## Supporting Information

for

## Synthesis, antimicrobial and cytotoxicity evaluation of new cholesterol congeners

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## Experimental section

## Chemistry

Melting points were determined on Electrothermal apparatus and are uncorrected. Flash chromatography was carried out on silica gel (Baker, 30-60 $\mu \mathrm{m}$ ). TLC Monitoring tests were carried out using plastic sheets precoated with silica gel $60 \mathrm{~F}_{245}$ (layer thickness 0.2 $\mathrm{mm})$ purchased from Merck. Spots were visualized by their fluorescence under UV-lamp ( $\lambda=245$ and 366 nm ) or staining with iodine vapor, $15 \% \mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{KMnO}_{4}$, or $\mathrm{Ce}(\mathrm{IV}) \mathrm{SO}_{4}$ in $\mathrm{H}_{2} \mathrm{SO}_{4}$. NMR spectra were recorded on Bruker 600 MHz spectrometer, Central Laboratory, King Abd El Aziz University, Jeddah, Saudi Arabia. IR-spectra were recorded on ATR-Alpha FT-IR spectrophotometer $400-4000 \mathrm{~cm}^{-1}$. Mass spectra were recorded on GCMS-QP 1000Ex Shimadzu spectrometers in the Microanalysis Unit at Cairo University.

## $3 \alpha$-Bromocholest-5-ene (2)

A mixture of $1(5.0 \mathrm{~g}, 12.9 \mathrm{mmol}), \mathrm{PPh}_{3}(4.8 \mathrm{~g}, 18.3 \mathrm{mmol})$ in $\mathrm{DCM}(50 \mathrm{~mL})$ was stirred at ambient temperature, while $\mathrm{CBr}_{4}(5.0 \mathrm{~g}, 15.0 \mathrm{mmol})$ was added portionwise and stirring was continued overnight. The mixture was evaporated in vacuo and the residue was purified by flash chromatography (petroleum ether) to afford $2(4.3 \mathrm{~g}, 74 \%)$ as colorless crystals. $R_{\mathrm{f}} 0.67$ (petroleum ether); Mp. $72{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 5.92 (dd, 1H, J 1.8, 9.6 Hz ), 5.59 (dd, 1H, J 5.4, 7.2 Hz ), 5.39 (t, 1H, J 2.4, 4.8 Hz ), $2.21-2.14(\mathrm{~m}, 2 \mathrm{H}), 2.11,2.08(2 \mathrm{t}, 1 \mathrm{H}, J 10.8,5.4 \mathrm{~Hz}), 2.03,2.01(2 \mathrm{t}, 1 \mathrm{H}, J 3.6,6.6 \mathrm{~Hz})$, $1.87-1.81(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{dd}, 1 \mathrm{H}, \mathrm{J} 4.8,12.6 \mathrm{~Hz}), 1.69-1.48(\mathrm{~m}, 6 \mathrm{H}), 1.45-1.24(\mathrm{~m}, 5 \mathrm{H})$, $1.20-0.98(\mathrm{~m}, 10 \mathrm{H}), 0.95\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19\right), 0.91\left(\mathrm{~d}, 3 \mathrm{H}, \mathrm{J}_{20,21} 6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right), 0.87,0.86$ (2d, $6 \mathrm{H}, J_{25,26}=J_{25,27} 3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27$ ), 0.70 (s, $3 \mathrm{H}, \mathrm{CH}_{3}-18$ ); ${ }^{13} \mathrm{C}$ NMR (150 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 141.48\left(\mathrm{C}-5_{\mathrm{Chol}}\right), 128.98,125.05,123.18,56.96,56.15,48.39,42.46$, $39.81,39.52,36.19,35.81,35.19,33.78,31.78,31.77$, 28.25, 28.02, 24.19, 23.83, 23.05, 22.83, 22.57, 20.96, 18.79, 18.71 ( 25 C ), $11.98\left(\mathrm{CH}_{3}-18\right)$; $\mathrm{EI}-\mathrm{MS}(m / z, \%)$ for $\mathrm{C}_{27} \mathrm{H}_{45} \mathrm{Br}$ (448.27); 449.40 ( $\mathrm{M}+1,2 \%$ ), 370.40 (3\%), 369.40 (17\%), 368.40 (53\%).

## 3 $\beta$-Azidocholest-5-ene (3)

A mixture of $2(4.3 \mathrm{~g}, 9.5 \mathrm{mmol})$ and $\mathrm{NaN}_{3}(3.0 \mathrm{~g}, 46.1 \mathrm{mmol})$ in DMF $(25 \mathrm{~mL})$ was stirred at $90-100{ }^{\circ} \mathrm{C}$ for 48 h then diluted with $\mathrm{H}_{2} \mathrm{O}(25 \mathrm{~mL})$. The mixture was extracted with ethyl acetate ( $3 \times 50 \mathrm{~mL}$ ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether) to afford $3(2.47 \mathrm{~g}, 63 \%)$ as colorless crystals. $R_{\mathrm{f}} 0.26$ (petroleum ether); Mp. $98{ }^{\circ} \mathrm{C}$; IR (v́, $\mathrm{cm}^{-1}$ ): $2081\left(\mathrm{~N}_{3}\right.$ str); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 5.39\left(\mathrm{t}, 1 \mathrm{H}, J 2.3,4.8 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}\right), 3.87(1 \mathrm{H}, J 3.0,6.0 \mathrm{~Hz}$, $\mathrm{H}-3_{\mathrm{Chol}}$ ), $2.51(2 \mathrm{t}, 1 \mathrm{H}, J 2.4,4.8 \mathrm{~Hz}), 2.20,2.17(2 \mathrm{t}, 1 \mathrm{H}, J 2.4,4.8 \mathrm{~Hz}), 2.03,2.00(2 \mathrm{t}$, $1 \mathrm{H}, J 3.0,3.6,6.6,7.2 \mathrm{~Hz}), 1.99-1.94(\mathrm{~m}, 1 \mathrm{H}), 1.92-1.80(\mathrm{~m}, 1 \mathrm{H}), 1.78,1.76(2 \mathrm{t}, 1 \mathrm{H}, J$ $3.0,3.6,6.6,7.2 \mathrm{~Hz}), 1.74-1.66(\mathrm{~m}, 1 \mathrm{H}), 1.68-1.55(\mathrm{~m}, 4 \mathrm{H}), 1.54-1.50(\mathrm{~m}, 1 \mathrm{H})$, $1.46-1.33(\mathrm{~m}, 5 \mathrm{H}), 1.27-1.22(\mathrm{~m}, 1 \mathrm{H}), 1.19-0.96(\mathrm{~m}, 10 \mathrm{H}), 1.00\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19\right), 0.91$ $\left(\mathrm{d}, 3 \mathrm{H}, J_{20,21} 6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right), 0.87,0.86\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26\right.$, $\mathrm{CH}_{3}-27$ ), 0.68 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 138.07\left(\mathrm{C}-5_{\text {Chol }}\right.$ ), 123.17 (C-6 $\left.{ }_{\text {Chol }}\right), 58.28,56.58,56.09,50.09,42.30,39.71,39.52,37.09,36.18,36.06$,
35.81, 33.62, 31.82, 31.77, 28.23, 28.02, 26.09, 24.26, 23.84, 22.84, 22.57, 20.72, 18.99, 18.71 (24 C), $11.86\left(\mathrm{CH}_{3}-18\right)$; EI-MS ( $\mathrm{m} / 2, \%$ ) for $\mathrm{C}_{27} \mathrm{H}_{45} \mathrm{~N}_{3}$ (411.36); $412.40(\mathrm{M}+1$, 2\%), 411.40 (M, 4\%), 393.40 (2\%), 383.40 (49\%), 368.40 (78\%);

General procedure for the CuAAC reactions.
A mixture of the relevant azido derivative ( 0.5 mmol ), the alkyne ( 0.45 mmol ), $\mathrm{CuSO}_{4} \cdot 5 \mathrm{H}_{2} \mathrm{O}(0.2 \mathrm{mmol})$ and L -ascorbic acid ( 1.4 mol ) in $\mathrm{THF} / \mathrm{H}_{2} \mathrm{O}(5: 1,6 \mathrm{~mL})$ was stirred under gentle reflux. The mixture was evaporated in vacuo after 3 h and the residue was purified.

## (2E)-1-[4-(\{1-[(3 $\beta$ )-Cholest-5-en-3-yl]-1H-1,2,3-triazol-4-yl\}methoxy)phenyl]-3-

 phenylprop-2-en-1-one (6a)Yield: (40\%) as colorless powder after flash chromatography using (toluene:ethyl acetate, $12: 1$ );. $R_{\mathrm{f}} 0.18$ (toluene:ethyl acetate, $12: 1$ ); Mp $174-175{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( 600 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 8.04(\mathrm{~d}, 2 \mathrm{H}, J 9.0 \mathrm{~Hz}, \mathrm{Ar}), 7.85\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}\right), 7.81\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}\right.$, $\mathrm{CH}=\mathrm{CHCO}$ ), $7.67-7.64(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 7.54\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}, \mathrm{CH}=\mathrm{CHCO}\right), 7.42-7.37$ (m, 3H, Ar), 7.07 (d, 2H, J $8.4 \mathrm{~Hz}, \mathrm{Ar}$ ), 5.45 (br. s, $1 \mathrm{H}, \mathrm{H}-6_{\mathrm{Chol}}$ ), 5.31 (s, 2H, $\mathrm{OCH}_{2}$ ), 4.93 (br.s, 1H), 2.95 (d, 1H, J 13.8 Hz ), 2.49 (d, 1H, J 15.6 Hz ), 2.22-2.13 (m, 2H), 2.01-1.97 (m, 2H), 1.85-1.78 (m, 1H), 1.67-1.39 (m, 6H), 1.31-1.21 (m, 4H), 1.11-0.90 $(\mathrm{m}, 14 \mathrm{H}), 0.87\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 6.0 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right), 0.86,0.85\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 3.0 \mathrm{~Hz}\right.$, $\mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27$ ), $0.66\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(150 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 188.40(\mathrm{C}=\mathrm{O})$, 162.01 ( $\mathrm{CH}=\mathrm{CHCO}$ ), 144.10, 142.24, 137.91, 135.01, 131.43, 130.79, 130.37, 128.93, $128.38,124.53,122.64,121.61,114.72$ (12 C-Ar, $\mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}, \mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}$, $\mathrm{CH}=C \mathrm{HCO}$ ), 62.21, 56.71, 56.52, 56.10, 49.97, 42.24, 39.50, 39.47, 37.05, 36.13, 35.83, $35.41,32.62,31.87,31.62,28.21,27.98,27.18,24.19,23.97,22.82,22.56,20.58,19.25$, $18.62(25 \mathrm{C}), 11.81\left(\mathrm{CH}_{3}-18\right)$; EI-MS $\left(\mathrm{m} / \mathrm{z}, \%\right.$ ) for $\mathrm{C}_{45} \mathrm{H}_{59} \mathrm{~N}_{3} \mathrm{O}_{2}$ (673.46): $675.70(\mathrm{M}+2$, $4 \%), 674.70(\mathrm{M}+1,15 \%), 673.6$ (M, 31\%), 663.50 (3\%), 422.45 (100\%).
(2E)-1-[4-(\{1-[(3ß)-Cholest-5-en-3-yl]-1H-1,2,3-triazol-4-yl\}methoxy)phenyl]-3-(4-methoxyphenyl)prop-2-en-1-one (6b)
Yield: ( $41 \%$ ) as colorless powder after flash chromatography using (toluene:ethyl acetate, 7:1). $R_{\mathrm{f}} 0.25$ (toluene:ethyl acetate, $7: 1$ ); Mp. $178-179{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.40(\mathrm{~d}, 2 \mathrm{H}, J 8.4 \mathrm{~Hz}, \mathrm{Ar}), 7.84\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}\right), 7.78\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}\right.$, $C \mathrm{H}=\mathrm{CHCO}), 7.59(\mathrm{~d}, 2 \mathrm{H}, J 8.4 \mathrm{~Hz}, \mathrm{Ar}), 7.42\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}, \mathrm{CH}=C \mathrm{HCO}\right), 7.06(\mathrm{~d}$, $2 \mathrm{H}, J 8.4 \mathrm{~Hz}, \mathrm{Ar}), 6.92$ (d, 2H, J $8.4 \mathrm{~Hz}, \mathrm{Ar}), 5.44\left(\mathrm{~d}, 1 \mathrm{H}, J 4.2 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Chol}}\right), 5.30(\mathrm{~s}, 2 \mathrm{H}$, $\left.\mathrm{OCH}_{2}\right), 4.92(\mathrm{~d}, 1 \mathrm{H}, J 2.4 \mathrm{~Hz}), 3.85\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 2.97-2.94(\mathrm{~m}, 1 \mathrm{H}), 2.49(\mathrm{~d}, 1 \mathrm{H}, J$ $16.2 \mathrm{~Hz}), 2.21-2.19(\mathrm{~d}, 1 \mathrm{H}, J 13.8 \mathrm{~Hz}), 2.16,2.13,2.12(3 \mathrm{t}, 1 \mathrm{H}, J 7.2,3.6 \mathrm{~Hz})$, 2.01-1.97 (m, 2H), 1.84-1.77 (m, 2H), 1.67-1.65 (m, 1H), 1.58-1.300.88 (m, 6H), $1.33-1.20(\mathrm{~m}, 5 \mathrm{H}), 1.12-1.01(\mathrm{~m}, 9 \mathrm{H}), 0.99-0.91(\mathrm{~m}, 2 \mathrm{H}), 0.87\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 6.0 \mathrm{~Hz}\right.$, $\mathrm{CH}_{3}-21$ ), $0.86,0.85$ ( $2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27$ ), 0.65 ( $\mathrm{s}, 3 \mathrm{H}$, $\left.\mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 188.44(\mathrm{C}=\mathrm{O}), 161.83,161.53,143.94,142.31$, 137.91, 131.71, 130.67, 130.14, 127.76, 124.54, 122.63, 119.28, 114.65, 114.38 (12 $\left.\mathrm{C}-\mathrm{Ar}, \mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}, \mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}, C H=C H C O\right), 62.21,56.71,56.51,56.09$, $55.39,49.97$, 42.25, 39.05, 39.47, 37.05, 36.13, 35.84, 35.41, 32.62, 31.86, 31.62, 28.21, 27.99, 27.18, 24.20, 24.00, 22.82, 22.57, 20.58, 19.25, 18.62 (26 C), $11.82\left(\mathrm{CH}_{3}-18\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}, \%$ ) for $\mathrm{C}_{46} \mathrm{H}_{61} \mathrm{~N}_{3} \mathrm{O}_{3}$ (703.47): $705.60(\mathrm{M}+2,7 \%), 704.65(\mathrm{M}+1,23 \%)$, 703.65 (M, 41\%), 688.40 (3\%), 422.45 ( $100 \%$ ).
(2E)-1-[4-(\{1-[(3及)-Cholest-5-en-3-yl]-1H-1,2,3-triazol-4-yl\}methoxy)phenyl]-3-[4-(dimethylamino)phenyl]prop-2-en-1-one (6c)

