Supporting Information for Angew. Chem. Int. Ed.

Non-peptidic $\alpha_v\beta_3$ Integrin Antagonist Libraries: On-bead Screening and Mass Spectrometric Identification without Tagging

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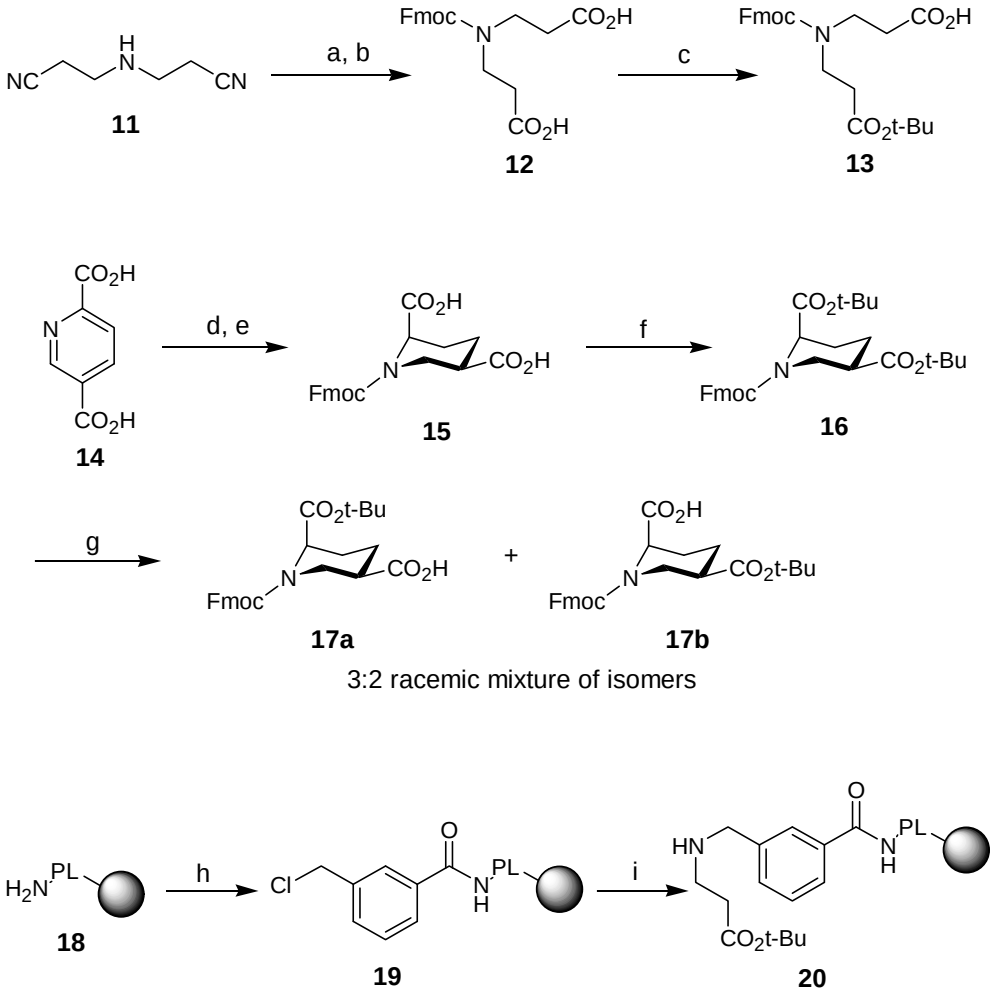

a) $Ba(OH)_2$, H_2O, 70 °C, 16 h, 70%; b) FmocCl (1.0 equiv), Na_2CO_3 (3.0 equiv), H_2O/dioxane, 0 °C → RT, 5 h, 63%; c) $Cl_3C(C{=}NH)O$*t*Bu (4.9 equiv), CH_2Cl_2/DMF, RT, 24 h, 49%; d) H_2, PdO_2 (0.05 equiv), 13% HCl in H_2O, 3 d, quant.; e) FmocCl (1.0 equiv), Na_2CO_3 (3.0 equiv), H_2O/dioxane, 0 °C → RT, 15 h, 66%; f) $Cl_3C(C{=}NH)O$*t*Bu (6.6 equiv), CH_2Cl_2/DMF, RT, 4 d, 87%; g) 5 Vol-% TFA, CH_2Cl_2, RT, 10 h, 54%; h) 3-(chloromethyl)benzoylchloride (6.8 equiv), DIEA (14 equiv), CH_2Cl_2, RT, 75 min; i) *tert*-butyl-3-aminopropionate (150 equiv), DMF, 45 °C, 12 h, 91% purity (HPLC, 220 nm).

General. Reactions on solid supports were performed in syringes with a fritted disc (2, 5 or 10 mL) from Vetter-Laborbedarf, Tübingen, Germany. Melting points were uncorrected. ^{1}H

and ^{13}C NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 as the solvent and internal reference. Thin layer chromatography was performed on silica gel 60 F_{254} plates from Merck. Flash chromatography was performed on silica gel 60 (230-400 mesh ASTM) from Merck. Analytical HPLC analyses were performed on a YMC column, 4.6 mm × 25 mm, 5 μm C_{18}, 1 mL/min, 30 min linear gradient from H_2O (0.1% TFA) and CH_3CN (0.1% TFA), 220 nm. Mass spectra were obtained on a LCQ Finnigan mass spectrometer.

