



Supporting Information

for

Preparation of β -cyclodextrin-based dimers with selectively methylated rims and their use for solubilization of tetracene

Konstantin Lebedinskiy, Volodymyr Lobaz and Jindřich Jindřich

Beilstein J. Org. Chem. **2022**, *18*, 1596–1606. doi:10.3762/bjoc.18.170

Synthetic procedures, characterization, ^1H , ^{13}C DEPT, 2D NMR, IR, UV–vis spectra of synthesized compounds; UV–vis spectra of tetracene solutions in DMSO; ITC thermograms

Contents

I Synthesis and characterization	S5
6 ^A -Azido-6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis- <i>tert</i> -butyldimethylsilyl-β-cyclodextrin (1).....	S5
Fig. S1 ¹ H NMR spectrum of 1 in CDCl ₃ at 25 °C	S6
Fig. S2 DEPT- ¹³ C NMR spectrum of 1 in CDCl ₃ at 25 °C.....	S7
Fig. S3 COSY spectrum of 1 in CDCl ₃ at 25 °C.....	S8
Fig. S4 HSQC spectrum of 1 in CDCl ₃ at 25 °C	S9
Fig. S5 IR spectrum of 1 in KBr pellet	S10
Fig. S6 UV–vis spectrum of 1 in CHCl ₃	S10
6 ^A -Azido-6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis- <i>tert</i> -butyldimethylsilyl-per-2,3- <i>O</i> -methyl-β-cyclodextrin (2) .	S11
Fig. S7 ¹ H NMR spectrum of 2 in CDCl ₃ at 25 °C	S12
Fig. S8 DEPT- ¹³ C NMR spectrum of 2 in CDCl ₃ at 25 °C.....	S13
Fig. S9 COSY spectrum of 2 in CDCl ₃ at 25 °C.....	S14
Fig. S10 HSQC spectrum of 2 in CDCl ₃ at 25 °C.....	S15
Fig. S11 IR spectrum of 2 in KBr pellet	S16
Fig. S12 UV–vis spectrum of 2 in CHCl ₃	S16
6 ^A -Azido-6 ^A -deoxy-per-2,3- <i>O</i> -methyl-β-cyclodextrin (3)	S17
Fig. S13 ¹ H NMR spectrum of 3 in CDCl ₃ at 25 °C	S18
Fig. S14 DEPT- ¹³ C NMR spectrum of 3 in CDCl ₃ at 25 °C.....	S19
Fig. S15 COSY spectrum of 3 in CDCl ₃ at 25 °C.....	S20
Fig. S16 HSQC spectrum of 3 in CDCl ₃ at 25 °C.....	S21
Fig. S17 IR spectrum of 3 in KBr pellet	S22
Fig. S18 UV–vis spectrum of 3 in CDCl ₃	S22
Bis-1,3-[1-(6 ^A -deoxy-2,3-per- <i>O</i> -methyl-β-cyclodextrin-6 ^A -C-yl)-1,2,3-triazol-4-yl]methoxymethylene (4)	S23

Fig. S19 ^1H -NMR spectrum of 4 in D_2O at 25 °C.....	S24
Fig. S20 DEPT- ^{13}C -NMR spectrum of 4 in D_2O at 25 °C.....	S25
Fig. S21 COSY spectrum of 4 in D_2O at 25 °C	S26
Fig. S22 HSQC spectrum of 4 in D_2O at 25 °C.....	S27
Fig. S23 NOESY spectrum of 4 in D_2O at 25 °C.....	S28
Fig. S24 IR spectrum of 4 in KBr pellet	S29
Fig. S25 UV–vis of 4 in CHCl_3	S29
<i>N,N'</i> - Bis(6 ^A -deoxy-2,3-per- <i>O</i> -methyl- β -cyclodextrin-6 ^A -C-yl)urea (5)	S30
Fig. S26 ^1H -NMR spectrum of 5 in D_2O at 25 °C.....	S30
Fig. S27 DEPT- ^{13}C -NMR spectrum of 5 in D_2O at 25 °C	S31
Fig. S28 COSY spectrum of 5 in D_2O at 25 °C	S32
Fig. S29 HSQC spectrum of 5 in D_2O at 25 °C.....	S33
Fig. S30 IR spectrum of 5 in KBr pellet	S34
Fig. S31 UV–vis spectrum of 5 in CHCl_3	S34
6 ^A -Azido-6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis- <i>tert</i> -butyl-dimethylsilyl-per-2,3- <i>O</i> -acetyl- β -cyclodextrin (6)..	S35
Fig. S32 ^1H -NMR spectrum of 6 in CHCl_3 at 25 °C	S36
Fig. S33 DEPT- ^{13}C -NMR spectrum of 6 in CHCl_3 at 25 °C.....	S37
Fig. S34 COSY spectrum of 6 in CHCl_3 at 25 °C.....	S38
Fig. S35 HSQC spectrum of 6 in CHCl_3 at 25 °C	S39
Fig. S36 IR spectrum of 6 in KBr pellet	S40
Fig. S37 UV–vis spectrum of 6 in CHCl_3	S40
6 ^A -Azido-6 ^A -deoxy-per-2,3- <i>O</i> -acetyl- β -cyclodextrin (7).....	S41
Fig. S38 ^1H -NMR spectrum of 7 in $[\text{d}_4]$ -MeOH at 25 °C	S42
Fig. S39 DEPT- ^{13}C -NMR spectrum of 7 in $[\text{d}_4]$ -MeOH at 25 °C.....	S43
Fig. S40 COSY spectrum of 7 in $[\text{d}_4]$ -MeOH at 25 °C	S44
Fig. S41 HSQC spectrum of 7 in $[\text{d}_4]$ -MeOH at 25 °C	S45

Fig. S42 IR spectrum of 7 in KBr pellet	S46
Fig. S43 UV–vis spectrum of 7 in CHCl ₃	S46
6 ^A -Azido-6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis-methyl-per-2,3- <i>O</i> -acetyl-β-cyclodextrin (8).....	S47
Fig. S44 ¹ H-NMR spectrum of 8 in CDCl ₃ at 25 °C	S48
Fig. S45 DEPT- ¹³ C-NMR spectrum of 8 in CDCl ₃ at 25 °C.....	S49
Fig. S46 COSY spectrum of 8 in CDCl ₃ at 25 °C	S50
Fig. S47 HSQC spectrum of 8 in CDCl ₃ at 25 °C	S51
Fig. S48 IR spectrum of 8 in KBr pellet	S52
Fig. S49 UV–vis spectrum of 8 in CHCl ₃	S52
Bis-1,3-[1-(6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis-methyl-per-2,3- <i>O</i> -acetyl-β-cyclodextrin-6 ^A -C-yl)-1,2,3-triazol-4-yl]methoxymethylene (9)	S53
Fig. S50 ¹ H-spectrum of 9 in CDCl ₃ at 25 °C	S54
Fig. S51 DEPT- ¹³ C-NMR spectrum of 9 in CDCl ₃ at 25 °C.....	S55
Fig. S52 COSY spectrum of 9 in CDCl ₃ at 25 °C.....	S56
Fig. S53 HSQC spectrum of 9 in CDCl ₃ at 25 °C	S57
Fig. S54 NOESY spectrum of 9 in CDCl ₃ at 25 °C	S58
Bis-1,3-[1-(6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis-methyl-β-cyclodextrin-6 ^A -C-yl)-1,2,3-triazol-4-yl]methoxymethylene (10).....	S59
Fig. S55 ¹ H-NMR spectrum of 10 in D ₂ O at 25 °C.....	S60
Fig. S56 DEPT- ¹³ C-NMR spectrum of 10 in D ₂ O at 25 °C.....	S61
Fig. S57 COSY spectrum of 10 in D ₂ O at 25 °C	S62
Fig. S58 HSQC spectrum of 10 in D ₂ O at 25 °C.....	S63
Fig. S59 NOESY spectrum of 10 in D ₂ O at 25 °C.....	S64
Fig. S60 IR spectrum of 10 in KBr pellet	S65
Fig. S61 UV–vis spectrum of 10 in H ₂ O	S65
6-Azido-6-deoxy -6-per- <i>O</i> -methyl -β-cyclodextrin (11)	S66

Fig. S62 ^1H -NMR spectrum of 11 in $[d_6]$ -DMSO at 25 °C.....	S66
Fig. S63 DEPT- ^{13}C -NMR spectrum of 11 in $[d_6]$ -DMSO at 25 °C.....	S67
Fig. S64 COSY spectrum of 11 in $[d_6]$ -DMSO at 25 °C.....	S68
Fig. S65 HSQC spectrum of 11 in $[d_6]$ -DMSO at 25 °C.....	S69
Fig. S66 IR spectrum of 11 in KBr pellet.....	S70
Fig. S67 UV–vis spectrum of 11 in DMSO.....	S70
<i>N,N'</i> -Bis(6 ^A -deoxy-6 ^{B,C,D,E,F,G} - <i>O</i> -hexakis-methyl- β -cyclodextrin-6 ^A -C-yl)urea (12)	S71
Fig. S68 ^1H -NMR spectrum of 12 in D_2O at 25 °C.....	S72
Fig. S69 DEPT- ^{13}C -NMR spectrum of 12 in D_2O at 25 °C.....	S73
Fig. S70 COSY spectrum of 12 in D_2O at 25 °C.....	S74
Fig. S71 HSQC spectrum of 12 in D_2O at 25 °C.....	S75
Fig. S72 IR spectrum of 12 in KBr pellet.....	S76
Fig. S73 UV–vis spectrum of 12 in DMSO.....	S76
II UV experiments with tetracene.....	S77
Fig. S74 UV–vis spectrum of tetracene in DMSO at different concentrations	S77
Fig. S75 Concentration dependence of tetracene's light absorbance in DMSO at 476 nm	S77
Fig. S76 UV–vis spectrum of 5-times diluted saturated tetracene solutions with the studied CDs and without any supramolecular host (O).....	S78
Fig. S77 UV–vis spectrum of 10-times diluted saturated tetracene solutions with the studied CDs and without any supramolecular host (O).....	S78
III ITC experiments	S79
Fig. 78 ITC thermograms.....	S79
IV References for SI.....	S81

I Synthesis and characterization

6-Azido-6-deoxy- β -cyclodextrin was prepared by two-step synthesis, starting with the tosylation of β -cyclodextrin [1] and subsequent azidation [2]. Per-6-O-methyl- β -cyclodextrin (**18**) and per-2,3-O-methyl- β -cyclodextrin (**17**) were prepared according to the procedures described in [3]. Per-2,3,6-O-methyl- β -cyclodextrin (**16**) was synthesized according to the method proposed by Zhou [4].

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-*tert*-butyldimethylsilyl- β -cyclodextrin (**1**)

6^A-Azido-6^A-deoxy- β -CD (5.6 g, 4.828 mmol) was dried under vacuum at 85 °C for 3 h. Then, imidazole (4.8 g, 63.7252 mmol) was added, and the mixture was dissolved in dry DMF (100 mL). The reaction mixture was stirred under argon. A portion of *tert*-butyldimethylsilyl chloride (4.8 g, 31.863 mmol), dissolved in THF (15 mL), was added dropwise to the reaction mixture. The course of the reaction was followed by TLC (EtOAc/EtOH/H₂O 30/5/4) every 15 min after 1 h since the start of the reaction. The main product has R_F = 0.6, while all spots with lower R_F represent undersilylated compounds and all spots with higher R_F indicate oversilylated compounds. The reaction was allowed to proceed for approximately 1.5 h until all undersilylated cyclodextrins had disappeared. Then, the reaction mixture was poured into cold water, and the bulky precipitate was filtered and washed several times on the frit with distilled water. The powder-like solid was put into a Petri dish and moved to a desiccator for several days. The compound was dried under a vacuum and dissolved in 50 mL of methanol under heating. Then the compound was precipitated by the addition of 200 mL of acetonitrile. The compound was filtered off, and the recrystallization process was repeated until all by-products had disappeared. After drying, we obtained 3.32 g of pure product (79% yield).

^1H -NMR (400 MHz, CDCl_3) δ =6.57-6.83 (H-O², 7H); 5.2-5.33 (H-O³, 7H); 4.88-4.98 (H-C¹, 7H); 4.01-4.09 (H-C⁴; 3.35-4.09 H-C³, H-C⁵, H-C⁴, H-C²); 0.89 (*t*-butyl-Si, 54H); 0.06 (methyl-Si, 36H). ^{13}C -NMR (100 MHz, CDCl_3) δ =101,64-102,32 (C¹); 81.16-83.16 (C²); 70.44-73.86 (C³, C⁴, C⁵); 61.38-62.62 (C^{6B,C,D,E,F,G}); 51.47 (C^{6A}); 25.78 (C-*t*-butyl-Si); -5 (C-methyl-Si); HRMS (ESI): m/z calcd for $\text{C}_{78}\text{H}_{153}\text{N}_3\text{O}_{34}\text{Si}_6+\text{Na}^+$: 1866,88 [M+Na⁺]; found: 1866.88; $[\alpha]_{\text{CHCl}_3}$ = +114.3° (the data are consistent with the literature [5]).

Fig. S1 ^1H NMR spectrum of **1** in CDCl_3 at 25 °C.

6-azido-6-deoxy-6-TBS-b-CD.1.fid

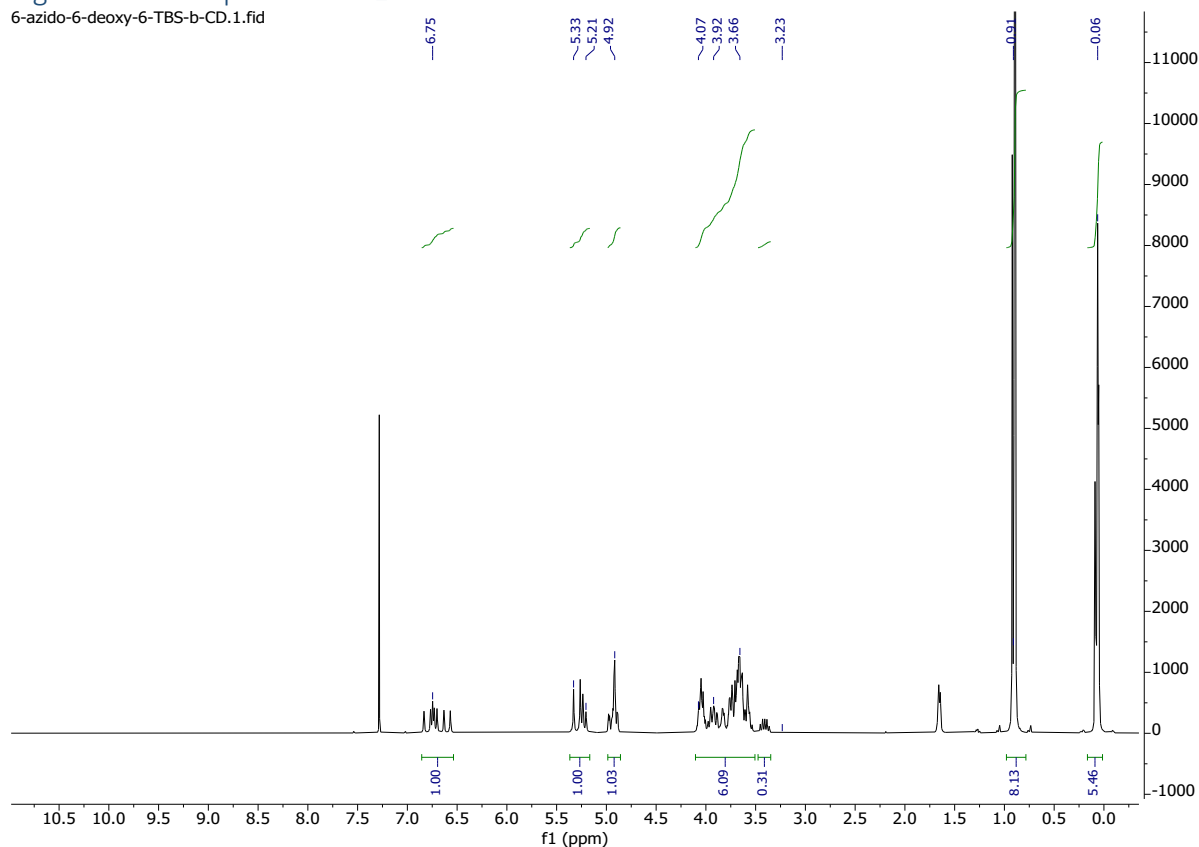


Fig. S2 DEPT- ^{13}C NMR spectrum of **1** in CDCl_3 at 25 $^\circ\text{C}$.
6-azido-6-deoxy-6-TBS-b-CD.4.fid

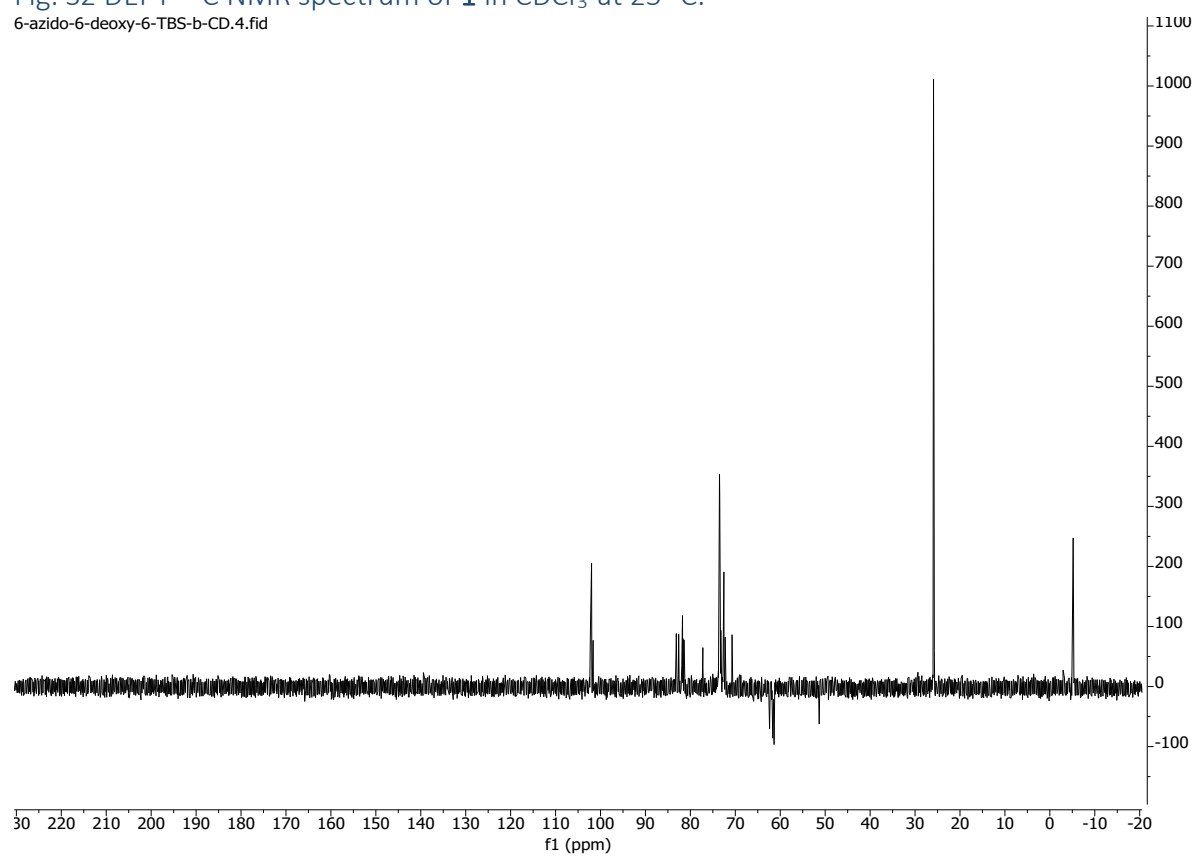


Fig. S3 COSY spectrum of **1** in CDCl₃ at 25 °C.

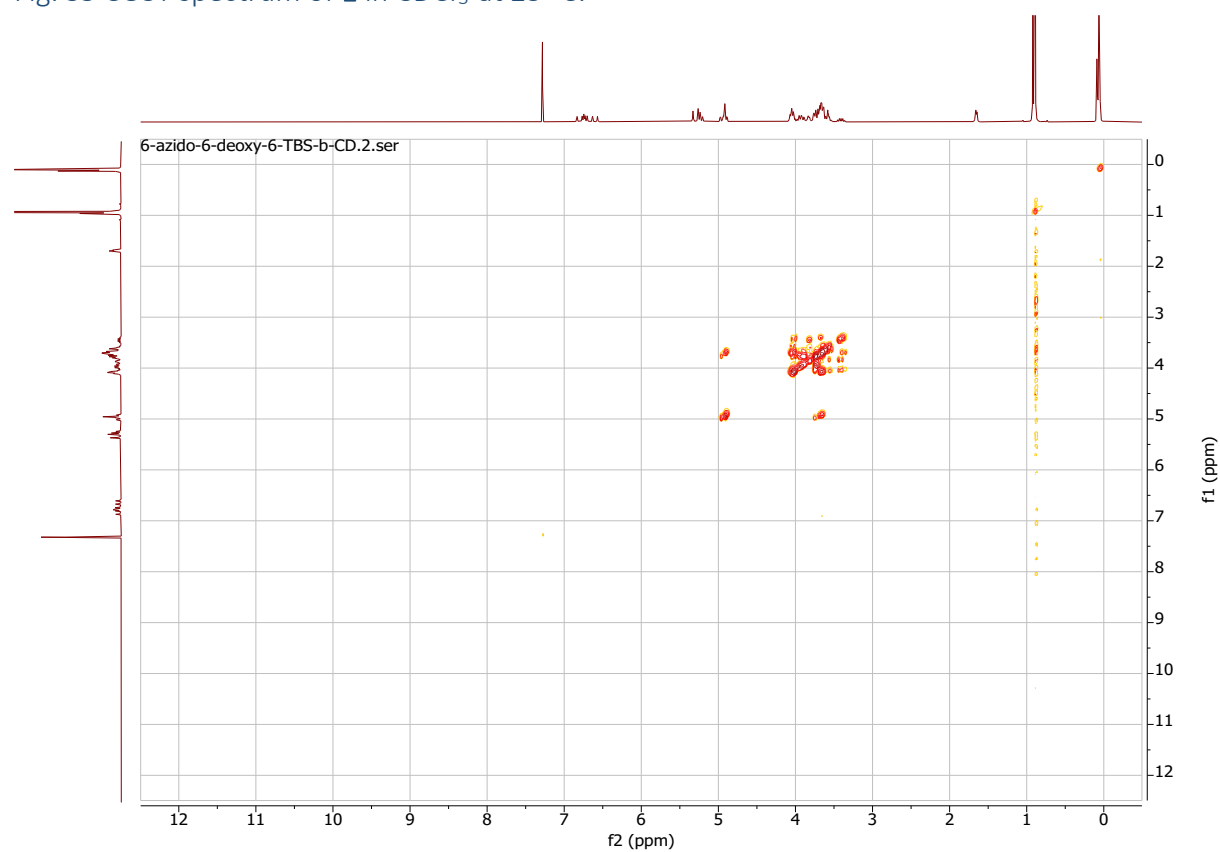


Fig. S4 HSQC spectrum of **1** in CDCl₃ at 25 °C.

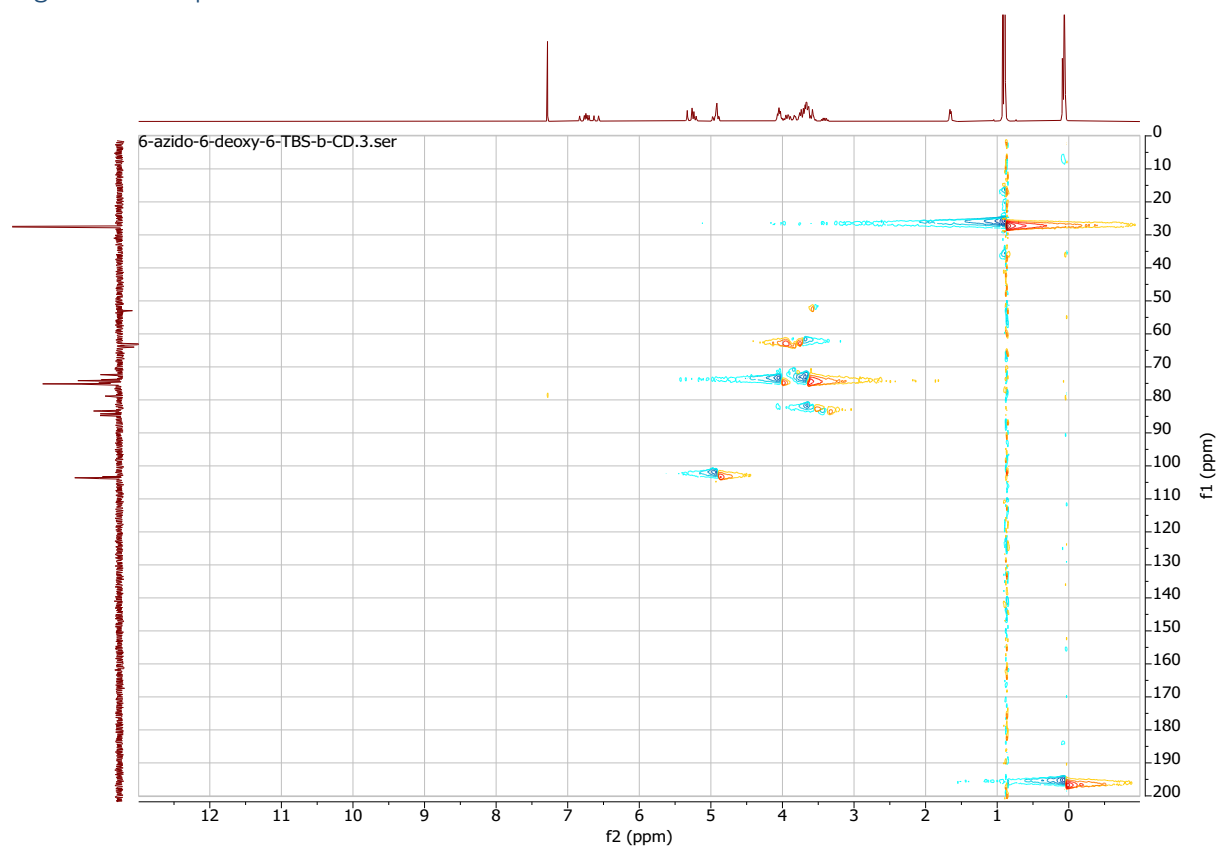


Fig. S5 IR spectrum of **1** in KBr pellet.

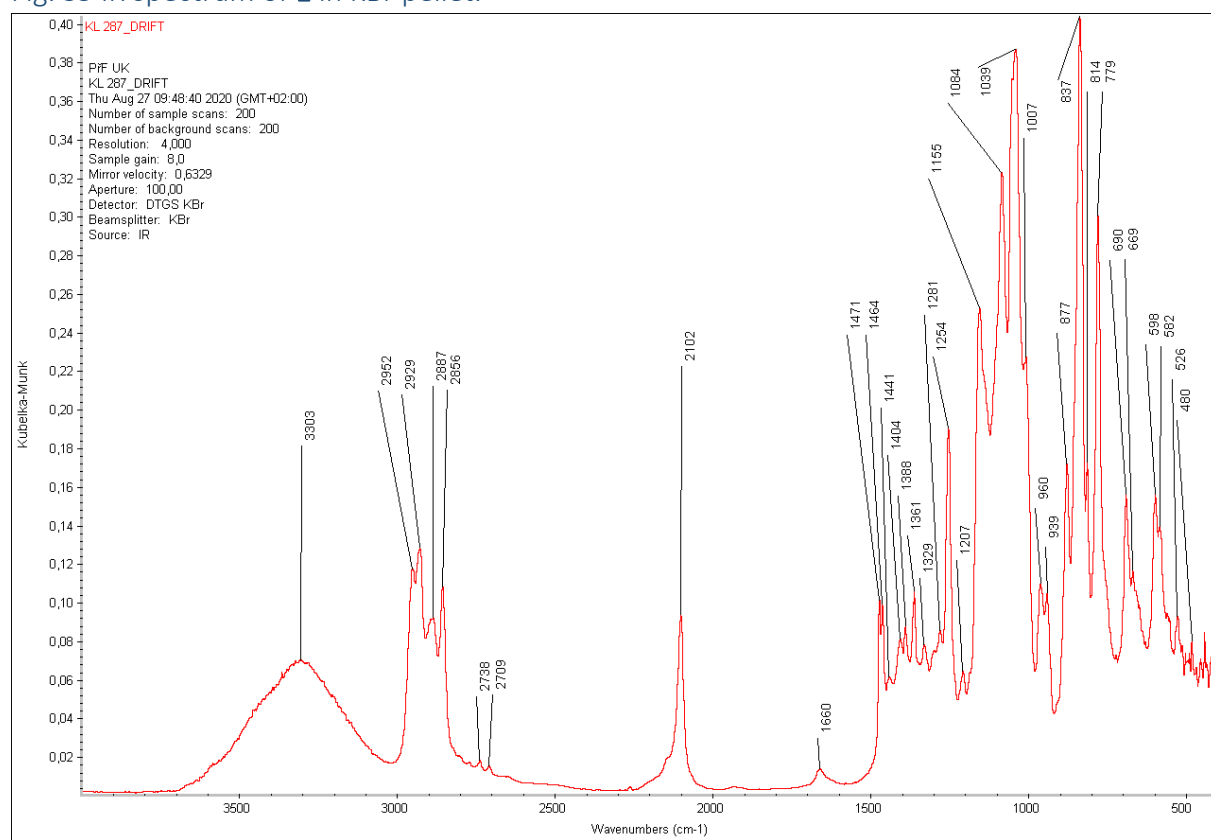
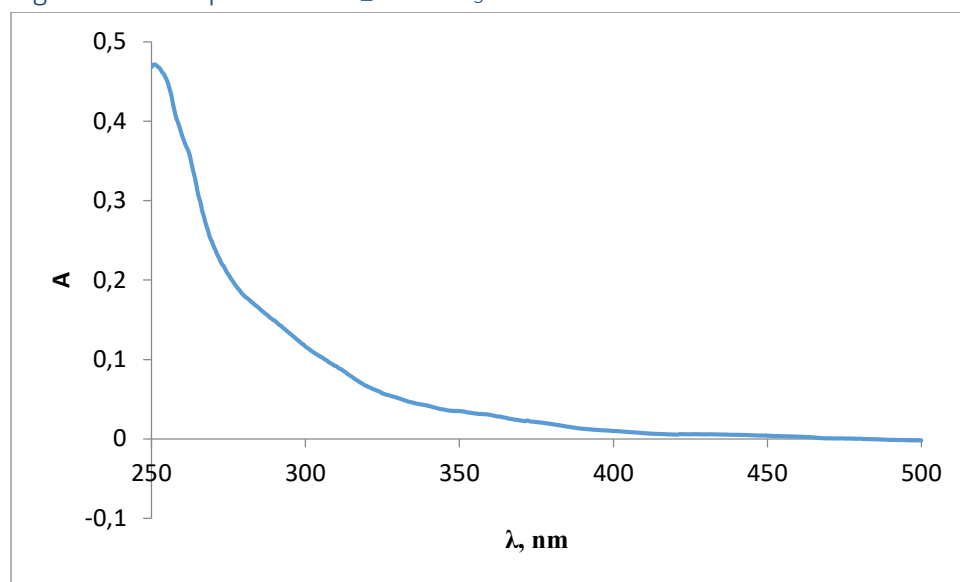


Fig. S6 UV-vis spectrum of **1** in CHCl₃.



6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O-tert*-butyldimethylsilyl-per-2,3-*O*-methyl-β-cyclodextrin (2)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O-tert*-butyldimethylsilyl-β-cyclodextrin (**1**, 3.5 g, 1.9 mmol) together with methyltriphenylphosphine bromide (0.286 g, 0.8 mmol) and ground KOH (5.32 g, 95 mmol) were dissolved in THF (84 mL). The flask was set up in a magnetic stirrer and allowed to stir for 1 h. Then methyl iodide (6.55 mL, 46.2 mmol) was added dropwise. After 2 h, an ice bath was applied to the system, and a portion of NaH (60% suspension in oil, 2.12 g, 53.2 mmol) was added slowly to the reaction mixture. After 1 h, the ice bath was removed, and the reaction continued at room temperature overnight. A portion of methanol (2 mL) was added to quench the reaction, and then all solids were filtered off. The filtrate was dried and moved to a column (50 g silica gel). An elution started with a hexane/ethyl acetate 4/1 mixture and switched to a 5/2 mixture when TLC indicated the presence of the product. The extraction from the column gave 3.3 g of the product (85% yield).

¹H-NMR (400 MHz, CDCl₃) δ=5.10-5.24 (H-C¹, 7H); 4.07-4.19 (H-C^{6B,C,D,E,F,G}, 6H); 3.47-3.88 (H-C³, H-C⁴; H-C⁵, Me-O-C²; Me-O-C³, H-C^{6A}); 3.05-3.20 (H-C², 7H); 0.91 (*t*-butyl-Si, 54H); 0.01 (methyl-Si, 36H); ¹³C-NMR (100 MHz, CDCl₃) δ=98.31-99.21 (C¹); 77.15-82.78 (C², C³, C⁴); 71.00, 72.43 (C⁵); 61.86-63.00 (C^{6B,C,D,E,F,G}); 61.55 (Me-O-C²); 58.63 (MeO-C³); 51.88 (C^{6A}); 68.00 (*t*-Bu-Si); -5.36 (Me-Si). HRMS (ESI): *m/z* calcd for C₉₁H₁₇₉N₃O₃₄Si₆+Na⁺: 2063.10 [M+Na⁺] found: 2063.10. [α]_D²⁰CHCl₃= +108,3° (the data are consistent with the literature [5]).

Fig. S7 ^1H NMR spectrum of **2** in CDCl_3 at 25 $^\circ\text{C}$.

