

**Supporting Information
for
Orthogonal dual thiol–chloroacetyl and thiol–ene
couplings for the sequential one-pot assembly of
heteroglycoclusters**

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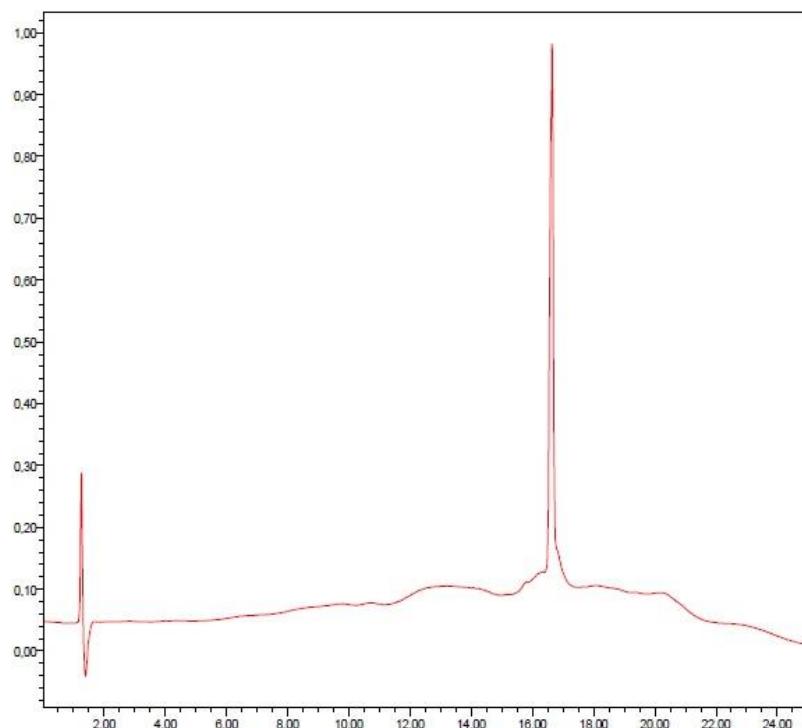
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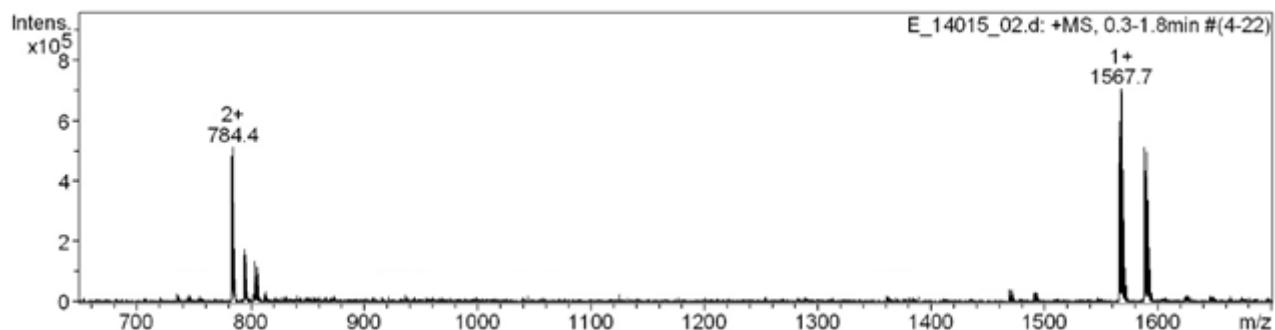
*Corresponding author

HPLC chromatograms and mass spectra of all compounds

Compound 3.

