# Supporting Information

**for**

**Revisiting the bromination of 3**-hydroxycholest-5-ene with CBr4/PPh3 and the subsequent azidolysis of the resulting bromide, disparity in stereochemical behavior**

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1. **X-ray crystallography**

Due to the known stereochemistry of the cholesterol skeleton no need for *ab initio* absolute structure determination (viz. based on Flack parameter) is not needed. Single-crystal X-ray data for diene **2** was measured using a Bruker-Nonius Kappa CCD diffractometer with an APEX-II detector with graphite-monochromatized Mo-*K*α (λ = 0.71073 Å) radiation at 170 K. Data collection and reduction were performed using the program COLLECT [1]and *HKL DENZO AND SCALEPACK*[2], respectively, and the intensities were corrected for absorption using *SADABS*[3]. Single-crystal X-ray data for bromide **3** was measured using a Rigaku SuperNova dual-source Oxford diffractometer equipped with an Eos detector using mirror-monochromated Mo-*K*α (λ = 0.71073 Å) radiation at 120 K. The data collection and reductionwere performed using the program *CrysAlisPro*and Gaussian face index absorption correction method was applied[4]. The structures were solved with intrinsic phasing (SHELXT) [5] and refined by full-matrix least squares on *F*2 using the *OLEX2* software[6], which utilizes the *SHELXL* module[7].For the azide **4** only a partial data collection was performed (see below) verifying the structure to be the known azide, 3*a*-azidocholest-5-ene[8].

**Crystal data for the diene 2**

C27H44, M = 368.62, colourless block, 0.24 x 0.30 x 0.40 mm, orthorhombic, space group *P*212121, a = 7.5850(2) Å, b = 15.9238(4) Å, c = 19.4795(4) Å, V = 2352.77(10) Å3, Z = 4, Dcalc = 1.041 gcm‑3, F000 = 824, µ = 0.06 mm‑1, T = 170(1) K, θmax = 28.7°, 5169 total reflections, 3861 with Io > 2σ(Io), Rint = 0.052, 5169 data, 249 parameters, no restraints, GooF = 1.03, 0.28 < d∆ρ < ‑0.17 eÅ‑3, *R*[*F*2 > 2*σ*(*F*2)] = 0.053, *wR*(*F*2) = 0.131. CCDC-2204245.

**Crystal data for the bromide 3**

C27H45Br, M = 449.54, colourless plate, 0.06 x 0.17 x 0.25 mm3, monoclinic, space group *P*21, a = 11.4127(12) Å, b = 7.5896(9) Å, c = 28.603(5) Å, β = 90.077(13)°, V = 2477.5(6) Å3, Z = 4, Dcalc = 1.205 gcm‑3, F000 = 968, µ = 1.67 mm‑1, T = 120.0(1) K, θmax = 25.8°, 11562 total reflections, 5812 with Io > 2σ(Io), Rint = 0.109, 11562 data, 467 parameters, 130 restraints, GooF = 1.06, 1.51 < d∆ρ < ‑1.68 eÅ‑3, *R*[*F*2 > 2*σ*(*F*2)] = 0.098, *wR*(*F*2) = 0.309. CCDC-2204246.

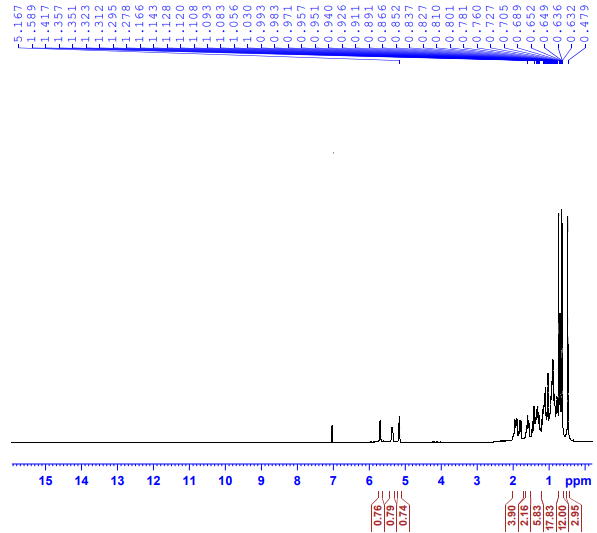
**Verification of the structure of the azide 4**

The physical habit (colorless plates), the unit cell (*a* = 13.2746(14) Å, *b* = 6.1854(6) Å, *c* = 14.9159(15) Å, *β* = 93.285(9)°, *V* = 1222.7(2) Å3) and the space group (*P*21) matched that previously reported for 3*a*-azidocholest-5-ene [8]. A partial (30%) data set was collected and a figure base on it is shown in (Figure S1) confirming the studied sample to be the 3*a*-azidocholest-5-ene.

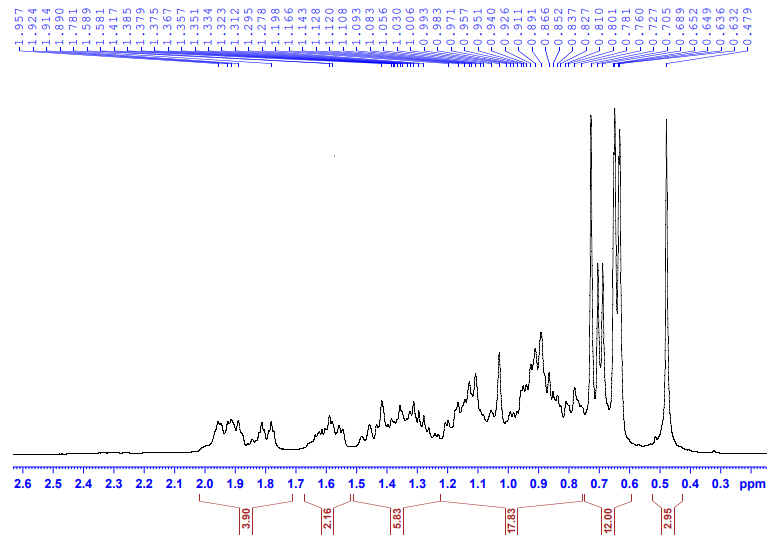


**Fig. S1.** The ORTEP plot of the 3*a*-azidocholest-5-enefrom a partial data set with thermal displacement parameter at 50% probability level.

