Supporting Information

A 'dual click' strategy for the fabrication of bioselective, glycosylated self-assembled monolayers as glycocalyx models

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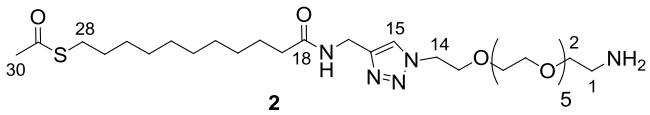
N-[(20-Amino-hexaethylene glycolyl)-1H-[1,2,3]-triazole-4-yl-methyl]-11-thioacetyl-undecanoic acid amide (2)



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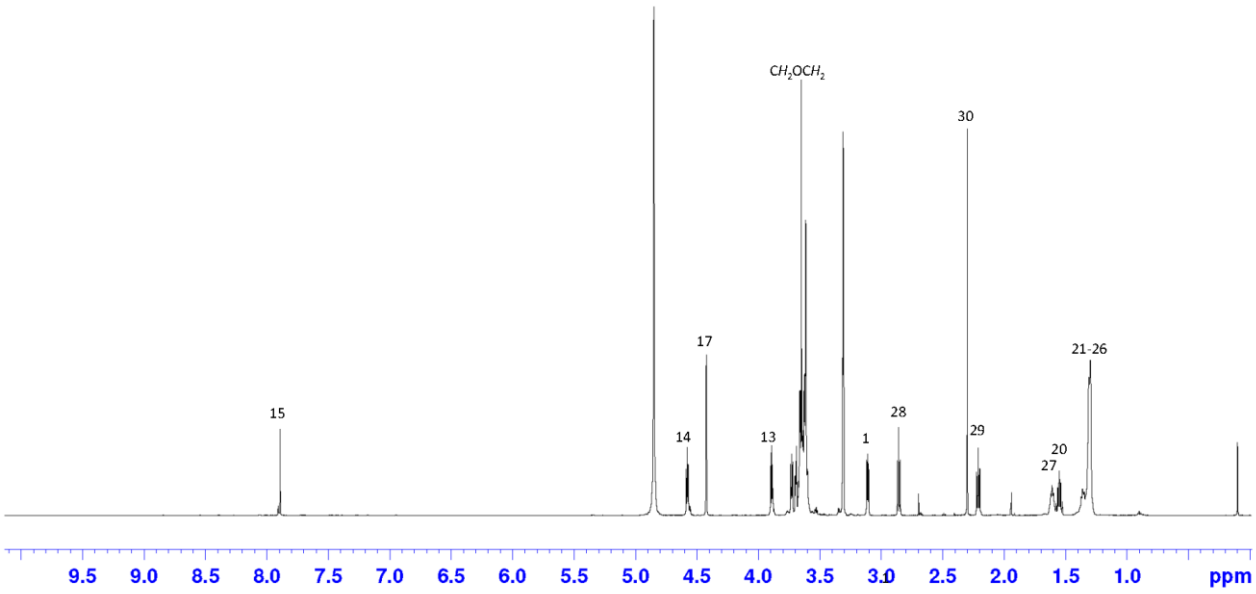


Figure S1. ^{1}H NMR spectrum (600 MHz, MeOH-d_4, 298 K) of compound **2**.