Yield: ( $68 \%$ ) as fluorescent green mass after flash chromatography (toluene:ethyl acetate, 7:1). $R_{\mathrm{f}} 0.19$ (toluene:ethyl acetate, $7: 1$ ); Mp. $168{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 8.01 (d, 2H, J $8.4 \mathrm{~Hz}, ~ A r), 7.82$ (s, $1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}$ ), 7.77 (d, $1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}, C \mathrm{H}=\mathrm{CHCO}$ ), 7.53 (d, 2H, J $9.0 \mathrm{~Hz}, ~ A r), 7.33$ (d, 1H, J $\left.{ }_{\alpha, \beta} 15.6 \mathrm{~Hz}, \mathrm{CH}=C \mathrm{HCO}\right), 7.04(\mathrm{~d}, 2 \mathrm{H}, J 9.0 \mathrm{~Hz}$, Ar), 6.67 (d, 2H, J 9.0 Hz, Ar), 5.43 (br.s, $\left.1 \mathrm{H}, J 4.8 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}\right), 5.28\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2}\right)$, 4.91 (br.d, 1H, J 2.4 Hz ), 3.03 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{NMe}_{2}$ ), 2.95 ( $\mathrm{s}, 1 \mathrm{H}$ ), 2.48 (d, 1H, J 16.2 Hz ), 2.18-2.09 (m, 2H), 2.00-1.95 (m, 2H), 1.84-1.79 (m, 1H), 1.67-1.63 (m, 1H), 1.56-1.39 $(\mathrm{m}, 5 \mathrm{H}), 1.32-1.21(\mathrm{~m}, 4 \mathrm{H}), 1.11-0.88(\mathrm{~m}, 14 \mathrm{H}), 0.86\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right)$,
$0.85,0.84\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27\right), 0.64\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 188.64(\mathrm{C}=\mathrm{O}), 161.55(\mathrm{CH}=\mathrm{CHCO}), 151.95,145.12,137.93$, 132.27, 130.54, 130.33, 124.59, 122.85, 122.63, 116.45, 114.56, 111.86 (12 C-Ar, $\mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}, \mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}, \mathrm{CH}=\mathrm{CHCO}$ ), $62.22,56.74,56.51,56.10,49.98$, $42.28,40.17,39.51,37.09,36.15,35.88,35 . .45,32.65,31.89,31.67,28.25,28.03,27.22$, 24.24, 24.05, 22.85, 22.60, 20.61, 19.28, 18.65 ( 27 C ), $11.84\left(\mathrm{CH}_{3}-18\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}$, \%) for $\mathrm{C}_{47} \mathrm{H}_{64} \mathrm{~N}_{4} \mathrm{O}_{2}$ (716.50): $717.40(\mathrm{M}+1,13 \%)$, $716.40(\mathrm{M}, 19 \%)$, 703.40 (28\%), 422.40 (88\%).
(2E)-1-[4-(\{1-[(3ß)-Cholest-5-en-3-yl]-1H-1,2,3-triazol-4-yl\}methoxy)phenyl]-3-(2-furyl)prop-2-en-1-one (7a)
Yield: (47\%) as yellow crystals upon flash chromatography (toluene:ethyl acetate, 4:1). $R_{\mathrm{f}} 0.33$ (toluene:ethyl acetate, $4: 1$ ); Mp. $162-164{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(600 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ): $\delta 8.04$ $\left(\mathrm{d}, 2 \mathrm{H}, J 9.0 \mathrm{~Hz}, \mathrm{H}-3_{\mathrm{Ar}}, \mathrm{H}-5_{\mathrm{Ar}}\right), 7.84\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\mathrm{Triaz}}\right), 7.58\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.0 \mathrm{~Hz}\right.$, $\mathrm{CH}=\mathrm{CHCO}$ ), 7.52 (d, $1 \mathrm{H}, J_{4,5} 1.8 \mathrm{~Hz}, \mathrm{H}-5_{\mathrm{Fur}}$ ), $7.46\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.0 \mathrm{~Hz}, \mathrm{CH}=\mathrm{CHCO}\right)$, 7.06 (d, 2H, J $9.0 \mathrm{~Hz}, \mathrm{H}-2_{\mathrm{Ar}}, \mathrm{H}-6_{\text {Ar }}$ ), $6.70\left(\mathrm{~d}, 1 \mathrm{H}, J_{3,4} 3.0 \mathrm{~Hz}, \mathrm{H}-3_{\mathrm{Fur}}\right.$ ), 6.15 (dd, 1H, $J_{3,4}$ $3.0, J_{4,5} 1.8 \mathrm{~Hz}, \mathrm{H}-4_{\text {Fur }}$ ), 5.44 (br.d, $1 \mathrm{H}, J 4.8 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}$ ), 5.31 (s, $2 \mathrm{H}, \mathrm{OCH}_{2}$ ), 4.93 (br.d, 1H, J 3.0 Hz ), 2.97-2.94 (m, 1H), 2.51-2.48 (m, 1H), 2.21-2.19 (m, 1H), 2.16-2.10 (3t, 1H, J 3.6, 4.2 Hz), 2.05-1.95 (m, 2H), 1.85-1.79 (m, 1H), 1.68-1.65 (m, $2 H), 1.60-1.39(\mathrm{~m}, 5 \mathrm{H}), 1.37-1.21(\mathrm{~m}, 5 \mathrm{H}), 1.16-1.00(\mathrm{~m}, 10 \mathrm{H}), 0.99-0.82(\mathrm{~m}, 2 \mathrm{H})$, $0.88\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 7.8 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right), 0.87,0.86\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26\right.$, $\left.\mathrm{CH}_{3}-27\right), 0.66\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 187.85(\mathrm{C}=\mathrm{O}), 161.98$ $(\mathrm{CH}=\mathrm{CHCO}), 151.81,144.72,142.30,137.92,131.45,130.73,130.11,124.56,122.62$, 119.02, 115.91, 114.70, 112.61 ( $6 \mathrm{C}-\mathrm{Ar}, 4 \mathrm{C}-\mathrm{Fur}, \mathrm{CH}=C \mathrm{HCO}, \mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}$, $\mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Triaz }}$ ), $62.22,56.72,56.52,56.09,49.99,42.26,39.51,39.49,37.07,36.14$, $35.85,35.42,32.62,31.87,31.63,28.21,28.00,27.20,24.20,23.99,22.83,22.57,20.58$, 19.26, 18.63 ( 25 C ), $11.83\left(\mathrm{CH}_{3}-18\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}$, \%) for $\mathrm{C}_{43} \mathrm{H}_{57} \mathrm{~N}_{3} \mathrm{O}_{3}$ (663.44): 665.60 $(\mathrm{M}+2,4 \%), 664.60(\mathrm{M}+1,15 \%), 663.60(\mathrm{M}, 29 \%), 449.50$ ( $10 \%$ ), 422.50 ( $100 \%$ ).
(2E)-1-[4-(\{1-[(3及)-Cholest-5-en-3-yl]-1H-1,2,3-triazol-4-yl\}methoxy)phenyl]-3-(2-thienyl)prop-2-en-1-one (7b)
Yield: ( $60 \%$ ) as yellowish powder upon flash chromatography (toluene:ethyl acetate, 6:1). $R_{\mathrm{f}} 0.35$ (toluene:ethyl acetate, $4: 1$ ); $\mathrm{Mp} 172-174{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $8.02\left(\mathrm{~d}, 2 \mathrm{H}, J 9.0 \mathrm{~Hz}, \mathrm{H}-3_{\mathrm{Ar}}, \mathrm{H}-5_{\mathrm{Ar}}\right), 7.93\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}, \mathrm{CH}=\mathrm{CHCO}\right), 7.84(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{H}-5_{\text {Triaz }}$ ), $7.40\left(\mathrm{~d}, 1 \mathrm{H}, J_{4,5} 4.8 \mathrm{~Hz}, \mathrm{H}-5_{\text {Thioph }}\right), 7.35\left(\mathrm{~d}, 1 \mathrm{H}, J_{\alpha, \beta} 15.6 \mathrm{~Hz}, \mathrm{CH}=\mathrm{CHCO}\right), 7.34$ $\left(\mathrm{d}, 1 \mathrm{H}, J_{3,4} 3.6 \mathrm{~Hz}, \mathrm{H}-3_{\text {Thioph }}\right), 7.08$ (dd, $1 \mathrm{H}, J_{3,4} 3.6, J_{4,5} 4.8 \mathrm{~Hz}, \mathrm{H}-4_{\text {Thioph }}$ ), 7.07 (d, 2H, J $9.0 \mathrm{~Hz}, \mathrm{H}-2_{\mathrm{Ar}}, \mathrm{H}-6_{\mathrm{Ar}}$ ), 5.44 (br.d, $1 \mathrm{H}, J 4.8 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Chol}}$ ), 5.31 (s, 2H, OCH $)_{2}$, 4.93 (br.d, $1 \mathrm{H}, J 2.4 \mathrm{~Hz}$ ), 2.95 (br.dd, 1H, J 2.4, 16.2 Hz), 2.49 (br.d, 1H, J 15.6 Hz ), 2.24-2.18 (m, $1 \mathrm{H}), 2.16,2.14,2.11(3 \mathrm{t}, 1 \mathrm{H}, J 3.6,7.2 \mathrm{~Hz}), 2.33-1.96(\mathrm{~m}, 2 \mathrm{H}), 1.85-1.79(\mathrm{~m}, 1 \mathrm{H})$, 1.75-1.70 (m, 1H), 1.66 (br.d, 1H, J 13.2 Hz ), 1.58-1.38 (m, 6H), 1.37-1.28 (m, 3H), $1.27-1.20(\mathrm{~m}, 1 \mathrm{H}), 1.14-1.01(\mathrm{~m}, 9 \mathrm{H}), 0.98-0.82(\mathrm{~m}, 3 \mathrm{H}), 0.87\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 6.6 \mathrm{~Hz}\right.$, $\mathrm{CH}_{3}-21$ ), $0.87,0.86$ ( $2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27$ ), 0.66 (s, 3 H , $\left.\mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR (150 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 187.80(\mathrm{C}=\mathrm{O}), 161.99(\mathrm{CH}=\mathrm{CHCO}), 140.55$, 137.91, 136.55, 131.86, 131.35, 130.69, 128.50, 128.30, 124.55, 122.64, 120.39, 114.72 ( $6 \mathrm{C}-\mathrm{Ar}, 4 \mathrm{C}-$ Thioph, $\mathrm{CH}=\mathrm{CHCO}, \mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}, \mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Triaz }}$ ), 62.22, 56.72 , $56.51,56.10,49.97,42.25,39.50,39.48,37.06,36.13,35.84,35.41,32.62,31.87,31.62$, 28.22, 27.99, 27.19, 24.20, 23.99, 22.83, 22.57, 20.58, 19.25, 18.62 (25 C), 11.82 $\left(\mathrm{CH}_{3}-18\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}, \%$ ) for $\mathrm{C}_{43} \mathrm{H}_{57} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{~S}$ (679.42): $681.50(\mathrm{M}+2,4 \%), 680.50$ ( $\mathrm{M}+1,9 \%$ ), $679.50(\mathrm{M}, 19 \%), 570.50(3 \%), 422.50$ (66\%).

## 6-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)hexan-1-ol (11a)

Yield: ( $90 \%$ ) as creamy foam upon flash chromatography (toluene:acetone, 7:3). $R_{\mathrm{f}} 0.34$ (toluene:acetone, 7:3); IR (v́, cm $\left.{ }^{-1}\right): 3345\left(\mathrm{OH}_{s t r}\right), 1071,1023\left(\mathrm{C}-\mathrm{O}-\mathrm{C}_{s t r}\right) ;{ }^{1} \mathrm{H}$ NMR (600 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.53$ (s, 1H, H-5 Triaz), 5.35 (dd, $1 \mathrm{H}, J 2.4,3.0 \mathrm{~Hz}, \mathrm{H}-6$ Chol $), 4.68$ (s, 2 H , $\mathrm{OCH}_{2}$ ), $4.34\left(\mathrm{t}, 2 \mathrm{H}, J 7.2 \mathrm{~Hz}, \mathrm{CH}_{2}-1_{\mathrm{Hex}}\right), 3.63\left(\mathrm{t}, 2 \mathrm{H}, J 6.6 \mathrm{~Hz}, \mathrm{CH}_{2}-6_{\mathrm{Hex}}\right), 3.35-3.30(\mathrm{~m}$, $1 \mathrm{H}, \mathrm{H}-3_{\text {Chol }}$ ), 2.42-2.39 (m, 1H), 2.27-2.23 (dd, 1H, J 11.4, 10.8 Hz ), 2.02-1.81 (m, OH, $9 H), 1.60-1.32(\mathrm{~m}, 17 \mathrm{H}), 1.27-1.23(\mathrm{~m}, 1 \mathrm{H}), 1.20-1.01(\mathrm{~m}, 7 \mathrm{H}), 1.00(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{CH}_{3}-19_{\text {Chol }}$ ), 0.91 (d, $3 \mathrm{H}, J 6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21_{\text {Chol }}$ ), $0.87,0.86$ ( $2 \mathrm{~d}, 6 \mathrm{H}, J 3.0 \mathrm{~Hz}$, $\mathrm{CH}_{3}-26_{\text {Chol }}, \mathrm{CH}_{3}-27_{\text {Chol }}$ ), 0.67 (s, $3 \mathrm{H}, \mathrm{CH}_{3}-18_{\text {Chol }}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$
$145.96\left(\mathrm{C}-4_{\text {Triaz }}\right), 140.67\left(\mathrm{C}-5_{\text {Chol }}\right), 122.13,121.84\left(\mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}\right), 78.96\left(\mathrm{C}-3_{\text {Chol }}\right)$, $62.54,61.69\left(2 \mathrm{OCH}_{2}\right), 56.75,56.14\left(\mathrm{C}-14_{\mathrm{Chol}}, \mathrm{C}-17_{\mathrm{Chol}}\right), 50.17,50.15,42.32,39.77$, $39.52,39.03,37.16,36.85,36.18,35.79,32.33,31.94,31.88,30.19,28.31,28.23,28.02$, 26.11, $25.08(19 \mathrm{C}), 24.29\left(\mathrm{CH}_{2}-15_{\mathrm{Chol}}\right), 23.82\left(\mathrm{CH}_{2}-23_{\mathrm{Chol}}\right), 22.83,22.57\left(\mathrm{CH}_{3}-26_{\mathrm{Chol}}\right.$, $\left.\mathrm{CH}_{3}-27_{\mathrm{CHol}}\right), 21.07\left(\mathrm{CH}_{2}-11_{\mathrm{Chol}}\right)$, $19.37\left(\mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 18.72\left(\mathrm{CH}_{3}-21_{\mathrm{Chol}}\right), 11.86$ $\left(\mathrm{CH}_{3}-18_{\text {Cho51 }}\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}, \%$ ) for $\mathrm{C}_{36} \mathrm{H}_{61} \mathrm{~N}_{3} \mathrm{O}_{2}$ (567.48): $568.10(\mathrm{M}+1,46), 567.10$ (M, 48), 564.10 (26), 555.10 (62.8), 505.10 (58.4).