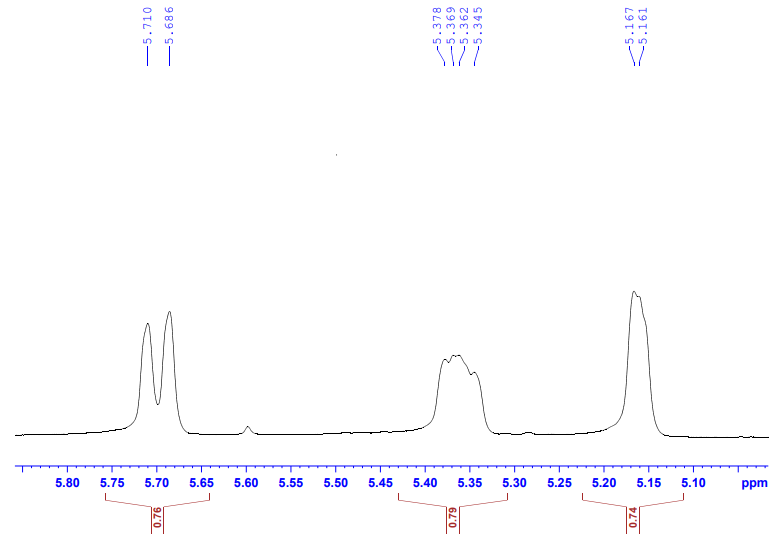
1. **NMR spectra**



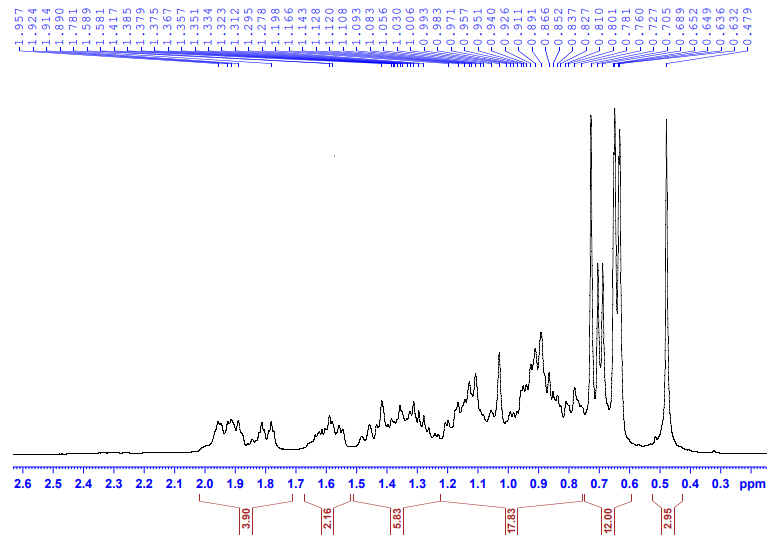
**Fig. S2.** 1H NMR spectrum (400 MHz, CDCl3) of compound **2**. A spectrum for this compound was previously published in [9], but incorrectly assigned to 3*α*-bromocholest-5-ene.



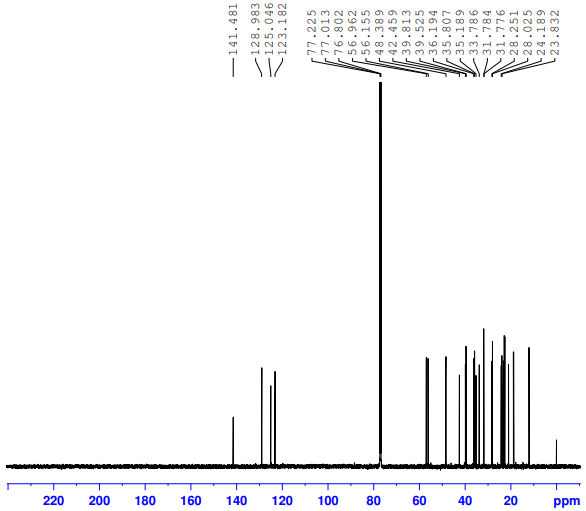
**Fig. S3.** Cross-section in the 1H NMR spectrum (400 MHz, CDCl3) of compound **2**.



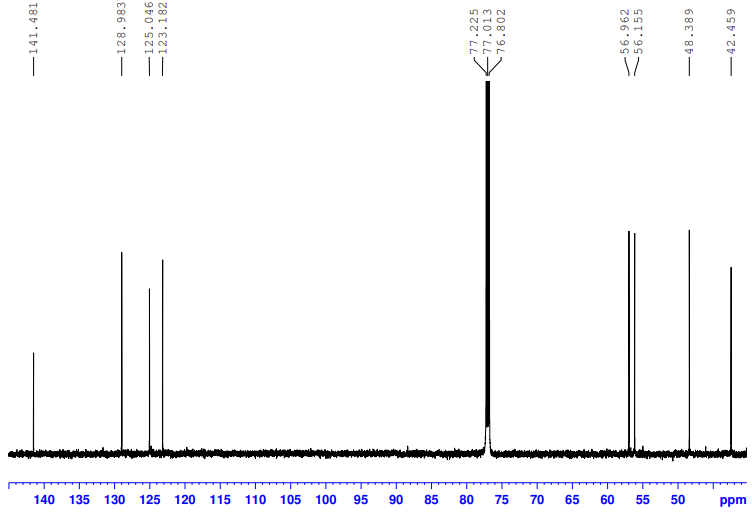
**Fig. S4.** Cross-section in the 1H NMR spectrum (400 MHz, CDCl3) of compound **2**.



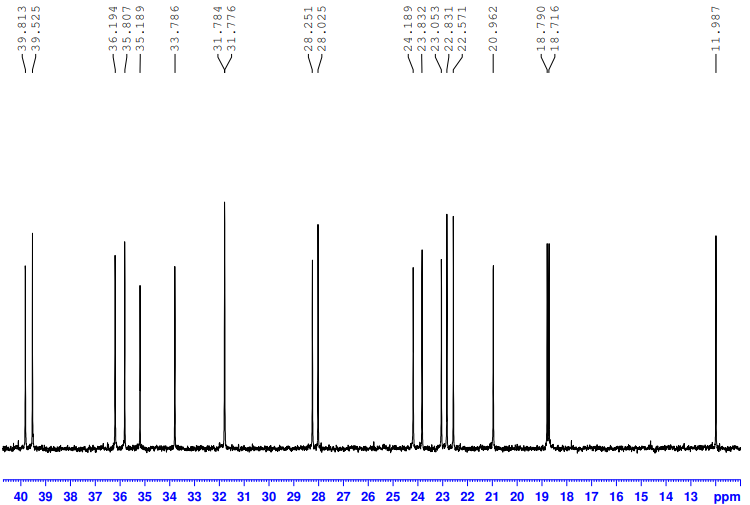
**Fig. S5.** Cross-section in the 1H NMR spectrum (400 MHz, CDCl3) of compound **2**.



