

Supporting information

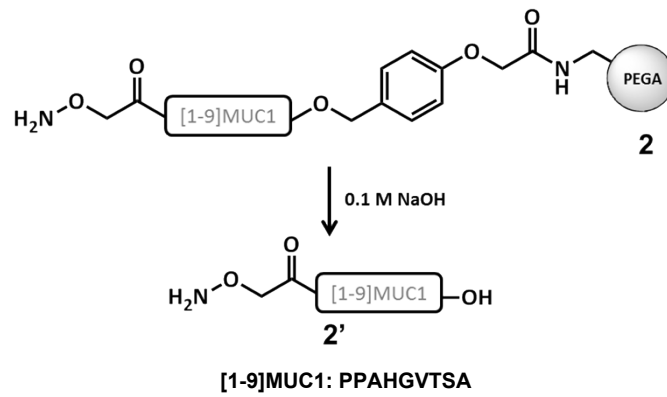
Solid phase oxime ligations for the iterative synthesis of polypeptide conjugates

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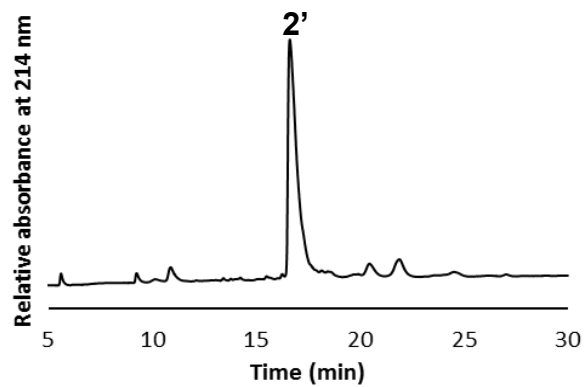
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☞ C-terminal peptide resin 2	
p S2	
☞ Internal peptide aldehyde 3	p S3
☞ N-Terminal segments 4	
- Peptide aldehyde 4a (PADRE-[1-20]MUC1-CHO)	p S4
- Peptide aldehyde 4b ([1-20]MUC1-CHO)	p S5
☞ Ligation intermediates	
- <i>N</i> -Aloc-protected Aoa-containing polypeptide 6'	p S6
- Aoa-containing polypeptide 7'	p S7
☞ Final products	
- 1a	p S8
- 1b	p S9

↳ C-terminal peptide resin 2



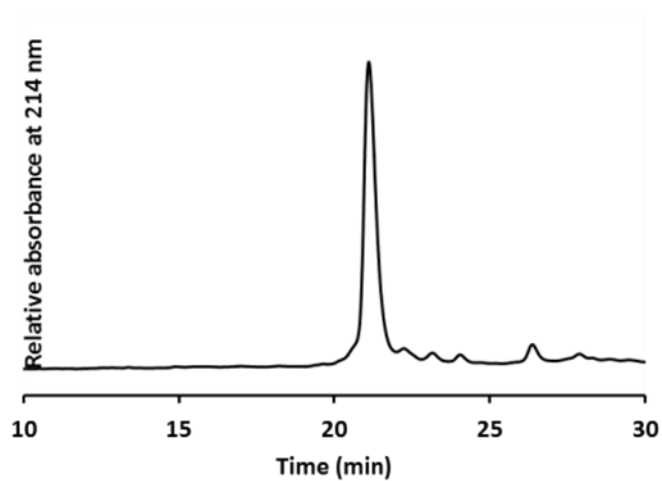
- HPLC analytical gradient: 3-30% B/A over 30 min. Retention time: 16.3 min.
MALDI/TOF $[M+H]^+$ $m/z = 909.3$ (calcd for $C_{38}H_{61}N_{12}O_{14}$, 909.4).