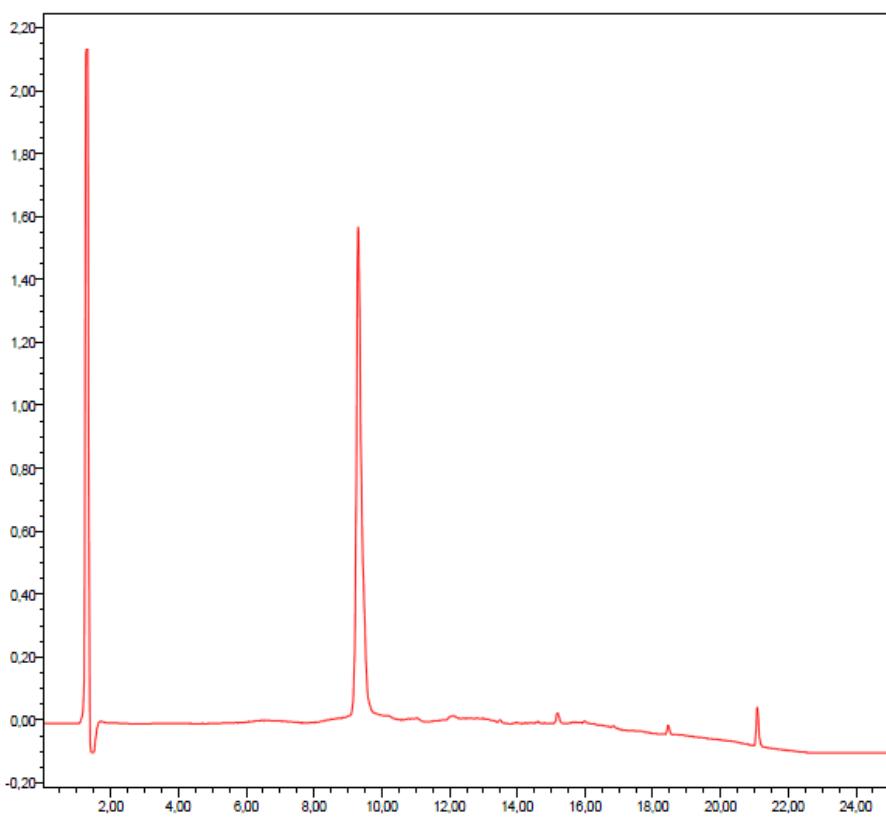


Analytical RP-HPLC: $t_R = 16.64$ min (gradient: 5 to 100% B in 20 min, $\lambda = 214$ nm).

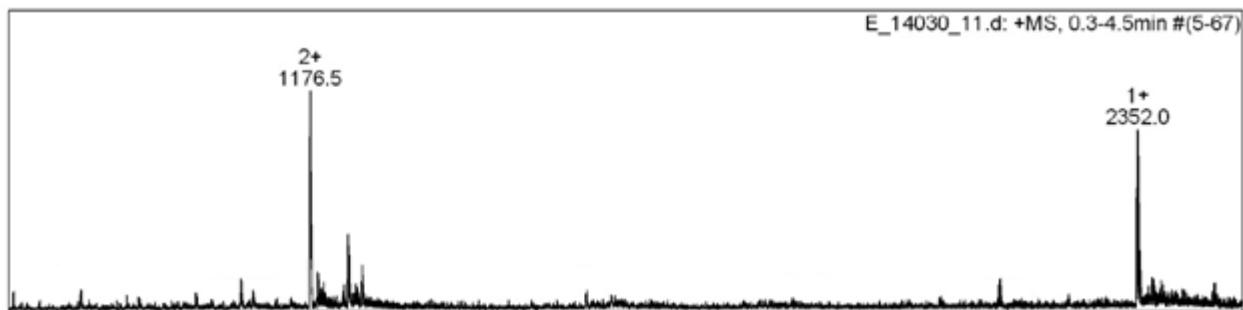


ESIMS⁺ (m/z): $[M + H]^+$ calcd for C₇₀H₁₁₁Cl₂N₁₆O₂₀, 1567.7; found, 1567.7.

Compound 4.

