

## Supplementary data

### Development of amino acids functionalized SBA-15 for the improvement of protein adsorption

Raquel Gutiérrez-Climente<sup>1,2\*</sup>, Margaux Clavié<sup>2†</sup>, Jérémie Gouyon<sup>2</sup>, Giang Ngo<sup>3</sup>, Yoann Ladner<sup>2</sup>, Pascal Etienne<sup>4</sup>, Pascal Dumy<sup>2</sup>, Pierre Martineau<sup>3</sup>, Martine Pugnière<sup>3</sup>, Catherine Perrin<sup>2</sup>, Gilles Subra<sup>2\*</sup>, Ahmad Mehdi<sup>1\*</sup>

<sup>1</sup> ICGM, Univ. Montpellier, CNRS, ENSCM, 34000 Montpellier, France

<sup>2</sup> IBMM, Univ. Montpellier, CNRS, ENSCM, 34000 Montpellier, France; [margaux.clavie@umontpellier.fr](mailto:margaux.clavie@umontpellier.fr) (M.C.); [jeremie.gouyon@univ-lorraine.fr](mailto:jeremie.gouyon@univ-lorraine.fr) (J.G.); [yoann.ladner@umontpellier.fr](mailto:yoann.ladner@umontpellier.fr) (Y.L.); [Pascal.Dumy@enscm.fr](mailto:Pascal.Dumy@enscm.fr) (P.D.); [catherine.perrin@umontpellier.fr](mailto:catherine.perrin@umontpellier.fr) (C.P.)

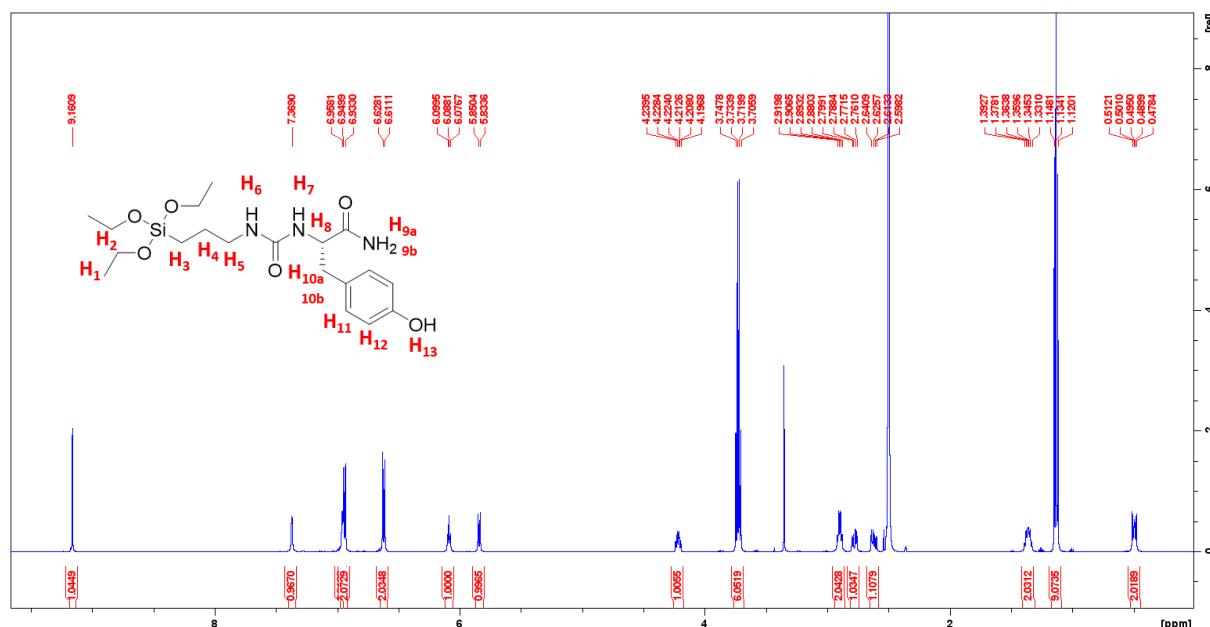
<sup>3</sup> IRCM, Univ. Montpellier, Inserm, ICM, 34000 Montpellier, France; [thi-hong-giang.ngo@inserm.fr](mailto:thi-hong-giang.ngo@inserm.fr) (G.N.); [pierre.martineau@inserm.fr](mailto:pierre.martineau@inserm.fr) (P.M.); [martine.pugniere@inserm.fr](mailto:martine.pugniere@inserm.fr) (M.P.)

<sup>4</sup> I2C, Univ. Montpellier, CNRS, ENSCM, 34000 Montpellier, France; [pascal.etienne@umontpellier.fr](mailto:pascal.etienne@umontpellier.fr)

\* Correspondence: [raquel.gutierrez-climente@enscm.fr](mailto:raquel.gutierrez-climente@enscm.fr) (R.G.-C.); [gilles.subra@umontpellier.fr](mailto:gilles.subra@umontpellier.fr) (G.S.); [ahmad.mehdi@umontpellier.fr](mailto:ahmad.mehdi@umontpellier.fr) (A.M.)

† These two authors contributed equally to the work.

