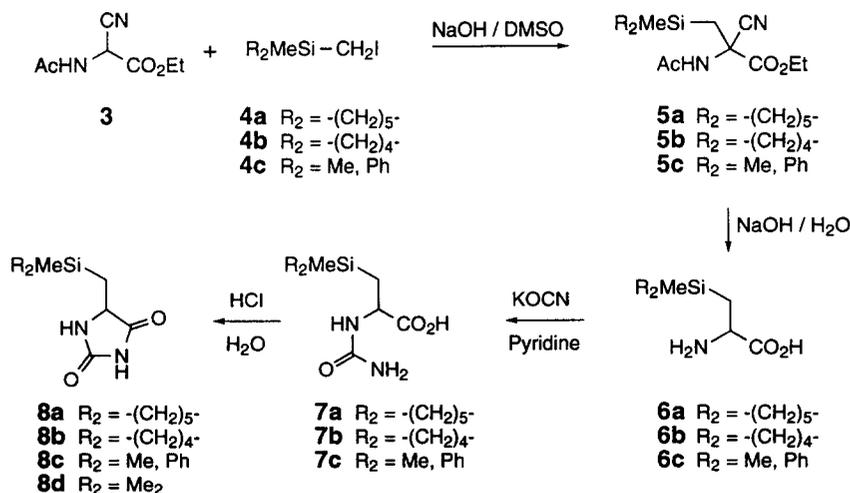


and carbamoylases — responsible for the enantiomer-selective degradation of either the L- or the D-hydantoin **1** to the respective enantiomerically pure α -amino acids (Scheme 1). A number of optically pure unusual and unnatural α -amino acids have been prepared by this “hydantoinase” process so far. The method has also been applied to the synthesis of D-3-(trimethylsilyl)alanine (D-TMS-Ala),⁴ a compound that was successfully used as a bioisoster for phenylalanine in renin inhibitors.⁵ Since silylated amino acids others than TMS-Ala could be of substantial interest as substitutes for natural lipophilic amino acids, too, we planned to use the “hydantoinase” process for the preparation of the optically active amino acids D-**6a–c** and L-**6a–c**. In the following we describe the synthesis of the racemic precursor compounds **6a–c** and their respective hydantoin derivatives **8a–c**.

RESULTS AND DISCUSSION

For the synthesis of the compounds **8a–c**, we followed a reaction sequence that was earlier used for the preparation of TMS-substituted hydantoin **8d** (Scheme 2).⁶ Treatment of cyanoacetate derivative **3** with the iodomethyl-substituted silanes **4a–c**^{11,12} in the presence of base provided the respective alkylated derivatives **5a–c** in moderate yields. These compounds were hydrolyzed with aqueous NaOH and gave rise to the amino acids **6a–c** after decarboxylation of the intermediary malonic acid derivatives. It is crucial for the hydrolysis step to use at least three equivalents of base and to heat the reaction mixture for a prolonged period of time (usually 12–48 h). The use of less NaOH or shorter reaction times gave incomplete transformations. As a result, considerable amounts of *N*-acetyl amino acids were isolated. Conversion of the amino acids **6a–c** to the corresponding hydantoin **8a–c** was attained by their treatment with KOCN in pyridine/H₂O and the subsequent cyclization of the crude *N*-carbamoylamino acids **7a–c** with HCl.¹³ The overall yields of the hydantoin **8a–c** summed up to approximately 20–23% (10% for the phenyl-substituted compound **8c**) when the reaction



Scheme 2

sequences were performed stepwise with isolation and purification of the intermediary amino acids **6a–c**. When purification of these intermediates was omitted, the yields increased to 40–48% (20% for **8c**). The significantly lower amounts that were obtained in the preparation of the (dimethyl)phenylsilyl-substituted compound **8c** was attributed to the fairly labile Ph–Si bond. Particularly in the hydrolysis step, under the prolonged action of hydroxide base, an ample amount of insoluble material was formed, and the yield of the desired product decreased drastically.

The synthetic pathway towards silicon-containing α -amino acids and hydantoins presented in this paper is straightforward and leads to the desired products — except for **6c/8c** — in reasonable overall yields. Problematic in the reaction sequence are two steps: the initial alkylation reaction (formation of **5a–c** from **3** and **4a–c**) and in the preparation of the phenyl-substituted silicon compound **6c**, as already mentioned above, the hydrolysis step. The alkylation reaction seems to be difficult mostly for steric reasons: with smaller and more reactive electrophiles, like, *e.g.*, MeI but also with Me₃SiCH₂I, the yields were considerably higher (up to 90% as compared to approximately 45%). We have also tested alternative glycine enolate equivalents (enolates of *N*-benzylidene glycine or of phthalimido-protected glycine) that thus gave inferior results.

