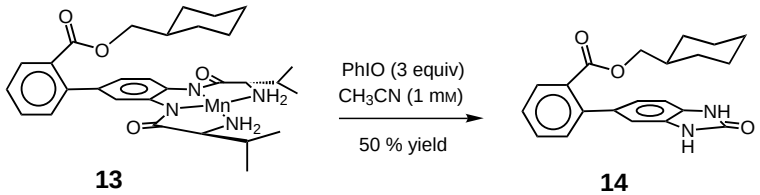
the ligands are stable under the oxidation conditions. For instance, system **5** was not oxidized under the reaction conditions, suggesting that the deactivation of the metal complex is not the result of ligand degradation. In contrast, the bis(valine) complex **13**, when submitted to the same reaction conditions (3 equiv PhIO), led to complete degradation of the ligand segment yielding the cyclic urea derivative **14** as the major product (Scheme 4).[15]



Scheme 4. Complete degradation of the bis(valine)manganese complex **13** in the presence of iodosylbenzene.

The simplicity of covalently assembled models of this type render them suitable probes for the rapid evaluation of novel metal complexes with regard to their capability to functionalize C–H bonds. We are currently studying possibilites for predictable positioning of the substrate to the metal through noncovalent recognition forces in order to attain a truly catalytic oxidation species.

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Solid-Phase Synthesis of Unprotected N-Glycopeptide Building Blocks for SPOT Synthesis of N-linked Glycopeptides

Laurence Jobron and Gerd Hummel*

Several approaches to the chemical synthesis of N-linked glycopeptides have been reported.[1] For the synthesis of glycosylated amino acids, the carbohydrate moiety is usually protected but unprotected glycosylamines have also been used.[2, 3] Using unprotected glycosylamines generally results in low yields[4, 5] and the compounds have to be purified by column chromatography. We present here a new and efficient method for the solid-phase synthesis of unprotected N-glycopeptide building blocks on a continous surface (SPOT synthesis). SPOT synthesis on cellulose[6] is a highly effective

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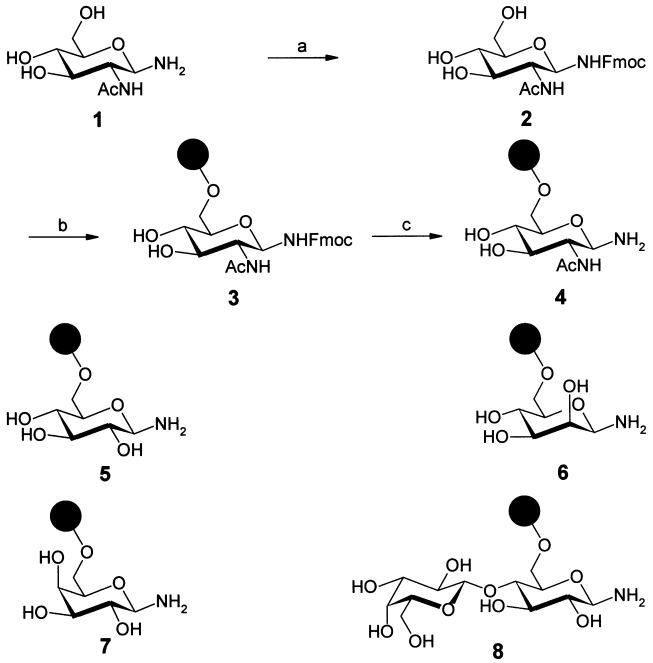
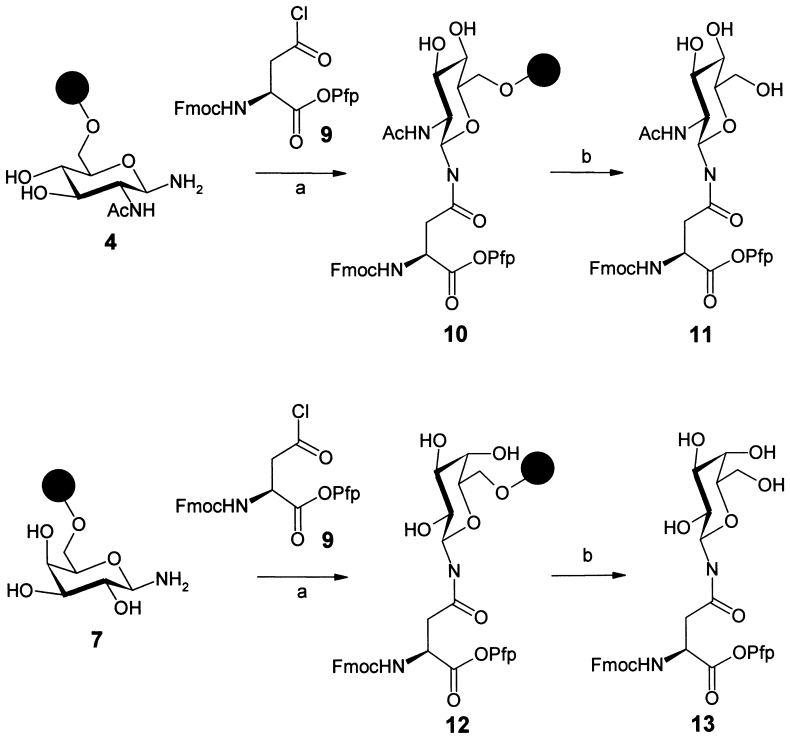
method for the rapid preparation of spatially addressed peptides.