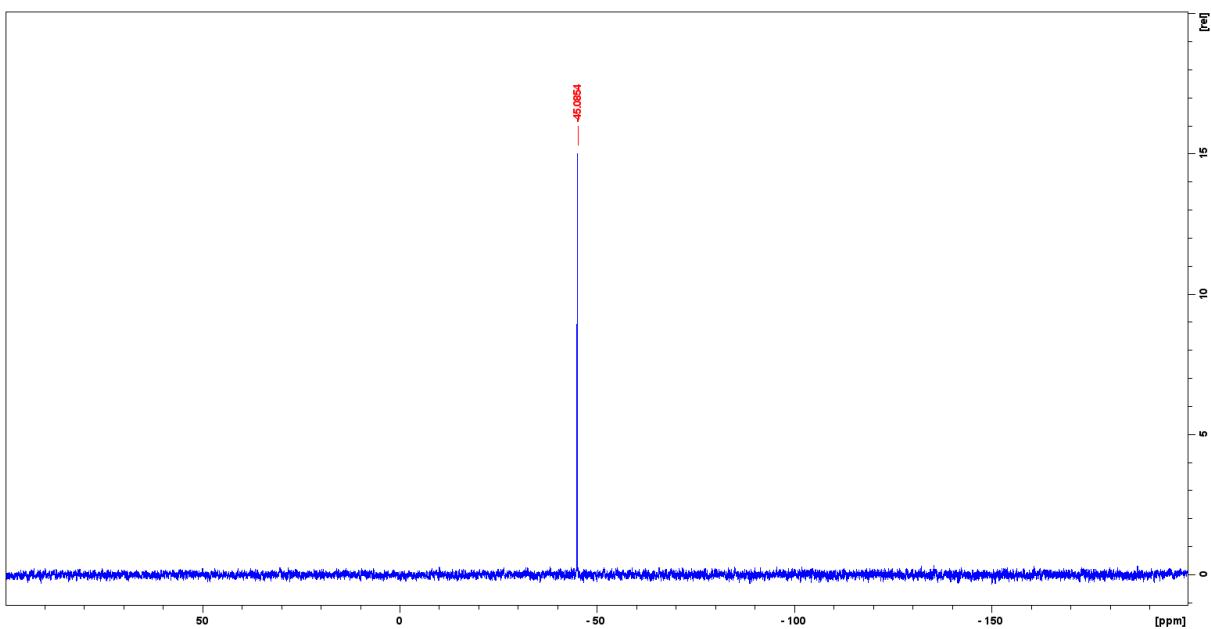
#### Compound 1:



**Figure S1.** <sup>1</sup>H NMR spectra of silylated tyrosinamide using DIEA as base

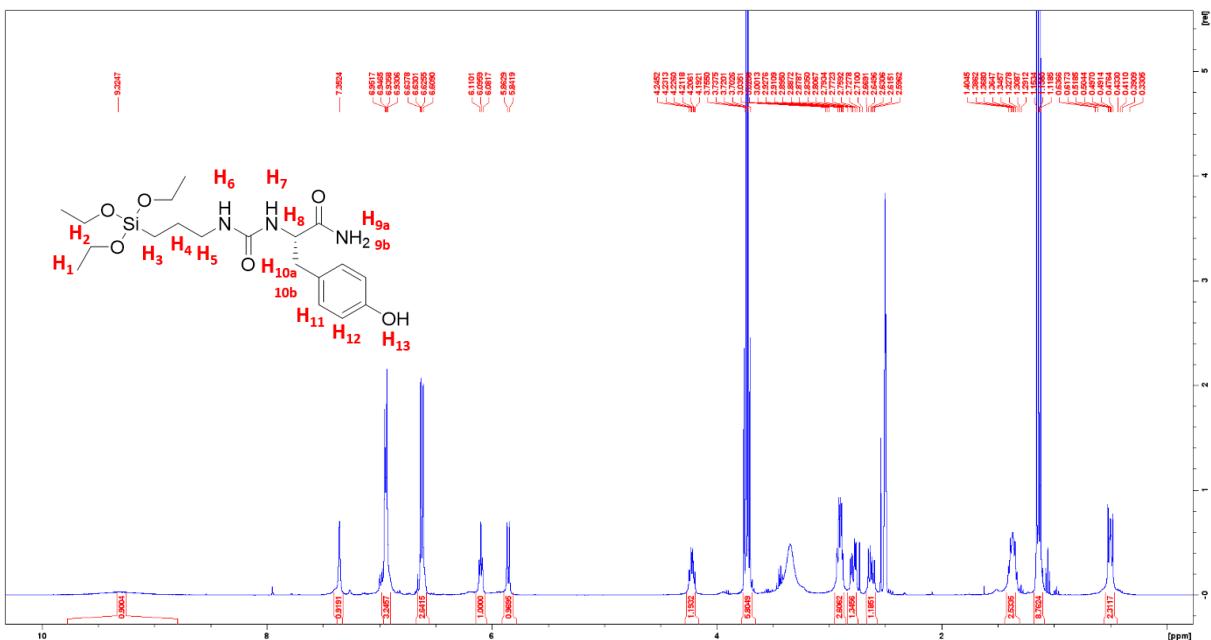
<sup>1</sup>H NMR (500MHz, DMSO-d<sub>6</sub>, 25°C):  $\delta$ (ppm) 0.49 (m, 2H, H<sub>3</sub>) ; 1.13 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.36 (m, 2H, H<sub>4</sub>) ; 2.62 (dd, 1H, J = 7.5 Hz, 13.8 Hz, H<sub>10a</sub>) ; 2.78 (dd, 1H, J = 5.3 Hz, 13.8 Hz, H<sub>10b</sub>) ; 2.90 (q, 2H, J = 6.4 Hz, H<sub>5</sub>) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.22 (m, 1H, H<sub>8</sub>) ; 5.84 (d, 1H, J = 8.2 Hz, H<sub>7</sub>) ; 6.09 (t, 1H, J = 5.4 Hz, H<sub>6</sub>) ; 6.62 (d, 2H, J = 8.5 Hz, H<sub>11</sub>) ; 6.94 (d, 2H, J = 8.4 Hz, H<sub>12</sub>) ; 6.96 (s, 1H, H<sub>9a</sub>) ; 7.37 (s, 1H, H<sub>9b</sub>) ; 9.16 (s, 1H, H<sub>13</sub>).

