

Preparation of silver nanoparticles functionalized with β -cyclodextrin and their use for loading vitamin D molecules

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Analysis of β -CD NMR Spectra

The ^1H NMR spectrum of β -CD, obtained in deuterated dimethyl sulfoxide (DMSO), is characterized by six groups of signals in the range of 3.23-3.32; 3.45-3.53; 3.56-3.60; 4.47-4.49; 4.77-4.78; and 5.66-5.73 ppm (Fig. 1). The lowest-field doublet signal in the range of 5.71-5.73 ppm with a splitting of 4 Hz belongs to the proton of the hydroxyl group at the C-2 atom (OH-2). The proton of the OH group of the adjacent atom (OH-3), located in the internal cavity of the CD molecule, also resonates in the downfield region ($\delta = 5.66$ ppm, doublet). The doublet signal in the region of 4.77-4.78 ppm corresponds to the H-1 proton. The location of this proton in a weaker field compared to the protons of other CH groups is due to the influence of the oxygen atom. The hydroxyl group OH-6 resonates, splitting into a triplet centered at 4.48 ppm. In the strong field region (3.56-3.60 ppm), an accumulation of signals of the H-6 a, b methylene group is observed. The high-intensity signal at 3.45 ppm corresponds to the H-3 and H-5 protons of the glucopyranose unit. In the range from 3.23 to 3.32 ppm, the methine protons H-2 and H-4 appear.

The carbon spectrum of β -CD (Fig. 2) consists of five signals from the ^{13}C nuclei of the elementary unit. The upfield signal is due to the C-6 carbon atom ($\delta = 60.41$ ppm). The signals at 72.49, 72.85, and 73.51 ppm are due to the C-5, C-2, and C-3 atoms, respectively. Downfield signals (82.02 and 102.41 ppm) are due to the carbon atoms (C-4 and C-1, respectively), directly linked to the adjacent glucopyranose unit via an oxygen bridge. To obtain more complete and accurate information on homo- (^1H - ^1H) and heteronuclear (^1H - ^{13}C) correlations, two-dimensional NMR spectra were acquired and interpreted in COSY, HSQC, and HMBC formats. The interactions between the ^1H nuclei can be determined using the COSY spectrum shown in Fig. 3. The presence of spin interaction, mediated through 3 bonds, between the proton at the carbon atom of the glucopyranose unit and the proton of the corresponding hydroxyl group is indicated by crosspeaks with coordinates (3.30; 5.79) H2-OH2; (3.63; 4.58) H6-OH6. The correlation with coordinates (3.34; 4.87) corresponds to interaction through 3 bonds between the H-1 and H-2 protons. A similar relationship is observed for the H2-H3, H3-H4, and H4-H5 protons. The interactions of the ^1H - ^{13}C nuclei, mediated through 1, 2, and 3 bonds, can be traced using the HMBC (Fig. 4) and HSQC spectra (Fig. 5). Heteronuclear interactions through 1 bond (Fig. 5) are characteristic of the nuclei H1-C1 (4.81; 102.46), H2-C2 (3.29; 72.66), H3-C3 (3.61; 73.26), H4-C4 (3.33; 81.82), H5-C5 (3.54; 72.01), H6-C6 (3.62; 60.16). The following interactions are characteristic of the hydroxyl proton at the C2 carbon atom: OH2-C2 and OH2-C3, determined by fragment a (5.74; 72.41), as well as OH2-C1 - the peak with coordinates (5.74; 102.23). It should be noted that the first type of interaction occurs through 2 bonds, and the next two - through 3. The hydroxyl group at the third carbon atom (OH-3) also interacts with neighboring ^{13}C nuclei through two (OH3-C3) and three bonds (OH3-C2; OH3-C4), as evidenced by peaks b (5.68; 72.32) and c (5.68; 81.75). Peak e (4.82; 72.38) corresponds to H1-C2 and H1-C3 interactions, realized through 2 and 3 bonds, respectively. Also, this proton is characterized by a correlation with

the carbon atom C4 d (4.80; 81.39). The hydroxyl group OH-6 is determined by the peaks (4.52; 59.97) and (4.52; 72.13), which correspond to the bonds OH6–C6 (through two bonds) and OH6–C5 (through three bonds). The peak (3.62; 72.53) indicates the interactions of the proton-carbon nuclei H6–C5 (through two bonds). Also, this proton is characterized by correlations with the C-4 atom (3.62; 81.77). Protons H-2 and H-4 interact with carbon atoms C3 and C5, as confirmed by the cross peak (3.33; 73.30). For H-2, a correlation with the C-1 atom at the point (3.33; 102.19) was also determined.