D-glucose, D-mannose, D-galactose, D-lactose, and *N*-acetyl-D-glucosamine were treated as previously reported[4, 7–10] to give the corresponding β-D-glycosylamines. For temporary amine protection, the glycosylamines were treated with fluoren-9-ylmethoxycarbonyl succinimide ester (Fmoc-Osu) in pyridine. The protected derivatives were obtained after trituration with a mixture of water and dichloromethane. Each of the unprotected sugar derivatives was immobilized on a triphenylmethyl (trityl) chloride derivatized polystyrene resin (1.6 mmol g^{-1}) (shown for GlcNAc, Scheme 1).[11] The loading of the glycosylamines on the solid support was determined by UV spectrophotometric analysis of the 9-fluorenylmethyl–piperidine adduct and ranged from 0.4 to 0.8 mmol g^{-1} depending on the glycosylamine. Removal of the Fmoc protecting group with piperidine in DMF gave compounds **4** to **8**.

In order to prepare glycosylated asparagine building blocks on the solid support, we decided to use the acid chloride N^{α}-Fmoc-Asp(Cl)-OPfp described by Bock et al.[12, 13] (Pfp = pentafluorophenol). Condensation of the unprotected glycosylamines **4** and **7** with the acid choride **9** gave the corresponding derivatives **10** and **12**; no reaction with the Pfp ester was observed (Scheme 2). In contrast to the solution phase synthesis, the glycosylamine hydroxyl groups had to be protected prior to this reaction in order to provide sufficient solubility.[13] After cleavage from the resin by treatment with 2% trifluoroacetic acid (TFA) in CH_2Cl_2, the glycosylated asparagine building blocks **11** and **13** were obtained in high yield (70–80%) and purity (>90%) (NMR and MS data are given in Table 1).



Scheme 1. Reagents and conditions: a) Fmoc-Osu, pyridine, RT, 18 h; b) trityl chloride resin, pyridine, 60 °C, 8 h; c) 20% piperidine, DMF, RT, 30 min. RT = room temperature.



Scheme 2. Reagents and conditions: a) *N*-ethylmorpholine, THF, 0 °C–RT, 2 h; b) 2% TFA, CH_2Cl_2, 20 °C, 10 min.

Table 1. Selected ^{1}H NMR signals (300 MHz, CD_3OD) and electrospray ionization (ESI) MS data.