6-azido-6-deoxy-6-TBS-2,3-permethyl-beta-CD.1.fid

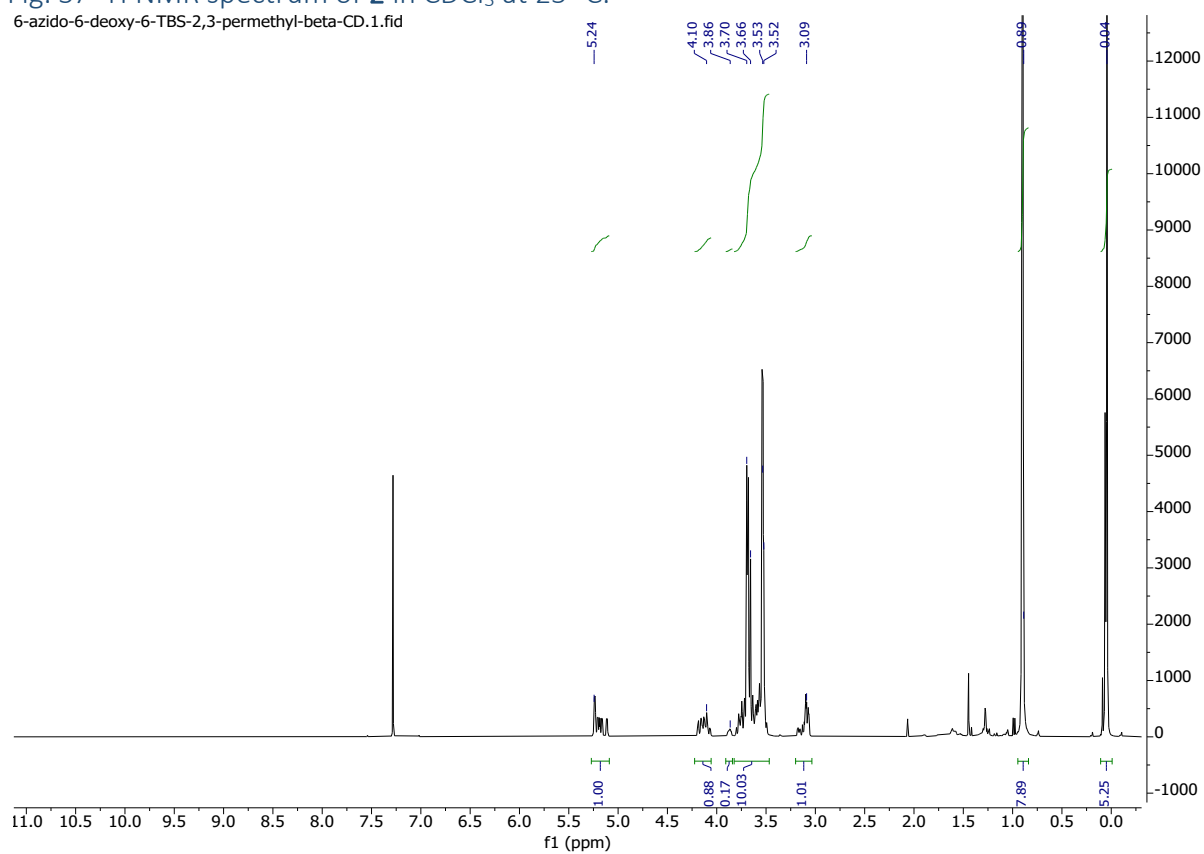


Fig. S8 DEPT- ^{13}C NMR spectrum of **2** in CDCl_3 at 25 $^\circ\text{C}$.
6-azido-6-deoxy-6-TBS-2,3-permethyl-beta-CD.2.fid

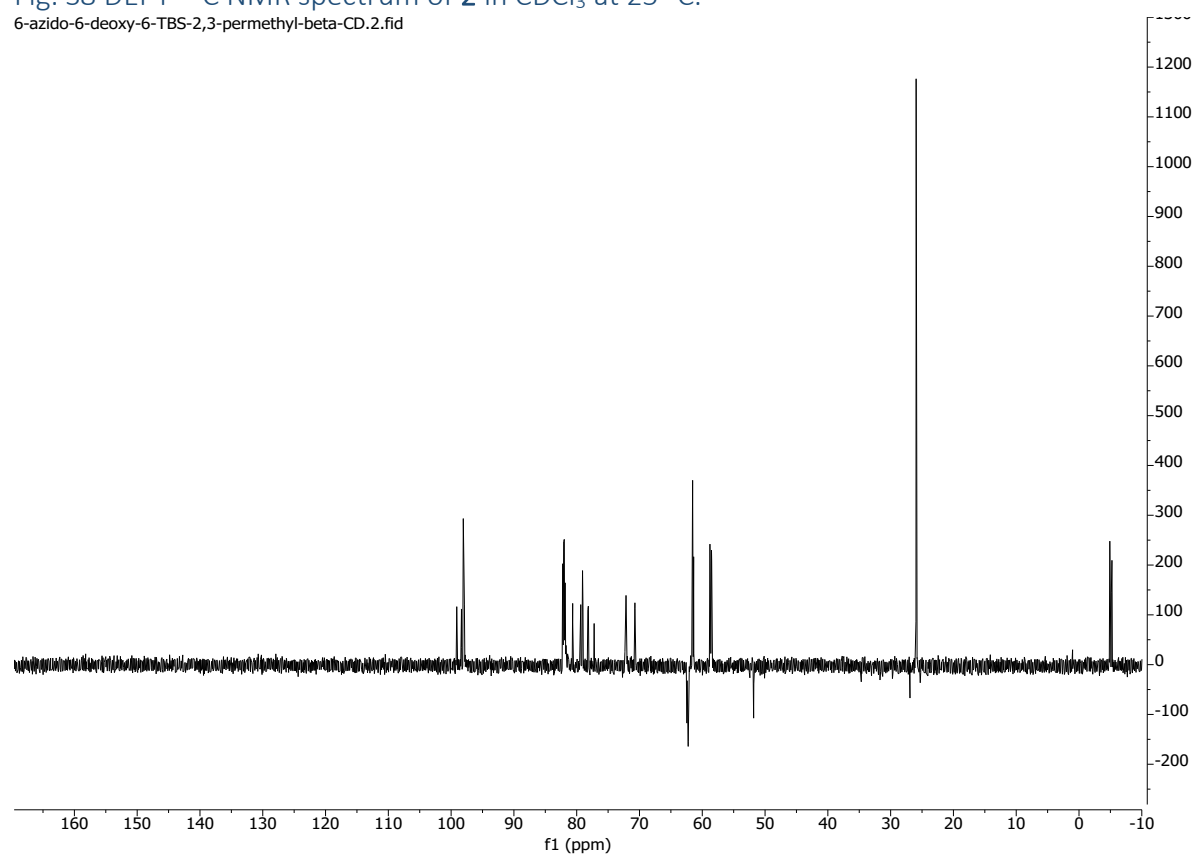


Fig. S9 COSY spectrum of **2** in CDCl₃ at 25 °C.

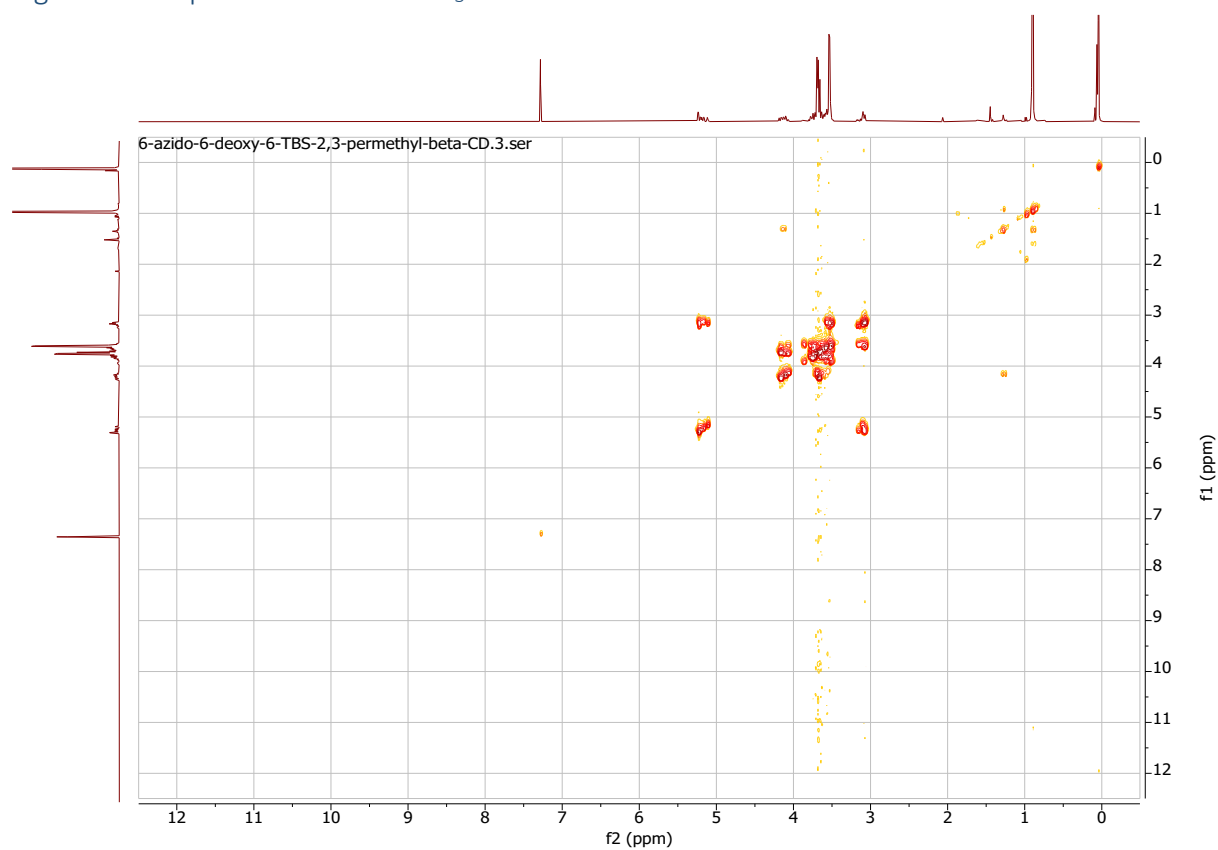


Fig. S10 HSQC spectrum of **2** in CDCl₃ at 25 °C.

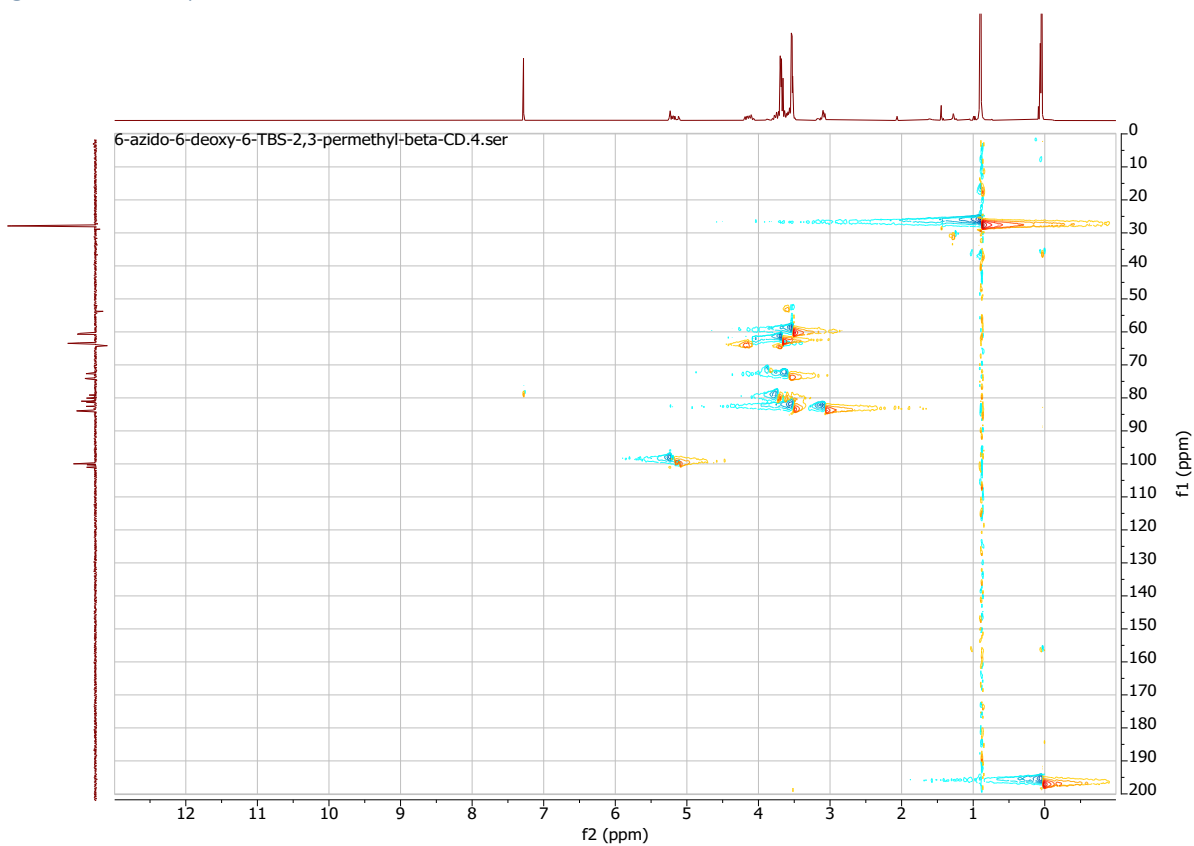


Fig. S11 IR spectrum of **2** in KBr pellet.

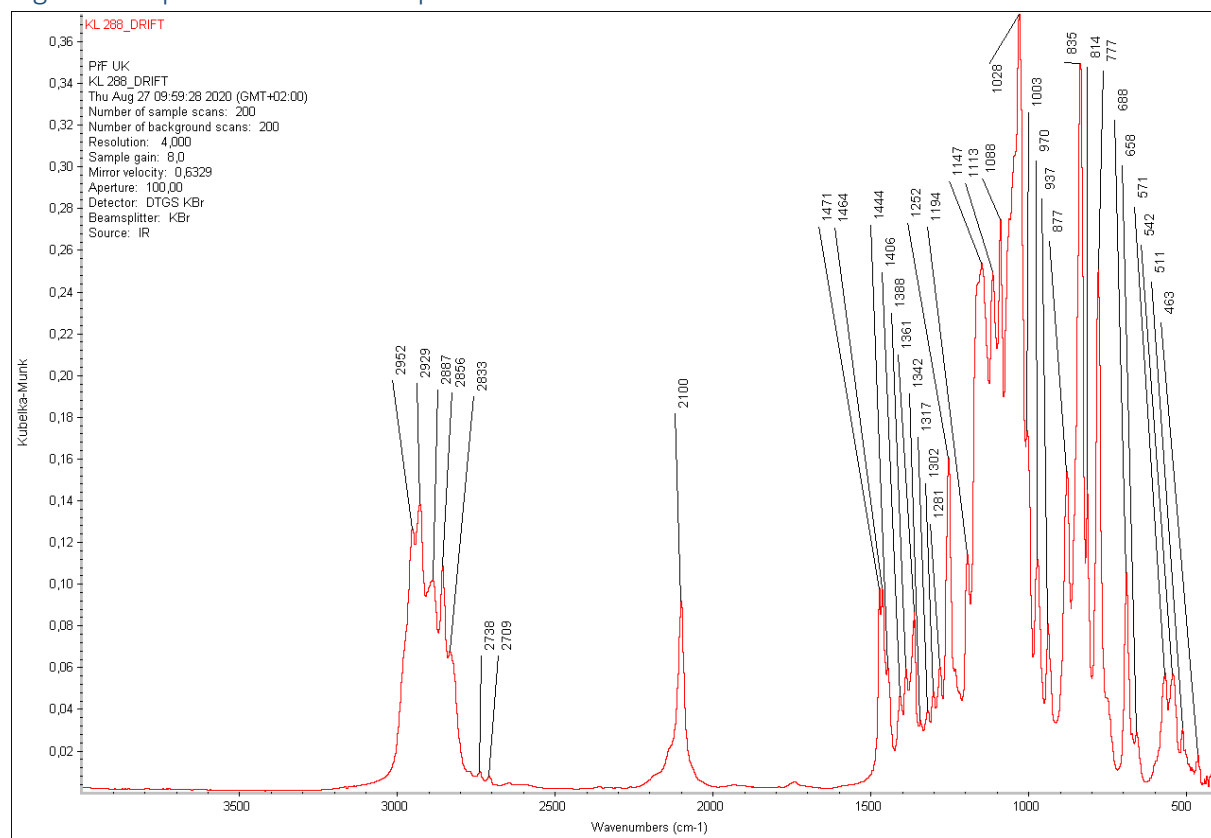
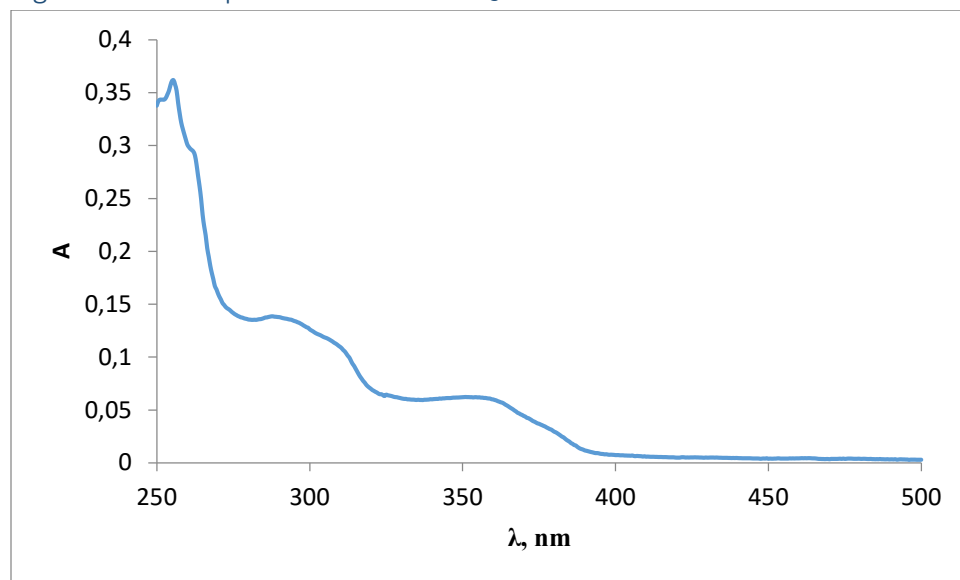


Fig. S12 UV-vis spectrum of **2** in CHCl₃.



6^A-Azido-6^A-deoxy-per-2,3-*O*-methyl-β-cyclodextrin (**3**)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O*-*tert*-butyldimethylsilyl-per-2,3-*O*-methyl-β-cyclodextrin (**2**, 1.4 g, 0.686 mmol) together with NH₄F (1.37 g, 37 mmol) were dissolved in methanol (40 mL) in a small flask. The flask with the mixture was set in a magnetic stirrer and refluxed overnight. After, the compound was dried, dissolved in chloroform and moved to a silica gel column (50 g). The mixture of chloroform/methanol 8/1 was used to wash out the main product (0.81 g; 87% yield) from the column.

¹H-NMR (400 MHz, CDCl₃) δ=5.0-5.21 (H-C¹, 7H); 4.3-4.64 (HO-C⁶, 6H); 3.25-4.01 (H-C⁶, H-C⁵, Me-O-C², H-C⁴, Me-O-C³, H-C³); 3.15-3.23 (H-C², 7H). ¹³C-NMR (100 MHz, CDCl₃) δ=98.23-99.41 (C¹); 78.93-82.36 (C², C³, C⁴); 71.00-72.48 (C⁵); 61.75, 61.41, 61.22 (C^{6B,C,D,E,F,G}); 60.00-61.55 (Me-O-C³); 58.31-59.19 (Me-O-C²); 51.54 (C^{6A}). HRMS (ESI): *m/z* calcd for C₅₅H₉₇N₃O₃₄+H⁺: 1356.6 [M+H⁺] found: 1356.60078. [α]_DCHCl₃= +140.8° (the data are consistent with the literature [5]).

Fig. S13 ^1H NMR spectrum of **3** in CDCl_3 at 25 $^\circ\text{C}$.

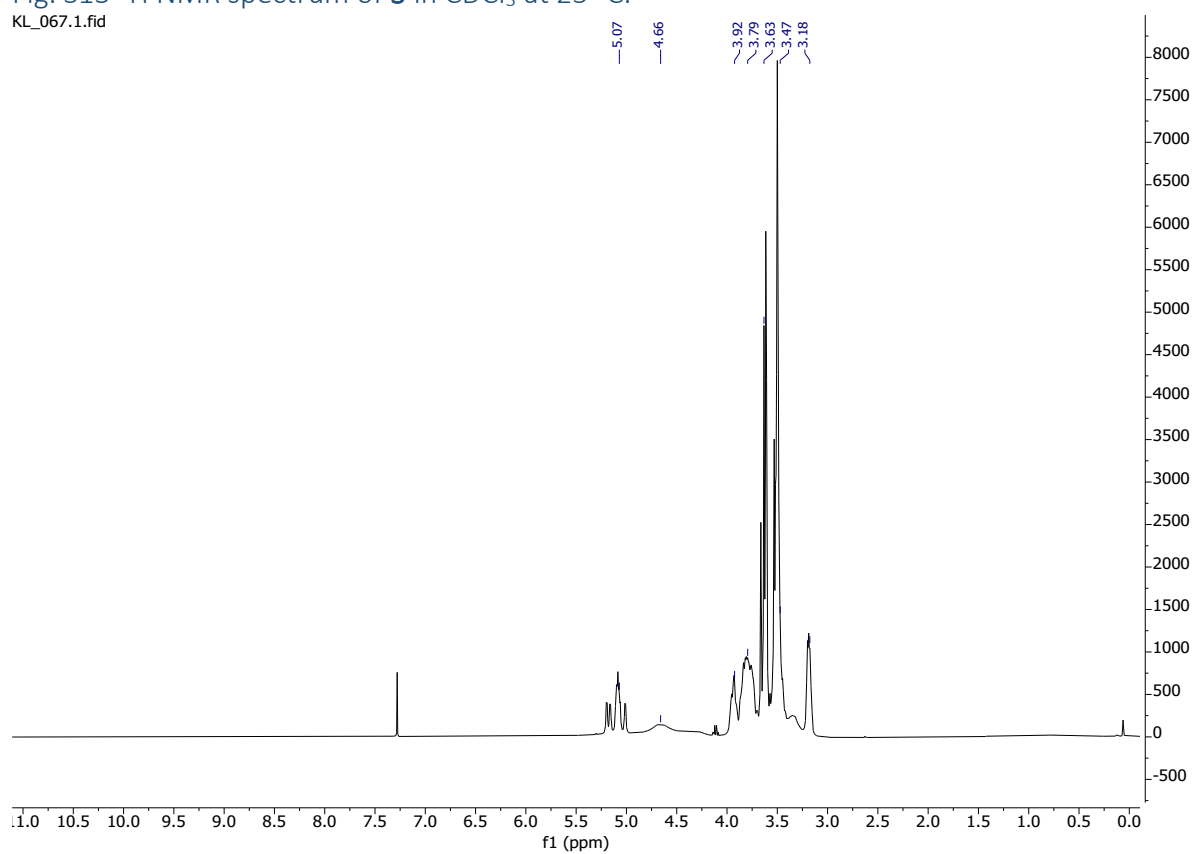


Fig. S14 DEPT- ^{13}C NMR spectrum of **3** in CDCl_3 at 25 $^\circ\text{C}$.
KL_067.2.fid

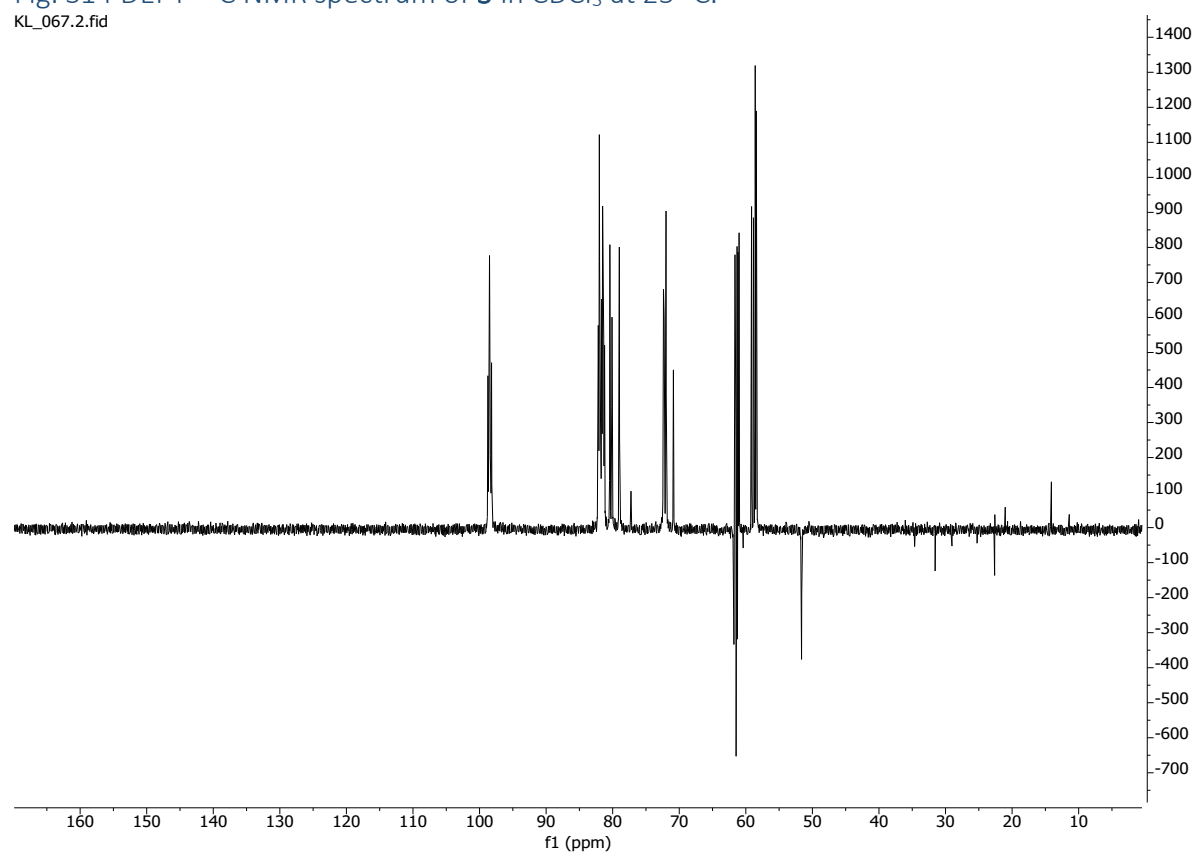


Fig. S15 COSY spectrum of **3** in CDCl₃ at 25 °C.

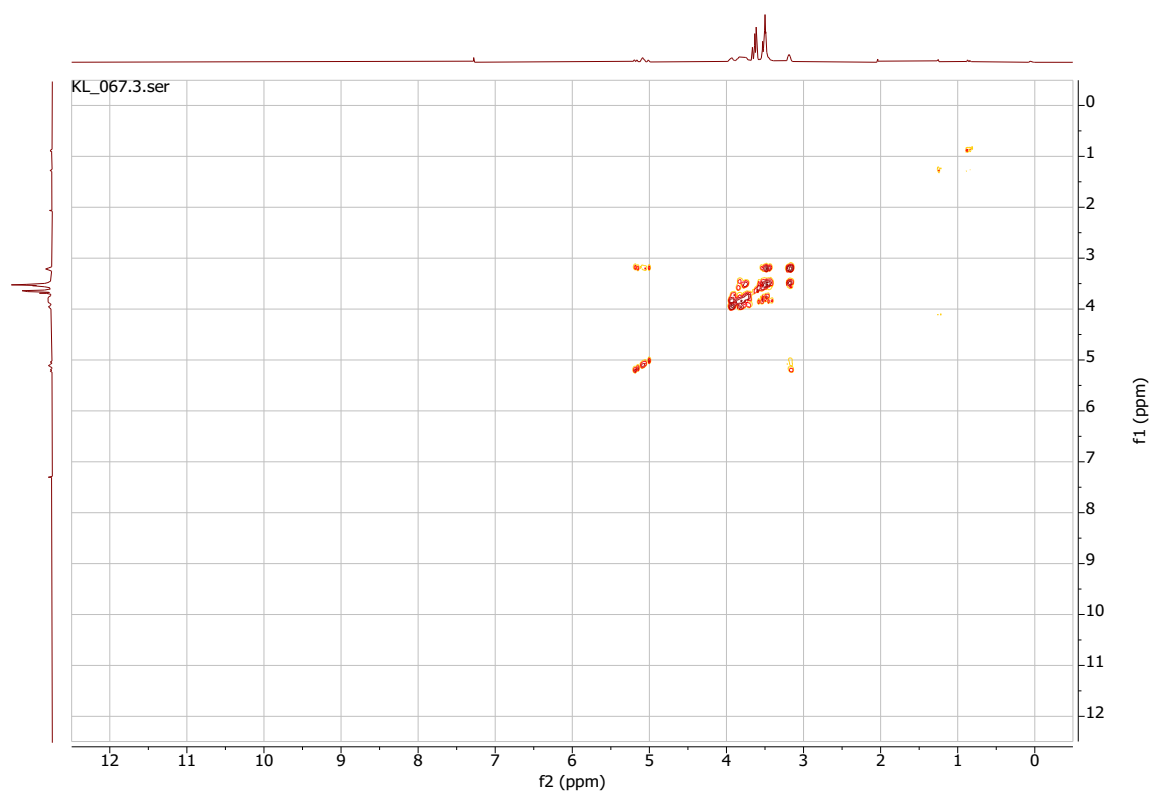


Fig. S16 HSQC spectrum of **3** in CDCl₃ at 25 °C.

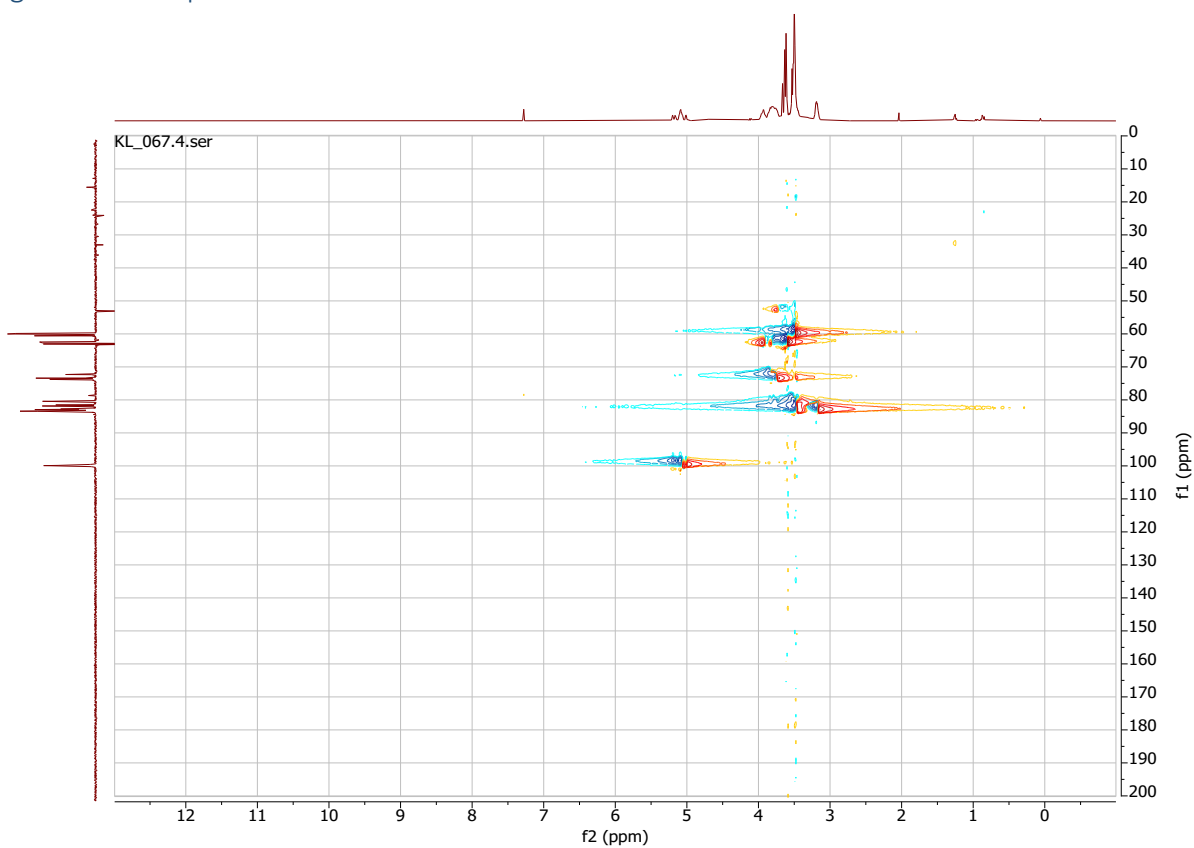


Fig. S17 IR spectrum of **3** in KBr pellet.

