Supplemental Information

From Pico to Nano: Biofunctionalization of Cube-octameric Silsesquioxanes by Peptides and Miniproteins

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Electronic Supplemental Information

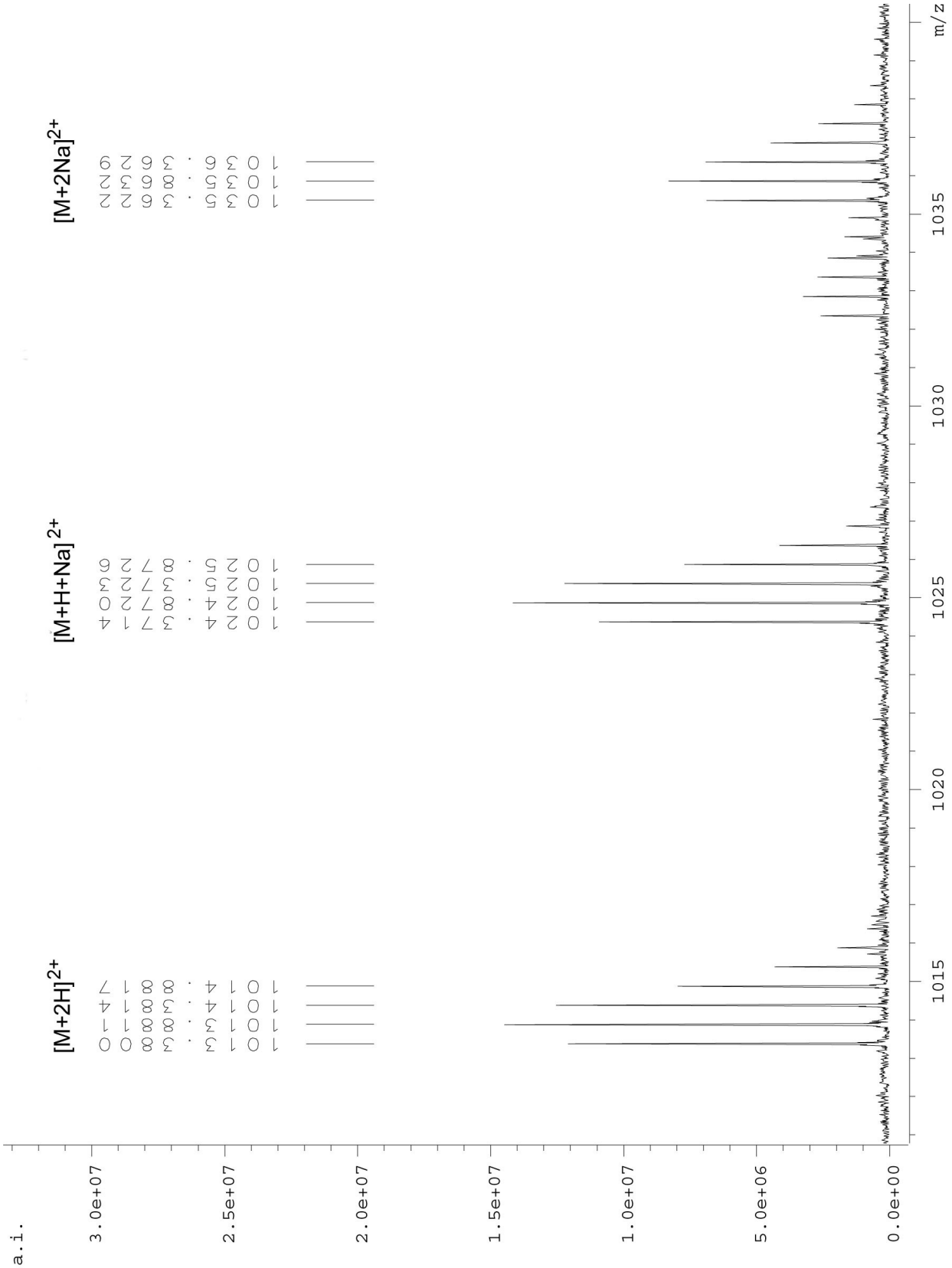


Fig. S1: HR-MS spectrum of **2**.

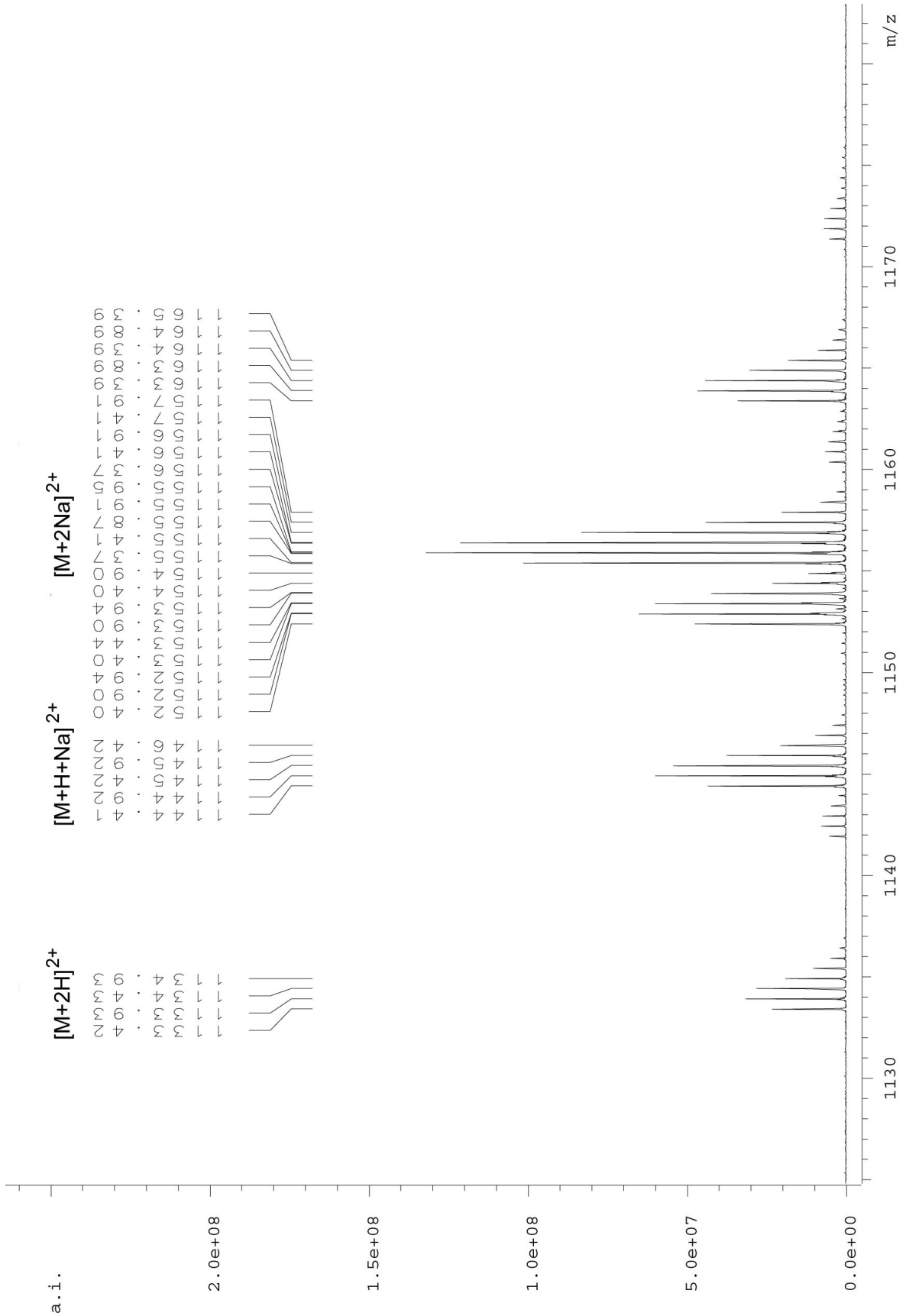


Fig. S2: HR-MS spectrum of **3**.