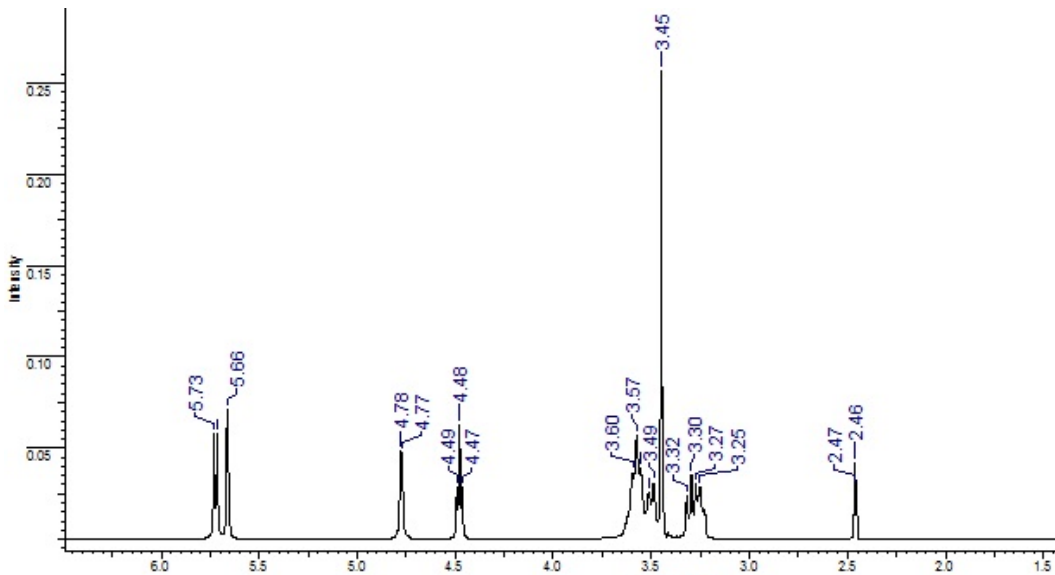


Figure S1. ^1H NMR spectra of β -CD (DMSO)

