Supplementary Material

Efficient monoacylation of symmetrical secondary alkanediamines and synthesis of unsymmetrical diacylated alkanediamines.
A new L-proline-based organocatalyst

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1. General S2
2. $^1$H and $^{13}$C NMR spectra of the new compounds 9, 11-13, 19-29, and 34-35 S3
General:

All reagents and solvents were purchased from commercial sources. Reactions were conducted in flame-dried glassware under an argon atmosphere. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded at 300 or 400 MHz and at 75 or 101 MHz in CD\(_3\)OD or DMSO-\(d_6\). Chemical shifts are given in ppm and reported to the residual solvent peak (CD\(_3\)OD 3.31 ppm and 49.00 ppm; DMSO-\(d_6\) 2.50 ppm and 39.52 ppm). Data are reported as follows: chemical shift (\(\delta\)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, and integration. Analytical TLC were performed on silica gel 60 F\(_{254}\) plates. Column chromatographies were carried out on silica gel 60 (63-200 μm). High-resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and Q-Tof detection. Melting points were measured with a Büchi apparatus and are reported uncorrected.

For the description of compounds 8, 10, 30, 31, 32, 33, see reference 18 in the manuscript.
tert-Butyl (S)-1-(6-aminohexylcarbamoyl)-5-(benzylamino-pentylcarbamoyl)carbamate (9)
tert-Butyl (S)-1-(6-aminohexylcarbamoyl)-2-phenylethylcarbamate (11)
(R)-N-(2-Aminoethyl)-2-(2-methoxynaphthalen-6-yl)propanamide (12)
(R)-N-(6-Aminohexyl)-2-(2-methoxynaphthalen-6-yl)propanamide (13)
**tert-Butyl (S)-6-aminobenzylcarbamoyl-1-(1,4-diazepan-1-yl)-1-oxohexan-2-ylcarbamate (19)**

![Chemical Structure](image)

![NMR Spectra](image)
tert-Butyl (S)-6-aminobenzylcarbamoyl-1-(piperazin-1-yl)-1-oxohexan-2-ylcarbamate (20)
Benzyl (S)-1-(1,4-diazepan-1-yl)-1-oxo-3-phenylpropan-2-ylcarbamate (21)
tert-Butyl (S)-1-oxo-3-phenyl-1-(piperazin-1-yl)propan-2-ylcarbamate (22)
(R)-1-(1,4-Diazepan-1-yl)-2-(2-methoxynaphthalen-6-yl)propan-1-one (23)
(R)-2-(2-Methoxynaphthalen-6-yl)-1-(piperazin-1-yl)propan-1-one (24)
(R)-2-(2-Methoxynaphthalen-6-yl)-N-methyl-N-(2-(methylamino)ethyl)propanamide (25)
(3,4-Dimethoxyphenyl)(piperazin-1-yl)methanone (26)
(2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)(piperazin-1-yl)methanone (27)
(Piperazin-1-yl)(thiophen-2-yl)methanone (28)
4-methyl-1-(piperazin-1-yl)pentan-1-one (29)
tert-butyl (S)-1-(2-aminoethyl-(2-pyrrolidine carbamoyl)-carbamoyl)-2-phenylethylcarbamate (34)
tert-butyl (S)-1-(2-aminoethyl-[1-benyl-(2-pyrrolidine carbamoyl)carbamoyl]-2-phenylethylcarbamate (35).