11: ^{1}H NMR: δ = 1.93 (s, 3H, CH_3), 2.05 (m, 2H, Asp H_β, $H_{\beta'}$), 3.63 (m, 1H, Fmoc-CH), 3.80 (m, 2H, Fmoc-CH_2), 4.19 (m, 1H, 6-H), 4.37 (m, 1H, Asp H_α), 4.46 (d, 1H, $J_{1,2}$ = 9.3 Hz, 1-H), 7.33, 7.65, 7.78 (m, 8H, Fmoc arom. H); MS: *m/z*: 723.9 [M^+]

13: ^{1}H NMR: δ = 1.85 (m, 2H, Asp H_β, $H_{\beta'}$), 3.60 (m, 1H, Fmoc-CH), 3.87 (m, 2H, Fmoc-CH_2), 4.20 (m, 1H, 6-H), 4.38 (m, 1H, Asp H_α), 4.40 (d, 1H, $J_{1,2}$ = 7.4 Hz, 1-H), 7.34, 7.65, 7.78 (m, 8H, Fmoc arom. H); MS: *m/z*: 682.8 [M^+]

16: ^{1}H NMR: δ = 1.95 (s, 3H, CH_3), 2.04 (m, 2H, Glu H_β, $H_{\beta'}$), 2.39 (m, 2H, Glu H_γ, $H_{\gamma'}$), 3.65 (m, 1H, Fmoc-CH), 3.81 (m, 2H, Fmoc-CH_2), 4.19 (m, 1H, 6-H), 4.24 (m, 1H, Gly $H_{\alpha'}$), 4.40–4.48 (m, 2H, Gly H_α, Glu H_α), 4.96 (d, 1H, $J_{1,2}$ = 9.7 Hz, 1-H), 7.35, 7.68, 7.79 (m, 8H, Fmoc arom. H); MS: *m/z*: 629.0 [M^+]

17: ^{1}H NMR: δ = 1.96 (m, 1H, Glu H_β), 2.06 (m, 1H, Glu $H_{\beta'}$), 2.40 (m, 2H, Glu H_γ, $H_{\gamma'}$), 3.60 (m, 1H, Fmoc-CH), 3.80 (m, 2H, Fmoc-CH_2), 4.09 (m, 1H, 6-H), 4.23 (m, 1H, Gly $H_{\alpha'}$), 4.37–4.50 (m, 2H, Gly H_α, Glu H_α), 4.90 (d, 1H, $J_{1,2}$ = 8.3 Hz, 1-H), 7.35, 7.69, 7.79 (m, 8H, Fmoc arom. H); MS: *m/z*: 587.9 [M^+]

18: ^{1}H NMR: δ = 2.00 (m, 1H, Glu H_β), 2.06 (m, 1H, Glu $H_{\beta'}$), 2.32 (m, 2H, Glu H_γ , $H_{\gamma'}$), 3.68 (m, 1H, Fmoc-CH), 4.00 (m, 2H, Fmoc-CH_2), 4.18 (m, 1H, 6-H), 4.22 (m, 1H, Gly $H_{\alpha'}$), 4.34–4.44 (m, 2H, Gly H_α, Glu H_α), 4.42 (d, 1H, $J_{1,2}$ = 8.0 Hz, 1-H), 7.34, 7.66, 7.79 (m, 8H, Fmoc arom. H); MS: *m/z*: 587.9 [M^+]

19: ^{1}H NMR: δ = 1.96 (m, 1H, Glu H_β), 2.07 (m, 1H, Glu $H_{\beta'}$), 2.40 (m, 2H, Glu H_γ, $H_{\gamma'}$), 3.30 (m, 1H, Fmoc-CH), 3.90 (m, 2H, Fmoc-CH_2), 4.14 (m, 1H, 6-H), 4.22 (m, 1H, Gly $H_{\alpha'}$), 4.34–4.44 (m, 2H, Gly H_α, Glu H_α), 4.74 (d, 1H, $J_{1,2}$ = 1.0 Hz, 1-H), 7.35, 7.69, 7.79 (m, 8H, Fmoc arom. H); MS: m/z: 587.9 [M^+]

20: ^{1}H NMR: δ = 1.98 (m, 1H, Glu H_β), 2.08 (m, 1H, Glu $H_{\beta'}$), 2.40 (m, 2H, Glu H_γ, $H_{\gamma'}$), 3.50 (m, 1H, Fmoc-CH), 3.90 (m, 2H, Fmoc-CH_2), 4.08 (m, 1H, 6-H), 4.23 (m, 1H, Gly $H_{\alpha'}$), 4.34 (d, 1H, $J_{1,2}$ = 7.3 Hz, 1-Hb), 4.38–4.47 (m, 2H, Gly H_α, Glu H_α), 4.92 (d, 1H, $J_{1,2}$ = 8.8 Hz, 1-H), 7.36, 7.70, 7.79 (m, 8H, Fmoc arom. H); MS: *m/z*: 749.9 [M^+]