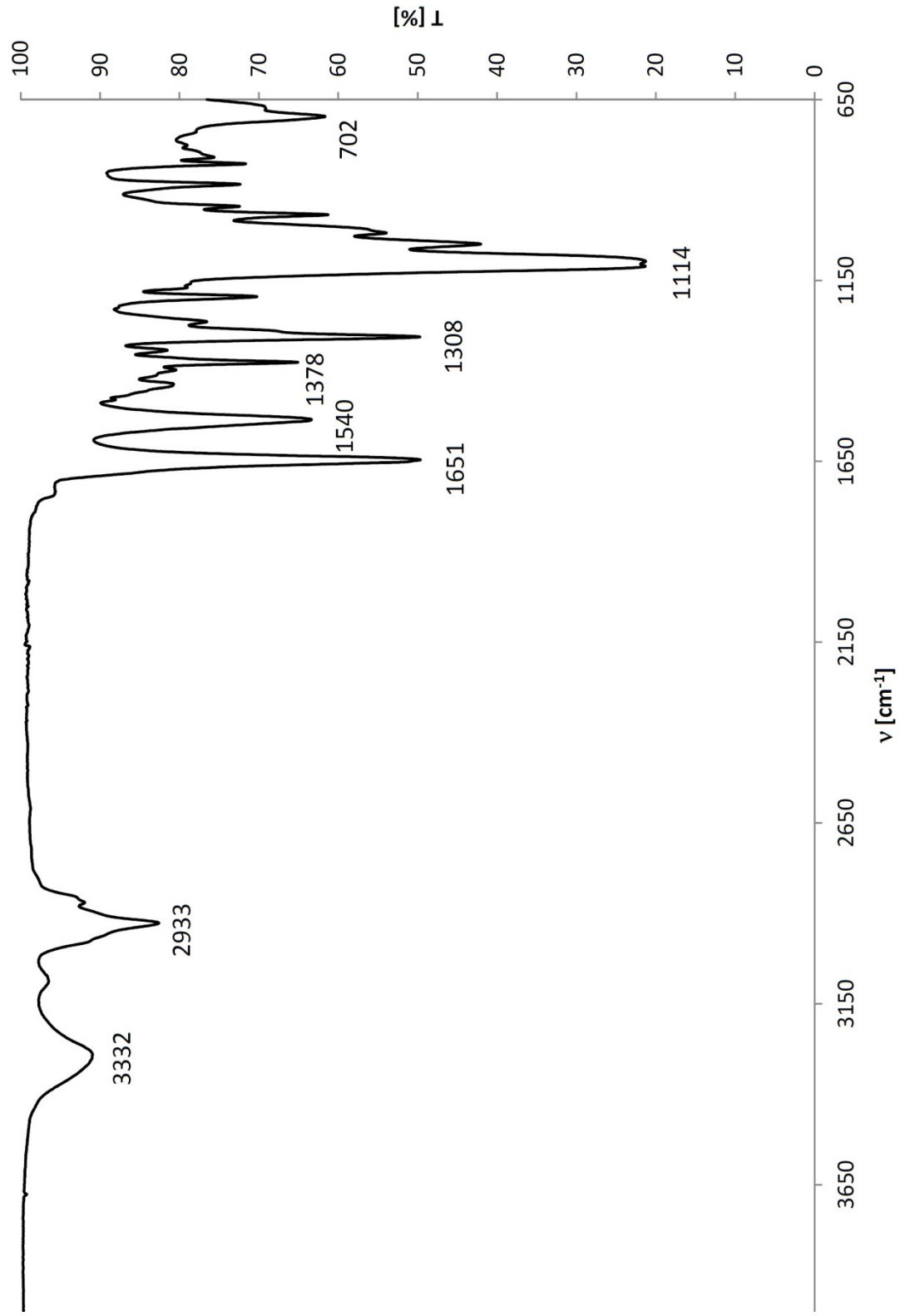


Fig. S3: ATR-IR spectrum of **2**

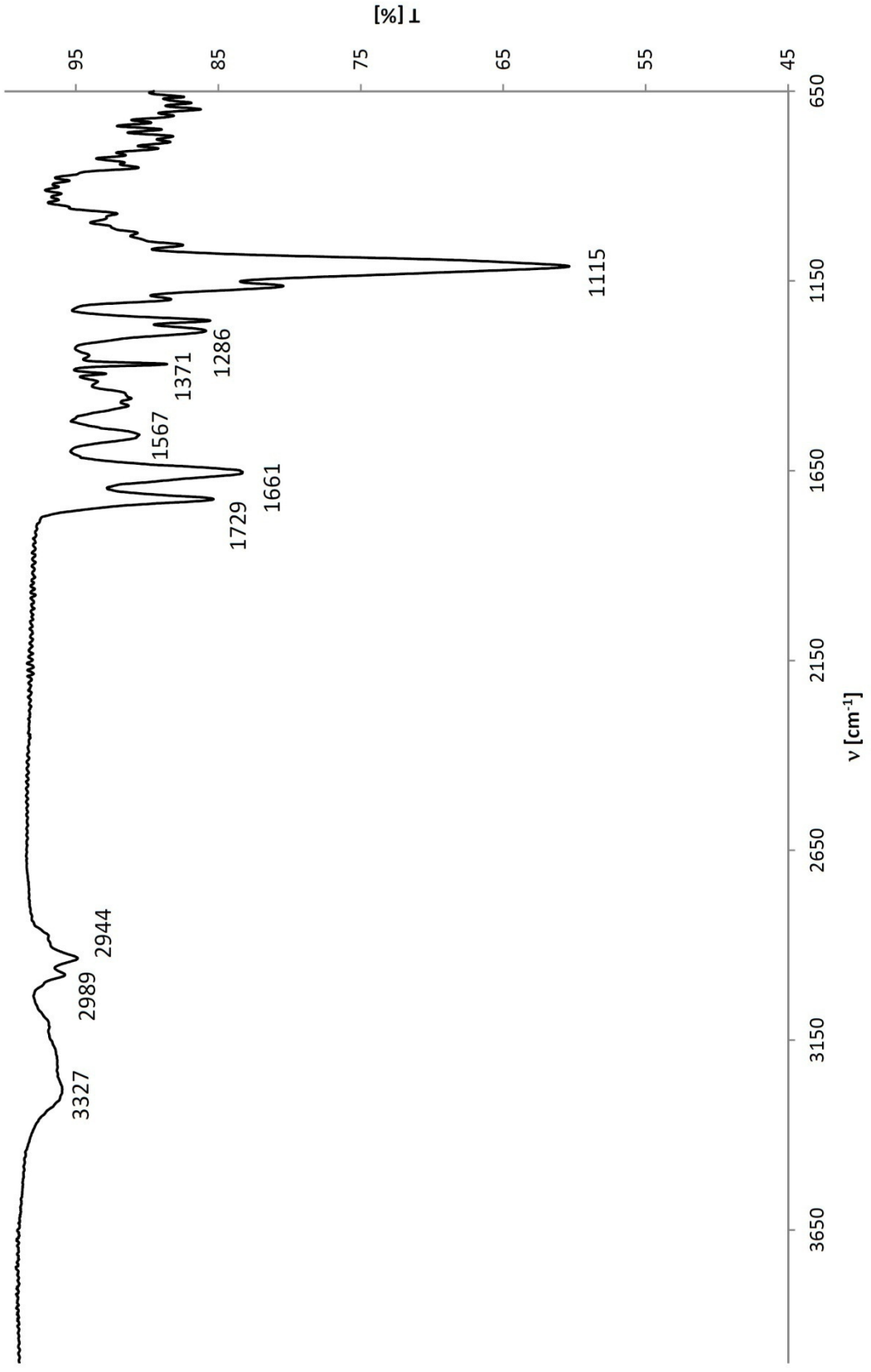


Fig. S4: ATR-IR spectrum of **3**.

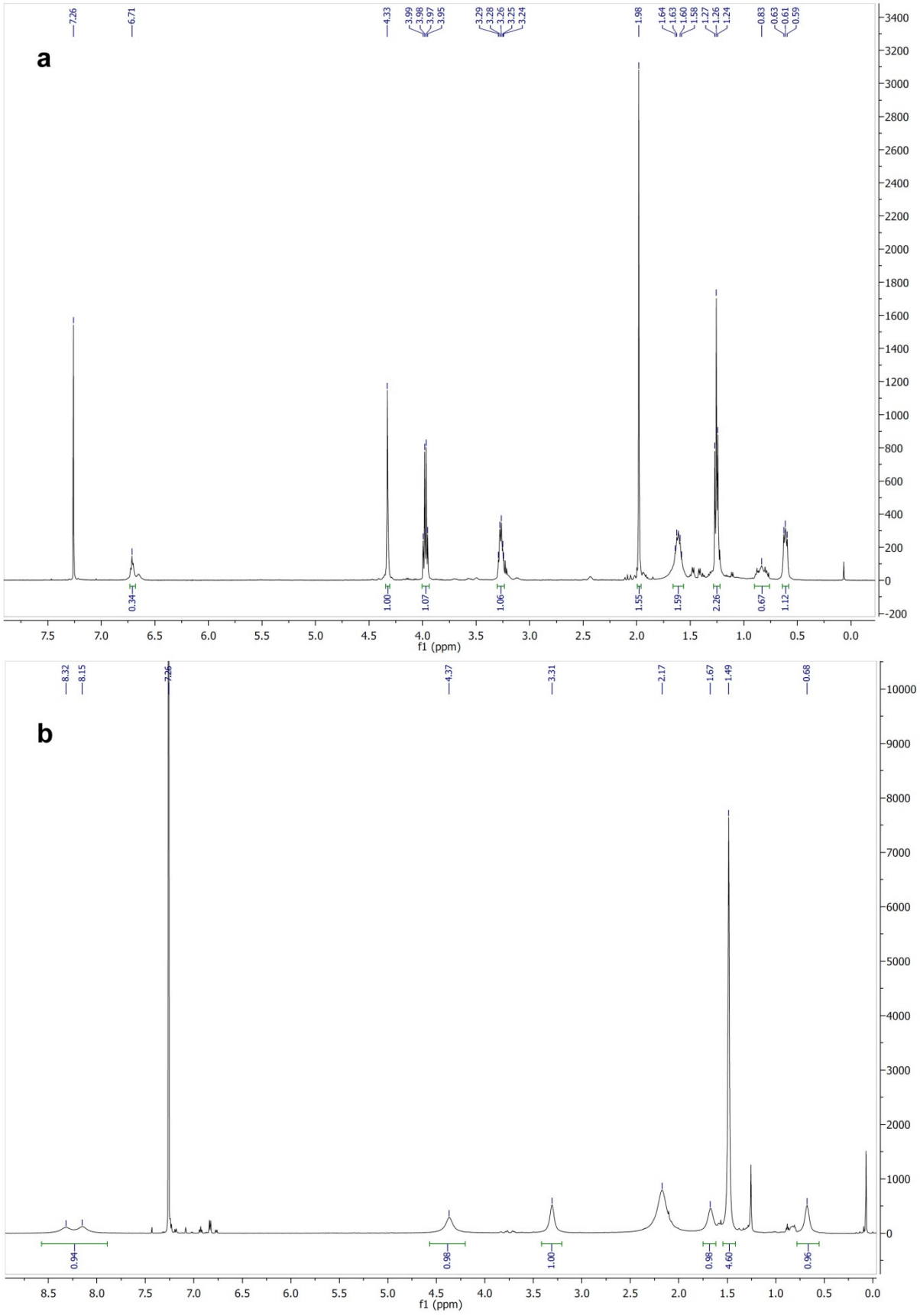


Fig. S5: (a) ^{1}H-NMR of **2**, (b) ^{1}H-NMR of **3**.

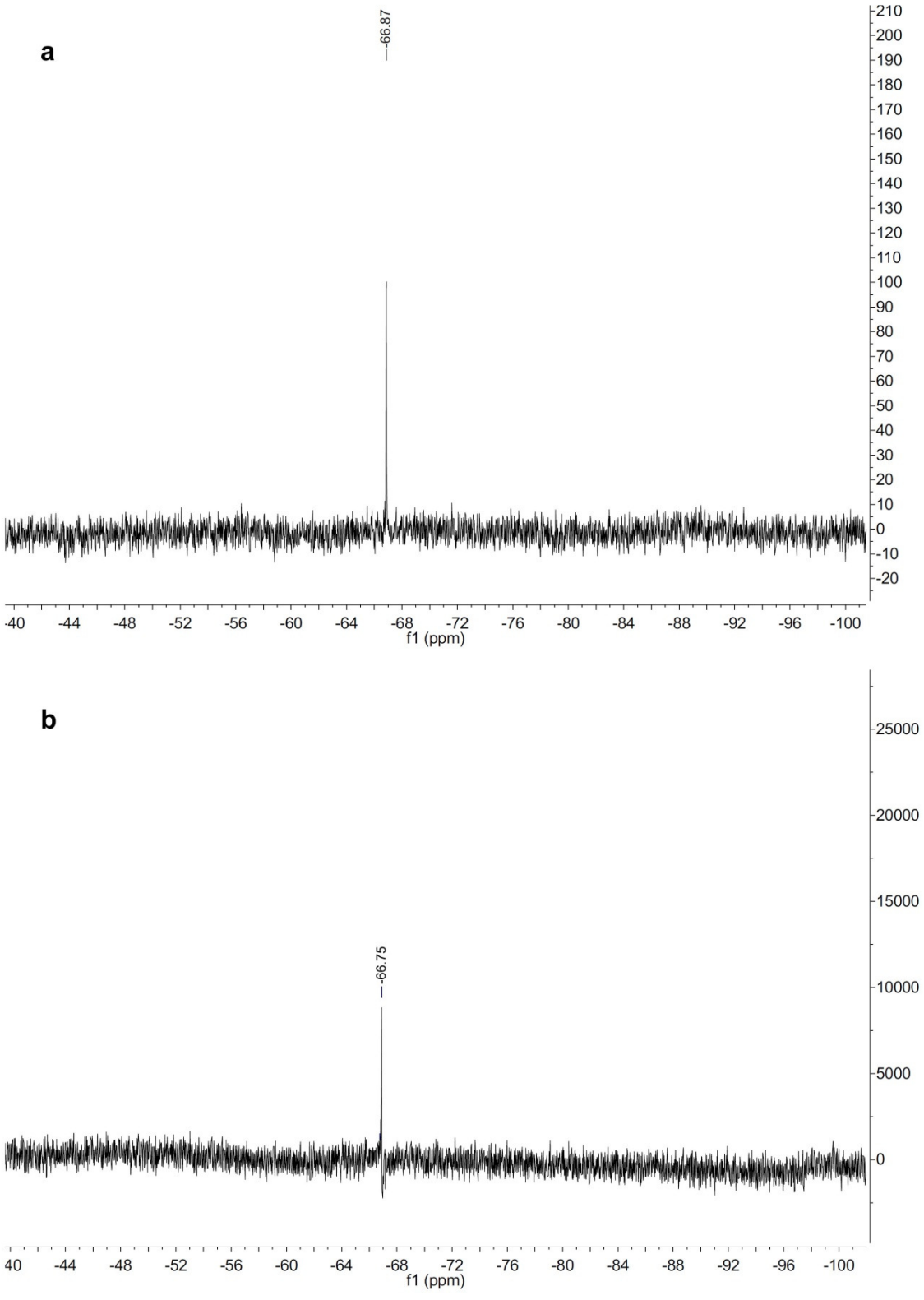


Fig. S6: (a) ^{29}Si-NMR of **2**, (b) ^{29}Si-NMR of **3**, the NMR spectra were base-line corrected using MestReNova.

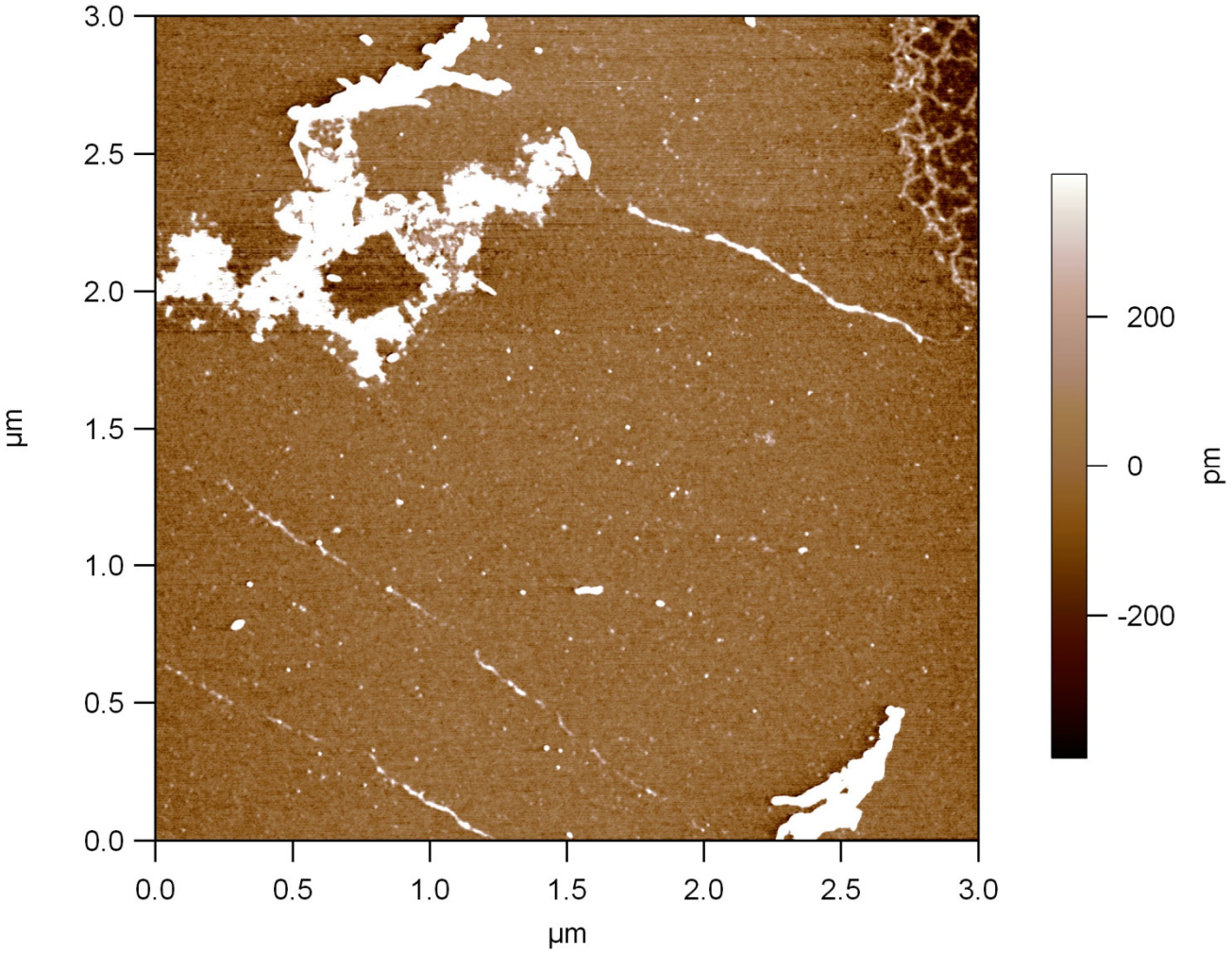
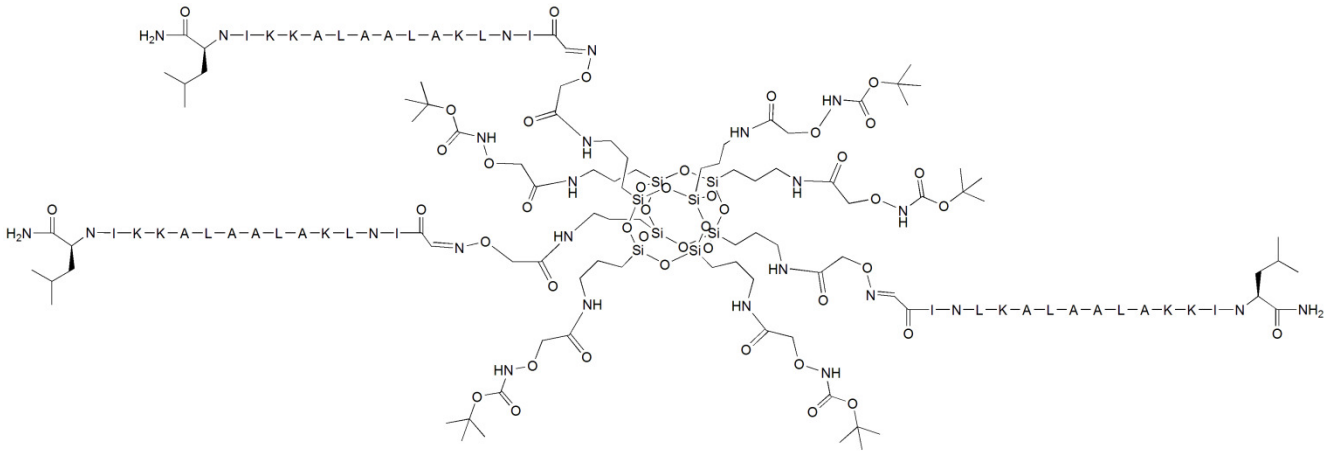