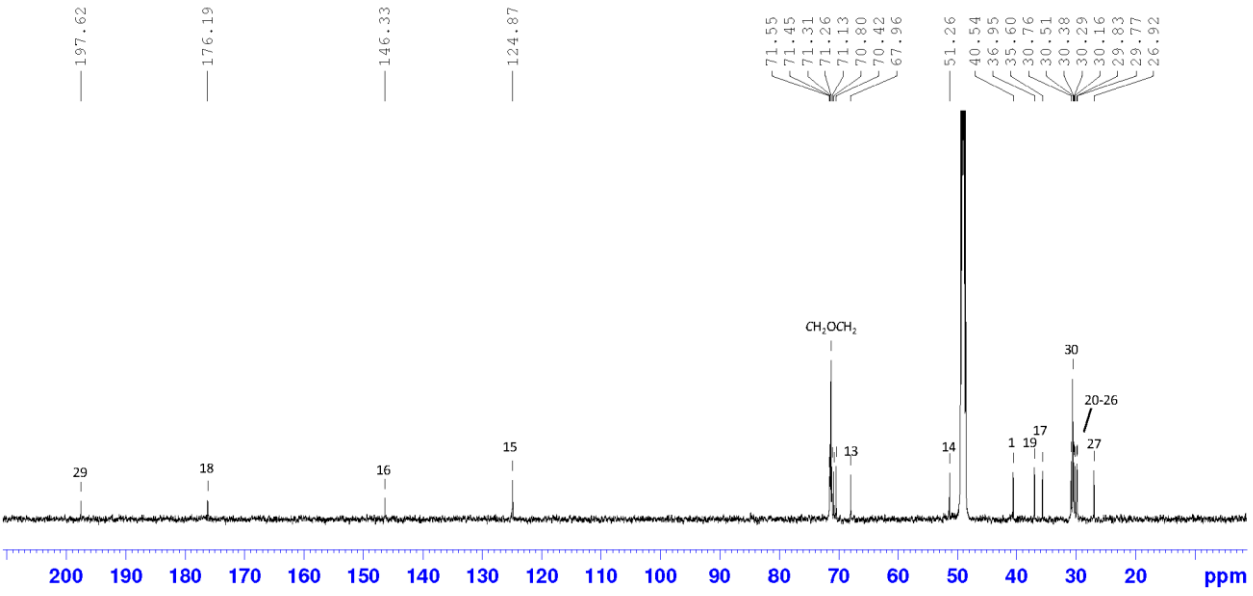
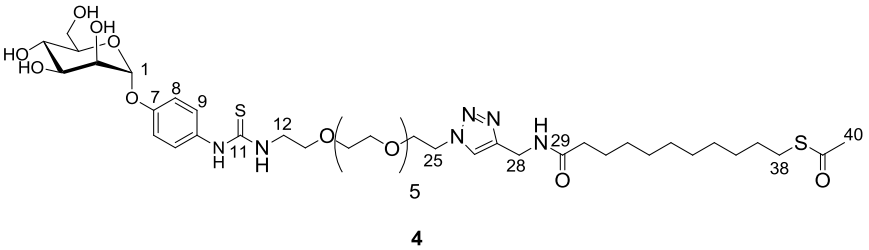


Figure S2. ^{13}C NMR spectrum (150 MHz, MeOH-d_4, 298 K) of compound **2**.

_N_-{20-[_p_-(α-D-Mannopyranosyloxy)-phenylthioureido-hexaethylene glycolyl]-1_H_-[1,2,3]-triazole-4-yl-methyl}-11-thioacetyl-undecanoic acid amide (4)



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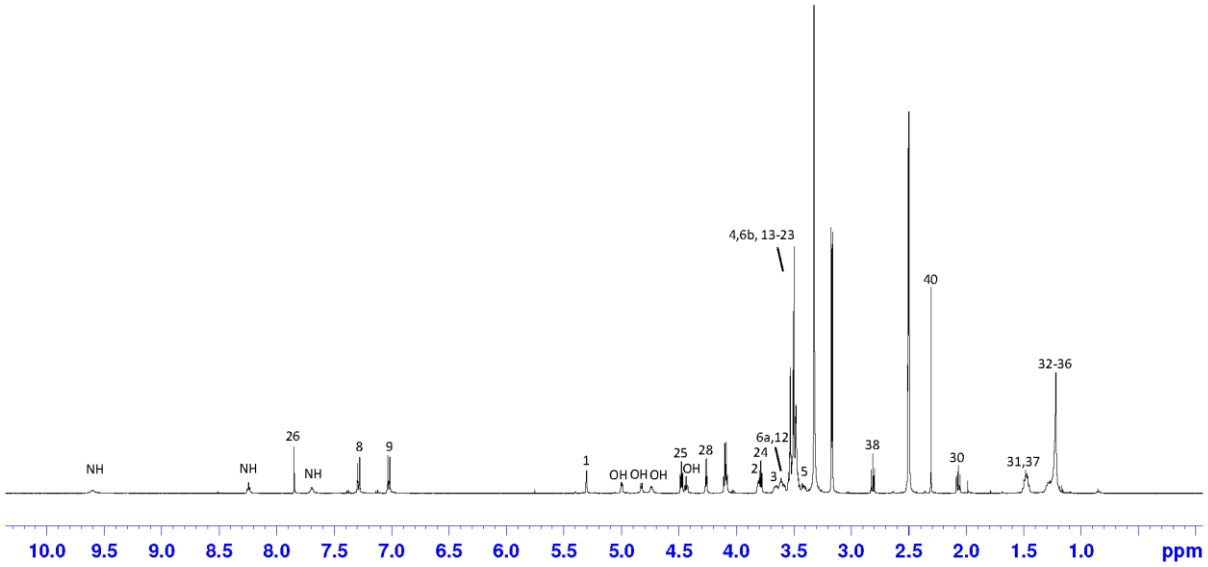


Figure S3. ^{1}H NMR spectrum (500 MHz, MeOH-d_4, 300 K) of compound **4**.