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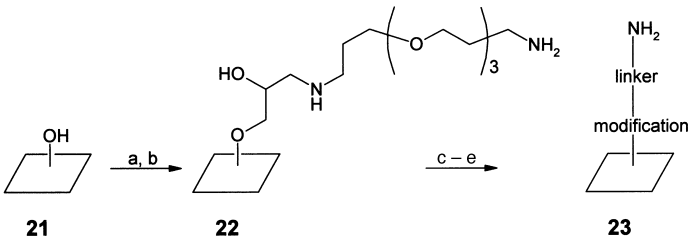
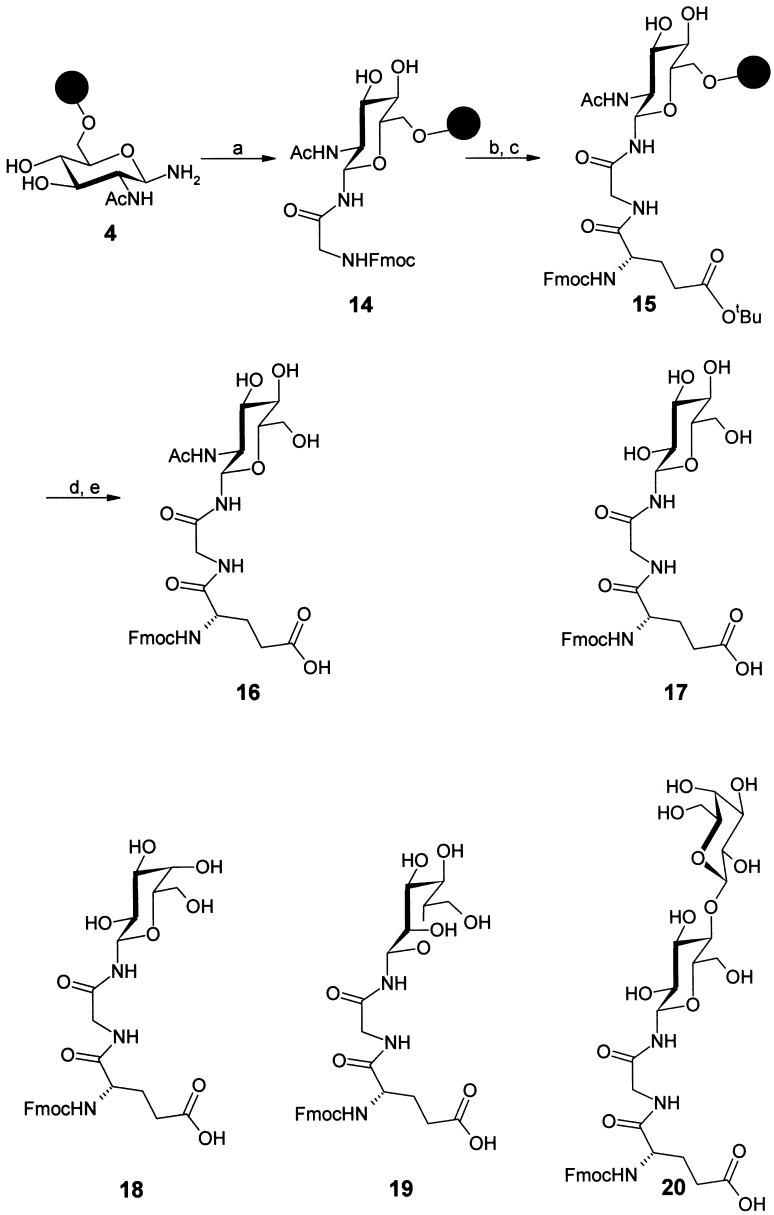
In order to introduce diversity in the array of saccharides, glycosylated glutamine building blocks were also prepared (shown for GlcNAc, Scheme 3). Glycosylamines **4** to **8** were coupled with commercially available N^{α}-Fmoc-Gly-OPfp in DMF. After 3 hours, the resin was washed, and treatment with piperidine in DMF gave the corresponding amines. A second coupling with commercially available N^{α}-Fmoc-Glu(O-*t*Bu)OPfp was performed as described above. After cleavage from the resin with 2% TFA in CH_2Cl_2 and deprotection of the *tert*-butyl esters with 50% TFA in CH_2Cl_2, derivatives **16** to **20** were obtained in good yields (75–90%) and high purity (>95%)(NMR and MS data are given in Table 1).