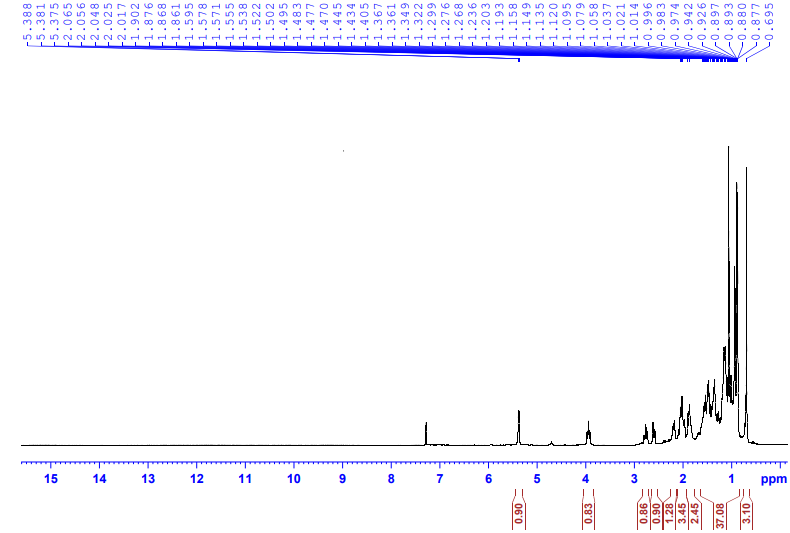
**Fig. S6.** 13C {1H} NMR spectrum (150 MHz, CDCl3) of compound **2**. This spectrum was slightly adapted from [9] (“Synthesis, antimicrobial and cytotoxicity evaluation of new cholesterol congeners”, © 2015 M. R. E. S. Aly et al., published by the Beilstein-Institut, distributed under the terms of the Creative Commons Attribution 2.0 Generic License, [https://creativecommons.org/licenses/by/2.0)](https://creativecommons.org/licenses/by/2.0)" \t "_blank). This spectrum was incorrectly assigned to 3*α*-bromocholest-5-ene in [9].



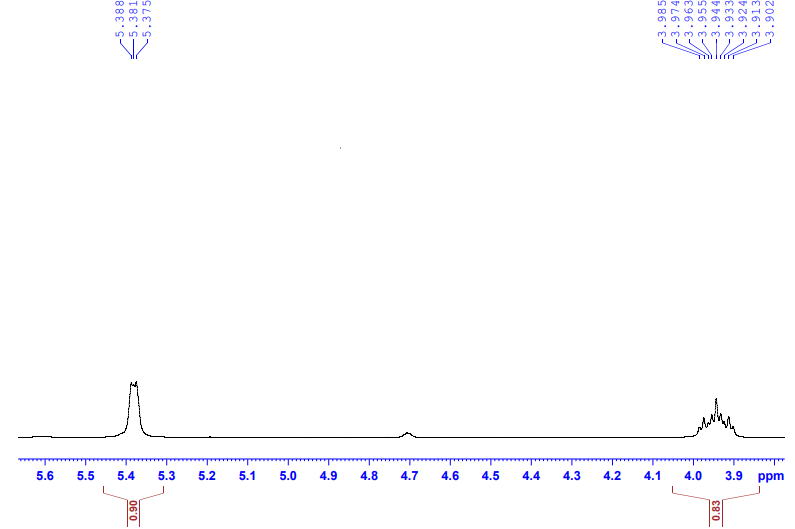
**Fig. S7.** Cross-section in the 13C {1H} NMR spectrum of compound **2**.



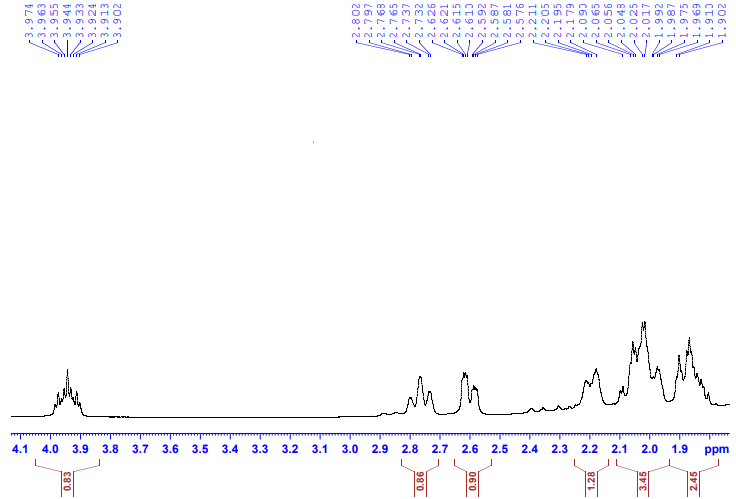
**Fig. S8.** Cross-section in the 13C {1H} NMR spectrum of compound **2**.



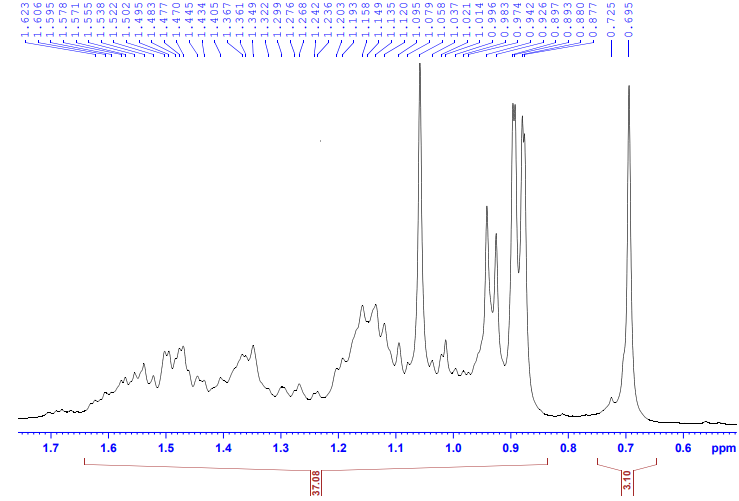
**Fig. S9.** 1H NMR spectrum (400 MHz, CDCl3) of compound **3**.