## 11-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)undecan-1-ol (11b)

Yield: ( $67 \%$ ) as colorless mass upon flash chromatography (toluene:ethyl acetate, 3:2). $R_{\mathrm{f}}$ 0.25 (toluene:ethyl acetate, $3: 2$ ); $\mathrm{Mp} 94{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.52(\mathrm{~s}, 1 \mathrm{H}$, $\mathrm{H}-5_{\text {Triaz }}$ ), 5.35 (dd, $\left.1 \mathrm{H}, J 2.4,3.0 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}\right), 4.68\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2}\right), 4.32(\mathrm{t}, 2 \mathrm{H}, J 7.8 \mathrm{~Hz}$, $\mathrm{CH}_{2}-1_{\text {Hex }}$ ), 3.63 (t, $2 \mathrm{H}, J_{10,11} 3,6.6, J_{\text {gem }} 10.2 \mathrm{~Hz}, \mathrm{CH}_{2}-11_{\text {Hex }}$ ), $3.35-3.30(\mathrm{~m}, 1 \mathrm{H}$, $\mathrm{H}-3_{\text {Chol }}$ ), 2.42-2.39 (m, 1H), 2.27-2.22 (dd, 1H), 2.03-1.79 (m, OH, 8H), 1.60-1.43 (m, $9 H), 1.34-1.26(\mathrm{~m}, 19 \mathrm{H}), 1.18-1.04(\mathrm{~m}, 6 \mathrm{H}), 1.03-0.96(\mathrm{~m}, 2 \mathrm{H}), 1.00(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{CH}_{3}-19_{\text {Chol }}$ ), 0.91 (d, $3 \mathrm{H}, J 6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21_{\text {Chol }}$ ), $0.87,0.86(2 \mathrm{~d}, 6 \mathrm{H}, J 2.4,3.0 \mathrm{~Hz}$, $\mathrm{CH}_{3}-26_{\text {Chol }}, \mathrm{CH}_{3}-27_{\text {Chol }}$ ), 0.67 (s, $3 \mathrm{H}, \mathrm{CH}_{3}-18_{\text {Chol }}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $145.90\left(\mathrm{C}-4_{\text {Triaz }}\right), 140.66\left(\mathrm{C}-5_{\text {Chol }}\right), 122.05,121.82\left(\mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}\right)$, $78.90\left(\mathrm{C}-3_{\text {Chol }}\right)$, 62.98, $61.71\left(2 \mathrm{OCH}_{2}\right), 56.75,56.14\left(\mathrm{C}-14_{\text {Chol }}, \mathrm{C}-17_{\text {Chol }}\right), 50.33,50.14,42.31,39.76$, $39.51,39.04,37.16,36.84,36.18,35.78,32.76,31.93,31.88,30.26,29.47,29.35,29.34$, 29.29, 28.92, 28.31, 28.23, 28.01, 26.44, 25.71 (24-C), $24.29\left(\mathrm{CH}_{2}-15_{\text {Chol }}\right), 23.82$ $\left(\mathrm{CH}_{2}-23_{\mathrm{Chol}}\right)$, 22.82, $22.57\left(\mathrm{CH}_{3}-26_{\mathrm{Chol}}, \mathrm{CH}_{3}-27_{\mathrm{CHol}}\right), 21.06\left(\mathrm{CH}_{2}-11_{\mathrm{Chol}}\right), 19.37$ $\left(\mathrm{CH}_{3}-19_{\text {Chol }}\right)$, $18.71\left(\mathrm{CH}_{3}-21_{\text {Chol }}\right), 11.86\left(\mathrm{CH}_{3}-18_{\text {Chol }}\right) . \mathrm{C}_{41} \mathrm{H}_{71} \mathrm{~N}_{3} \mathrm{O}_{2}(638.02)$

## (3ß)-3-\{[1-(6-Bromohex-1-yl)-1H-1,2,3-triazol-4-yl]methoxy $\}$ cholest-5-ene (12)

A mixture of $11 \mathrm{a}(0.4 \mathrm{~g}, 0.7 \mathrm{mmol}), \mathrm{PPh}_{3}(0.25 \mathrm{~g}, 0.9 \mathrm{mmol})$ in $\mathrm{DCM}(5 \mathrm{~mL})$ was treated with $\mathrm{CBr}_{4}(0.35 \mathrm{~g}, 1.0 \mathrm{mmol})$ and stirred at ambient temperature overnight. The reaction mixture was evaporated in vacuo and the residue was purified by flash chromatography (toluene:acetone, $7: 1$ ) to afford $\mathbf{1 2}(0.26 \mathrm{~g}, 59 \%)$ as faint greenish crystals. $R_{\mathrm{f}} 0.56$ (toluene:acetone, $4: 1$ ); Mp. $126^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.55\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}\right.$ ),
5.35 (dd, 1H, J $2.4 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}$ ), $4.70\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2}\right), 4.35\left(\mathrm{t}, 2 \mathrm{H}, J 7.2 \mathrm{~Hz}, \mathrm{CH}_{2}-1_{\text {Hex }}\right)$, 3.39 ( $\mathrm{t}, 2 \mathrm{H}, J 6.6, J_{\mathrm{gem}} 10.2 \mathrm{~Hz}, \mathrm{CH}_{2}-6_{\mathrm{Hex}}$ ), $3.34-3.31\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-3_{\mathrm{Chol}}\right), 2.42-2.39$, 2.27-2.23 (2m, 2H), 2.02-1.82 (m, 10H), 1.53-1.33 (m, 16H), 1.27-1.23 (m, 1H, J 4.2, $3.0 \mathrm{~Hz}), 1.16-1.05(\mathrm{~m}, 7 \mathrm{H}), 1.00\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 0.91\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 6.8 \mathrm{~Hz}\right.$, $\mathrm{CH}_{3}-21_{\text {Chol }}$ ), $0.87,0.86$ ( $2 \mathrm{~d}, 6 \mathrm{H}, J 2.4,3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26_{\text {Chol }}, \mathrm{CH}_{3}-27_{\text {Chol }}$ ), 0.67 (s, 3 H , $\mathrm{CH}_{3}-18_{\text {Chol }}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 145.71\left(\mathrm{C}-4_{\text {Triaz }}\right), 140.65\left(\mathrm{C}-5_{\mathrm{Chol}}\right), 122.31$, $121.85\left(\mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}\right), 78.98\left(\mathrm{C}-3_{\text {Chol }}\right), 61.64\left(\mathrm{OCH}_{2}\right), 56.75,56.14\left(\mathrm{C}-14_{\text {Chol }}\right.$, $\mathrm{C}-17_{\text {Chol }}$, $50.22,50.14,42.32,39.77,39.52,39.04,37.16,36.85,36.18,35.79,33.55$, $32.37,31.94,31.88,30.09,28.31,28.23,28.02,27.49$, 25.65 (20C), $24.29\left(\mathrm{CH}_{2}-15_{\mathrm{Chol}}\right)$, $23.81\left(\mathrm{CH}_{2}-23_{\mathrm{Chol}}\right)$, 22.83, $22.57\left(\mathrm{CH}_{3}-26_{\mathrm{Chol}}, \mathrm{CH}_{3}-27_{\mathrm{CHol}}\right)$, $21.06\left(\mathrm{CH}_{2}-11_{\mathrm{Chol}}\right), 19.37$ $\left(\mathrm{CH}_{3}-19_{\text {Chol }}\right), 18.72\left(\mathrm{CH}_{3}-21_{\text {Chol }}\right), 11.86\left(\mathrm{CH}_{3}-18_{\text {Chol }}\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}$, \%) for $\mathrm{C}_{36} \mathrm{H}_{60} \mathrm{BrN}_{3} \mathrm{O}$ (629.39): 630.00 ( $\mathrm{M}+1,55 \%$ ), 629.00 (M, 64\%), 623.00 ( $43 \%$ ); 615.00 ( $47 \%$ ), 584 (58\%).

## (3ß)-3-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)cholest-5-ene

 (13)Yield: ( $96 \%$ ) as amorphous colorless mass upon flash chromatography (toluene:ethyl acetate, 7:1). $R_{\mathrm{f}} 0.32$ (toluene:ethyl acetate, $7: 1$ ); Mp 192-194 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( 600 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.78$ (s, $1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}$ ), 5.50 (br.t, $1 \mathrm{H}, J 2.4,4.8 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}$ ), 5.33 (br.t, $1 \mathrm{H}, J$ $3.0,5.4 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Chol}}$ ), 4.89 (br.d, 1H, J 1.8 Hz ), 4.70 (d, 2H, J 3.0 Hz, OCH 2 ), 3.28-3.24 (m, 1H), 2.94 (br.d, 1H, J 14.4 Hz ), 2.52 (br.d, 1H, J 15.6 Hz ), 2.40-2.38, 2.37-2.37 (2m, 1H), 2.25-2.20 (m, 2H), 2.14, 2.12, 2.10 (3 t, 1H, J 3.6, 2.7 Hz), 2.07-1.93 (m, 4H), $1.91-1.79(\mathrm{~m}, 4 \mathrm{H}), 1.67-1.40(\mathrm{~m}, 16 \mathrm{H}), 1.39-1.21(\mathrm{~m}, 9 \mathrm{H}), 1.18-1.04(\mathrm{~m}, 15 \mathrm{H})$, $1.01-0.95(\mathrm{~m}, 7 \mathrm{H}), 0.94-0.88(\mathrm{~m}, 1 \mathrm{H}), 0.91,0.89\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{20,21} 6.6 \mathrm{~Hz}, 2 \mathrm{CH}_{3}-21\right)$, $0.86-0.85\left(\mathrm{~m}, 12 \mathrm{H}, 2 \mathrm{CH}_{3}-26,2 \mathrm{CH}_{3}-27\right), 0.68,0.67\left(2 \mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR ( 150 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 145.00,140.62$, 138.17 ( $\mathrm{C}-4_{\text {Triaz }}, 2 \mathrm{C}-5_{\text {Chol }}$ ), 124.37, $122.04,121.86$ (C-5 Triaz, $2 \mathrm{C}-6_{\text {Chol }}$ ), $78.46,61.90,56.74,56.50,56.34,56.17,50.20,50.09,42.34,42.32$, $39.86,39.63,39.53,39.51,39.00,37.40,37.06,36.86,37.06,36.86,36.24,36.20,35.91$, $35.82,35.40,32.87,31.96,31.91,31.67,28.69,28.27,28.26,28.04,28.03,27.26,24.31$,
24.24, 24.07, 23.86, 22.84, 22.83, 22.61, 22.59, 21.10, 20.64, 19.42, 19.31, 18.75, 18.66 (49 C), 11.88 ( $2 \mathrm{CH}_{3}-18$ ); $\mathrm{C}_{57} \mathrm{H}_{93} \mathrm{~N}_{3} \mathrm{O}$ (835.73).
(3ß)-Cholest-5-en-3-yl

## 3,4,6-tri- $O$-acetyl-2-deoxy-2-dimethylmaleimido- $\beta$-D-

 glucopyranoside (15)A mixture of $\mathbf{1}(0.4 \mathrm{~g}, 1.0 \mathrm{mmol})$ and $\mathbf{1 4}(0.7 \mathrm{~g}, 1.2 \mathrm{mmol})$ in $\mathrm{CH}_{3} \mathrm{CN}(5 \mathrm{~mL})$ was stirred under $\mathrm{N}_{2}$ at ambient temperature then TMSOTf ( $0.01 \mathrm{M}, 1.0 \mathrm{~mL}, 1.0 \mathrm{~mol} \%$ ) was added dropwise. Stirring was continued for 15 min then $\mathrm{Et}_{3} \mathrm{~N}$ was added and the mixture was evaporated in vacuo. The residue was purified by flash chromatography (toluene:ethyl acetate, 6:1) and the fractions including the product were collected and acetylated $\left(\mathrm{Pyr} / \mathrm{Ac}_{2} \mathrm{O}, 2: 1,3 \mathrm{~mL}\right)$ then worked up and purified again under the same conditions. This acetylation removed the unreacted cholesterol and easily afforded pure $15(0.6 \mathrm{~g}, 74 \%)$ as colorless crystals. $R_{\mathrm{f}} 0.46$ (toluene:ethyl acetate, $4: 1$ ); Mp. $94{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( 600 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 5.60\left(\mathrm{dd}, 1 \mathrm{H}, J_{2,3} 10.8, J_{3,4} 9.0 \mathrm{~Hz}, \mathrm{H}-3_{\mathrm{Glu}}\right), 5.31-5.29\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-6_{\text {Chol }}\right), 5.30$ $\left(\mathrm{d}, 1 \mathrm{H}, J_{1,2} 8.4 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}\right), 5.09\left(\mathrm{dd}, 1 \mathrm{H}, J_{3,4} 9.0, J_{4,5} 9.6 \mathrm{~Hz}, \mathrm{H}-4_{\mathrm{Glu}}\right.$ ), 4.29 (dd, $1 \mathrm{H}, J_{\mathrm{gem}}$ $12.0, J_{5,6} 4.8 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}$ ), 4.11 (dd, $1 \mathrm{H}, J_{\text {gem }} 12.0, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6_{\text {Glu }}$ ), 4.05 (dd, $1 \mathrm{H}, J_{1,2}$ $8.4, J_{2,3} 10.8 \mathrm{~Hz}, \mathrm{H}-2_{\text {Glu }}$ ), $3.81-3.78\left(2 \mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-5_{\mathrm{Glu}}\right), 3.47-3.43\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-3_{\text {Chol }}\right), 2.09$, 2.02, 1.96, $1.92\left(4 \mathrm{~s}, 15 \mathrm{H}, 3 \mathrm{COCH}_{3}, 2 \mathrm{CH}_{3}\right), 2.07-1.93(\mathrm{~m}, 7 \mathrm{H}), 1.84-1.80(\mathrm{~m}, 3 \mathrm{H})$, $1.55-1.32(\mathrm{~m}, 11 \mathrm{H}), 1.28-1.22(\mathrm{~m}, 1 \mathrm{H}), 1.14-0.96(\mathrm{~m}, 6 \mathrm{H}), 0.94\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19_{\text {Chol }}\right)$, 0.90 (d, $3 \mathrm{H}, J 6.8 \mathrm{~Hz}, \mathrm{CH}_{3}-21_{\text {Chol }}$ ), $0.86,0.85\left(2 \mathrm{~d}, 6 \mathrm{H}, J 2.4,3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-26_{\text {Chol }}\right.$, $\mathrm{CH}_{3}-27_{\text {Chol }}$, $0.66\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18_{\mathrm{Chol}}\right.$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 170.84,170.30$, 169.56, 163.76 ( $5 \mathrm{C}=\mathrm{O}$ ), $140.22\left(\mathrm{C}-5_{\mathrm{Chol}}\right)$, 137.38 ( $\mathrm{C}=\mathrm{C}_{\text {Maleimido }}$ ), $122.17\left(\mathrm{C}-6_{\text {Chol }}\right)$, 96.86 $\left(\mathrm{C}-1_{\mathrm{Glu}}\right), 79.56\left(\mathrm{C}-3_{\mathrm{Chol}}\right), 71.58\left(\mathrm{C}-5_{\mathrm{Glu}}\right), 71.01\left(\mathrm{C}-3_{\mathrm{Glu}}\right), 69.06\left(\mathrm{C}-4_{\mathrm{Glu}}\right), 62.18\left(\mathrm{C}-6_{\mathrm{Glu}}\right)$, 56.70, $56.11\left(\mathrm{C}-14_{\text {Chol }}, \mathrm{C}-17_{\mathrm{Chol}}\right)$, $54.68\left(\mathrm{C}-2_{\mathrm{Glu}}\right)$, 50.07, 42.29, 39.71, 39.50, 38.69, $37.11,36.62,36.16,35.76,31.89,31.82,29.35,28.21,28.00(14 \mathrm{C}), 24.27\left(\mathrm{CH}_{2}-15_{\mathrm{Chol}}\right)$, $23.80\left(\mathrm{CH}_{2}-23_{\mathrm{Chol}}\right)$, 22.82, $22.56\left(\mathrm{CH}_{3}-26_{\mathrm{Chol}}, \mathrm{CH}_{3}-27_{\mathrm{CHol}}\right), 21.01\left(\mathrm{CH}_{2}-11_{\mathrm{Chol}}\right), 20.81$, 20.66, $20.56\left(3 \mathrm{CH}_{3} \mathrm{CO}\right)$, $19.37\left(\mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 18.70\left(\mathrm{CH}_{3}-21_{\mathrm{Chol}}\right), 11.84\left(\mathrm{CH}_{3}-188_{\text {Chol }}\right)$, $8.84\left(2 \mathrm{CH}_{3 \text { Maleimid }}\right)$; EI-MS $(\mathrm{m} / \mathrm{z}, \%)$ for $\mathrm{C}_{45} \mathrm{H}_{67} \mathrm{NO}_{10}$ (781.48): $783.00(\mathrm{M}+2,26 \%)$, 782.00 ( $\mathrm{M}+1,24 \%$ ), 781.00 (M, 44\%), 755.00 (35\%), 711 (41\%).