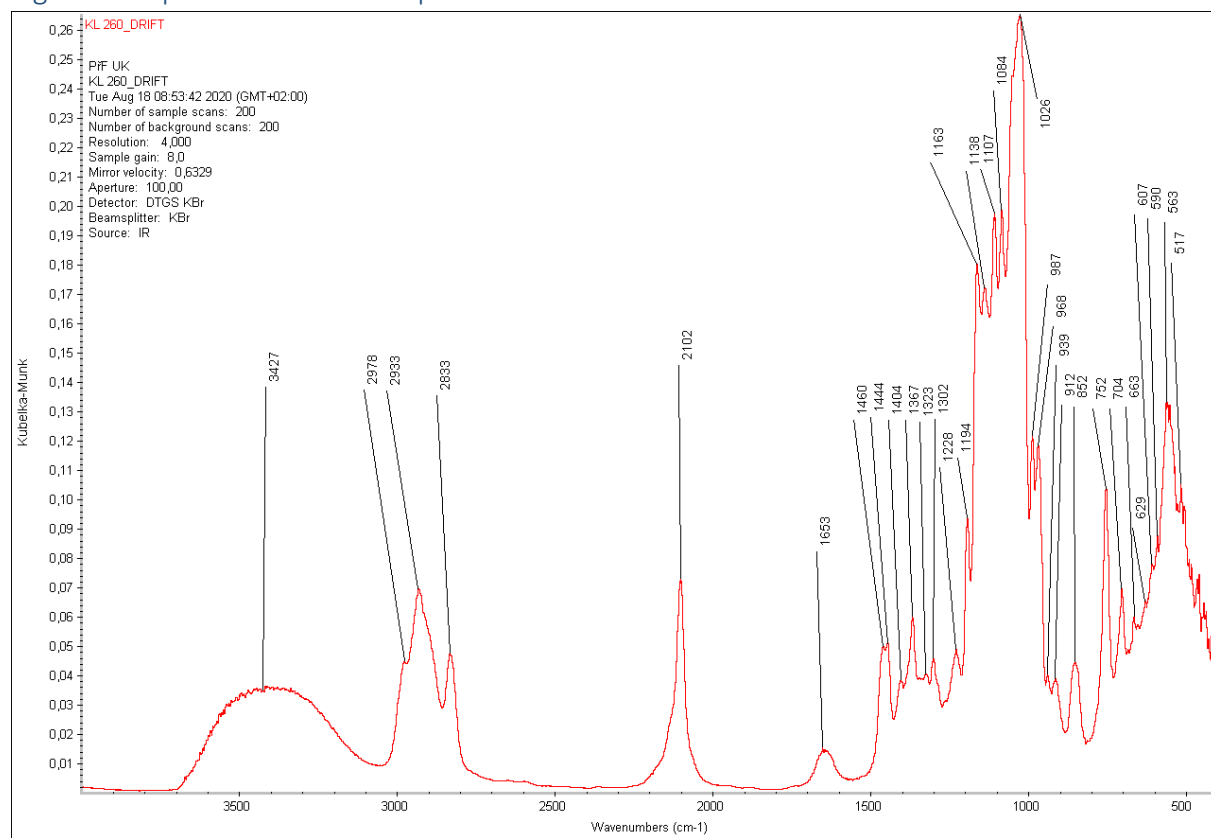
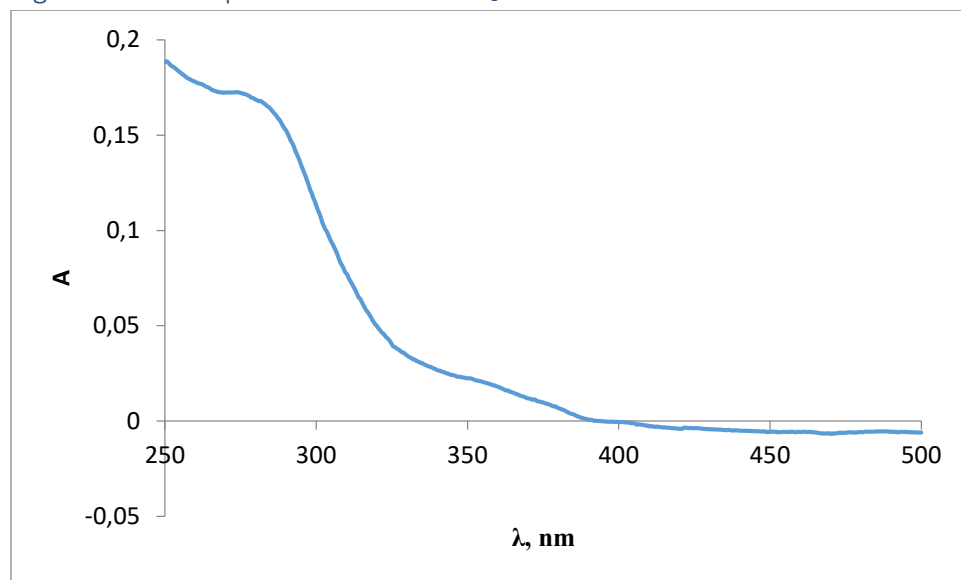


Fig. S18 UV-vis spectrum of **3** in CHCl₃.



Bis-1,3-[1-(6^A-deoxy-2,3-per-*O*-methyl- β -cyclodextrin-6^A-C-yl)-1,2,3-triazol-4-yl]methoxymethylene (**4**)

6^A-Azido-6^A-deoxy-per-2,3-*O*-methyl- β -cyclodextrin (**3**, 1.00 g; 0.7377 mmol) was dissolved in DMF (25 mL), and the solution was bubbled by argon for 30 minutes. Then, portions of 0.5 M propargyl ether solution in DMF (0.664 mL; 0.332 mmol), copper sulfate hydrate (0.184 g; 0.7377 mmol), and sodium ascorbate (0.142 g; 0.7377 mmol) were added to the reaction mixture, and the reaction was allowed at the room temperature overnight. The solvent was removed in vacuo at 90 °C, and a column chromatography (30 g silica gel) with acetonitrile/water/conc. aq. NH₃ 12/1/1 gave 0.78 g of the desirable product (84% yield).

¹H-NMR (400 MHz, D₂O) δ =8.0 (s, H-triazole 2H); 5.09-5.35 (H-C¹, 14H); 5.04, 4.57 (H-C^{6A}, 4H); 4.67 (s, -CH₂-triazole, 4H); 4.20 (H-C^{5A}, 2H); 2.97-3.97 (H-C^{6B,C,D,E,F,G}; H-C^{5B,C,D,E,F,G}; Me-O-C²; H-C⁴; Me-O-C³; H-C³; H-C²). ¹³C-NMR (100 MHz, D₂O) δ =126.85 (C-triazole); 96.77-97.66 (C¹); 70.24-81.44 (C², C³, C⁴, C⁵); 63.97, 60.53 (C^{6B,C,D,E,F,G}); 62.84 (-CH₂-triazole); 51.71 (C^{6A}). HRMS (ESI): *m/z* calcd for C₁₁₈H₂₀₀N₆O₆₉+2H⁺: 1404.13 [M+2H⁺] found: 1404.12527. $[\alpha]_{\text{CHCl}_3}$ = +159.4°.

Fig. S19 ^1H -NMR spectrum of **4** in D_2O at 25 $^\circ\text{C}$.

KL_189_b.1.fid

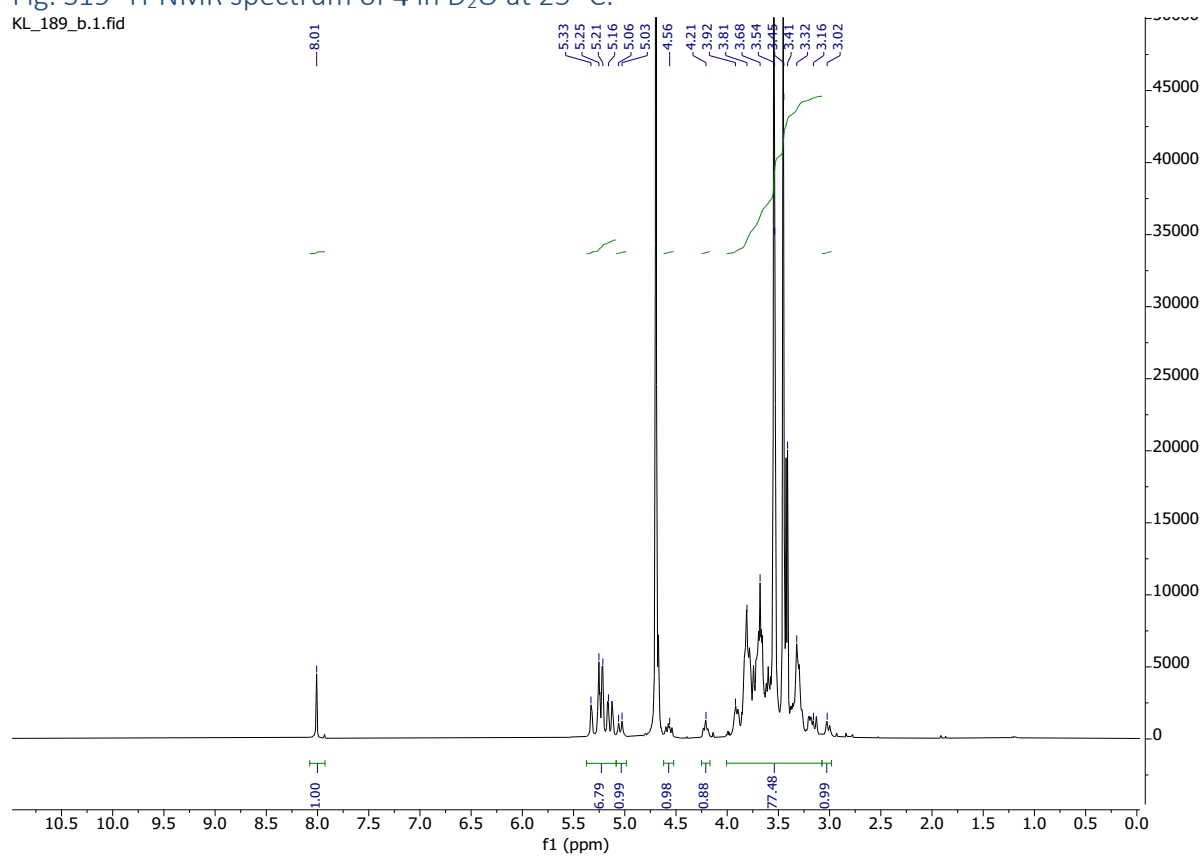


Fig. S20 DEPT- ^{13}C -NMR spectrum of **4** in D_2O at 25 °C.

KL_189_b/carbon_13

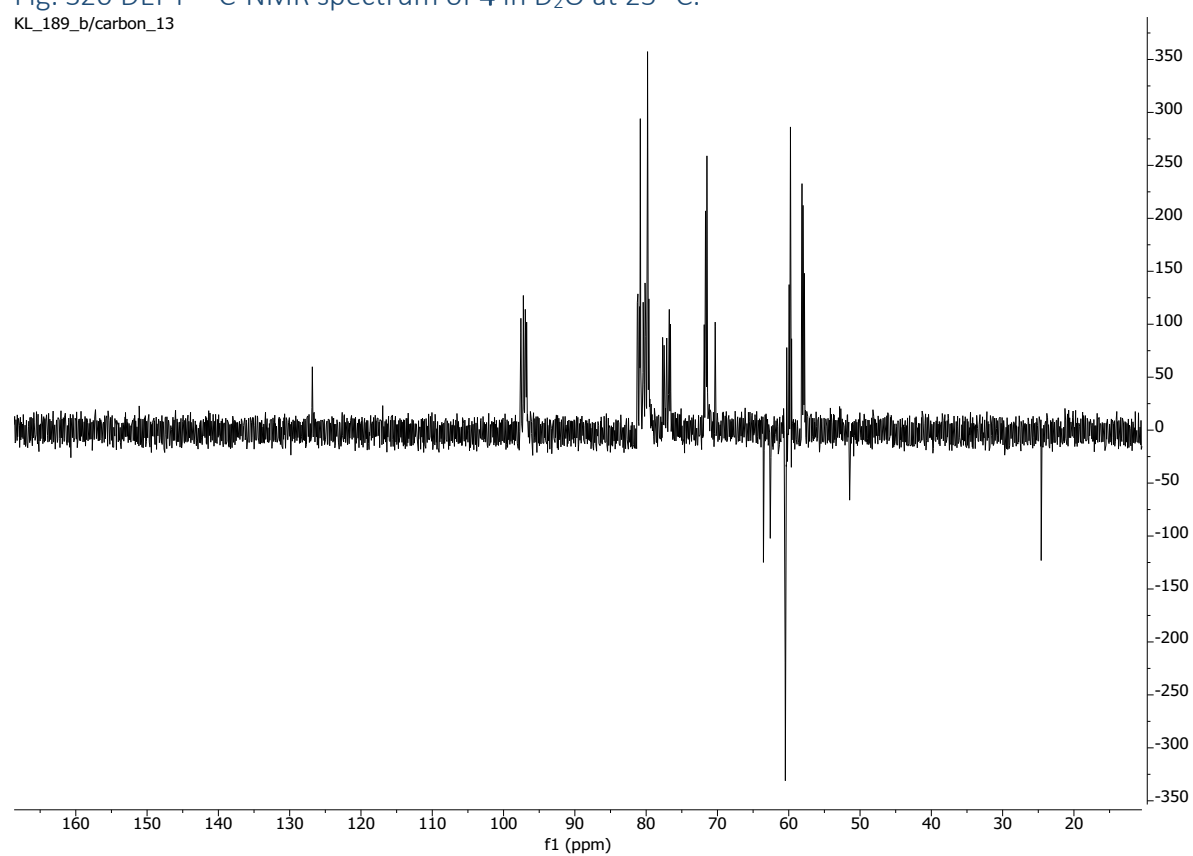


Fig. S21 COSY spectrum of **4** in D₂O at 25 °C.

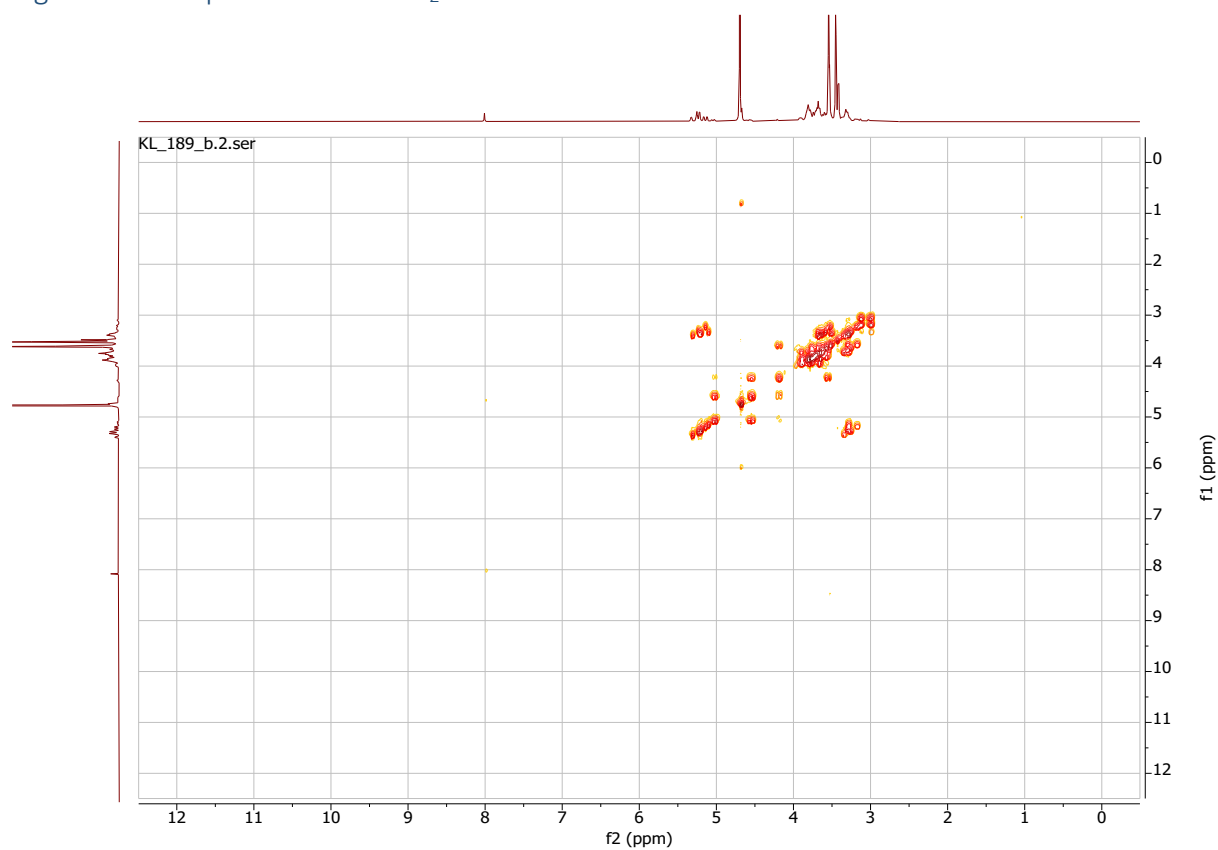


Fig. S22 HSQC spectrum of **4** in D₂O at 25 °C.

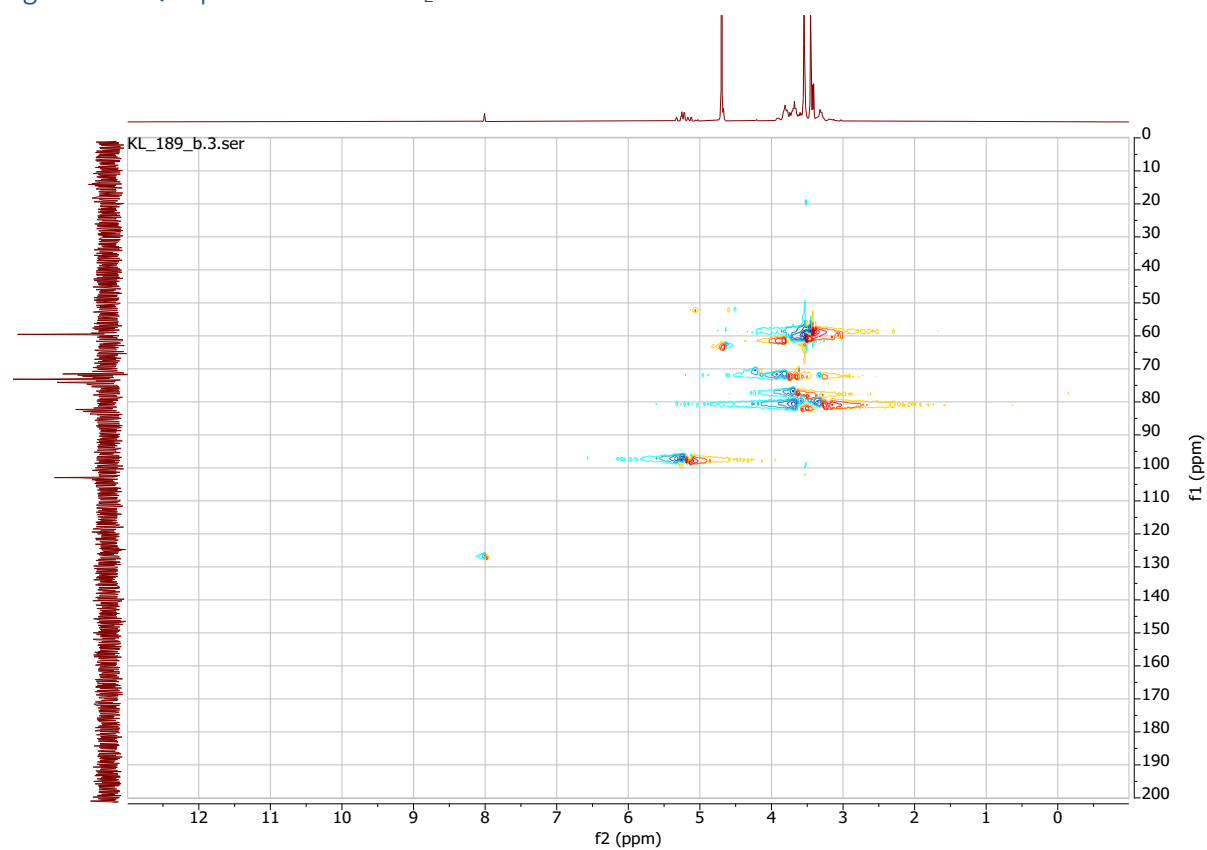


Fig. S23 NOESY spectrum of **4** in D₂O at 25 °C.

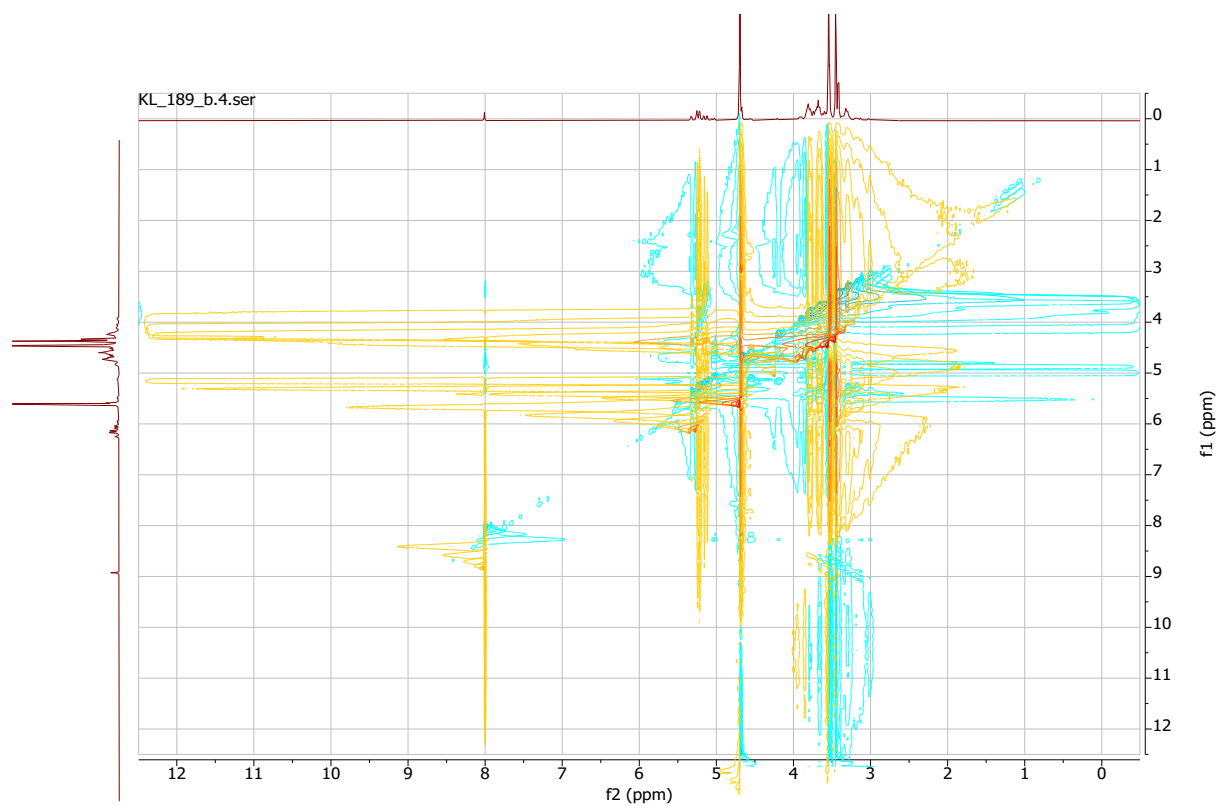


Fig. S24 IR spectrum of **4** in KBr pellet.

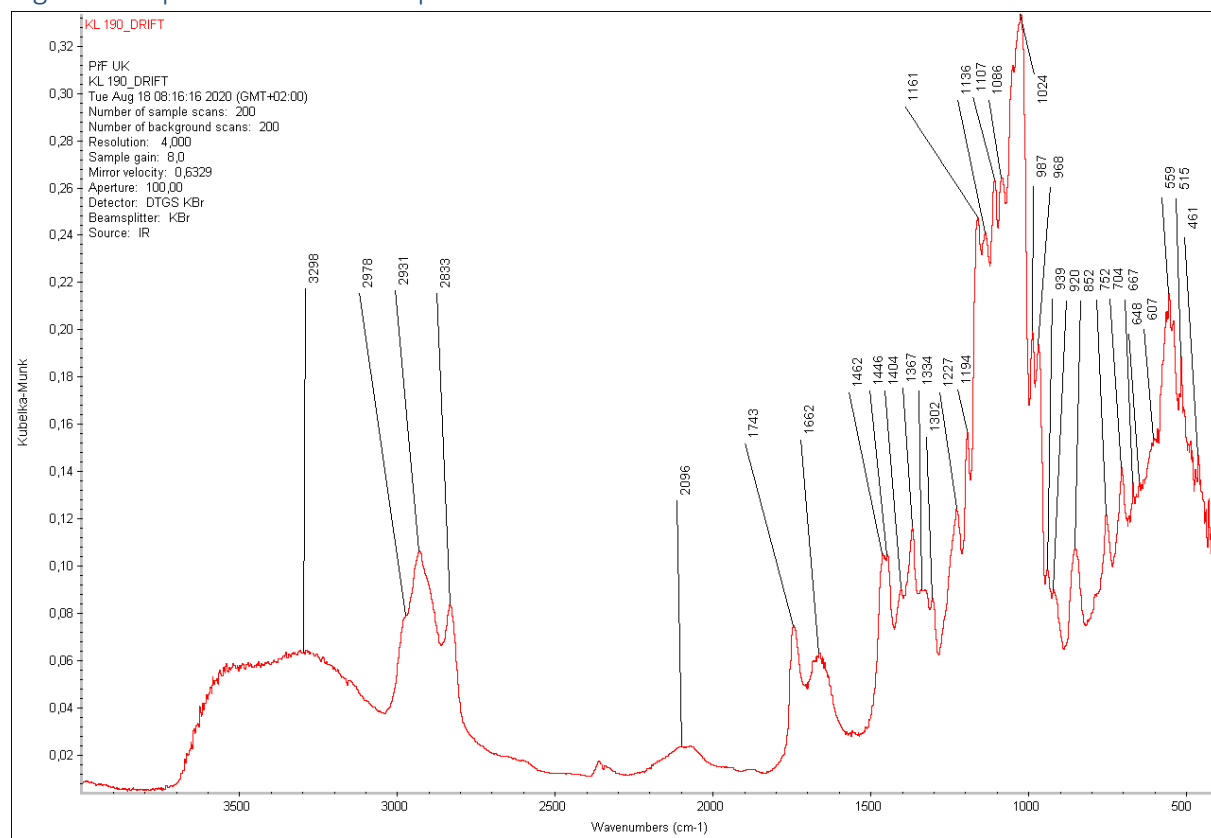
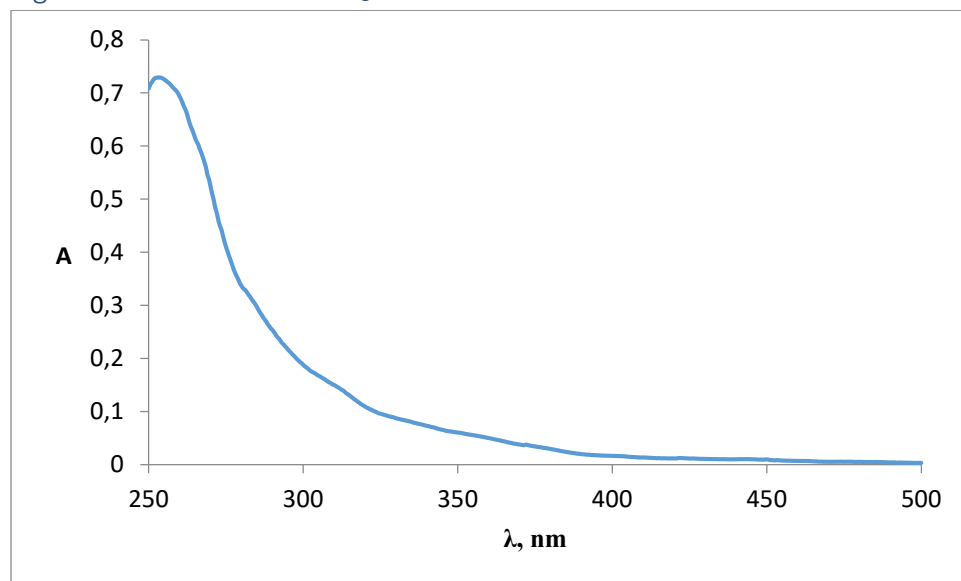


Fig. S25 UV-vis of **4** in CHCl₃.



N,N'- Bis(6^A-deoxy-2,3-per-*O*-methyl-β-cyclodextrin-6^A-C-yl)urea (**5**).

6^A-Azido-6^A-deoxy-per-2,3-*O*-methyl-β-cyclodextrin (**3**, 0.91 g; 0.67 mmol) together with triphenylphosphine (0.265 g; 1.01 mmol) were dissolved in dry DMF (19 mL). The reaction mixture was bubbled with dry CO₂ overnight. Then all solvent was distilled off under vacuum, and the residue was purified by column chromatography with acetonitrile/water/conc. aq NH₃ 12/1/1 (0.49 g; 54% yield).

¹H-NMR (400 MHz, D₂O) δ=5.21 (H-C¹, 14H); 3.22-3.88 (H-C², H-C³, H-C⁴, H-C⁵, H-C⁶); 3.53 (s, Me-O-C²), 3.43 (s, Me-O-C³). ¹³C-NMR (100 MHz, D₂O) δ=97.40 (C¹); 81.14 (C³); 77.34 (C⁴); 71.76 (C⁵); 60.04 (Me-O-C²); 60.62 (C⁶); 58.30 (Me-O-C³). HRMS (ESI): *m/z* calcd for C₁₁₃H₁₉₆N₂O₆₉+2H⁺: 1344.10 [M+2H⁺] found: 1344.096; [α]_DCHCl₃= +155.4°.

Fig. S26 ¹H-NMR spectrum of **5** in D₂O at 25 °C.

KL_222_2_D2O.1.fid

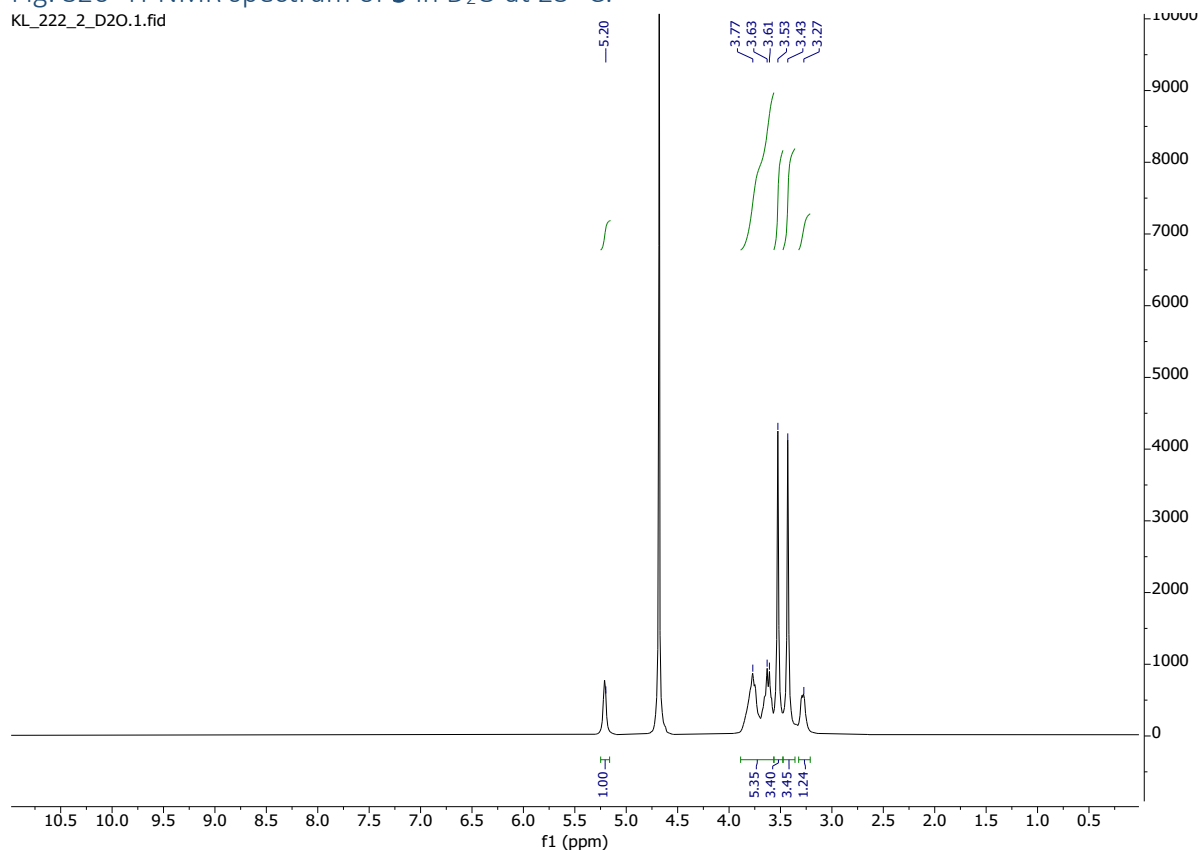


Fig. S27 DEPT- ^{13}C -NMR spectrum of **5** in D_2O at 25 °C.

KL_222_2_D2O.4.fid

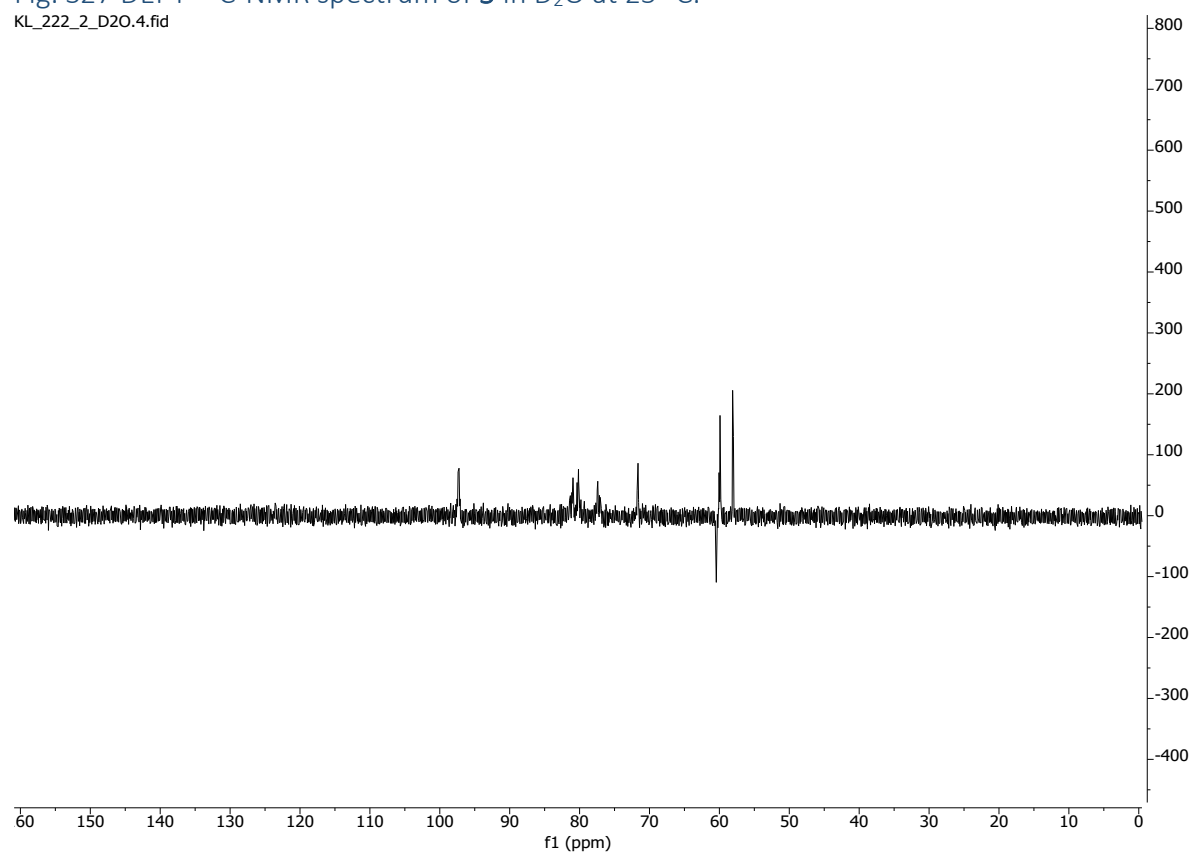


Fig. S28 COSY spectrum of **5** in D₂O at 25 °C.