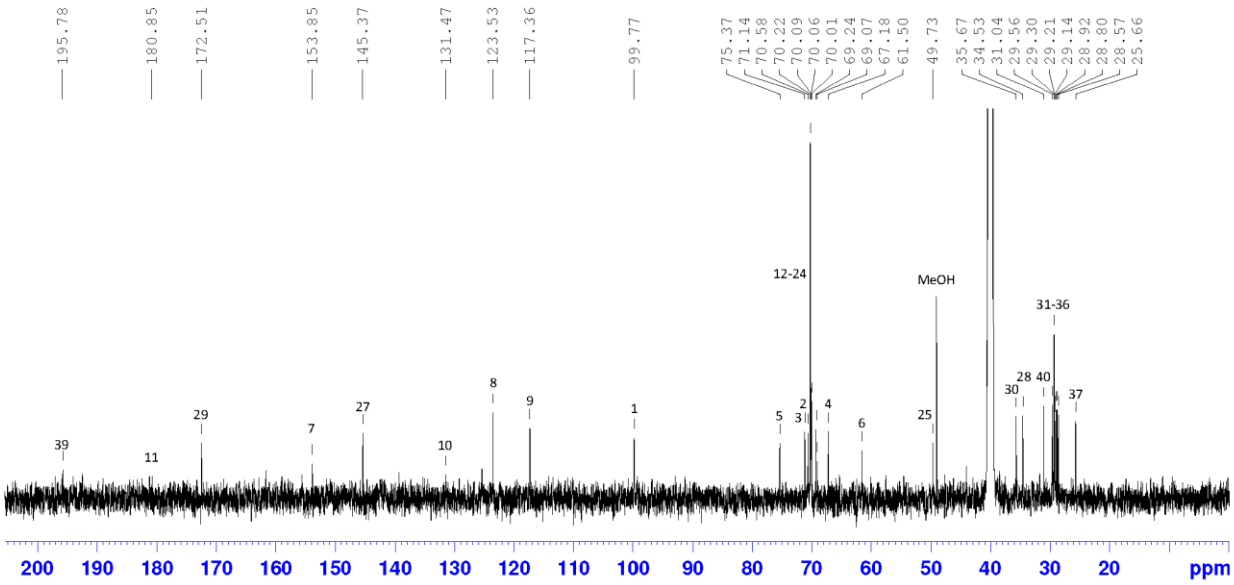
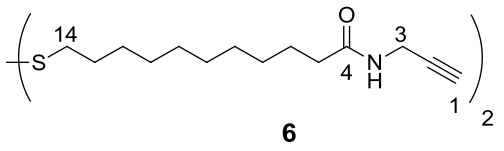


Figure S4. ^{13}C NMR spectrum (125 MHz, MeOH-d_4, 300 K) of compound **4**.

Bis-[*N*-(propynyl)-11,11'-disulphanediyl diundecanoic acid diamide (6)



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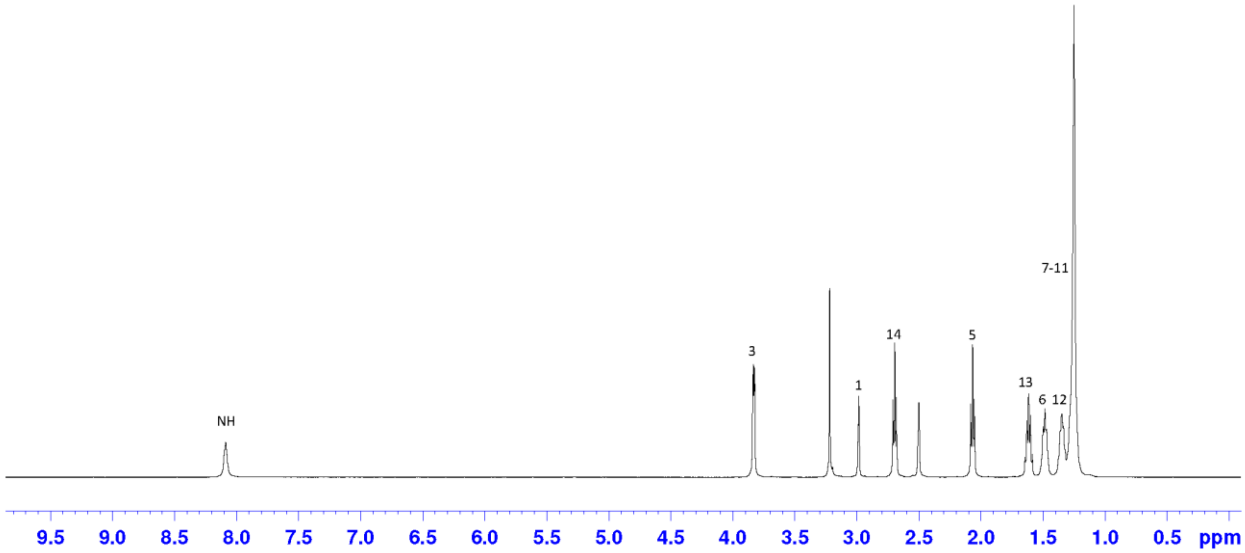


Figure S5. ^{1}H NMR spectrum (500 MHz, DMSO-d_6, 320 K) of compound **6**.