Compound 12: Diammonium 3,3-Iminodipropanoate[1] (3.0 g, 15 mmol) and Na_2CO_3 (4.8 g, 45 mmol) were dissolved in H_2O (50 mL) followed by evaporation of the H_2O. The residue was resolved in a mixture of H_2O (30 mL) and dioxane (17 mL). A solution of FmocCl (3.9 g, 15 mmol) was added to the stirring reaction mixture at 0 °C. The temperature was kept at 0 °C for 15 min, after which time the reaction mixture was allowed to warm to room temperature and stirred for 5 h. The reaction mixture was diluted with H_2O (500 mL) and extracted with Et_2O (3 × 100 mL). The aqueous layer was acidified with conc. HCl to pH 1. The precipitate was collected by filtration, washed thoroughly with H_2O, and dried in *vacuo* to yield compound **12** (3.6 g, 63%) as a white solid: mp: 140 °C; ^1H NMR (250 MHz, DMSO): δ = 12.2 (s, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 2H), 4.54-4.18 (m, 3H), 3.31 (br s, 4H), 2.20 (br s, 2H), 1.94 (br s, 2H); ^{13}C NMR (DMSO, 125.0 MHz): δ = 172.7, 154.9, 143.9, 140.8, 127.6, 127.0, 124.8, 120.1, 66.5, 46.7, 43.7, 43.2, 33.1, 32.7; HPLC (10-90% within 30 min) R_t = 18.6 min; ESI-MS: *m/z* 805.0 (100) [$2M + K^+$], 789.9 (60) [$2M + Na^+$], 422.1 (10) [$M + K^+$], 406.1 (10) [$M + Na^+$], 383.9 (10) [$M + H^+$].

Compound 13: *tert*-Butyl 2,2,2-trichloroethanimidoate (8.0 mL, 9.6 g, 45 mmol) was added to a solution of compound **12** (3.55 g, 9.27 mmol) in anhydrous CH_2Cl_2 (40 mL) and DMF (4 mL) at room temperature. After stirring for 24 h the solvent was removed under reduced pressure. Compound **13** (1.99 g, 49%) was isolated by flash chromatography as a yellow solid: mp: 98 °C; ^1H NMR (250 MHz, DMSO): δ = 7.86 (d, *J* = 7.0 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 4.48-3.41 (m, 2H), 4.27 (t, *J* = 5.8 Hz, 1H), 3.42-3.08 (m, 4H), 2.44-2.02 (m, 4H), 1.37 (br. s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 176.2, 170.8, 155.8, 143.9, 141.3, 127.6, 127.0, 124.8, 119.9, 80.8, 67.1, 47.2, 44.3, 43.7, 34.7, 34.4, 33.5, 28.0; HPLC (10-90% within 30 min) R_t = 26.5 min; ESI-MS: *m/z* 916.9 (90) [$2M + K^+$], 900.9 (40) [$2M + Na^+$], 462.0 (100) [$M + Na^+$].

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[1] P. R. Ashton, S. E. Boyd, C. L. Brown, N. Jayaraman, S. A. Nepogodiev, F. Stoddart, *Chem. Eur. J.* **1996**, *2*, 1115-1128

Compound 15: The transformation of *rac-cis*-Piperidine-2,5-dicarboxylic acid[2] (2.70 g, 15.6 mmol) according to the procedure described above and isolation by flash chromatography yielded compound **15** (4.08 g, 66%) as a white solid: mp: 180-183 °C; ^{1}H NMR (250 MHz, DMSO, 300 K): δ = 12.73 (br s, 2H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.68-7.54 (m, 2H), 7.47-7.24 (m, 4H), 4.68 (br d, *J* = 4.6 Hz, 0.5H), 4.63 (br d, *J* = 4.8 Hz, 0.5H), 4.45-4.18 (m, 3H), 4.10 (m_c, 1H), 2.99 and 2.84 (2 × t, *J* = 12.7 Hz, 1H), 2.32 (m_c, 1H), 2.21-2.07 (m, 1H), 1.99-1.86 (m, 1H), 1.62 (m_c, 1H), 1.34-1.12 (m, 1H); ^{13}C NMR (62.5 MHz, DMSO, 300 K): δ = 174.1, 172.2, 155.2, 155.0, 143.8, 143.1, 140.7, 127.7, 127.1, 125.0, 120.1, 67.1, 53.4, 53.1, 46.6, 42.6, 42.5, 25.5, 25.3, 23.7; HPLC (10-90% within 30 min) R_t = 20.8 min; ESI-MS: *m/z* 829.0 (100) [2*M* + K^+], 812.9 (80) [2*M* + Na^+], 418.1 (60) [*M* + Na^+], 395.9 (15) [*M* + H^+].