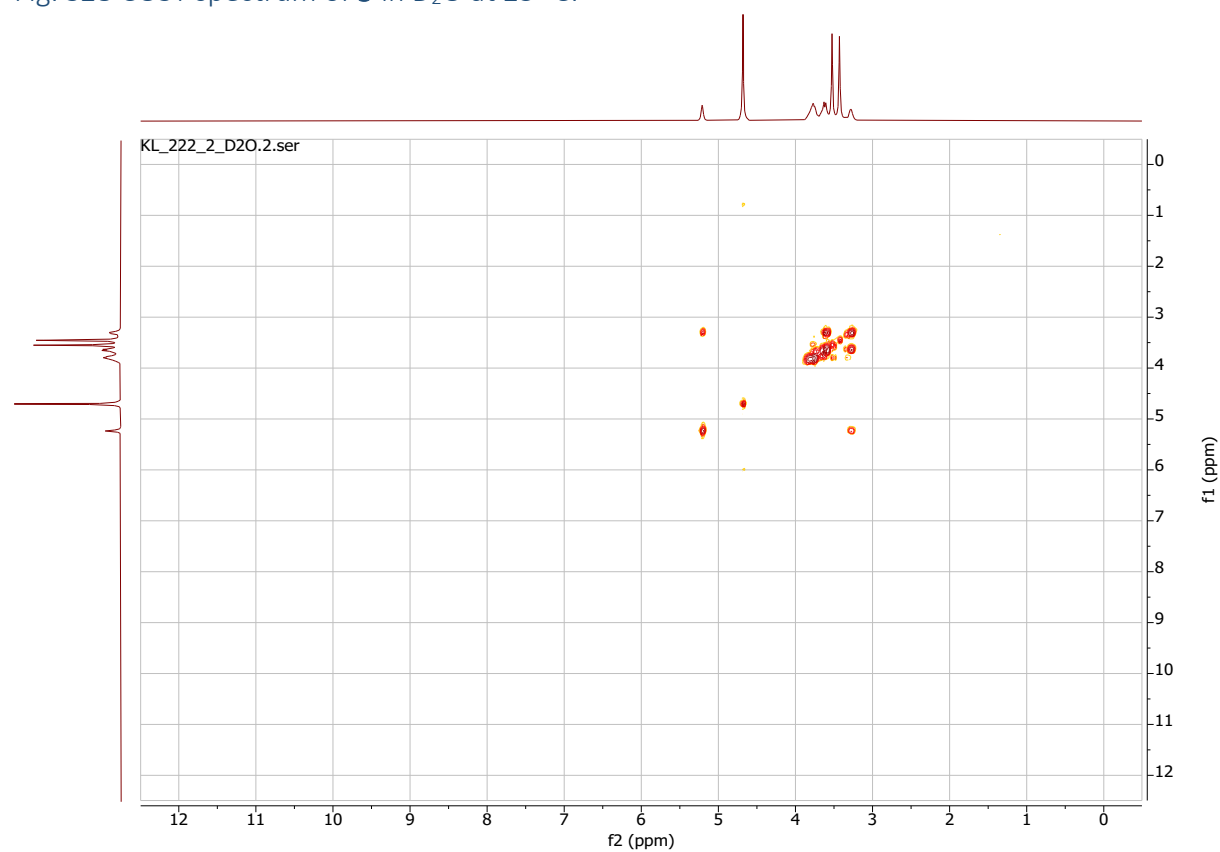


Fig. S30 IR spectrum of **5** in KBr pellet.

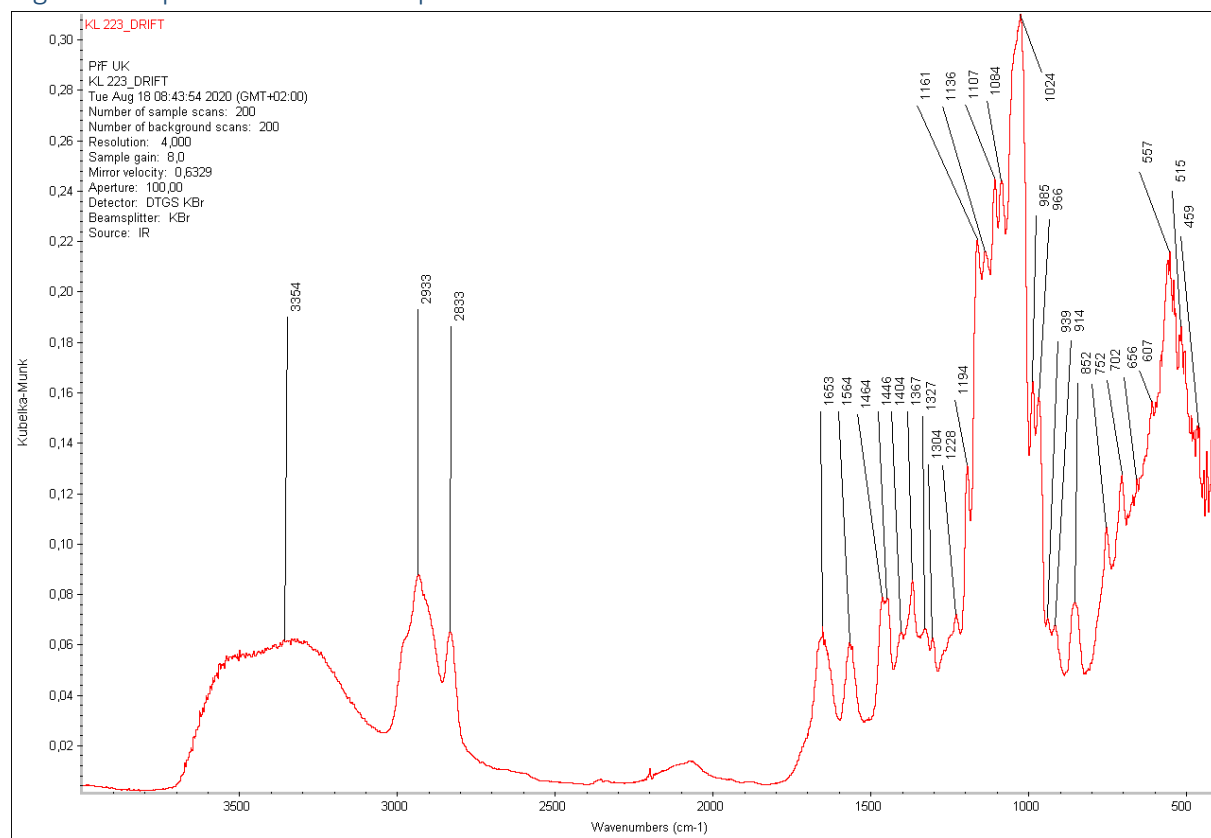
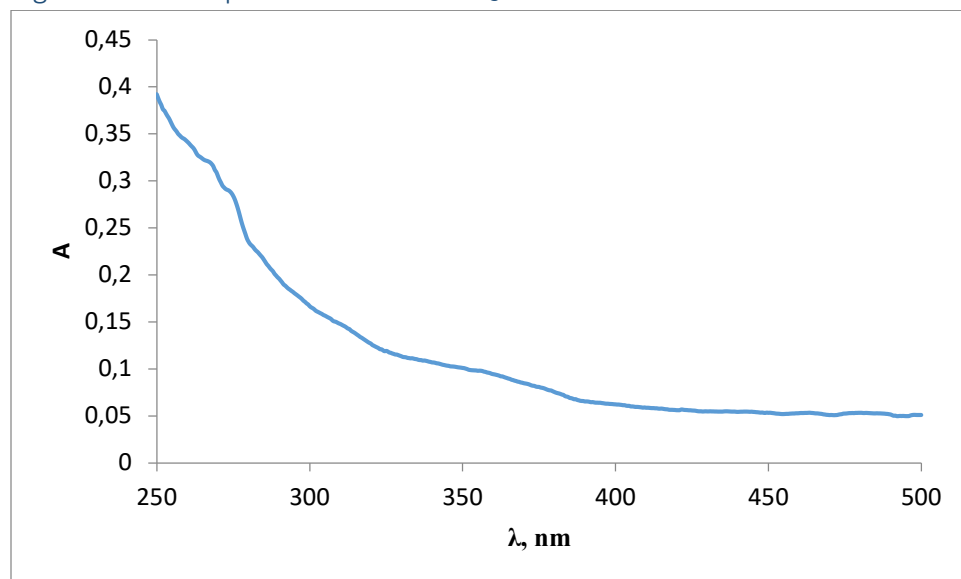


Fig. S31 UV-vis spectrum of **5** in CHCl₃.



6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O*-*tert*-butyl-dimethylsilyl-per-2,3-*O*-acetyl-β-cyclodextrin (**6**)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O*-*tert*-butyldimethylsilyl-β-cyclodextrin (**1**, 1.27 g, 0.6887 mmol) was dissolved in pyridine/acetic anhydride 2/1 mixture (25 mL). The reaction mixture was allowed to stir at 80 °C overnight. After this, the reaction mixture was diluted by chloroform and washed in a dropping funnel successively with 1 M hydrochloric acid, saturated NaHCO₃ solution, and brine (all 50 mL). Drying of the organic part gave the pure compound (1.64 g; 97% yield).

¹H-NMR (400 MHz, CDCl₃) δ=5.27-5.45 (H-C³, 7H); 5.11-5.21 (H-C¹, 7H), 3.50-4.27 (H-C²; H-C⁶; H-C⁴; H-C⁵); 2.0-2.13 (Me-C(O), 42H); 0.84-0.94 (t-Bu-Si, 54H); 0.04-0.09 (Me-Si, 36H). ¹³C-NMR (100 MHz, CDCl₃) δ=95.96-97.36 (C¹); 74.9-77.12 (C⁴); 70.33-72.31 (C³, C², C⁵); 61.42-62.18 (C^{6B,C,D,E,F,G}); 51.49 (C^{6A}); 25.87 (t-Bu-Si); 20.91 (Me-C(O)); -5.67 (Me-Si). HRMS (ESI): *m/z* calcd for C₁₀₆H₁₈₁N₃O₄₈Si₆+Na⁺: 2455.03 [M+Na⁺]; found: 2455.04. [α]_{CHCl₃} = +90°.

Fig. S32 ^1H -NMR spectrum of **6** in CDCl_3 at 25 $^\circ\text{C}$.

6-azido-6-deoxy-6-TBS-2,3-peracetyl-b-CD.1.fid

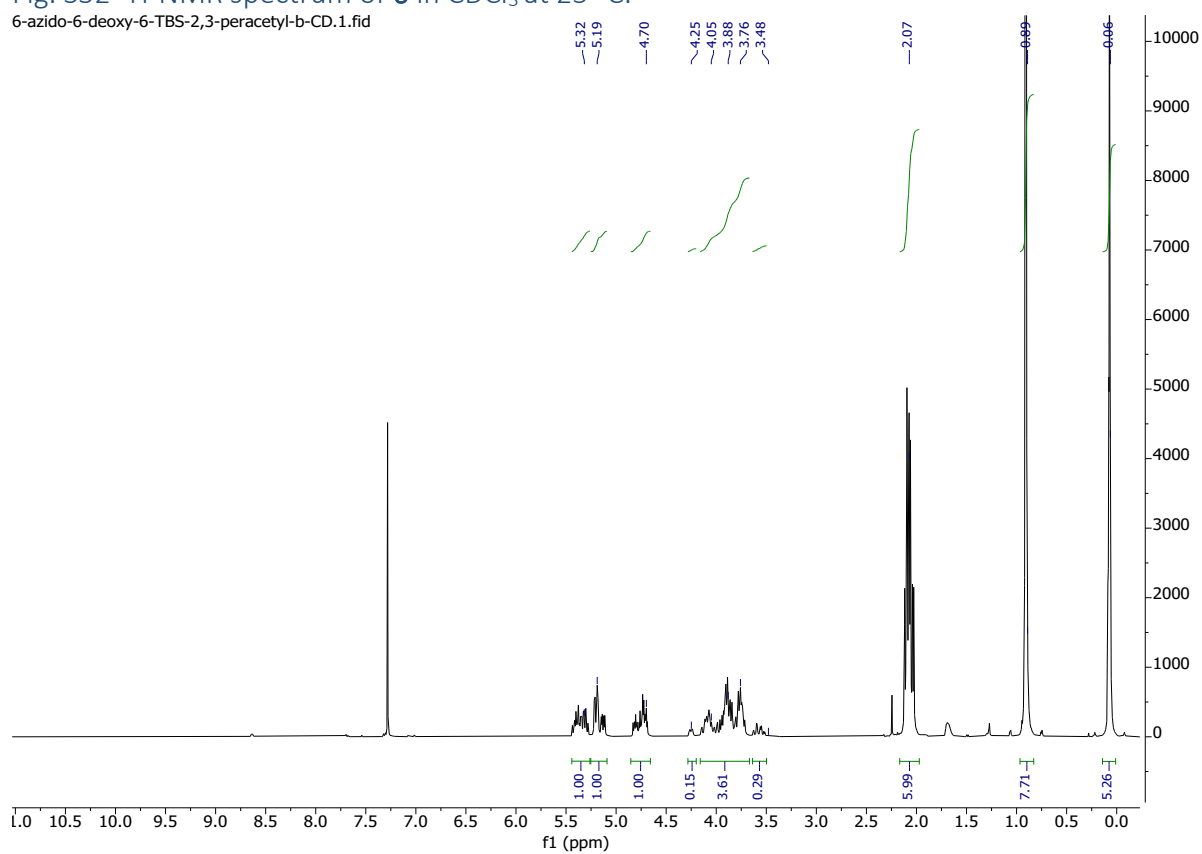


Fig. S33 DEPT- ^{13}C -NMR spectrum of **6** in CDCl_3 at 25 $^\circ\text{C}$.
KL_289_dried.2.fid

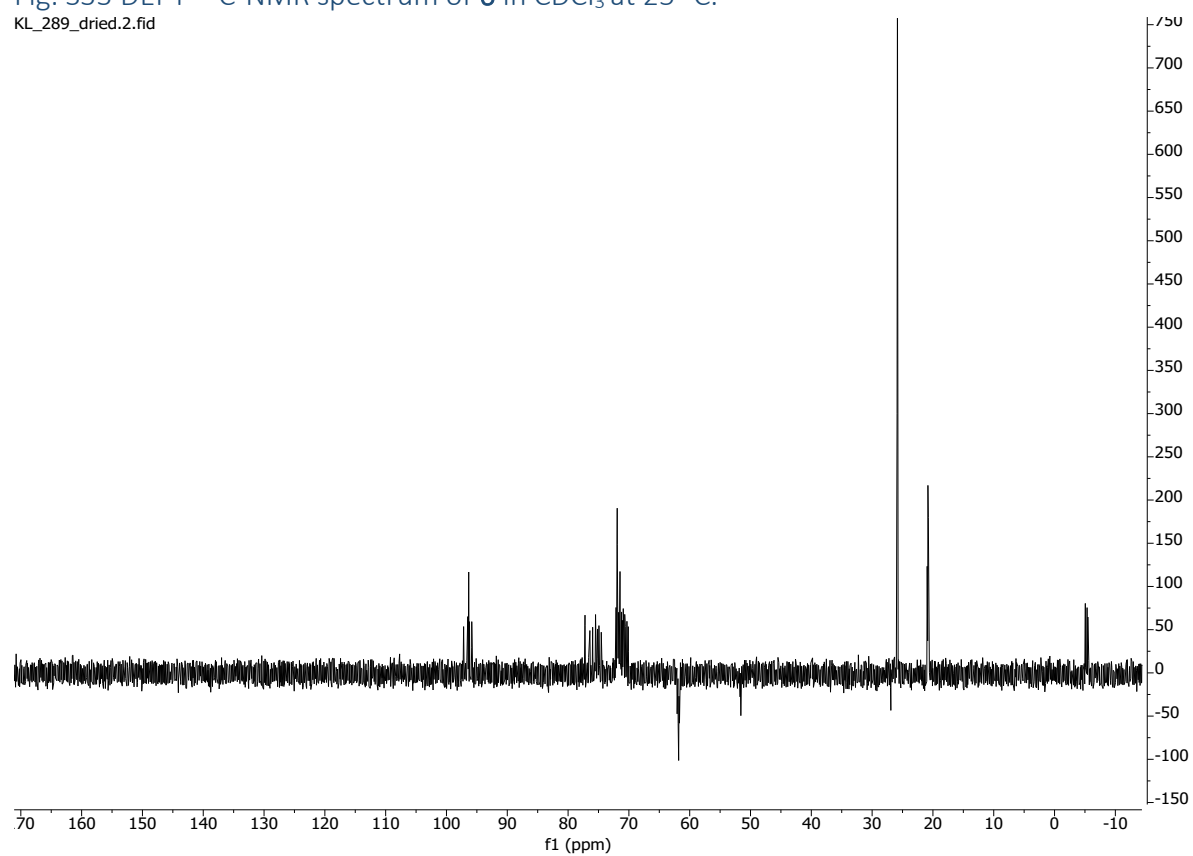


Fig. S34 COSY spectrum of **6** in CDCl₃ at 25 °C.

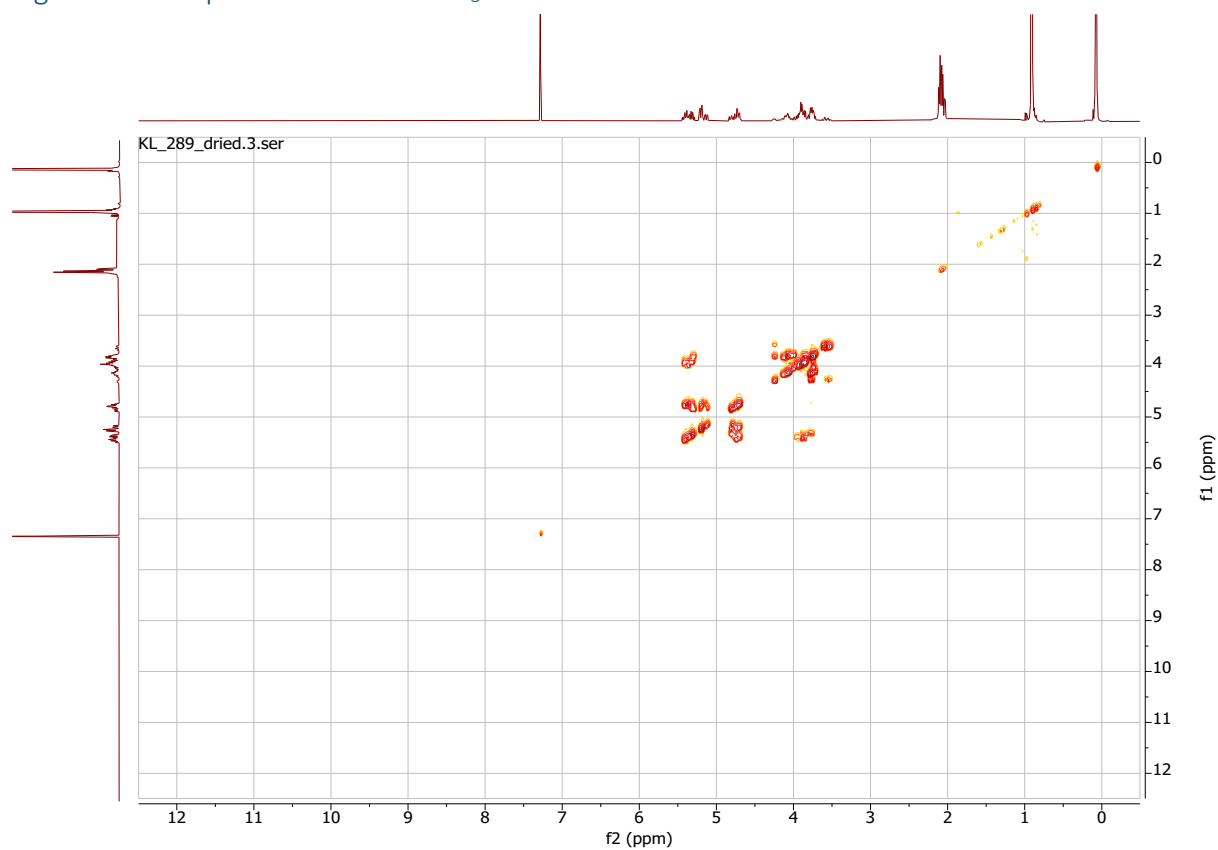


Fig. S35 HSQC spectrum of **6** in CDCl₃ at 25 °C.

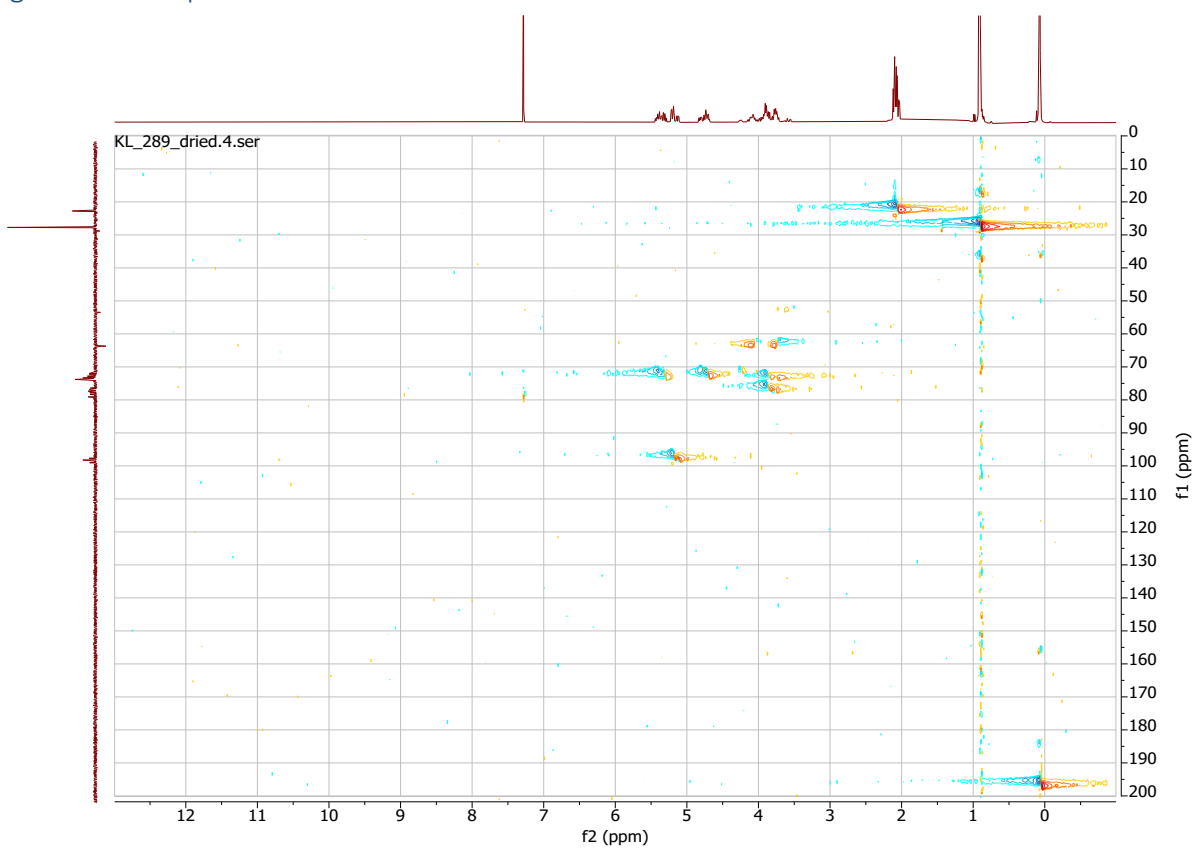


Fig. S36 IR spectrum of **6** in KBr pellet.

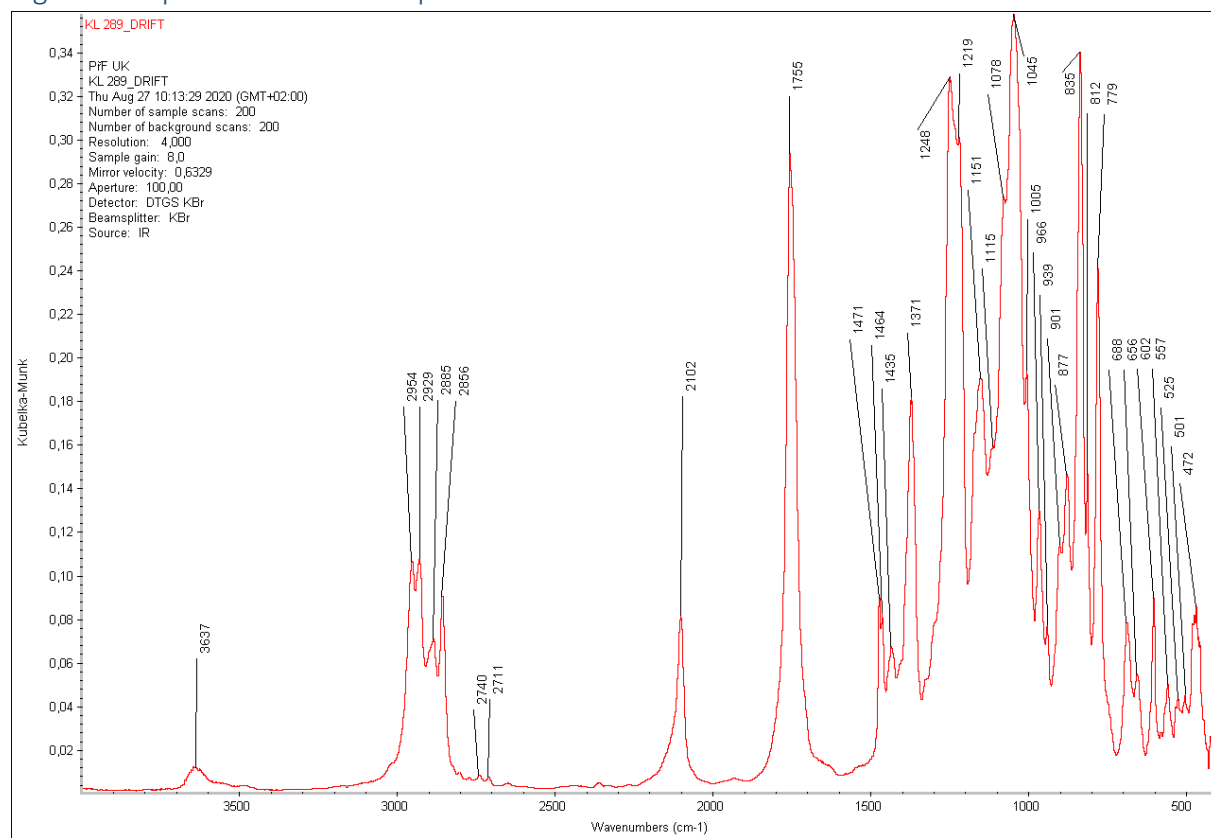
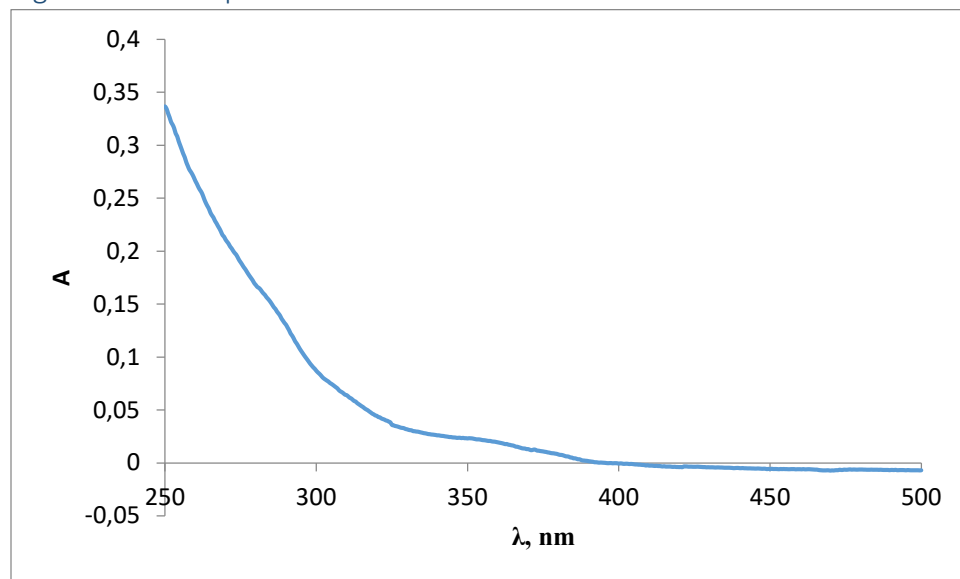


Fig. S37 UV-vis spectrum of **6** in CHCl₃.



6^A-Azido-6^A-deoxy-per-2,3-*O*-acetyl-β-cyclodextrin (7)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O-tert*-butyl-dimethylsilyl-per-2,3-*O*-acetyl-β-cyclodextrin (**6**, 1.64 g, 0.676 mmol) was dissolved in DCM (24 mL). The flask with the reaction mixture was set up in a magnetic stirrer at room temperature, and boron trifluoride etherate (1.6 mL, 12.96 mmol) was added dropwise to the reaction mixture. After 3 h, the reaction mixture was washed with ice-cold NaHCO₃ solution in a dropping funnel, concentrated on rotavap. The product was isolated by chromatography on a silica gel column (100 g). The main product was eluted with chloroform/methanol mixture 9/1 in the 88% yield (1.03 g).

¹H-NMR (400 MHz, [d₄] MeOH) δ=5.38-5.48 (H-C³, 7H); 5.13-5.24 (H-C¹, 7H); 4.75-4.82 (H-C², 7H); 3.68-4.15 (H-C⁴, H-C⁵, H-C⁶); 2.05-2.15 (Me-C(O), 42H). ¹³C-NMR (100 MHz, [d₄] MeOH) δ=96.17-96.78 (C¹); 75.43-76.93 (C⁴); 72.38 (C⁵); 70.43-71.32 (C², C³); 60.37 (C^{6B,C,D,E,F,G}); 51.25 (C^{6A}); 19.62 (Me-C(O)). HRMS (ESI): *m/z* calcd for C₇₀H₉₇N₃O₄₈+Na⁺:1770.51 [M+Na⁺]; found 1770.51; [α]_{CHCl₃}= +118,5°.

Fig. S38 ^1H -NMR spectrum of **7** in $[\text{d}_4]\text{-MeOH}$ at 25 $^\circ\text{C}$.

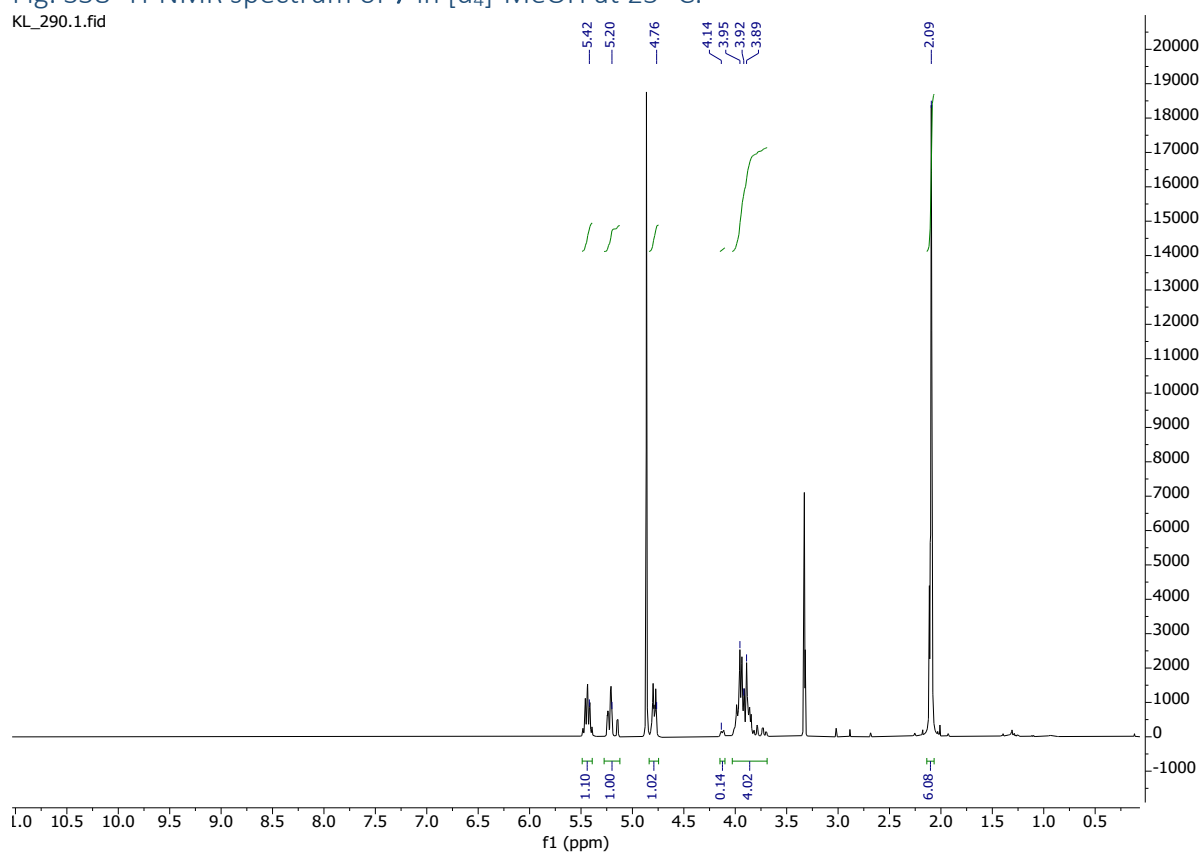


Fig. S39 DEPT- ^{13}C -NMR spectrum of **7** in $[\text{d}_4]\text{-MeOH}$ at 25 °C.