## (3ß)-Cholest-5-en-3-yl 2-deoxy-2-dimethylmaleimido- $\beta$-D-glucopyranoside (16)

A mixture of $\mathbf{1 5}(0.23 \mathrm{~g}, 0.3 \mathrm{mmol})$ and $\mathrm{NaOMe} / \mathrm{MeOH}(0.005 \mathrm{M}, 20 \mathrm{~mL})$ was stirred at ambient temperature for 75 min then neutralized with Amberlite IR $120\left(\mathrm{H}^{+}\right)$resin, filtered and evaporated in vacuo. The residue was purified by flash chromatography using solvent gradient of toluene then (toluene:acetone 5:4) to afford 16 ( $0.16 \mathrm{~g}, 84 \%$ ) as colorless mass. $R_{\mathrm{f}} 0.17$ (toluene:acetone 5:4); Mp. $220{ }^{\circ} \mathrm{C}$; IR (v́, $\mathrm{cm}^{-1}$ ): 3524-3461 $\left(\mathrm{O}-\mathrm{H}_{s t r}\right), 1701\left(\mathrm{C}=\mathrm{O}_{s t r}\right) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{MeOH}-d_{4}$ ): $\delta 5.28-5.28\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-6_{\text {Chol }}\right)$, $5.10\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 8.4 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}\right.$ ), 4.05 (dd, $1 \mathrm{H}, J_{1,2} 8.4, J_{2,3} 10.8 \mathrm{~Hz}, \mathrm{H}-2_{\mathrm{Glu}}$ ), 3.87 (dd, $\left.1 \mathrm{H}, J_{\mathrm{gem}} 12.0, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}\right), 3.70-3.67\left(\mathrm{~m}, 2 \mathrm{H}_{\mathrm{Glu}}\right), 3.49-3.44\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-3_{\text {Chol }}\right)$, 3.35-3.30 (m, 4H), 2.10-2.09, 2.08-2.07 (2m, 1H), 2.04-2.01 (m, 1H, J 3.6, 7.2 Hz), $1.96\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3 \text { Maleimide }}\right), 1.95-1.81(\mathrm{~m}, 4 \mathrm{H}), 1.62-1.58(\mathrm{~m}, 1 \mathrm{H}), 1.53-1.33(\mathrm{~m}, 9 \mathrm{H})$, $1.29-1.24(\mathrm{~m}, 1 \mathrm{H}), 1.18-0.97(\mathrm{~m}, 9 \mathrm{H}), 0.94\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 0.92(\mathrm{~d}, 3 \mathrm{H}, J 6.6 \mathrm{~Hz}$, $\mathrm{CH}_{3}-21_{\text {Chol }}$ ), $0.87,0.86$ ( $2 \mathrm{~d}, 6 \mathrm{H}, J 2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26_{\text {Chol }}, \mathrm{CH}_{3}-2_{\text {Chol }}$ ), 0.69 (s, 3 H , $\mathrm{CH}_{3}-18_{\text {Chol }}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{MeOH}-d_{4}$ ): $\delta 141.55\left(\mathrm{C}-5_{\mathrm{Chol}}\right), 138.40\left(\mathrm{C}=\mathrm{C}_{\text {Maleimid }}\right)$, $123.05\left(\mathrm{C}-6_{\text {Chol }}\right), 98.16\left(\mathrm{C}-1_{\text {Glu }}\right), 79.88,78.25,72.90,72.55,62.75,58.56,58.16,57.57$, $51.68,43.51,41.15,40.71,39.99,38.44,37.80,37.39,37.14,33.23,33.03,30.54,29.34$, 29.18, 25.32, 24.96, 23.21, 22.95, 22.16 ( 27 C ), $19.80,19.24\left(\mathrm{CH}_{3}-19\right.$ Chol, $\mathrm{CH}_{3}-21_{\text {Chol }}$, $12.31\left(\mathrm{CH}_{3}-18\right)$, $8.80\left(2 \mathrm{CH}_{3}\right.$ Maleimide $)$; $\mathrm{EI}-\mathrm{MS}(\mathrm{m} / \mathrm{z}, \%)$ for $\mathrm{C}_{39} \mathrm{H}_{61} \mathrm{NO}_{7}$ (655.44): 651.00 (M-4, 23\%), 634.00 ( $26 \%$ ), 604.00 ( $26 \%$ ), 502.00 ( $30 \%$ ).

## (3ß)-Cholest-5-en-3-yl 2-Acetamido-2-deoxy- $\beta$-D-glucopyranoside (17)

A mixture of $16(0.1 \mathrm{~g}, 0.15 \mathrm{mmol})$ and $\mathrm{NaOH}(0.2 \mathrm{~g}, 5.0 \mathrm{mmol})$ in dioxane $/ \mathrm{MeOH} / \mathrm{H}_{2} \mathrm{O}$ (6:3:1, 10 mL ) was stirred at ambient temperature for 8 h , then the acidity of the mixture was adjusted at pH 5 by 1 N HCl and stirring was continued overnight. The mixture was neutralized by $\mathrm{Na}_{2} \mathrm{CO}_{3}$ then evaporated in vacuo. The residue was stirred with $\mathrm{Pyr} / \mathrm{Ac}_{2} \mathrm{O}$ $(2: 1,5 \mathrm{~mL})$ overnight then evaporated in vacuo and the residue was stirred with $\mathrm{NaOMe} / \mathrm{MeOH}(0.005 \mathrm{M}, 20 \mathrm{~mL})$ for 2 h . The mixture was neutralized with Amberlite IR $\left(\mathrm{H}^{+}\right)$resin, filtered and evaporated in vacuo. The residue was purified by flash chromatography (toluene:acetone, 5:4) to afford 17 ( $30 \mathrm{mg}, 37 \%$ ) as amorphous colorless mass. $R_{\mathrm{f}} 0.17$ (toluene:acetone $5: 4$ ); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{MeOH}-d_{4}$ ): $\delta 5.28-5.27$ (m,
$\left.1 \mathrm{H}, \mathrm{H}-6_{\text {Chol }}\right), 5.10\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 8.4 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}\right), 4.05\left(\mathrm{dd}, 1 \mathrm{H}, J_{1,2} 8.4, J_{2,3} 10.8 \mathrm{~Hz}\right.$, $\mathrm{H}-2_{\mathrm{Glu}}$ ), 3.87 (dd, $1 \mathrm{H}, J_{\text {gem }} 12.0, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}$ ), $3.70-3.67$ (m, 2H), 2.10-2.09, 2.08-2.07 ( $2 \mathrm{~m}, 1 \mathrm{H}$ ), 2.03-2.01 (m, 1H), $1.96\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 1.95-1.81(\mathrm{~m}, 6 \mathrm{H})$, $1.60-1.25(\mathrm{~m}, 13 \mathrm{H}), 1.18-0.99(\mathrm{~m}, 10 \mathrm{H}), 0.94\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19\right), 0.92\left(\mathrm{~d}, 3 \mathrm{H}, J_{20,21} 6.0\right.$ $\mathrm{Hz}, \mathrm{CH}_{3}-21$ ), $0.87,0.86$ (2d, $6 \mathrm{H}, J_{25,26}=J_{25,27} 2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27$ ), 0.69 (s, 3 H , $\left.\mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 183.10\left(\mathrm{COCH}_{3}\right), 141.64\left(\mathrm{C}-5_{\mathrm{Chol}}\right), 123.06$ ( $\left.\mathrm{C}-6_{\text {Chol }}\right), 98.15\left(\mathrm{C}-1_{\text {Glu }}\right), 79.87,78.25,72.90,72.54,58.56,58.16,57.57,51.68,43.50$, $41.14,40.71,39.99,38.44,37.80,37.38,37.14,33.23,33.03,30.54,29.34,29.18,25.32$, 24.95, 23.20, 22.95, 22.16, 19.80, 19.24 (30 C), $12.30\left(\mathrm{CH}_{3}-18\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}, \%$ ) for $\mathrm{C}_{35} \mathrm{H}_{59} \mathrm{NO}_{6}$ (589.43): $590.00(\mathrm{M}+1,30 \%), 589.00(\mathrm{M}, 30 \%), 572.00$ ( $40 \%$ ), 514.00 (43\%).

## 6-Azidohex-1-yl

## 3,4,6-tri- $O$-acetyl-2-deoxy-2-dimethylmaleimido- $\beta$-D-

## glucopyranoside (18)

A mixture of $\mathbf{1 4}(0.7 \mathrm{~g}, 1.2 \mathrm{mmol})$ and $\mathbf{9 a}(0.15 \mathrm{~g}, 1.0 \mathrm{mmol})$ in DCM ( 5 mL$)$ was stirred under $\mathrm{N}_{2}$ then treated with TMSOTf $(0.01 \mathrm{M}, 1.2 \mathrm{~mL})$ and stirring was continued for 45 min. The mixture was neutralized with $\mathrm{Et}_{3} \mathrm{~N}$ and evaporated in vacuo. The residue was purified by flash chromatography (toluene:ethyl acetate, 4:1) to afford $\mathbf{1 8}(0.4 \mathrm{~g}, 71 \%)$ as syrup. $R_{\mathrm{f}} 0.5$ (toluene:ethyl acetate, 2:1); IR (v́, $\mathrm{cm}^{-1}$ ): $2096\left(\mathrm{~N}_{3 s t r}\right), 1714\left(\mathrm{C}=\mathrm{O}_{\text {str }}\right), 1223$, $1034\left(\mathrm{C}-\mathrm{O}-\mathrm{C}_{s t r}\right) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 5.59$ (dd, $1 \mathrm{H}, J_{2,3} 10.2, J_{3,4} 9.0 \mathrm{~Hz}$, $\left.\mathrm{H}-3_{\mathrm{Glu}}\right), 5.18\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 8.4 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}\right), 5.10\left(\mathrm{dd}, 1 \mathrm{H}, J_{3,4} 9.0, J_{4,5} 9.6 \mathrm{~Hz}, \mathrm{H}-4_{\mathrm{Glu}}\right), 4.29$ (dd, $1 \mathrm{H}, J_{\text {gem }} 12.0, J_{5,6} 4.8 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}$ ), 4.13 (dd, $1 \mathrm{H}, J_{\text {gem }} 12.0, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6{ }_{\mathrm{Glu}}$ ), 4.05 (dd, $1 \mathrm{H}, J_{1,2} 8.4, J_{2,3} 10.2 \mathrm{~Hz}, \mathrm{H}-2_{\text {Glu }}$ ), $3.81-3.77\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}-1_{\mathrm{Hex}}\right), 3.41(\mathrm{~m}, 1 \mathrm{H}$, $\mathrm{H}-5_{\mathrm{Glu}}$ ), $3.21\left(\mathrm{dd}, 2 \mathrm{H}, J 7.2,6.6 \mathrm{~Hz}, \mathrm{CH}_{2}-6_{\mathrm{Hex}}\right.$ ), 2.09, 2.01, $1.91\left(3 \mathrm{~s}, 9 \mathrm{H}, 3 \mathrm{COCH}_{3}\right), 1.95$ (s, $6 \mathrm{H}, 2 \mathrm{CH}_{3}$ ), $1.52-1.49\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}-2_{\mathrm{Hex}}, \mathrm{CH}_{2}-5_{\mathrm{Hex}}\right), 1.30-1.21\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}-3_{\text {Hex }}\right.$, $\mathrm{CH}_{2}-4_{\mathrm{Hex}}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 170.79,170.26,169.52(5 \mathrm{C}=\mathrm{O}), 98.20$ $\left(\mathrm{C}-1_{\mathrm{Glu}}\right), 71.35,70.97,69.79,68.99,62.08,54.49,51.39,51.29,29.12,28.76,26.32$, 25.37 ( 13 C ), 20.80, 20.66, $20.57\left(3 \mathrm{COCH}_{3}\right), 8.81\left(2 \mathrm{CH}_{3}\right)$; EI-MS ( $\mathrm{m} / \mathrm{z}, \%$ ) for $\mathrm{C}_{24} \mathrm{H}_{34} \mathrm{~N}_{4} \mathrm{O}_{10}$ (538.22): 539.10 ( $\mathrm{M}+1,77 \%$ ), 538.10 (M, 100\%), 520.10 ( $77 \%$ ), 490.10 (71\%).

## 6-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)hex-1-yl 3,4,6-tri-O-

 acetyl-2-deoxy-2-dimethylmaleimido- $\beta$-D-glucopyranoside (19)Compounds 10 and 18 were clicked according to the general procedure and the residue was purified by flash chromatography (toluene:acetone, 4:1) to afford 19 ( $67 \%$ ) as syrup. $R_{\mathrm{f}} 0.36$ (toluene:acetone, $4: 1$ ); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.49$ (s, $1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}$ ), 5.58 (dd, $1 \mathrm{H}, J_{2,3} 10.8, J_{3,4} 9.6 \mathrm{~Hz}, \mathrm{H}-3_{\mathrm{Glu}}$ ), $5.34\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-6_{\mathrm{Chol}}\right), 5.17\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 8.4 \mathrm{~Hz}\right.$, $\left.\mathrm{H}-1_{\mathrm{Glu}}\right), 5.09\left(\mathrm{dd}, 1 \mathrm{H}, J_{3,4} 9.6, J_{4,5} 9.0 \mathrm{~Hz}, \mathrm{H}-4_{\mathrm{Glu}}\right), 4.66\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2}\right), 4.29-4.26(\mathrm{~m}$, $3 \mathrm{H}), 4.13$ (dd, 1H, $\left.J_{\text {gem }} 12.0, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6\right), 3.80-3.76$ (m, 2H), 3.42-3.48 (m, 1H), 3.33-3.29 (m, 1H), 2.41-2.38 (2m, 1H), 2.60-2.22(m, 1H), 2.09-1.89 (m, 8H), 2.08, 2.00, $1.90\left(3 \mathrm{~s}, 9 \mathrm{H}, 3 \mathrm{CH}_{3} \mathrm{CO}\right), 1.93$ (s, $6 \mathrm{H}, 2 \mathrm{CH}_{3 \text { Maleimid }}$ ), 1.86-1.80 (m, 3H), 1.57-1.42 $(\mathrm{m}, 8 \mathrm{H}), 1.34-1.24(\mathrm{~m}, 9 \mathrm{H}), 1.17-1.04(\mathrm{~m}, 7 \mathrm{H}), 0.99\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19_{\text {Chol }}\right), 0.90(\mathrm{~d}, 3 \mathrm{H}, J$ $6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21_{\mathrm{Chol}}$ ), $0.85,0.84\left(2 \mathrm{~d}, 6 \mathrm{H}, J 3.0 \mathrm{~Hz}, \mathrm{CH}_{3}-2_{\text {Chol }}, \mathrm{CH}_{3}-27_{\mathrm{Chol}}\right.$ ), 0.66 (s, 3 H , $\mathrm{CH}_{3}-18_{\mathrm{Chol}}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 170.76,170.23,169.51$ ( $5 \mathrm{C}=\mathrm{O}$ ), 145.97, 140.70 125.31, $122.09,121.85$ ( $\mathrm{C}-5_{\text {Chol }}, \mathrm{C}-6_{\text {Chol }}, \mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Triaz }}, \mathrm{C}=\mathrm{C}_{\text {Maleimid }}$ ), 98.20 $\left(\mathrm{H}-1_{\text {Glu }}\right), 78.98\left(\mathrm{C}-3_{\text {Chol }}\right), 71.77,70.98,69.70,68.98,62.06,61.72,56.77,56.16,54.50$, $50.17,42.34,39.79,39.53,39.05,37.19,36.87,36.20,35.80,31.96,31.90,30.21,29.40$, 29.05, 28.33, 28.25, 28.03, 26.14, $25.25(28 \mathrm{C}), 24.31\left(\mathrm{CH}_{2}-15_{\mathrm{Chol}}\right), 23.84\left(\mathrm{CH}_{2}-23_{\mathrm{Chol}}\right)$, 22.84, $22.58\left(\mathrm{CH}_{3}-26_{\mathrm{Chol}}, \mathrm{CH}_{3}-27_{\mathrm{CHol}}\right)$, $21.08\left(\mathrm{CH}_{2}-11_{\mathrm{Chol}}\right)$, 20.82, 20.67, 20.57 (3 $\left.\mathrm{COCH}_{3}\right), 19.39\left(\mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 18.74\left(\mathrm{CH}_{3}-21_{\mathrm{Chol}}\right), \quad 11.88\left(\mathrm{CH}_{3}-18_{\text {Chol }}\right), 8.85 \quad(2$ $\mathrm{CH}_{3 \text { Maleimide }}$ ); $\mathrm{C}_{54} \mathrm{H}_{82} \mathrm{~N}_{4} \mathrm{O}_{11}$ (963.25).