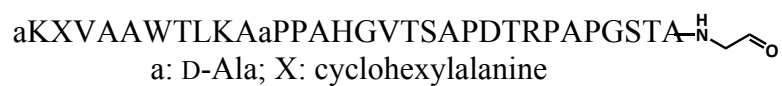
Internal peptide aldehyde 3



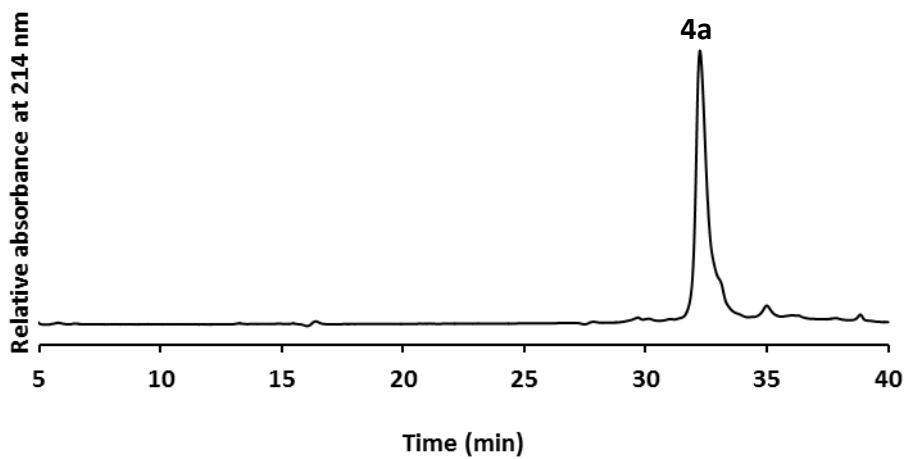
- HPLC analytical gradient: 10-35% B/A over 40 min. Retention time: 21.1 min.
MALDI-TOF: $[M+H]^+$ $m/z = 2085.0$ (calcd for $C_{88}H_{138}N_{27}O_{32}$, 2085.0).



Peptide aldehyde **4a** (PADRE-[1-20]MUC1-CHO)
PADRE (pan DR epitope)



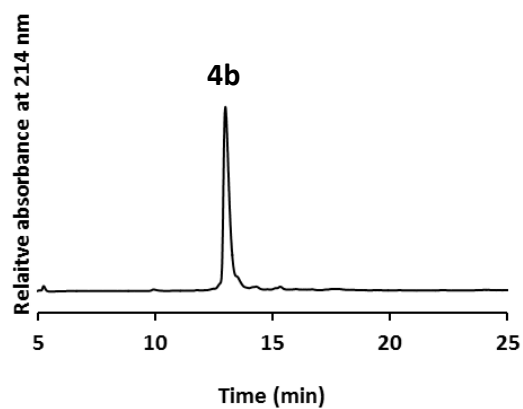
- HPLC analytical gradient: 10-35% B/A over 40 min. Retention time: 32.2 min.
MALDI-TOF: $[M+H]^+$ $m/z = 3192.8$ (calcd for $C_{144}H_{232}N_{41}O_{41}$ 3191.7).



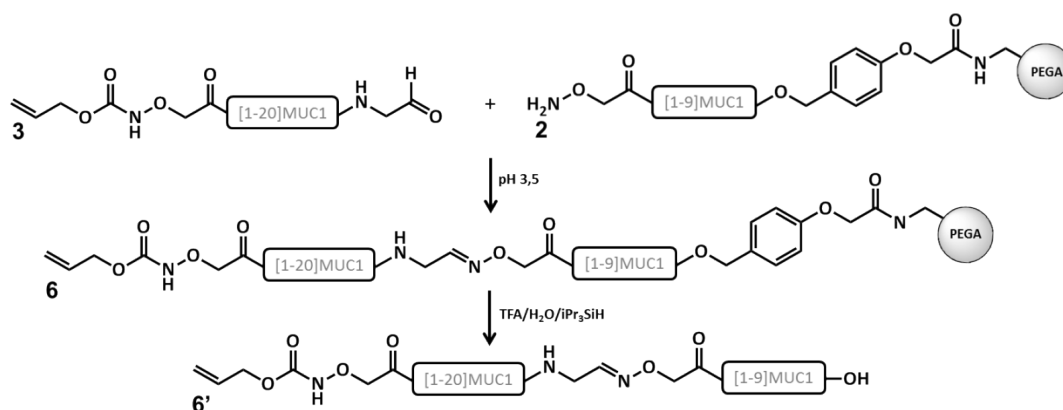
Peptide aldehyde **4b** ([1-20]MUC1-CHO)