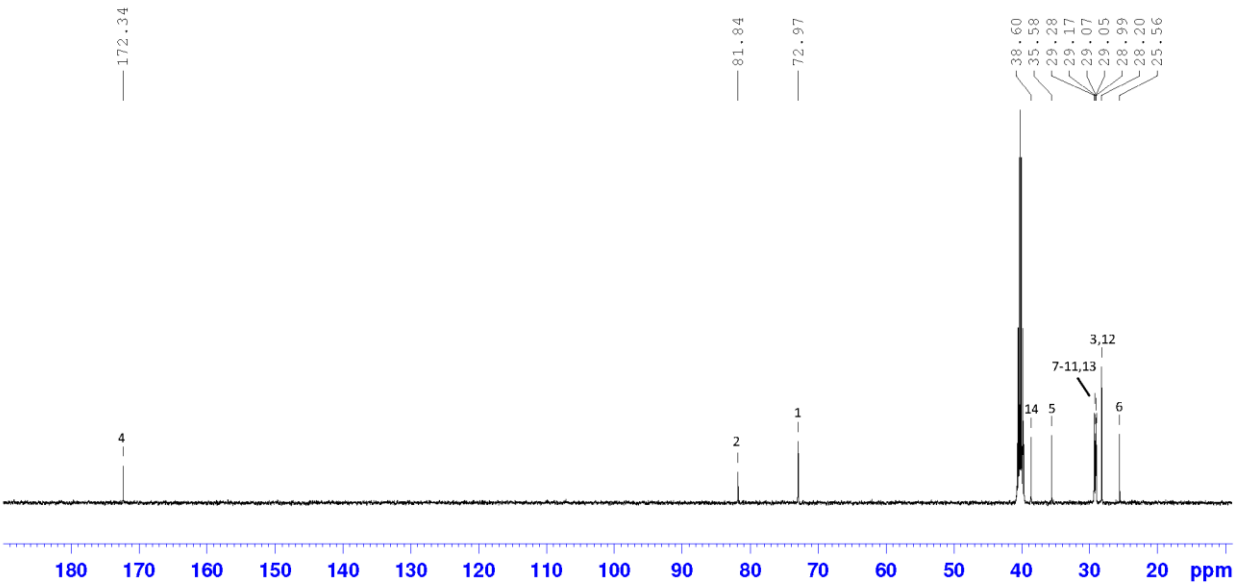
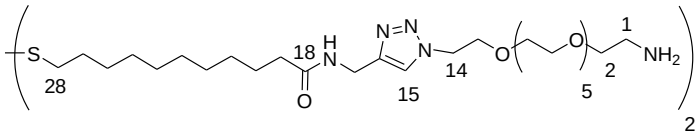


Figure S6. ^{13}C NMR spectrum (125 MHz, DMSO-d_6, 320 K) of compound **6**.

Bis-{*N*-[(20-amino-hexaethylene glycolyl)-1*H*-[1,2,3]-triazole-4-yl-methyl]}-11,11'-disulphanediyl diundecanoic acid diamide (7)