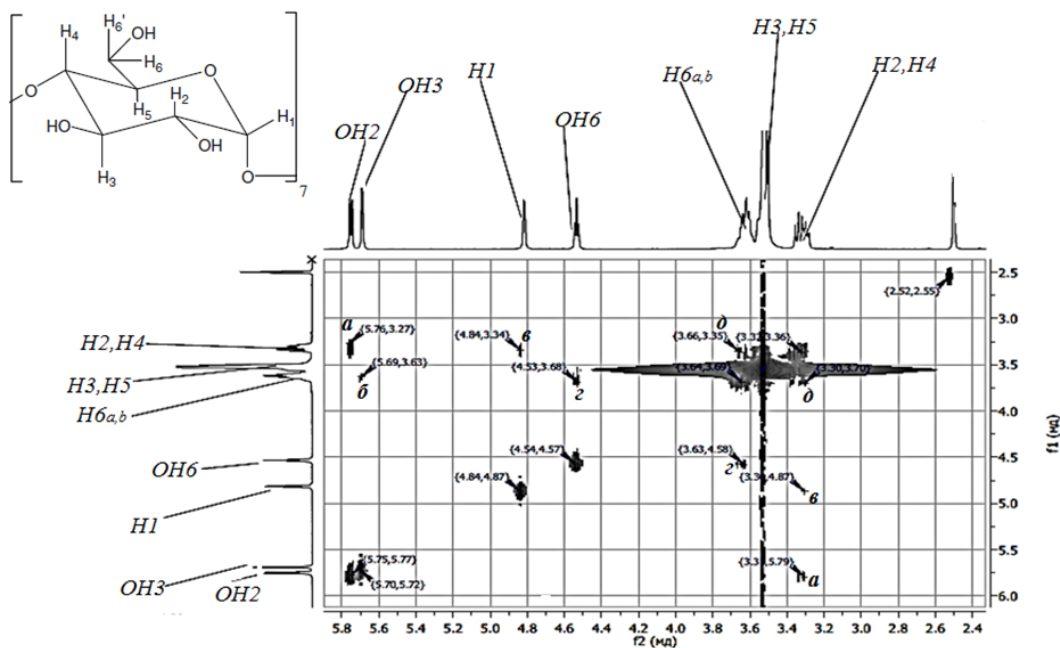


Figure S2. COSY (^1H - ^1H) NMR spectra of β -CD (DMSO)

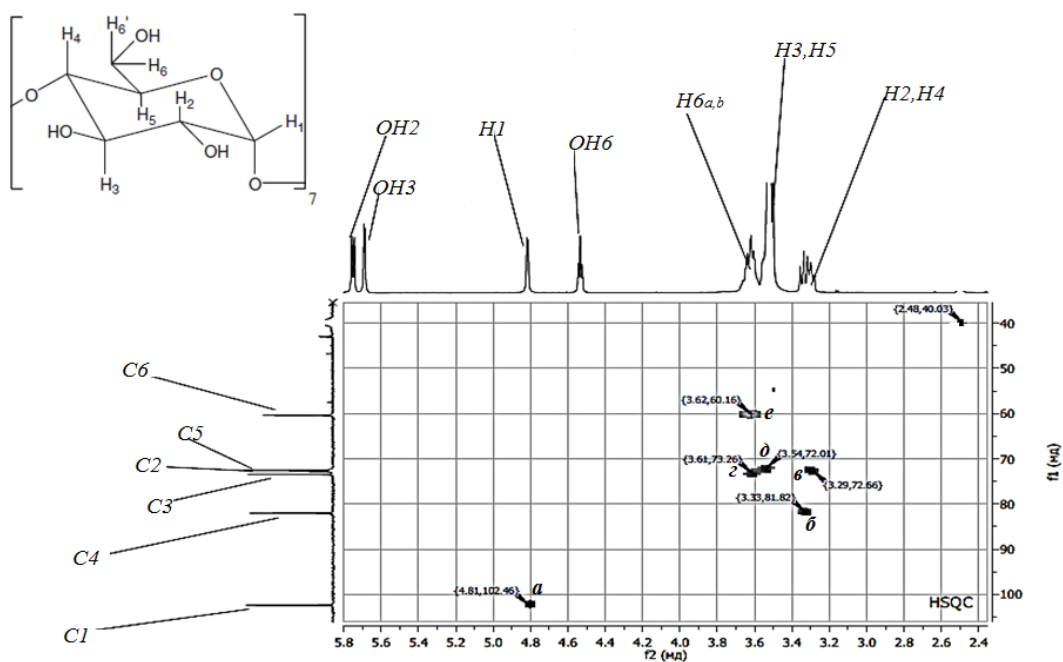


Figure S3. HSQC (^1H - ^{13}C) NMR spectra of β -CD (DMSO)