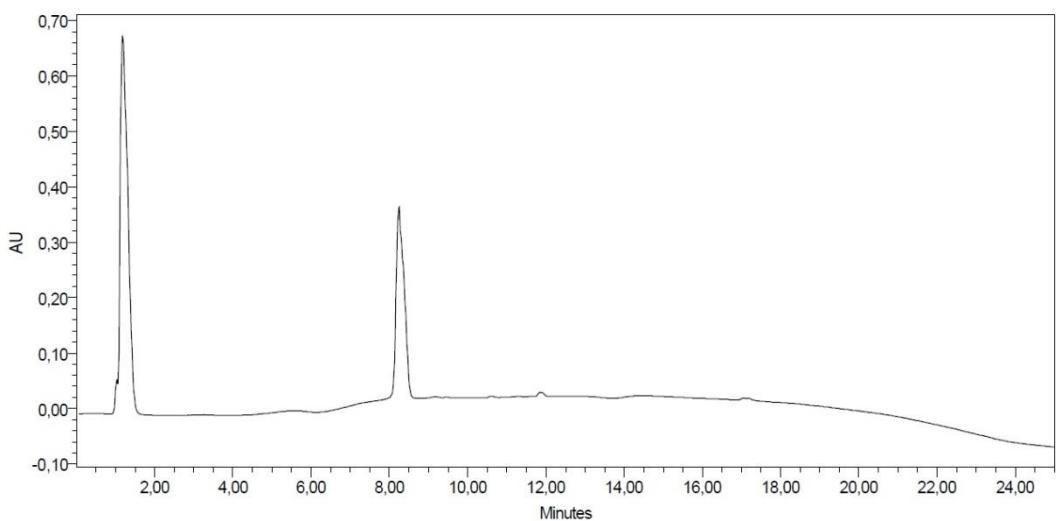


Analytical RP-HPLC: $t_R = 9.71$ (gradient: 5 to 100% B in 20 min, $\lambda = 214$ nm).



ESIMS⁺ (m/z): [M + H]⁺ calcd. for C₉₄Cl₂H₁₅₉N₁₆O₄₀S₄, 2351.9; found, 2352.0.

Compound 5.

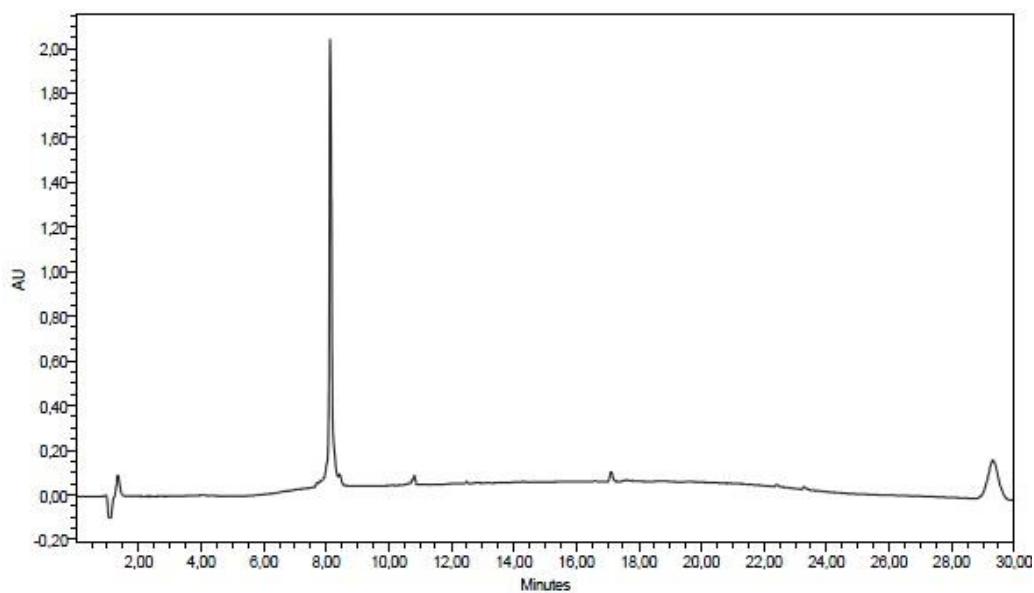


RP-HPLC: $t_R = 8.24$ (gradient: 5 to 100% B in 20 min, $\lambda = 214$ nm).