Residual DIEA: 0%



**Figure S2.**  $^{29}\text{Si}$  NMR spectra of silylated tyrosinamide using DIEA as base

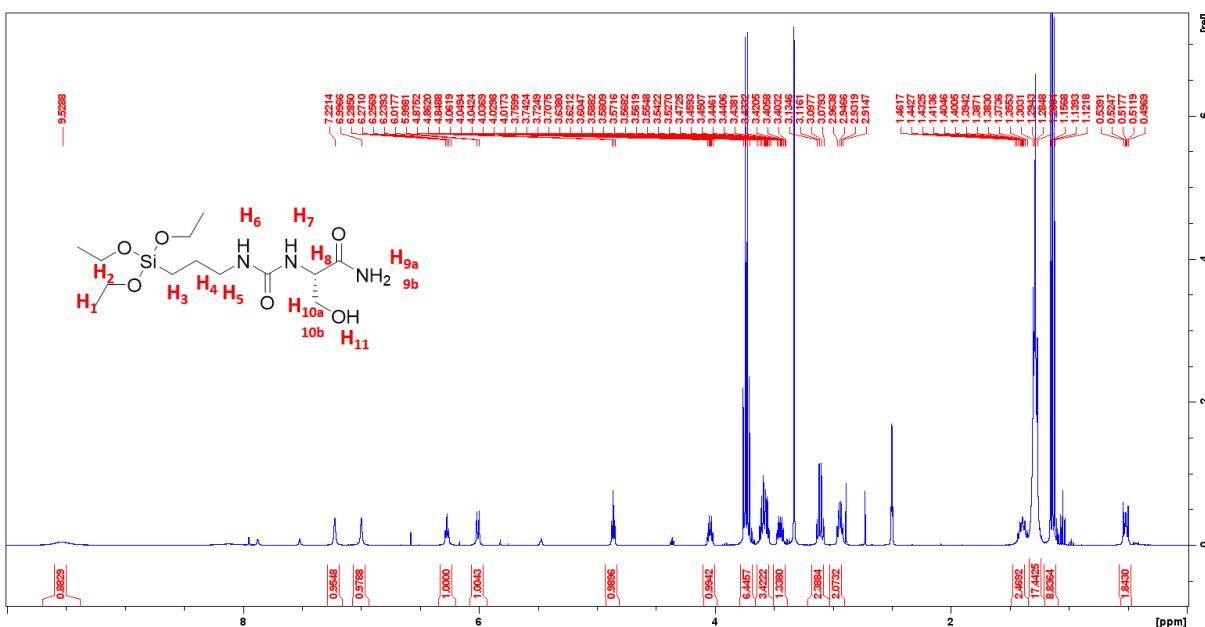
$^{29}\text{Si}$  NMR (99.4MHz, DMSO-d<sub>6</sub>, 25°C):  $\delta$ (ppm) -45.0



**Figure S3.**  $^1\text{H}$  NMR spectra of silylated tyrosinamide using NaHCO<sub>3</sub> as base

$^1\text{H}$  RMN (500MHz, DMSO-d<sub>6</sub>, 25°C):  $\delta$ (ppm) 0.49 (m, 2H, H<sub>3</sub>) ; 1.13 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.36 (m, 2H, H<sub>4</sub>) ; 2.62 (dd, 1H, J = 7.5 Hz, 13.8 Hz, H<sub>10a</sub>) ; 2.78 (dd, 1H, J = 5.3 Hz, 13.8 Hz, H<sub>10b</sub>) ; 2.90 (q, 2H, J = 6.4 Hz, H<sub>5</sub>) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.22 (m, 1H, H<sub>8</sub>) ; 5.84 (d, 1H, J = 8.2 Hz, H<sub>7</sub>) ; 6.09 (t, 1H, J = 5.4 Hz, H<sub>6</sub>) ; 6.62 (d, 2H, J = 8.5 Hz, H<sub>11</sub>) ; 6.94 (d, 2H, J = 8.4 Hz, H<sub>12</sub>) ; 6.96 (s, 1H, H<sub>9a</sub>) ; 7.35 (s, 1H, H<sub>9b</sub>).