Fig. S7: AFM image of aggregated and randomly distributed COSS particles **1**.

a



b

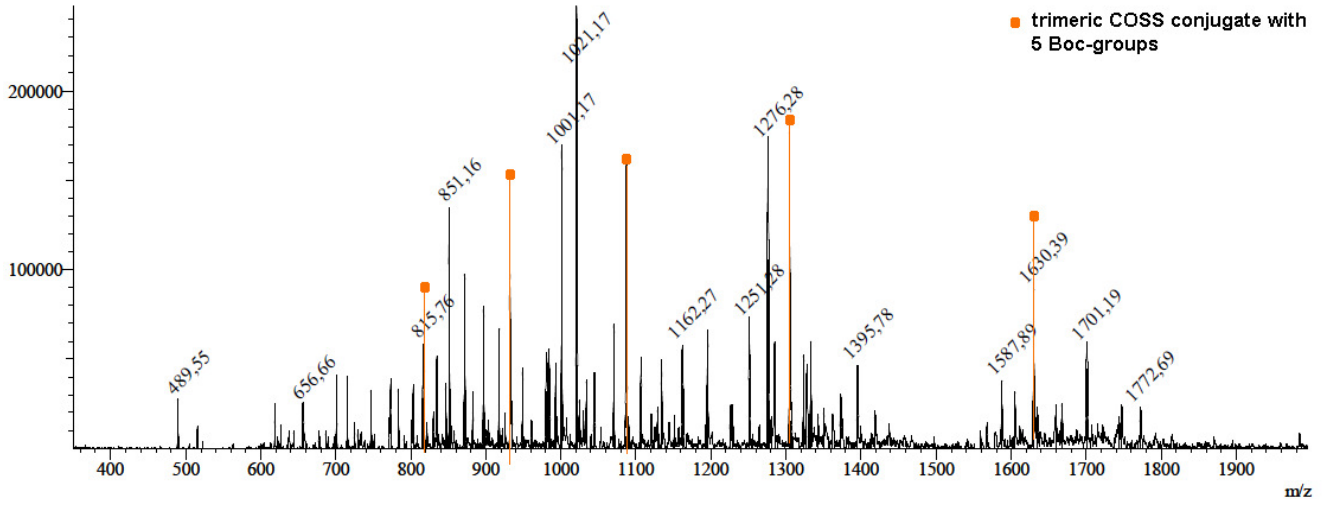
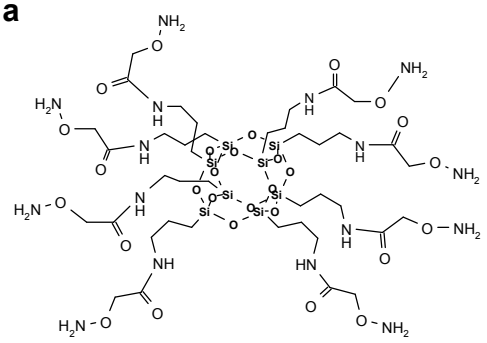


Fig. S8: (a) proposed structure of reaction intermediates in the synthesis of **6**. (b) ESI-MS spectrum of the reaction mixture after 30 min.

a

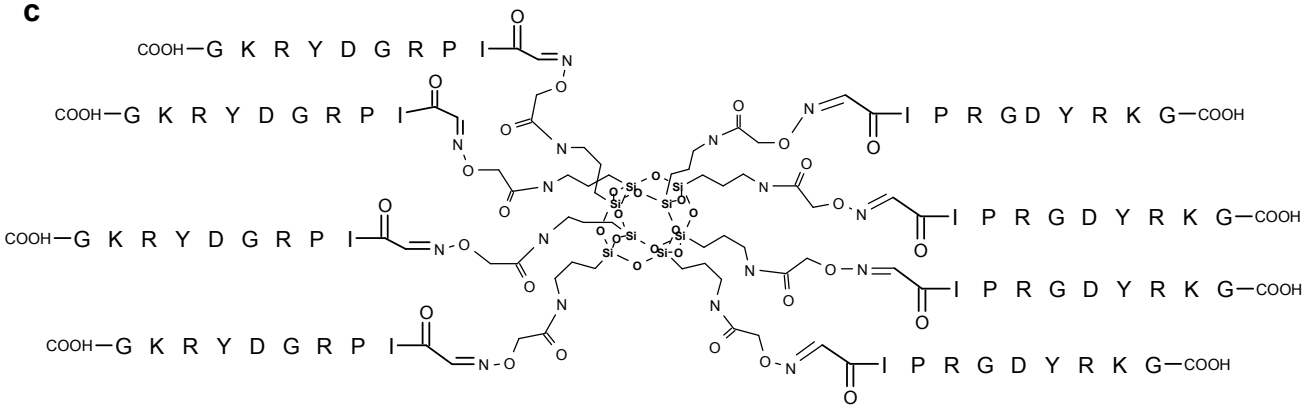


Molecular Weight =1465.93
Molecular Formula =$C_{40}H_{88}N_{16}O_{28}Si_8$

b

Molecular Weight =1117.24
Molecular Formula =$C_{48}H_{76}N_{16}O_{15}$

c



d

Monoconjugate
Molecular Weight =2565.15
Molecular Formula =$C_{88}H_{162}N_{32}O_{42}Si_8$

Diconjugate
Molecular Weight =3664.37
Molecular Formula =$C_{136}H_{236}N_{48}O_{56}Si_8$

Triconjugate
Molecular Weight =4763.60
Molecular Formula =$C_{184}H_{310}N_{64}O_{70}Si_8$

Tetraconjugate
Molecular Weight =5862.82
Molecular Formula =$C_{232}H_{384}N_{80}O_{84}Si_8$

Pentaconjugate
Molecular Weight =6962.04
Molecular Formula =$C_{280}H_{458}N_{96}O_{98}Si_8$

Hexaconjugate
Molecular Weight =8061.27
Molecular Formula =$C_{328}H_{532}N_{112}O_{112}Si_8$

Heptaconjugate
Molecular Weight =9160.49
Molecular Formula =$C_{376}H_{606}N_{128}O_{126}Si_8$

Octaconjugate
Molecular Weight =10259.72
Molecular Formula =$C_{424}H_{680}N_{144}O_{140}Si_8$

Fig. S9: (a) unprotected aminooxy COSS particle, (b) periodate oxidized **p4**, (c) possible conjugation products **4**.

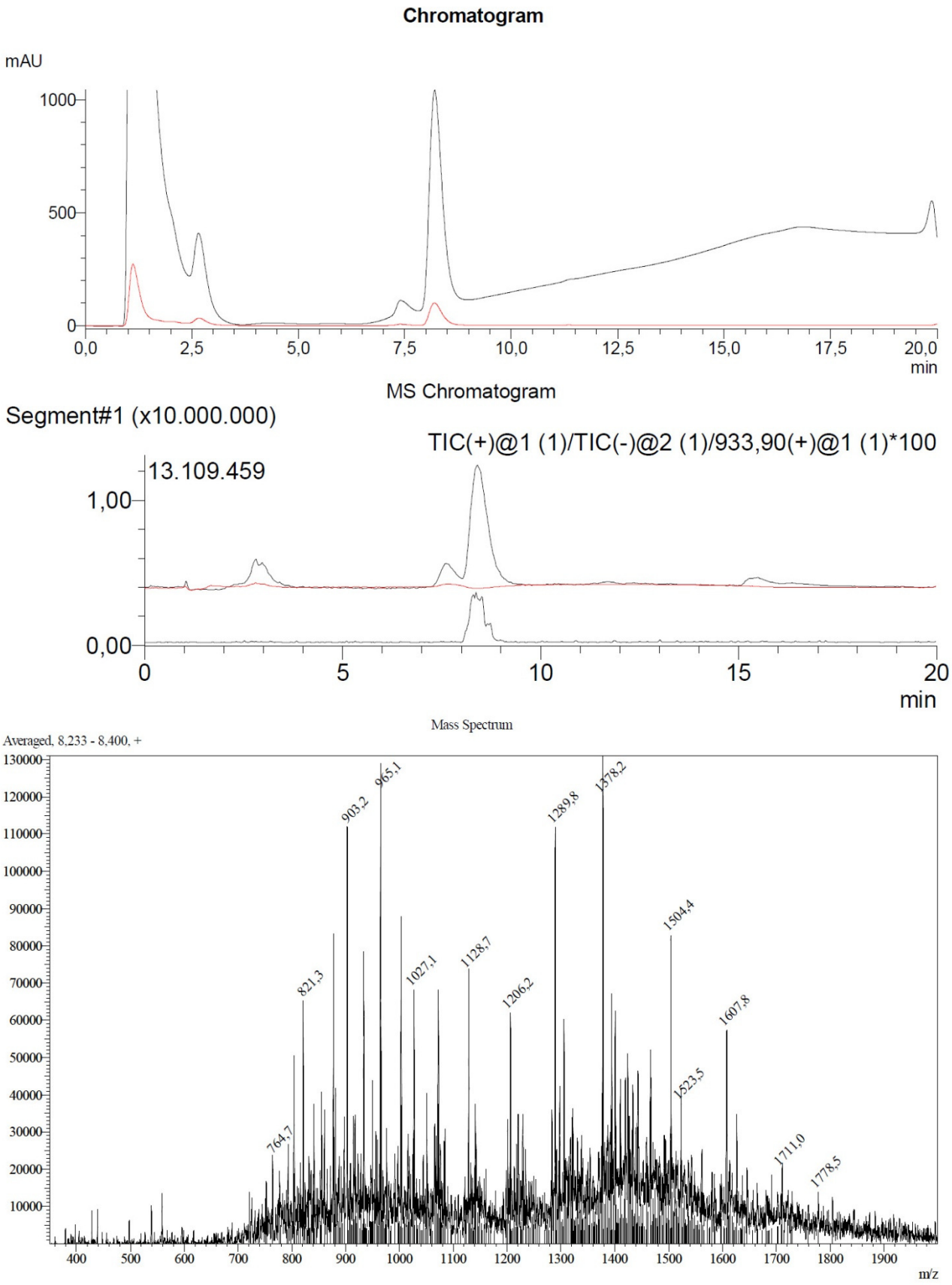


Fig. S10: LC-MS monitoring of the synthesis of **4**: analysis after overnight reaction.