EXPERIMENTAL

General Remarks. Unless otherwise stated: all org. solvents were distilled prior to use. All moisture-sensitive reactions were carried out under a blanket of Ar. Extracts were dried (MgSO₄) and evaporated *in vacuo*. Column chromatography (SiO₂): silica gel *Merck 60* (40–63 μ m). M.p.: *Mettler FP-5/FP-52*; *d* = decomposition. IR: *Perkin-Elmer 781*; as KBr pellets; data in $\bar{\nu}$ (cm⁻¹) with *s* (strong), *m* (middle), and *w* (weak) with respect to the most intense absorption. ¹H NMR: at 300 MHz in CDCl₃; *Bruker AC-300* or *Bruker ARX-300*; δ in ppm relative to CHCl₃ (δ = 7.26) or DMSO (δ = 2.49); *J* in Hz; multiplicities denoted as *s* = singlet, *d* = doublet, *t* = triplet, *q* = quadruplet, *quint.* = quintuplet, and *m* = multiplet. ¹³C NMR: at 75.6 MHz in CDCl₃; *Bruker ARX-300*; δ in ppm relative to CDCl₃ (δ = 77.0) or DMSO (δ = 39.7); multiplicities from DEPT90 and DEPT135 experiments. CI-MS (chemical ionization mass spectrometry) with NH₃ as the reactant gas: *Finnigan SSQ 700* or *Finnigan MAT 90*; ESI-MS (electrospray ionization mass spectrometry): *Finnigan TSQ 700*; signals at *m/z* > 50 and >10% rel. abundance, for ESI-MS: base peak and quasi-molecular ions only; data in *m/z* (relative abundance of major isotope in percent, where appropriate). Elemental analyses: *Elementar Vario EL*.

Ethyl 2-Acetamido-2-cyano-3-(1-methyl-1-silacyclohex-1-yl)propionate (5a): A soln. of ethyl *N*-acetamidocyanoacetate (**3**, 1.17 g, 6.88 mmol) in DMSO (10 ml) was added at 23°C to a soln. of NaOEt (0.47 g, 6.86 mmol) in DMSO (10 ml). After 4 h, 1-(iodomethyl)-1-methylsilacyclohexane¹¹ (**4a**, 1.47 g, 5.80 mmol) was added dropwise and the resultant mixture was stirred at 23°C for 48 h. It was quenched with H₂O, extracted with Et₂O, and chromatographed (AcOEt/hexane 1:1) to give **5a** (0.85 g, 2.87 mmol, 49%) as colorless crystals. M.p.: 97.8–98.6°C (AcOEt/hexane). IR: 3270s, 3190m, 3020m, 2990m, 2910s, 2850m, 2790w, 1760s, 1710w, 1695m, 1660s, 1535s, 1480w, 1460w, 1445m, 1405m, 1390m, 1375m, 1360m, 1340w,

1300s, 1265s, 1205s, 1180s, 1160w, 1125w, 1115w, 1095w, 1020s, 995m, 970w, 910s, 870w, 845s, 820s, 795s, 780m, 760w, 705w, 685m, 645w. ¹H NMR: 6.21 (s, HN); 4.36, 4.26 (2dq, *J* = 10.7, 7.1, MeCH₂); 2.05 (s, MeCO); 1.77, 1.49 (AB, *J* = 14.6, SiCH₂); 1.75–1.40 (m, CH₂CH₂CH₂); 1.37 (t, *J* = 7.1, MeCH₂); 0.67 (*q*-like *m*, '*J*' = 7.1, 2 SiCH₂); 0.18 (s, MeSi). ¹³C NMR: 169.3 (s, MeCO); 167.3 (s, CO₂Et); 117.3 (s, C≡N); 63.7 (t, OCH₂); 54.5 (s, CC≡N); 29.6 (t, Si(CH₂)₂CH₂); 24.0 (t, 2 SiCH₂CH₂); 23.8 (t, SiCH₂); 22.6 (*q*, MeCO); 13.8 (*q*, MeCH₂); 13.1 (t, 2 SiCH₂); -4.3 (*q*, MeSi). CI-MS: 314 (100, [*M* + NH₄]⁺), 297 (12, [*M* + H]⁺), 270 (5), 256 (15), 225 (17). Anal. Calcd. for C₁₄H₂₄N₂O₃Si (296.45): C 56.72, H 8.16, N 9.45 Found: C 55.85, H 7.93, N 9.65.