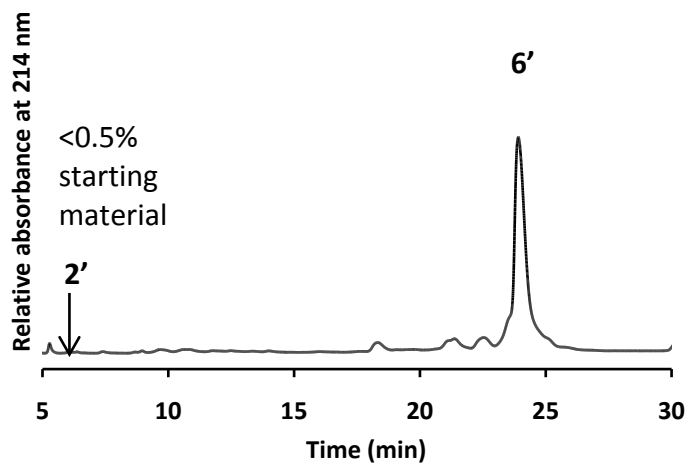
- HPLC analytical gradient: 10-35% B/A over 40 minutes. Retention time: 13.0 min.
MALDI-TOF: $[M+H]^+$ $m/z = 1927.9$ (calcd for $C_{82}H_{130}N_{26}O_{28}$, 1928.0).



N-Alloc-protected Aoa-containing polypeptide **6'**

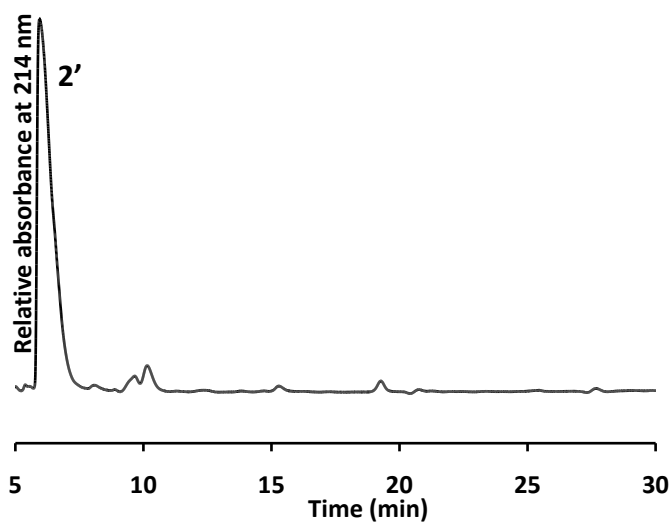


- HPLC analytical gradient : 10-35% B/A over 40 minutes. Retention time: 23.9 min.
MALDI-TOF: $[\text{M}+\text{H}]^+$ $m/z = 2976.9$ (calcd for $\text{C}_{126}\text{H}_{196}\text{N}_{39}\text{O}_{45}$, 2975.4).