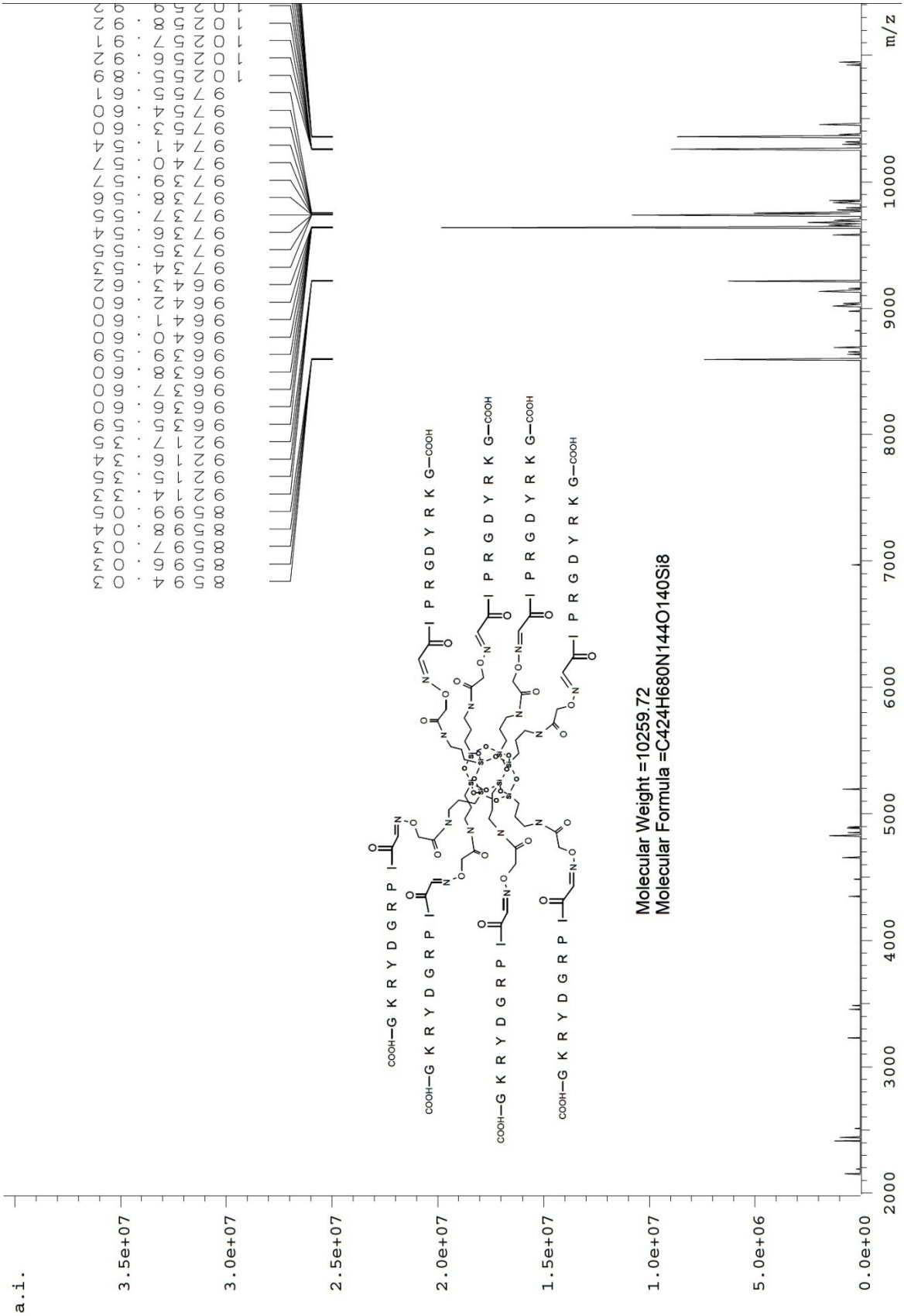


Fig. S11: Synthesis of **4**: deconvoluted ESI MS spectrum of the reaction mixture.

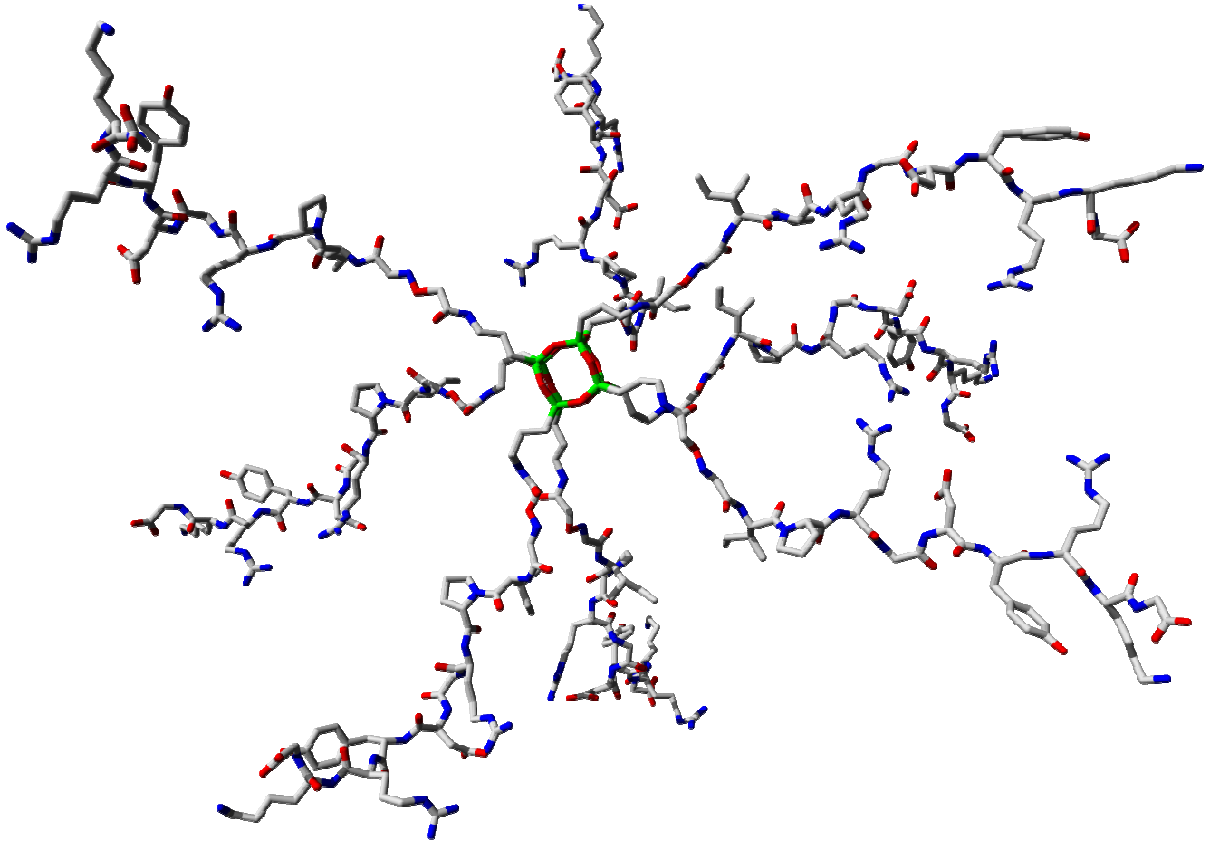
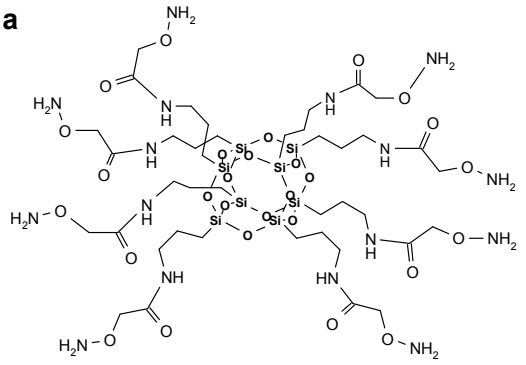


Fig. S12: 3D representation (sticks) of compound **4**. The model was generated using the YASARA structure package. After modelling of the COSS core atoms and connectivities an energy minimization procedure was applied. The respective peptide structures (compare **p4**) were attached, and the core coordinates were fixed. The resulting conjugate **4** was simulated in 0.9 % (m/v) NaCl aq. at pH 7 and 298 K for 0.1 ns using the AMBER03 force field. Blue: nitrogen, green: silicon, red: oxygen, grey: carbon, hydrogen was left out for clarity. Representative diameters were measured as distances of *C*-terminal carboxylic carbons of peptide ligands attached to opposing corners of the COSS cage. The measured values were: 7.21 nm, 6.69 nm, 6.16 nm, and 5.61 nm. The resulting average diameter was 6.42 ± 0.69 nm.

a

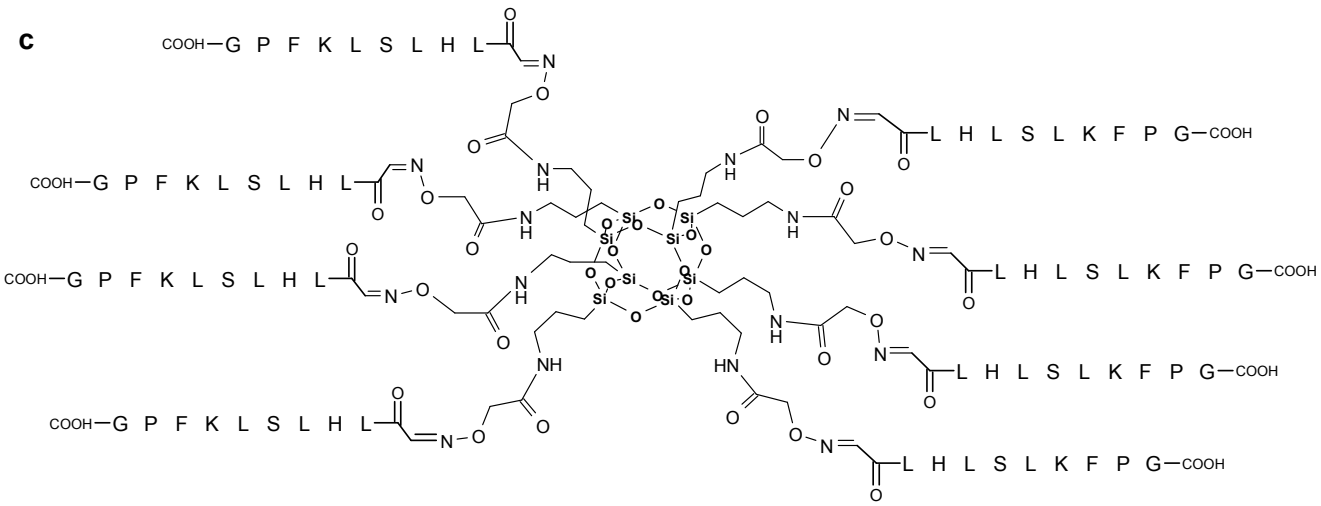


Molecular Weight =1465.93
Molecular Formula =$C_{40}H_{88}N_{16}O_{28}Si_8$

b

Molecular Weight =1067.26
Molecular Formula =$C_{51}H_{78}N_{12}O_{13}$

c



d

Monoconjugate
Molecular Weight =2515.17
Molecular Formula =$C_{91}H_{164}N_{28}O_{40}Si_8$

Diconjugate
Molecular Weight =3564.42
Molecular Formula =$C_{142}H_{240}N_{40}O_{52}Si_8$

Triconjugate
Molecular Weight =4597.65
Molecular Formula =$C_{193}H_{314}N_{51}O_{64}Si_8$

Tetraconjugate
Molecular Weight =5662.92
Molecular Formula =$C_{244}H_{392}N_{64}O_{76}Si$-

Pentaconjugate
Molecular Weight =6712.16
Molecular Formula =$C_{295}H_{468}N_{76}O_{88}Si_8$

Hexaconjugate
Molecular Weight =7761.41
Molecular Formula =$C_{346}H_{544}N_{88}O_{100}Si_8$

Heptaconjugate
Molecular Weight =8810.66
Molecular Formula =$C_{397}H_{620}N_{100}O_{112}Si_8$

Octaconjugate
Molecular Weight =9859.91
Molecular Formula =$C_{448}H_{696}N_{112}O_{124}Si_8$

Fig. S13: (a) unprotected aminooxy COSS particle, (b) periodate oxidized **p5**, (c) possible conjugation products **5**.