To demonstrate the suitability of the new building blocks, they were used in the SPOT synthesis on cellulose of an N-linked glycopeptide library. Cellulose membranes (Whatman 50) were modified by treatment with epibromohydrin and 4,7,10-trioxa-1,13-tridecanediamine to provide homogeneous amino functionalization (**22**, Scheme 4).[14] For analytical purposes, the photo-labile linker system 4-[4(1-Fmoc-aminoethyl)-2-methoxy-5-nitrophenoxyl]-butanoic acid was coupled with the amine by activation with *N* - [(dimethylamino) - 1*H* - 1,2,3 - triazol[4,5 - *b*]pyridin-1-ylmethylene]-*N*-methylmethanaminium hexafluorophosphate *N*-oxide (HATU) and *N*-methyl-imidazole (NMI) in *N*-methyl-2-pyrrolidone (NMP). After acetylation of the remaining free amine functional groups, the Fmoc-protected photo-labile linker was treated with piperidine in DMF to give **23**.



Scheme 4. Reagents and conditions: a) epibromohydrin, RT; b) 4,7,10-trioxa-1,13-tridecanediamine, RT; c) photo-labile linker (0.5 M in NMP), HATU, NMI, RT, 2 × 15 min; d) 10% Ac_2O, 20% DIPEA, DMF, RT, 30 min; e) 20% piperidine, DMF, RT, 2 × 10 min. DIPEA = *N*,*N*′-diisopropylethylamine.



Scheme 3. Reagents and conditions: a) N^{α}-Fmoc-Gly-OPfp, DMF, RT, 3 h; b) 20% piperidine, DMF, RT, 30 min; c) N^{α}-Fmoc-Glu-(O-*t*Bu)-OPfp, DMF, RT, 3 h; d) 2% TFA, CH_2Cl_2, RT, 10 min; e) 50% TFA, CH_2Cl_2, RT, 30 min.

The first amino acid N^{α}-Fmoc-Gly-OPfp was coupled on the continuous surface in NMP (Scheme 5). The remaining free amine functions were acetylated with a solution of 10% acetic anhydride in MeOH. Fmoc deprotection yielded derivative **24**. In the second coupling step, the seven sugar building blocks described above were used. Pfp-activated sugar derivatives **11** and **13** were coupled to the free amine in NMP. The free acids **16** to **20** were coupled in the presence of PfpOH and diisopropylcarbodiimide (DIC) in NMP. After acetylation and Fmoc deprotection, derivatives **25a–g** were obtained (**a–g** are the corresponding derivatives of compounds **11**, **13**, and **16–20**). The last amino acid was also coupled as described. The side-chain protective groups were removed with TFA in CH_2Cl_2. For analytical purposes, derivatives **27a–g**, **28a–g**, and **29a–g** were cleaved from the continuous surface by UV irradiation and obtained in high purity (>90%) (MS data are given in Table 2).

In conclusion, a practical way for the stereoselective synthesis of unprotected N-linked glycopeptide building blocks has been described. SPOT synthesis on a continuous surface allowed the rapid nanomolar preparation of N-glycopeptide libraries which can be used in solid- and solution-phase screening systems and can be applied to the synthesis of bigger libraries.