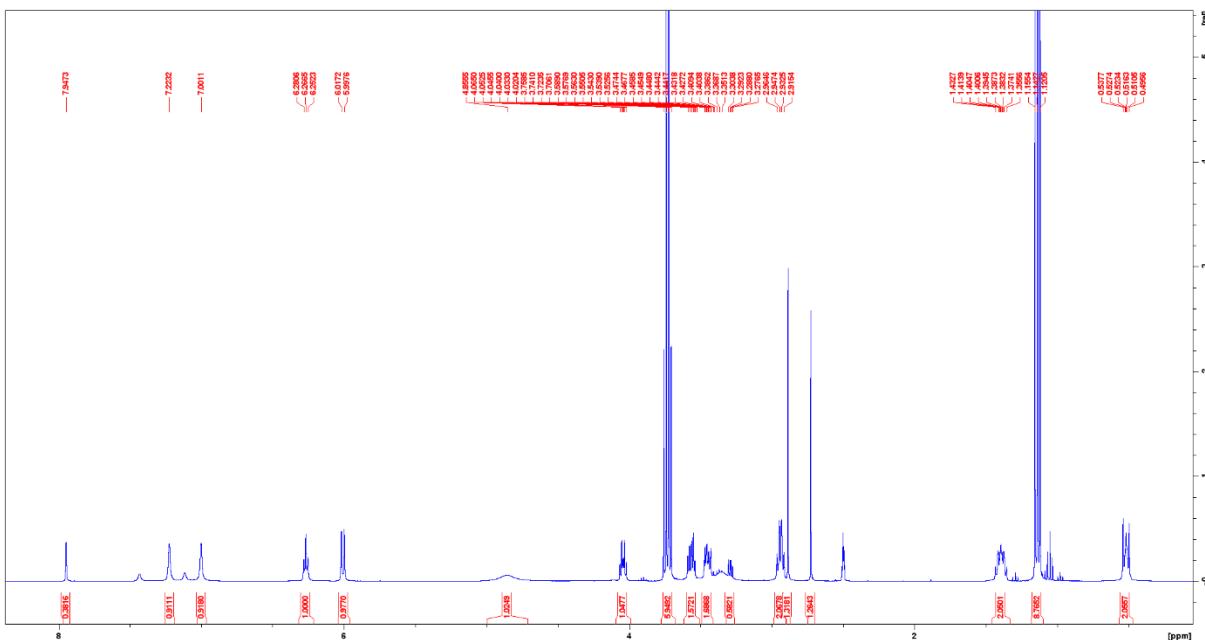
**Compound 2:**



**Figure S4.** <sup>1</sup>H NMR spectra of silylated serinamide using DIEA as base

<sup>1</sup>H RMN (500MHz, DMSO-d6, 25°C): δ(ppm) 0.52 (m, 2H, H<sub>3</sub>) ; 1.14 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.28 (m, 17H, CH<sub>3</sub> DIEA) ; 1.39 (m, 2H, H<sub>4</sub>) ; 2.94 (q, 2H, J = 7.0 Hz, H<sub>5</sub>) ; 3.10 (q, 3H, J = 7.5 Hz, CH<sub>2</sub> DIEA) ; 3.45 (m, 1H, H<sub>10a</sub>) ; 3.58 (m, 3H, H<sub>10b</sub> + 2CH DIEA) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.04 (m, 1H, H<sub>8</sub>) ; 4.86 (t, 1H, J = 5.3 Hz, H<sub>11</sub>) ; 6.00 (d, 1H, J = 7.8 Hz, H<sub>7</sub>) ; 6.27 (t, 1H, J = 5.5 Hz, H<sub>6</sub>) ; 6.99 (s, 1H, H<sub>9a</sub>) ; 7.22 (s, 1H, H<sub>9b</sub>) ; 9.52 (s, 1H, NH<sup>+</sup> DIEA).

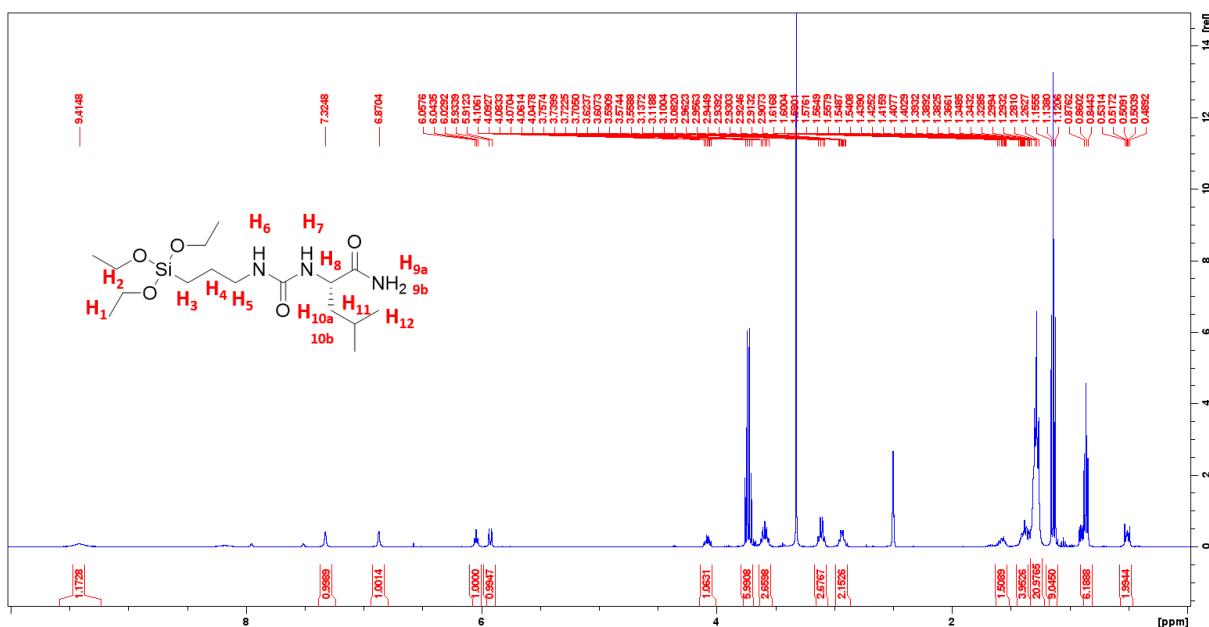
Residual DIEA: 25%



**Figure S5.** <sup>1</sup>H NMR spectra of silylated serinamide using NaHCO<sub>3</sub> as base

<sup>1</sup>H RMN (500MHz, DMSO-d6, 25°C): δ(ppm) 0.52 (m, 2H, H<sub>3</sub>) ; 1.14 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.39 (m, 2H, H<sub>4</sub>) ; 2.94 (q, 2H, J = 7.0 Hz, H<sub>5</sub>) ; 3.45 (m, 1H, H<sub>10a</sub>) ; 3.58 (m, 3H, H<sub>10b</sub> + 2CH DIEA) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.04 (m, 1H, H<sub>8</sub>) ; 4.86 (s, 1H, H<sub>11</sub>) ; 6.00 (d, 1H, J = 7.8 Hz, H<sub>7</sub>) ; 6.27 (t, 1H, J = 5.5 Hz, H<sub>6</sub>) ; 6.99 (s, 1H, H<sub>9a</sub>) ; 7.22 (s, 1H, H<sub>9b</sub>).