Compound 16: The transformation of compound **15** (3.0 g, 7.6 mmol) according to the procedure described above and isolation by flash chromatography yielded compound **16** (3.37 g, 87%) as a colorless oil: ^{1}H NMR (250 MHz, DMSO, 300 K): δ = 7.88 (d, *J* = 7.4 Hz, 2H), 7.67-7.53 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36-7.24 (m, 2H), 4.59 (br d, *J* = 4.3 Hz, 0.5H), 4.51 (br d, *J* = 4.9 Hz, 0.5H), 4.48-4.19 (m, 3H), 4.08 (br d, *J* = 12.7 Hz, 0.5H), 3.91 (br d, *J* = 12.0 Hz, 0.5H), 2.85 (t, *J* = 12.6 Hz, 0.5H), 2.78 (t, *J* = 12.8 Hz, 0.5H), 2.39-2.14 (m, 1H), 2.14-2.01 (m, 1H), 1.94-1.78 (m, 1H), 1.68-1.49 (m, 1H), 1.38 (br s, 18H), 1.26-1.05 (m, 1H); ^{13}C NMR (62.5 MHz, DMSO, 300 K): δ = 169.8, 167.9, 153.4, 153.2, 142.0, 141.8, 138.9, 125.9, 125.2, 123.1, 118.3, 79.7, 79.5, 78.4, 65.3, 65.0, 51.9, 51.7, 44.8, 39.1, 25.8, 23.6, 21.6; HPLC (10-90% within 30 min) R_t = 36.7 min; ESI-MS: *m/z* 530.1 (100) [*M* + Na^+].

Compound 17a and 17b: TFA (8.0 mL) was added to a solution of Compound **16** (3.37 g, 6.64 mmol) in CH_2Cl_2 (150 mL). After stirring for 10 h at room temperature the reaction was stopped by the addition of a saturated aqueous solution of $NaHCO_3$ (40 mL). The pH was adjusted to 6 by the addition of solid $NHCO_3$. The organic layer was separated and the solvent was removed under reduced pressure. Isolation by flash chromatography yielded compound 1**7a** and 1**7b** (1.61 g, 54%; 62:38 mixture of isomers) as a colorless oil.

Separation of the isomers **17a** and **17b** (394 mg) by HPLC (90% CH_3CN in H_2O) yielded pure **17a** (209 mg, 53%) as a white solid and **17b** (150 mg, 38%) as a colorless oil.

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[2] L. I. Mastafanova, K. F. Turchin, M. I. Evstratova, Y. N. Sheinker, L. N. Yakhontov, *Chem. Heterocycl. Compd.* **1985**, *21*, 305-309.

Compound 17a: mp: 124 °C; ^{1}H NMR (500 MHz, DMSO, 300 K): δ = 7.88 (d, *J* = 7.5 Hz, 2H), 7.66-7.54 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.35-7.25 (m, 2H), 4.63 (br d, *J* = 5.0 Hz, 0.5H), 4.50 (br d, *J* = 4.8 Hz, 0.5H), 4.42-4.20 (m, 3H), 4.15-4.02 (m, 1H), 2.96 (t, *J* = 12.7 Hz, 0.5H), 2.80 (t, *J* = 12.7 Hz, 0.5H), 2.32 (m_c, 1H), 2.10 (m_c, 1H), 1.92 (m_c, 1H), 1.61 (m_c, 1H), 1.39 und 1.38 (2 × s, 9H), 1.27-1.12 (m, 1H); ^{13}C NMR (125 MHz, DMSO, 300 K): δ = 173.9, 169.7, 155.2, 155, 143.7, 140.7, 127.6, 127.0, 124.8, 120.1, 81.4, 81.3, 67.0, 53.7, 53.5, 46.6, 42.5, 42.4, 39.6, 39.4, 27.5, 25.5, 23.4, 23.3; HPLC (10-90% within 30 min) R_t = 29.8 min; ESI-MS: *m/z* 941.0 (50) [2*M* + K^+], 924.9 (15) [2*M* + Na^+], 474.0 (100) [*M* + Na^+].

Compound 17b: ^{1}H NMR (500 MHz, DMSO, 300 K): δ = 7.87 (d, *J* = 7.3 Hz, 2H), 7.67-7.55 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35-7.27 (m, 2H), 4.65 (br d, *J* = 5.2 Hz, 0.5H), 4.61 (br d, *J* = 5.7 Hz, 0.5H), 4.47-4.21 (m, 3H), 4.09 (br d, *J* = 13.4 Hz, 0.5H), 3.92 (br d, *J* = 12.8 Hz, 0.5H), 2.87 (t, *J* = 12.7 Hz, 0.5H), 2.81 (t, *J* = 12.6 Hz, 0.5H), 2.30 and 2.21 (2 × m_c, 1H), 2.11 (m_c, 1H), 1.87 (m_c, 1H), 1.60 (m_c, 1H), 1.41 and 1.39 (2 × s, 9H), 1.29-1.13 (m, 1H); ^{13}C NMR (125 MHz, DMSO, 300 K): δ = 172.1, 171.6, 155.2, 143.8, 140.8, 127.7, 127.1, 125.0, 80.3, 67.2, 66.8, 53.4, 53.0, 46.7, 46.6, 42.5, 41.0, 27.7, 25.4, 25.1, 23.6; HPLC (10-90% within 30 min) R_t = 30.4 min; ESI-MS: *m/z* 941.0 (60) [2M + K^+], 696.7 (60) [3M + H^+ + Na^+], 474.0 (100) [M + Na^+].