KL_290.2.fid

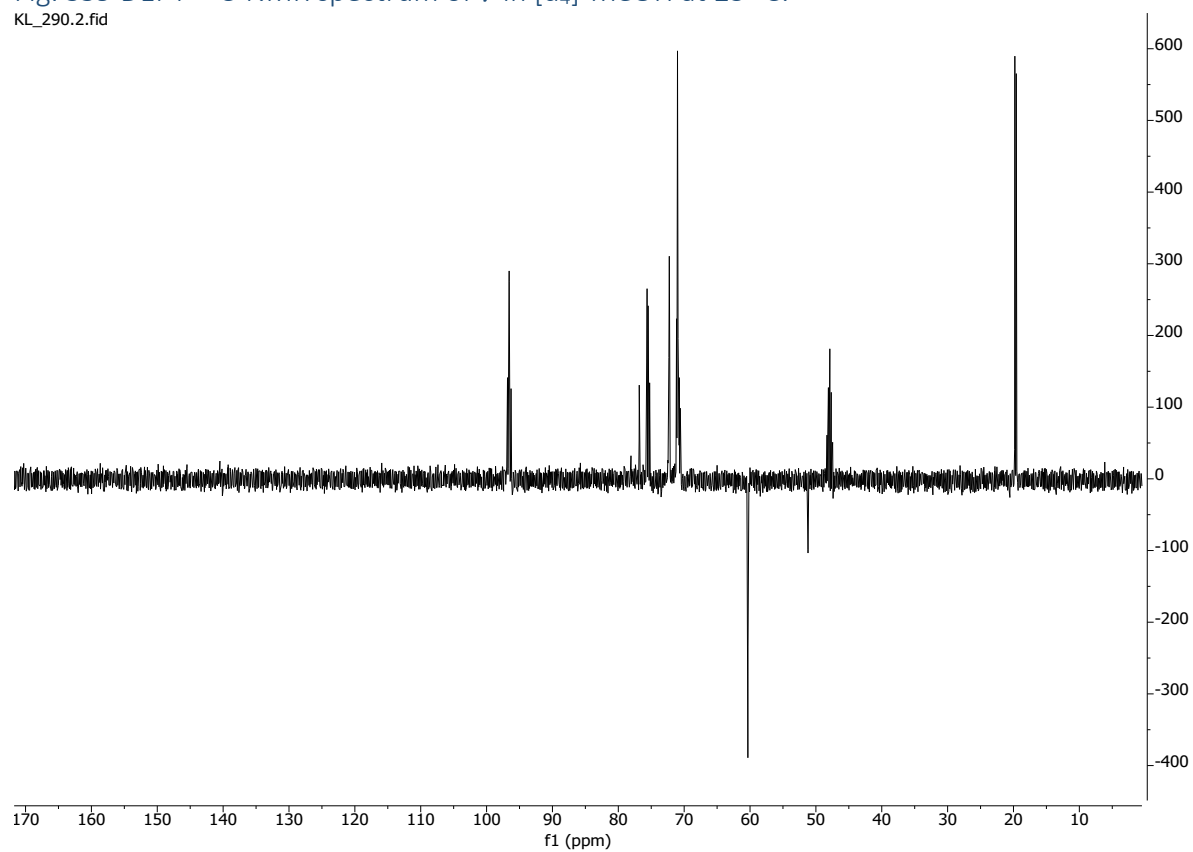


Fig. S40 COSY spectrum of **7** in [d₄]-MeOH at 25 °C.

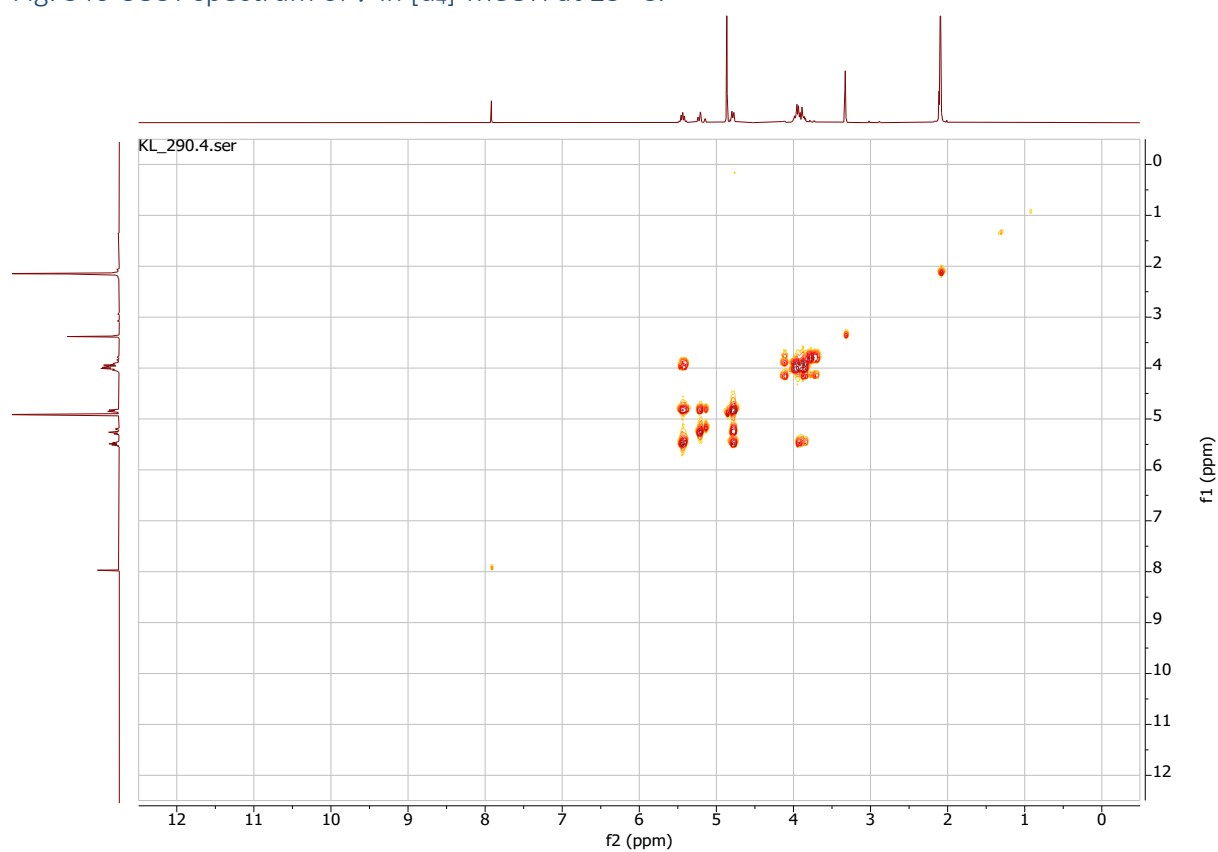


Fig. S41 HSQC spectrum of **7** in [d₄]-MeOH at 25 °C.

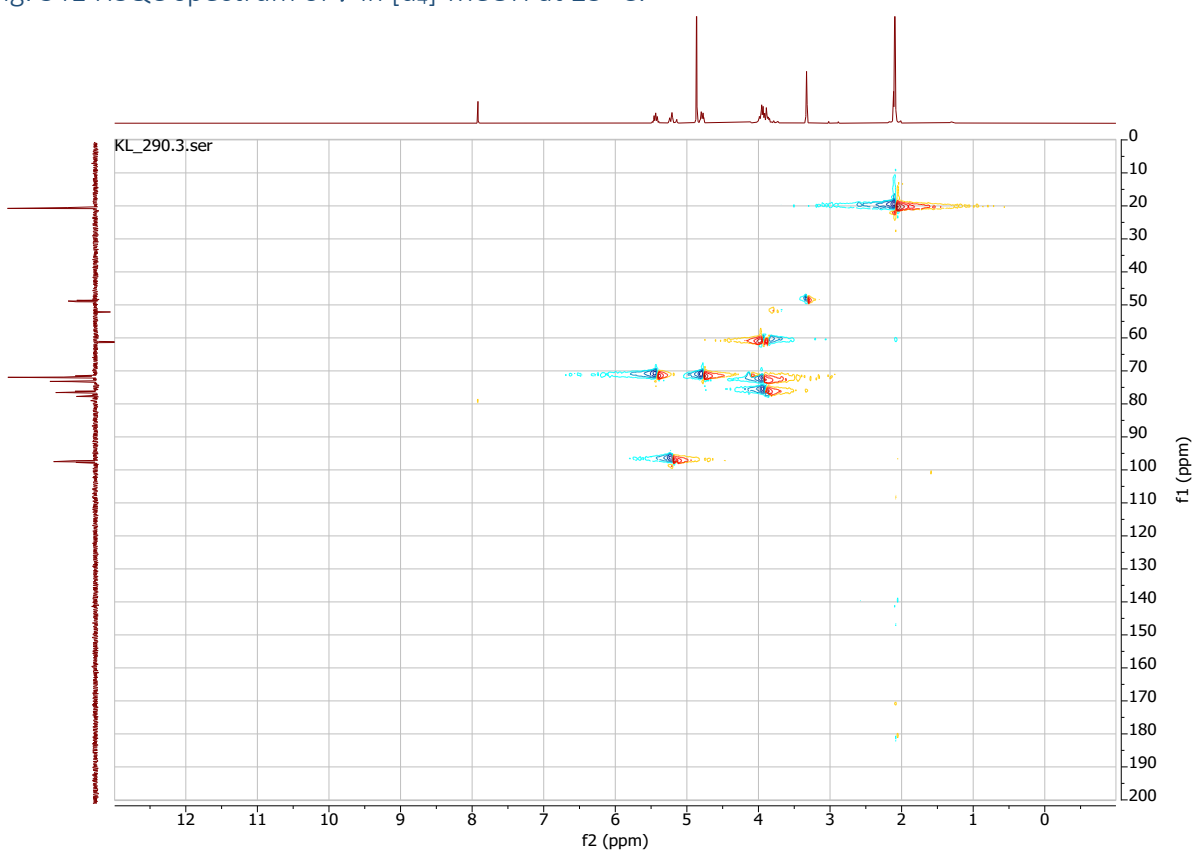


Fig. S42 IR spectrum of **7** in KBr pellet.

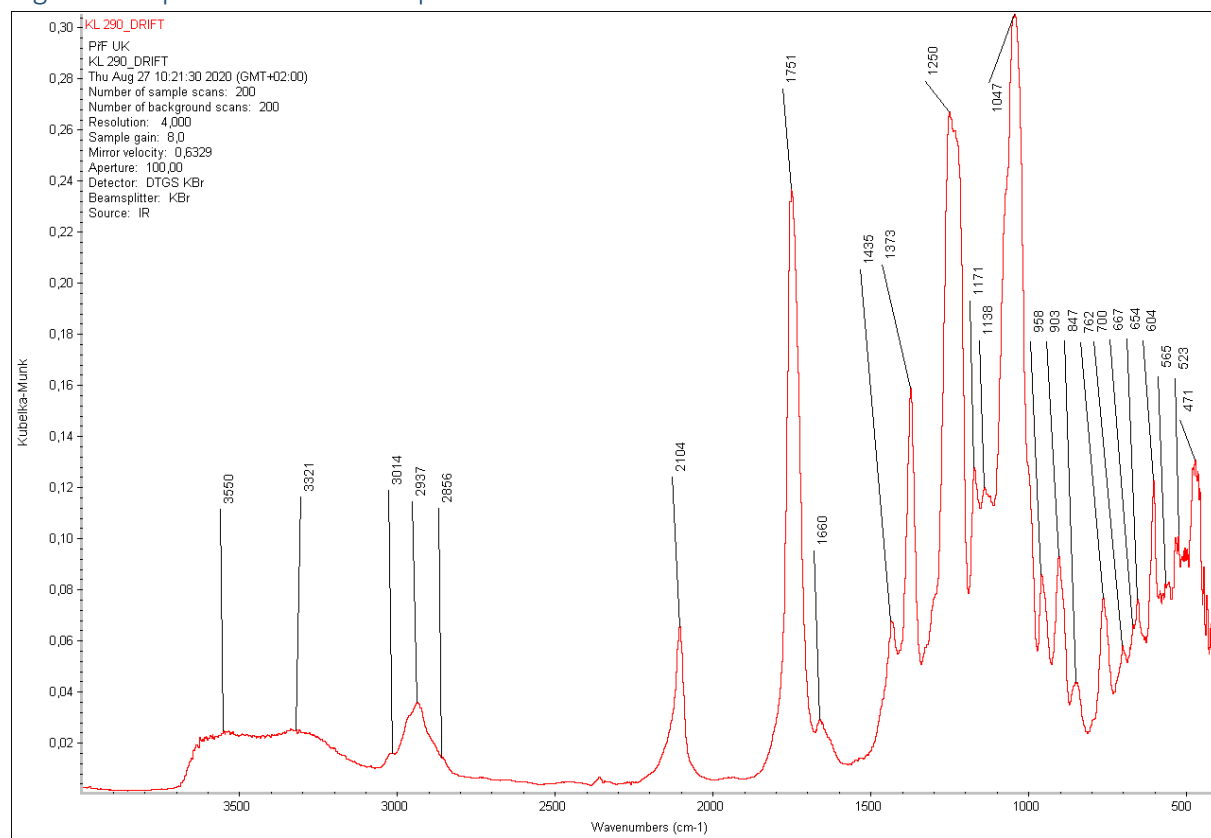
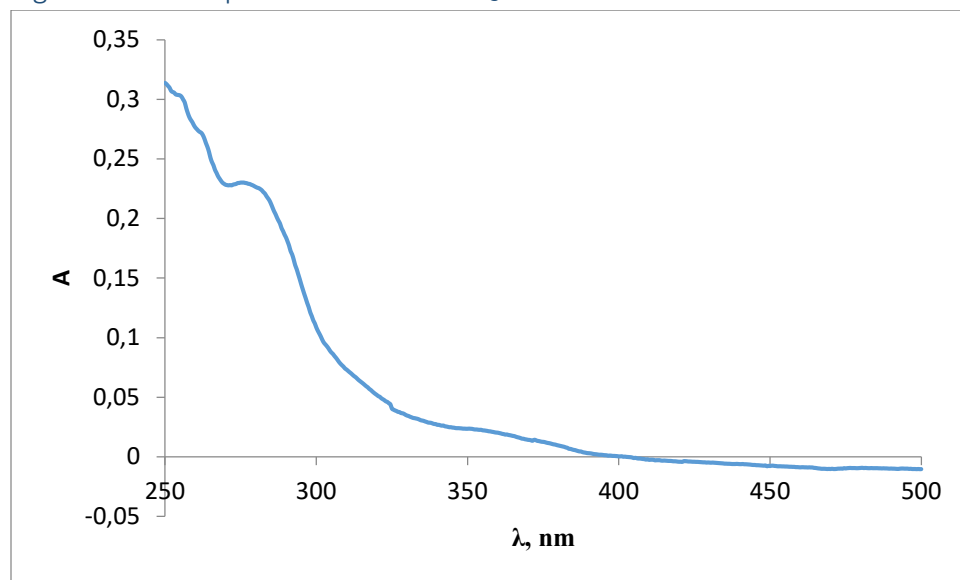


Fig. S43 UV-vis spectrum of **7** in CHCl₃.



6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl-per-2,3-O-acetyl-β-cyclodextrin (8)

6^A-Azido-6^A-deoxy-per-2,3-O-acetyl-β-cyclodextrin (**7**, 2.64 g, 1.51 mmol) was dissolved in purified methyl *p*-toluenesulfonate (26 mL, 177 mmol) in a 100 mL flask. The flask was set in a magnetic stirrer at room temperature under the argon flow. After this, a portion of *N,N*-diisopropylethylamine (6.5 mL, 38 mmol) was slowly added to the reaction mixture. Then the process was allowed to proceed at 100 °C. Every two hours, the pH of the reaction mixture was checked by an indicator paper, and small portions of *N,N*-diisopropylethylamine (0,5 mL, 2,9 mmol) were added to maintain the basicity. The reaction mixture was finally left overnight when the pH of the mixture had stopped decreasing. After this, the reaction mixture was diluted by chloroform and washed successively with 9/1 ethanol/water solution of NaI, 1 M HCl, saturated solution of NaHCO₃, saturated solution of Na₂S₂O₃, and brine (all 50 mL). The organic layer was concentrated and applied to a silica gel column (40 g of silica gel). The product (2.25 g; 81% yield) was eluted with chloroform/methanol 75/1 mixture.

¹H-NMR (400 MHz, CDCl₃) δ=5.28-5.43 (H-C³, 7H); 5.12-5.23 (H-C¹, 7H); 4.65-4.83 (H-C², 7H); 4.16- 3.55 (H-C⁴, H-C⁵, H-C⁶, 28H); 3.42 (Me-O-C⁶, 18H); 2.02-2.12 (Me-C(O), 42H). ¹³C-NMR (100 MHz, CDCl₃) δ=96.36 (C¹); 75.55-76.40 (C⁴); 69.80-72.01 (C², C³, C⁵, C^{6B,C,D,E,F,G}); 59.41 (Me-O-C⁶); 51.98 (C^{6A}); 20.74 (Me-C(O)). HRMS (ESI): *m/z* calcd for C₇₆H₁₀₉N₃O₄₈+NH₄⁺: 1849.65 [M+NH₄⁺]; found: 1849.64870; [α]_DCHCl₃= +132.8°.

Fig. S44 ^1H -NMR spectrum of **8** in CDCl_3 at 25 $^\circ\text{C}$.
KL_276.2.fid

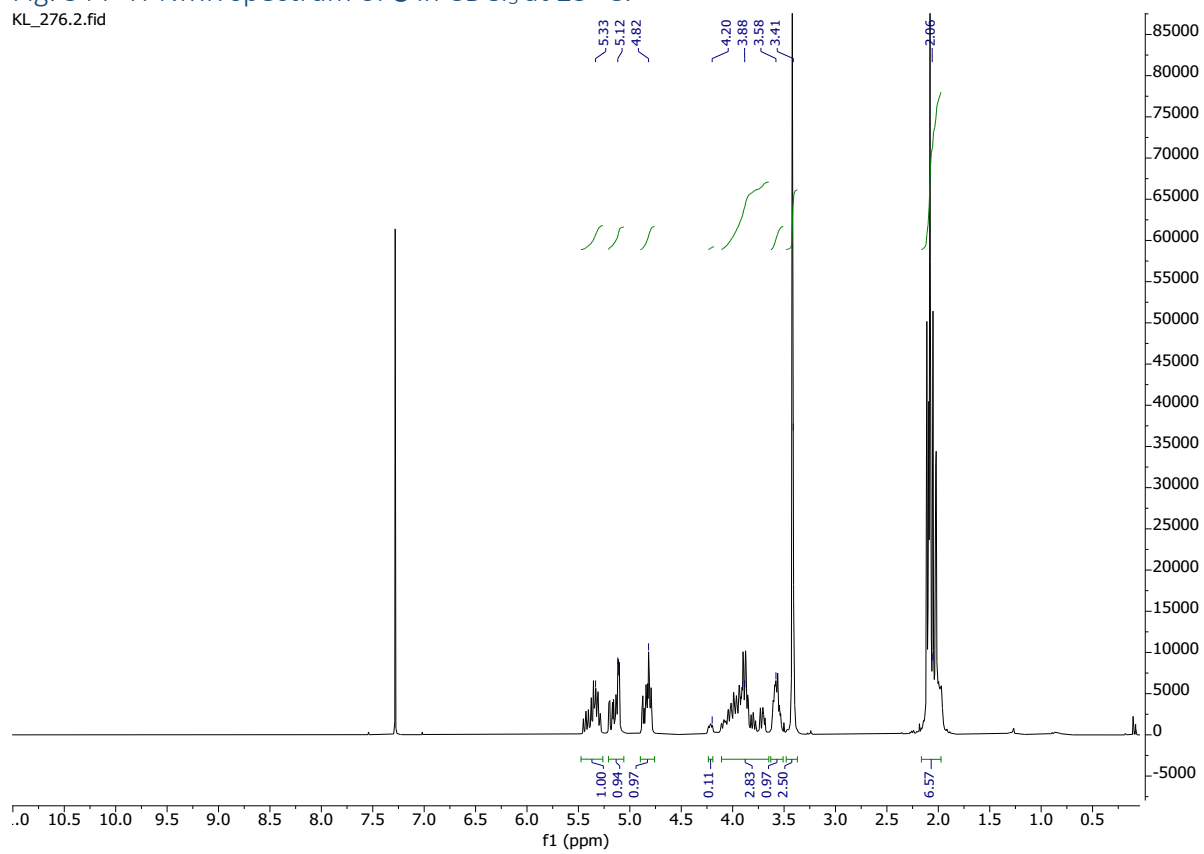


Fig. S45 DEPT- ^{13}C -NMR spectrum of **8** in CDCl_3 at 25 $^\circ\text{C}$.
KL_276.5.fid

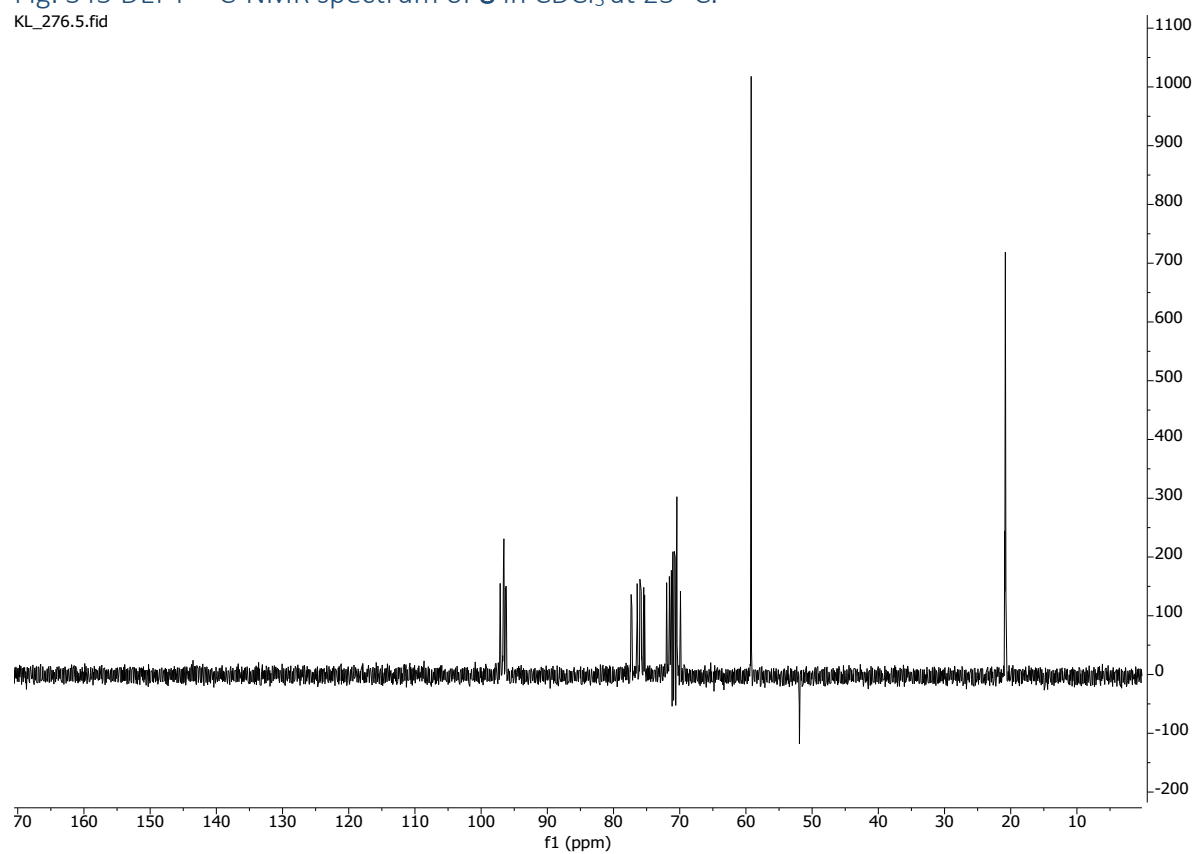


Fig. S46 COSY spectrum of **8** in CDCl₃ at 25 °C.

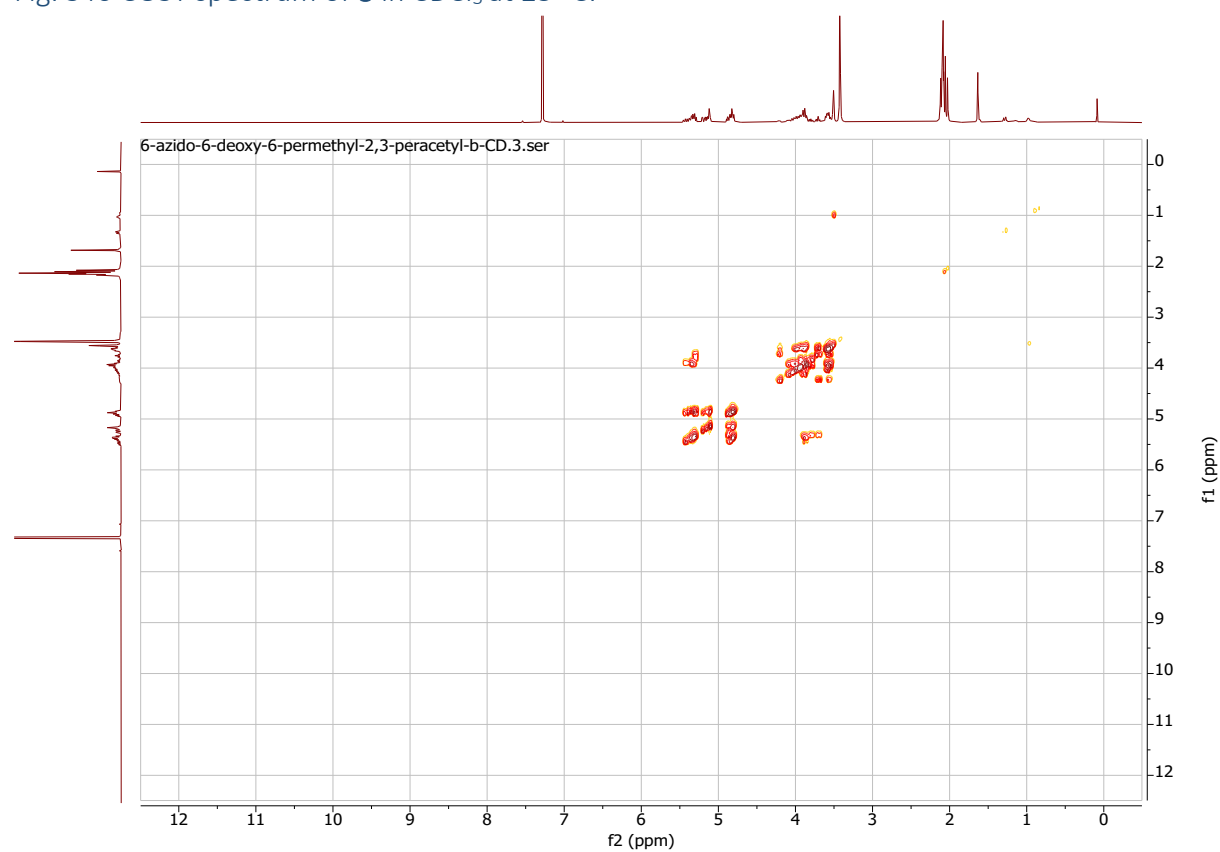


Fig. S47 HSQC spectrum of **8** in CDCl₃ at 25 °C.

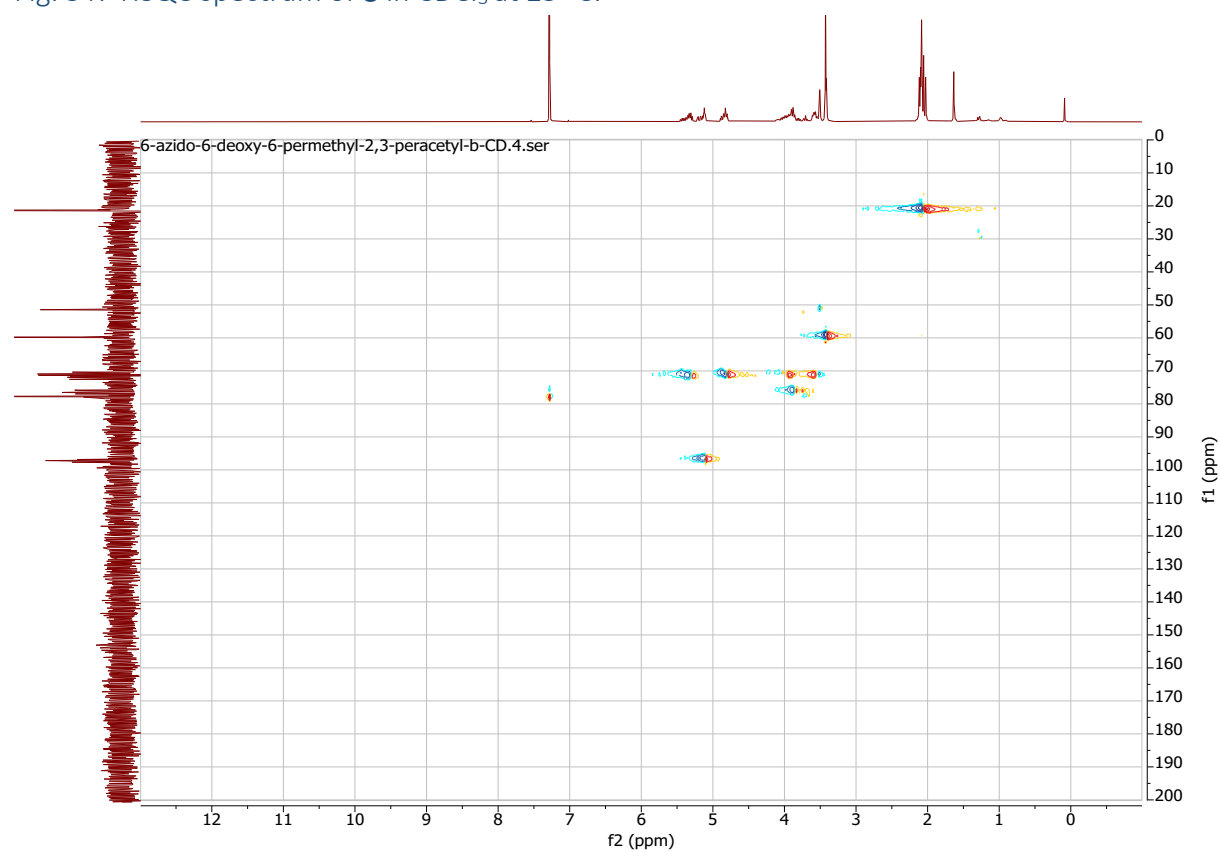


Fig. S48 IR spectrum of **8** in KBr pellet.

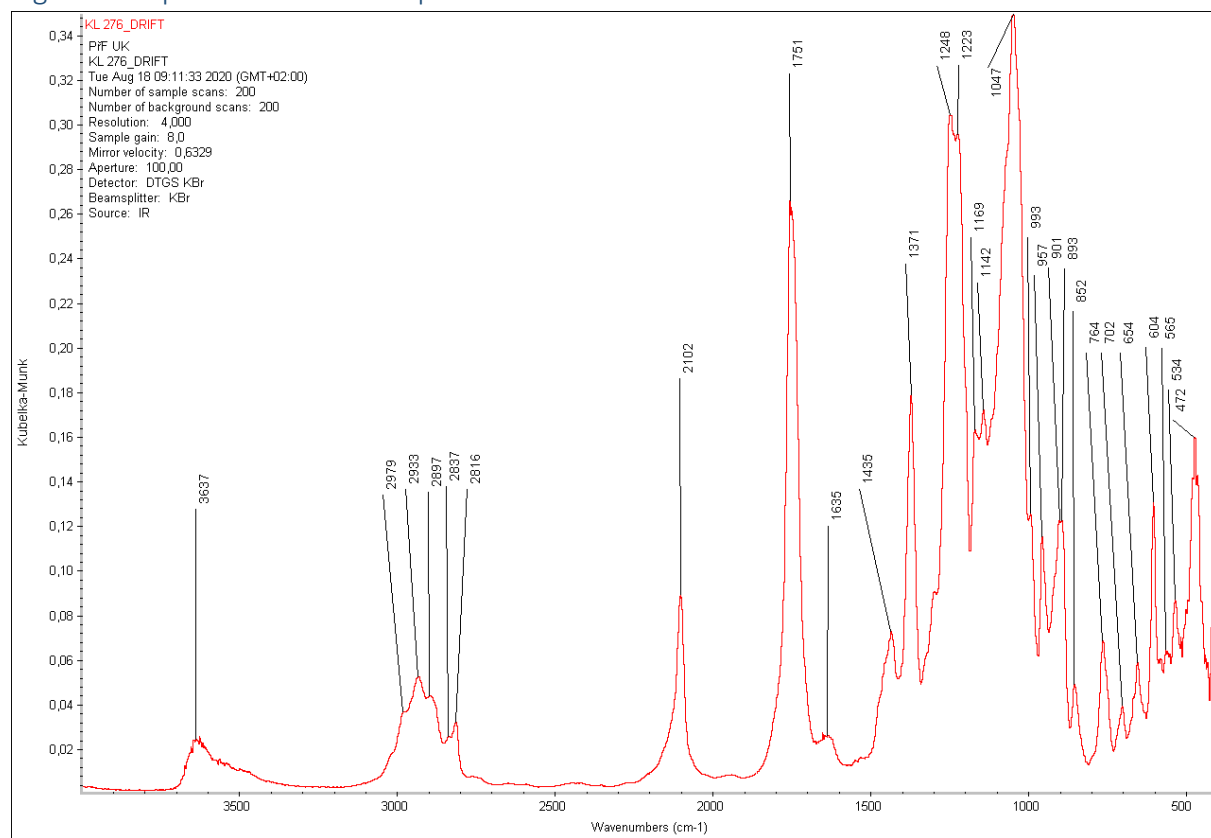
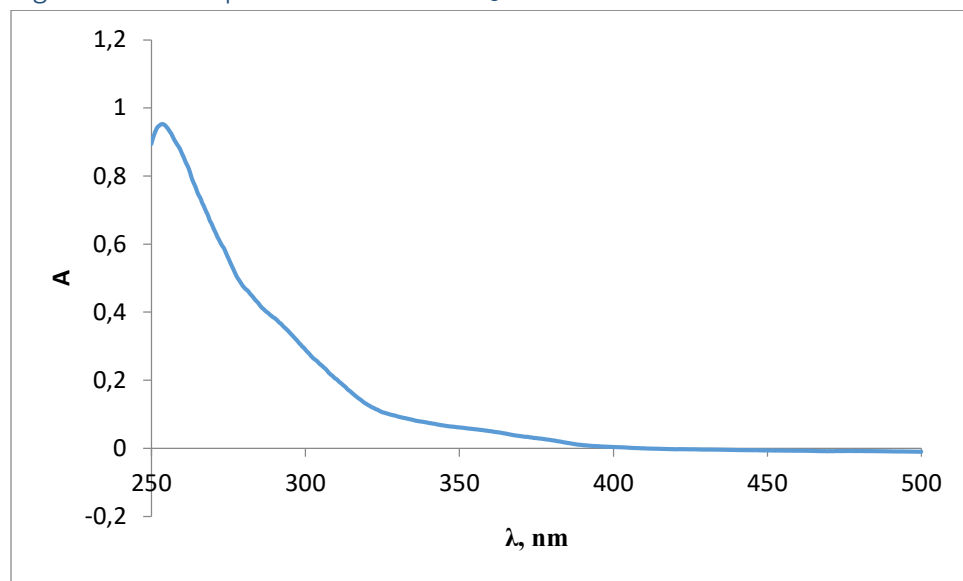


Fig. S49 UV-vis spectrum of **8** in CHCl₃.



