

Supplementary Material

The new approach to organocatalysts. Synthesis of a library of *N*-lipidated oligopeptides immobilized on cellulose and screening of their catalytic activity

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1. Elemental Analysis of Selected Peptides Immobilized on Cellulose

C, H, N analyses of randomly selected elements of library

1.1. (9Z,12R)-12-hydroxyoctadec-9-enoyl-EHS-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose;

7{10,E,S,H}:

C 50.82%; H 6.71%; N 7.04%

1.2. (9Z,12R)-12-hydroxyoctadec-9-enoyl-SEH-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose;

17{10,S,E,H}:

C 50.81%; H 6.70%; N 7.03%

1.3. (9Z,12R)-12-hydroxyoctadec-9-enoyl-HES-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose;

17{10,H,E,S}:

C 50.84%; H 6.73%; N 7.02%

1.4. decanoyl-SEH-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose; **12{12,S,E,H}:**

C 48.42%; H 6.24%; N 7.51%

1.5. decanoyl-EHS-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose; **17{12,E,H,S}:**

C 48.40%; H 6.21%; N 7.54%

1.6. decanoyl-EHS-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose; **17{12,E,S,H}:**

C 48.41%; H 6.22%; N 7.52%

1.7. octadecanoyl-EHS-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose; **17{12,E,H,S}:**

C 50.76%; H 6.81%; N 7.02%

1.8. octadecanoyl-HES-NH-C₆H₄-NH-1,3,5-triazinyl-cellulose; **17{12,H,E,S}:**

C 50.78%; H 6.82%; N 7.00%

2. Synthesis of incomplete structures of chemzymes for blank experiments

2.1. Synthesis of *O*-lipidated cellulose 18-21. General procedure

Four sheets [3 x 6 cm] of Whatman-7 filter paper were immersed in 1M NaOH (10 ml) and gently shaken for 15 minutes. An excess of the solution was removed, then the wet sheets were washed successively with mixture of THF/water (1:1 v/v) (3 x 25 ml), THF (2 x 25 ml), blotted with dry filter paper and finally each sheet was immersed in the solution of appropriate carboxylic acid (10 mmol) in THF (25 ml) activated by treatment with solution of DMT/NMM/TosO⁻ (**8**) (4.13 g, 10 mmol) and NMM (0.33 ml, 3 mmol) at 0-5° C. The mixture was gently shaken at room temperature for 24 h. An excess of acylating reagent was removed and the cellulose was successively washed by gentle shaking in DMF (3 x 25 ml) and DCM (3 x 25 ml), then dried in vacuum desiccator affording cellulose *O*-acylated with Fmoc-Ala-OH (**18**), hexadecanoic acid (**19**), (*E*)-octadec-9-enoic acid (**20**), nonanoic acid (**21**), decanoic acid (**22**).

2.2. Cellulose 23, modified with 2,4-dichloro-6-methoxy-1,3,5-triazine (DCMT), *m*-phenylenediamine (**17**) and then *N*-acylated with hexadecanoic acid

The vigorously stirred solution of DMT/NMM/TosO⁻ (**8**) (4.13 g, 10 mmol) in DCM (25 ml) was cooled to 0-5° C, treated with hexadecanoic acid -(10 mmol) and NMM (0.33 ml, 3 mmol). Stirring was continued at 0-5°C for 4 h and one sheet of cellulose modified with 2,4-dichloro-6-methoxy-1,3,5-triazine (DCMT) and *m*-phenylenediamine (**17**) was immersed into

suspension and gently shaken at room temperature for 24 h. An excess of acylating reagent was removed and the cellulose was successively washed by gentle shaking in DMF (3 x 25 ml) and DCM (3 x 25 ml), then dried in vacuum desiccator affording **23** (**17** *N*-acylated with hexadecanoic acid).

2.3. **17** modified with *N*-acylated amino acids **24-32**

The Fmoc-protected amino acid (10.0 mmol), *N*-methyl-*N*-(4,6-dimethoxy-1,3,5 triazin-2-yl) morpholinium tetrafluoroborate (DMT/NMM/BF₄⁻), (3.28 g, 10 mmol) were dissolved in DMF (25 ml) and then NMM (2,2 ml, 20 mmol) was added. Functionalized cellulose sheets **17** were immersed in the mixture and gently shaken for 24 h. An excess of acylating reagent was removed, then sheets were successively washed by gentle shaking in DMF (3 x 25 ml) and DCM (3 x 15 ml), then dried in vacuum desiccator.

Fmoc-protecting group was removed by treatment with 25% solution of piperidine in DMF (10 ml) and gently shaken for 20 minutes, then washing with DMF (3 x 15 ml), DCM (1 x 15 ml). Aminoacylated **17** was immediately used in the next synthetic stage.

The second amino acid was incorporated as described above.

Acylation with carboxylic acids.

The vigorously stirred solution of DMT/NMM/TosO⁻ (**8**) (4.13 g, 10 mmol) in DCM (25 ml) was cooled to 0-5° C, treated with carboxylic acid (10 mmol) and NMM (0.55 ml, 5 mmol). Stirring was continued at 0-5°C for 4 h and **17** acylated with amino acids (peptides) were immersed into suspension and gently shaken at room temperature for 24 h. After this, the plates were soaked, washed with DCM (4 x 25 ml), DMF (2 x 25 ml) and DCM (2 x 25 ml) then soaked and dried in vacuum dessicator.

The procedure used for acylation gave **17** *N*-acylated with Fmoc-Ala-OH (**24**), **17** *N*-acylated with Fmoc-Phe-OH (**25**), **17** *N*-acylated with Fmoc-Pro-Ala-OH (**26**), **17** *N*-acylated with Boc-Gly-OH (**27**), **17** *N*-acylated with *N*'-decanoylo-Phe-OH (**28**), **17** *N*-acylated with *N*'-hexadecanoyl-Phe-OH (**29**), **17** *N*-acylated with *N*'-decanoyl-Ala-OH (**30**), **17** *N*-acylated with *N*'-decanoyl-Ala-Ala-OH (**31**), and **17** *N*-acylated with *N*'-decanoyl-Ala-Phe-OH (**32**).