

7 Experimental part

Analytical Methods

^1H NMR- and **^{13}C NMR-spectra** were recorded on *Bruker AC 250* (250.1 and 62.9 MHz for ^1H and ^{13}C , respectively) and *AC 500* or *Joel Eclipse 500* (500 and 126 MHz for ^1H and ^{13}C , respectively) spectrometers at 20 °C. ^1H and ^{13}C chemical shifts are expressed as ppm down field from tetramethylsilane ($\delta=0.00$) or using solvent signal of the proton as internal standard (^1H : $\delta(\text{CHCl}_3) = 7.24$ ppm, $\delta(\text{CH}_3\text{OH}) = 3.31$ ppm, $\delta(\text{DMSO}) = 2.49$ and ^{13}C : $\delta(\text{CDCl}_3) = 77.0$ ppm, $\delta(\text{CD}_3\text{OD}) = 49.0$ ppm, $\delta([\text{D}_6]\text{DMSO}) = 39.7$ ppm). ^{13}C -NMR-spectra have been recorded with broadband ^1H -decoupling. Two-dimensional correlation experiments that correlate $^1\text{H}/^1\text{H}$ -NMR-spectra (COSY) and $^1\text{H}/^{13}\text{C}$ -NMR-spectra (HETCORR, HMBC) have been made in order to determine exact structures.

IR spectra (IR) were recorded as KBr pellets on *Nicolet 5SXC* FTIR-Interferometer equipped with DTGS-detector. Settings and characteristic absorptions ν (in cm^{-1}) are listed for every experiment.

Mass-spectra (MS) were registered on *Perkin-Elmer Varian* Type: MAT 711 (EI, 80 eV, 8 kV), MAT CH7A (EI, 80 eV, 3 kV) and CH5DF (FAB, 3 kV). Setting and conditions (EI/FAB, Temperature; EI= Electron ionisation, FAB= Fast Atom Bombardment) as well as values for molecular- and fragmentation-cations are given for single experiments. High-resolution mass spectra (HMRS) were measured from the molecular peak. In case of low intensity of the molecular cation (<200 mV) the fragmentation-cation with highest mass is taken as reference mass.

Elemental analyses were performed on a *Perkin-Elmer* Elemental-Analyzer 240.

Melting points were registered on a *Reichert* ThermoVar melting point microscope and have not been corrected.

Optical rotation were registered on a *Perkin-Elmer* 241-Polarimeter at room temperature.

Specific optical rotations were calculated from:

$$[\alpha]_D^{20} = \frac{\alpha \cdot 100}{c \cdot d}$$

D = Sodium-D-line ($\lambda = 589.3$ nm); d = layer thickness (in dm, always = 1); c = concentration in g/100 ml

Solvent and concentration are given in brackets.

X-ray analyses were performed on a *Bruker* SMARTCCD diffractometer at Institut fuer Chemie - Anorganische und Analytische Chemie, Freie Universitaet Berlin, in the group of Prof. Hartl. The data were processed with ORTEP 3.2 and SHELLXL programmes.

Chromatography

Reactions were monitored with thin-layer chromatography (TLC) on TLC plates purchased from Merck (Silica gel 60 on Aluminium plate, fluorescence indicator F₂₅₄, 0.25 mm layer thickness) and from Macherey-Nagel (Polygram Aluminium oxide, activity III, neutral, N/UV₂₅₄).

Preparative separations and purifications of products from mixtures were performed by means of **column chromatography**. Silica gel 60 (0.040-0.063 mm particle size, 230-400 mesh ASTM) purchased from Merck-Schuchardt and neutral Aluminium oxide (6% water, activity III) purchased from Fluka were used as stationary phase. Eluent system mixtures are given for single experiments.