Bis-1,3-[1-(6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl-per-2,3-O-acetyl-β-cyclodextrin-6^A-C-yl)-1,2,3-triazol-4-yl]methoxymethylene (**9**)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl-per-2,3-O-acetyl-β-cyclodextrin (**8**, 1 g; 0.546 mmol) was dissolved in DMF (25 mL), and the solution was bubbled by argon for 30 minutes. Then, portions of 0.5 M propargyl ether solution in DMF (0.49 mL; 0.2457 mmol), copper sulfate hydrate (0.136 g; 0.546 mmol), and sodium ascorbate (0.105 g; 0.546 mmol) were added to the reaction mixture, and the reaction mixture was allowed to stir at room temperature. After 72 hours, the temperature increased to 50 °C, and the reaction mixture was stirred for another 48h. After that, the solvent was removed in vacuo at 90 °C, and a column chromatography (30 g silica gel) with chloroform/methanol 50/1 to 25/1 mixture gave 0.6 g of the desirable product (60% yield).

¹H-NMR (400 MHz, CDCl₃) δ=7.68 (s, H-triazole, 2H); 5.23-5.44 (H-C³, 14H); 5.05-5.2 (H-C¹, 14H); 4.63-4.96 (H-C², -CH₂-triazole, 18H); 3.27-4.37 (H-C⁴, H-C⁵, H-C⁶, Me-O-C⁶); 2.02-2.12 (Me-C(O), 42H). ¹³C-NMR (100 MHz, CDCl₃) δ=125.63 (C-triazole); 95.65-96.94 (C¹); 75.13-76.37 (C⁴); 69.63-72.10 (C³, C⁵, C², C⁶); 63.77 (-CH₂-triazole); 20.51-20.90 (Me-C(O)). HRMS (ESI): *m/z* calcd for C₁₅₈H₂₂₄N₆O₉₇+H⁺+Na⁺: 1889.15 [M+H⁺+Na⁺]; found 1889.15856.

Fig. S50 ^1H -spectrum of **9** in CDCl_3 at 25 $^\circ\text{C}$.

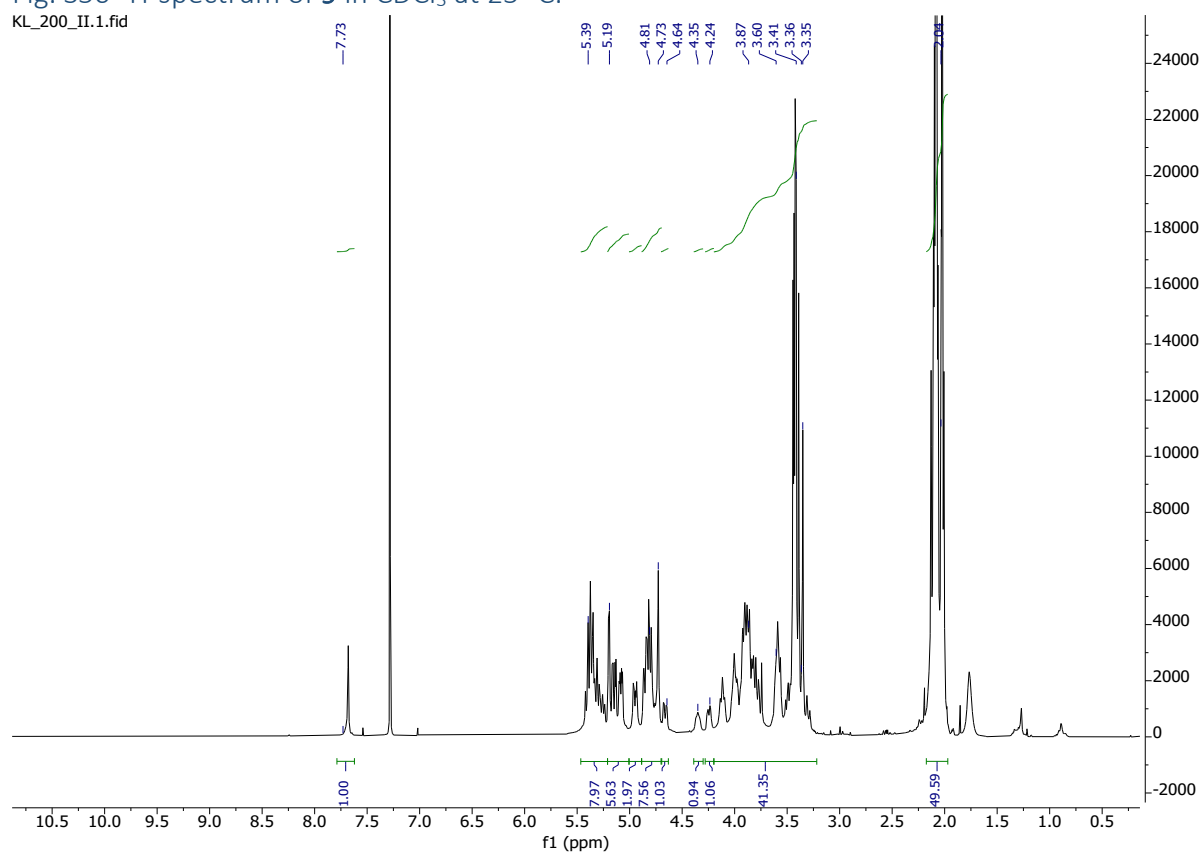


Fig. S51 DEPT- ^{13}C -NMR spectrum of **9** in CDCl_3 at 25 $^\circ\text{C}$.
KL_200_II.5.fid

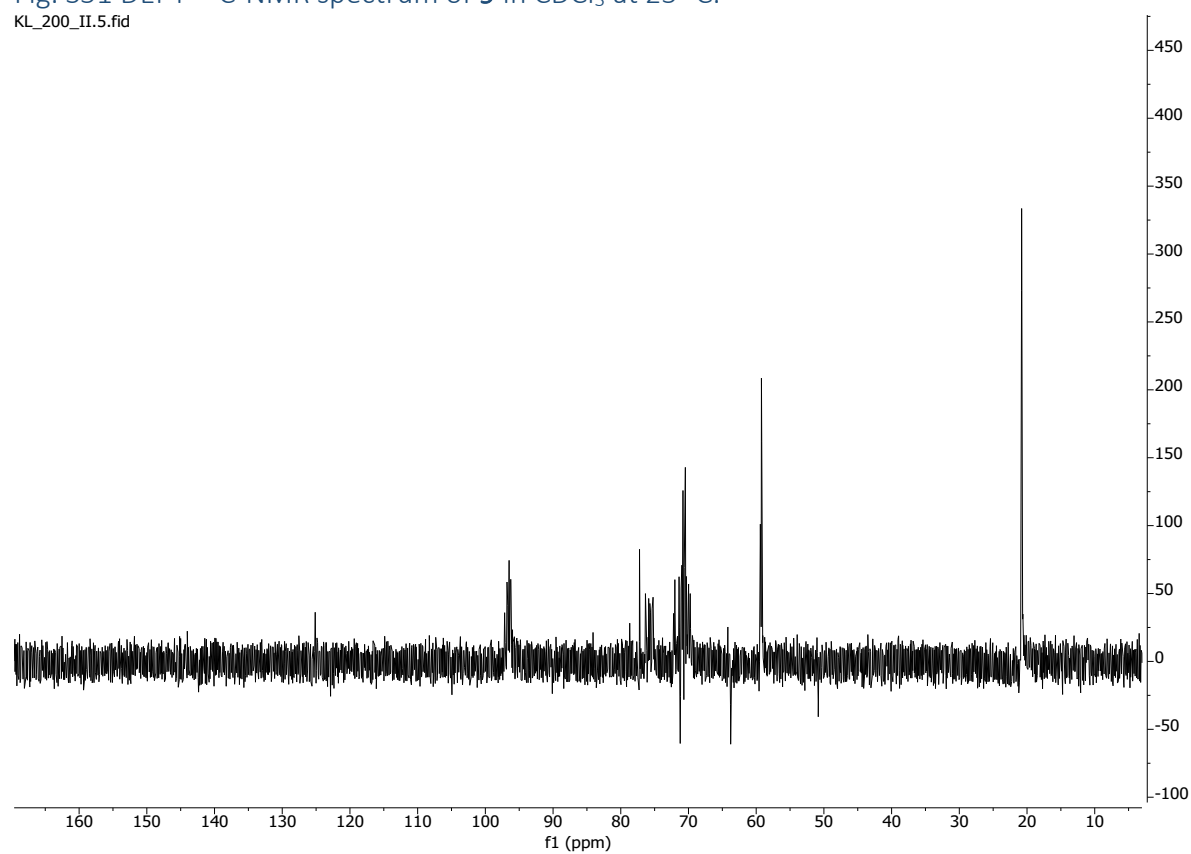


Fig. S52 COSY spectrum of **9** in CDCl₃ at 25 °C.

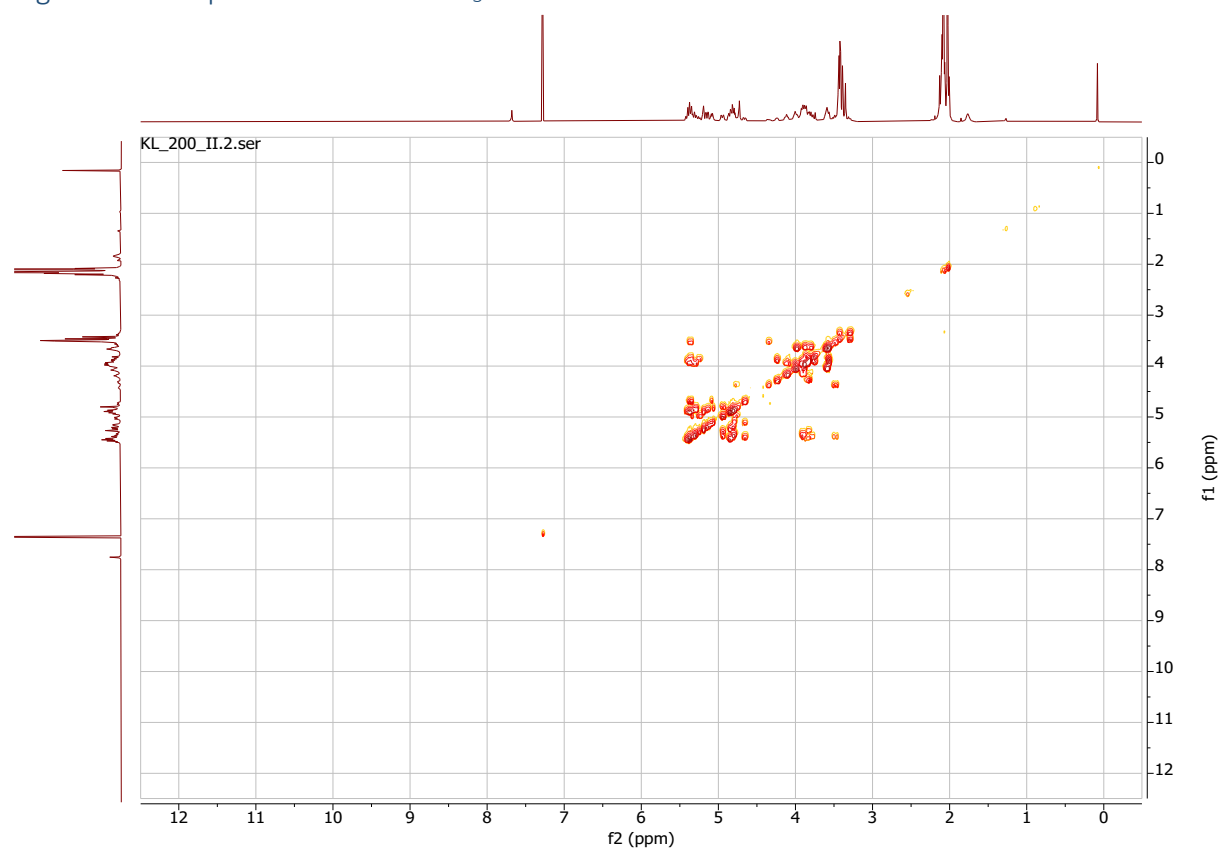


Fig. S53 HSQC spectrum of **9** in CDCl₃ at 25 °C.

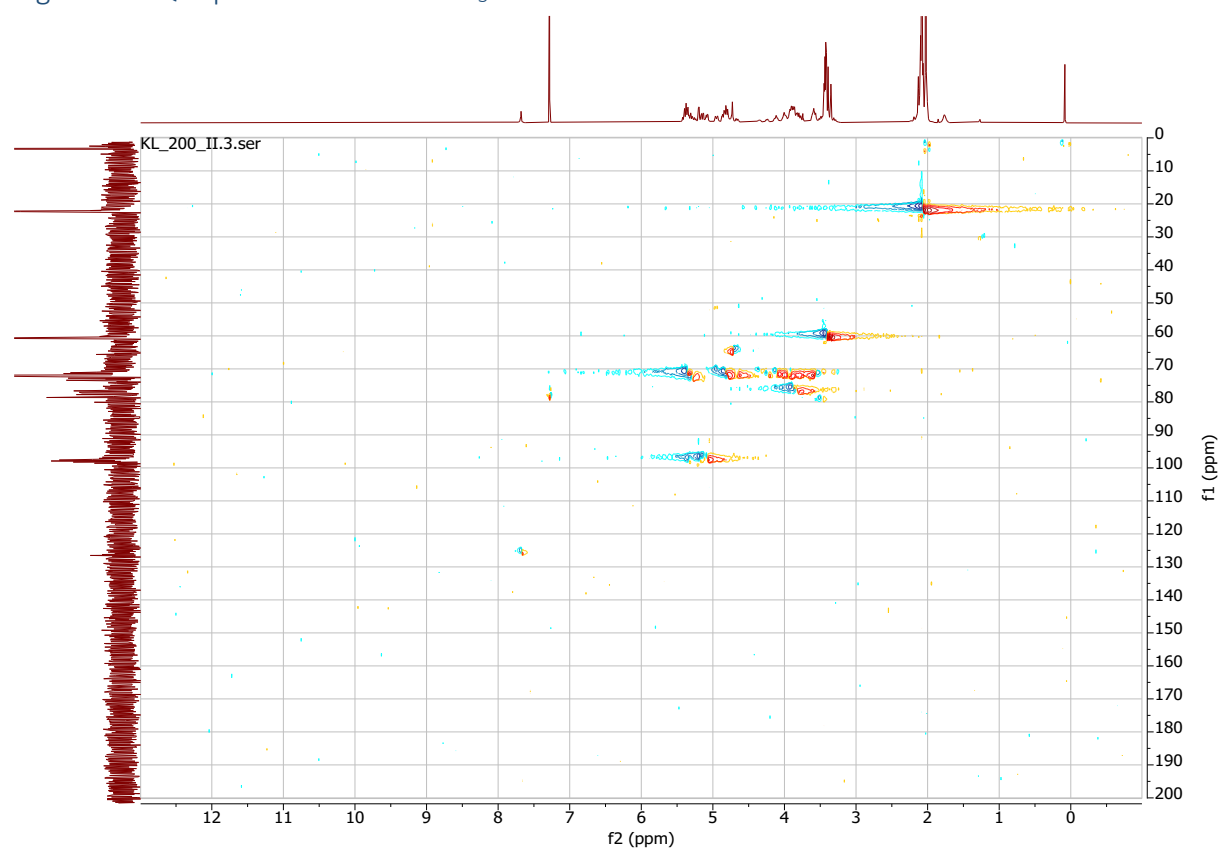
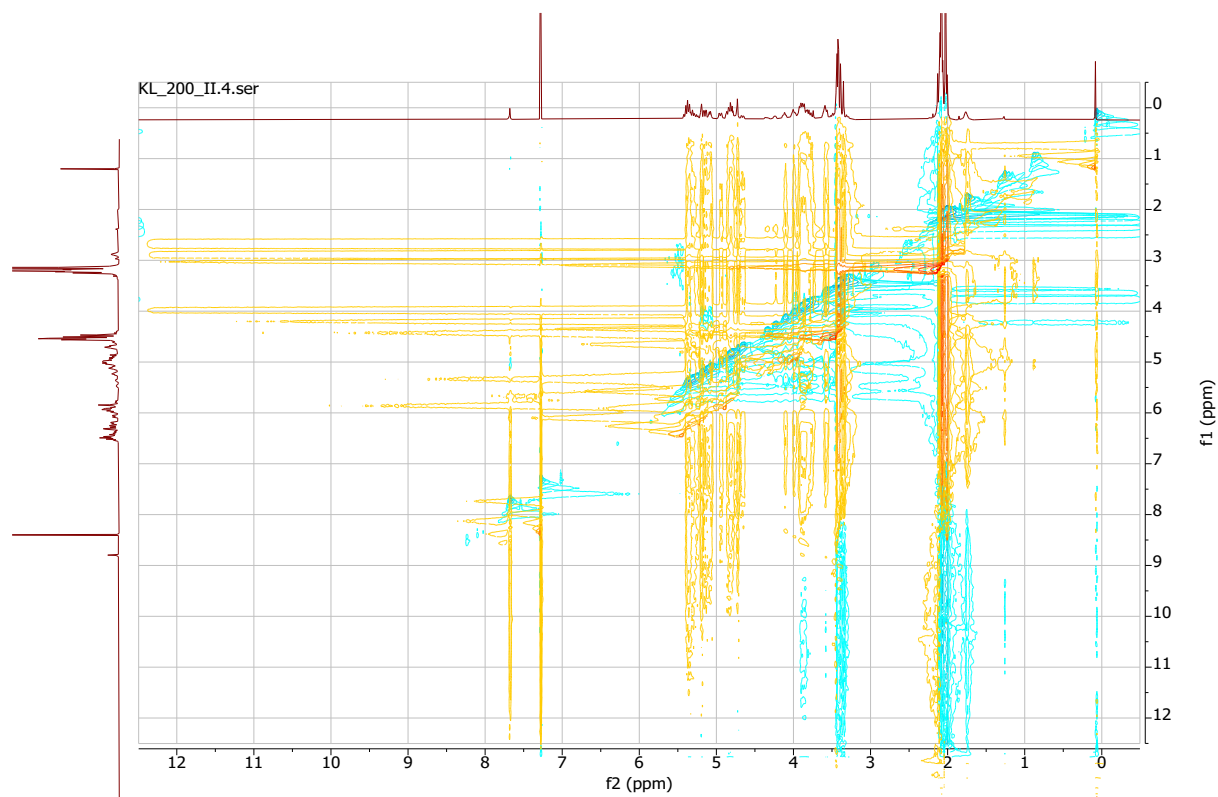


Fig. S54 NOESY spectrum of **9** in CDCl₃ at 25 °C.



Bis-1,3-[1-(6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl-β-cyclodextrin-6^A-yl)-1,2,3-triazol-4-yl]methoxymethylene (**10**)

Bis-1,3-[1-(6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl-per-2,3-O-acetyl-β-cyclodextrin-6^A-C-yl)-1,2,3-triazol-4-yl]methoxymethylene (**9**, 0.6 g; 0.165 mmol) was treated by 1 mL of 1 M solution of sodium methoxide in 20 mL of methanol for 1 h at room temperature. The solution was neutralized by 10 g of Amberlite 120 resin and dried to get the final product (0.38 g; 97% yield).

¹H-NMR (400 MHz, D₂O) δ=8,04 (s, H-triazole, 2H); 4,88-5,1 (H-C¹, H-C^{6A}, 18H); 4.69 (–CH₂-triazole overlapped with H₂O); 4.48-4.56 (H-C^{6A}, 2H, diastereotopic); 4.17-4.23 (H-C^{5A}, 2H); 3,41-4.06 (H-C², H-C³, H-C⁴, H-C⁵, H-C⁶); 3,05-3,35 (Me-O-C⁶, 18H); 2.64-2.98 (H-C⁶ 4H). ¹³C-NMR (100 MHz, D₂O) δ=126.48 (C-triazole); 101.34-102.13 (C¹); 80.44-83.27 (C²); 69.08-73.04 (C³, C⁴, C⁵, C⁶); 62.78 (–CH₂-triazole, C⁶); 58.43 (Me-C⁶); 51.21 (C^{6A}). HRMS (ESI): *m/z* calcd for C₁₀₂H₁₆₈N₆O₆₉+2H⁺: 1291.99 [M+2H⁺] found: 1291.99549; [α]_{DMF}=+106.3°.

Fig. S55 ^1H -NMR spectrum of **10** in D_2O at 25 $^\circ\text{C}$.

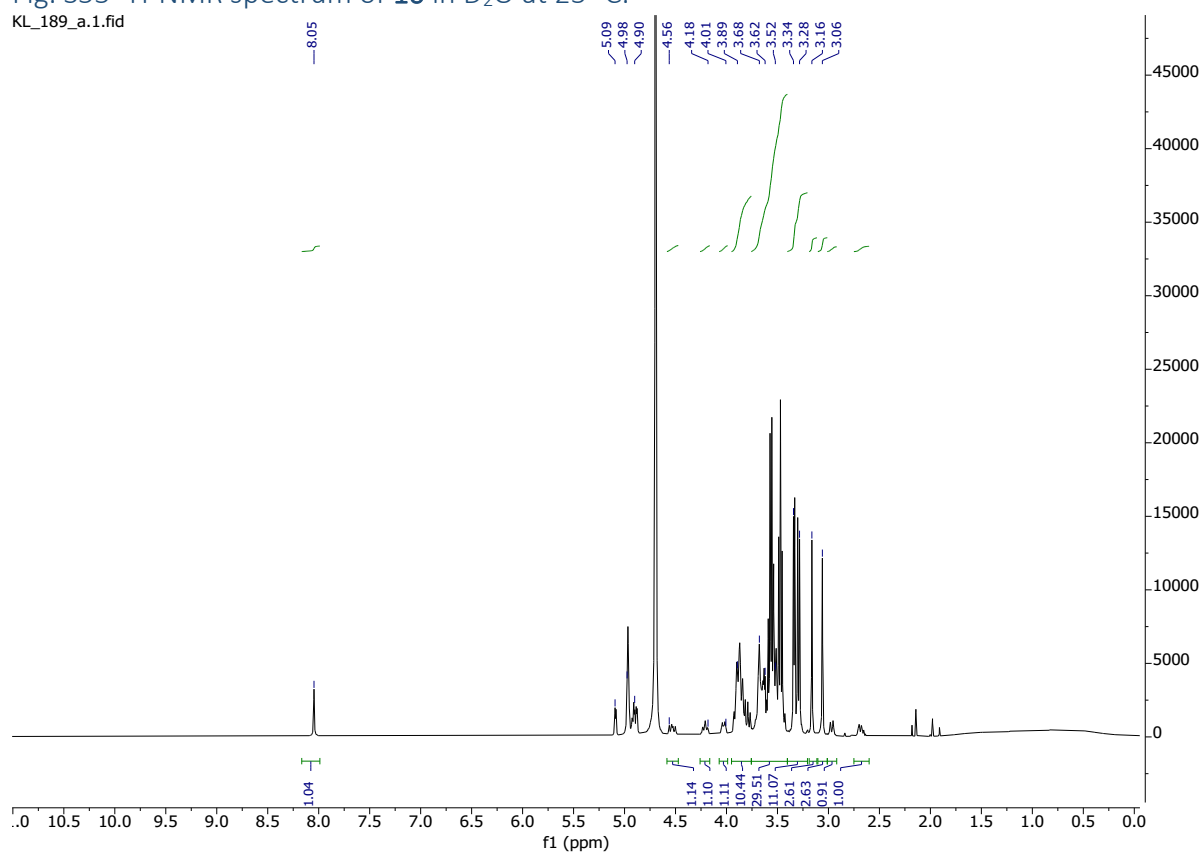


Fig. S56 DEPT- ^{13}C -NMR spectrum of **10** in D_2O at 25 °C.

KL_200_deac/C13

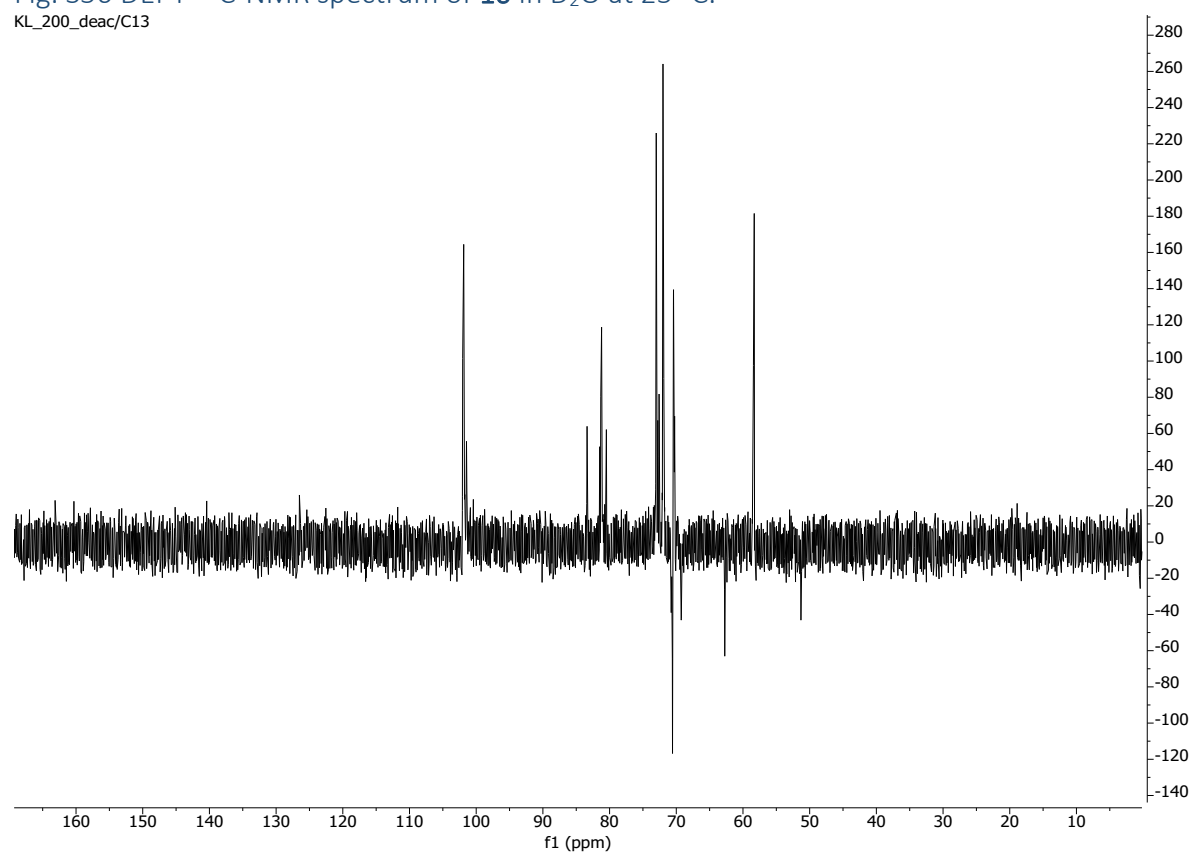


Fig. S57 COSY spectrum of **10** in D₂O at 25 °C.

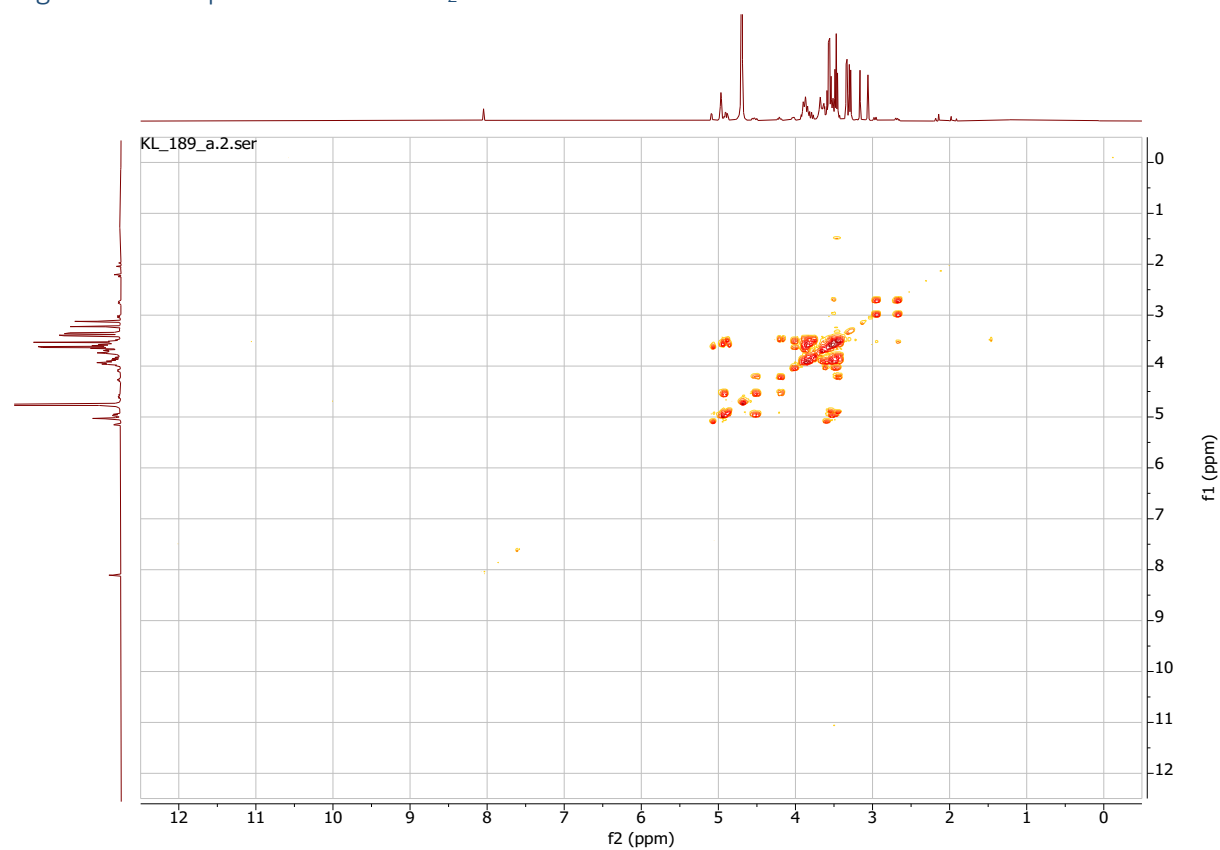


Fig. S58 HSQC spectrum of **10** in D₂O at 25 °C.

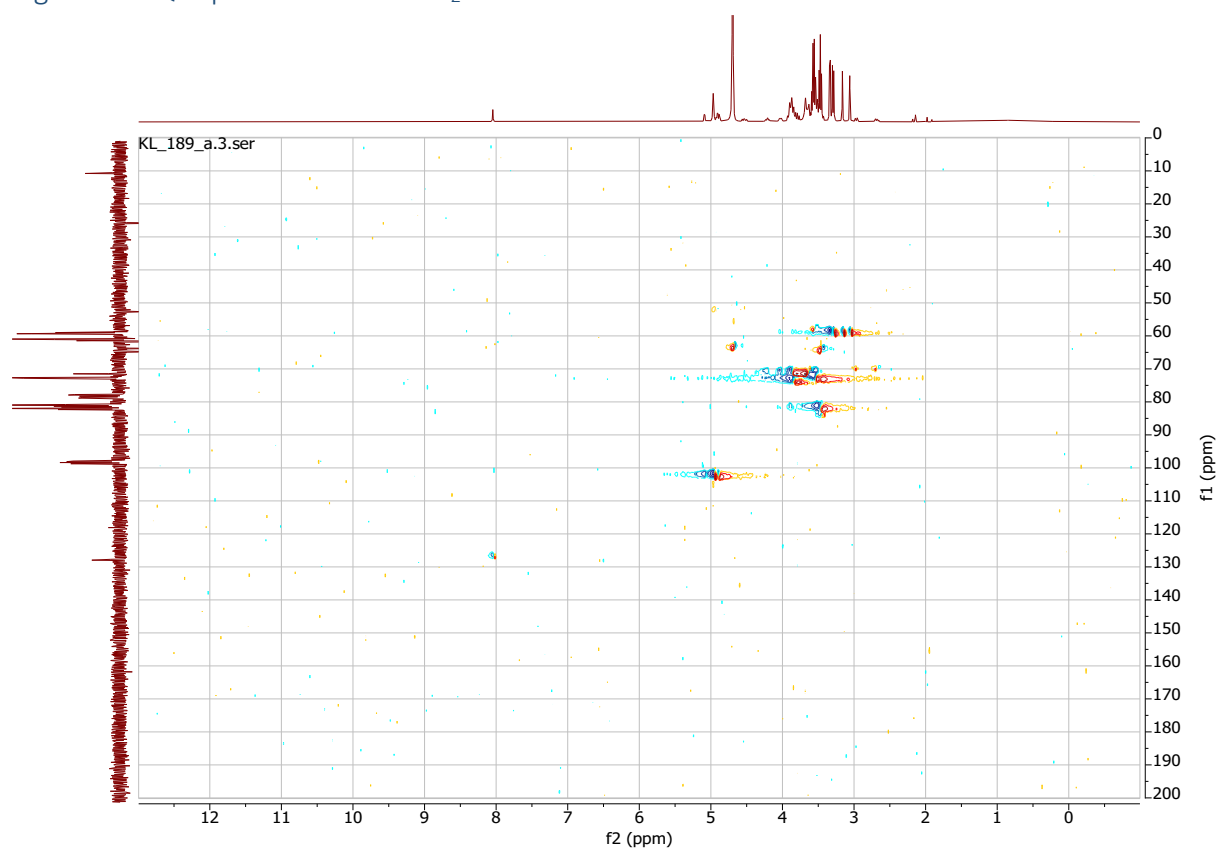


Fig. S59 NOESY spectrum of **10** in D₂O at 25 °C.

