Trifluoroacetyl as an Orthogonal Protecting Group for Guanidines

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Table of contents:

General Methods. Commercially available compounds were used without further purification. When necessary solvents were dried according to literature procedures[1]. Peptide and library synthesis on solid phase were performed in glass vessels with sinter frits or polypropylene filtration tubes with polyethylene frits on a Visiprep SPE Vacuum Manifold (Supelco). Reaction vessels were agitated either on a shaker (Stuart Scientific Flash Shaker SF1) or on a blood tube rotator (Stuart Scientific Blood Tube Rotator SB1). Thin layer chromatography (TLC) was performed on aluminium-backed plates silica gel 60 F_{254}. Column chromatography was performed on 40-60 mesh silica. All melting points were determined in open capillary tubes using a Gallenkamp Electrothermal Melting Point Apparatus and are uncorrected. Optical rotations were measured on a PolAAr-2001 Polarimeter. Proton NMR spectra were obtained at 300 MHz on a Bruker AC 300 and at 400 MHz on a Bruker DPX 400. Carbon NMR spectra were recorded at 75 MHz on a Bruker AC 300 and at 100 MHz on a Bruker DPX 400. Chemical shifts are reported in ppm on the δ scale relatively to the signal of the solvent used. Coupling constants are given in Hz. Mass spectra were obtained on a VG analytical 70-250-SE normal geometry double focussing mass spectrometer. All electrospray (ES) spectra were recorded on a Micromass Platform quadrupole mass analyser with an electrospray ion source using acetonitrile or methanol as solvent. MALDI-TOF spectra were recorded on a Dynamo

DE-linear-MALDI-TOF mass spectrometer. UV absorbance of ninhydrin and Fmoc assays were measured on a Hewlett-Packard 8452A Diode Array Spectrometer using two way quartz cells. Absorbance values were recorded at 570 nm (ninhydrin) and 302 nm (Fmoc).

Abbreviations: Aloc, allyloxycarbonyl; Boc, *tert*-butyloxycarbonyl; CBS, carboxylate binding site; Cbz, benzyloxycarbonyl; DIC, *N*, *N*′-diisopropylcarbodiimide; DBU, 1,8 diazabicyclo[5.4.0] undec-7-ene; Ddpe, 1-(4,4-dimethyl-2,6-dioxocyclohex-1-ylidene)phenylethyl; DIPEA, diisopropylethylamine; DMAP, 4-(dimethylamino)pyridine; DMF, *N*, *N*-dimethylformamide; DMS, dimethylsulfide; DMSO, dimethyl sulphoxide; EDC, 1-(3-dimethylaminopropyl)-3-ethylcardodiimide hydrochloride; EDT, ethanedithiol; FC, flash chromatography; Fmoc, 9-fluorenyloxycarbonyl; HOBt, 1-hydroxybenzotriazole; PyBOP, benzotriazole-1-yl-oxy-tris-pyrrolino-phosphonium hexafluorophosphate; TFA, trifluoroacetic acid; TFAc, trifluoroacetyl; TIS, triisopropyl silane.

Materials. (2-Amino-ethyl)-carbamic acid *tert*-butyl ester, (3-Amino-propyl) carbamic acid *tert*-butyl ester, (3-Amino-propyl) carbamic acid benzyl ester (**1**), (2-Isothiocyanatoethyl) carbamic acid allyl ester, (2-Isothiocyanatoethyl) carbamic acid *tert*-butyl ester, (3-Isothiocyanatopropyl) carbamic acid *tert*-butyl ester (**2**) were synthesised according to literature procedures[2,3].

References

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