6-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)hex-1-yl 2-deoxy-2-dimethylmaleimido- $\beta$-D-glucopyranoside (20)
Compound 19 ( $0.24 \mathrm{~g}, 0.0 .25 \mathrm{mmol}$ ) was treated with NaOMe and worked up as described for 16 then purified by flash chromatography (toluene:acetone, 1:1) to afford $20(0.15 \mathrm{~g}, 75 \%)$ as colorless foam. $R_{\mathrm{f}} 0.21$ (toluene:acetone, 5:4); ${ }^{1} \mathrm{H}$ NMR ( 600 MHz , $\left.\mathrm{MeOH}-d_{4}\right): \delta 7.92\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}\right), 5.35$ (dd, $1 \mathrm{H}, J 2.4,3.0 \mathrm{~Hz}, \mathrm{H}-6_{\text {Chol }}$ ), 4.94 (d, 1 H , $J_{1,2} 8.4 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}$ ), $4.63\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{OCH}_{2}\right), 4.35\left(\mathrm{dd}, 2 \mathrm{H}, J 7.2 \mathrm{~Hz}, \mathrm{H}-3_{\mathrm{Glu}}, \mathrm{H}-4_{\mathrm{Glu}}\right), 4.07$ (dd, $1 \mathrm{H}, J_{1,2} 8.4, J_{2,3} 10.8 \mathrm{~Hz}, \mathrm{H}-2_{\text {Glu }}$ ), $3.88\left(\mathrm{dd}, 1 \mathrm{H}, J_{\text {gem }} 12.0, J_{5,6} 1.8 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}\right.$ ), $3.82-3.79(\mathrm{~m}, 1 \mathrm{H}), 3.72-3.68(\mathrm{~m}, 2 \mathrm{H}), 3.41-3.37(\mathrm{~m}, 1 \mathrm{H}), 3.34-3.32(\mathrm{~m}, 1 \mathrm{H}), 3.31-3.26$
$(\mathrm{m}, 1 \mathrm{H}), 2.39-2.38,2.37-2.36(2 \mathrm{~m}, 1 \mathrm{H}), 2.22-2.17(\mathrm{~m}, 1 \mathrm{H}), 2.06-2.02(\mathrm{~m}, 1 \mathrm{H})$, $1.98-1.78(\mathrm{~m}, 7 \mathrm{H}), 1.93\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3 \text { maleimid }}\right), 1.64-1.34(\mathrm{~m}, 12 \mathrm{H}), 1.32-0.90(\mathrm{~m}, 15 \mathrm{H})$, $1.01\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 0.93\left(\mathrm{~d}, 3 \mathrm{H}, J 6.0 \mathrm{~Hz}, \mathrm{CH}_{3}-2_{\text {Chol }}\right), 0.88,0.87(2 \mathrm{~d}, 6 \mathrm{H}, J 1.8$ $\mathrm{Hz}, \mathrm{CH}_{3}-26_{\text {Chol }}, \mathrm{CH}_{3}-27_{\text {Chol }}$ ), 0.71 (s, $3 \mathrm{H}, \mathrm{CH}_{3}-18_{\text {Chol }}$ ); ${ }^{13} \mathrm{C}$ NMR ( 150 MHz , $\left.\mathrm{MeOH}-d_{4}\right): \delta 174.28(2 \mathrm{C}=\mathrm{O}), 146.53\left(\mathrm{C}-4_{\text {Triaz }}\right), 141.83$ ( $\mathrm{C}-5_{\text {Chol }}$ ), $138.40\left(\mathrm{C}=\mathrm{C}_{\text {Maleimid }}\right)$, $124.90\left(\mathrm{C}-5_{\text {Triaz }}\right), 122.90\left(\mathrm{C}-6_{\text {Chol }}\right), 99.80\left(\mathrm{C}-1_{\text {Glu }}\right), 80.18,78.25,72.76,72.59,70.18$, 62.76, 61.93, 58.39, 58.20, 57.60, 51.74, 51.24, 43.53, 41.18, 40.73, 40.12, 38.44, 37.98, $37.41,37.17,33.27,33.09,31.32,30.18,29.39,29.36,29.19,27.04,26.45,25.35,24.99$, 23.23, 22.98, $22.22(34 \mathrm{C}), 19.87\left(\mathrm{CH}_{3}-19_{\mathrm{Chol}}\right), 19.28\left(\mathrm{CH}_{3}-21_{\mathrm{Chol}}\right), 12.36\left(\mathrm{CH}_{3}-18_{\mathrm{Chol}}\right)$, 8.63 ( $2 \mathrm{CH}_{3 \text { Maleimid }}$ ); EI-MS ( $\mathrm{m} / \mathrm{z}$, \%) for $\mathrm{C}_{48} \mathrm{H}_{76} \mathrm{~N}_{4} \mathrm{O}_{8}$ (836.56): 831.10(9.2\%), 830.10 ( $9.8 \%$ ), 825.10 ( $9.3 \%$ ), $687.110 .5 \%$ ), 642.10 ( $10.5 \%$ ).

## 6-Azidohex-1-yl $O$-(2,3,4,6-tetra- $O$-acetyl- $\alpha$-D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri- $O$ -acetyl- $\boldsymbol{\beta}$-D-glucopyranoside (22)

A mixture of $21(0.68 \mathrm{~g}, 0.85 \mathrm{mmol})$ and $9 \mathrm{a}(0.1 \mathrm{~g}, 0.7 \mathrm{mmol})$ in dry DCM ( 5 mL ) was stirred under $\mathrm{N}_{2}$ at ambient temperature, while TMSOTf $(0.01 \mathrm{M}, 2 \mathrm{~mol} \%)$ was added dropwise. The mixture was neutralized by $\mathrm{Et}_{3} \mathrm{~N}$ after 1h then evaporated in vacuo. The residue was purified by flash chromatography (toluene:ethyl acetate, 3:2) to afford 22 $(0.1 \mathrm{~g}, 19 \%)$ as colorless syrup. $R_{\mathrm{f}} 0.32$ (toluene:ethyl acetate, 3:2); IR (v́, $\mathrm{cm}^{-1}$ ): 2096 $\left(\mathrm{N}_{3 s t r}\right), 1742\left(\mathrm{C}=\mathrm{O}_{s t r}\right), 1212\left(\mathrm{C}-\mathrm{O}_{\text {Pyran } s t r}\right), 1027\left(\mathrm{CH}_{2}-\mathrm{O}_{s t r}\right) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 5.40\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 4.2 \mathrm{~Hz}, \mathrm{H}-1 \mathrm{~b}\right), 5.35(\mathrm{t}, 1 \mathrm{H}, J 9.6,10.2 \mathrm{~Hz}), 5.24(\mathrm{t}, 1 \mathrm{H}, J 9.0 \mathrm{~Hz}), 5.04$ (t, 1H, J 10.2, 9.6 Hz ), 4.84 (dd, 1H, J 10.2, 4.2 Hz ), 4.80 (dd, 1H, J 7.8, 9.0 Hz), 4.53-4.45 (m, 2H), 4.25-4.20 (m, 2H), $4.02(\mathrm{dd}, 1 \mathrm{H}, J 2.4,12.6 \mathrm{~Hz}, \mathrm{H}-6), 4.00(\mathrm{t}, 1 \mathrm{H}, J$ $9.6,9.0 \mathrm{~Hz}), 3.96-3.93$ (m, 1H), 3.67-3.65 (m, 1H), 3.48-3.44 (m, 1H), 3.36 (dd, 1H, J $6.6,13.2 \mathrm{~Hz}), 3.26-3.23(\mathrm{~m}, 2 \mathrm{H}), 2.13,2.12,2.09,2.06,2.03,2.01,2.00,1.99(7 \mathrm{~s}, 21 \mathrm{H}, 7$ $\mathrm{COCH}_{3}$ ), 1.59-1.55 (m, 4H, CH2 $-2_{\text {Hex }}, \mathrm{CH}_{2}-5_{\text {Нех }}$ ), $1.37-1.32$ ( $\mathrm{m}, 4 \mathrm{H}, \mathrm{CH}_{2}-3_{\text {Hex }}$, $\mathrm{CH}_{2}-4_{\mathrm{Hex}}$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 170.52,170.51,170.46,170.23,169.94$, 169.57, $169.40\left(7 \mathrm{COCH}_{3}\right), 100.23\left(\mathrm{C}-1_{\mathrm{a}}\right), 95.45\left(\mathrm{C}-1_{\mathrm{b}}\right), 75.37,72.67,72.15,72.03$, $69.94,69.85,68.28,69.41,67.95,62.79,61.45,51.28,29.18,28.71,26.32,25.35$ (10
$\left.\mathrm{C}_{\text {Glu }}, 6 \mathrm{CH}_{2}-\mathrm{Hex}\right), 20.88,20.81,20.65,20.60,20.57,20.54,20.53\left(7 \mathrm{COCH}_{3}\right)$; $\mathrm{C}_{32} \mathrm{H}_{47} \mathrm{~N}_{3} \mathrm{O}_{18}$ (761.72).

## 6-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)hex-1-yl O-(2,3,4,6-tetra- $O$-acetyl- $\alpha$-D-glucopyranosyl)-(1 $\rightarrow 4$ )-2,3,6-tri- $O$-acetyl- $\beta$-D-glucopyranoside (23)

A mixture of $22(0.22 \mathrm{~g}, 0.3 \mathrm{mmol})$ and $10(0.15 \mathrm{~g}, 0.35 \mathrm{mmol})$ was clicked and worked up according to the general procedure. The residue was purified by flash chromatography (toluene:acetone, 4:1) to afford $23(0.21 \mathrm{~g}, 62 \%)$ as colorless oil. $R_{\mathrm{f}} 0.34$ (toluene:acetone, $4: 1$ ); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.52$ (s, $1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}$ ), $5.40(\mathrm{~d}, 1 \mathrm{H}$, $J_{1,2} 4.2 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{b}}$ ), 5.37-5.34(m,2H), $5.24(\mathrm{t}, 1 \mathrm{H}, J 9.6,9.0 \mathrm{~Hz}), 5.05(\mathrm{t}, 1 \mathrm{H}, J 10.2,9.6$ $\mathrm{Hz}), 4.84\left(\mathrm{dd}, 1 \mathrm{H}, J_{1,2} 4.2, J_{2,3} 10.8 \mathrm{~Hz}, \mathrm{H}-2 \mathrm{~b}\right), 4.80(\mathrm{dd}, 1 \mathrm{H}, J 7.8,9.0 \mathrm{~Hz}), 4.67(\mathrm{~s}, 2 \mathrm{H}$, $\left.\mathrm{OCH}_{2}\right), 4.49\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 7.8 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{a}}\right), 4.47\left(\mathrm{dd}, 1 \mathrm{H}, J_{\mathrm{gem}} 12.0, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}\right), 4.31$ (t, 2H, J 7.2 Hz), 4.24 (d, 1H, $J_{\text {gem }} 12.6, J_{5,6} 3.6 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}$ ), 4.21 (dd, 1H, $J_{\text {gem }} 12.0, J_{5,6}$ $4.2 \mathrm{~Hz}, \mathrm{H}-\mathbf{6}_{\mathrm{Glu}}$ ), $4.06\left(\mathrm{dd}, 1 \mathrm{H}, J_{\text {gem }} 12.6, J_{5,6} 2.4 \mathrm{~Hz}, \mathrm{H}-6_{\mathrm{Glu}}\right.$ ), $3.99(\mathrm{t}, 1 \mathrm{H}, J 9.6,9.0$ Hz), 3.97-3.94 (2m, 1H), 3.84-3.81 (m, 1H), 3.68-3.65 (m, 1H), 3.47-3.41 (m, 1H), 3.36-3.30 (m, 1H, H-3 Chol ), 2.41-2.39 ( $2 \mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-4_{\text {Chol }}$ ), 2.26-2.22 (m, $1 \mathrm{H}, \mathrm{H}-7_{\text {Chol }}$ ), 2.13, 2.10, 2.04, 2.02, 2.00, 1.99 ( $6 \mathrm{~s}, 21 \mathrm{H}, 7 \mathrm{COCH}_{3}$ ), 2.07-1.84 (m, $6 \mathrm{H}-\mathrm{Chol}$ ), 1.57-1.04 (m, 28H, 20 H -Chol, $4 \mathrm{CH}_{2}-\mathrm{Hex}$ ), 0.98 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19$ ), 0.90 (d, $3 \mathrm{H}, \mathrm{J}_{20,21}$ $\left.6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right), 0.86,0.85\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27\right), 0.67(\mathrm{~s}$, $3 \mathrm{H}, \mathrm{CH}_{3}-18$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 170.59,170.51,170.28,170.01,169.64$, $169.46\left(7 \mathrm{COCH}_{3}\right), 140.68\left(\mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}\right), 121.85\left(\mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-4_{\text {Chol }}\right), 100.30\left(\mathrm{C}-1_{\mathrm{a}}\right)$, $95.52\left(\mathrm{C}-1_{\mathrm{b}}\right), 78.98,75.41,72.72,72.20,72.12,70.01,69.86,69.35,68.48,68.01,62.82$, 61.70, 61.50, 56.77, 56.15, 50.16, 42.33, 39.78, 39.53, 39.04, 37.18, 36.86, 36.20, 35.80, $31.95,31.89,30.21,29.72,29.17,28.32,28.25,28.03,26.20,25.32,24.31,23.83,22.84$, 22.58, 21.08 (39 C), 20.94, 20.90, 20.72, 20.70, 20.64, $20.61\left(7 \mathrm{COCH}_{3}\right), 19.39$ $\left(\mathrm{CH}_{3}-19\right), 18.73\left(\mathrm{CH}_{3}-21\right), 11.88\left(\mathrm{CH}_{3}-18\right) ; \mathrm{C}_{62} \mathrm{H}_{95} \mathrm{~N}_{3} \mathrm{O}_{19}(1186.43)$.