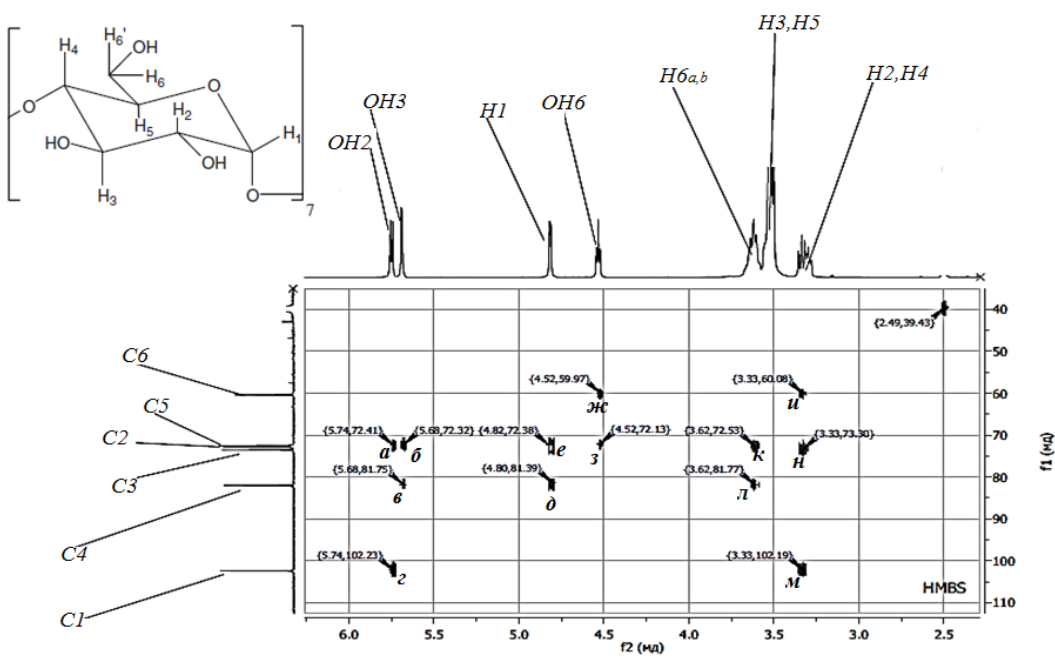
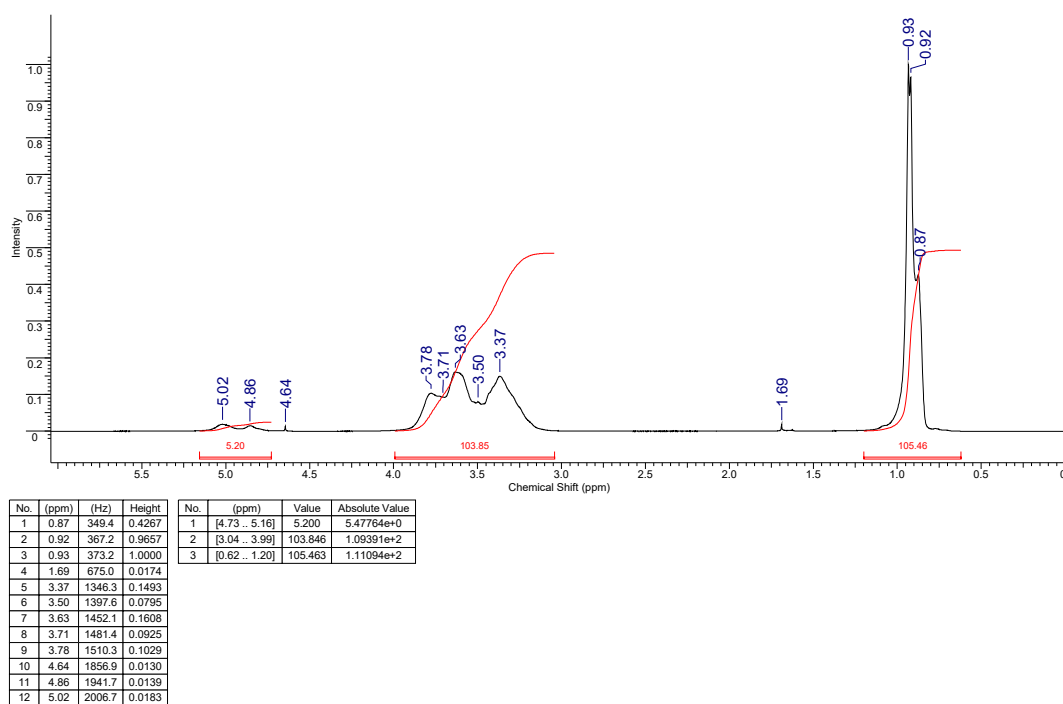
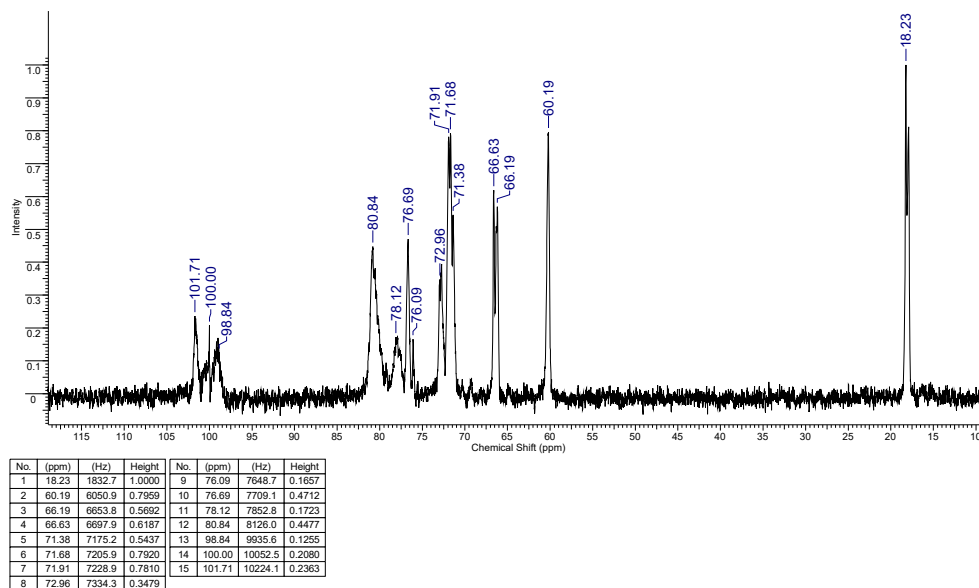