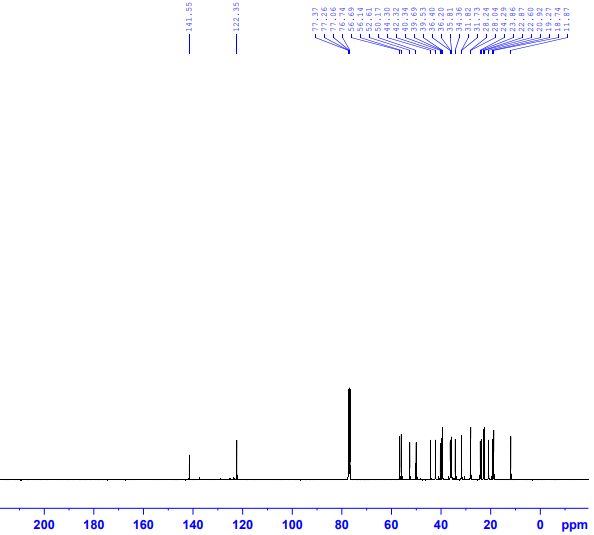
**Fig. S10.** Cross-section in the 1H NMR spectrum of compound **3**.



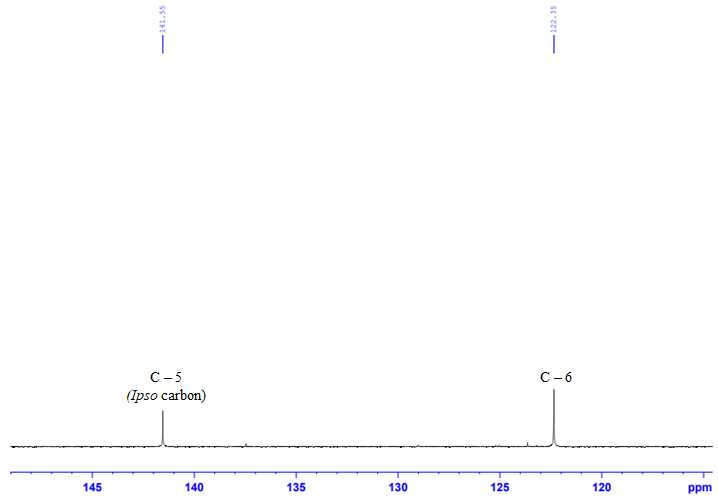
**Fig. S11.** Cross-sections in the 1H NMR spectrum of compound **3**.



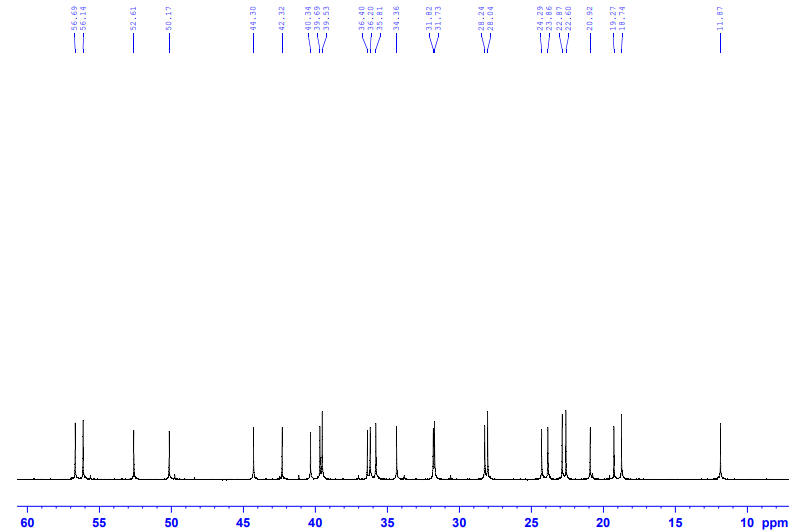
**Fig. S12.** Cross-sections in the 1H NMR spectrum of compound **3**.



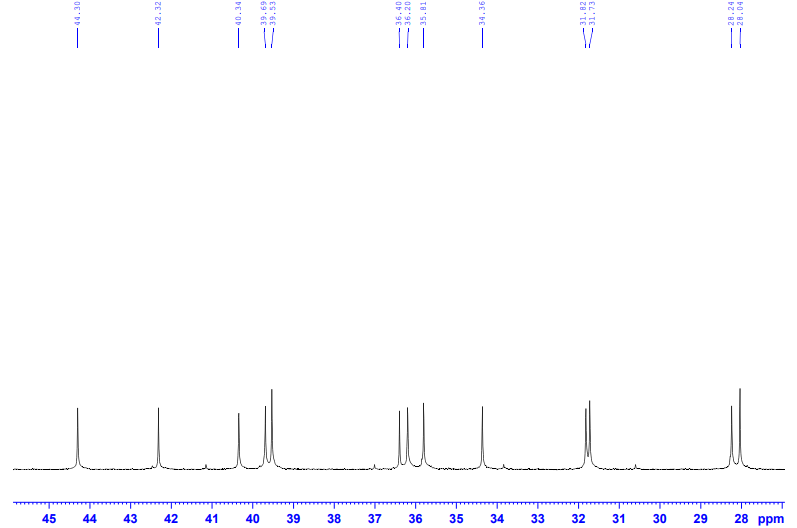
**Fig. S13.** 13C {1H} NMR spectrum (100 MHz, CDCl3) of compound **3**.



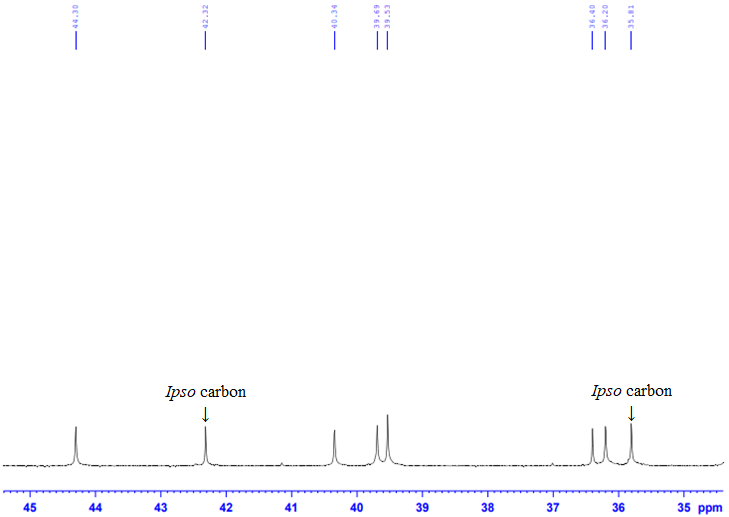
**Fig. S14.** Cross-section in the 13C {1H} NMR spectrum (100 MHz, CDCl3) of compound **3**.