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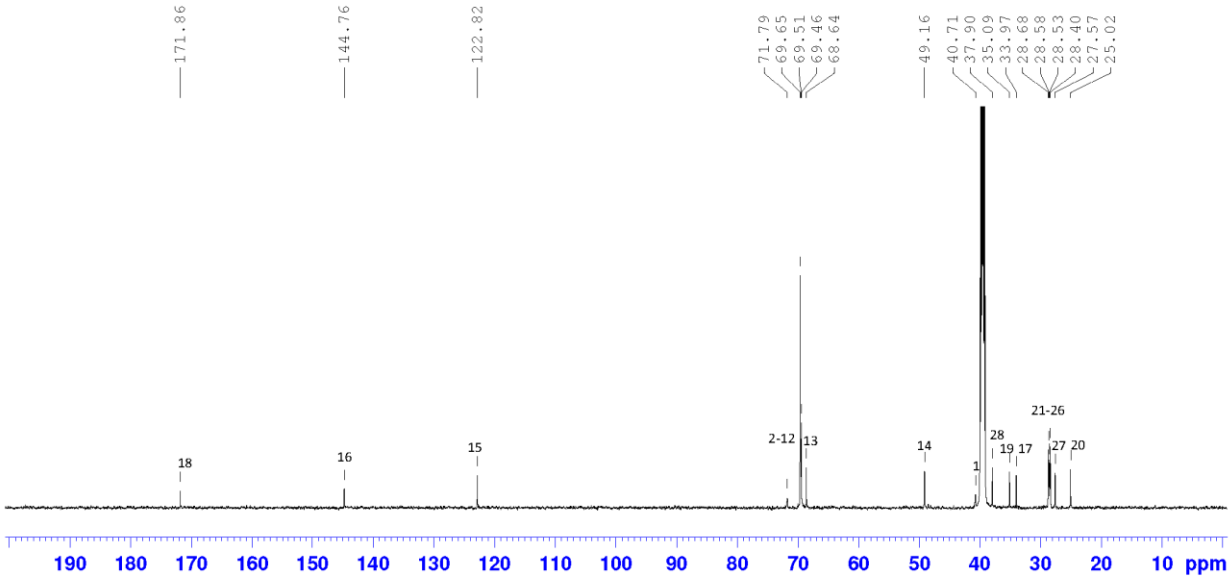

Figure S7. ^{1}H NMR spectrum (600 MHz, DMSO-d_6, 320 K) of compound **7**.

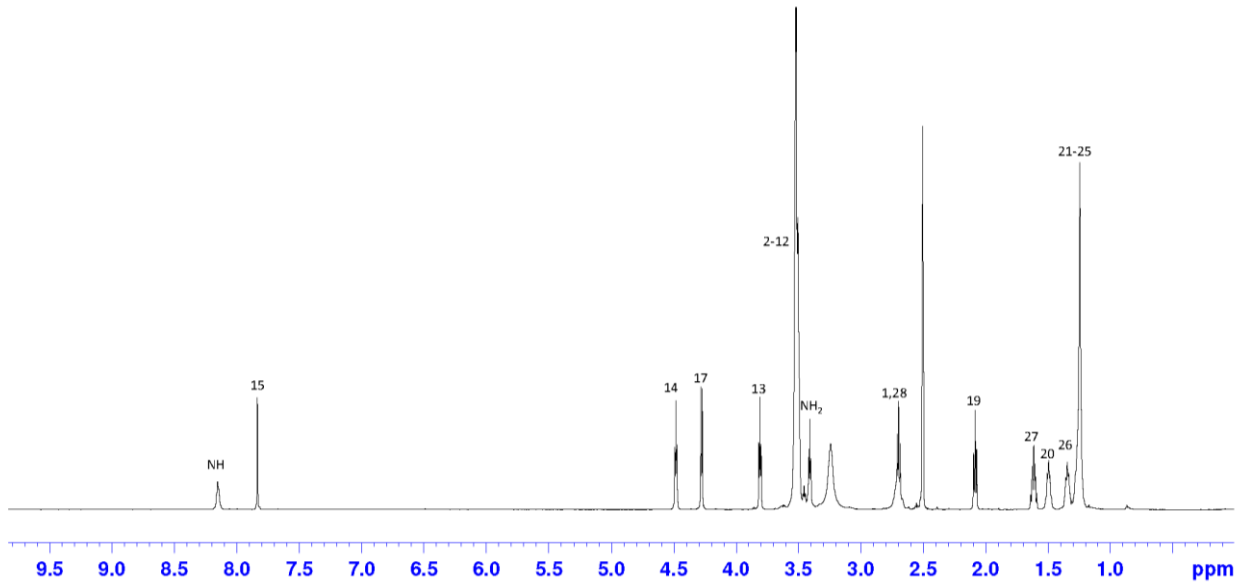

Figure S8. ^{13}C NMR spectrum (150 MHz, DMSO-d_6, 320 K) of compound **7**.

Bis-{*N*-[20-(*p*-(α-D-Mannopyranosyloxy)-phenylthioureido-hexaethylene glycolyl]-1*H*-[1,2,3]-triazole-4-yl-methyl]}-11,11'-disulphanediyl diundecanoic acid diamide (8)