Figure S4. HMBC (^1H - ^{13}C) NMR spectra of β -CD (DMSO)



(a)



(b)

Figure S5. ¹H(a), ¹³C(b) NMR spectra of β-CD-AgNPs (D₂O)

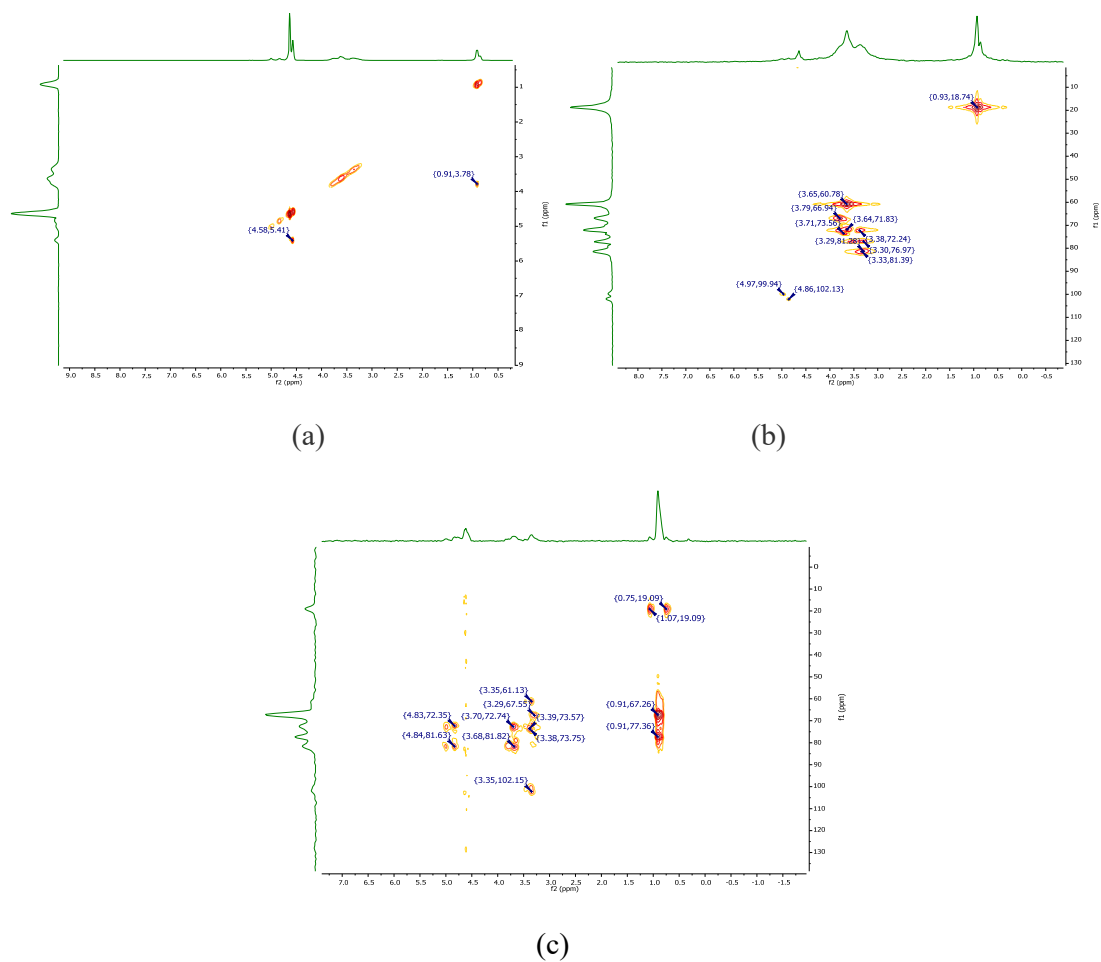
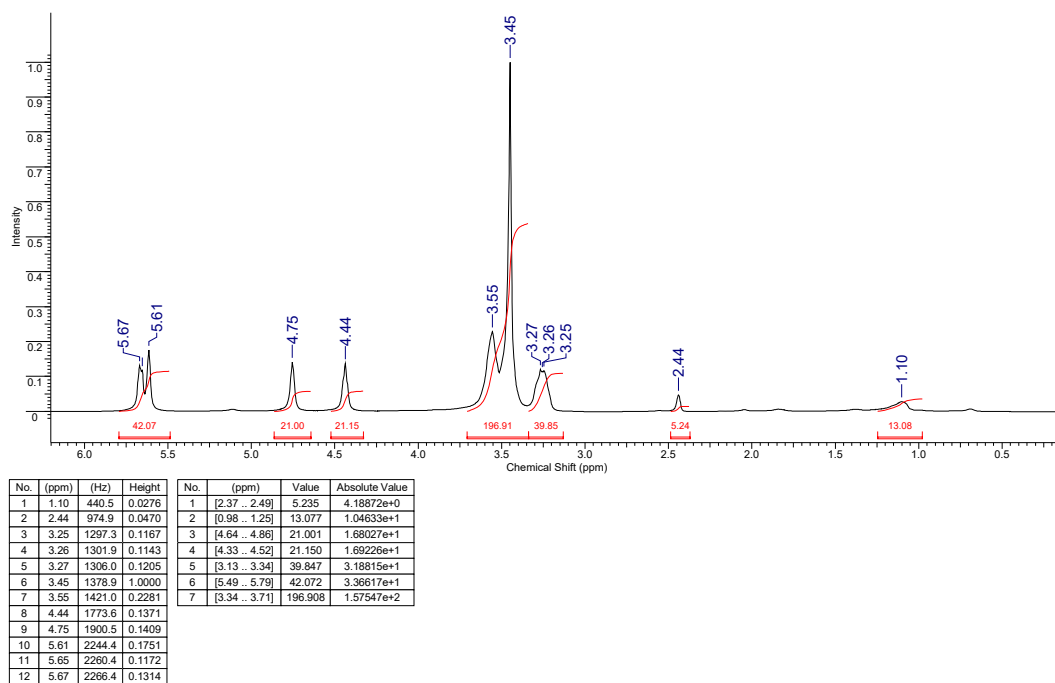
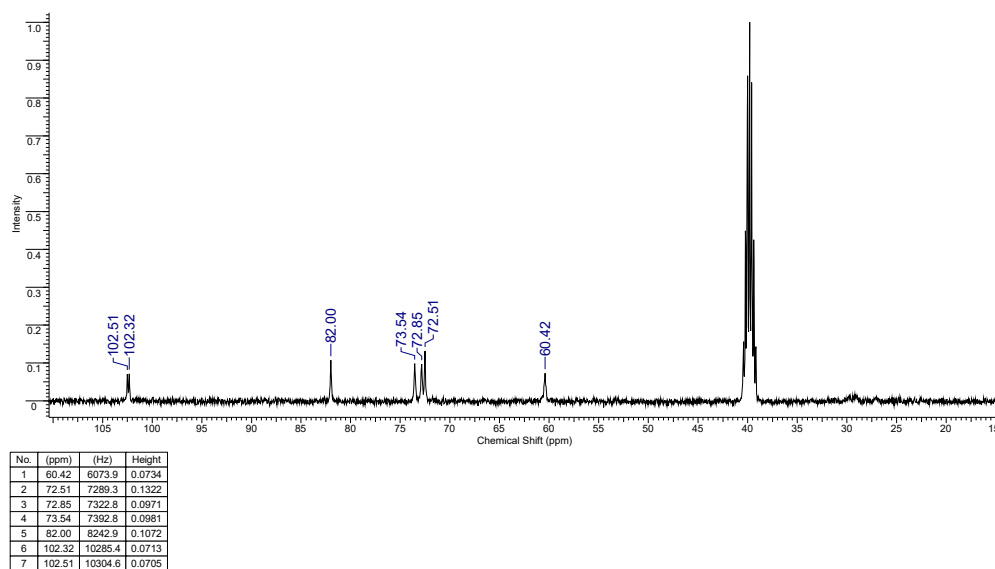