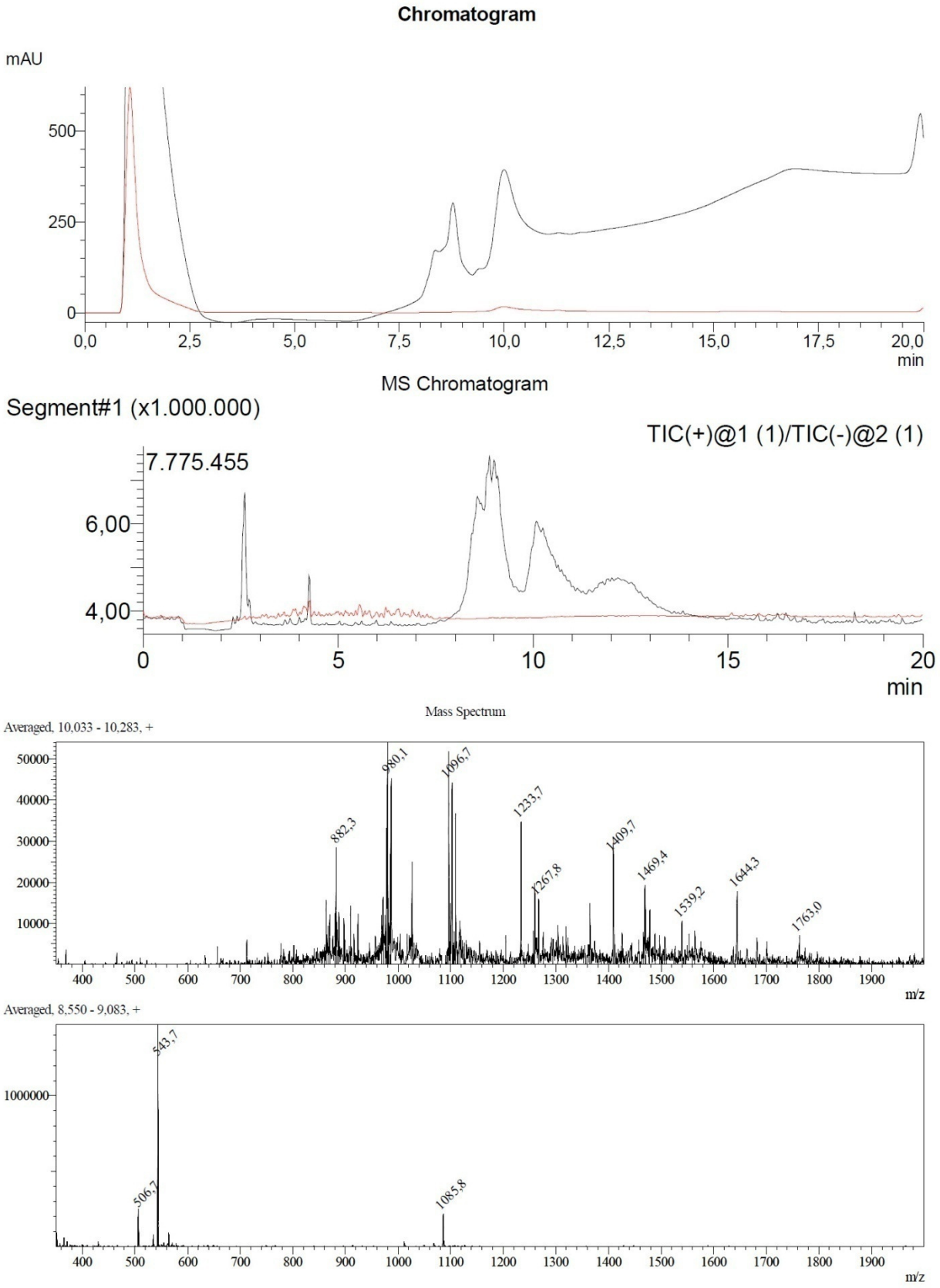


Fig. S14: LC-MS monitoring of the synthesis of **5**: analysis after overnight reaction.

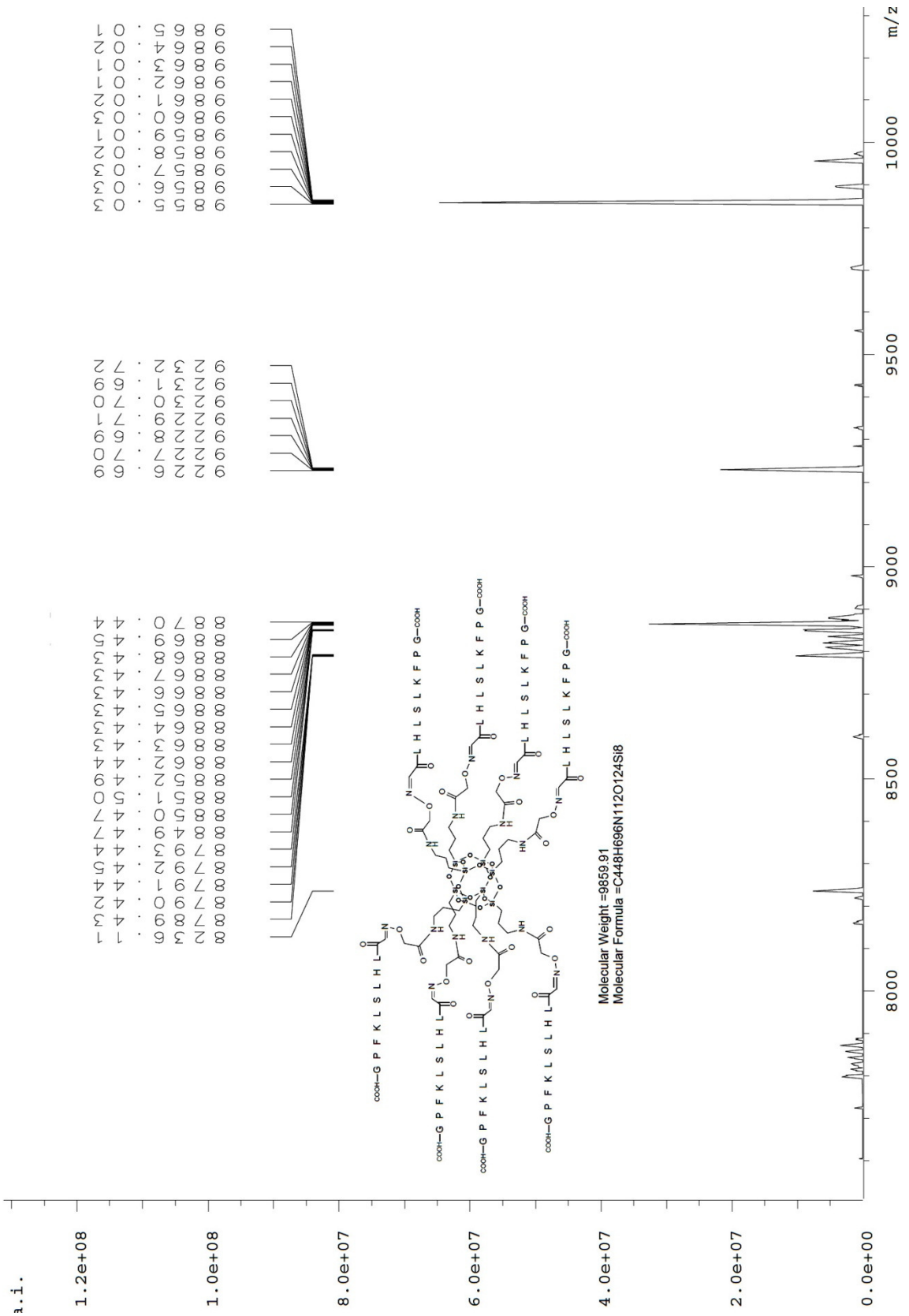


Fig. S15: Synthesis of **5**: deconvoluted ESI MS spectrum of the reaction mixture.

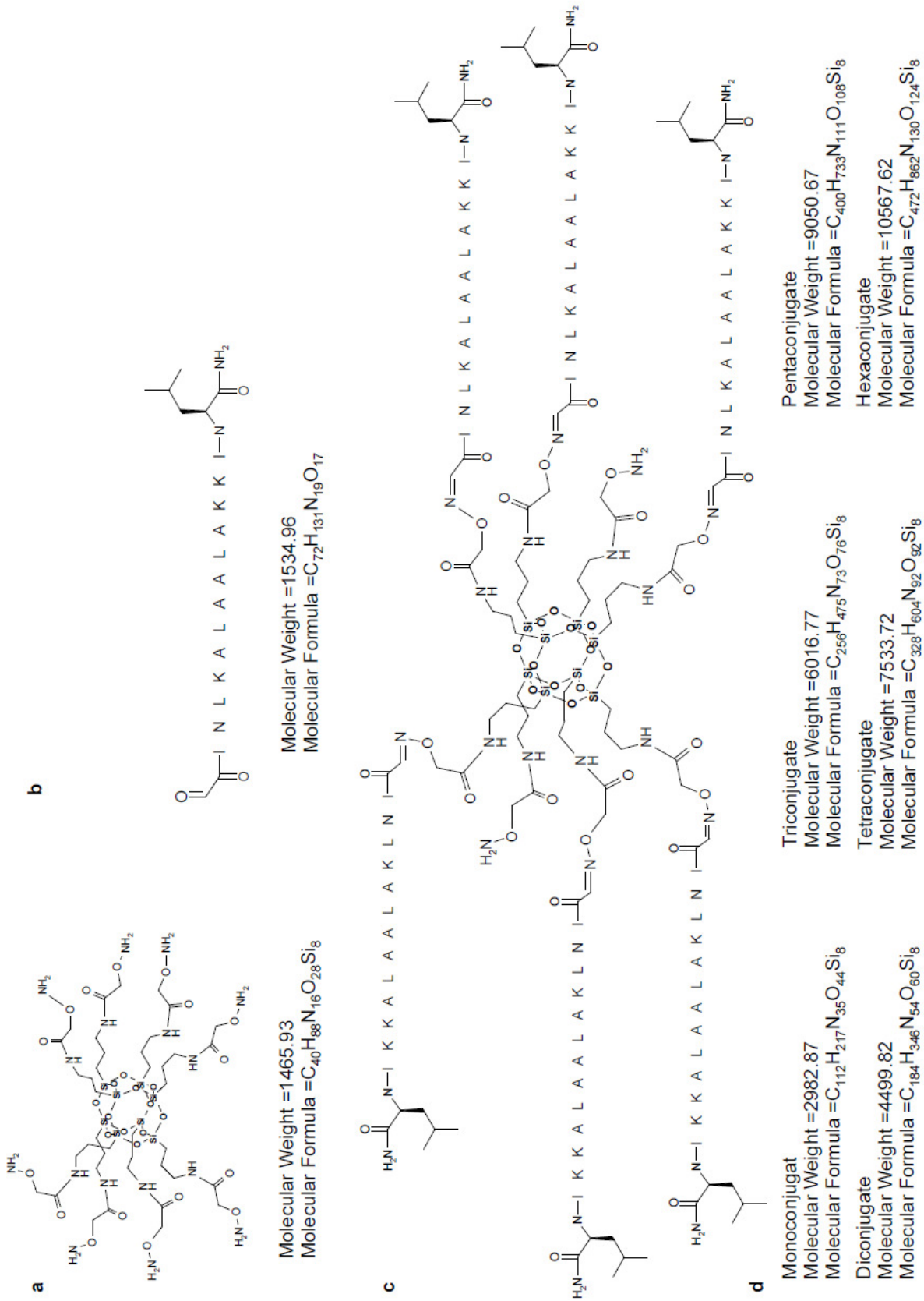


Fig. S16: (a) unprotected aminooxy COSS particle, (b) periodate oxidized **p6**, (c) possible conjugation products **6**.

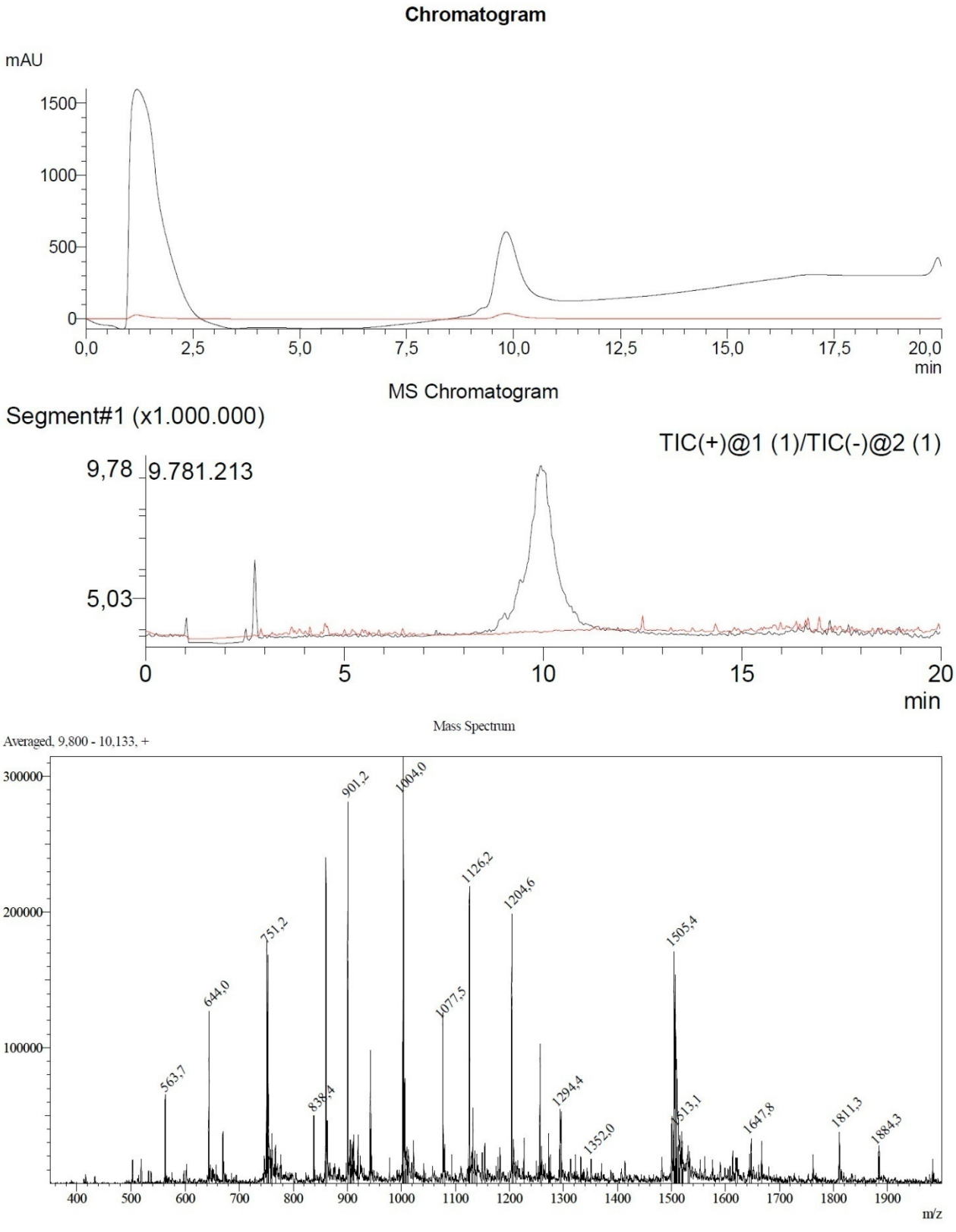


Fig. S17: LC-MS monitoring of the synthesis of **6**: analysis after overnight reaction.