Resin-bound buiding block A[6]: Fmoc-aminoethyl-photolinker TentaGel resin (0.358 g, 0.26 mmol/g, 93 μmol) was deprotected according to procedure A (see below) and washed with DMF (6 × 7 mL), Et_2O (3 × 7 mL), and anhydrous CH_2Cl_2 (4 × 7 mL). A solution of Chloro[3-(chloromethyl)phenyl]methanone (0.120 g, 0.633 mmol) and DIEA (0.224 mL, 0.163 g, 1.27 mmol) in anhydrous CH_2Cl_2 (4 mL) was added to the resin. After shaking for 75 min at room temperature the reaction was stopped by washing the resin with CH_2Cl_2 (6 × 7 mL). The resin was shrunk in Et_2O (3 × 7 mL), dried in *vacuo* and suspended in a 1:1 mixture of *tert*-butyl-3-aminopropionate. After shaking the resin for 12 h at 45 °C it was washed with DMF (6 × 7 mL), CH_2Cl_2 (3 × 7 mL), and Et_2O (4 × 10 mL). The dried resin (10 mg) was suspended in a mixture of ACN (0.8 mL) and H_2O (0.2 mL) in a syringe with a fritted disc. Photolysis was performed by irradiation of the sample with a 150 W high pressure Hg lamp (TQ 150 Z2 from Heraeus). The samples were irradiated for 1 h with gentle mixing by a magnetic stirrer. The supernatant was analyzed by HPLC and ESI-MS after photolysis.

HPLC (10-90% within 30 min) R_t = 12.4 min, 91% purity (220 nm); ESI-MS: *m/z* 301.0 (30) [M + Na^+], 278.9 (40) [M + H^+].

Building block A[4]: L-Cysteic acid monohydrate (2.50 g, 13.4 mmol) and DIEA (7.0 mL, 5.3 g, 41 mmol.) were dissolved in H_2O (30 mL). A solution of FmocCl (4.15 g, 16.0 mmol)

in dioxane (16 mL) was added to the stirring reaction mixture at 0 °C within 1 h. The temperature was kept at 0 °C for 1 h, after which time the reaction mixture was allowed to warm to room temperature and stirred for 130 min. The reaction mixture was extracted with hexane (2 × 20 mL) and Et_2O (1 × 20 mL). A Et_2O layer (30 mL) was put on top of the aqueous layer and the biphasic mixture was gently stirred overnight. The aqueous layer was separated and the solvent was removed under reduced pressure to yield building block **A**^{4} (9.92 g, quant.) as a colorless oil: ^{1}H NMR (250 MHz, DMSO, contains 2.7 equiv DIEA): δ = 7.88 (d, *J* = 7.3 Hz, 2H), 7.68 (br d, *J* = 7.4 Hz, 2H), 7.48-7.27 (m, 5H), 4.28-4.12 (m, 4H), 3.52 (m_c, 5.4H), 3.03 (br q, *J* = 7.3 Hz, 5.4H), 2.85 (br d, *J* = 5.0 Hz, 2H), 1.31-1.16 (m, 40.5H); HPLC (10-90% within 30 min) R_t = 13.1 min; ESI-MS: *m/z* 821.0 (100) [2M+K^+], 804.9 (80) [2M+Na^+], 414.2 (20) [M+Na^+], 391.9 (10) [M+H^+].

Solid phase synthesis

General procedure 1 (HATU couplings): The resin (1.0 g) was washed with DMF (7 × 10 mL) and treated with a 0.1 M solution of Fmoc-protected amino acid (3.0 equiv), HATU (2.8 equiv), and collidine (30 equiv) in DMF. The suspension was shaken for 3-12 h and washed with DMF (5 × 10 mL).

General procedure 2 (Fmoc deprotections): The resin was treated with a solution of 20% piperidine in DMF (2 × 7 mL) for 20 and 30 min and washed with DMF (7 × 10 mL).

General procedure 3 (incorporation of Fmoc-azaGly (building block B^1)): The resin (1.12 g, 0.18 mmol/g, 0.20 mmol) was washed with anhydrous CH_2Cl_2 (3 × 7 mL) and a solution of 5-(9*H*-fluoren-9-ylmethoxy)-1,3,4-oxadiazol-2(3*H*)-one (**B^1**) (0.176 g, 0.629 mmol) in anhydrous CH_2Cl_2 (5 mL) was added. The reaction mixture was shaken at room temperature for 3 h and washed with CH_2Cl_2 (3 × 7 mL), DMF (5 × 7 mL).

General procedure 4 (incorporation of Fmoc-azaSar (building block B^2)): The resin (0.372 g, 0.18 mmol/g, 67 μmol) was washed with anhydrous CH_2Cl_2 (3 × 5 mL) and a solution of Fmoc-azaSar-Cl (**B^2**) (0.112 g, 0.339 mmol) in anhydrous CH_2Cl_2 (3 mL) was added. The reaction mixture was shaken at room temperature for 10 min. A solution of DIEA (69 μL, 52 mg, 0.40 mmol) in CH_2Cl_2 (0.9 mL) was then added to the reaction mixture in 3 equal portions over a period of 1 h. After shaking for 1 h, the resin was washed with CH_2Cl_2 (3 × 7 mL), DMF (5 × 7 mL).

General procedure 5 (incorporation of Fmoc-azaAla (building block B^3)): The resin (0.577 g, 0.17 mmol/g, 98.1 μmol) was washed with anhydrous DMF (3 × 5 mL) and a solution of Fmoc-azaAla-Cl (**B^3**) (0.164 g, 0.496 mmol) and DIEA (92 μL, 69 mg, 0.54 mmol) in anhydrous DMF (5 mL) was then added. The reaction mixture was shaken at room temperature for 15 h and washed with DMF (5 × 7 mL).