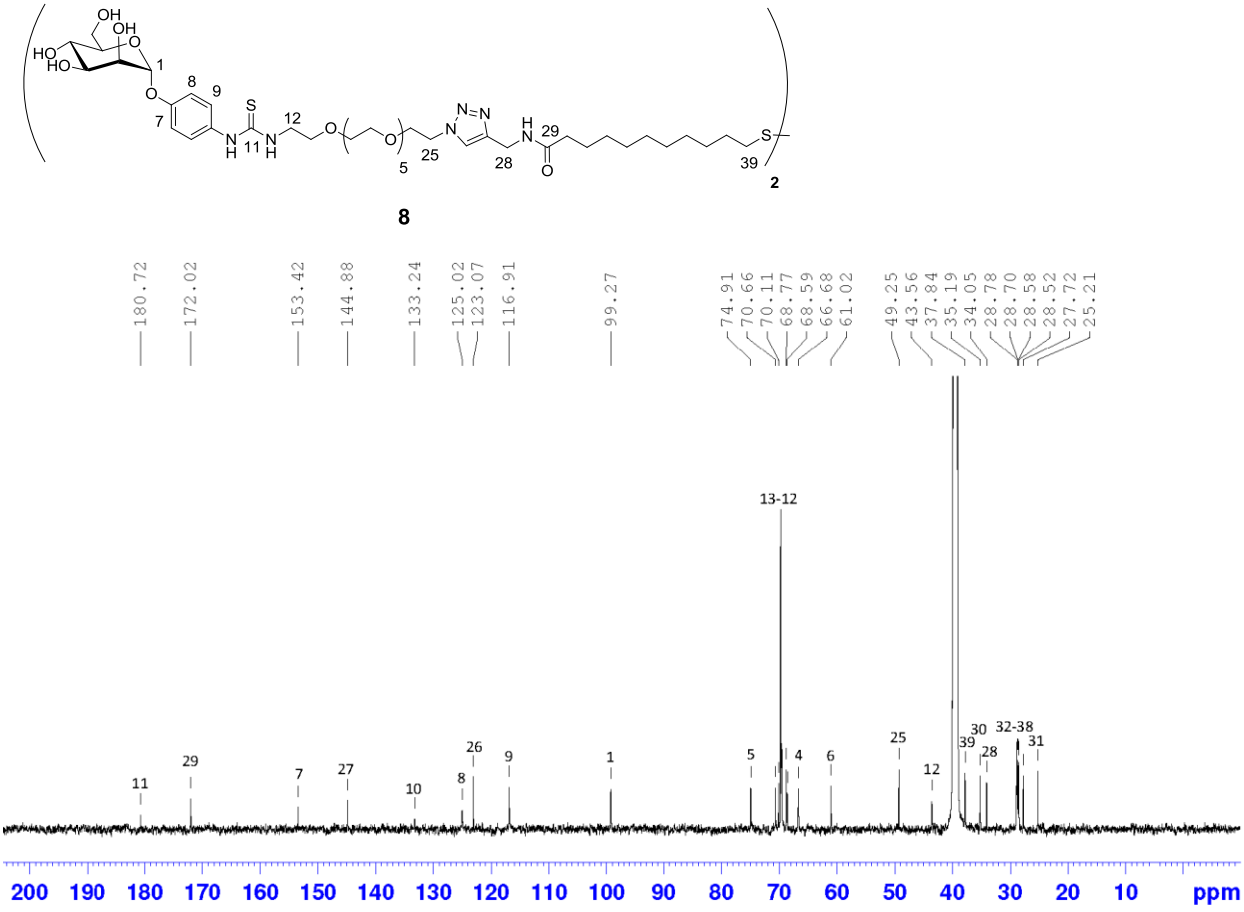

Figure S9. ^{1}H NMR spectrum (600 MHz, DMSO-d_6, 298 K) of compound **8**.