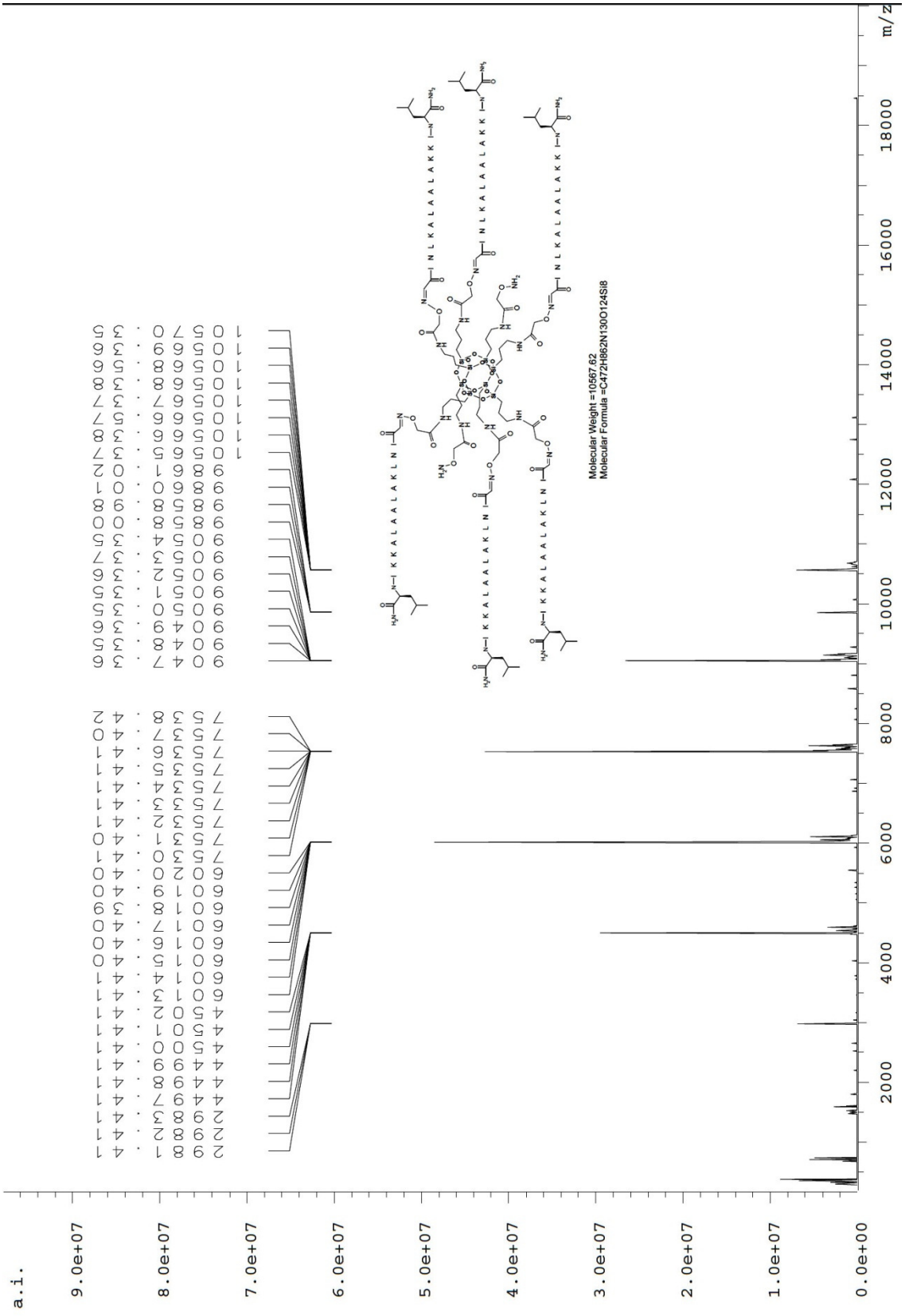


Fig. S18: Synthesis of **6**: deconvoluted ESI MS spectrum of the reaction mixture.

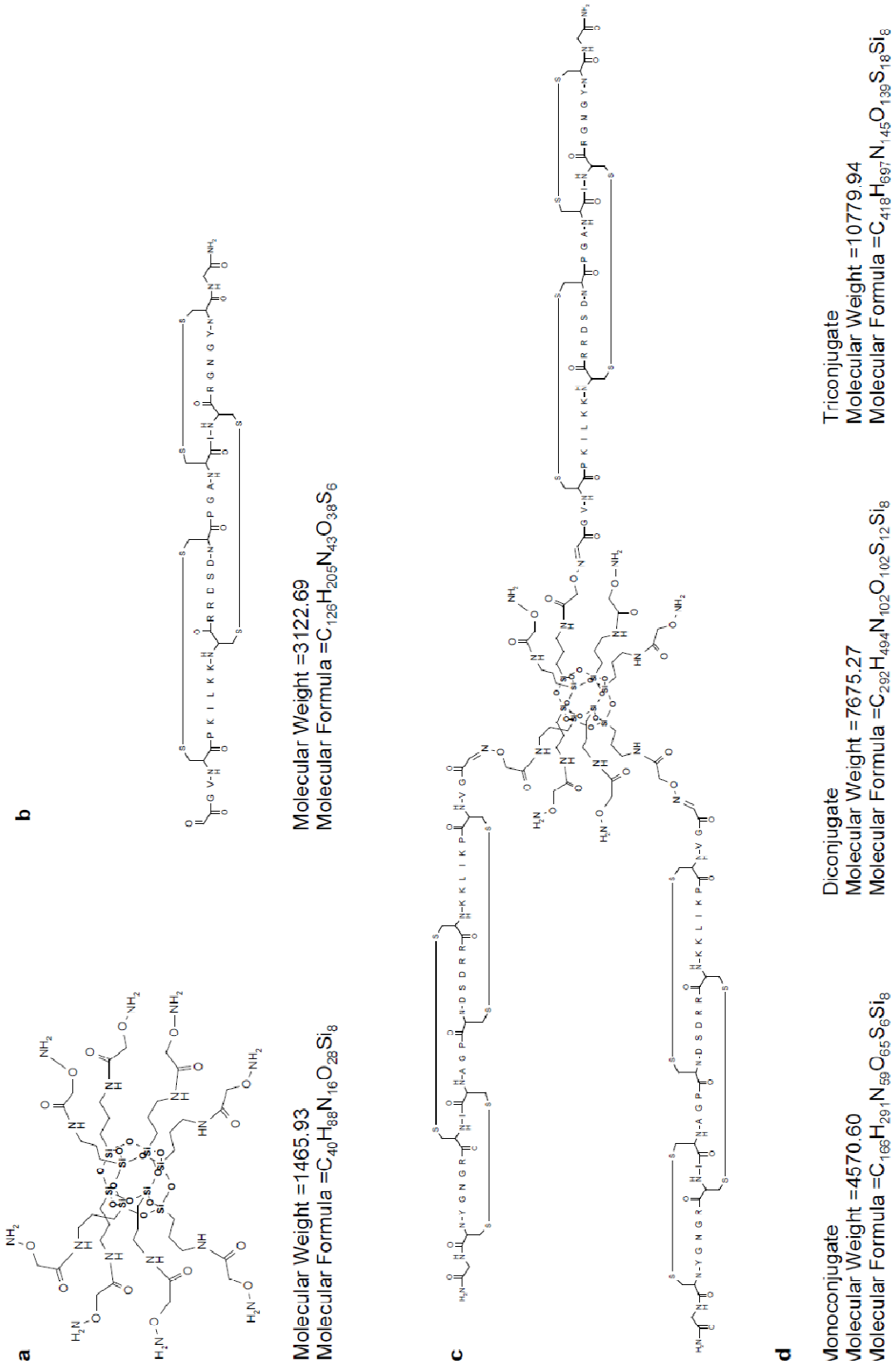


Fig. S19: (a) unprotected aminooxy COSS particle, (b) periodate oxidized **p7**, (c) possible conjugation products.

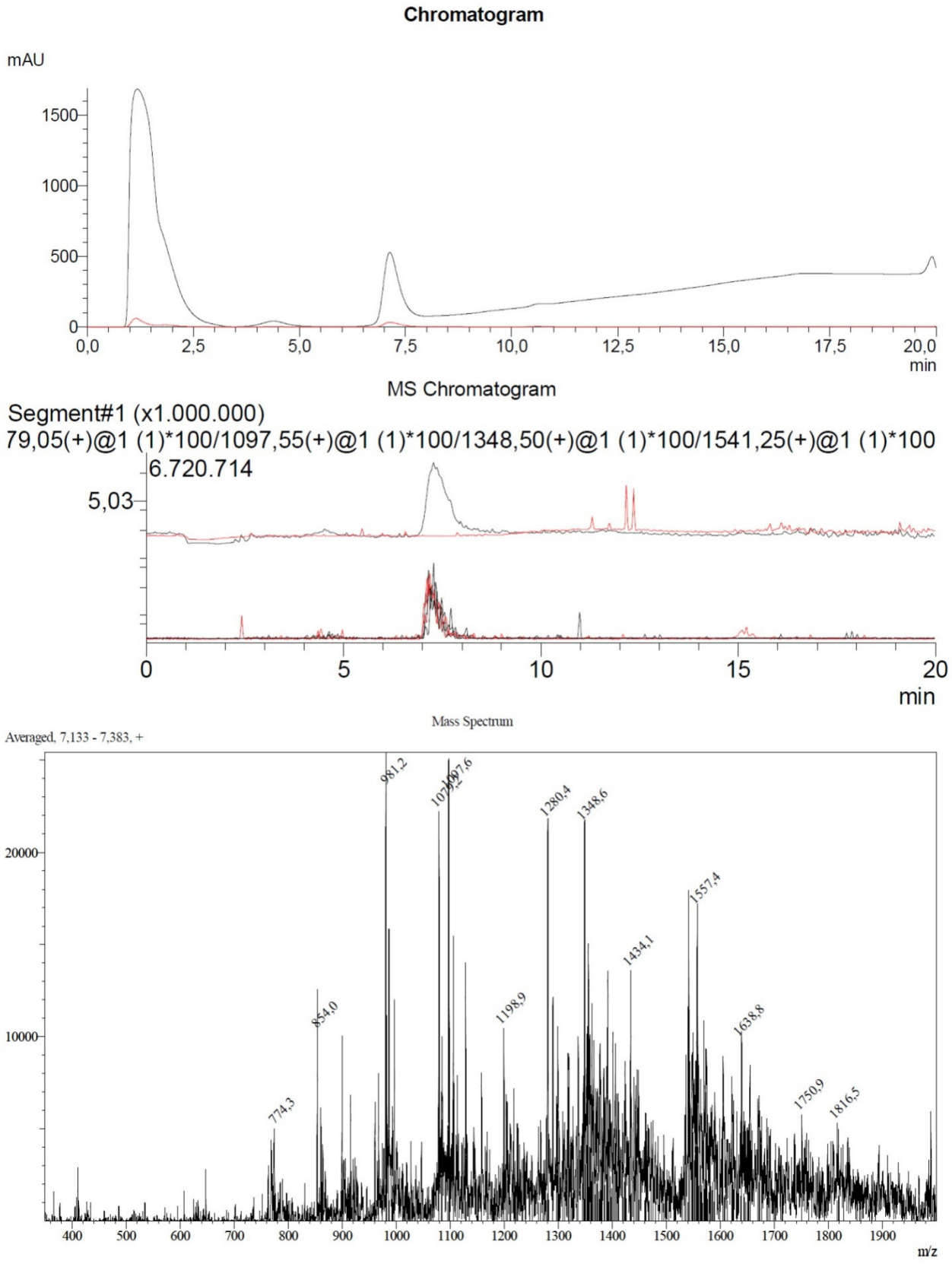


Fig. S20: LC-MS monitoring of the synthesis of **7**: analysis after overnight reaction.