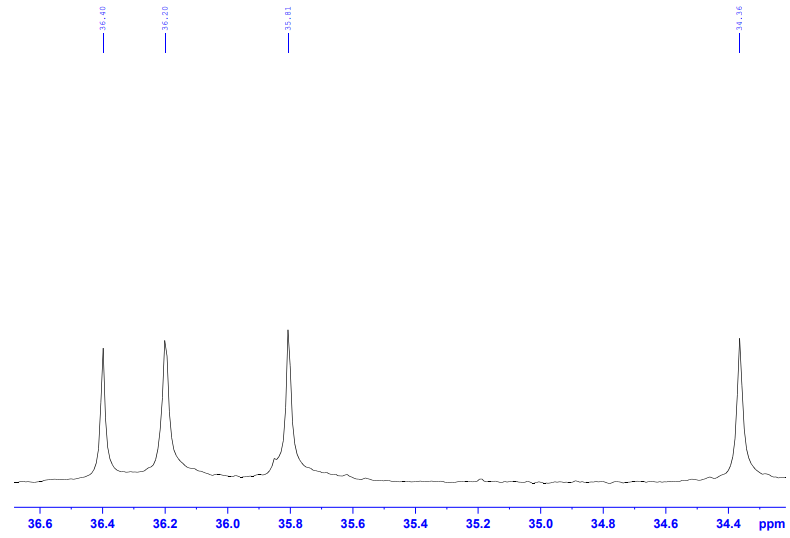
**Fig. S15.** Cross-section in the 13C {1H} NMR spectrum (100 MHz, CDCl3) of compound **3**.



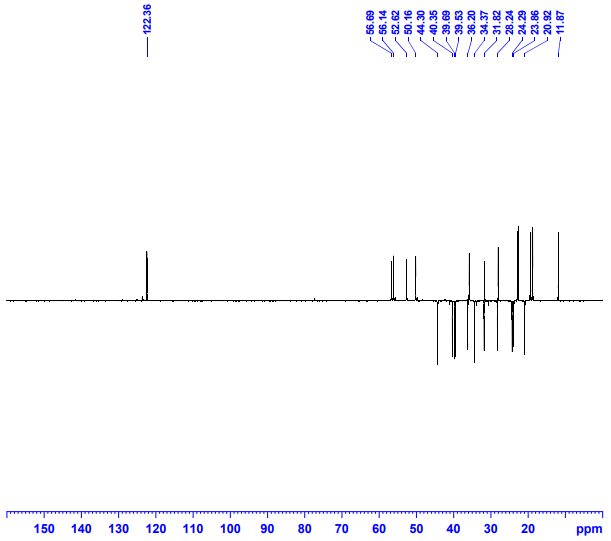
**Fig. S16.** Cross-section in the 13C {1H} NMR spectrum (100 MHz, CDCl3) of compound **3**.



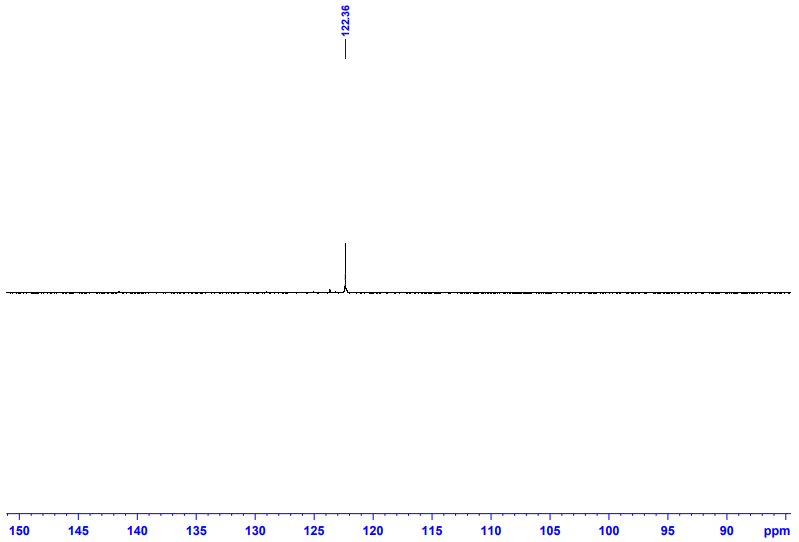
**Fig. S17.** Cross-section in the 13C {1H} NMR spectrum (100 MHz, CDCl3) of compound **3**.



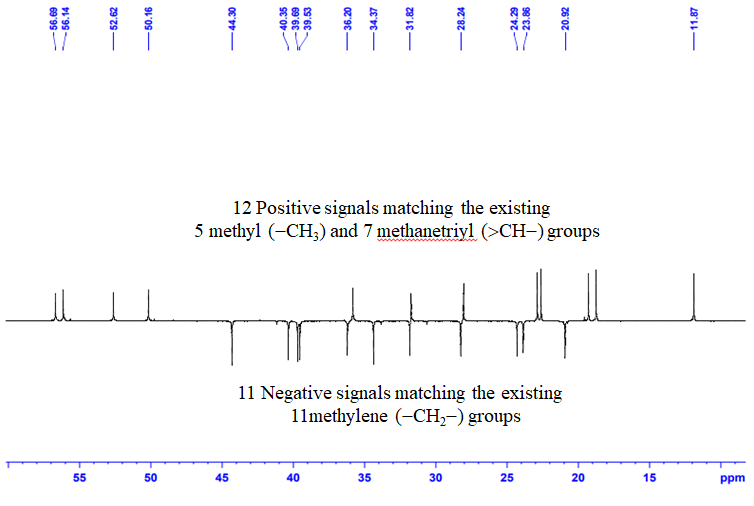
**Fig. S18.** Cross-section in the 13C {1H} NMR spectrum (100 MHz, CDCl3) of compound **3**.