Ethyl 2-Acetamido-2-cyano-3-(1-methyl-1-silacyclopent-1-yl)propionate (5b): Analogously to the preparation of **5a**, **3** (3.13 g, 18.4 mmol) was deprotonated with NaOEt (1.25 g, 18.4 mmol) and alkylated with 1-(iodomethyl)-1-methylsilacyclopentane¹¹ (**4b**, 3.72 g, 15.5 mmol). The solid obtained after work-up was recrystallized (AcOEt) and gave **5b** (2.00 g, 7.08 mmol, 46%) as colorless crystals. M.p.: 129.8–131.5°C (AcOEt). IR: 3260s, 3030m, 3000m, 2930s, 2850m, 2800w, 1760s, 1710m, 1660s, 1650s, 1550m, 1540s, 1505m, 1480m, 1450m, 1405m, 1390m, 1375s, 1360m, 1300s, 1270s, 1200s, 1155m, 1115m, 1090m, 1075s, 1020s, 960w, 925w, 865s, 835s, 805s, 785s, 775s, 710m, 670m, 655m. ¹H NMR: 6.21 (s, HN); 4.36, 4.26 (2dq, *J* = 10.7, 7.1, MeCH₂); 2.05 (s, MeCO); 1.78, 1.58 (AB, *J* = 14.6, SiCH₂); 1.61–1.54 (m, 2 SiCH₂CH₂); 1.37 (t, *J* = 7.1, MeCH₂); 0.70–0.56 (m, 2 SiCH₂); 0.26 (s, MeSi). ¹³C NMR: 169.3 (s, MeCO); 167.1 (s, CO₂Et); 117.3 (s, C≡N); 63.8 (t, OCH₂); 54.6 (s, CC≡N); 26.9, 26.8 (2t, 2 SiCH₂CH₂); 24.5 (t, SiCH₂); 22.6 (*q*, MeCO); 13.8 (*q*, MeCH₂); 12.4, 12.3 (2t, 2 SiCH₂); -2.5 (*q*, MeSi). CI-MS: 300 (100, [*M* + NH₄]⁺), 283 (20, [*M* + H]⁺), 256 (7), 242 (13). Anal. Calcd. for C₁₃H₂₂N₂O₃Si (282.42): C 55.29, H 7.85, N 9.92. Found: C 54.76, H 7.77, N 10.03.

Ethyl 2-Acetamido-2-cyano-3-[(dimethyl)phenylsilyl]propionate (5c): Analogously to the preparation of **5a**, **3** (1.17 g, 6.88 mmol) was deprotonated with NaOEt (0.47 g, 6.86 mmol) and alkylated with (iodomethyl)dimethylphenylsilane¹² (**4c**, 1.58 g, 5.70 mmol). The solid obtained after work-up was chromatographed (AcOEt/hexane 1:1) and gave **5c** (0.80 g, 2.51 mmol, 44%) as colorless crystals. The analogous reaction performed with KO^t-Bu instead of NaOEt as the base delivered the same product in 33% yield. M.p.: 89.9–92.1°C (AcOEt/hexane). IR: 3240s, 3190m, 3065m, 3040m, 3020m, 2980m, 2930m, 2890m, 2840w, 2220w, 1765s, 1750s, 1700m, 1660s, 1650s, 1605m, 1565w, 1535s, 1485w, 1470w, 1445m, 1425m, 1415m, 1395m, 1370m, 1360m, 1300s, 1270s, 1245s, 1210s, 1160w, 1115s, 1095w, 1040w, 1020s, 1000m, 970w, 955w, 870w, 845s, 820s, 790s, 775m, 725s, 700s, 630w. ¹H NMR: 7.59–7.56 (m, 2 arom. H); 7.45–7.43 (m, 3 arom. H); 5.76 (s, HN); 4.11 (*q*, *J* = 7.1, MeCH₂); 2.04 (s, MeCO); 1.90, 1.62 (AB, *J* = 14.8, SiCH₂); 1.25 (t, *J* = 7.1, MeCH₂); 0.53, 0.40 (2s, Me₂Si). ¹³C NMR: 169.3 (s, MeCO); 167.0 (s, CO₂Et); 136.4 (s, arom. C); 133.8 (d, 2 arom. C); 130.1 (d, arom. C); 128.4 (d, 2 arom. C); 117.4 (s, C≡N); 63.4 (t, OCH₂); 54.4 (s, CC≡N); 24.9 (t, SiCH₂); 22.0 (*q*, MeCO); 13.7 (*q*, MeCH₂); -2.8, -3.0 (2*q*, Me₂Si). CI-MS: 336 (6, [*M* + NH₄]⁺), 319 (4, [*M* + H]⁺), 303 (9), 292 (10), 278 (9), 241 (100). Anal. Calcd. for C₁₆H₂₂N₂O₃Si (318.45): C 60.35, H 6.96, N 8.80. Found: C 59.97, H 6.86, N 8.93.