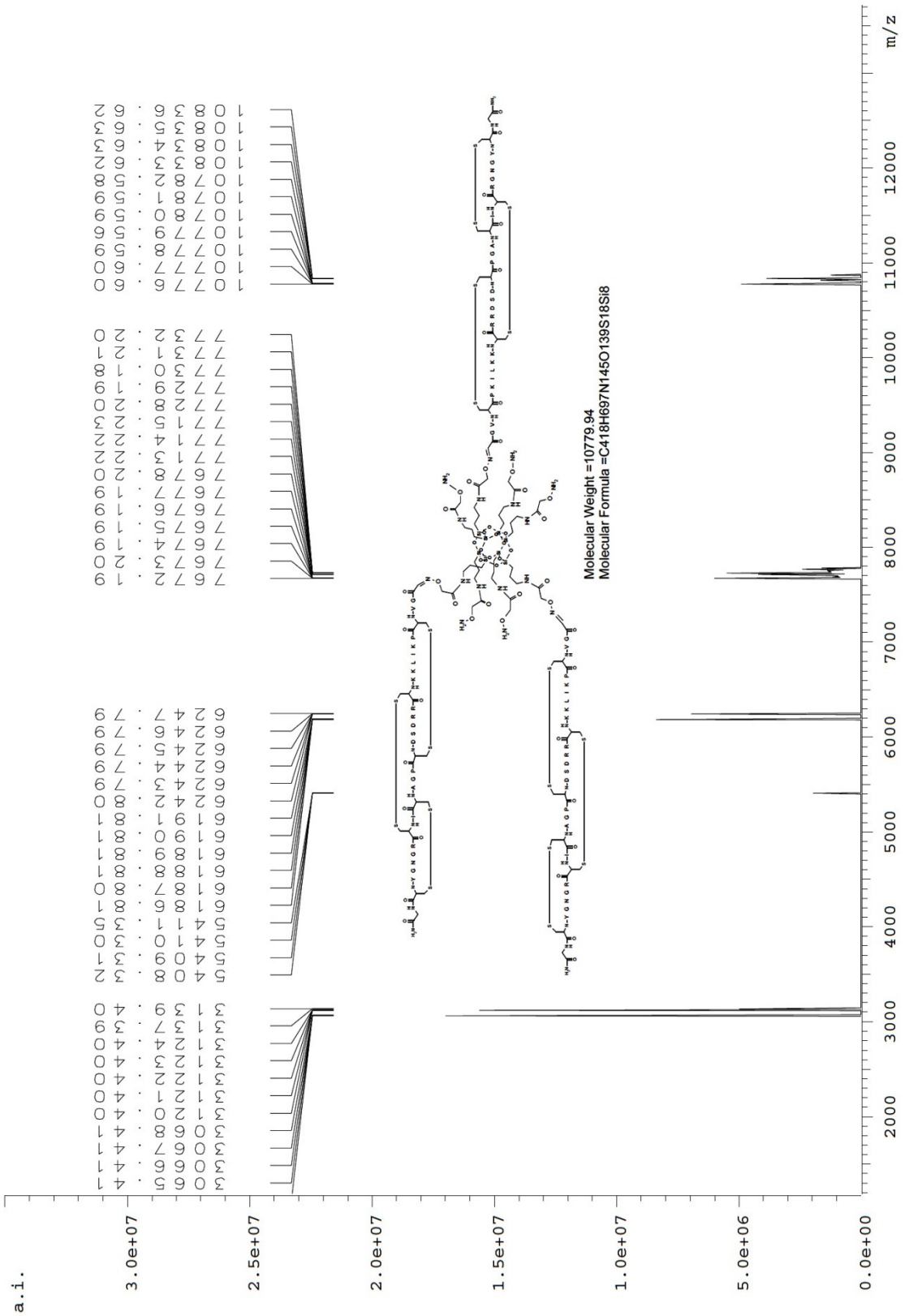
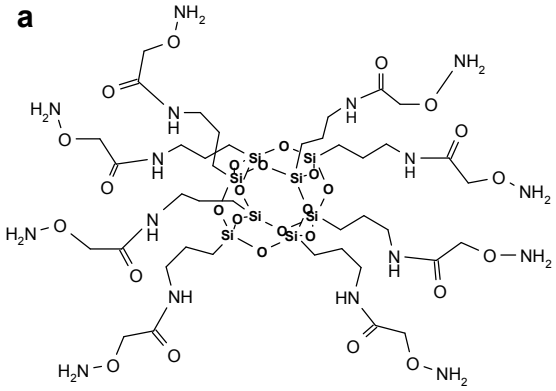


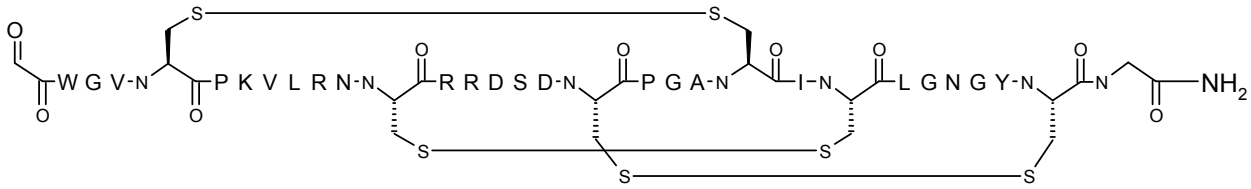
Fig. S21: Synthesis of **7**: deconvoluted ESI MS spectrum of the reaction mixture.

a



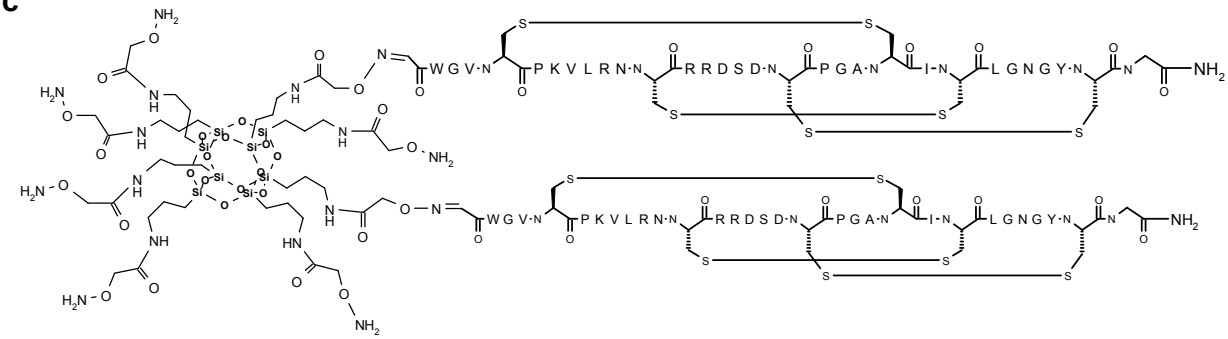
Molecular Weight =1465.93
Molecular Formula =$C_{40}H_{88}N_{16}O_{28}Si_8$

b



Molecular Weight =3265.79
Molecular Formula =$C_{134}H_{206}N_{44}O_{40}S_6$

c



d

Monoconjugate
Molecular Weight =4713.70
Molecular Formula =$C_{174}H_{292}N_{60}O_{67}S_6Si_8$

Diconjugate
Molecular Weight =7961.48
Molecular Formula =$C_{308}H_{496}N_{104}O_{106}S_{12}Si_8$

Fig. S22: (a) unprotected aminooxy COSS particle, (b) periodate oxidized **p8**, (c) possible conjugation products **8**.

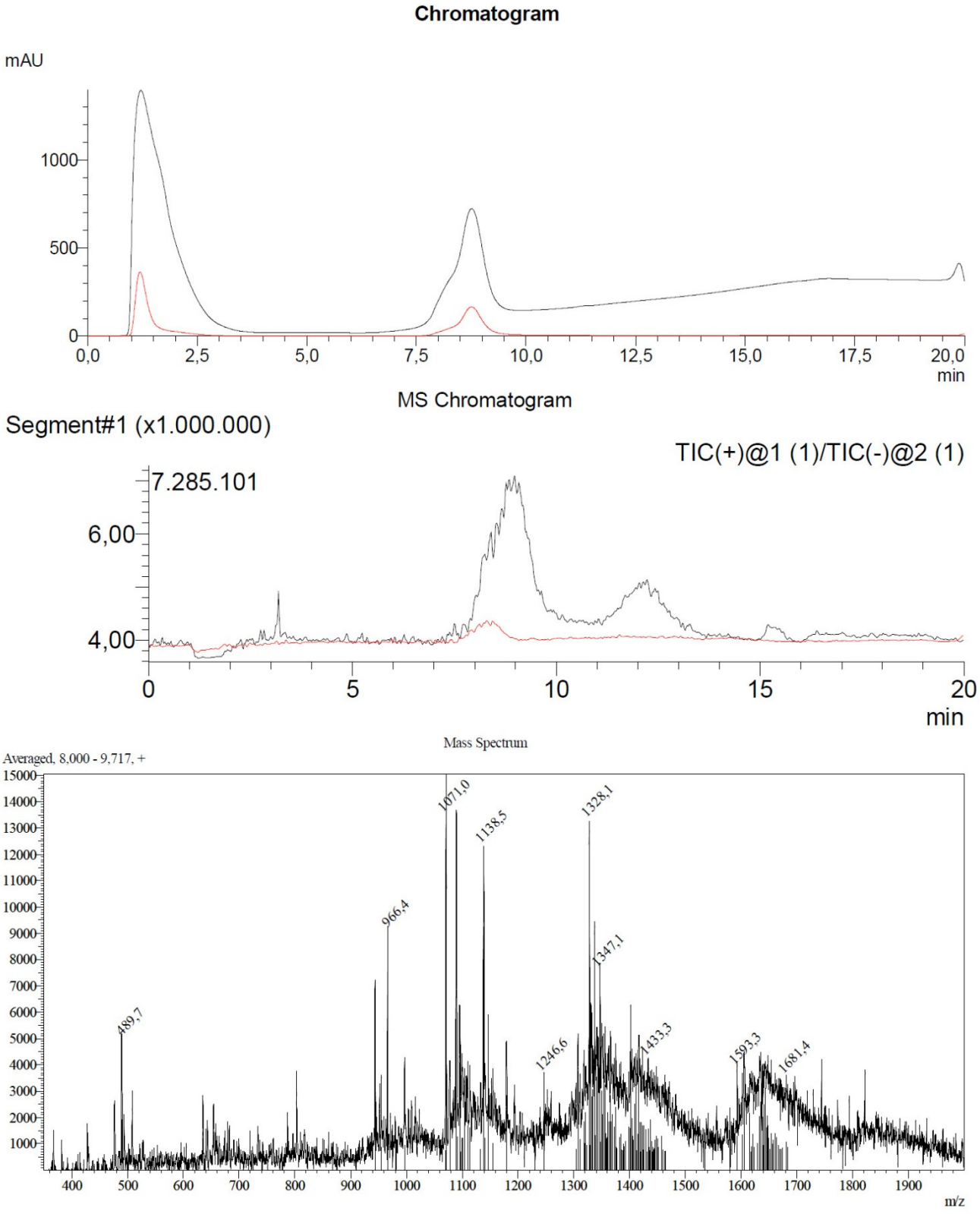


Fig. S23: LC-MS monitoring of the synthesis of **8**: analysis after overnight reaction.