## 6-(4-\{[(3ß)-Cholest-5-en-3-yloxy]methyl\}-1H-1,2,3-triazol-1-yl)hex-1-yl O-( $\alpha$-D-

 glucopyranosyl)-( $1 \rightarrow \mathbf{4}$ )- $\boldsymbol{\beta}$-D-glucopyranoside (24)Compound $23(0.17 \mathrm{~g}, 0.14 \mathrm{mmol})$ was treated with $\mathrm{NaOMe} / \mathrm{MeOH}$ then worked up as described for the synthesis of 16. The residue was purified by flash chromatography (ethyl acetate: $\mathrm{iPrOH}: \mathrm{H}_{2} \mathrm{O}, 6: 2.5: 1$ ) to afford $24(0.1 \mathrm{~g}, 78 \%)$ as amorphous colorless mass. $R_{\mathrm{f}} 0.37$ (ethyl acetate: $\mathrm{iPrOH}: \mathrm{H}_{2} \mathrm{O}, 6: 2.5: 1$ ); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{MeOH}-d_{4}$ ): $\delta 7.96$ (s, 1H, H-5 $5_{\text {Triaz }}$ ), $5.36-5.35\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{H}-6_{\text {Chol }}\right.$ ), $5.14\left(\mathrm{~d}, 1 \mathrm{H}, \mathrm{J}_{1,2} 3.6 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{b}}\right), 4.62(\mathrm{~s}, 2 \mathrm{H}$, $\mathrm{OCH}_{2}$ ), $4.40(\mathrm{t}, 2 \mathrm{H}, J 7.8,6.0 \mathrm{~Hz}), 4.25(2 \mathrm{~d}, 1 \mathrm{H}, J 7.8,13.8 \mathrm{~Hz}), 3.88-3.86(\mathrm{~m}, 2 \mathrm{H})$, $3.82-3.78(\mathrm{~m}, 3 \mathrm{H}), 3.68-3.58(\mathrm{~m}, 4 \mathrm{H}), 3.54-3.50(\mathrm{~m}, 2 \mathrm{H}), 3.43(\mathrm{dd}, 1 \mathrm{H}, J 9.6,3.6 \mathrm{~Hz})$, 3.36-3.33 (m, 1H, H-3 Chol $)$, 3.25 (t, 1H, J 9.6, 9.0 Hz ), 3.21 (dd, 1H, J 9.0, 7.8 Hz ), 2.39-2.37 (m, 1H, H-4 Chol $), 2.20$ (t, 1H, J 12.6, $12.0 \mathrm{~Hz}, \mathrm{H}-7_{\text {Chol }}$ ), 2.05-1.82 (m, 6H), 1.61-1.05 (m, $28 \mathrm{H}, 20 \mathrm{H}-\mathrm{Chol}, 4 \mathrm{CH}_{2}-\mathrm{Hex}$ ), 1.01 (s, $3 \mathrm{H}, \mathrm{CH}_{3}-19$ ), 0.93 (d, 3H, J $\mathrm{J}_{20,21}$ $\left.6.6 \mathrm{~Hz}, \mathrm{CH}_{3}-21\right), 0.88,0.87\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27\right), 0.71(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{CH}_{3}-18\right) ;{ }^{13} \mathrm{C}$ NMR (150 MHz, $\left.\mathrm{MeOH}-d_{4}\right): \delta 141.82\left(\mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Chol }}\right), 122.90$ $\left(\mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-4_{\text {Chol }}\right), 104.33\left(\mathrm{C}-1_{\mathrm{a}}\right), 104.08\left(\mathrm{C}-1_{\mathrm{b}}\right), 81.39,80.23,77.88,76.60,75.10$, $74.81,74.73,74.69,74.19,71.52,70.63,62.77,62.19,58.19,57.60,51.73,43.53,41.18$, $40.72,40.11,38.43,37.98,37.41,37.16,33.27,33.08,31.25,30.52,29.39,29.36,29.19$, 27.21, 26.45, 25.35, 24.98, 23.23, 22.98, 22.21, 19.87, 19.28, 15.48 (41 C), 12.35 $\left(\mathrm{CH}_{3}-18\right) ; \mathrm{C}_{48} \mathrm{H}_{81} \mathrm{~N}_{3} \mathrm{O}_{12}$ (892.17).

## General procedure for propargylation of $\mathbf{2 5}$ and 29.

A solution of the proper lactoside ( 1.0 mmol ) and propargyl bromide ( 5.0 mmol ) in dry $\mathrm{Et}_{2} \mathrm{O} / \mathrm{DMF}(1: 1,10 \mathrm{~mL})$ was stirred in ice bath under dry atmosphere, while $\mathrm{NaH}(60 \%$, 13.0 mmol ) was added portionwise. The mixture was allowed to reach ambient temperature gradually and stirring was continued overnight then treated carefully with $\mathrm{MeOH}(10 \mathrm{~mL})$ and coevaporated with toluene $-\mathrm{H}_{2} \mathrm{O}$ azeotrope in vacuo. The residue was taken in ethyl acetate $(50 \mathrm{~mL})$, washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, evaporated in vacuo and the residue was purified by flash chromatography using toluene as eluent.

## Benzyl $O$-[2,4,6-tri- $O$-benzyl-3- $O$-(prop-2-yn-1-yl)- $\beta$-D-galactopyranosyl]-(1 $\rightarrow$ 4)-

 2,3,6-tri- $O$-benzyl- $\boldsymbol{\beta}$-D-glucopyranoside (26)Yield: (quant.) as syrup; IR (v́, $\left.\mathrm{cm}^{-1}\right): 2286\left(\equiv \mathrm{C}-\mathrm{H}_{s t r}\right), 2113\left(\mathrm{C} \equiv \mathrm{C}_{s t r}\right), 1059\left(\mathrm{C}-\mathrm{O}-\mathrm{C}_{s t r}\right)$; ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.38-7.22(\mathrm{~m}, 35 \mathrm{H}, 7 \mathrm{Ph}), 5.01(\mathrm{~d}, 1 \mathrm{H}, J 10.8 \mathrm{~Hz}$, $\left.\mathrm{CH}_{2} \mathrm{Ph}\right), 4.96\left(\mathrm{~d}, 1 \mathrm{H}, J 11.4, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.95\left(\mathrm{~d}, 1 \mathrm{H}, J 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.91(\mathrm{~d}, 1 \mathrm{H}, J 10.8$, $\left.\mathrm{CH}_{2} \mathrm{Ph}\right), 4.77-4.71(\mathrm{~m}, 4 \mathrm{H}), 7.66\left(\mathrm{~d}, 1 \mathrm{H}, J 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.58(\mathrm{~d}, 1 \mathrm{H}, J 12.6 \mathrm{~Hz}$, $\left.\mathrm{CH}_{2} \mathrm{Ph}\right), 4.57\left(\mathrm{~d}, 1 \mathrm{H}, J 11.4 \mathrm{~Hz}, \mathrm{C}_{2} \mathrm{Ph}\right), 4.48\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 7.8 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}\right), 4.42(\mathrm{~d}, 1 \mathrm{H}$, $J_{1,2} 7.8 \mathrm{~Hz}, \mathrm{H}-1_{\text {Gal }}$ ), $4.41\left(\mathrm{~d}, 1 \mathrm{H}, J 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.34\left(\mathrm{~d}, 1 \mathrm{H}, J 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right)$, 4.29-4.28 (m, 2H), 4.23 (d, 1H, J $12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}$ ), 3.95 (dd, 1H, J 9.6 Hz ), 3.92 (d, 1H, $J_{\text {gem }} 3.0 \mathrm{~Hz}, \equiv \mathrm{C}-\mathrm{CHH}$ ), 3.80 (dd, $\left.1 \mathrm{H}, J_{\text {gem }} 10.8, J_{5,6} 4.2 \mathrm{~Hz}, \mathrm{H}-6\right), 3.72$ (dd, $1 \mathrm{H}, J_{\text {gem }} 10.2$, $\left.J_{5,6}<1 \mathrm{~Hz}, \mathrm{H}-6\right), 3.68\left(\mathrm{dd}, 1 \mathrm{H}, J_{1,2} 7.8, J_{2,3} 9.6 \mathrm{~Hz}, \mathrm{H}-2\right), 3.57-3.45(\mathrm{~m}, 4 \mathrm{H}), 3.39-3.34$ $(\mathrm{m}, 3 \mathrm{H}), 2.45(\mathrm{t}, 1 \mathrm{H}, J 1.8,2.4 \mathrm{~Hz}, \equiv \mathrm{C}-\mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 139.15$, $139.08,138.80,138.64,138.38,138.13,137.60\left(7 \mathrm{C}_{\text {ter }}-\mathrm{Ph}\right)$, 129.79, 129.04, 128.39, $128.33,128.29,128.25,128.17,128.13,128.09,128.00,127.90,127.84,127.82,127.80$, 127.74, 127.71, 127.70, 127.55, 127.48, 127.36, 127.11 ( $35 \mathrm{C}_{\text {sec }}-\mathrm{Ph}$ ), $102.77\left(\mathrm{C}-1_{\mathrm{Glu}}\right.$ ), $102.54\left(\mathrm{C}-1_{\mathrm{Gal}}\right), 83.00,82.00,81.80,80.45,80.02,75.41,75.19,75.17,75.08,74.75$, $74.38,74.19,73.41,73.19,73.02,71.00,68.25,68.10(19 \mathrm{C}), 58.43\left(\equiv \mathrm{C}-\mathrm{CH}_{2}\right) ; \mathrm{C}_{64} \mathrm{H}_{66} \mathrm{O}_{11}$ (1011.3).

## Benzyl $O$-[2,3,6-tri- $O$-benzyl-4-O-(prop-2-yn-1-yl)- $\beta$-D-galactopyranosyl]-(1 $\rightarrow$ 4)-

 2,3,6-tri- $\boldsymbol{O}$-benzyl- $\boldsymbol{\beta}$-D-glucopyranoside (30)Yield: (quant.) as syrup; $R_{\mathrm{f}} 0.11$ (toluene); IR (v́, $\left.\mathrm{cm}^{-1}\right)$ : $2292\left(\equiv \mathrm{C}-\mathrm{H}_{\text {str }}\right), 2114\left(\mathrm{C} \equiv \mathrm{C}_{\text {str }}\right)$, $1059\left(\mathrm{C}-\mathrm{O}-\mathrm{C}_{s t r}\right) ;{ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.38-7.22(\mathrm{~m}, 35 \mathrm{H}, 7 \mathrm{Ph}), 5.00(\mathrm{~d}, 1 \mathrm{H}$, $\left.J 10.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.95\left(\mathrm{~d}, 1 \mathrm{H}, J 12.6, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.91\left(\mathrm{~d}, 1 \mathrm{H}, J 10.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right)$, 4.98-4.74 (m, 5H), 4.68 (d, 1H, J $\left.12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.66\left(\mathrm{~d}, 1 \mathrm{H}, J 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.56$ (dd, 1H, $\left.J_{\text {gem }} 12.0, J_{5,6} 1.8 \mathrm{~Hz}, \mathrm{H}-6\right), 4.50-4.36(\mathrm{~m}, 7 \mathrm{H}), 4.04(\mathrm{~s}, 1 \mathrm{H}, \equiv \mathrm{C}-\mathrm{CHH}), 3.96$ (dd, 1H, J 9.0, 7.8 Hz ), $3.81(\mathrm{~d}, 1 \mathrm{H}, J 10.2 \mathrm{~Hz}), 3.74(\mathrm{~d}, 1 \mathrm{H}, J 10.8 \mathrm{~Hz}), 3.68(\mathrm{dd}, 1 \mathrm{H}, J$ $9.0,7.8 \mathrm{~Hz}), 3.63(\mathrm{dd}, 1 \mathrm{H}, J 8.4,7.8 \mathrm{~Hz}), 3.56(\mathrm{dd}, 1 \mathrm{H}, J 9.0 \mathrm{~Hz}), 3.47(\mathrm{~m}, 1 \mathrm{H})$, $3.43-3.36(\mathrm{~m}, 4 \mathrm{H}), 2.39(\mathrm{~d}, 1 \mathrm{H}, J 1.8,2.4 \mathrm{~Hz}, \equiv \mathrm{C}-\mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) : $\delta$ $139.10,138.79,138.68,138.41,138.27,137.60,134.50\left(7 \mathrm{C}_{t e r}-\mathrm{Ph}\right)$, 129.79, 129.04,
128.48, 128.42, 128.39, 128.30, 128.27, 128.11, 128.08, 127.91, 127.83, 127.80, 127.71, 127.668, 127.64, 127.58, 126.56, 127.48, 127.27 ( $35 \mathrm{C}_{\text {sec }}-\mathrm{Ph}$ ), 102.61 ( $\mathrm{C}-1_{\mathrm{Glu}}$ ), 102.55 ( $\mathrm{C}-1_{\text {Gal }}$ ), $83.00,82.40,81.90,80.52,80.08,76.52,75.45,75.31,75.22,75.07,74.46$, $73.48,73.14,73.01,72.90,72.33,71.00,68.35$ (19C), $59.49\left(\equiv \mathrm{C}-\mathrm{CH}_{2}\right) ; \mathrm{C}_{64} \mathrm{H}_{66} \mathrm{O}_{11}$ (1011.3).

## Benzyl $O$-[2,6-di- $O$-benzyl-3- $O$-(prop-2-yn-1-yl)- $\beta$-D-galactopyranosyl]-(1 $\rightarrow \mathbf{4}$ )-2,3,6-

 tri- $O$-benzyl- $\beta$-D-glucopyranoside (34)A mixture of diol $33(0.6 \mathrm{~g}, 0.7 \mathrm{mmol})$ and $\mathrm{Bu}_{2} \mathrm{SnO}(0.2 \mathrm{~g}, 0.8 \mathrm{mmol})$ in dry $\mathrm{MeOH}(10$ mL ) was gently refluxed then evaporated in vacuo. The residue was refluxed, in toluene $(10 \mathrm{~mL})$, with TBAI ( $0.27 \mathrm{~g}, 0.7 \mathrm{mmol}$ ) and propargyl bromide ( $80 \% \mathrm{w} / \mathrm{w}$ in toluene, 1.7 mmol ). The mixture was evaporated in vacuo after 2 h and the residue was purified by flash chromatography using solvent gradient of petroleum ether, toluene then (toluene:acetone, $5: 1$ ) to afford $34(0.57 \mathrm{~g}, 92 \%)$ as syrup; $R_{\mathrm{f}} 0.29$ (toluene:acetone, $5: 1$ ); $\mathrm{C}_{57} \mathrm{H}_{60} \mathrm{O}_{11}$ (921.17).