General procedure 6 (guanylation): A solution of *N*,*N*'-bis-Boc-1-guanylpyrazole (**D^1**) (0.328 g, 1.06 mmol, 19 equiv) in $CHCl_3$ (3.0 mL) was added to the resin (0.347 g, 0.16 mmol/g, 56 μmol). The reaction mixture was shaken at room temperature for 20 h at 50 °C and washed with CH_2Cl_2 (7 × 7 mL).

General procedure 7 (pyrimidylation): The resin (30 mg, 0.20 mmol/g, 6.0 µmol) was suspended in a solution of 2-fluoropyrimidine (**D**^{2}) (8.9 mg, 90 µmol, 15 equiv) and DIEA (15 µL, 12 mg, 90 µmol, 15 equiv) in anhydrous DMF (180 µL). After shaking the reaction mixture for 24 h the resin was washed with DMF (6 × 1 mL), CH_2Cl_2 (4 × 1 mL) and Et_2O (4 × 1 mL) and dried in *vacuo* for 6 h. The dried resin was suspended in a solution of 2-fluoropyrimidine (**D**^{2}) (18 mg, 0.18 mmol, 30 equiv) and $BF_3 \cdot Et_2O$ (9 µl) in anhydrous DMF (180 µl). After shaking the reaction mixture for 7 d the resin was washed with DMF (6 × 1 mL).

General procedure 8 (*tert*-butyl deprotection): The resin (0.7 g) was washed with CH_2Cl_2 (2 × 10 mL) and treated with a 50:50:5-mixture of CH_2Cl_2, TFA and TIPS (10 mL) for 1.5 h at room temperature. The resin was washed with CH_2Cl_2 (3 × 10 mL), neutralized with a solution of 20% DIEA in CH_2Cl_2 (10 mL), washed with CH_2Cl_2 (5 × 10 mL), shrunk in Et_2O (4 × 10 mL), and dried in *vacuo*.

Table 1. Flowchart of the combinatorial solid phase synthesis of the aza-RGD libraries

Step	Function	Procedure
1	Fmoc-deprotection	2
2	Coupling of building blocks **A**$^{1\text{-}5}$ (for **A**^{6} see above)	1
3	Fmoc-deprotection	2
4	Pool, mix, and split	
5	Incorporation of aza-building blocks **B**$^{1\text{-}3}$	3, 4, or 5
6	Fmoc-deprotection	2
7	Pool, mix, and split	
8	Coupling of building blocks **C**$^{1\text{-}10}$	1
9	Fmoc-deprotection	2
10	Pool, mix, and split	
11	Guanylation (**D**^{1}) or pyrimidylation (**D**^{2})	6 or 7
12	*tert*-Butyl deprotection	8

On-bead screening

Binding buffer: TRIS (6.06 g, 50.0 mmol)**,** NaCl (14.6 g, 250 mmol), $CaCl_2 \cdot (H_2O)_6$ (0.219 g, 1.00 mmol), $MgCl_2 \cdot (H_2O)_6$ (0.203 g, 1.00 mmol), $MnSO_4$ (1.7 mg, 10 µmol), BSA fraction V (1.00 g), and Tween 20 (1.00 mL) were dissolved in H_2O (800 mL). The pH-value was adjusted to 7.4 by adding 2N HCl and the volume was set to 1000 mL by adding H_2O.

Bocking buffer: BSA fraction V (330 mg) was dissolved in binding buffer (10 mL).

Anti-biotin solution: The monoclonal anti-biotin alkaline phosphatase conjugate (A-6561, Sigma) was diluted to 1:10000 in binding buffer.

AP-developer: TRIS (12.1 g, 100 mmol), NaCl (5.84 g, 100 mmol), and $MgCl_2 \cdot (H_2O)_6$ (1.02 g, 5.00 mmol) were dissolved in H_2O (800 mL). The pH-value was adjusted to 9.5 by adding 2N HCl and the volume was set to 1000 mL by adding H_2O.

BCIP-solution: BCIP (2.0 mg) was suspended in DMF (400 µl) and added to AP-developer (10 mL).

On-bead screenings protocol of aza-RGD-library with 180 different beads: A 2 mL syringe with a fritted disc was loaded with the TentGel Macrobead-bound aza-RGD-library (14.3 mg, ca. 940 beads, 5.2-fold excess). The resin was suspended in blocking buffer (1.6 mL) and shaken at 120 rpm for 1 h at 37 °C. The resin was washed with binding buffer (3× 1.6 mL, each 10 min) followed by incubation with biotinylated soluble αvβ3 receptor (0.4 µg/mL in binding buffer, 1.6 mL) for 1 h at 37 °C. Then the library was washed with binding buffer (3 × 1.6 mL, each 10 min), incubated with anti-biotin solution (1.6 mL) at 37 °C and washed with binding buffer (5 × 1.6 mL, each 4 min). Finally, the beads were treated with BCIP solution (1.6 mL) at room temperature. After 25 min the staining reaction was stopped by washing the resin with H_2O (5 × 2 mL, each 3 min)