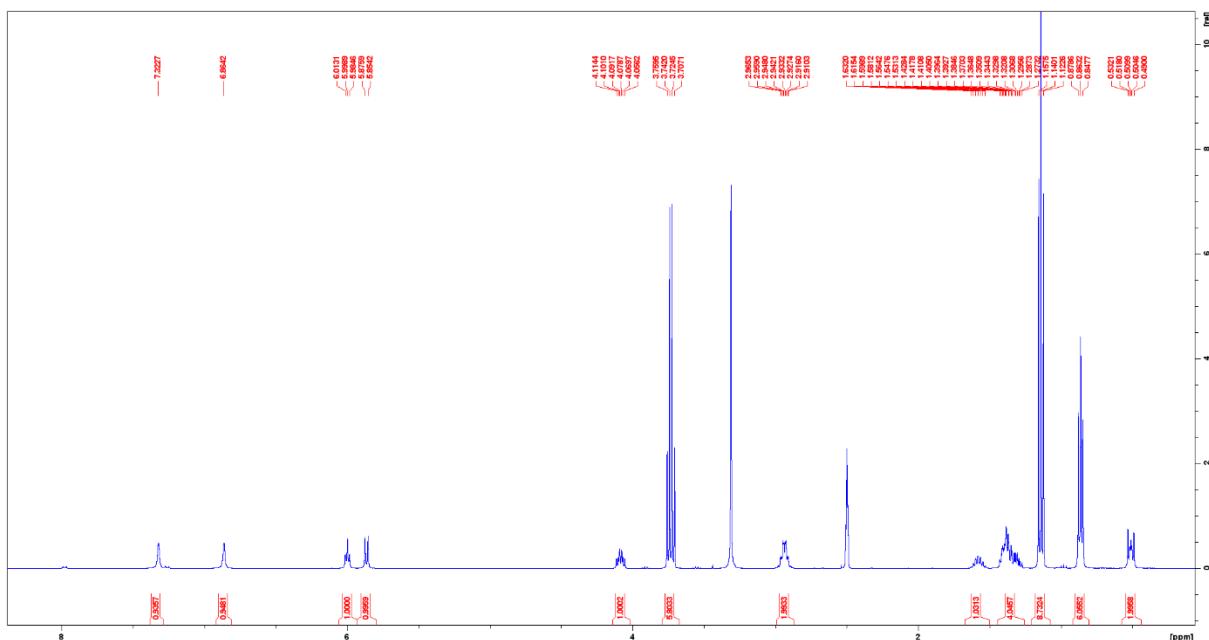
### Compound 3:



**Figure S6.**  $^1\text{H}$  NMR spectra of silylated leucinamide using DIEA as base

<sup>1</sup>H RMN (500MHz, DMSO-d6, 25°C): δ(ppm) 0.50 (m, 2H, H<sub>3</sub>) ; 0.86 (t, 6H, J = 6.5 Hz, H<sub>12</sub>) ; 1.14 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.28 (m, 20H, CH<sub>3</sub> DIEA – H<sub>10a</sub> – H<sub>10b</sub>) ; 1.38 (m, 2H, H<sub>4</sub>) ; 1.57 (m, 1H, H<sub>11</sub>) ; 2.93 (m, 2H, H<sub>5</sub>) ; 3.11 (m, 3H, CH<sub>2</sub> DIEA) ; 3.59 (m, 3H, 2CH DIEA) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.07 (m, 1H, H<sub>8</sub>) ; 5.92 (d, 1H, J = 8.6 Hz, H<sub>7</sub>) ; 6.04 (t, 1H, J = 5.8 Hz, H<sub>6</sub>) ; 6.87 (s, 1H, H<sub>9a</sub>) ; 7.32 (s, 1H, H<sub>9b</sub>) ; 9.41 (s, 1H, NH<sup>+</sup> DIEA).

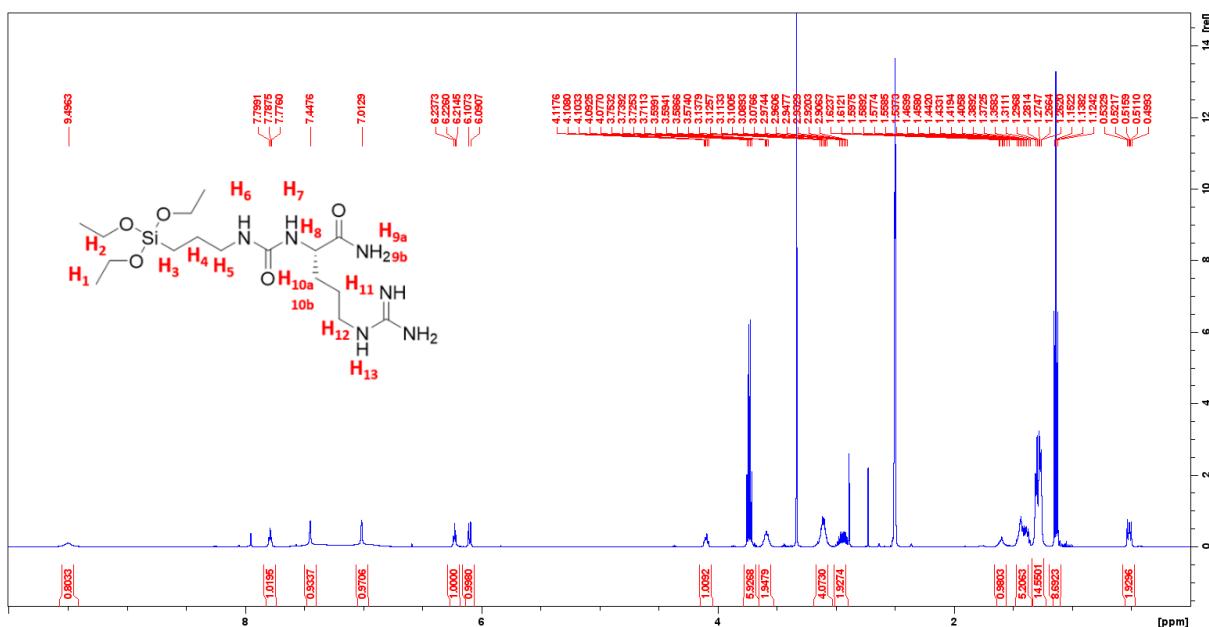
Residual DIEA: 57%



**Figure S7.**  $^1\text{H}$  NMR spectra of silylated leucinamide using  $\text{NaHCO}_3$  as base

<sup>1</sup>H RMN (500MHz, DMSO-d6, 25°C): δ(ppm) 0.50 (m, 2H, H<sub>3</sub>) ; 0.86 (t, 6H, J = 6.5 Hz, H<sub>12</sub>) ; 1.14 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.28-1.42 (m, H<sub>4</sub> - H<sub>10a</sub> - H<sub>10b</sub>) ; 1.57 (m, 1H, H<sub>11</sub>) ; 2.93 (m, 2H, H<sub>5</sub>) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.07 (m, 1H, H<sub>8</sub>) ; 5.92 (d, 1H, J = 8.6 Hz, H<sub>7</sub>) ; 6.04 (t, 1H, J = 5.8 Hz, H<sub>6</sub>) ; 6.87 (s, 1H, H<sub>9a</sub>) ; 7.32 (s, 1H, H<sub>9b</sub>).