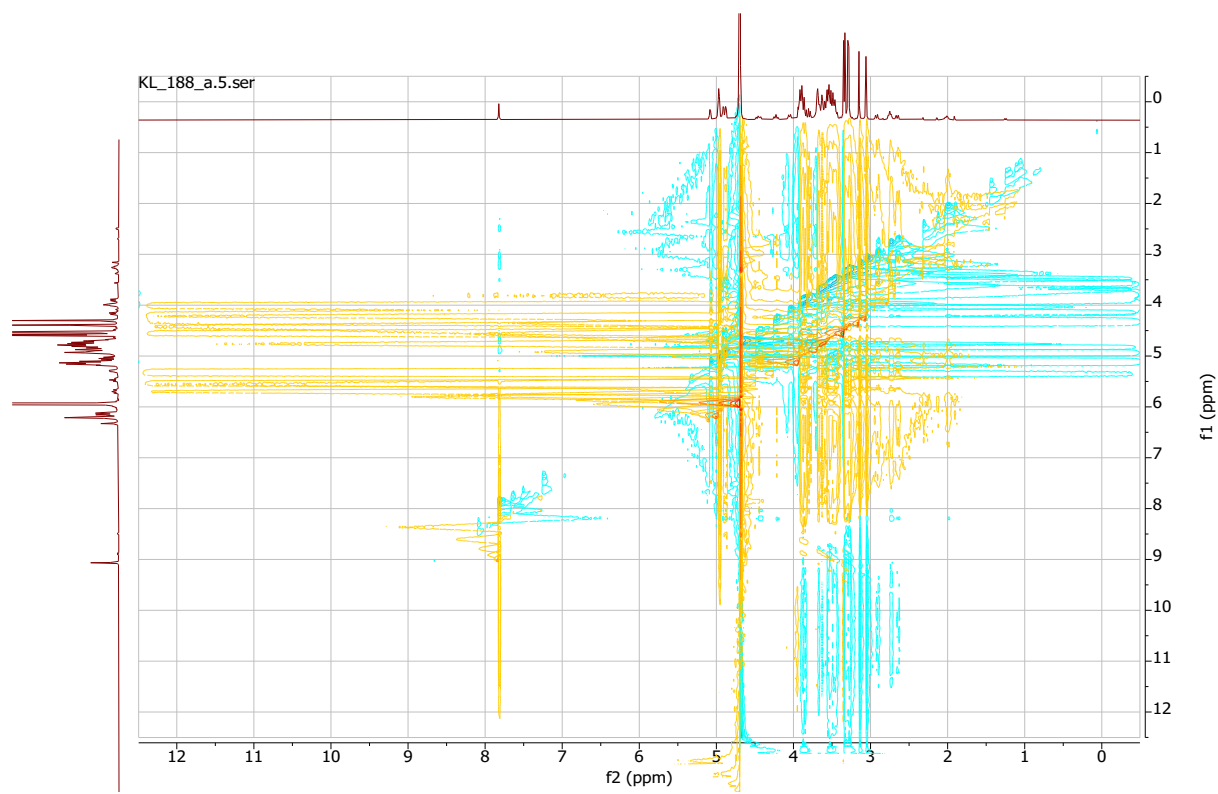


Fig. S60 IR spectrum of **10** in KBr pellet.

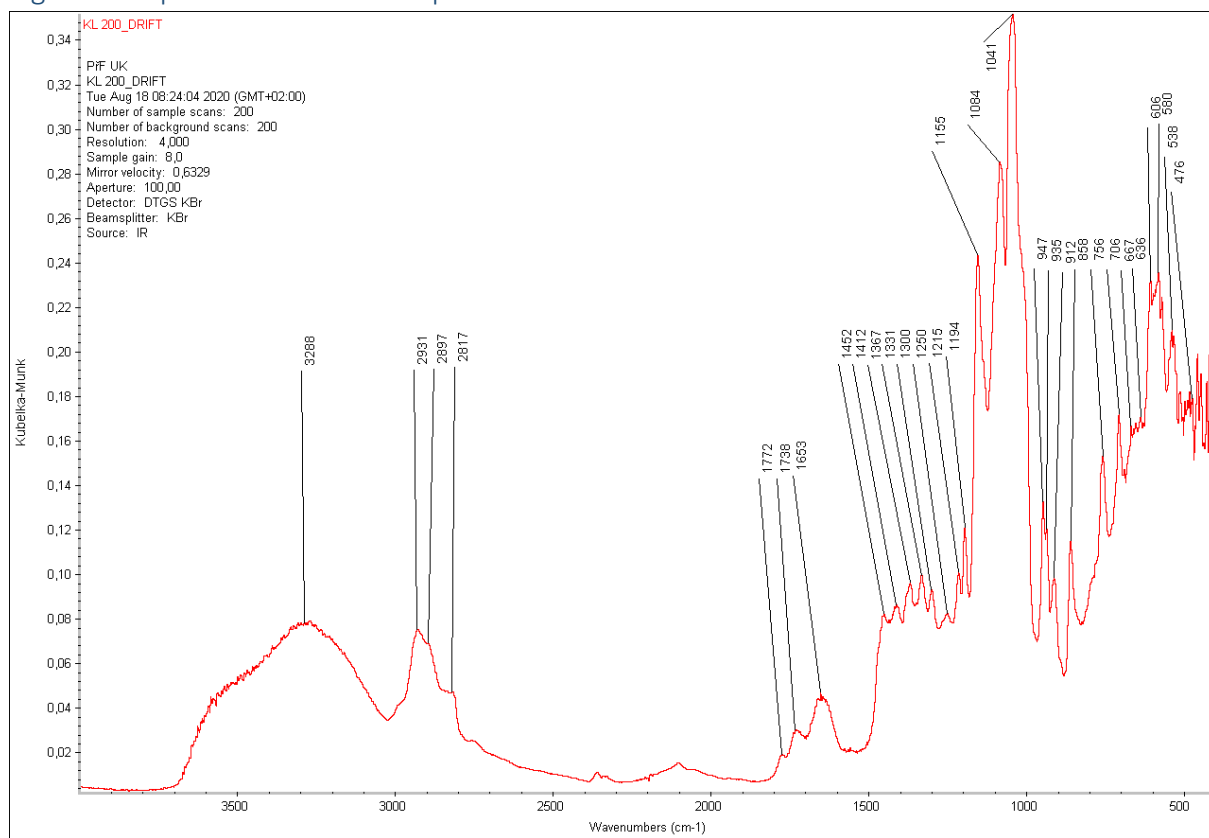
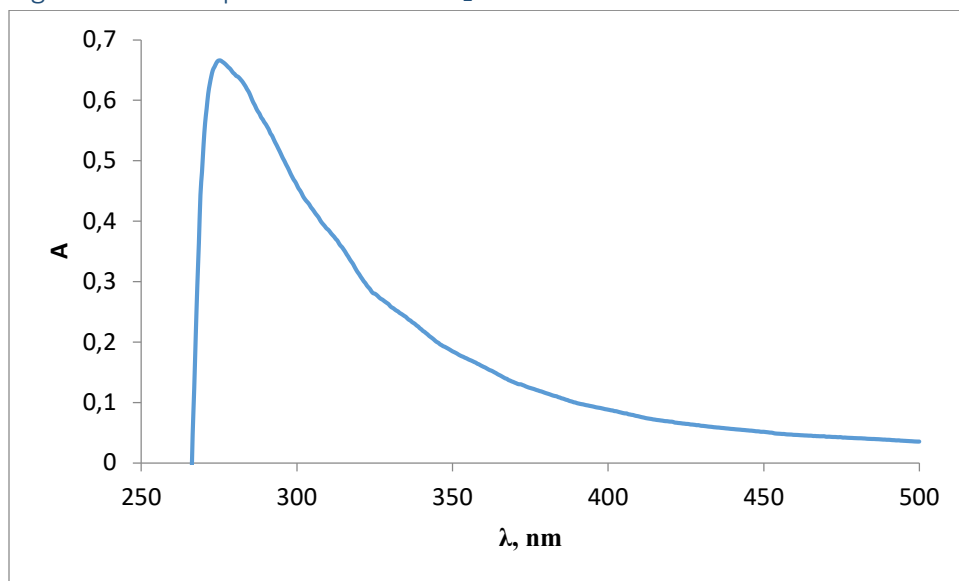


Fig. S61 UV-vis spectrum of **10** in H₂O.



6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl - β -cyclodextrin (**11**)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-O-methyl-per-2,3-O-acetyl- β -cyclodextrin (**8**, 0.8 g; 0.643 mmol) was treated by 1 mL of 1 M solution of sodium methoxide in 20 mL of methanol for 1 h at room temperature. The solution was neutralized by 10 g of Amberlite 120 resin and dried to get the final product in the quantitative yield.

¹H-NMR (400 MHz, [d₆] DMSO) δ = 6.08-6.47 (HO-C², HO-C³, 14H); 4.71-4.84 (H-C¹, 7H); 3.15-3.79 (H-C², H-C³, H-C⁴, H-C⁵, H-C⁶, Me-O-C⁶ (overlapped with H₂O). ¹³C-NMR (100 MHz, [d₆] DMSO) δ =103.28 (C¹); 82.65-83.94 (C²); 70.60-73.44 (C³, C⁴, C⁵, C⁶); 69.51, 61.00 (C⁶); 58.54 (Me-C⁶, C^{6A}). HRMS (ESI): *m/z* calcd for C₄₈H₈₁N₃O₃₄+NH₄⁺: 1261.50 [M+NH₄⁺]; found: 1261.49846. [α]DMF=+140.8°.

Fig. S62 ¹H-NMR spectrum of **11** in [d₆]-DMSO at 25 °C.

KL_142_deac.1.fid

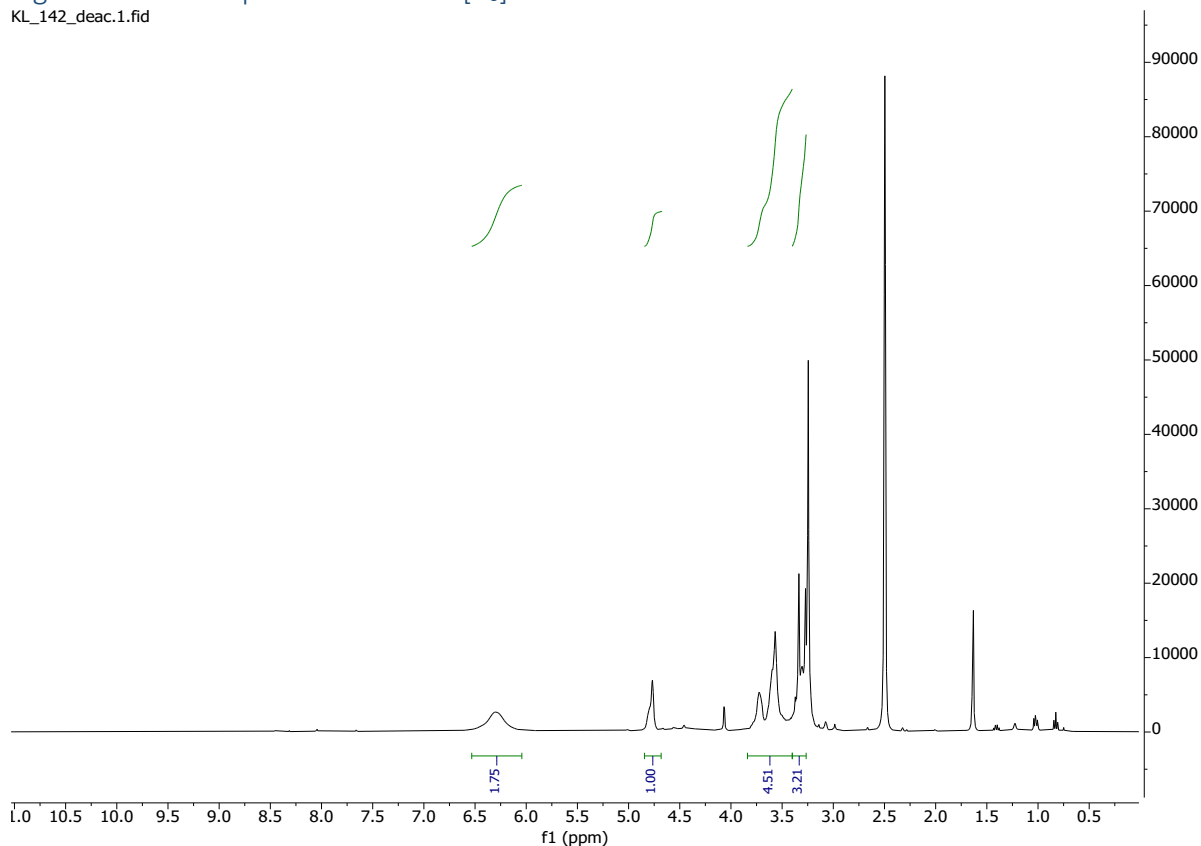


Fig. S63 DEPT- ^{13}C -NMR spectrum of **11** in $[\text{d}_6]$ -DMSO at 25 °C.

KL_142_deac.2.fid

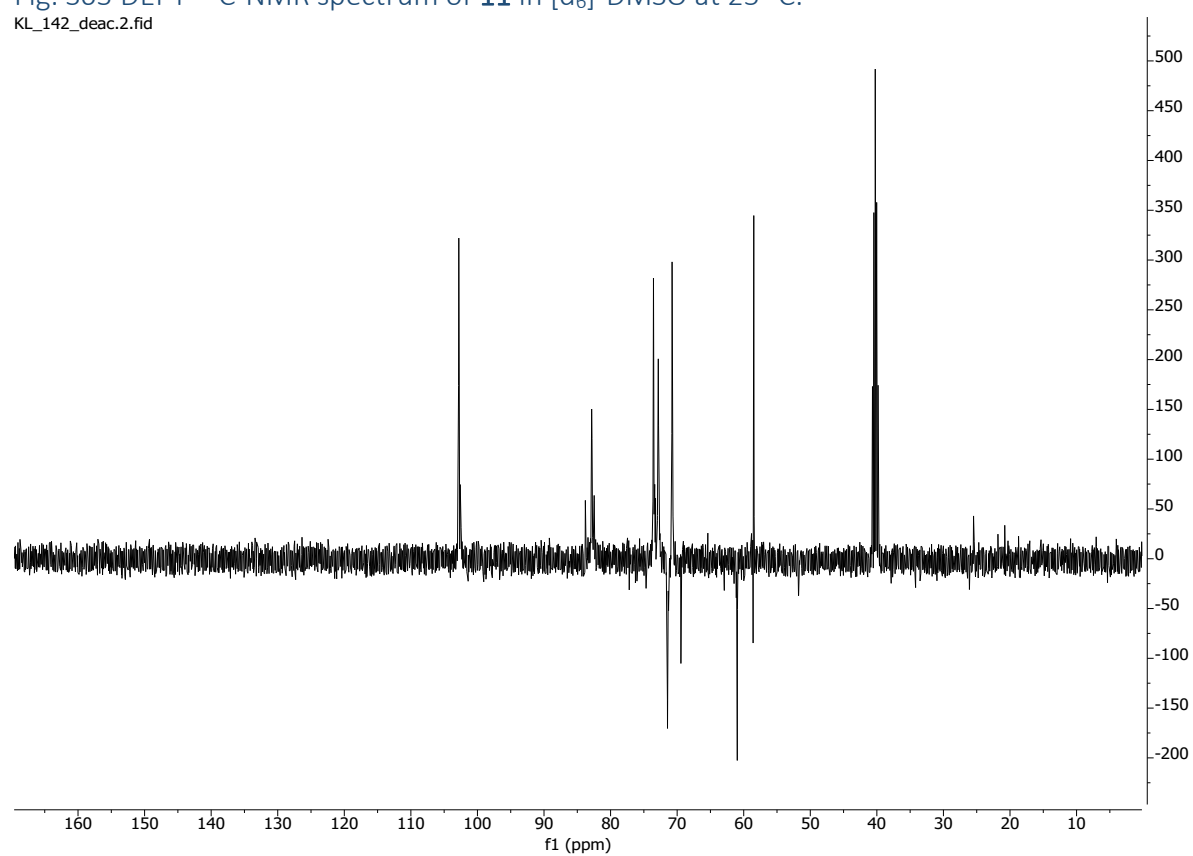


Fig. S64 COSY spectrum of **11** in [d₆]-DMSO at 25 °C.

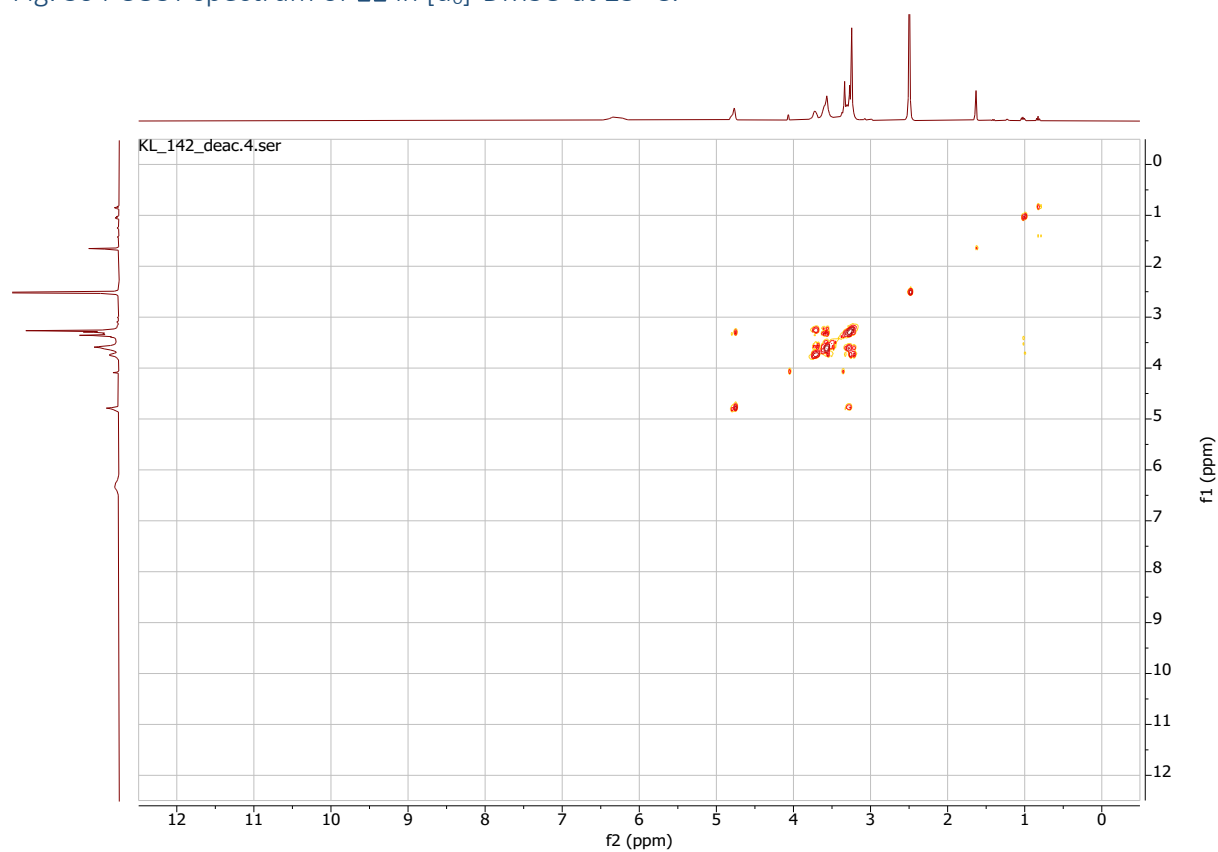


Fig. S65 HSQC spectrum of **11** in [d₆]-DMSO at 25 °C.

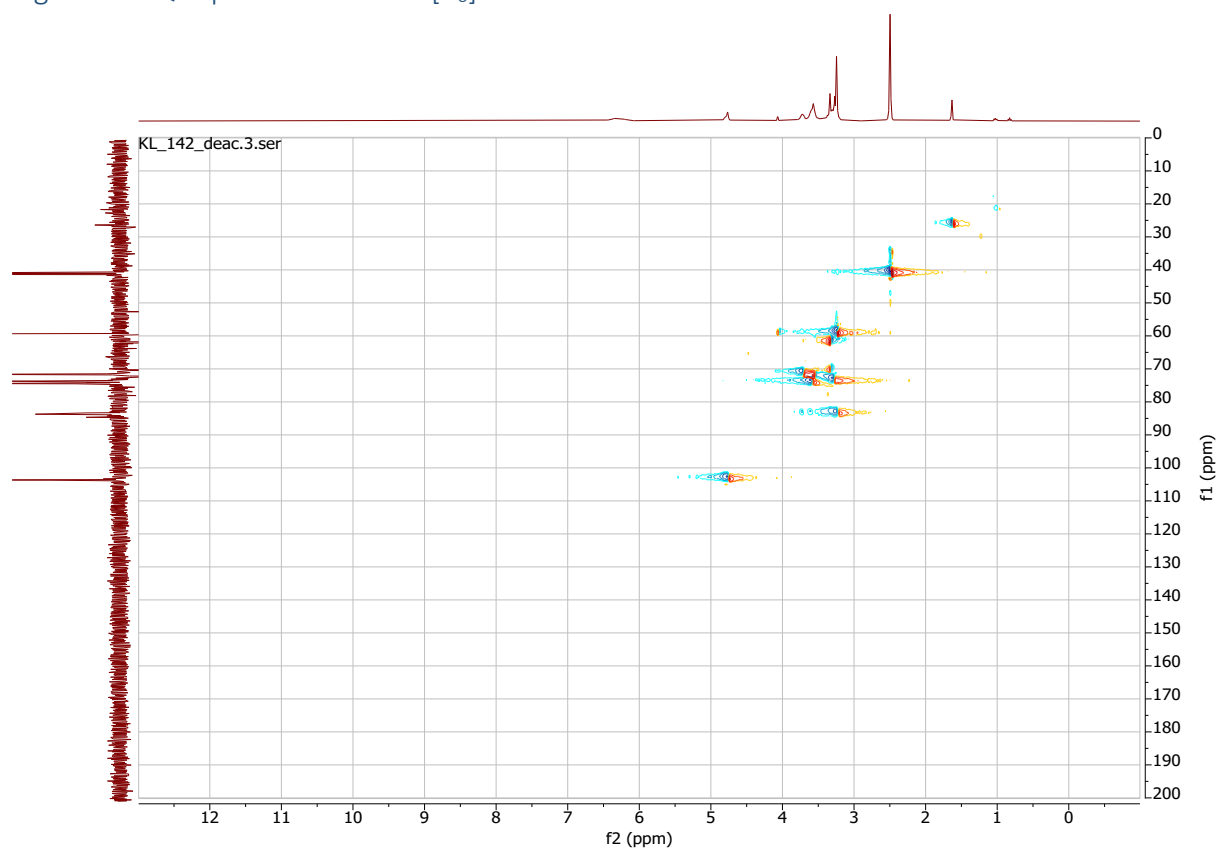


Fig. S66 IR spectrum of **11** in KBr pellet.

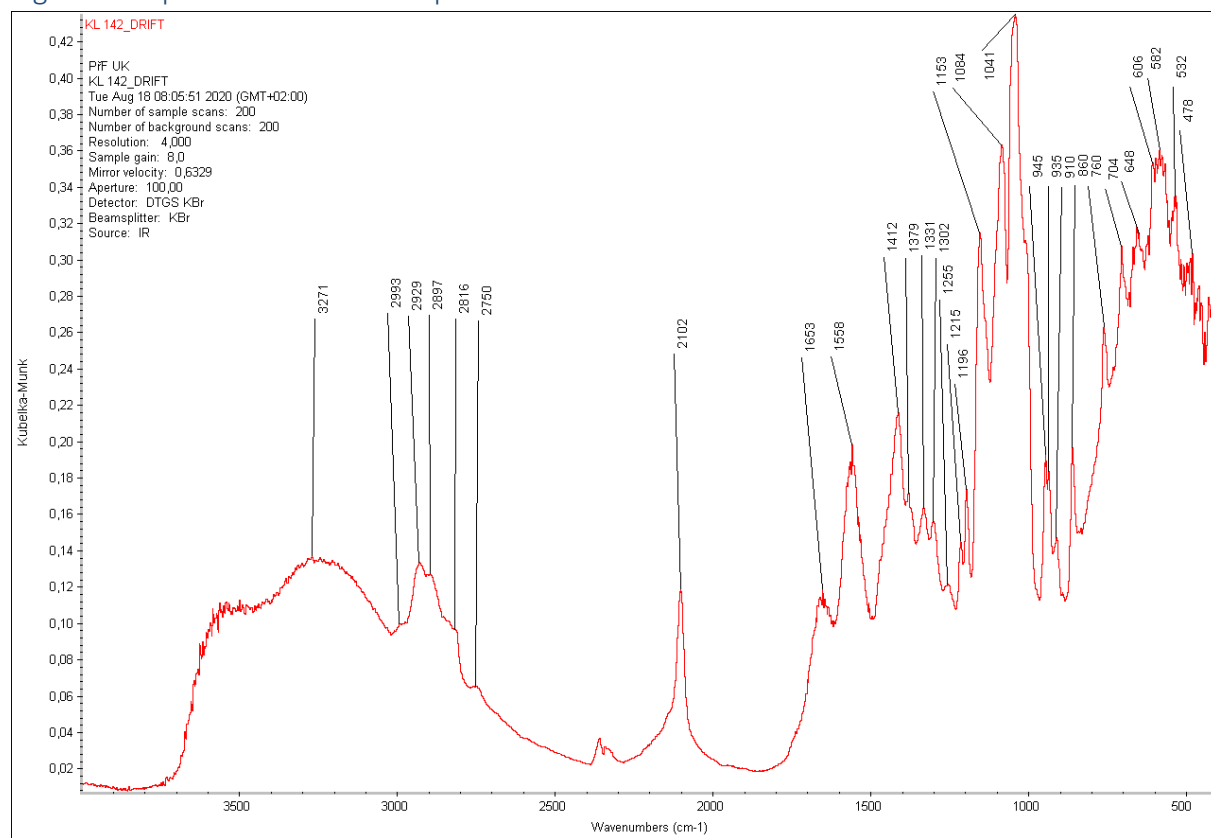
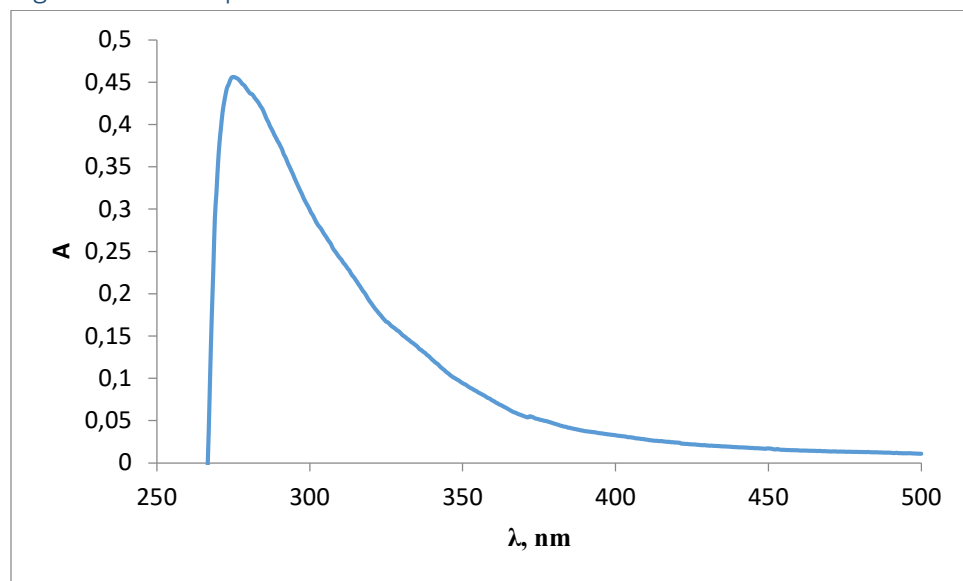


Fig. S67 UV-vis spectrum of **11** in DMSO.



N,N'-Bis(6^A-deoxy-6^{B,C,D,E,F,G}-*O*-hexakis-methyl-β-cyclodextrin-6^A-C-yl)urea (12)

6^A-Azido-6^A-deoxy-hexakis-6^{B,C,D,E,F,G}-*O*-methyl-β-cyclodextrin (**11**, 0.1 g; 0.0804 mmol) together with triphenylphosphine (0.05 g; 0.1907 mmol) and lithium iodide (0.023 g; 0.1717 mmol) were dissolved in dry DMF (19 mL). The reaction mixture was bubbled by dry CO₂ at 40 °C overnight. The solvent was distilled off, and column chromatography (10 g silica gel) with acetonitrile/water/ conc. aq. NH₃ 12/3/1 afforded 0.04 g of the desirable product (41% yield).

¹H-NMR (400 MHz, D₂O) δ=4.93-4.99 (H-C¹, 14H); 3.45-3.91 (H-C², H-C³, H-C⁴, H-C⁵, H-C⁶); 3.33 (Me-O-C⁶, 36H). ¹³C-NMR (100 MHz, D₂O) δ=101.92 (C¹); 81.47 (C²); 72.96 (C⁴); 72.15 (C⁵); 71.13 (C⁶); 70.38 (C⁵); 58.63 (Me-C⁶). HRMS (ESI): *m/z* calcd for C₉₇H₁₆₄N₂O₆₉+2H⁺: 1231.98 [M+2H⁺]; found: 1231.96992; [α]_{DMF}=+115.4°.

Fig. S68 ^1H -NMR spectrum of **12** in D_2O at 25 $^\circ\text{C}$.

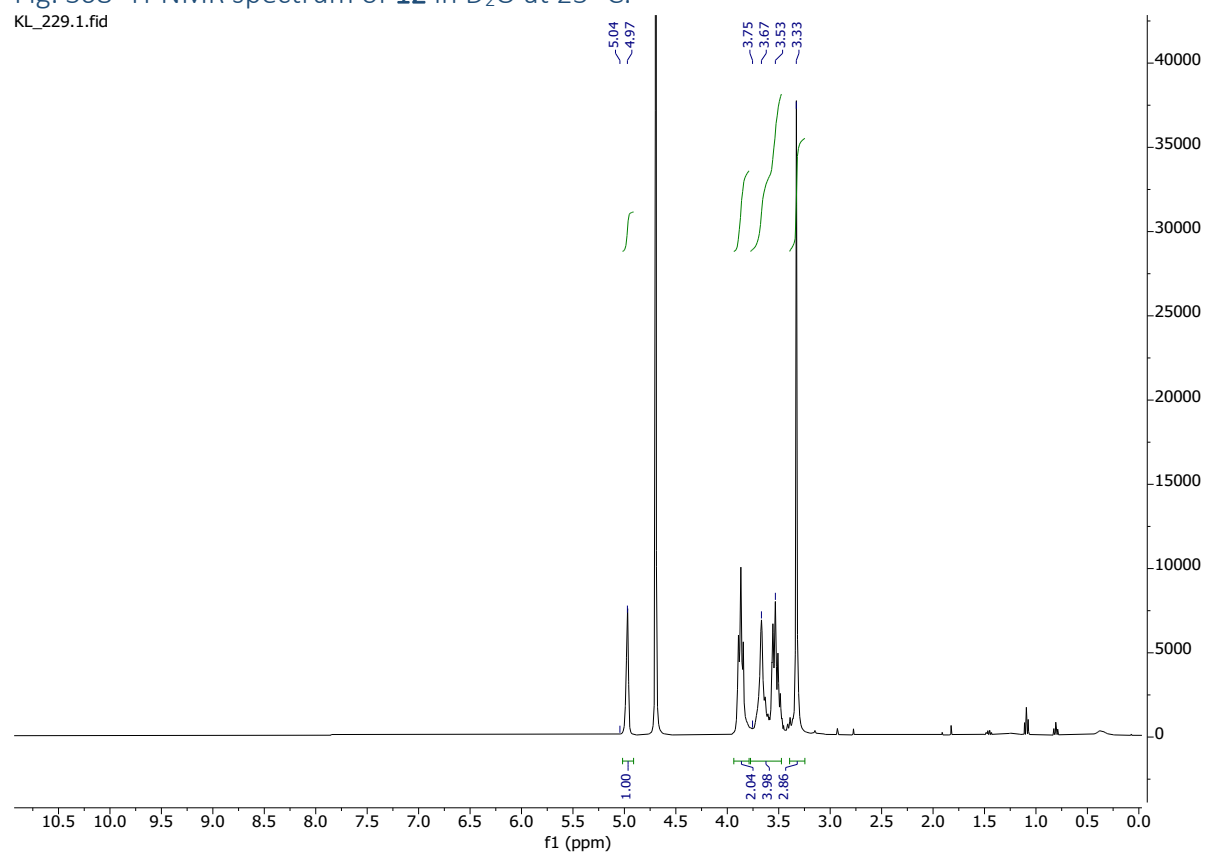


Fig. S69 DEPT- ^{13}C -NMR spectrum of **12** in D_2O at 25 °C.
KL_229.6.fid

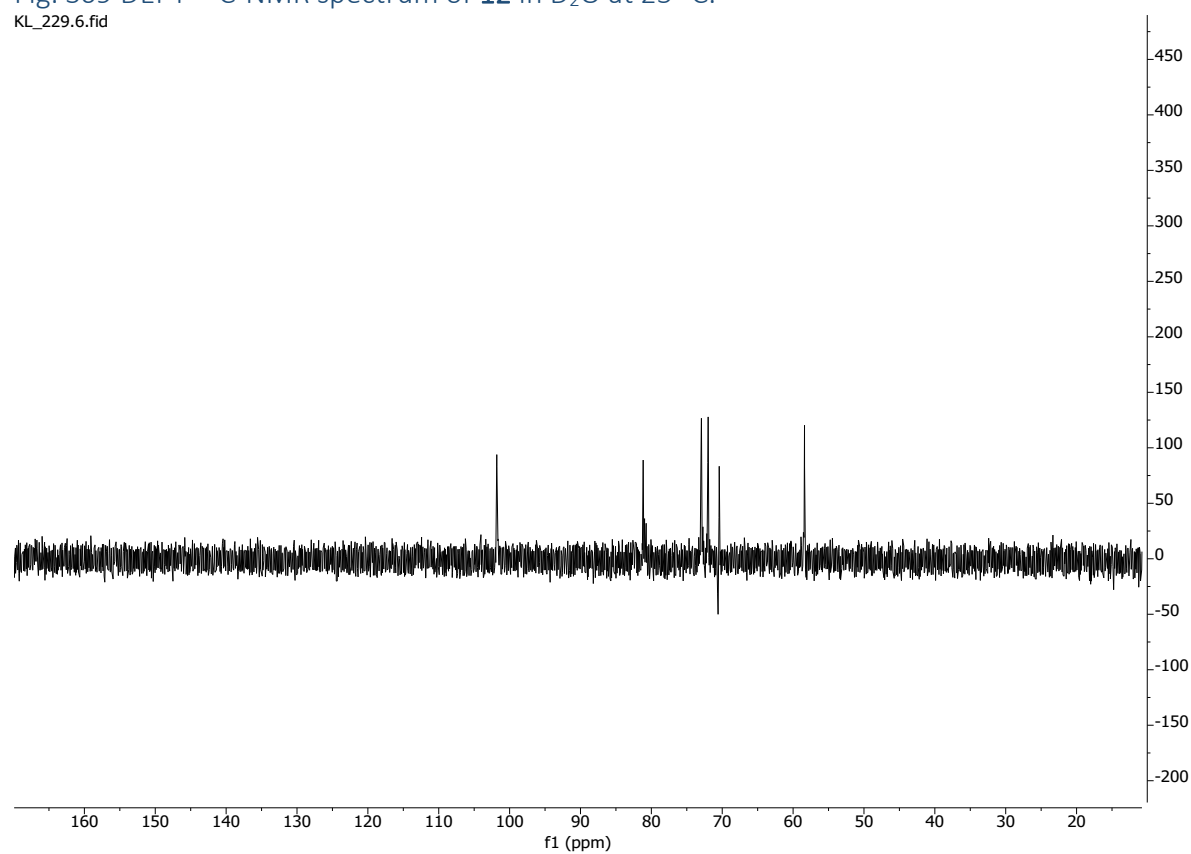


Fig. S70 COSY spectrum of **12** in D₂O at 25 °C.