3-(1-Methyl-1-silacyclohex-1-yl)alanine (6a): A soln. of **5a** (0.77 g, 2.60 mmol) and NaOH (2.0 g, 50.0 mmol) in H₂O (20 ml) was refluxed for 12 h. It was cooled to 0°C and acidified with conc. aq. HCl soln. to pH = 6. The thus formed precipitate was filtered off and chromatographed (CH₂Cl₂/EtOH/AcOH 14:4:1) to give **6a** (0.45 g, 2.23 mmol, 86%) as colorless crystals. M.p.: 239.8–241.3(d)°C (H₂O). IR: 3400m, 3000s, 2910s, 2850s, 2610m, 2520m, 1745s, 1590m, 1500m, 1445m, 1400w, 1345w, 1250s, 1205m, 1180s, 1160s, 1075w, 1025w, 990m, 910m, 860m, 810s, 800s, 755m, 720m, 705w, 675w. ¹H NMR (DMSO/DCl): 3.69 (dd, *J* = 12.1, 4.1, CH); 1.68–1.40 (*m*, 2 SiCH₂CH₂); 1.41–1.22 (*m*, Si(CH₂)₂CH₂); 1.17, 1.01 (*AB* of *ABX*, *J*_{AB} = 14.3, *J*_{AX} = 4.2, *J*_{BX} = 12.2, SiCH₂); 0.65–0.45 (*m*, 2 SiCH₂); 0.01 (*s*, MeSi). ¹³C NMR (DMSO/DCl): 171.7 (*s*, CO₂H); 50.2 (*d*, CH); 29.5 (*t*, Si(CH₂)₂CH₂); 24.0, 23.9 (*2t*, 2 SiCH₂CH₂); 16.8, 13.1, 12.7 (*3t*, 3 SiCH₂); –4.4 (*q*, MeSi). CI-MS: 202 ([*M* + H]⁺). Anal. Calcd. for C₉H₁₉NO₂Si (201.34): C 53.69, H 9.51, N 6.96. Found: C 53.22, H 9.22, N 6.83.

3-(1-Methyl-1-silacyclopent-1-yl)alanine (6b): Analogously to the preparation of **6a**, **5b** (1.9 g, 6.73 mmol) was hydrolyzed with NaOH (2.0 g, 50.0 mmol) and gave, after recrystallization of the crude product (H₂O), **6b** (0.92 g, 4.89 mmol, 73%) as colorless crystals. M.p.: 252(d)°C (H₂O). IR: 3420m, 3040s, 2920s, 2850s, 1675s, 1600s, 1550s, 1430s, 1395s, 1345m, 1320m, 1245s, 1170s, 1130s, 1075s, 1025s, 885w, 860m, 830s, 775s, 740m, 705m, 650m, 635w. ¹H NMR (DMSO/DCl): 3.66 (dd, *J* = 12.4, 4.2, CH); 1.24 (*s*, 2 SiCH₂CH₂); 1.11, 0.91 (*AB* of *ABX*, *J*_{AB} = 14.1, *J*_{AX} = 4.2, *J*_{BX} = 13.3, SiCH₂); 0.33–0.20 (*m*, 2 SiCH₂); –0.08 (*s*, MeSi). ¹³C NMR (DMSO/DCl): 172.7 (*s*, CO₂H); 52.3 (*d*, CH); 28.2, 28.1 (*2t*, 2 SiCH₂CH₂); 19.5, 14.2, 13.5 (*3t*, 3 SiCH₂); –1.4 (*q*, MeSi). CI-MS: 188 ([*M* + H]⁺). Anal. Calcd. for C₈H₁₇NO₂Si (187.32): C 51.30, H 9.15, N 7.48. Found: C 51.08, H 9.11, N 7.32.