## Benzyl $O$-(2,4,6-tri- $O$-benzyl-3- $O$-( $(\{1-[(3 \beta)$-cholest-5-en-3-yl]-1H-1,2,3-triazol-4-

 yl\}methyl)- $\beta$-D-galactopyranosyl)-(1 $\rightarrow \mathbf{4}$ )-2,3,6-tri- $O$-benzyl- $\beta$-D-glucopyranosideA mixture of $\mathbf{3}(0.2 \mathrm{~g}, 0.5 \mathrm{mmol})$ and $26(0.42 \mathrm{~g}, 0.41 \mathrm{mmol})$ was clicked and worked up according to the general procedure. The residue was purified by flash chromatography (toluene:ethyl acetate, 5:1) to afford $27(0.53 \mathrm{~g}, 89 \%)$ as syrup. $R_{\mathrm{f}} 0.27$ (toluene:ethyl acetate, $5: 1$ ); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.71\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}\right.$ ), $7.42-7.11$ (m, 35, 7 Ph), 5.28 ( $\mathrm{m}, 1 \mathrm{H}, \mathrm{H}-6_{\text {Chol }}$ ), 5.00 (d, $1 \mathrm{H}, J_{\text {gem }} 10.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}$ ), 4.94 (d, $1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}$, $\left.\mathrm{CH}_{2} \mathrm{Ph}\right), 4.91\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.90\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 10.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right)$, 4.86-4.84 (m, 3H, OCHH, CH2 $\underline{H}_{2} \mathrm{Ph}$ ), 4.79 (d, $\left.1 \mathrm{H}, J_{\text {gem }} 11.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.74\left(\mathrm{~d}, 1 \mathrm{H}, J_{\mathrm{gem}}\right.$ $\left.10.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.72\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 11.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.70\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 10.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right)$, $4.65\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.54\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.51\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }}\right.$ $\left.11.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.47\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 7.8 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Glu}}\right), 4.43\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 8.4 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{Gal}}\right), 4.41$ $\left(\mathrm{d}, 1 \mathrm{H}, J_{\text {gem }} 12.6 \mathrm{~Hz}, \mathrm{C}_{2} \mathrm{Ph}\right), 4.31\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, \underline{C H}_{2} \mathrm{Ph}\right), 4.20\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 11.4\right.$
$\left.\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 3.93(\mathrm{t}, 1 \mathrm{H}, J 9,9.6 \mathrm{~Hz}), 3.86\left(\mathrm{~d}, 1 \mathrm{H}, J 2.4 \mathrm{~Hz}, \mathrm{H}-4_{\mathrm{Gal}}\right), 3.77(\mathrm{dd}, 1 \mathrm{H}, J \mathrm{gem}$ $11.4, J 5,64.8 \mathrm{~Hz}, \mathrm{H}-6_{\text {Sug. }}$.), 3.72-3.69 (m, 2H), 3.54-3.45 (m, 4H), 3.38-3.31 (m, 3H), 2.89 (d, 1H, J 15.6 Hz ), 2.37-2.35 (m, 2H), 2.18 (d, 1H, J 13.8 Hz ), 2.13-2.05 (m, 1H), $1.92-1.87(\mathrm{~m}, 2 \mathrm{H}), 1.79-1.74(\mathrm{~m}, 2 \mathrm{H}), 1.62(\mathrm{~d}, 1 \mathrm{H}, J 13.8 \mathrm{~Hz}), 1.56-1.52(\mathrm{~m}, 1 \mathrm{H})$, $1.44-1.33(\mathrm{~m}, 8 \mathrm{H}), 1.23-1.12(\mathrm{~m}, 4 \mathrm{H}), 1.05\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-19\right), 1.02-0.94(\mathrm{~m}, 5 \mathrm{H}), 0.89$, 0.88 (2d, s, 9H, $J_{25,26}=J_{25,27}=2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27, \mathrm{CH}_{3}-21$ ), $0.63\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18\right)$; ${ }^{13}{ }^{1}$ NMR (150 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 139.16,138.99,138.85,138.65,138.41,138.18,138.02$, 137.61, 129.07, 128.43, 128.39, 128.36, 128.33, 128.29, 128.27, 128.26, 128.19, 128.14, 128.09, 128.00, 127.94, 127.91, 127.78, 127.77, 127.70, 127.65, 127.62, 127.55, 127.52, 127.47, 127.46, 127.15, 127.10, 125.33, 124.22, 121.92, ( $42 \mathrm{C}-\mathrm{Ph}, \mathrm{C}-5_{\mathrm{Chol}}, \mathrm{C}-6_{\mathrm{Chol}}$, $\left.\mathrm{C}-4_{\text {Triaz }}, \mathrm{C}-5_{\text {Triaz }}\right), 102.71\left(\mathrm{C}-1_{\text {Glu }}\right), 102.50\left(\mathrm{C}-1_{\text {Gal }}\right), 83.02,82.72,81.81,79.82,75.38$, $75.18,75.09,75.08,74.79,73.70,73.33,73.14,72.97,70.96,68.28,68.08,64.84,56.59$, $56.31,55.95,50.02,42.16,39.55,39.41,37.04,36.20,35.77,35.36,32.75,31.82,31.55$, 28.15, 28.06, 27.11, 24.13, 23.89, 22.87, 22.61, 20.59, 19.23, 18.70 (42 C), 11.81 ( $\left.\mathrm{CH}_{3}-18\right) ; \mathrm{C}_{91} \mathrm{H}_{111} \mathrm{~N}_{3} \mathrm{O}_{11}$ (1423.05).

## Benzyl $O$-(2,3,6-tri- $O$-benzyl-4-O-(\{1-[(3 $\beta$ )-cholest-5-en-3-yl]-1H-1,2,3-triazol-4-

 yl\}methyl)- $\beta$-D-galactopyranosyl)-( $1 \rightarrow 4$ )-2,3,6-tri- $O$-benzyl- $\beta$-D-glucopyranoside (31)A mixture of $\mathbf{3}(0.2 \mathrm{~g}, 0.5 \mathrm{mmol})$ and $\mathbf{3 0}(0.5 \mathrm{~g}, 0.5 \mathrm{mmol})$ was clicked and worked up according to the general procedure. The residue was purified by flash chromatography (toluene:ethyl acetate, 9:1) to afford $31(0.51 \mathrm{~g}, 74 \%)$ as syrup. $R_{\mathrm{f}} 0.17$ (toluene:ethyl acetate, 9:1); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.75\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}\right.$ ), $7.38-7.24(\mathrm{~m}, 35 \mathrm{H}, 7$ Ph), 5.34 (br.t, $1 \mathrm{H}, J 2.4,4.8 \mathrm{~Hz}, \mathrm{H}-5_{\mathrm{Chol}}$ ), 5.30 (s, 1H), 5.01 (d, $1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, 0.5$ $\left.\mathrm{CH}_{2} \mathrm{Ph}\right), 4.96\left(\mathrm{~d}, 1 \mathrm{H}, J_{\mathrm{gem}} 10.2 \mathrm{~Hz}, 0.5 \mathrm{CH}_{2} \mathrm{Ph}\right), 4.95\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, 0.5 \mathrm{CH}_{2} \mathrm{Ph}\right)$, $4.90\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 11.4 \mathrm{~Hz}, 0.5 \mathrm{CH}_{2} \mathrm{Ph}\right), 4.86\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, 0.5 \mathrm{CH}_{2} \mathrm{Ph}\right.$ ), $4.80(\mathrm{~d}$, $1 \mathrm{H}, J_{\text {gem }} 10.8 \mathrm{~Hz}, 0.5 \mathrm{C}_{2} \mathrm{Ph}$ ), 4.76 (d, 1H, $J_{\text {gem }} 10.2 \mathrm{~Hz}, 0.5 \mathrm{C}_{2} \mathrm{Ph}$ ), $4.73-4.68$ (m, 10H, $\left.\mathrm{OCH}_{2}, 2.5 \mathrm{CH}_{2} \mathrm{Ph}\right), 4.65\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 11.4 \mathrm{~Hz}, 0.5 \mathrm{CH}_{2} \mathrm{Ph}\right), 4.50\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 7.8 \mathrm{~Hz}\right.$, $\left.\mathrm{H}-1_{\mathrm{a}}\right), 4.45\left(\mathrm{~d}, 1 \mathrm{H}, J_{1,2} 7.8 \mathrm{~Hz}, \mathrm{H}-1_{\mathrm{b}}\right), 4.40\left(\mathrm{~d}, 1 \mathrm{H}, J_{\mathrm{gem}} 12.0 \mathrm{~Hz}, 0.5 \mathrm{CH}_{2} \mathrm{Ph}\right), 4.36(\mathrm{~s}$, $1 \mathrm{H}), 4.02\left(\mathrm{dd}, 1 \mathrm{H}, J_{3,4} 3.0, J_{4,5}<1.0 \mathrm{~Hz}, \mathrm{H}-4_{\mathrm{b}}\right), 3.96\left(\mathrm{dd}, 1 \mathrm{H}, J 9.6,9.0 \mathrm{~Hz}, \mathrm{H}_{\text {Sug. }}\right.$ ), 3.79
(dd, $1 \mathrm{H}, J_{\text {gem }} 10.8, J_{5,6} 4.2 \mathrm{~Hz}, \mathrm{H}-6_{\text {Sug. }}$. $), 3.74$ (dd, $1 \mathrm{H}, J_{\text {gem }} 10.8, J_{5,6} 1.2 \mathrm{~Hz}, \mathrm{H}-6_{\text {Sug }}$.), 3.70 (dd, $1 \mathrm{H}, J_{1,2} 7.8, J_{2,3} 9.6 \mathrm{~Hz}, \mathrm{H}-2_{\text {Sug. }}$.), 3.58-3.54 (m, 2H), 3.48-3.46 (m, 1H), 3.42-3.35 (m, 4H), 2.80 (br.d, 1H, J 14.4 Hz ), 2.29 (d, 1H, J 15.6 Hz ), 2.02-1.89 (m, 5H), $1.72-1.69(\mathrm{~m}, 2 \mathrm{H}), 1.56-1.39(\mathrm{~m}, 4 \mathrm{H}), 1.37-1.25(\mathrm{~m}, 7 \mathrm{H}), 1.20-1.06(\mathrm{~m}, 3 \mathrm{H}), 1.05-0.93$ (m, 4H), 0.87, $0.86\left(2 \mathrm{~d}, 6 \mathrm{H}, J_{25,26}=J_{25,27} 2.4 \mathrm{~Hz}, \mathrm{CH}_{3}-26, \mathrm{CH}_{3}-27\right.$ ), (d, $3 \mathrm{H}, J_{20,21} 6.6 \mathrm{~Hz}$, $\mathrm{CH}_{3}-21$ ), 0.63 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{CH}_{3}-18$ ); ${ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 144.86, 140.92, 138.85, 138.71, 138.43, 138.38, 138.19, 138.06, 137.60, 136.43, 134.50, 133.43, 130.14, 129.79, 129.03, 128.59, 128.44, 128.42, 128.41, 128.39, 128.38, 128.31, 128.29, 128.27, 128.08, 128.06, 127.87, 127.86, 127.79, 127.70, 127.68, 127.66, 127.61, 127.56, 127.52, 127.48, 127.33, 127.02, 124.10, 122.39 (42 C-Ar, C-4 Triaz $, \mathrm{C}-5_{\text {Chol }}, \mathrm{C}-5_{\text {Triaz }}, \mathrm{C}-6_{\text {Chol }}$ ), 102.65 $\left(\mathrm{C}-1_{\mathrm{a}}\right), 102.60\left(\mathrm{C}-1_{\mathrm{b}}\right), 82.97,82.26,81.86,80.33,76.45,75.57,75.54,75.27,75.01$, $73.61,73.49,73.12,72.99,72.46,71.04,68.36,68.21,66.71,65.39,56.45,56.41,56.16$, 49.94, 42.21, 39.50, 36.98, 36.16, 35.80, 35.32, 32.67, 31.93, 31.61, 28.17, 28.05, 26.97, 24.18, 24.05, 22.86, 22.60, 20.57, 19.21, 18.69 (42 C ), $11.80\left(\mathrm{CH}_{3}-18\right) ; \mathrm{C}_{91} \mathrm{H}_{111} \mathrm{~N}_{3} \mathrm{O}_{11}$ (1423.05).

## Benzyl $O$-(2,6-di- $O$-benzyl-3- $O$-(\{1-[6-chloro-2-methylquinolin-4-yl]-1H-1,2,3-triazol-4-yl $\}$ methyl)- $\beta$-D-galactopyranosyl)-(1 $\rightarrow 4$ )-2,3,6-tri- $O$-benzyl- $\beta$-Dglucopyranoside (36)

A mixture of $\mathbf{3 4}(0.1 \mathrm{~g}, 0.45 \mathrm{mmol})$ and $35(0.3 \mathrm{~g}, 0.32 \mathrm{mmol})$ was clicked and worked up according to the general procedure. The residue was purified by flash chromatography (toluene:ethyl acetate, $4: 10$ ) to afford $36(0.28 \mathrm{~g}, 76 \%)$ as syrup. $R_{\mathrm{f}} 0.2$ (toluene:ethyl acetate, 4:1); ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{DMSO}-d_{6}$ ): $\delta 8.08(\mathrm{~d}, 1 \mathrm{H}, J 9.0 \mathrm{~Hz}, \mathrm{Ar}), 7.85(\mathrm{t}, 1 \mathrm{H}, J$ 3.6, 2.4 Hz, Ar), 7.80 (s, 1H, H-5 Triaz ), 7.72 (dd, 1H, J 2.4, 9.0 Hz, Ar), 7.39-7.36 9 (m, $4 \mathrm{H}, \mathrm{Ar}), 7.33-7.22(24 \mathrm{H}, \mathrm{Ar}), 7.15-7.13(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}), 7.08(\mathrm{t}, 1 \mathrm{H}, J 7.2,7.8 \mathrm{~Hz})$, $5.02-4.90(\mathrm{~m}, 5 \mathrm{H}), 4.79,4.71$ ( $2 \mathrm{~d}, 2 \mathrm{H}, J_{\text {gem }} 11.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}$ ), 4.77, 4.72 (2d, 2H, $J_{\text {gem }}$ $\left.10.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.65,4.59\left(2 \mathrm{~d}, 2 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.51-4.47(\mathrm{~m}, 3 \mathrm{H})$, 4.45-4.40 (m, 3H), $4.15(\mathrm{~d}, 1 \mathrm{H}, J 3.0 \mathrm{~Hz}), 4.02(\mathrm{t}, 1 \mathrm{H}, J 9.6 \mathrm{~Hz}), 3.83\left(\mathrm{dd}, 1 \mathrm{H}, J_{5,6} 4.8\right.$, $\left.J_{\text {gem }} 11.4 \mathrm{~Hz}, \mathrm{H}-6\right), 3.75\left(\mathrm{dd}, 1 \mathrm{H}, J_{5,6} 1.8, J_{\text {gem }} 10.8 \mathrm{~Hz}, \mathrm{H}-6\right), 3.68$ (dd, 1H, J 7.2, 9.6 $\mathrm{Hz}), 3.63(\mathrm{dd}, 1 \mathrm{H}, J 7.8,9.6 \mathrm{~Hz}), 3.58(\mathrm{t}, 1 \mathrm{H}, J 9.0 \mathrm{~Hz}), 3.53-3.46(\mathrm{~m}, 3 \mathrm{H}), 3.39-3.38$
(m, 2H), $2.79\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{MeOH}_{d 4}$ ): $\delta 159.54,147.80,146.15$, $140.09,139.11,138.59,138.55,138.31,138.01,137.52,133.65,131.72,130.86,129.06$, $128.43,128.40,128.35,128.29,128.19,128.12,128.11,128.00,127.91,127.74,127.71$, $127.69,127.64,127.58,127.54,127.47,127.29$, 124.25 , $121.76,121.23$, 117.69 (47 C-Ar $), 102.57\left(\mathrm{C}-1_{\text {Glu }}\right), 102.52\left(\mathrm{C}-1_{\text {Gal }}\right), 82.92,81.85,81.72,79.49,76.57,75.34,75.25$, $75.18,75.02,73.56,73.25,72.68,71.01,68.57,68.32,66.31,63.47(17 \mathrm{C}), 25.34\left(\mathrm{CH}_{3}\right)$; $\mathrm{C}_{67} \mathrm{H}_{67} \mathrm{ClN}_{4} \mathrm{O}_{11}(1139.83)$.