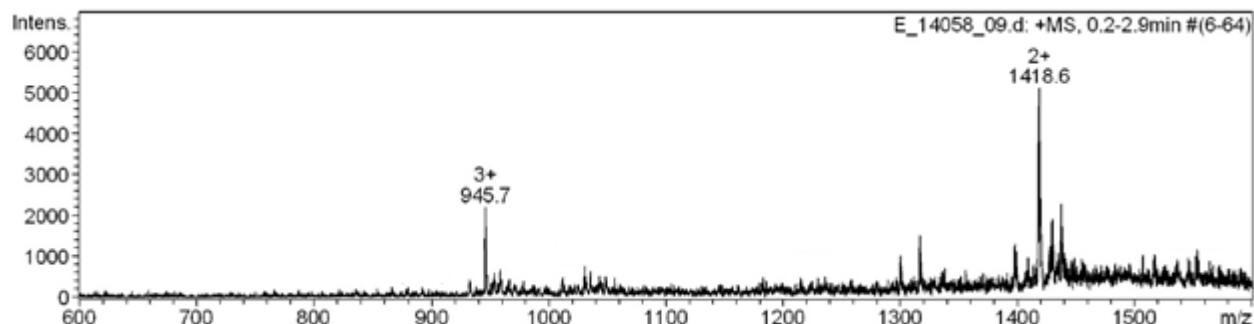


ESIMS⁺ (m/z): $[M + H]^+$ calcd for $C_{110}H_{187}N_{18}O_{50}S_6$, 2753.1; found, 2753.2.

Compound 8.

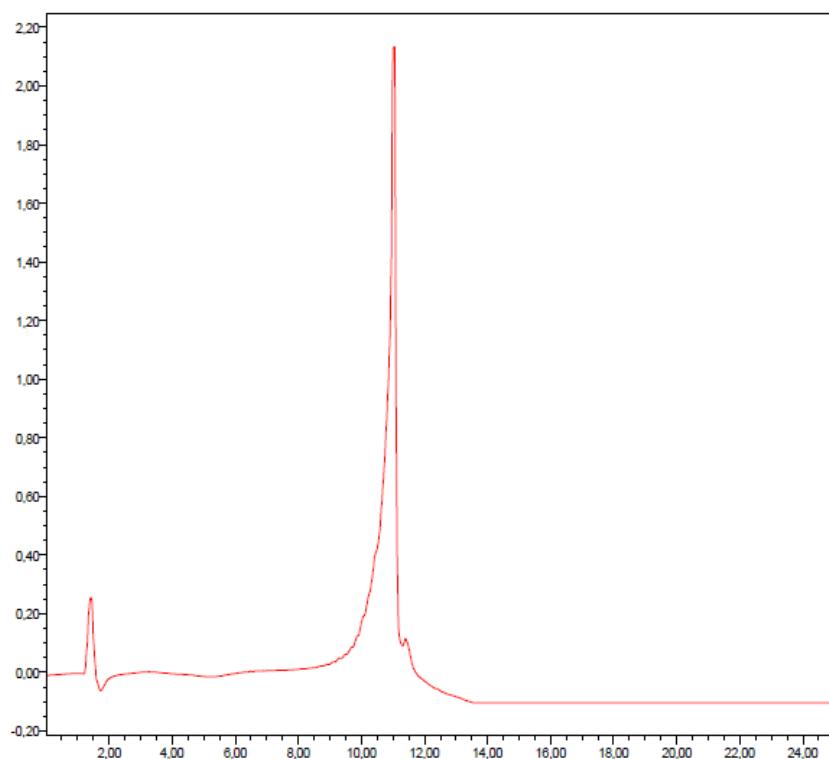


Analytical RP-HPLC: $t_R = 8.35$ min (gradient: 5 to 100% B in 20 min, , $\lambda = 214$ nm).