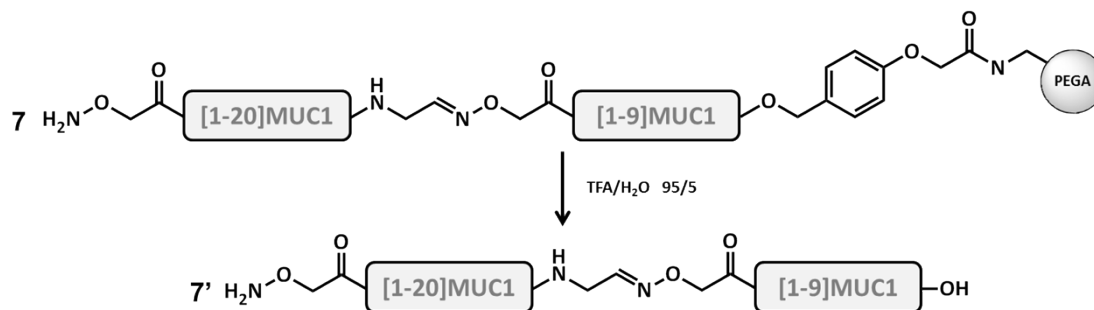


Starting material **2'** analyzed using the same gradient

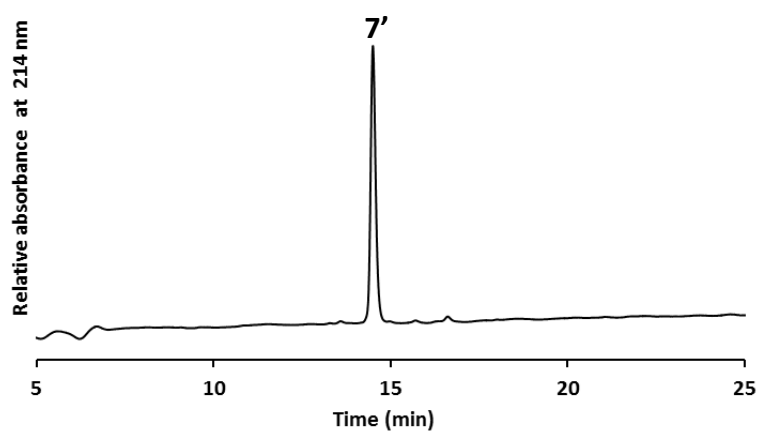
HPLC analytical gradient : 10-35% B/A over 40 minutes. Retention time: 6.2 min.



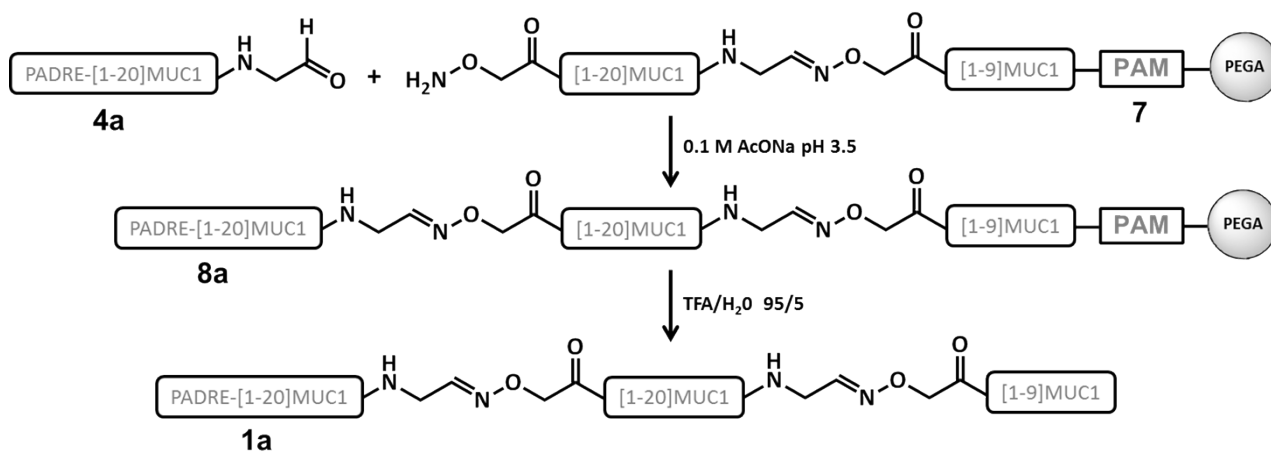
↻ Aoa-containing polypeptide 7'