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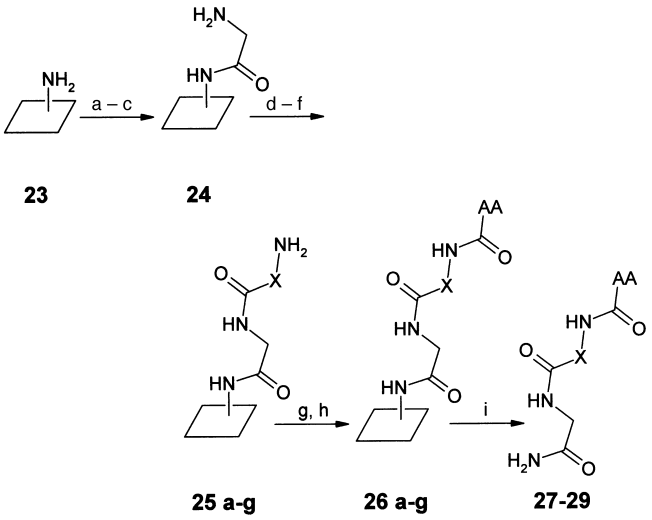

Scheme 5. Reagents and conditions: a) N^{α}-Fmoc-Gly-OPfp (0.6 M in NMP), RT, 2 × 15 min; b) 10% Ac_2O, MeOH, RT, 1 h; c) 20% piperidine, DMF, RT, 2 × 10 min; d) coupling of sugar building blocks: 1) if activated with Pfp, 0.6 M solution of the sugar in NMP, RT, 2 × 15 min; 2) if free of acid functionality, 0.6 M solution of the sugar in NMP, PfpOH, DIC, RT, 2 × 15 min; e) 10% Ac_2O, MeOH, RT, 1 h; f) 20% piperidine, DMF, RT, 2 × 10 min; g) N^{α}-Fmoc-AA-OPfp (0.6 M in NMP), RT, 2 × 15 min; h) TFA, CH_2Cl_2, RT, 2.5 h; i) UV light at 365 nm, 2 h. X = sugar building blocks 11, 13, 16–20, AA = different amino acids: N^{α}-Fmoc-Glu-(OH) **27a–g**, N^{α}-Fmoc-Thr-(OH) **28a–g**, N^{α}-Fmoc-Tyr-(OH) **29a–g**.

Table 2. ESI MS data.

Compound	m/z [M^+]	Compound	m/z [M^+]	Compound	m/z [M^+]
27a	743.1	**28a**	715.1	**29a**	777.1
27b	702.0	**28b**	674.1	**29b**	736.1
27c	841.1	**28c**	786.1	**29c**	848.1
27d	773.0	**28d**	745.0	**29d**	807.0
27e	773.0	**28e**	745.0	**29e**	807.0
27f	773.0	**28f**	745.0	**29f**	807.0
27g	935.1	**28g**	907.1	**29g**	969.1

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Can a Homometallic Chain Be Ferrimagnetic?**

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Dedicated to Professor Harald Krischner on the occasion of his 70th birthday

One-dimensional homometallic magnetic systems can behave either as antiferromagnetic (AF) or as ferromagnetic (F) chains depending on the sign of the nearest-neighbor exchange interactions.[1] The recent synthesis of molecular materials, however, has extended the range of magnetic behaviors that can be observed. For instance, regular alternating AF/F chains have been reported that show an overall AF behavior.[2] However, ferrimagnetic behavior has not been reported for homometallic chains because, in this case, the condition for the noncompensation of the individual spin moments is difficult to achieve. We have now found that the versatility of the azide ligand affords chains with Mn^{II} in which ferrimagnetic behavior is clearly observed.

From methanolic solutions of manganese(II) nitrate and the appropriate pyridine derivative, *trans*-$[\{Mn(N_3)_2(3\text{-Mepy})_2\}_n]$ **1** and *trans*-$[\{Mn(N_3)_2(Menic)_2\}_n]$ **2** were obtained upon addition of aqueous solutions of sodium azide (3-Mepy = 3-methylpyridine, Menic = methylnicotinate). Compounds **1** and **2** consist of one-dimensional systems[3] in which each manganese atom is coordinated by two *trans*-oriented pyridinic ligands and four azido ligands. Two azido bridges, oriented either end-to-end (EE) or end-on (EO), between neighboring manganese atoms build the one-dimensional system. Compound **1** shows azido bridges in the sequence $(\text{-EE-EE-EO-})_n$ but compound **2** shows the sequence $(\text{-EE-EO-EO-EO-EO-})_n$ (Figure 1). Bond lengths and angles in the bridging region lie in the range of values reported for conventional EE or EO bridges.[2, 4, 5] For the Mn^{II}-azido system, double EE azido bridges give AF interactions with

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