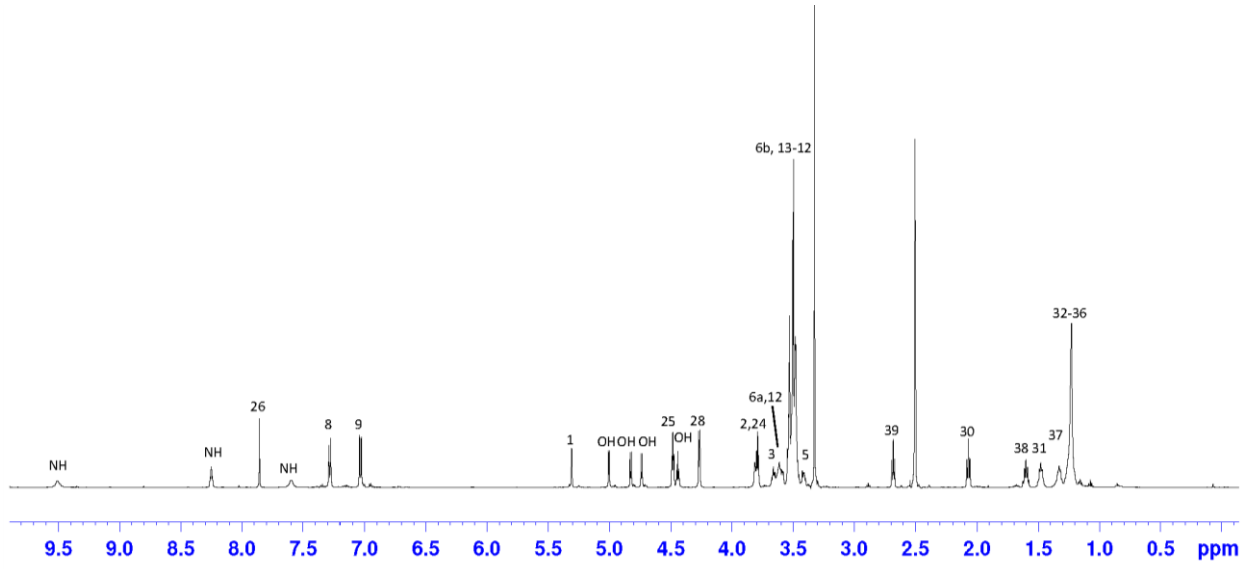

Figure S10. ^{13}C NMR spectrum (150 MHz, DMSO-d_6, 298 K) of compound **8**.

Assignment of IR bands

Table S1. Wavenumbers (cm^{-1}) and assignments of vibrational bands of compound **8**.
'Conventional SAM': substrate immersed into a solution of **8**.
'Click SAM': click reaction of monolayer of substance **7** on Au with substance **3** (see text of main manuscript for details).

neat substance		SAMs 'click'		SAMs 'conventional'		proposed vibrational mode
1101	vs	1132	vs	1128	vs	ν C-O ethylene glycol
1222	m	1188	s	1232	s	ν C=S
1346	w	1351	w	1351	w	ω CH_2 ethylene glycol
1508	s	1508	w	1508	m	δ CH ring
1547	s	1547	m	1541	s	δ NH (amide II)
1635	vs	1637	s	1653	s	ν C=O (amide I)
1693	s					ν C=O acetyl group
2852	s	2853	m	2870	s	ν CH_2 sym
2919	vs	2920	vs	2926	vs	ν CH_2 asym
3292	vs	3299	m			ν NH
3400-3600	vs, b	3400-3600	m, b	3300-3600	s, b	ν OH

ν: stretching mode, ω: wagging mode, δ: ip plane bending mode, vs: very strong, s: strong, m: medium, w: weak, b: broad, sym: symmetric, asym.: asymmetric.

Table S2. Wavenumbers (cm^{-1}) and assignments of vibrational bands of compound **7**.

neat substance		SAM		proposed vibrational mode
1105	s	1130	vs	ν C-O ethylene glycol
1346	w	1351	w	ω CH_2 ethylene glycol
1546	s	1547	m	δ NH (amide II)
1634	vs	1637	s	ν C=O (amide I)
2853	s	2853	s	ν CH_2 sym
2920	vs	2920	vs	ν CH_2 asym
3291	s	3297	m	ν NH

ν: stretching mode, ω: wagging mode, δ: ip plane bending mode, vs: very strong, s: strong, m: medium, w: weak, b: broad, sym: symmetric, asym. asymmetric.

Table S3. Wavenumbers (cm^{-1}) and assignments of vibrational bands of compound **3**.

neat substance		proposed vibrational mode
1498	m	δ CH ring
2117	s, b	ν CNS
2885-2966	w	ν CH aliph
3191	vs	ν OH
3377	s	ν OH
3538	m	ν OH

ν: stretching mode, vs: very strong, s: strong, m: medium, w: weak, b: broad, aliph: aliphatic.

S→*N*-Acetyl migration

We assume that the amino function of substance **2** is protected by possible *S*→*N*-acetyl migration during monolayer formation. This assumption was supported by the isolation of the respective *N*-acetylated derivative of **2** by semi-preparative HPLC on RP-NH_2 phase (Figure S11).