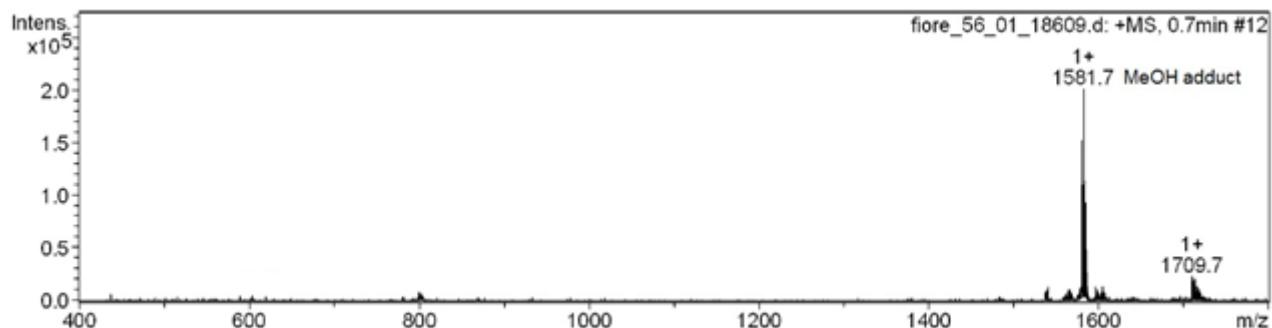


ESIMS⁺ (m/z): $[M + H]^+$ calcd for C₁₁₄H₁₉₃N₂₀O₅₀S₆, 2835.8; found, 2836.0.

Compound 9.

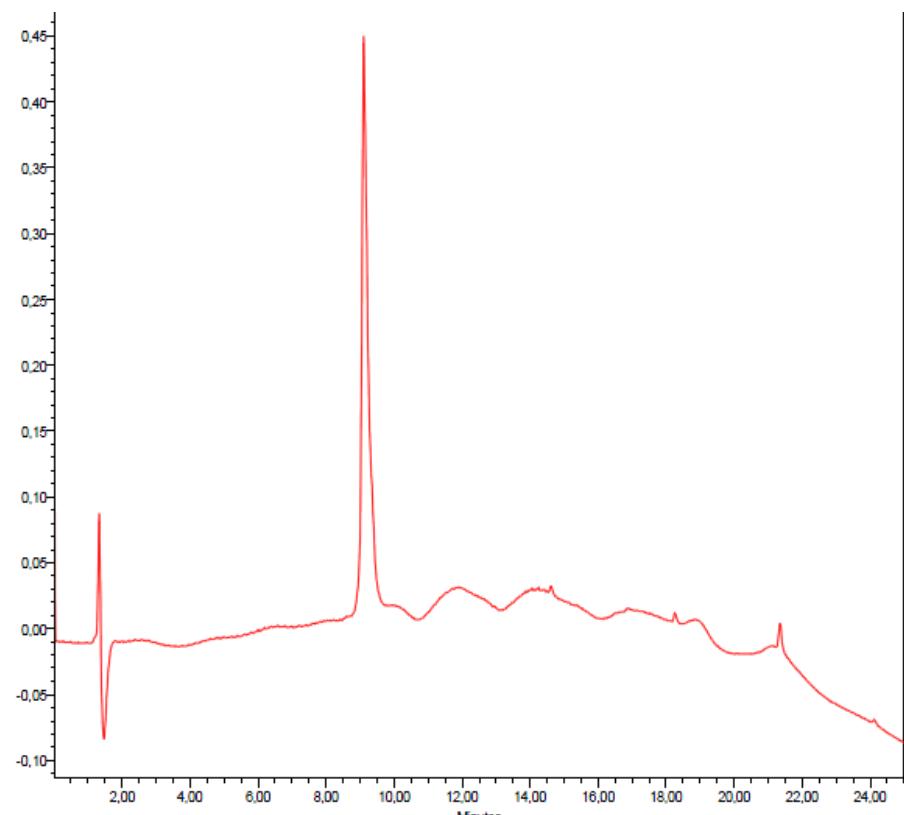


Analytical RP-HPLC: $t_R = 11.67$ min (gradient: 5 to 100% B in 20 min, , $\lambda = 214$ nm).

