Supporting information

Synthesis of γ -glutamyl derivatives of sulfur-containing amino acids in a multigram scale *via* a two-steps, one-pot procedure

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γ-glutamyl-S-methyl-L-cysteine 8

 $HO \xrightarrow{O}_{\frac{1}{N}H_2} O H_{\frac{1}{N}H_2} \xrightarrow{O}_{\frac{1}{N}} O H_{\frac{1}{N}} O H_{\frac{1}{N}}$

γ-glutamyl-S-allyl-L-cysteine 9

O N H о НО ÇOOH $\bar{N}H_2$

γ-glutamyl-S-benzyl-L-cysteine 10



γ-glutamyl-L-methionine 11

| • | S1.1A | ¹ H NMR (full spectrum) | | |
|---|-------|------------------------------------|--|--|
| | S1.1B | ¹ H NMR (excerpt) | | |
| | S1.2 | APT | | |
| | S1.3 | COSY | | |
| | S1.4 | HSQC | | |
| | S1.5 | HMBC | | |
| | S1.6A | ESI-MS (positive detection) | | |
| | S1.6B | ESI-MS (negative detection) | | |
| | S1.6C | ESI-MS/MS (positive detection) | | |
| | S1.6D | ESI-MS/MS (negative detection) | | |
| | S2.1A | ¹ H NMR (full spectrum) | | |
| | S2.1B | ¹ H NMR (excerpt) | | |
| | S2.2 | APT | | |
| | S2.3 | HSQC | | |
| | S2.4 | HMBC | | |
| | S2.5A | ESI-MS (positive detection) | | |
| | S2.5B | ESI-MS (negative detection) | | |
| | S2.5C | ESI-MS/MS (positive detection) | | |
| | S2.5D | ESI-MS/MS (negative detection) | | |
| | S3.1 | ¹ H NMR | | |
| | S3.2 | APT | | |
| | S3.3 | HSQC | | |
| | S3.4 | НМВС | | |
| | S3.5A | ESI-MS (positive detection) | | |
| | S3.5B | ESI-MS/MS (positive detection) | | |
| | S3.5C | ESI-MS/MS (positive detection) | | |
| | S4.1A | ¹ H NMR (full spectrum) | | |
| | S4.1B | ¹ H NMR (excerpt) | | |
| | S4.2 | APT | | |
| | S4.3 | COSY | | |
| | S4.4 | HSQC | | |
| | S4.5 | НМВС | | |
| | S4.6A | ESI-MS (positive detection) | | |
| | S4.6B | ESI-MS (negative detection) | | |
| | S4.6C | ESI-MS/MS (negative detection) | | |

S1.1A 1-H NMR of γ-glutamyl-S-methyl-L-cysteine 8



S1.1B 1-H NMR of γ-glutamyl-S-methyl-L-cysteine 8 (expansion 1.5 - 4.8 ppm) 4.395 4.374 4.374 4.352 4.352 -3.406 -3.390 -3.374 2.690 2.7124 2.7124 2.7124 -2.332 -2.312 -2.293 ~i-1.22 1.17 1.97 2.1 1.55 1.13 2.62

3.0

2.5

1.

2.0

3.5

4.0

4.5

ppm

S1.2 APT spectrum of γ-glutamyl-S-methyl-L-cysteine **8**

| 172.363 | | | 53.108 | |
|--|---------------------------------------|---------------------------------------|---|--|
| | | | | |
| &************************************* | ₽₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩ | ₽₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩ | orgeneziska, Algelander, hensperioren, medrander (Algelander), hensperioren anderen anderen anderen anderen and | м ¹ етория (¹ андатороди, 1944) |
| ppm | 150 | 100 | 50 | |









S1.6A ESI-MS spectrum of γ-glutamyI-S-methyI-L-cysteine **8** positive detection



S1.6B ESI-MS spectrum of γ-glutamyl-S-methyl-L-cysteine **8** negative detection



S1.6C

ESI-MS/MS spectrum of γ-glutamyl-S-methyl-L-cysteine **8**

positive detection



S1.6D

ESI-MS/MS spectrum of γ-glutamyl-S-methyl-L-cysteine **8**

negative detection













S2.5A ESI-MS spectrum of γ-glutamyl-S-allyl-L-cysteine **9** positive detection



S2.5B ESI-MS spectrum of γ-glutamyl-S-allyl-L-cysteine 9 negative detection



S2.5C ESI-MS/MS spectrum of γ-glutamyl-S-allyl-L-cysteine 9 positive detection



S2.5D

ESI-MS/MS spectrum of y-glutamyl-S-allyl-L-cysteine 9 negative detection











S3.5A ESI-MS spectrum of γ-glutamyl-S-benzyl-L-cysteine **10** positive detection

S3.5B ESI-MS spectrum of γ-glutamyl-S-benzyl-L-cysteine

10 negative detection

S3.5C

ESI-MS/MS spectrum of y-glutamyl-S-benzyl-L-cysteine

10 positive detection

S4.1A 1-H NMR spectrum of γ-glutamyl-L-methioine **11**

S4.6A ESI-MS spectrum of γ-glutamyl-L-methioine **11** positive detection

S4.6B ESI-MS spectrum of γ -glutamyl-L-methioine **11** negative detection

S4.6C ESI-MS/MS spectrum of γ-glutamyl-L-methioine **11** negative detection