3-[(Dimethyl)phenylsilyl]alanine (6c): Analogously to the preparation of **6a**, **5c** (0.62 g, 1.93 mmol) was hydrolyzed with NaOH (2.0 g, 50.0 mmol) and gave, after recrystallization of the crude product (H₂O), **6c** (0.30 g, 1.35 mmol, 70%, contaminated with inorganic impurities) as a colorless amorphous solid. M.p.: 213.7–215.3(d)°C (H₂O). IR: 3420m, 3060s, 1610s, 1515m, 1505m, 1485m, 1470w, 1455w, 1425s, 1415m, 1390s, 1345m, 1315m, 1245s, 1180m, 1140w, 1115m, 1020w, 995w, 885w, 835s, 810m, 780s, 740m, 725s, 700s, 665w, 635w, 620w. ¹H NMR (DMSO/DCl): 7.48–7.45 (*m*, 2 arom. H); 7.33–7.30 (*m*, 3 arom. H); 3.73 (dd, *J* = 12.0, 4.1, CH); 1.40, 1.26 (*AB* of *ABX*, *J*_{AB} = 14.4, *J*_{AX} = 4.2, *J*_{BX} = 12.3, SiCH₂); 0.27, 0.24 (*2s*, Me₂Si). ¹³C NMR (DMSO/DCl): 172.3 (*s*, CO₂H); 139.0 (*s*, arom. C); 134.9 (*d*, 2 arom. C); 130.8 (*d*, arom. C); 129.5 (*d*, 2 arom. C); 51.7 (*d*, CH); 19.6 (*t*, SiCH₂); –1.1, –1.5 (*2q*, Me₂Si). ESI-MS (MeOH): 246 ([*M* + Na]⁺), 224 ([*M* + H]⁺).

***N*-Carbamoyl-3-(1-methyl-1-silacyclohex-1-yl)alanine (7a) and 5-[(1-Methyl-1-silacyclohex-1-yl)methyl]imidazolidine-2,4-dione (8a):** From **6a**: A suspension of **6a** (0.20 g, 1.0 mmol) and KOCN (0.10 g, 1.2 mmol) in H₂O/pyridine (1:1, 4 ml) was heated to 60°C for 2 h (the reactants were dissolved completely). It was cooled to 23°C, pyridine was extracted with AcOEt, and the aq. layer acidified with aq. HCl soln. (6N, 1 ml) and AcOH (1 ml) (formation of a precipitate). The mixture was heated to reflux for 1 h, cooled to 4°C and stored at this temperature for 15 h to complete crystallization of the desired product. The precipitate was filtered off and dried to give **8a** (0.12 g, 0.55 mmol, 55%). The *N*-carbamoyl intermediate **7a** was ob-

tained, when the intermediary formed precipitate (after treatment of **6a** with KOCN and acidification) was filtered off, washed with H₂O, and dried. *From 3*: Analogously to the preparation of **5a**, **3** (14.36 g, 84.4 mmol) was deprotonated with NaOEt (6.7 g, 92.8 mmol) and alkylated with **4a** (18.64 g, 73.3 mmol). Analogously to the preparation of **6a**, the crude **5a** was directly hydrolyzed with NaOH (20 g, 0.50 mol, in 200 ml of H₂O, reflux for 48 h), and the thus obtained crude amino acid was subsequently treated as above with KOCN (7.3 g, 90 mmol) in H₂O/pyridine (1:1, 200 ml) and then with aq. HCl soln. (6N, 40 ml) and AcOH (40 ml) at reflux. Recrystallization (H₂O) of the crude product afforded **8a** (8.0 g, 35.3 mmol, 48%) as colorless crystals.