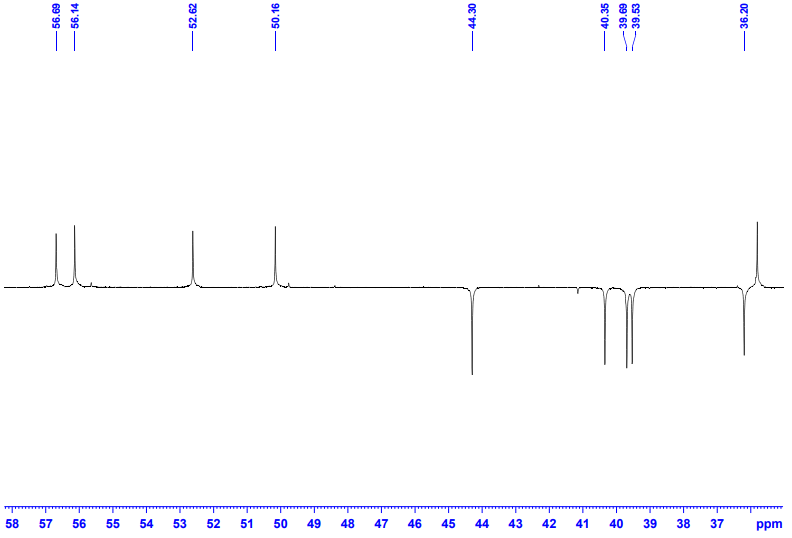
**Fig. S19.** DEPT-135º spectrum (100 MHz, CDCl3) of compound **3**.



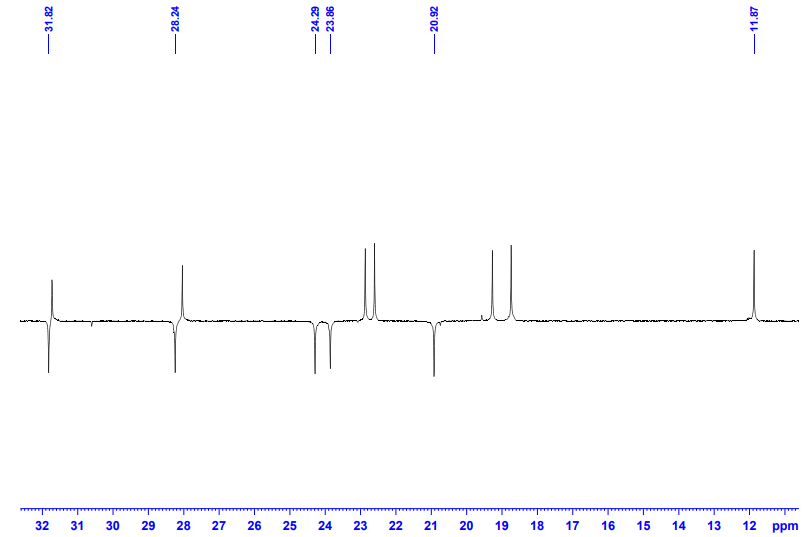
**Fig. S20.** Cross-section in the DEPT-135º spectrum (100 MHz, CDCl3) of compound **3**.



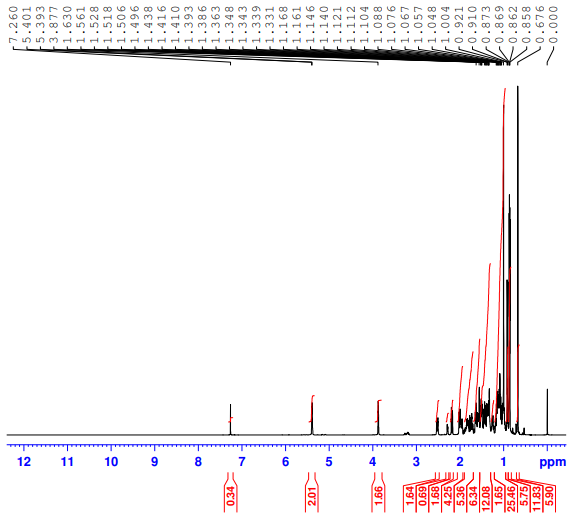
**Fig. S21.** Cross-section in the DEPT-135º spectrum (100 MHz, CDCl3) of compound **3**.