Figure S6 (a-c). COSY (a), HMQC (b), HMBC (c) spectra of β -CD-AgNPs, (D_2O)

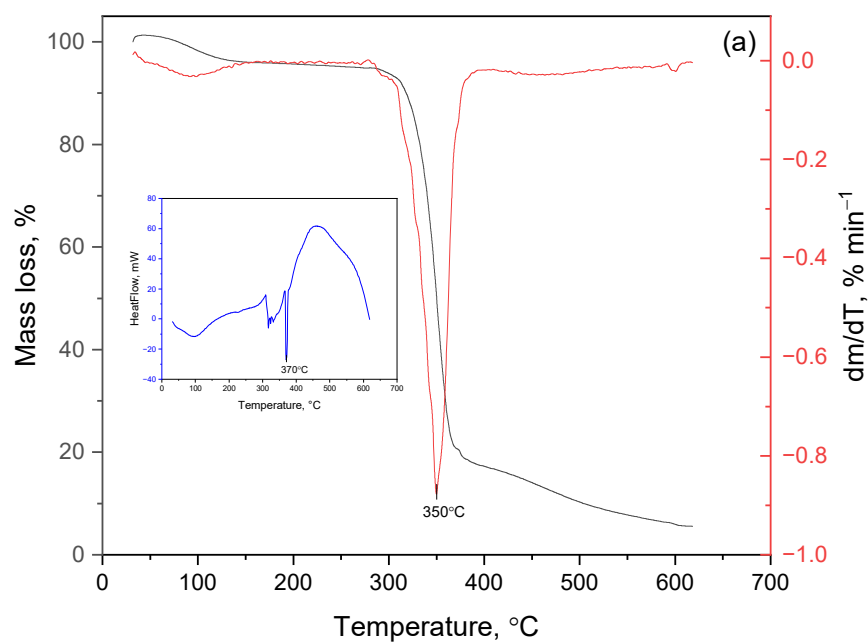


(a)