Data of **7a**: M.p.: 123(d)°C (H₂O). IR: no reasonable spectrum was obtained. ¹H NMR (DMSO): 5.92 (*d*, *J* = 6.7, HN); 5.39 (*s*, H₂N); 3.72 (*q*, *J* = 6.8, CH); 1.68–1.42 (*m*, 2 SiCH₂CH₂); 1.39–1.20 (*m*, Si(CH₂)₂CH₂); 1.01, 0.89 (*AB* of *ABX*, *J*_{AB} = 14.3, *J*_{AX} = 6.9, *J*_{BX} = 6.8, SiCH₂); 0.67–0.42 (*m*, 2 SiCH₂); 0.00 (*s*, MeSi). ¹³C NMR (DMSO): 176.5, 158.3 (2*s*, 2 C=O); 51.9 (*d*, CH); 30.0 (*t*, Si(CH₂)₂CH₂); 24.4 (*t*, 2 SiCH₂CH₂); 20.3, 13.8, 13.7 (3*t*, 3 SiCH₂); –3.8 (*q*, MeSi). CI-MS (compound decomposes): 30°C: 263 (100); 60°C: 279 (25), 263 (100); 150°C: 528 (19), 391 (20), 365 (35), 295 (8), 279 (100), 263 (13), 223 (4); 250°C: 536 (7), 462 (4), 367 (10), 314 (29), 279 (8), 255 (13), 227 (48), 202 (33), 184 (50), 158 (90), 145 (40), 132 (46), 130 (100), 114 (73). ESI-MS (MeOH): 479 (19), 463 (19), 369 (20), 338 (35), 327 (44), 311 (18), 283 (36), 245 (100, [*M* + H]⁺), 228 (34), 190 (75), 175 (68), 139 (48).

Data of **8a**: M.p.: 174.8–175.9°C (H₂O). IR: 3280*m*, 3180*m*, 3060*m*, 2910*s*, 2845*m*, 2790*w*, 2750*w*, 1775*s*, 1730*s*, 1695*m*, 1680*w*, 1645*w*, 1555*w*, 1535*w*, 1440*m*, 1415*s*, 1380*m*, 1335*m*, 1295*m*, 1255*m*, 1205*m*, 1185*m*, 1095*m*, 1040*w*, 1005*w*, 990*m*, 910*m*, 895*m*, 870*m*, 825*s*, 800*s*, 740*m*, 710*w*, 695*w*, 675*w*, 645*m*, 630*w*. ¹H NMR (DMSO): 10.53, 7.78 (2*s*, br., 2 HN); 4.08 (*t*, *J* = 6.3, CH); 1.62–1.23 (*m*, CH₂CH₂CH₂); 1.03, 0.94 (*AB* of *ABX*, *J*_{AB} = 14.8, *J*_{AX} = 7.1, *J*_{BX} = 6.2, SiCH₂); 0.62–0.51 (*m*, 2 SiCH₂); 0.05 (*s*, MeSi). ¹³C NMR (DMSO): 177.3, 157.3 (2*s*, 2 C=O); 55.1 (*d*, CH); 29.6 (*t*, Si(CH₂)₂CH₂); 24.0 (*t*, 2 SiCH₂CH₂); 17.3, 13.2, 13.1 (3*t*, 3 SiCH₂); –3.9 (*q*, MeSi). CI-MS: 244 (100, [*M* + NH₄]⁺), 227 (4, [*M* + H]⁺). Anal. Calcd. for C₁₀H₁₈N₂O₂Si (226.35): C 53.06, H 8.02, N 12.38. Found: C 52.88, H 7.94, N 12.11.

***N*-Carbamoyl-3-(1-methyl-1-silacyclopent-1-yl)alanine (7b) and 5-[(1-Methyl-1-silacyclopent-1-yl)methyl]imidazolidine-2,4-dione (8b)**: *From 6b*: Analogously to the preparation of **7a** and **8a**, **6b** (0.75 g, 4.0 mmol) was reacted with KOCN (0.39 g, 4.8 mmol) in H₂O/pyridine (1:1, 16 ml) then with aq. HCl soln. (6N, 4 ml) and AcOH (4 ml) to form **8b** (0.50 g, 2.35 mmol, 58%). *N*-Carbamoyl amino acid **7b** was collected, as described above, after acid treatment before heating to reflux. *From 3*: Analogously to the preparation of **8a**, **3** (11.41 g, 67.1 mmol) was deprotonated with NaOEt (4.56 g, 67.1 mmol) and alkylated with **4b** (13.60 g, 56.5 mmol). It was hydrolyzed with NaOH (80 g, 2.0 mol, in 400 ml of H₂O, reflux 48 h), treated with KOCN (5.2 g, 64.0 mmol) in H₂O/pyridine (1:1, 200 ml), then with aq. HCl soln. (54 ml) and AcOH (54 ml). Recrystallization (H₂O) of the crude product afforded **8b** (4.8 g, 22.5 mmol, 40%) as colorless crystals.