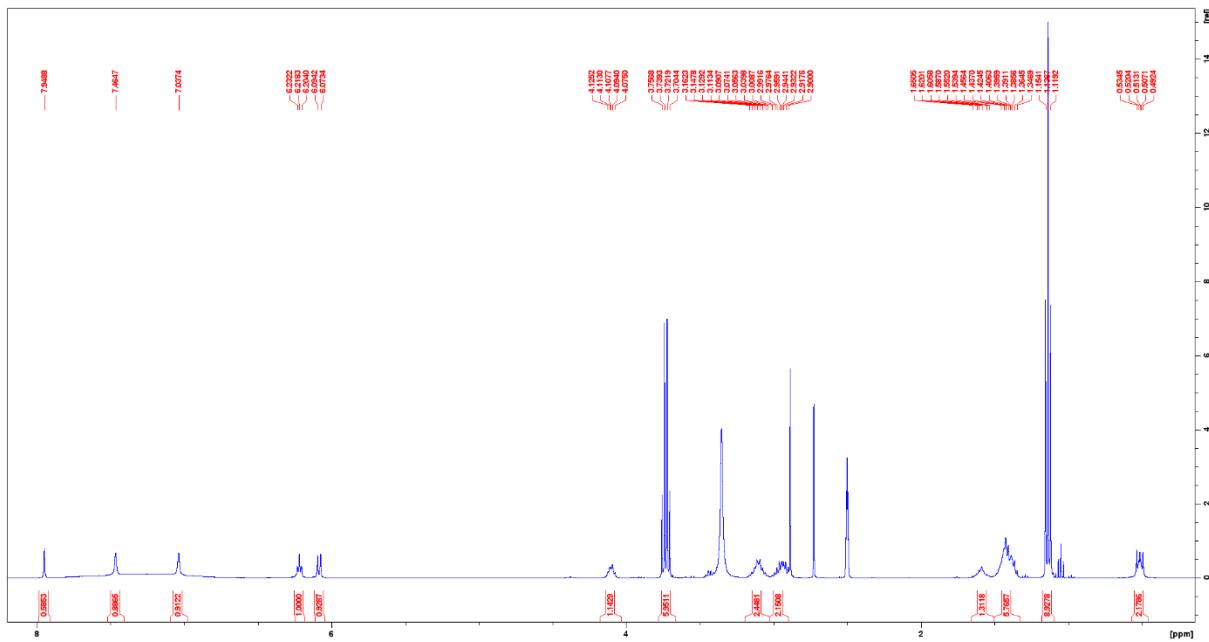
## Compound 4:



**Figure S8.**  $^1\text{H}$  NMR spectra of silylated argininamide using DIEA as base

<sup>1</sup>H RMN (500MHz, DMSO-d<sub>6</sub>, 25°C): δ(ppm) 0.52 (m, 2H, H<sub>3</sub>) ; 1.14 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.28 (m, 15H, CH<sub>3</sub> DIEA) ; 1.41 (m, 5H, H<sub>10a</sub> - H<sub>10b</sub> - H<sub>4</sub>) ; 1.59 (m, 1H, H<sub>12</sub>) ; 2.94 (m, 2H, H<sub>5</sub>) ; 3.10 (m, 4H, CH<sub>2</sub> DIEA - H<sub>11</sub>) ; 3.59 (m, 2H, 2CH DIEA) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.10 (m, 1H, H<sub>8</sub>) ; 6.10 (d, 1H, J = 7.8 Hz, H<sub>7</sub>) ; 6.22 (t, 1H, J = 5.5 Hz, H<sub>6</sub>) ; 7.01 (s, 1H, H<sub>9a</sub>) ; 7.45 (s, 1H, H<sub>9b</sub>) ; 7.78 (t, 1H, J = 5.8 Hz, H<sub>13</sub>) ; 9.49 (s, 1H, NH<sup>+</sup> DIEA).