Analytical and preparative **HPLC**-separations were performed on a system that is build from following components: Pump 64, refractometer and printer *Knauer*, injection system U6K9 from *Waters/Milipore*. Different sizes *Knauer* columns were used (analytical: ID 4 x 250 mm, preparative: ID 16 x 250 mm, ID 32 x 250 mm) filled with *Macherey-Nagel* Nucleosil 50-5. *Knauer* Variable UV-detector (at $\lambda=255$ nm or $\lambda= 220$ nm) and *Knauer* Differential-refracometer were used for detection.

Distillations of small amounts of compounds were performed on *Büchi* kugelrohr distillation apparatus; therefore given boiling points represent temperature of the apparatus oven.

Preparative procedures and reagents

Reactions which are water sensitive were performed in an apparatus that was dried by heating under vacuum and filling the apparatus with argon, during addition of reagents argon was flushed through the apparatus and reactions were performed under argon. Reaction mixtures were stirred with magnetic stirrer. Solvents were distilled prior to use; dried solvents were kept over molecular sieves 4 Å.

Drying and purification of solvents and reagents

Diethyl ether / Tetrahydrofuran (THF):

Solvent was refluxed with sodium and benzophenone under argon atmosphere. Dark blue solution was distilled under argon atmosphere.

Dichloromethane:

Solvent was heated with calcium hydride, then distilled and stored over molecular sieves 4 Å.

Toluene:

Solvent was refluxed with sodium under argon atmosphere, after one hour it was distilled and stored over molecular sieves 4 Å.

Triethylamine (TEA):

Solvent was heated with calcium hydride, then distilled and stored over KOH pellets.

Compounds which have been prepared according to literature procedures:

Cyclohexenylisocyanide **66**,^[38] Diazomethane,^[121] *p*-Methoxyphenylisocyanide **69**,^[39]
Siloxycyclopropanecarboxylates **53, 54, 55, 56, 57, 60**,^[67, 77, 78]

Purchased compounds:

Acetic acid (Merck, 96 %); L-Alanine methyl ester hydrochloride (Acros, 99 %); 2-Aminopyridine (Acros, ≥ 99 %); (Benzotriazol-1-yloxy)tris(dimethyl-amino)phosphonium-hexafluorophosphate (Fluka, > 98 %); Benzyl cyanoacetate (Lancaster, > 98 %); Benzylisocyanide (Aldrich, 98 %); N-Boc-L-alanine (Degussa AG, 98 %); *tert*-Butyl cyanoacetate (Merck, > 99 %); Di-*tert*-butyl dicarbonate (Acros, 99 %); *n*-Butylisocyanide

(Acros, > 98 %); N,N'-Dicyclohexylcarbodiimide (Acros, 99 %); Diethylamine (Merck, > 99 %); N,N-Diisopropylethylamine (Merck, > 98 %); 4-Dimethylaminopyridine (Acros, 99 %); Ethyleneglycol (Fluka, \geq 98 %); Hydrochloric acid (37 %); Lithium hydroxide monohydrate (Acros, 56% LiOH); 2,6-Lutidine (Fluka, 98 %); Methanol (Roth, \geq 99.9%); Methyl cyanoacetate (Lancaster, 99 %); Methyl isocyanoacetate (Acros, 95 %); Oxalylchloride (Merck, > 98 %); L-Phenylalanine (Acros, > 98.5 %); Potassium fluoride (Merck, > 98.5 %); Potassium hexafluorophosphate (Acros, 99 %); Ruthenium(IV) oxide hydrate (Fluka, 60 % Ru); Sodium cyanide (Acros, > 95.5 %); Sodium hydride (Merck, 60 % w/w dispersion in mineral oil); Sodium periodate (Merck, 99 %); Sulfur (Merck); 1,1,3,3-Tetramethylbutylisocyanide (Merck, > 97 %); Tetramethylurea (Acros, > 99 %); Triethylamine trihydrofluoride (Riedel-de-Haën, ca. 37 % HF); Trifluoroacetic acid (Acros, 99 %); (Trimethylsilyl)diazomethane (Aldrich, 2.0 M solution in hexanes); Trimethylsilyl trifluoromethanesulfonate (Acros, 99 %);