Photolytic cleavage of an aza-RGD mimetic from an isolated TentaGel Macrobead: The selected TentaGel Macrobeads were transferred in a polypropylene 1.5 mL reaction vessel and DMSO (1 mL) was added. The reaction vessel was rotated at 15 rpm for 48 h. Then the beads were washed with a 4:1 CH_3CN/H_2O solution (4 × 1 mL, each 3 h), with CH_3CN (2 × 1 mL, each 20 min), and with a 4:1 CH_2Cl_2/Et_2O solution (1 × 1 mL, 20 min) followed by the addition of a solution of Boc_2O (20 mg, 92 µmol) and DIEA (8.1 µl, 5.9 mg, 46 µmol) in CH_2Cl_2 (0.54 mL) and Et_2O (0.06 mL). After rotation for 12 h the beads were

washed with CH_3CN (3 × 1 mL, each 15 min) and separately transferred in a glass (not in a plastic!) 250 µL vial. A 4:1 CH_3CN/H_2O solution (100 µl) was added to the bead via a glass syringe. After 10 min the solution was exchanged. This washing step was repeated twice followed by the addition of a 4:1 CH_3CN/H_2O solution (100 µl) and sealing the vial with parafilm. The vial was irradiated with a 150 W high pressure Hg lamp (TQ 150 Z2 from Heraeus) for 4 h and after a 12 h disruption for 2 h. The supernatant was analyzed by LC-MS and ESI-MS^n.

Table 2. *Representative results of the mass spectrometric analysis of some randomly chosen beads*

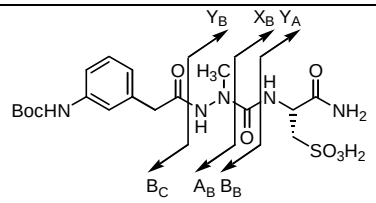
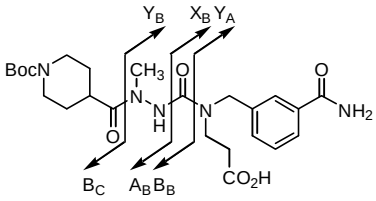
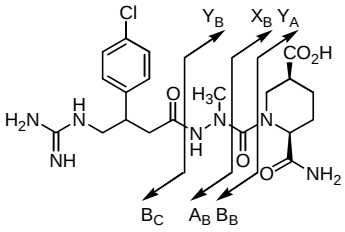
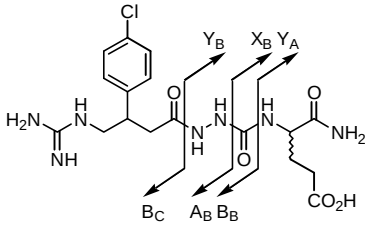
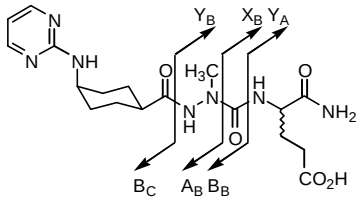
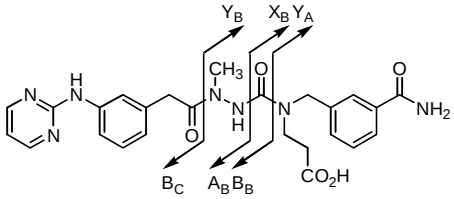
Structure	Result of MS analysis
	LC-MS: 496 $[M+Na]^+$, 374 $[M-Boc+H]^+$; MS^2 on $[M-Boc+H]^+$: 206 (30) $[B_B]$, 180 (100) $[A_B]$; MS^2 on $[M-Boc+Na]^+$: 202 (100) $[A_B]$
	LC-MS: 528 $[M+Na]^+$, 406 $[M-Boc+H]^+$; MS^2 on $[M-Boc+H]^+$: 295 (100) $[Y_B]$, 223 (45) $[Y_A]$, 184 (6) $[B_B]$; MS^2 on $[M-Boc+Na]^+$: 317 (5) $[Y_B]$, 245 (100) $[Y_A]$, 206 (3) $[B_B]$
	LC-MS: 482 $[M+H]^+$; MS^2 on $[M+H]^+$: 310 (100) $[B_B]$, 284 (30) $[A_B]$, 238 (15) $[B_C]$; MS^2 on $[M+Na]^+$: 332 (15) $[B_B]$, 306 (100) $[A_B]$, 267 (80) $[Y_B]$, 195 (100) $[Y_A]$
	LC-MS: 464 $[M+Na]^+$, 442 $[M+H]^+$; MS^2 on $[M+H]^+$: 296 (40) $[B_B]$, 270 (100) $[A_B]$, 238 (30) $[B_C]$; MS^2 on $[M+Na]^+$: 318 (50) $[B_B]$, 292 (100) $[A_B]$,260 (10) $[B_C]$
	LC-MS: 444 $[M+Na]^{+,}$ 422 $[M+H]^+$; MS^2 on $[M+H]^+$: 250 (100) $[A_B]$, 204 (5) $[B_C]$; MS^2 on $[M+Na]^+$: 298 (7) $[B_B]$, 272 (100) $[A_B]$
	LC-MS: 528 $[M+Na]^+$, 506 $[M+H]^+$; MS^2 on $[M+H]^+$: 284 (100) $[B_B]$, 223 (7) $[Y_A]$; MS^2 on $[M+Na]^+$: 306 (15) $[B_B]$, 245 (100) $[Y_A]$