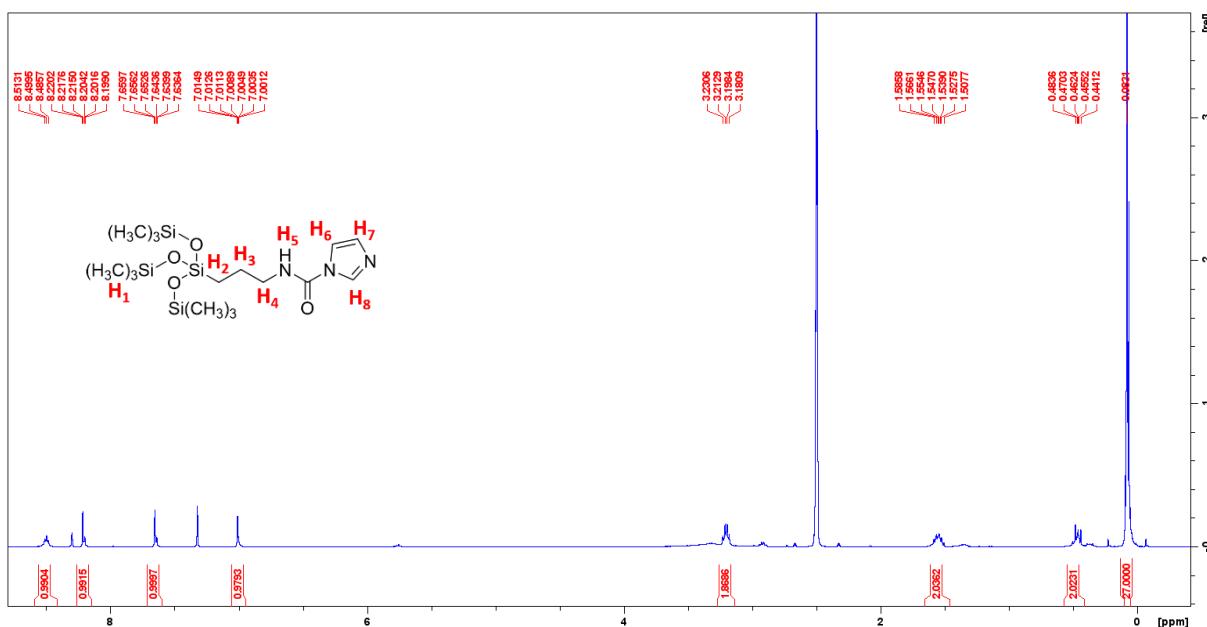
Residual DIEA: 50%



**Figure S9.**  $^1\text{H}$  NMR spectra of silylated serinamide using  $\text{NaHCO}_3$  as base

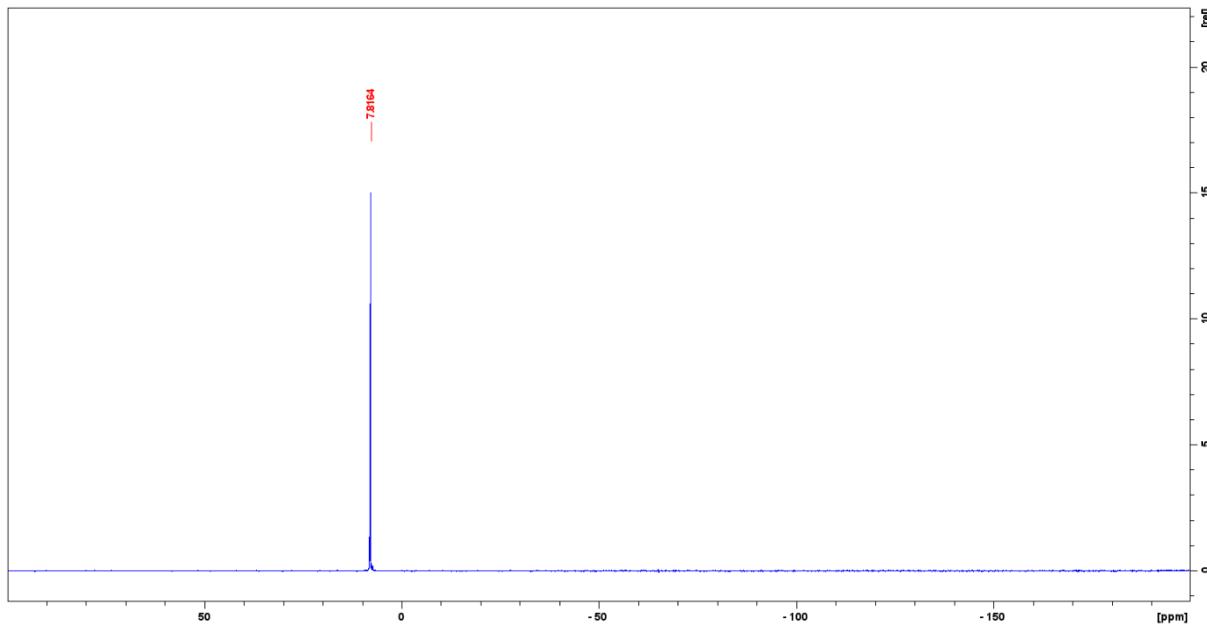
<sup>1</sup>H RMN (500MHz, DMSO-d<sub>6</sub>, 25°C): δ(ppm) 0.52 (m, 2H, H<sub>3</sub>) ; 1.14 (t, 9H, J = 7.0 Hz, H<sub>1</sub>) ; 1.41 (m, 5H, H<sub>10a</sub> - H<sub>10b</sub> - H<sub>4</sub>) ; 1.59 (m, 1H, H<sub>12</sub>) ; 2.94 (m, 2H, H<sub>5</sub>) ; 3.10 (m, 2H, H<sub>11</sub>) ; 3.73 (q, 6H, J = 7.0 Hz, H<sub>2</sub>) ; 4.10 (m, 1H, H<sub>8</sub>) ; 6.10 (d, 1H, J = 7.8 Hz, H<sub>7</sub>) ; 6.22 (t, 1H, J = 5.5 Hz, H<sub>6</sub>) ; 7.01 (s, 1H, H<sub>9a</sub>) ; 7.45 (s, 1H, H<sub>9b</sub>).

**Compound 5:**



**Figure S10.** <sup>1</sup>H NMR spectra of the synthesis of N-[3-tris(trimethylsiloxy)silylpropyl]-imidazole-1-carboxamide