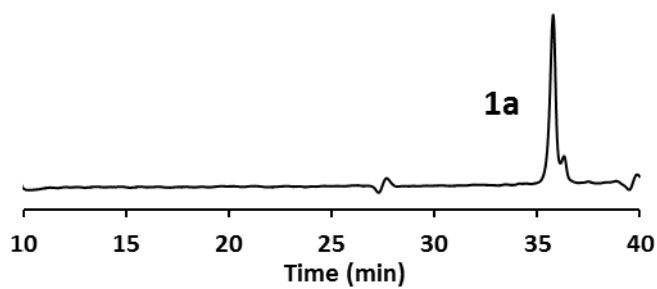
- HPLC analytical gradient: 3-39% B/A over 40 minutes. Retention time: 14.5 min.
MALDI-TOF: $[M+H]^+$ $m/z = 2892.6$ (calcd for C₁₂₂ H₁₉₂ N₃₉ O₄₃, 2891.4).



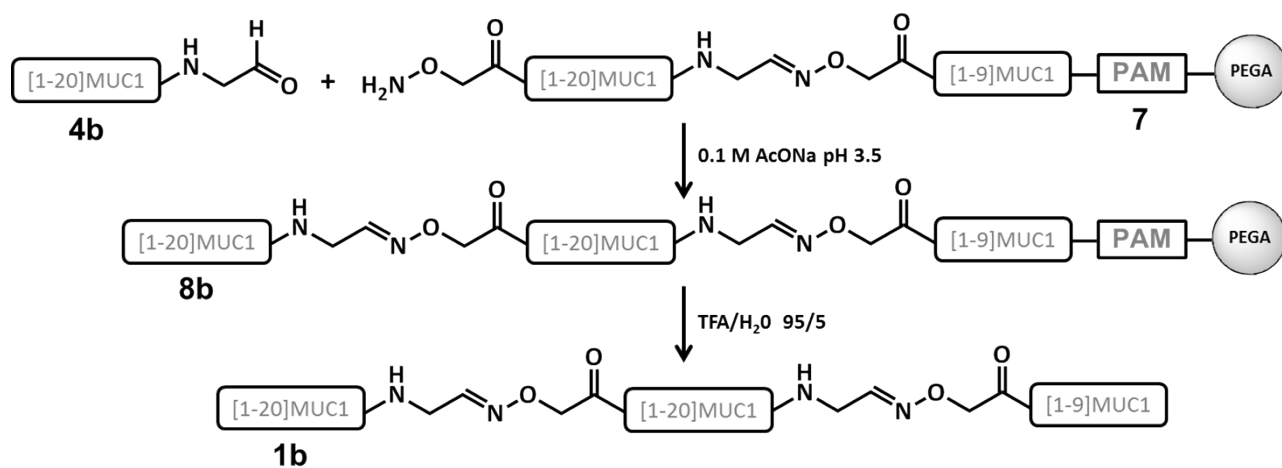
1a



- HPLC analytical gradient : 10-35% B/A over 40 min. Retention time: 35.8 min.
 MALDI-TOF: $[\text{M}+2\text{H}]^+ m/z = 3037.5$ ($[\text{M}]$: calcd for $\text{C}_{266}\text{H}_{419}\text{N}_{80}\text{O}_{83}$, 6063.1) average mass.



1b



- HPLC analytical gradient: 10-35% B/A over 40 min. Retention time: 17.3 min.
- MALDI-TOF: $[\text{M}+\text{H}]^+ m/z = 4802.7$ (calcd for $\text{C}_{204}\text{H}_{320}\text{N}_{65}\text{O}_{70}$, 4803.2), average mass.