Table 3a. *Mass spectrometric analysis of selected beads*

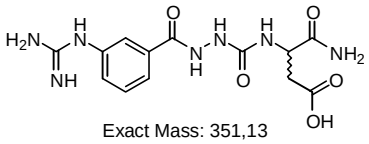
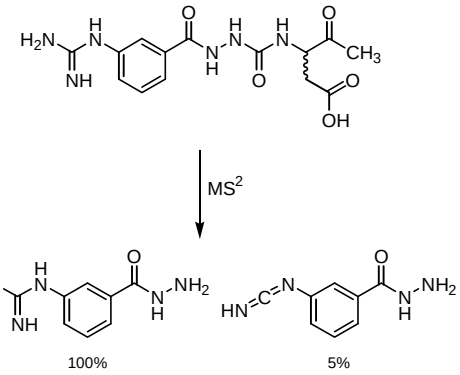
No.	Structure	Method	Result
5	 Exact Mass: 351,13	LC-MS (10→90)	R_t = 11.8 min; *m/z* = 352.1 (100) $[M+H]^+$, 194.0 (50). (Probably M+Boc)
		MS^n on $[M+H]^+$	 100% 5%
5	dto.	LC-MS (10→90)	R_t = 11.8 min; *m/z* = 352.1 (100) $[M+H]^+$, 194.1 (50). (Probably M+Boc)
5	dto.	LC-MS (10→90)	R_t = 11.9 min; *m/z* = 352.1 (100) $[M+H]^+$, 194.0 (50). (Probably M+Boc)
5	dto.	LC-MS (10→90)	R_t = 11.8 min; *m/z* = 352.0 (100) $[M+H^+]$, 194.0 (50). (Probably M+Boc)
5	dto.	LC-MS (10→90)	R_t = 11.8 min; *m/z* = 352.0 (100) $[M+H]^+$, 194.1 (50). (Probably M+Boc)

Table 3b. *Mass spectrometric analysis of selected beads*

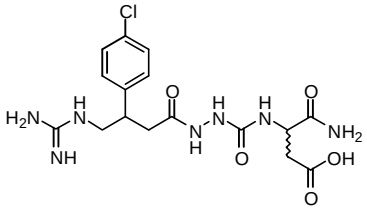
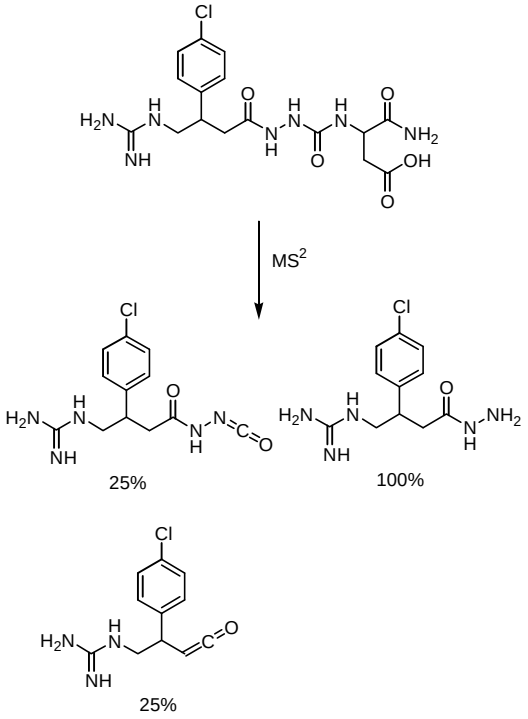
No.	Structure	Method	Result
7	 Exact Mass: 427,14	LC-MS (10→90)	R_t = 2.4 min *m/z* = 428.0 (80) $[M+H]^+$, 270 (100), 238.1 (40)
		MS^n on $[M+H]^+$	 25% 100% 25%
7	dto.	LC-MS (10→90)	R_t = 2.4 min; *m/z* = 450.0 (5) $[M+Na]^+$, 296.0 (45), 270.1 (100), 238.1 (40)
7	dto.	LC-MS (10→90)	R_t = 2.4 min; *m/z* = 466.0 (10) $[M+K]^+$, 296.0 (45), 270.1 (100), 238.1 (40)

Table 3c. *Mass spectrometric analysis of selected beads*

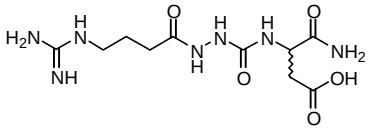
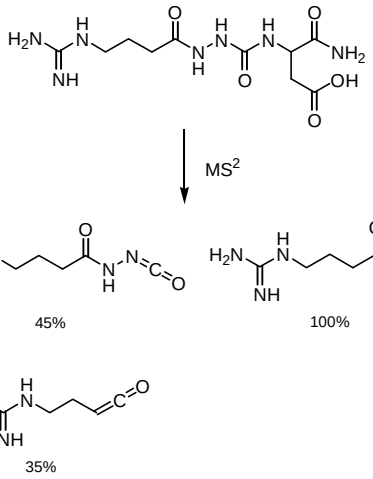
No.	Structure	Method	Result
6	 Exact Mass: 317,14	LC-MS (10→90)	R_t = 2.0 min; *m/z* = 356.0 (45) $[M+K]^+$, 318.1 (100) $[M+H]^+$, 186.0 (30), 160.1 (35), 128.0 (20)
		MS^n on $[M+H]^+$	
6	dto.	LC-MS	R_t = 2.0 min; *m/z* = 356.0 (55) $[M+K]^+$, 340.1 (45) $[M+Na]^+$, 318.2 (100) $[M+H]^+$, 186.0 (30), 160.1 (50), 128.0 (20)
6	dto.	LC-MS	R_t = 1.9 min; *m/z* = 356.3 (70) $[M+K]^+$, 318.2 (100) $[M+H]^+$, 186.1 (50), 160.1 (70), 128.0 (20)
6	dto.	LC-MS	R_t = 2.0 min; *m/z* = 356.1 (90) $[M+K]^+$, 318.1 (100) $[M+H]^+$, 186.0 (30), 160.1 (60), 128.0 (40)
6	dto.	LC-MS	R_t = 1.9 min; *m/z* = 356.3 (60) $[M+K]^+$, 318.1 (100) $[M+H]^+$, 186.1 (30), 160.0 (30), 128.0 (30)