Supplemental Information

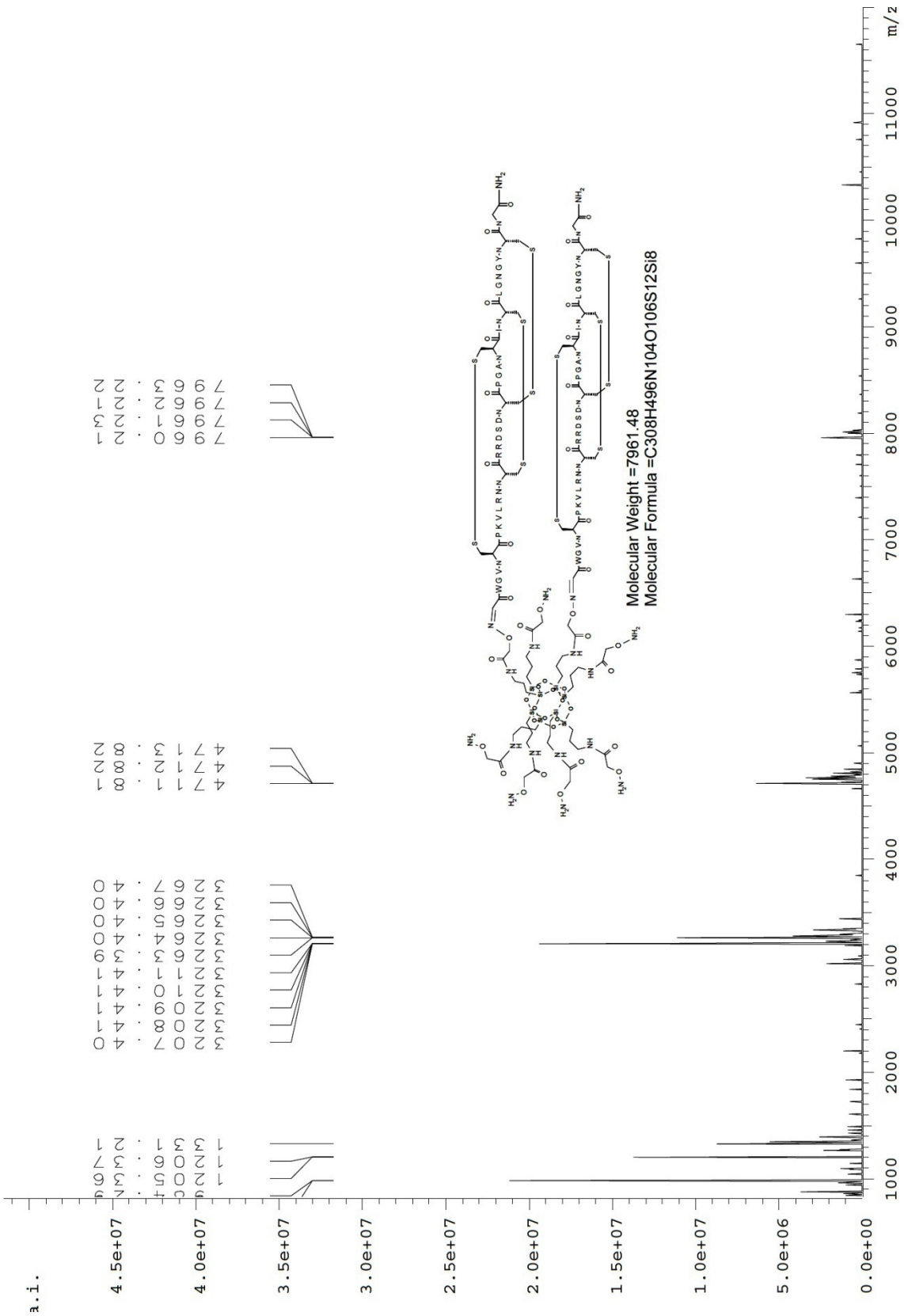
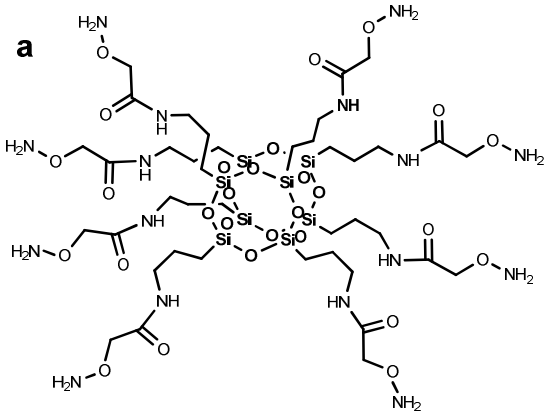


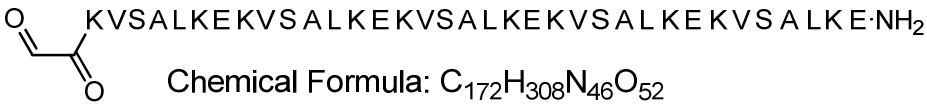
Fig. S24: Synthesis of **8**: deconvoluted ESI MS spectrum of the reaction mixture.

a



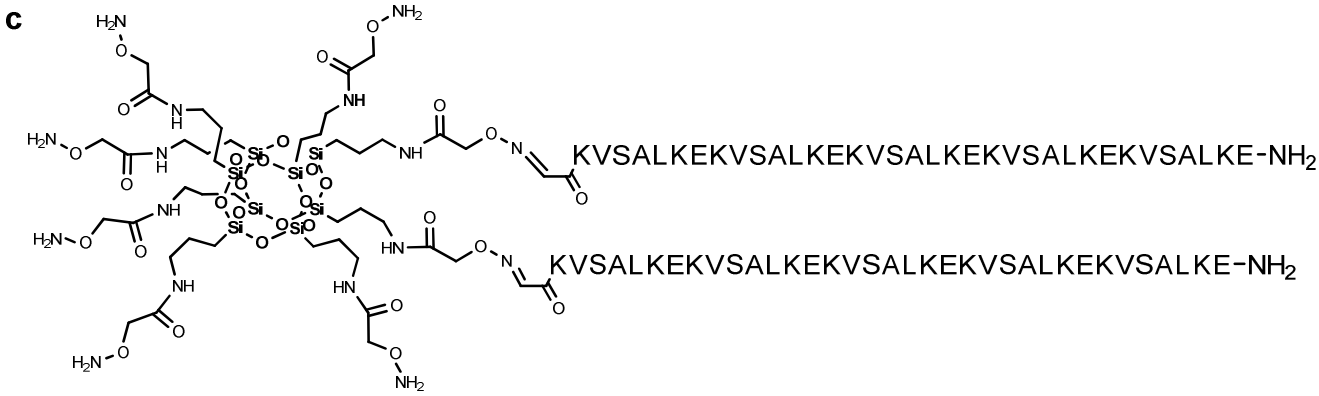
Chemical Formula: C40H88N16O28Si8 $C_{40}H_{88}N_{16}O_{28}Si_8$
Molecular Weight: 1465.901465.9011

b



Chemical Formula: $C_{172}H_{308}N_{46}O_{52}$
Molecular Weight: 3852.5629

c



d

Monoconjugate
Chemical Formula: $C_{212}H_{394}N_{62}O_{79}Si_8$
Molecular Weight: 5300.44

Diconjugate
Chemical Formula: $C_{384}H_{700}N_{108}O_{130}Si_8$
Molecular Weight: 9134.99

Fig. S25: (a) unprotected aminooxy COSS particle, (b) periodate oxidized **p9**, (c) possible conjugation products **9**.

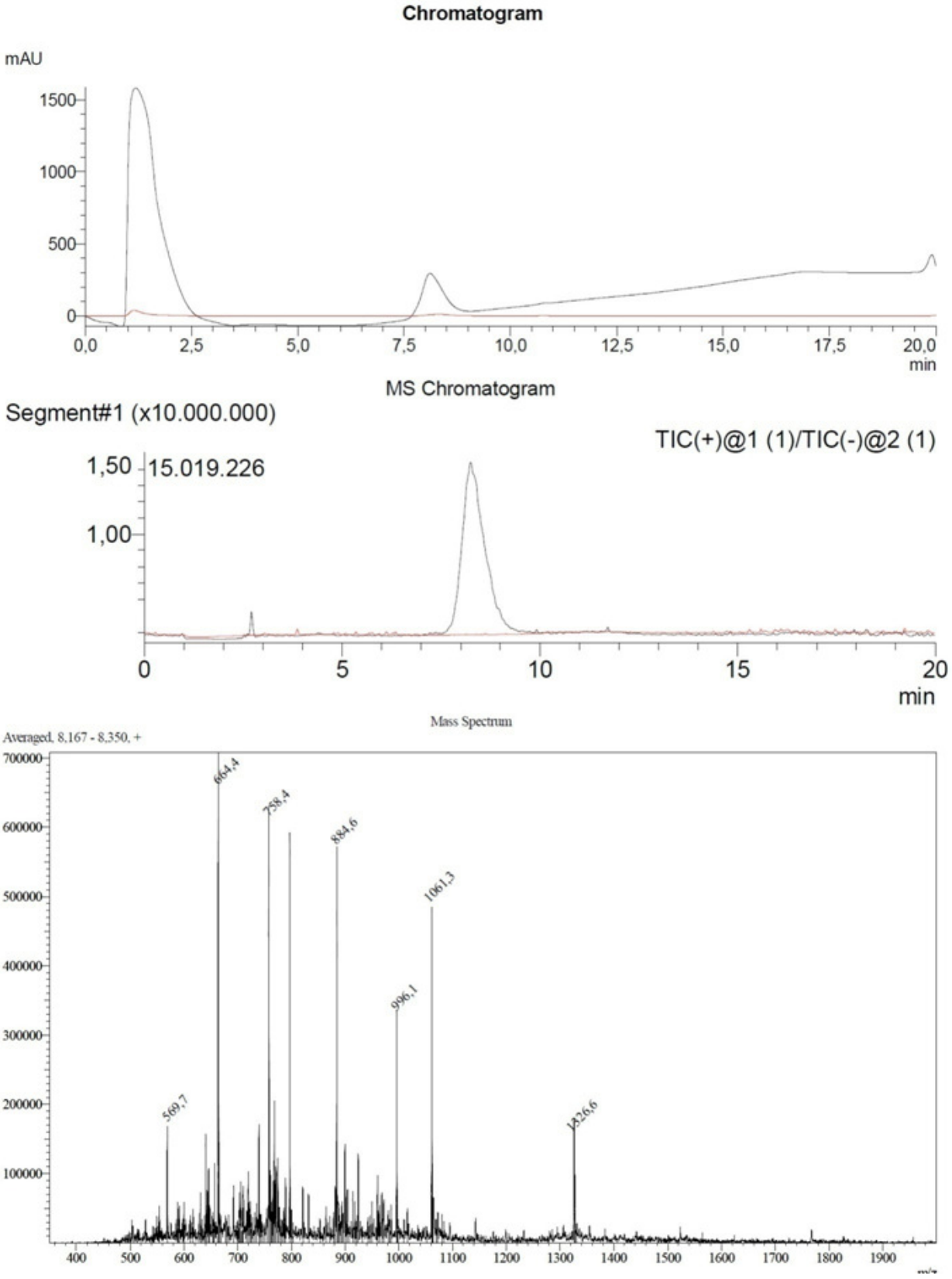


Fig. S26: LC-MS monitoring of the synthesis of **9**: analysis after overnight reaction.

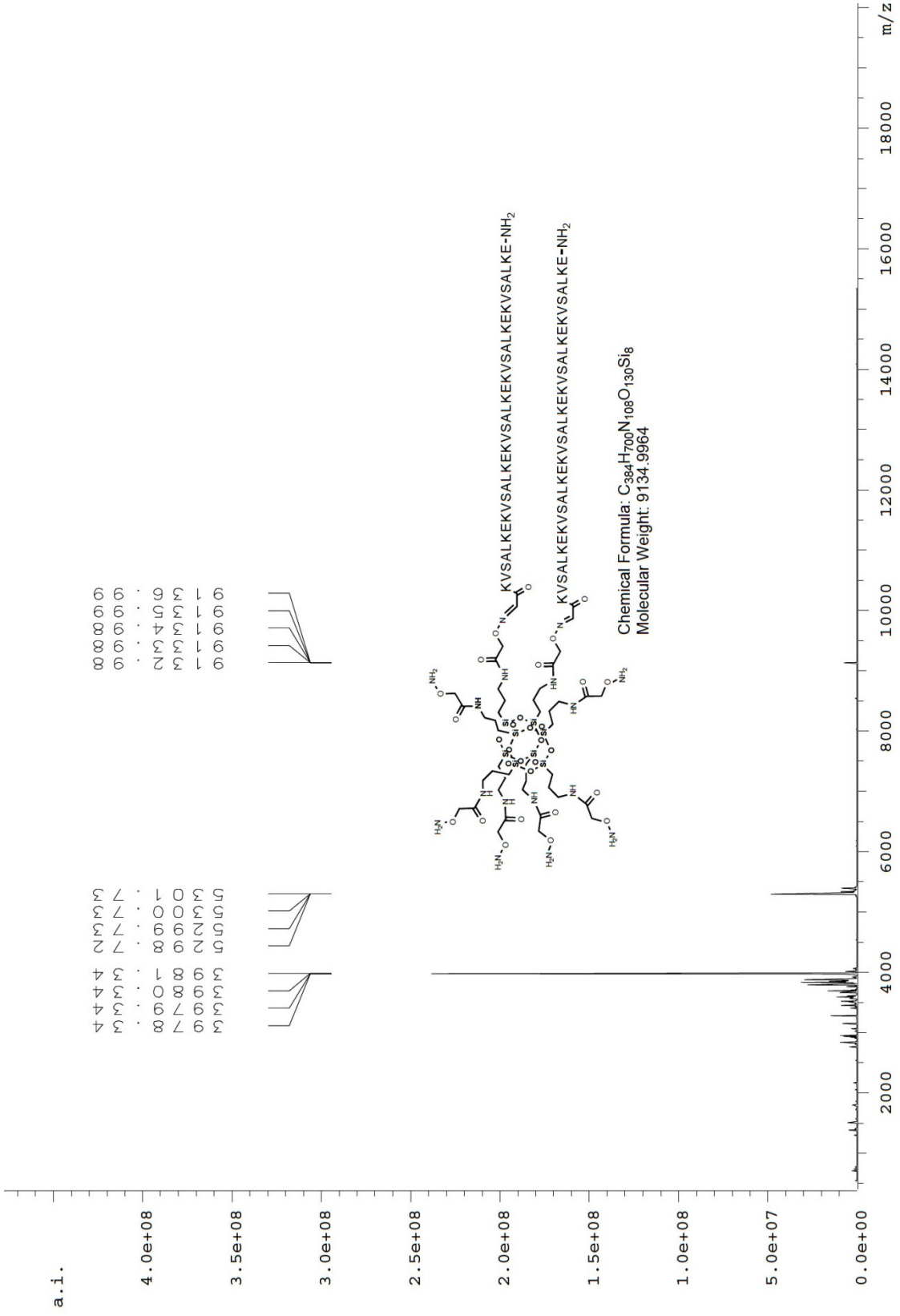


Fig. S27: Synthesis of **9**: deconvoluted ESI MS spectrum of the reaction mixture.