Data of **7b**: M.p.: 146(d)°C (H₂O). IR: 3410*s*, 3380*s*, 3230*s*, 2935*s*, 2835*m*, 2480*w*, 1880*w*, 1690*s*, 1680*s*, 1660*s*, 1640*s*, 1560*s*, 1550*s*, 1540*s*, 1470*m*, 1450*w*, 1415*m*, 1405*m*, 1315*m*, 1295*m*, 1240*s*, 1200*m*, 1175*m*, 1150*m*, 1075*s*, 1050*s*, 1030*s*, 910*w*, 860*m*, 830*m*, 810*s*, 775*m*, 725*w*, 710*w*, 685*w*, 650*w*, 620*w*. ¹H

NMR (DMSO): 6.10 (*d*, $J = 8.5$, HN); 5.53 (*s*, H_2N); 4.08 (*dt*, $J = 9.6, 6.0$, CH); 1.49 (*quint.*, $J = 3.7$, 2 $SiCH_2CH_2$); 1.06, 0.94 (*AB* of *ABX*, $J_{AB} = 14.5$, $J_{AX} = 5.9$, $J_{BX} = 9.8$, $SiCH_2$); 0.64–0.37 (*m*, 2 $SiCH_2$); 0.09 (*s*, MeSi). ^{13}C NMR (DMSO): 176.0, 158.1 (2*s*, 2 C=O); 49.6 (*d*, CH); 26.8, 26.7 (2*t*, 2 $SiCH_2CH_2$); 19.4, 12.0, 11.9 (3*t*, 3 $SiCH_2$); –2.7 (*q*, MeSi). CI-MS: 248 (25, $[M + NH_4]^+$), 231 (100, $[M + H]^+$), 213 (10, $[M + H - H_2O]^+ \triangleq [8b + H]^+$), 188 (86, $[M + H - CONH]^+ \triangleq [6b + H]^+$).

Data of **8b**: M.p.: 163.5–164.2°C (H_2O). IR: 3220*s*, 3060*s*, 2920*s*, 2850*m*, 2745*w*, 1770*s*, 1735*s*, 1695*w*, 1685*w*, 1555*w*, 1485*w*, 1450*m*, 1415*s*, 1380*m*, 1320*m*, 1305*m*, 1245*m*, 1205*s*, 1140*s*, 1070*s*, 1040*s*, 1005*m*, 945*w*, 890*m*, 860*m*, 835*s*, 805*s*, 785*m*, 760*m*, 740*m*, 715*w*, 700*w*, 650*m*, 635*m*. 1H NMR (DMSO): 10.55, 7.81 (2*s*, br. 2 HN); 4.15–4.10 (*m*, CH); 1.49 (*quint.*-like *m*, ' J ' = 3.7, 2 $SiCH_2CH_2$); 1.09, 1.03 (*AB* of *ABX*, $J_{AB} = 14.8$, $J_{AX} = 6.4$, $J_{BX} = 6.0$, $SiCH_2$); 0.62–0.43 (*m*, 2 $SiCH_2$); 0.10 (*s*, MeSi). ^{13}C NMR (DMSO): 177.1, 157.3 (2*s*, 2 C=O); 55.3 (*d*, CH); 26.7 (*t*, 2 $SiCH_2CH_2$); 18.3, 12.4, 12.3 (3*t*, 3 $SiCH_2$); –2.3 (*q*, MeSi). CI-MS: 230 (100, $[M + NH_4]^+$), 213 (17, $[M + H]^+$). Anal. Calcd. for $C_9H_{16}N_2O_2Si$ (212.33): C 50.91, H 7.60, N 13.19. Found: C 50.72, H 7.33, N 12.98.

***N*-Carbamoyl-3-[(dimethyl)phenylsilyl]alanine (7c) and 5-[(Dimethyl)phenylsilyl]methylimidazole-2,4-dione (8c)**: From **6c**: Analogously to the preparation of **7a** and **8a**, **6c** (0.22 g, 1.0 mmol) was reacted with KOCN (0.10 g, 1.2 mmol) in H_2O /pyridine (1:1, 4 ml) then with aq. HCl soln. (6*N*, 1 ml) and AcOH (1 ml) to form **8c** (0.12 g, 0.49 mmol, 49%). *N*-Carbamoyl amino acid **7c** was collected, as described above, after acid treatment before heating to reflux. From **3**: Analogously to the preparation of **8a**, **3** (5.71 g, 33.6 mmol) was deprotonated with NaOEt (2.65 g, 36.9 mmol) and alkylated with **4c** (8.34 g, 30.2 mmol). It was hydrolyzed with NaOH (80 g, 2.0 mol, in 400 ml of H_2O , reflux 48 h), treated with KOCN (1.65 g, 20.5 mmol) in H_2O /pyridine (1:1, 90 ml), then with aq. HCl soln. (6*N*, 11 ml) and AcOH (11 ml). Recrystallization (H_2O) of the crude product afforded **8c** (1.50 g, 6.04 mmol, 20%) as colorless crystals.