Table 3d. *Mass spectrometric analysis of selected beads*

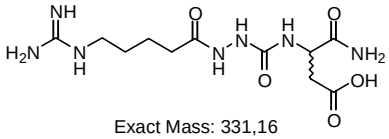
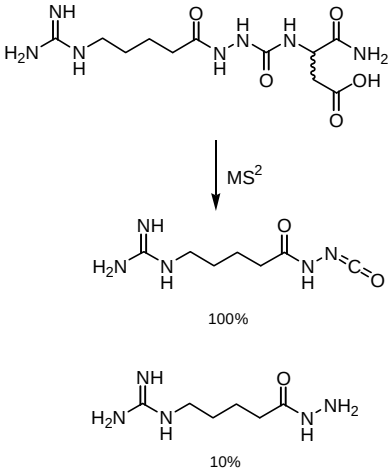
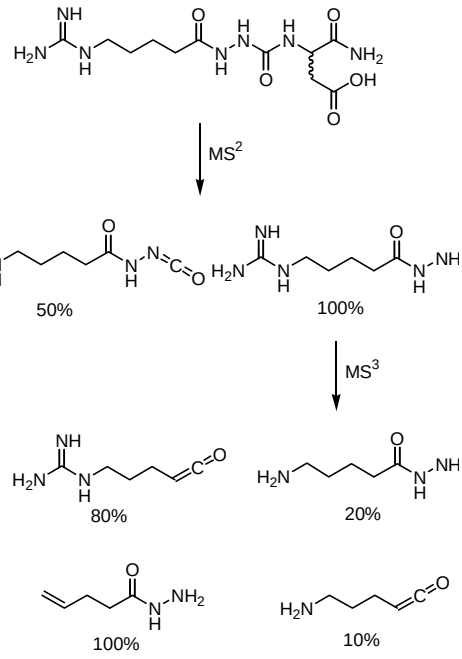
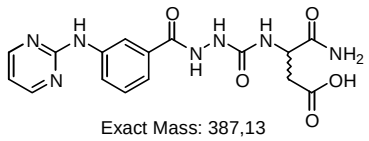
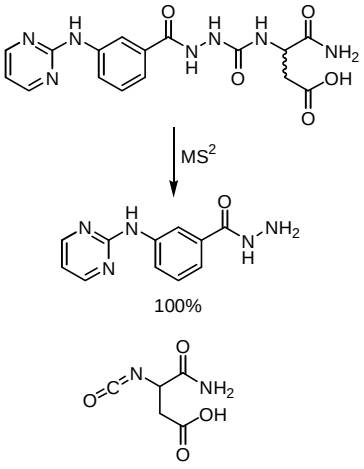
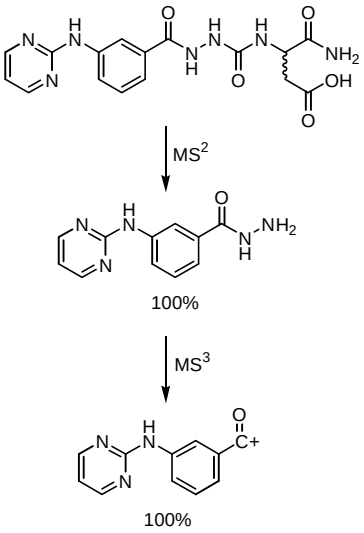
No.	Structure	Method	Result
8	 Exact Mass: 331,16	LC-MS (10→90)	R_t = 2.3 min; *m/z* = 370.0 (50) $[M+K]^+$, 354.0 (40) $[M+Na]^+$, 332.2 (100) $[M+H]^+$, 200 (50)
		MS^n on $[M+Na]^+$	
		MS^n on $[M+H]^+$	

Table 3e. *Mass spectrometric analysis of selected beads*

No.	Structure	Method	Result
9	 Exact Mass: 387,13	LC-MS (10→90)	R_t = 2.5 min; *m/z* = 198.0 (100), 230 (30), 170 (20)
		MS	*m/z* = 410.2 (100) $[M+Na]^+$
		MS^n on $[M+Na]^+$	
		MS^n on $[M+H]^+$	
9	dto.	LC-MS (10→90)	R_t = 2.4 min; *m/z* = 426.1 (20) $[M+K]^+$, 230 (30) 198.0 (100)