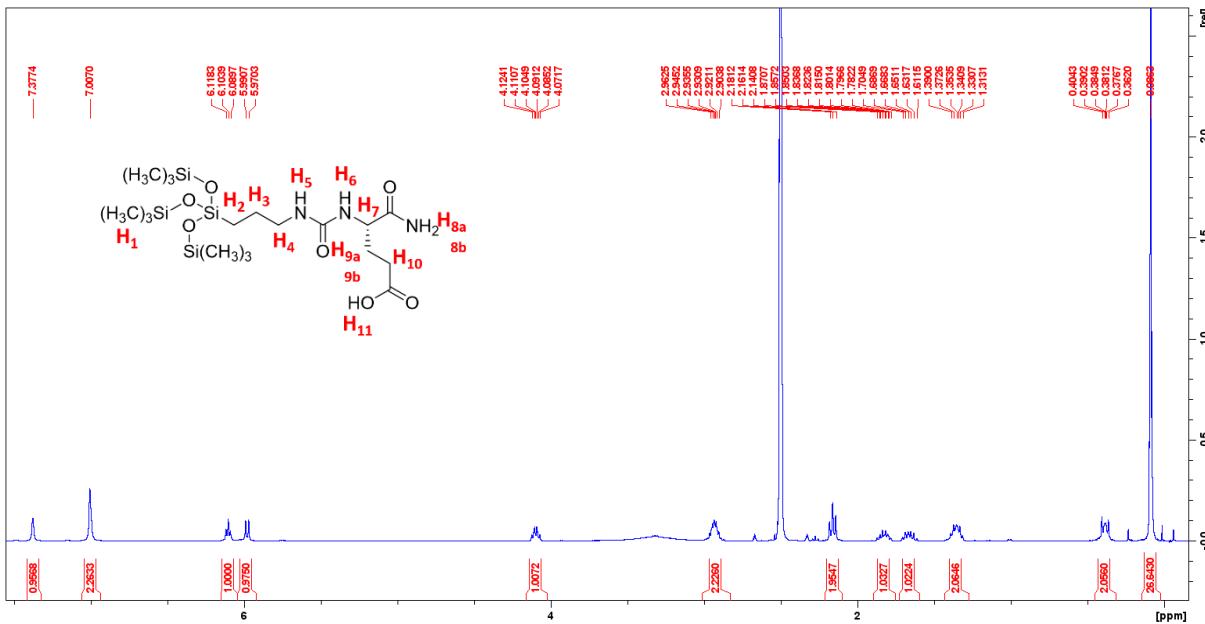
<sup>1</sup>H RMN (500MHz, DMSO-d<sub>6</sub>, 25°C): δ(ppm) 0.08 (s, 27H, H<sub>1</sub>) ; 0.46 (m, 2H, H<sub>2</sub>) ; 1.55 (3, 2H, H<sub>3</sub>) ; 3.20 (q, 2H, J = 5.8 Hz, H<sub>4</sub>) ; 7.01 (m, 1H, H<sub>8</sub>) ; 7.38 (s, 0.8H, traces of CDI) ; 7.66 (t, 1H, J = 1.5 Hz, H<sub>7</sub>) ; 8.21 (t, 1H, J = 1.1 Hz, H<sub>6</sub>) ; 8.30 (s, 0.4H, traces of CDI) ; 8.50 (t, 1H, J = 5.5 Hz, H<sub>5</sub>).



**Figure S11.** <sup>29</sup>Si NMR spectra of the synthesis of N-[3-tris(trimethylsiloxy)silylpropyl]-imidazole-1-carboxamide

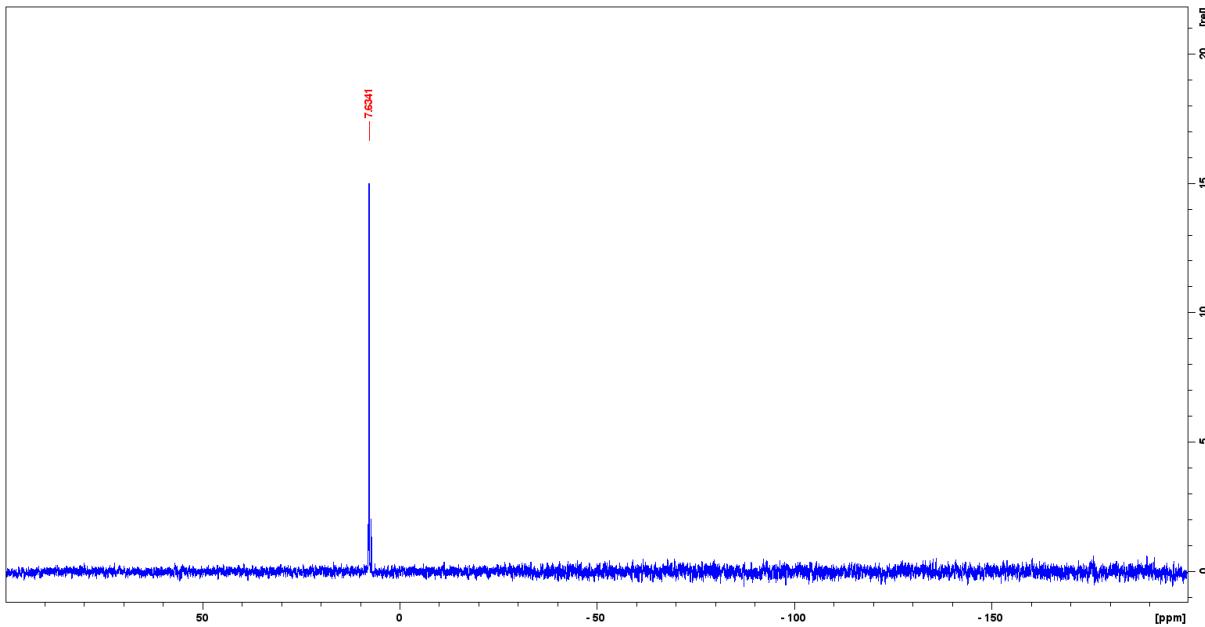
<sup>29</sup>Si RMN (99.4MHz, DMSO-d<sub>6</sub>, 25°C): δ(ppm) 7.81

## Compound 6:



**Figure S12.**  $^1\text{H}$  NMR spectra of silylated isoglutamine

<sup>1</sup>H RMN (500MHz, DMSO-d6, 25°C): δ(ppm) 0.08 (m, 2H, H<sub>1</sub>) ; 0.38 (m, 2H, H<sub>2</sub>) ; 1.35 (m, 2H, H<sub>3</sub>) ; 1.66 (m, 1H, H<sub>9a</sub>) ; 1.66 (m, 1H, H<sub>9b</sub>) ; 2.16 (t, 2H, J = 8.0 Hz, H<sub>10</sub>) ; 2.93 (m, 2H, H<sub>4</sub>) ; 4.09 (m, 1H, H<sub>7</sub>) ; 5.98 (d, 1H, J = 8.0 Hz, H<sub>6</sub>) ; 6.10 (t, 1H, J = 5.6 Hz, H<sub>7</sub>) ; 7.00 (s, 2H, H<sub>8a</sub> – H<sub>11</sub>) ; 7.37 (s, 1H, H<sub>8b</sub>).



**Figure S13.**  $^{29}\text{Si}$  NMR spectra of silylated isoglutamine

<sup>29</sup>Si RMN (99.4MHz, DMSO-d<sub>6</sub>, 25°C): δ(ppm) 7.63