Data of **7c**: M.p.: 150.0–150.4°C (H_2O). IR: 3520*s*, 3460*s*, 3360*s*, 3280*s*, 3110*m*, 3060*m*, 2960*m*, 2890*m*, 2710*m*, 2520*m*, 1715*s*, 1660*m*, 1645*m*, 1615*s*, 1565*s*, 1555*s*, 1505*m*, 1485*m*, 1470*w*, 1455*w*, 1430*m*, 1415*m*, 1390*m*, 1340*w*, 1250*s*, 1210*s*, 1170*s*, 1140*m*, 1110*s*, 1070*m*, 1020*w*, 1000*w*, 950*w*, 920*w*, 835*s*, 800*m*, 775*m*, 730*m*, 700*s*, 675*w*, 665*w*. 1H NMR (DMSO): 7.51–7.48 (*m*, 2 arom. H); 7.35–7.33 (*m*, 3 arom. H); 6.14 (*d*, $J = 8.5$, HN); 5.54 (*s*, H_2N); 4.08 (*dt*, $J = 9.6, 5.5$, CH); 1.21, 1.04 (*AB* of *ABX*, $J_{AB} = 14.6$, $J_{AX} = 5.3$, $J_{BX} = 10.1$, $SiCH_2$); 0.25, 0.23 (2*s*, Me_2Si). ^{13}C NMR (DMSO): 176.1, 158.2 (2*s*, 2 C=O); 138.8 (*s*, arom. C); 133.5 (*d*, 2 arom. C); 129.1 (*d*, arom. C); 127.9 (*d*, 2 arom. C); 49.4 (*d*, CH); 19.9 (*t*, $SiCH_2$); –2.1, –2.6 (2*q*, Me_2Si). CI-MS (100°): 284 (5, $[M + NH_4]^+$), 280 (18), 267 (47, $[M + H]^+$), 266 (100, $[M + NH_4 - H_2O]^+$), 249 (9, $[M + H - H_2O]^+ \triangleq [8c + H]^+$), 233 (20), 224 (82, $[M + H - CONH]^+ \triangleq [6c + H]^+$), 189 (67), 185 (30), 171 (58).

Data of **8c**: M.p.: 160.3–161.2°C (H_2O). IR: 3220*s*, 3180*s*, 3120*s*, 3060*s*, 2960*m*, 2900*m*, 2740*w*, 1770*s*, 1730*s*, 1695*m*, 1680*w*, 1645*w*, 1635*w*, 1485*w*, 1425*s*, 1415*s*, 1375*m*, 1325*w*, 1305*m*, 1245*m*, 1205*m*, 1195*m*, 1145*w*, 1110*m*, 1090*m*, 1040*m*, 1000*w*, 890*w*, 835*s*, 795*m*, 765*m*, 740*m*, 725*m*, 695*m*, 630*m*. 1H NMR (DMSO): 10.54, 7.74 (2*s*, br., 2 HN); 7.52–7.49 (*m*, 2 arom. H); 7.37–7.33 (*m*, 3 arom. H); 4.03 (*dt*, $J = 6.9, 1.5$, CH); 1.23, 1.09 (*AB* of *ABX*, $J_{AB} = 14.9$, $J_{AX} = 6.8$, $J_{BX} = 7.0$, $SiCH_2$); 0.31 (*s*, Me_2Si). ^{13}C NMR (DMSO): 177.2, 157.4 (2*s*, 2 C=O); 138.6 (*s*, arom. C); 133.5 (*d*, 2 arom. C); 129.2 (*d*, arom. C); 127.9 (*d*, 2

arom. C); 55.1 (*d*, CH); 19.1 (*t*, SiCH₂); -2.1, -2.2 (2*q*, Me₂Si). CI-MS: 266 (100, [*M* + NH₄]⁺), 249 (12, [*M* + H]⁺), 233 (5), 171 (55). Anal. Calcd. for C₁₂H₁₆N₂O₂Si (248.36): C 58.03, H 6.49, N 11.28. Found: C 57.88, H 6.33, N 11.13.

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