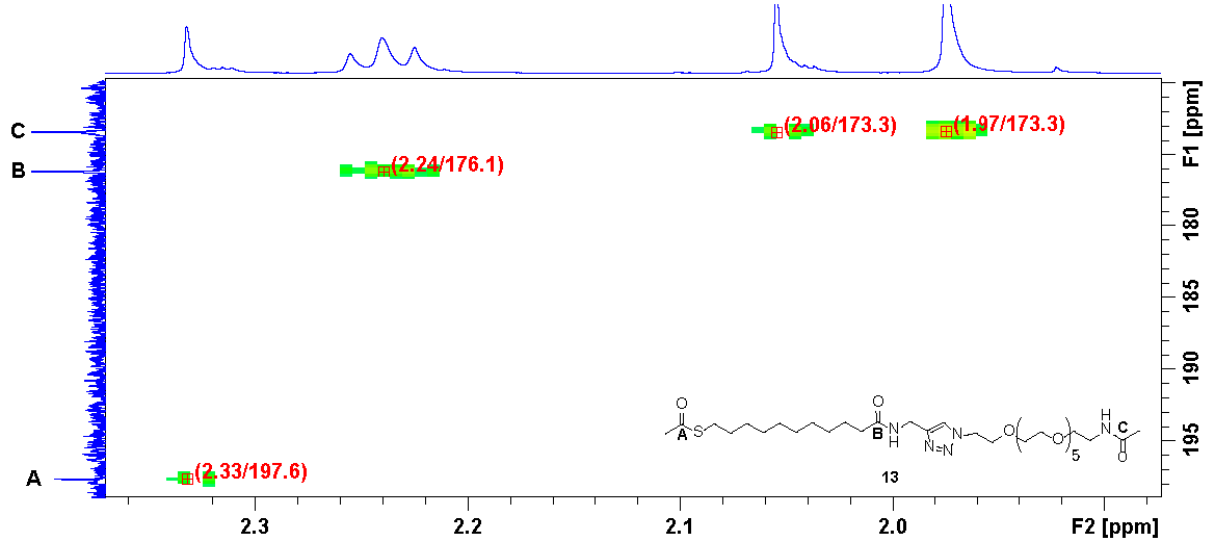

Figure S11. HMBC spectrum of the *N*-acetylated derivative of **2**. Additional to the expected cross peaks for the thioacetyl group (2.33/197.6) and for the amide C(O) (2.24/176.1) another two cross peaks (2.06/173.3) and (1.97/173.3) were detected, originating from a new *N*-acetyl group.

This *N*-acetyl-protected derivative of **2** was further investigated by ESI mass spectrometry, where the expected *m/z* peak was detected: $[M+Na]^+$ calc. for $C_{32}H_{59}N_5O_9SNa$: 712.3926; found: 712.3986.

As an additional *m/z* peak, the mono-acetylated compound (*S*- or *N*-acetylated) was detected: $[M+Na]^+$ calc. for $C_{30}H_{57}N_5O_8SNa$: 670.3826, found: 670.3875 (Figure S12).

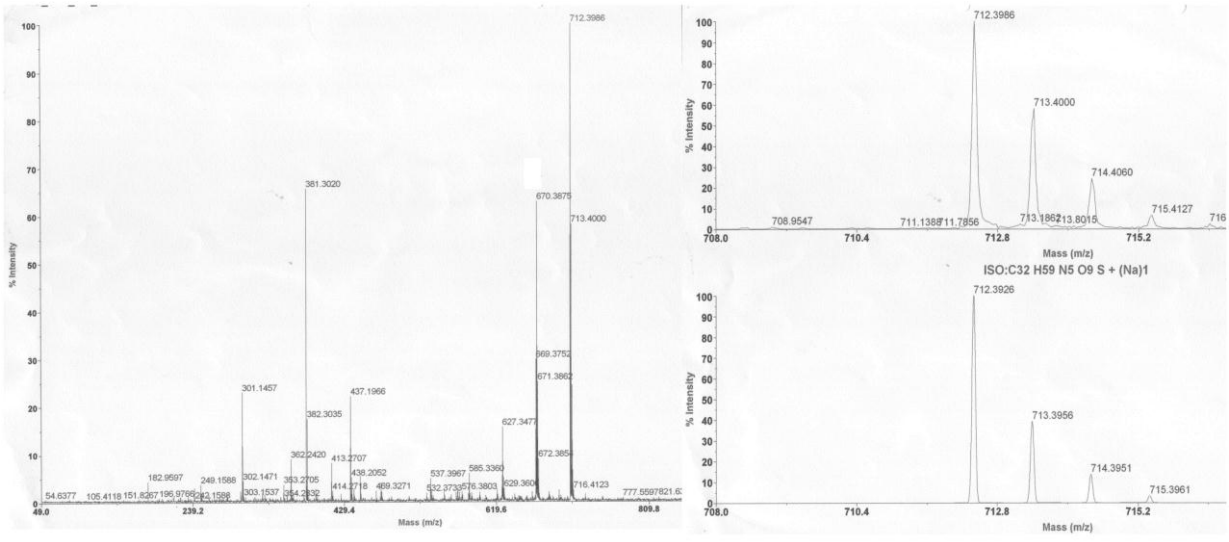

Figure S12. ESI MS spectrum of the *N*-acetylated derivative of **2**.