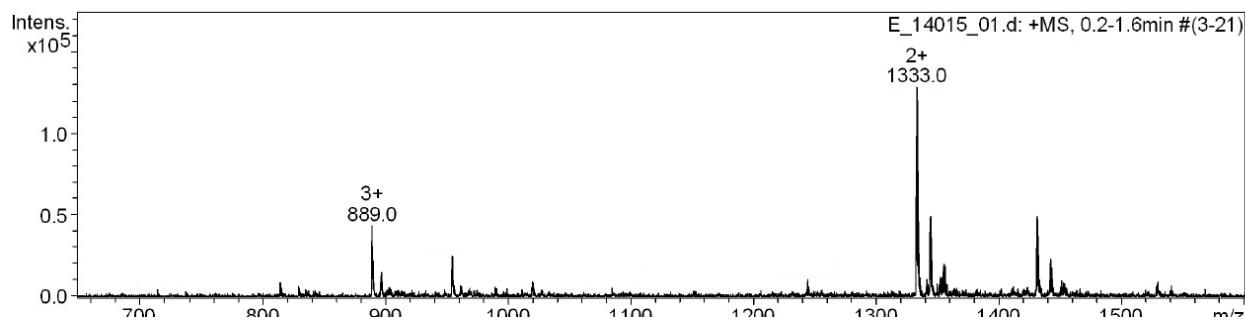


ESIMSM⁺ (m/z): $[M + \text{MeOH}]^+$ calcd for $C_{66}H_{105}\text{Cl}_4\text{N}_{16}\text{O}_{18}$, 1582.7; found, 1582.0.

Compound 11.

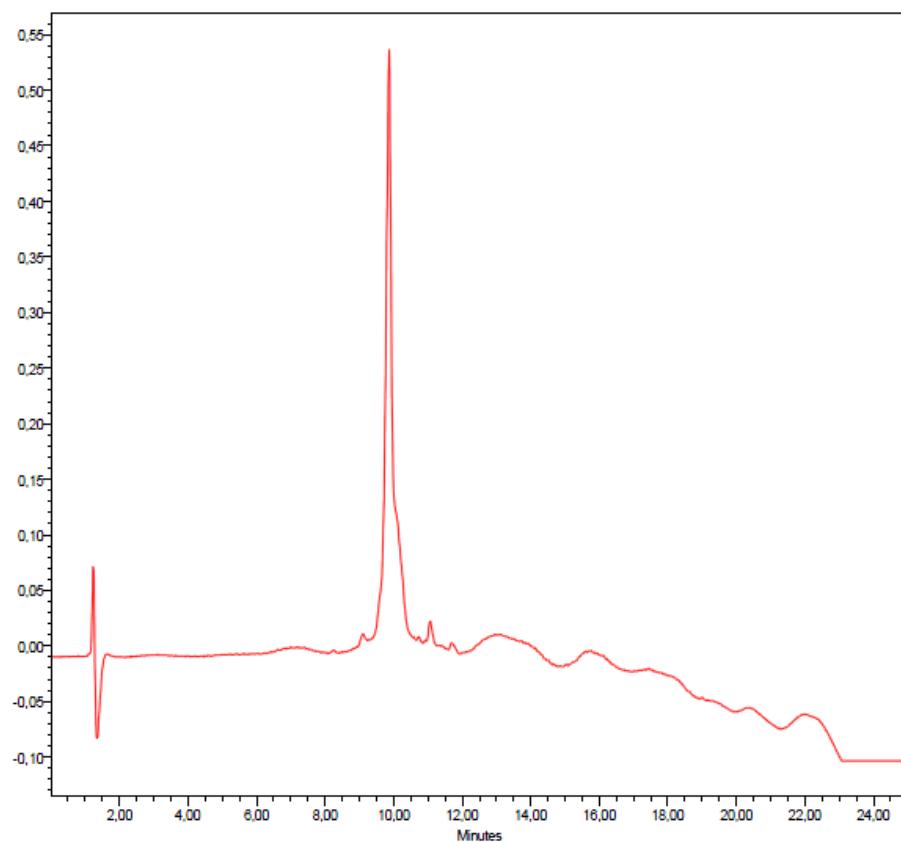


Analytical RP-HPLC: $t_R = 8.06$ min (gradient: 5 to 100% B in 20 min, , $\lambda = 214$ nm).



ESIMS⁺ (m/z): $[M + H]^+$ calcd for C₁₀₆H₁₈₀N₁₈O₄₈S₆, 2666.1; found, 2666.1.

Compound 13.



Analytical RP-HPLC: $t_R = 10.06$ min (gradient: 5 to 100% B in 20 min, $\lambda = 214$ nm).



ESIMS⁺ (m/z): [M + H]⁺ calcd for C₁₁₀H₁₈₄N₂₀O₄₈S₆, 2747.1; found, 2747.2.