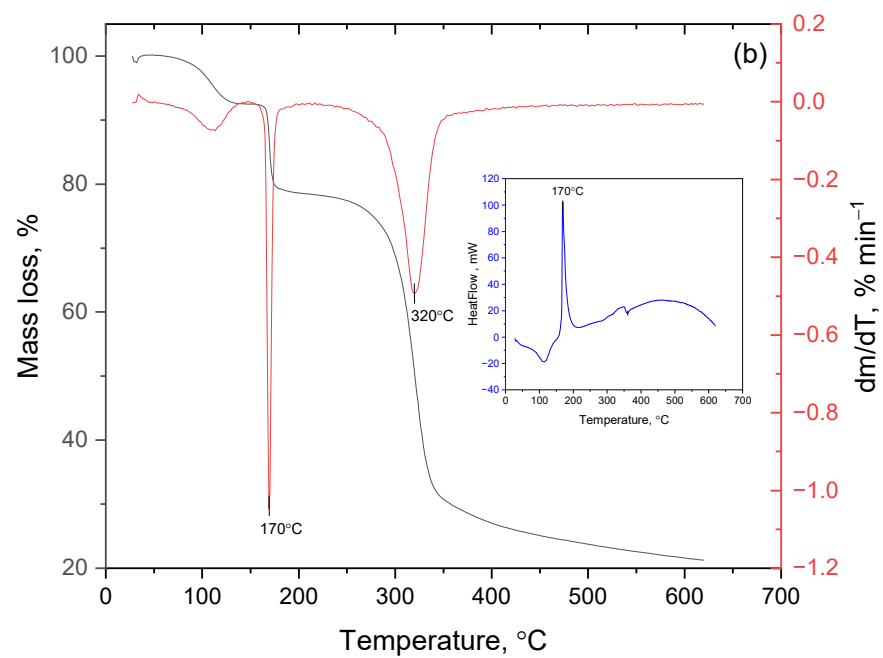


(b)

Figure S7 (a, b). ^1H (a) and ^{13}C (b) NMR spectra of VD_3 (DMSO)

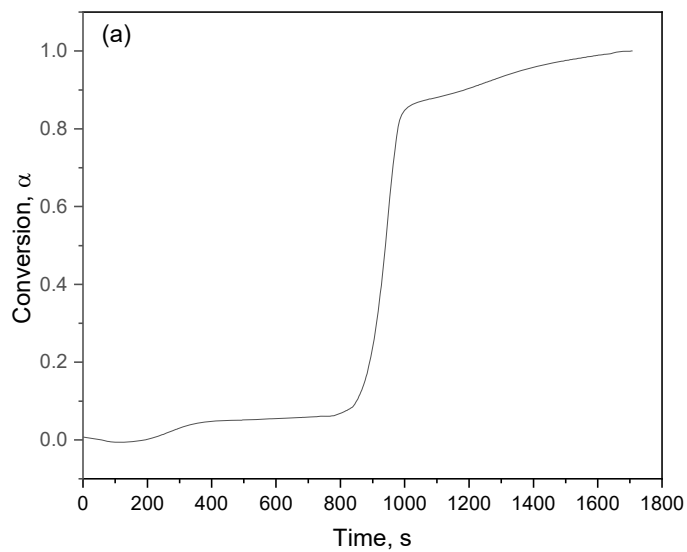


(a)



(b)

Figure S8 (a,b). Graphical dependences of mass change on temperature: (a) $\beta\text{-CD-Ag (15:1)}$ and (b) $\text{VD}_3\text{-}\beta\text{-CD-Ag (15:1:1)}$



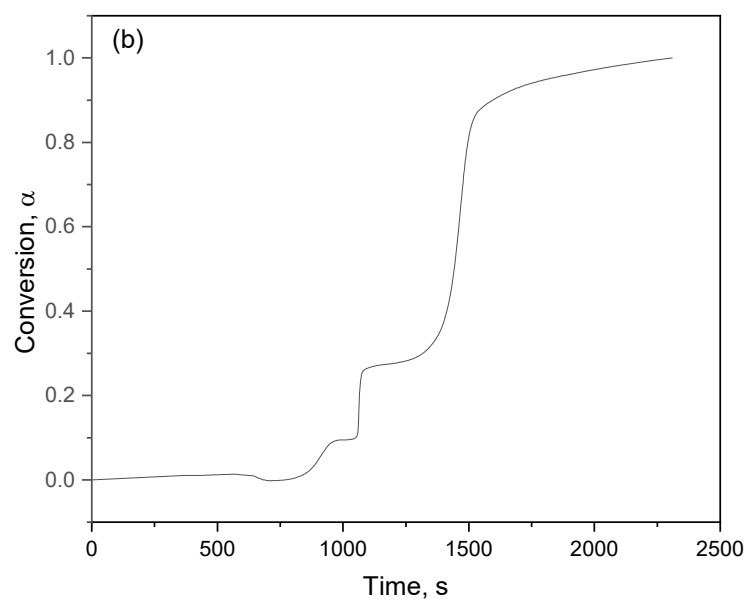


Figure S9. Kinetic curves of the dependence of the degree of transformation on time during thermal decomposition of β -CD-Ag (15:1) (a) and VD₃- β -CD-Ag (15:1:1) (b)