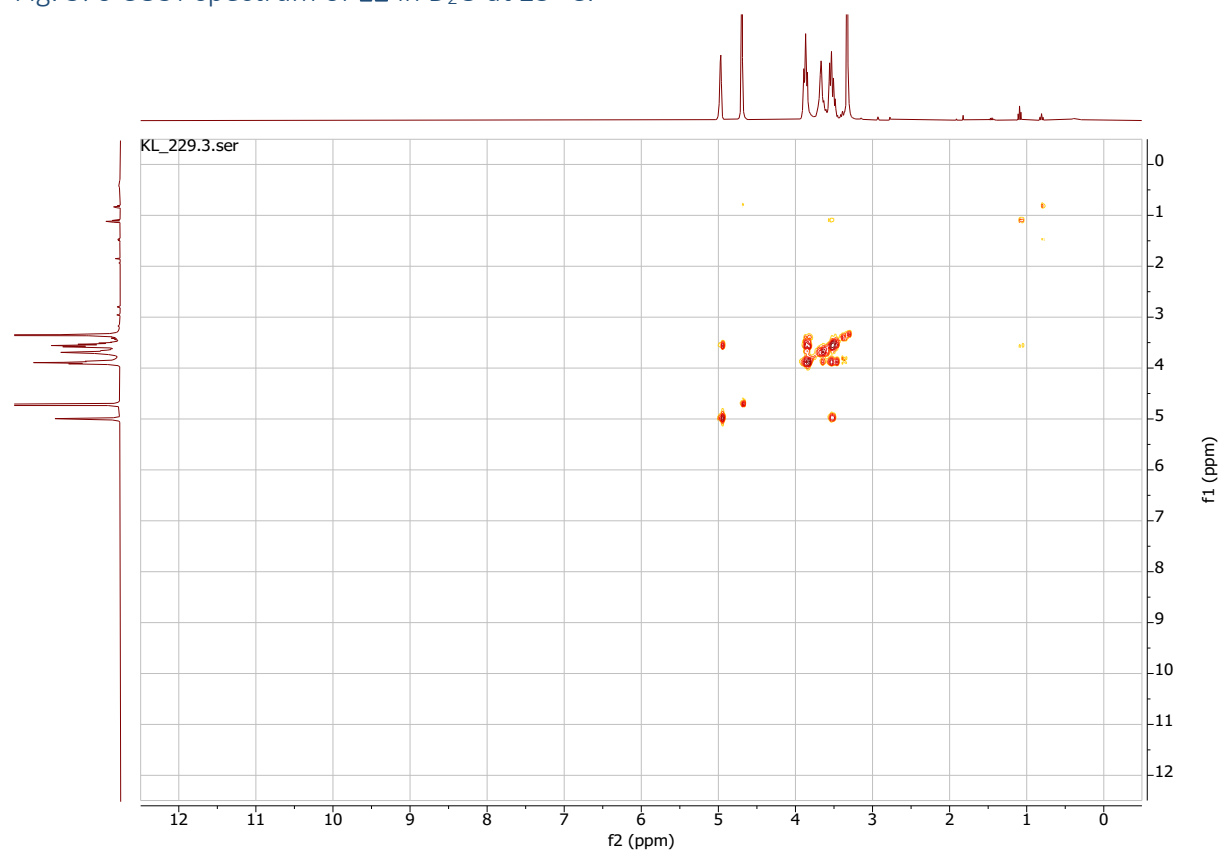


Fig. S71 HSQC spectrum of **12** in D₂O at 25 °C.

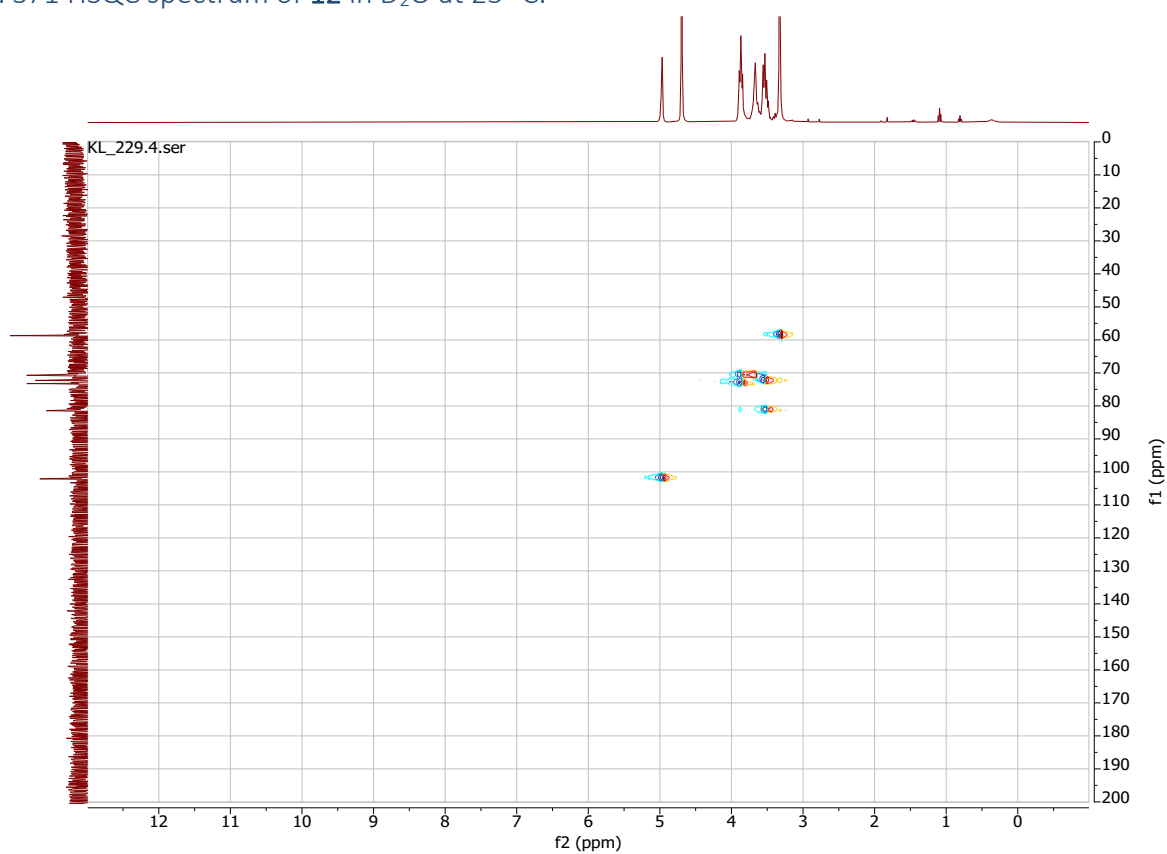


Fig. S72 IR spectrum of **12** in KBr pellet.

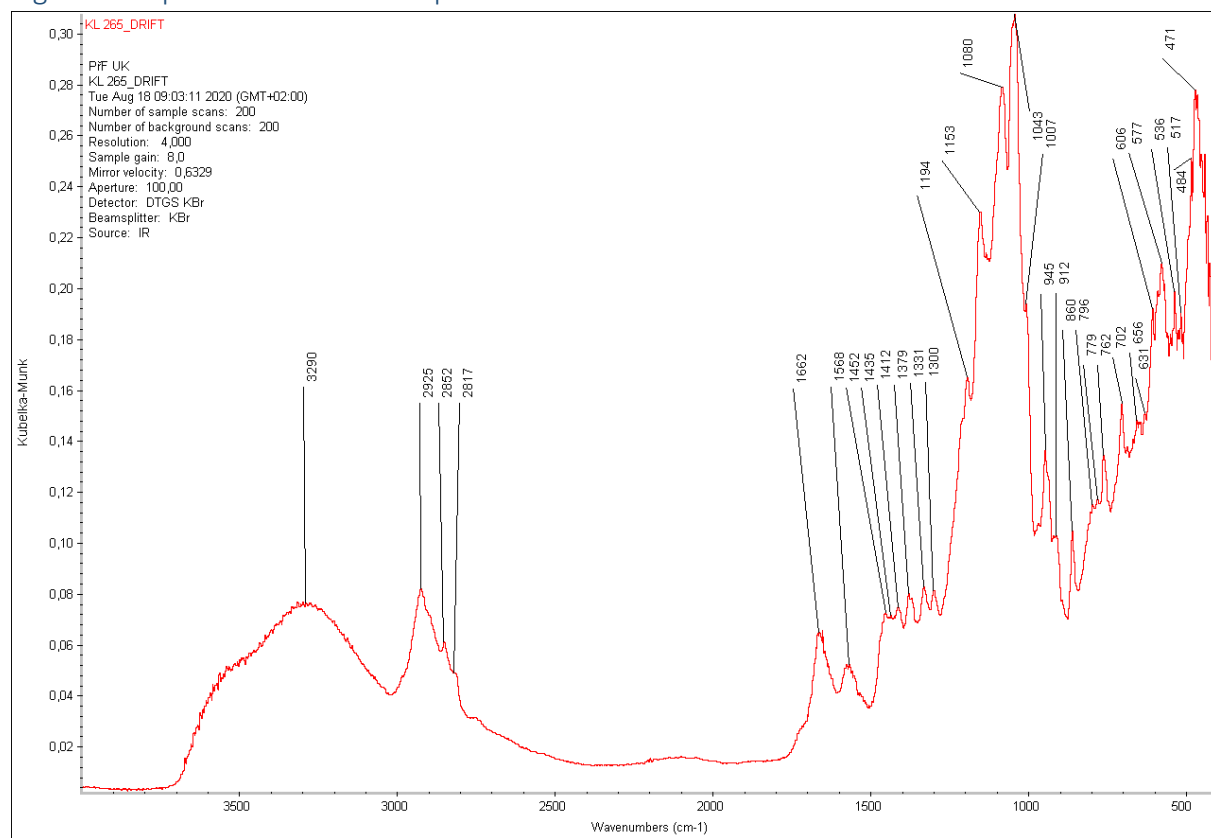
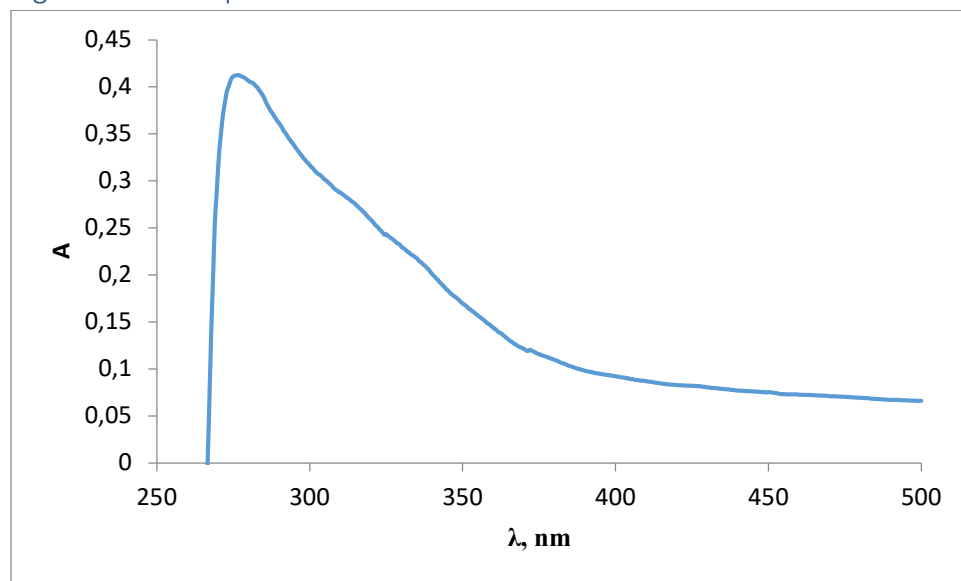


Fig. S73 UV-vis spectrum of **12** in DMSO.



II UV experiments with tetracene

Fig. S74 UV-vis spectrum of tetracene in DMSO at different concentrations.

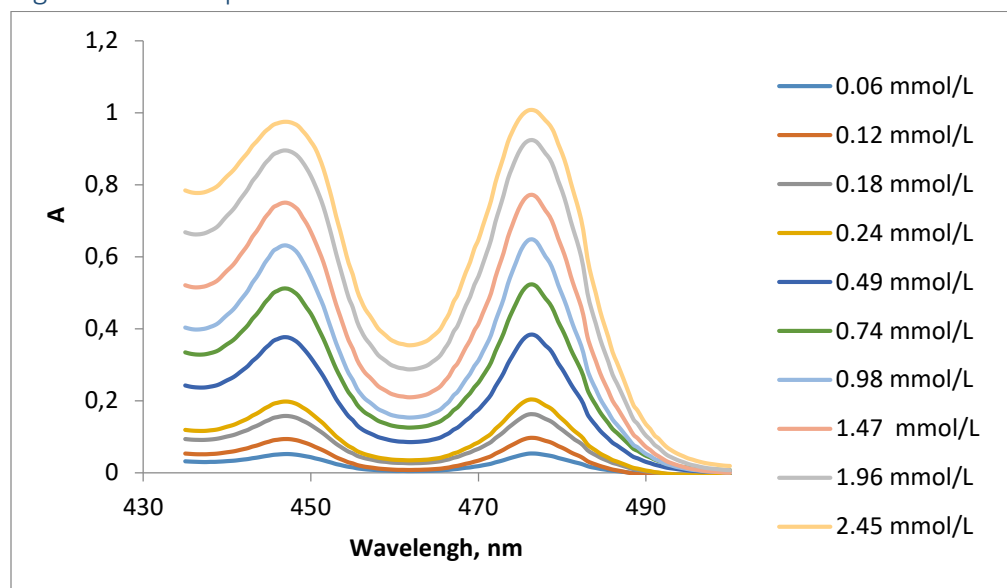


Fig. S75 Concentration dependence of tetracene's light absorbance in DMSO at 476 nm.

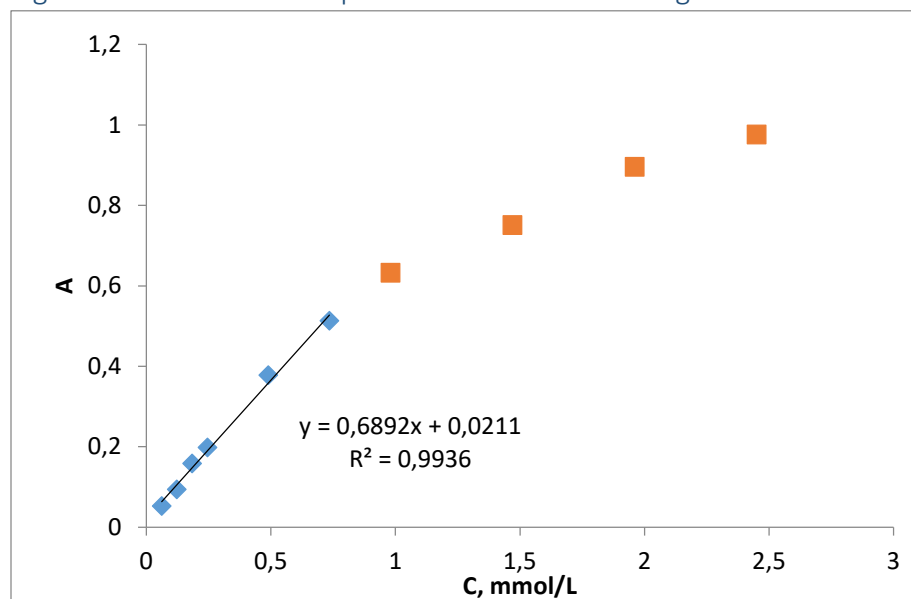


Fig. S76 UV-vis spectrum of 5-times diluted saturated tetracene solutions with the studied CDs and without any supramolecular host (O).

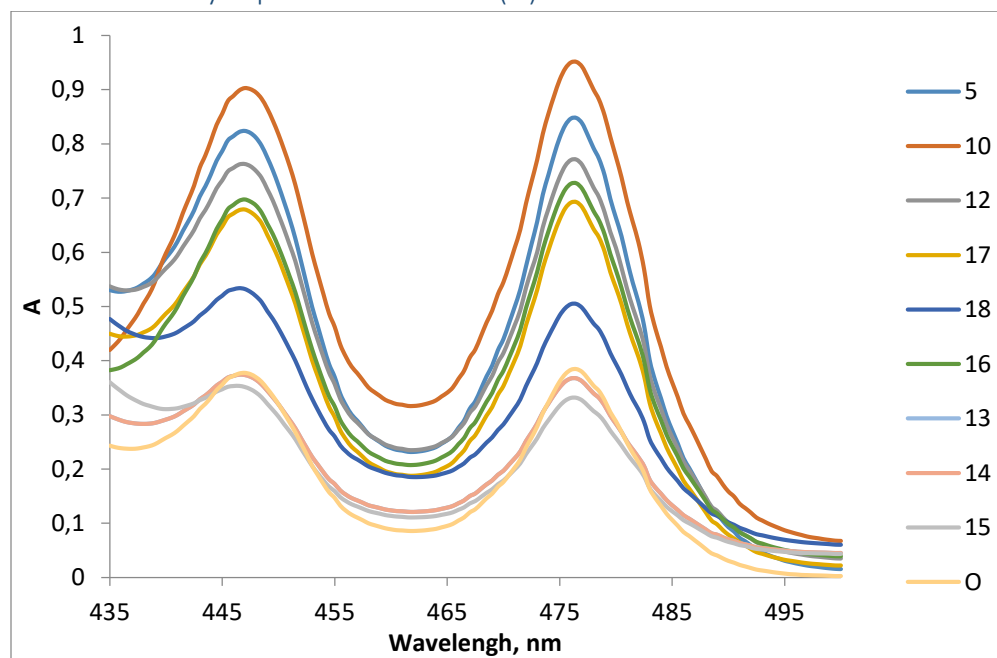
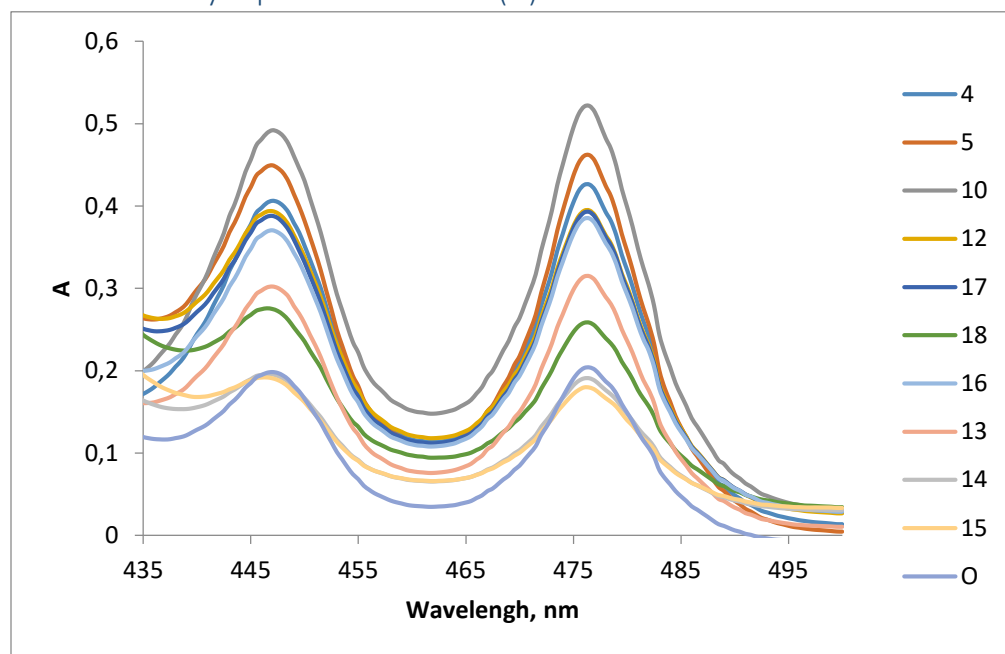
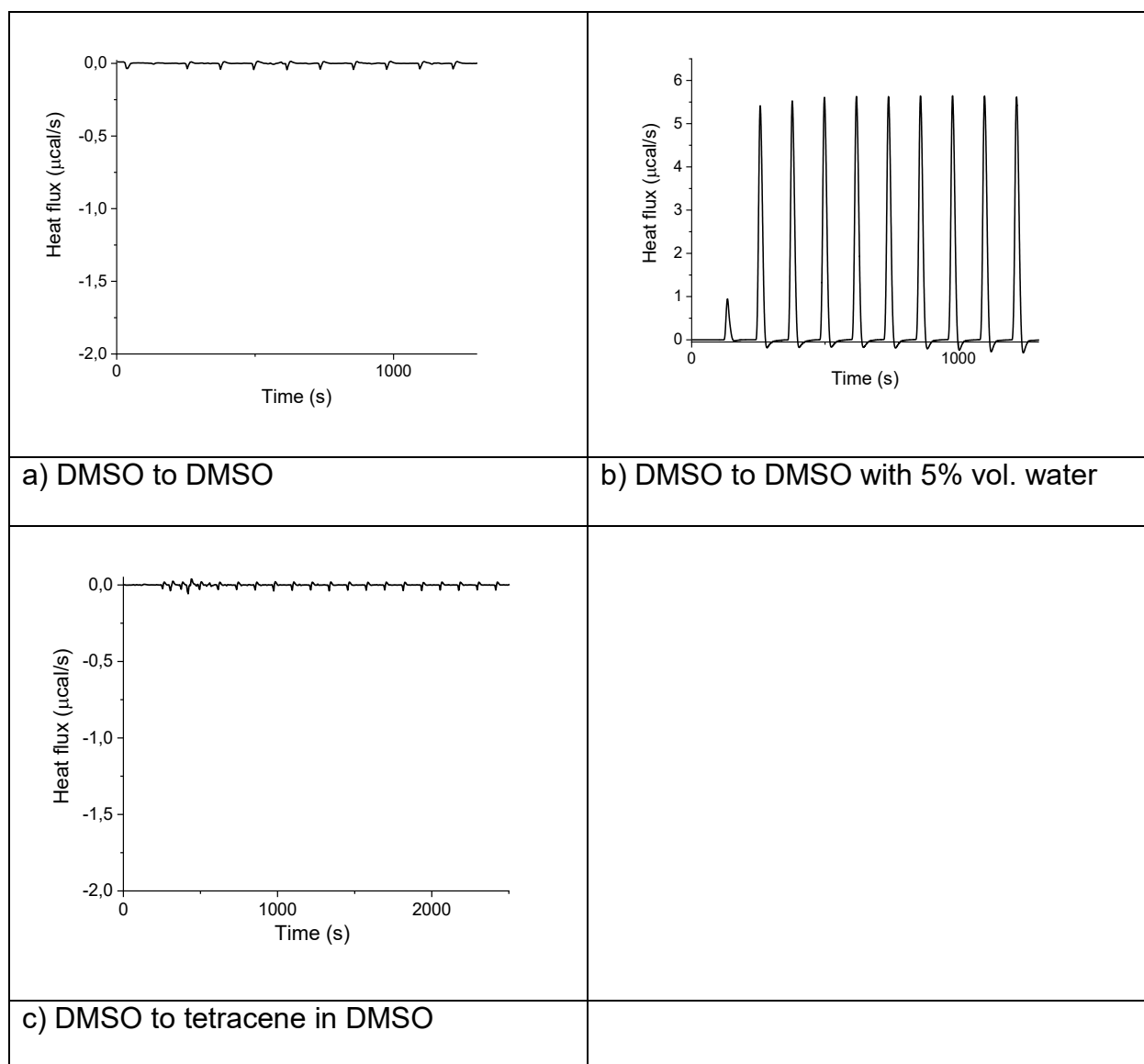


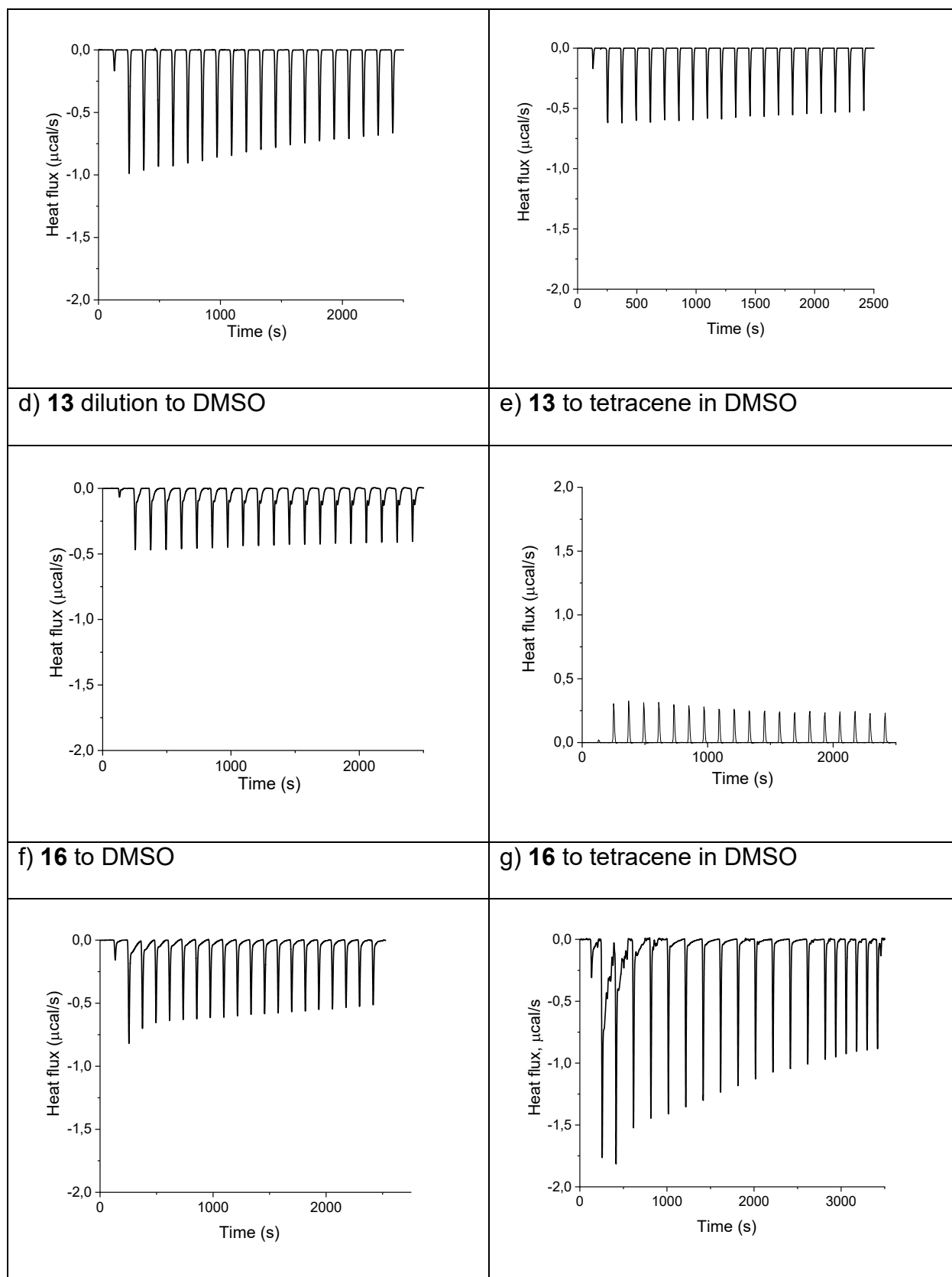
Fig. S77 UV-vis spectrum of 10-times diluted saturated tetracene solutions with the studied CDs and without any supramolecular host (O).

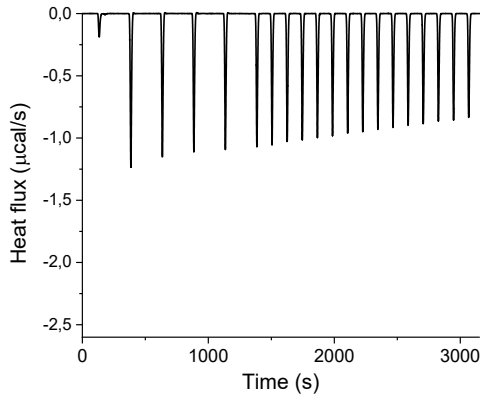
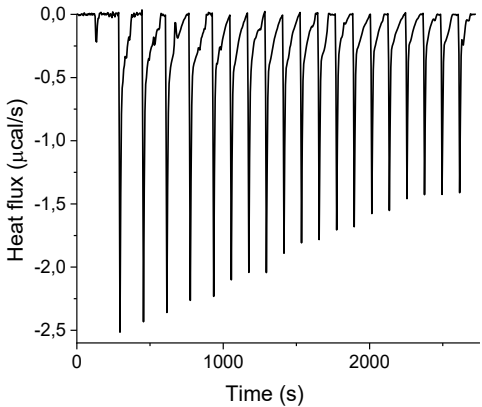
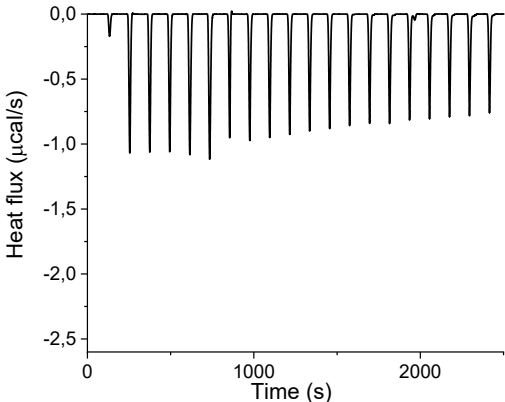
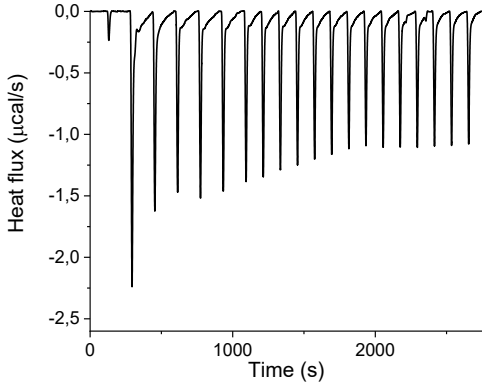


III ITC experiments

Fig. 78 ITC thermograms.





h) 4 to DMSO	i) 4 to tetracene in DMSO
	
j) 5 to DMSO	k) 5 to tetracene in DMSO
	
g) 10 to DMSO	h) 10 to tetracene in DMSO

IV References for SI

- [1] *Org. Synth.*, **2000**, 77, 220.
- [2] Tang, W.; Ng, S.-C. *Nat. Protoc.*, **2008**, 3, 691–697.
- [3] Zhou, Y.; Lindbäck, E.; Marinescu, L. G.; Pedersen, C. M.; Bols, M. *Eur. J. Org. Chem.*, **2012**, 2012, 4063–4070.

- [4] Varga, E.; Benkovics, G.; Darcsi, A.; Varnai, B.; Sohajda, T.; Malanga, M.; Beni, S. Electrophoresis, **2019**, 40, 2789–2798.
- [5] Carofiglio, T.; Cordioli, M.; Fornasier, R.; Jicsinszky, L.; Tonellato, U. *Carbohydr. Res.*, **2004**, 339, No. 7, 1361–1366.