## Benzyl $O$-(4-O-acetyl-2,6-di- $O$-benzyl-3- $O$-(\{1-[11-acetoxyundec-1-yl]-1H-1,2,3-triazol-4-yl $\}$ methyl)- $\beta$-D-galactopyranosyl)-(1 $\rightarrow 4$ )-2,3,6-tri- $O$-benzyl- $\beta$-Dglucopyranoside (39)

A mixture of $\mathbf{3 4}(0.16 \mathrm{~g}, 0.75 \mathrm{mmol})$ and $\mathbf{9 b}(0.5 \mathrm{~g}, 0.54 \mathrm{mmol})$ was clicked and worked up according to the general procedure. The residue was purified by flash chromatography (toluene:acetone, 3:1) to afford $38(0.44 \mathrm{~g}, 71 \%)$ as syrup; $R_{\mathrm{f}} 0.41$ (toluene:acetone, 5:3). Compound $38(15.0 \mathrm{mg}, 13.0 \mu \mathrm{~mol})$ was stirred with $\mathrm{Ac}_{2} \mathrm{O} /$ pyridine $(2: 1,1 \mathrm{~mL})$ at ambient temperature overnight then coevaporated with toluene $-\mathrm{H}_{2} \mathrm{O}$ azeotrope in vacuo. The residue was purified by flash chromatography (toluene:acetone, 7:1) to afford 39 $(14.0 \mathrm{mg}, 90 \%)$ as colorless mass. $R_{\mathrm{f}} 0.71$ (toluene:acetone, $5: 2$ ); ${ }^{1} \mathrm{H}$ NMR ( 600 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.42-7.16\left(\mathrm{~m}, 31 \mathrm{H}, 6 \mathrm{Ph}, \mathrm{H}-5_{\text {Triaz }}\right), 5.46\left(\mathrm{~d}, 1 \mathrm{H}, J_{3,4}=J_{4,5}<1.0 \mathrm{~Hz}, \mathrm{H}-4 \mathrm{~b}\right)$, 4.95 (d, 1H, J $\left.10.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.94\left(\mathrm{~d}, 1 \mathrm{H}, J 12.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.89\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 10.8\right.$ $\left.\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.80\left(\mathrm{~d}, 1 \mathrm{H}, J 12.6 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.74-4.68(\mathrm{~m}, 6 \mathrm{H}), 4.65\left(\mathrm{~d}, 1 \mathrm{H}, J_{\mathrm{gem}} 12.0\right.$ $\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{Ph}$ ), $4.57\left(\mathrm{~d}, 1 \mathrm{H}, J_{\text {gem }} 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}\right), 4.49-4.44(\mathrm{~m}, 3 \mathrm{H}), 4.39\left(\mathrm{~d}, 1 \mathrm{H}, J_{\mathrm{gem}}\right.$ $12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}$ ), 4.23 (d, $1 \mathrm{H}, J 12.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{Ph}$ ), 4.21 (dd, $1 \mathrm{H}, J 7.2 \mathrm{~Hz}$ ), 4.16 (dd, 1H, $J 7.2 \mathrm{~Hz}$ ), 4.05 (m, 2H, J 6.6, 7.2 Hz), 3.97 (t, 1H, J 9.6, 9.0 Hz ), 3.79 (dd, 1H, $J_{\text {gem }} 10.8$, $J 5,64.2 \mathrm{~Hz}, \mathrm{H}-6), 3.72\left(\mathrm{dd}, 1 \mathrm{H}, J_{\mathrm{gem}} 10.8, J_{5,6} 1.8 \mathrm{~Hz}, \mathrm{H}-6\right), 3.54(\mathrm{t}, 1 \mathrm{H}, J 9.0 \mathrm{~Hz}$ ), 3.49-3.42 (m, 4H), 3.36-3.34 (m, 1H), 3.31-3.30 (m, 1H), 2.04, $2.03\left(2 \mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{COCH}_{3}\right)$, 1.78 (t, 2H, J 6.6, $7.2 \mathrm{~Hz}, \mathrm{CH}_{2}$ ), 1.61 (t, 2H, J 7.2, $7.8 \mathrm{~Hz}, \mathrm{CH}_{2}$ ), 1.32-1.17 (m, 14H, 7 $\left.\mathrm{CH}_{2}\right) ;{ }^{13} \mathrm{C}$ NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 171.29,170.26,\left(2 \mathrm{COCH}_{3}\right), 145.14\left(\mathrm{C}-4_{\text {Triaz }}\right)$, $139.05,138.63,138.56,138.21,137.86,137.50,128.39,128.38,128.34,128.28,128.26$, 128.09, 127.98, 127.92, 127.88, 127.71, 127.70, 127.68, 127.61, 127.57, 127.49, 127.31,
122.68 (36 C-Ar, $\mathrm{C}-5_{\text {Triaz }}$ ), $102.49\left(\mathrm{C}-1_{\mathrm{a}}\right), 102.32\left(\mathrm{C}-1_{\mathrm{b}}\right), 82.83,81.75,79.54,79.37$, $76.46,75.26,75.14,75.06,75.03,73.39,73.20,71.54,70.98,68.15,67.08,66.87,64.64$, 63.92, 50.24 ( 10 C -sugar, $6 \mathrm{CH}_{2} \mathrm{Ph}, 3 \mathrm{CH}_{2}$ ), 30.26, 29.45, 29.44, 29.37, 29.22, 28.99, 28.58, 26.41, 25.89, 21.04, $20.92\left(2 \mathrm{COCH}_{3}, 9 \mathrm{CH}_{2}\right), \mathrm{C}_{72} \mathrm{H}_{87} \mathrm{~N}_{3} \mathrm{O}_{14}$ (1218.62).

## Benzyl O-(3-O-(\{1-[11-hydroxyundec-1-yl]-1H-1,2,3-triazol-4-yl\}methyl)- $\beta$-D-galactopyranosyl)-(1 $\rightarrow 4$ )- $\boldsymbol{\beta}$-D-glucopyranoside (40)

Compound 38 ( $0.34 \mathrm{~g}, 0.3 \mathrm{mmol}$ ) was stirred with $\mathrm{Pd} / \mathrm{C}-10 \% ~(50.0 \mathrm{mg})$ in deaereated $\mathrm{MeOH} / \mathrm{AcOH}(5: 1,6 \mathrm{~mL})$ under $\mathrm{H}_{2}$ overnight. The mixture was filtered through celite, washed with MeOH , evaporated in vacuo and the residue was purified by flash chromatography (ethyl acetate: $\mathrm{iPrOH}: \mathrm{H}_{2} \mathrm{O}, 5: 1.5: 0.5$ ) to afford $40(0.11 \mathrm{~g}, 62 \%)$ as colorless amorphous mass. $R_{\mathrm{f}} 0.28$ (ethyl acetate: $\mathrm{iPrOH}: \mathrm{H}_{2} \mathrm{O}, 5: 1.5: 0.5$ ); ${ }^{1} \mathrm{H}$ NMR ( 600 $\left.\mathrm{MHz}, \mathrm{MeOH}-d_{4}\right): \delta 8.05$ (s, $1 \mathrm{H}, \mathrm{H}-5_{\text {Triaz }}$ ), 5.11 (d, $0.55 \mathrm{H}, J_{1,2} 3.6 \mathrm{~Hz}, \mathrm{H}-1_{\alpha}$ ), 4.84 (dd, $1 \mathrm{H}, J_{\text {gem }} 12.6, J 5,6^{\circ}<1 \mathrm{~Hz}, \mathrm{H}-6$ ), 4.76 (dd, $1 \mathrm{H}, J_{\text {gem }} 12.6, J 5,6^{`} 2.4 \mathrm{~Hz}, \mathrm{H}-6$ ), 4.50 $\left(\mathrm{d}, 0.45 \mathrm{H}, J_{1,2} 7.8 \mathrm{~Hz}, 1-\mathrm{H}_{\beta}\right), 4.41\left(\mathrm{t}, 2 \mathrm{H}, J 7.8,8.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{OH}\right), 4.06(\mathrm{~m}, 1 \mathrm{H})$, 3.89-3.86 (m, 2H), 3.82-3.78 (m, 3H), 3.74-3.70 (m, 2H), 3.69-3.65 (m, 1H), 3.59-3.58 (m, 1H), 3.56 (dd, 1H, J 7.8, < 1.0 Hz ), 3.52 (t, 2H, J $6.6 \mathrm{~Hz}, \mathrm{~N}-\mathrm{CH}_{2}$ ), 3.45-3.43 (m, $2 \mathrm{H}), 1.90\left(\mathrm{q}, 2 \mathrm{H}, J 7.2 \mathrm{~Hz},-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{~N}\right), 1.50\left(\mathrm{q}, 2 \mathrm{H},-\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}\right), 1.32-1.29(\mathrm{~m}, 14 \mathrm{H}$, $\left.7 \mathrm{CH}_{2}\right) ;{ }^{13} \mathrm{C}$ NMR ( $\left.150 \mathrm{MHz}, \mathrm{MeOH}-d_{4}\right): \delta 145.96\left(\mathrm{C}-5_{\text {Triaz }}\right), 125.25\left(\mathrm{C}-4_{\text {Triaz }}\right), 105.01$ $\left(\mathrm{C}-1_{\mathrm{b}}\right), 98.08\left(\mathrm{C}-1_{\mathrm{a} \beta}\right), 93.67\left(\mathrm{C}-1_{\mathrm{a} \mathrm{\alpha}}\right), 82.81,81.20,76.90,76.54,76.47,75.95,73.55$, $73.27,71.75,66.99,66.95,63.72,63.04,62.62,62.59,62.14,62.05,51.69,33.68,31.27$, $30.73,30.62,30.61,30.57,30.37,30.12,27.48,26.97$ (22 C). $\mathrm{C}_{26} \mathrm{H}_{47} \mathrm{~N}_{3} \mathrm{O}_{12}$ (593.76).

## NMR spectral data

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Fig. S1. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 2.


Fig. S2. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 2 .


Fig. S3. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 3 .


Fig. S4. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 3 .


Fig. S5. ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{6 a}$.


Fig. S6. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{6 a}$.


Fig. S7. ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{6 b}$.

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Fig. S8. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{6 b}$.


Fig. S9. ${ }^{1}$ H NMR spectrum of compound $\mathbf{6 c}$.


Fig. S10. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{6 c}$.


Fig. S11. ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{7 a}$.


Fig. S12. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $7 \mathbf{7}$.


Fig. S13. ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{7 b}$.


Fig. S14. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{7 b}$.


Fig. S15. COSY spectrum of compound 7b.


Fig. S16. DEPT $-135^{\circ}$ spectrum of compound $\mathbf{7 b}$.


Fig. S17. ${ }^{1}$ H NMR spectrum of compound 11a.


Fig. S18. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 11a.


Fig. S19. ${ }^{1} \mathrm{H}$ NMR spectrum of compound $\mathbf{1 1 b}$.










Figs. S21. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 13.


Figs. S22. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 15.







Figs. S24. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 16.


Figs. S25. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 16.


Figs. S26. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 17.


Figs. S27. ${ }^{1}$ H NMR spectrum of compound 18.


Figs. S28. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 19.



Figs. S29. ${ }^{1}$ H NMR spectrum of compound 20.


Fig. S30. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{2 0}$.


Figs. S31. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 22.


Fig. S32. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 22 .


Figs. S33. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 23.


Fig. S34. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 23.


Figs. S35. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 24.


Fig. S36. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 24.

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Figs. S37. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 26.


Fig. S38. ${ }^{13} \mathrm{C}$ NMR spectrum of compound 26.


Figs. S39. ${ }^{1}$ H NMR spectrum of compound 27.


Figs. S40. ${ }^{13} \mathrm{C}$ NMR spectrum of 27.


Fig. S41. ${ }^{1}$ H NMR spectrum of compound $\mathbf{3 0}$.


Fig. S42. ${ }^{13} \mathrm{C}$ NMR spectrum of compound $\mathbf{3 0}$.



Figs. S45. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 36 .



Figs. S49. ${ }^{1} \mathrm{H}$ NMR spectrum of compound 40 .

## Biology

## Antimicrobial screening

The antimicrobial activity of target cholesterol derivatives was determined using a modified Kirby-Bauer disc diffusion method in the Microanalytical Unit, Faculty of Science at Cairo University. Ampicillin and amphotericin B were used as bacterial and fungal positive controls, respectively, while DMSO was used as solvent and negative control as well. Four microbial species were considered, E. coli ( $\mathrm{G}^{-}$bacteria), S. aureus ( $\mathrm{G}^{+}$bacteria), A. flavus (filamentous fungi) and C. albicans (yeast).

Briefly, $100 \mu \mathrm{~L}$ of the test organism were grown in 10 mL of fresh media until they reached a count of 108 cells $/ \mathrm{mL}$ for bacteria and 105 cells $/ \mathrm{mL}$ for fungi. $100 \mu \mathrm{~L}$ of the microbial suspension was spread onto Müller-Hinton agar plates. Paper discs (Schleicher \& Schüll, Spain) with a diameter of 8.0 mm were impregnated $10 \mu \mathrm{~L}$ of the test compound $(4.0 \mathrm{mM})$ and controls were treated similarly. Plates were incubated for 48 h at $35-37^{\circ} \mathrm{C}$ for bacterial strains, $25{ }^{\circ} \mathrm{C}$ for A. flavus and $30^{\circ} \mathrm{C}$ for C. albicans. Inhibition zone diameters were measured with slipping calipers. Measurements were taken in triplicates.

## Cytotoxicity screening

In vitro anticancer-drug discovery screening of newly synthesized triazoles was performed using the colorimetric cytotoxicity assay for anticancer-drug screening using prostate cancer cell line PC3 at the National Cancer Institute, Cairo University. Cells were plated in 96 -multiwell plates ( $10^{4}$ cells per well) for 24 h to allow attachment of cells to the walls. Monolayer cells were incubated with test compounds individually at concentrations of $5.0,10.0,20.0,30.0,40.0$ and $50.0 \mu \mathrm{M}$ at $37{ }^{\circ} \mathrm{C}$ under $5 \% \mathrm{CO}_{2}$ atmosphere. After 48 h , cells were fixed, washed then stained with sulforhodamine-B stain. Excess stain was washed with acetic acid and attached stain was recovered with tris-EDTA buffer. Color intensity was measured in an ELISA reader. The relation between surviving fraction and drug concentration was plotted to get the survival curve for each compound and measurements were taken in triplicates.

## Statistical analysis

All results were subjected to one-way ANOVA and the means were compared according to the Student-Newman-Keuls (SNK) multiple range test ( $p \leq 0.05$ ).


Fig. S51. Kill curve of compd. 6c against PC3 cell line.


Fig. S53. Kill curve of compd. 12 against PC3 cell line.


Fig. S55. Kill curve of compd. 16 against PC3 cell line.


Fig. S52. Kill curve of compd. 11a against PC3 cell line.


Fig. S54. Kill curve of compd. 13 against PC3 cell line.


Fig. S56. Kill curve of compd. 17 against PC3 cell line.


Fig. S57. Kill curve of compd. 24 against PC3 cell line.


Fig. S58. Kill curve of compd. 27 against PC3 cell line.


Fig. S59. Kill curve of compd. 40 against PC3 cell line.