**Fig. S22.** Cross-section in the DEPT-135º spectrum (100 MHz, CDCl3) of compound **3**.

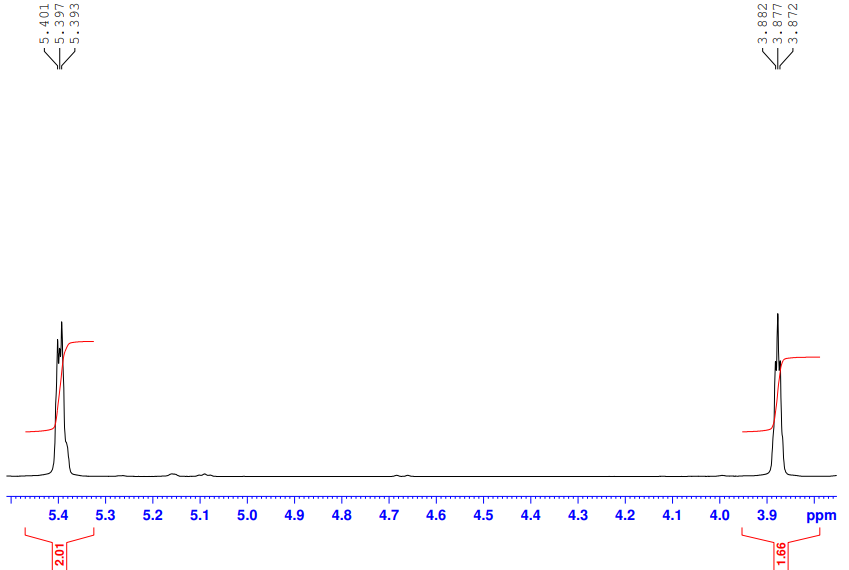


**Fig. S23.** Cross-section in the DEPT-135º spectrum (100 MHz, CDCl3) of compound **3**.

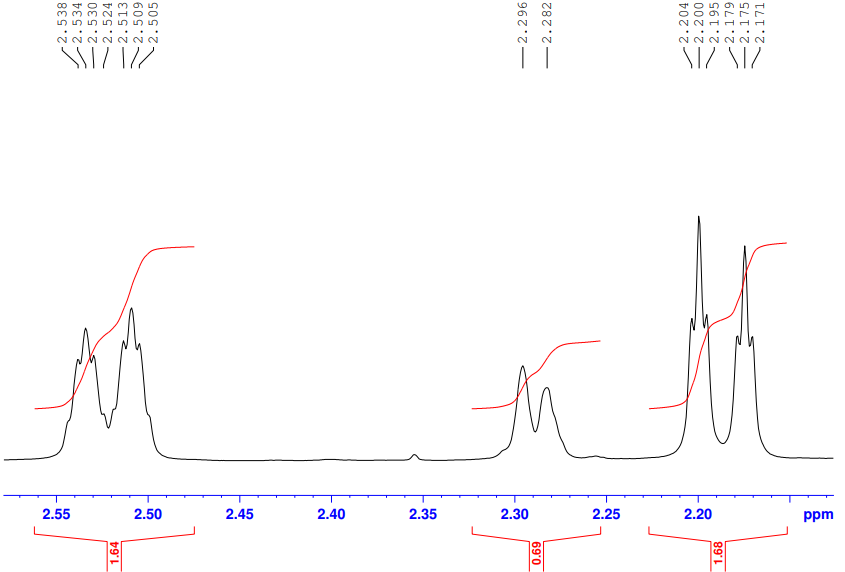


**Fig. S24.** 1H NMR spectrum (600 MHz, CDCl3) of compound **4**.This spectrum was slightly adapted from [9] (“Synthesis, antimicrobial and cytotoxicity evaluation of new cholesterol congeners”, © 2015 M. R. E. S. Aly et al., published by the Beilstein-Institut, distributed under the terms of the Creative Commons Attribution 2.0 Generic License, [https://creativecommons.org/licenses/by/2.0)](https://creativecommons.org/licenses/by/2.0)" \t "_blank). This spectrum was incorrectly assigned to 3*β*-azidocholest-5-ene in [9]. The weak signal at *δ* = 3.20 (H−3β) belongs to the *β*‒epimer (*ca.* 15%) [10].

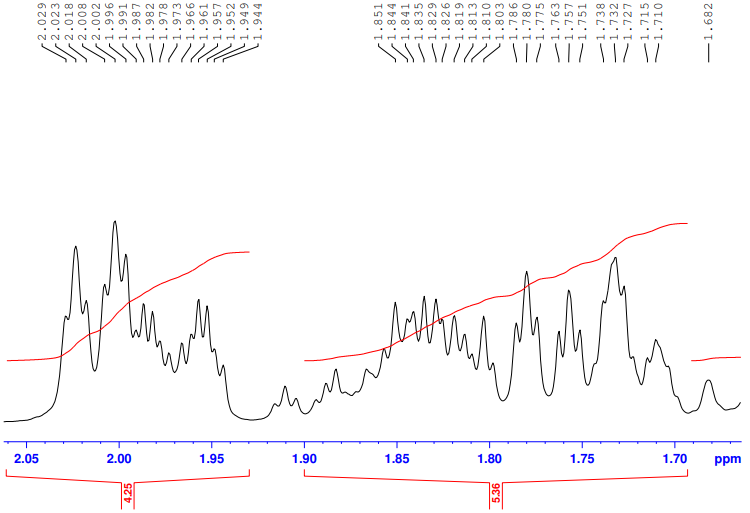
.



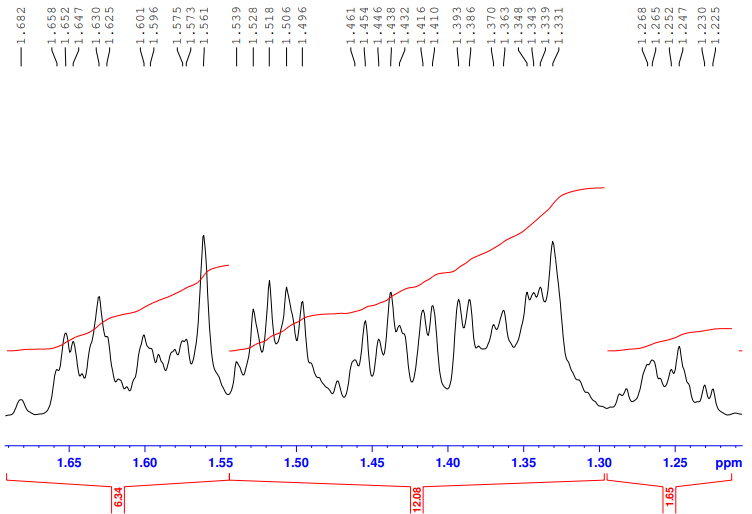
**Fig. S25.** Cross-section in the 1H NMR spectrum of compound **4**.



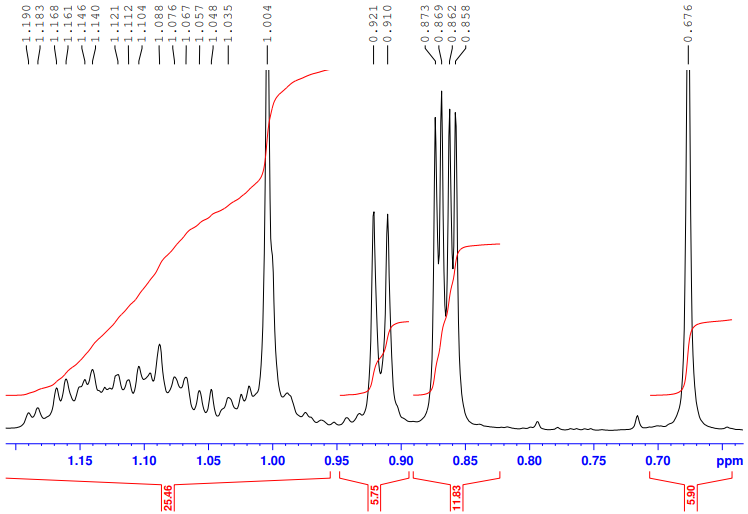
**Fig. S26.** Cross-section in the 1H NMR spectrum of compound **4**. The signal at *δ* = 2.28 ppm arise from two protons of the *β*‒epimer (*ca.* 15%) [10].



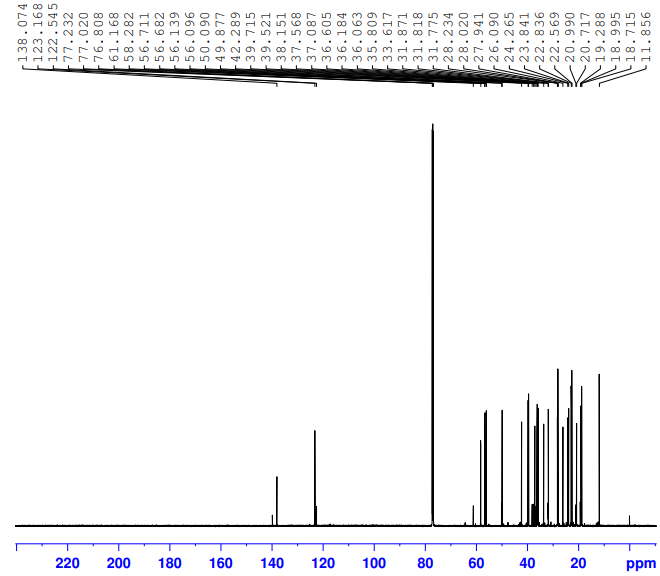
**Fig. S27.** Cross-section in the 1H NMR spectrum of compound **4**.



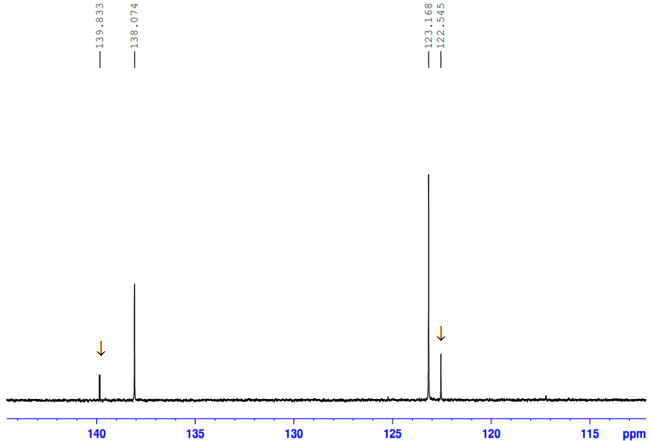
**Fig. S28.** Cross-section in the 1H NMR spectrum of compound **4**.



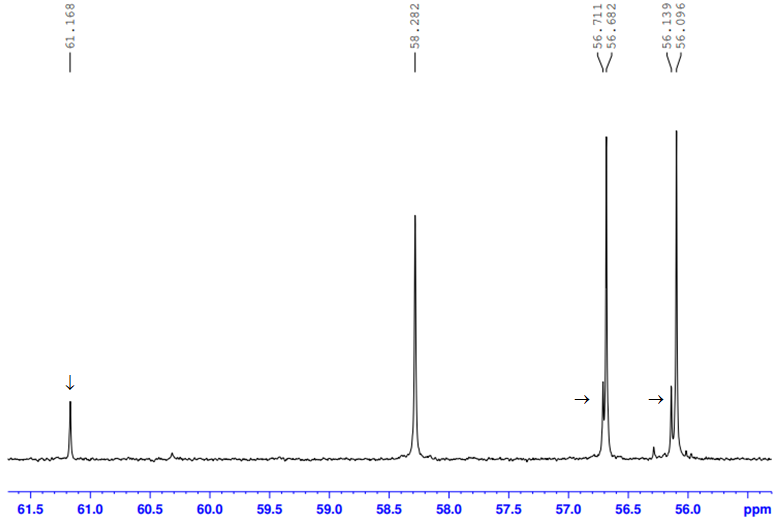
**Fig. S29.** Cross-section in the 1H NMR spectrum of compound **4**.



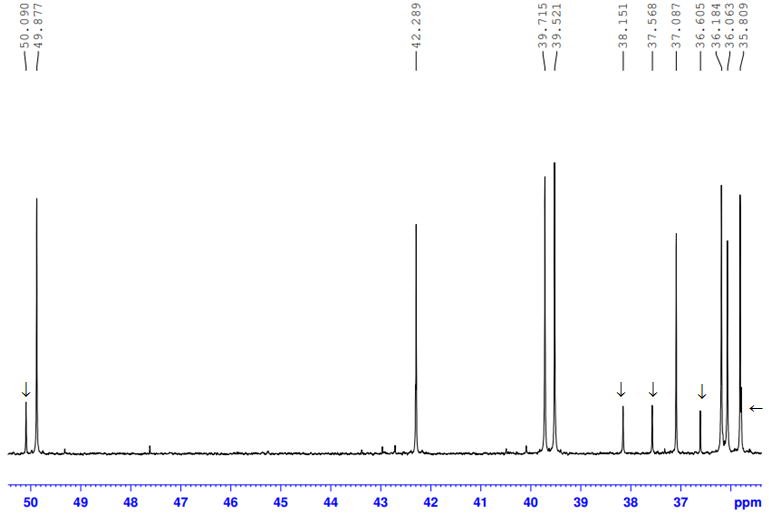
**Fig. S30.** 13C {1H} NMR spectrum (150 MHz, CDCl3) of compound **4**.This spectrum was slightly adapted from [9] (“Synthesis, antimicrobial and cytotoxicity evaluation of new cholesterol congeners”, © 2015 M. R. E. S. Aly et al., published by the Beilstein-Institut, distributed under the terms of the Creative Commons Attribution 2.0 Generic License, [https://creativecommons.org/licenses/by/2.0)](https://creativecommons.org/licenses/by/2.0)" \t "_blank). This spectrum was incorrectly assigned to 3*β*-azidocholest-5-ene in [9].



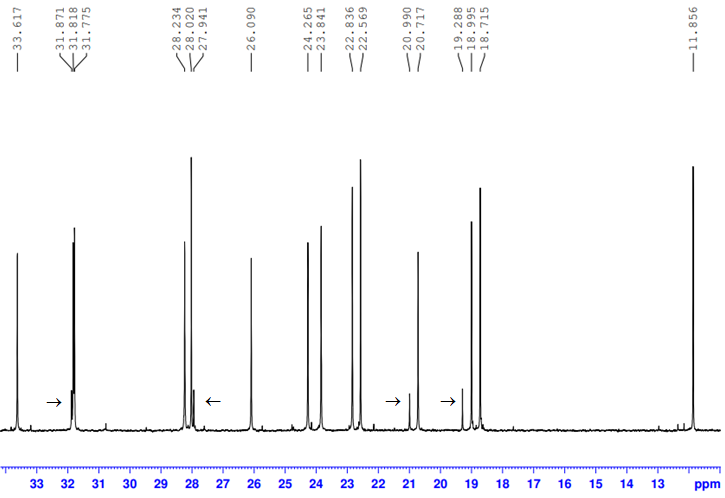
**Fig. S31.** Cross-section in the 13C {1H} NMR spectrum (150 MHz, CDCl3) of compound **4**. The arrows here and in the next cross-sections denote to the signals arising from the presence of trace of 3*β*-azidocholest-5-ene [10].



**Fig. S32.** Cross-section in the 13C {1H} NMR spectrum (150 MHz, CDCl3) of compound **4**.



**Fig. S33.** Cross-section in the 13C {1H} NMR spectrum (150 MHz, CDCl3) of compound **4**.



**Fig. S34 .** Cross-section in the 13C {1H} NMR spectrum (150 MHz, CDCl3) of compound **4**.

1. **References**

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