Supplemental Information for Halogen- and Hydrogen-bonded Self-Assembled Fibrillar Networks of Substituted 1,3:2,4-Dibenzylidene-d-sorbitols (DBS)

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List of General Abbreviations

aq.	Aqueous
^{o}C	degrees Celsius
^{13}C NMR	Carbon Nuclear Magnetic Resonance Spectroscopy
COSY	Proton-Proton Correlation Spectroscopy
δ_C	Chemical Shift
equiv	Equivalents
g	Grams
h	Hours
^{1}H NMR	Proton Nuclear Magnetic Resonance Spectroscopy
HRESIMS	High-Resolution Electrospray Ionization Mass Spectroscopy
J	Coupling constant
JMOD	J-Modulated Spin-Echo Nuclear Magnetic Resonance Spectroscopy
mg	Milligrams
MHz	Megahertz
min	Minutes
ml	Milliliters
mmol	Millimoles
NMR	Nuclear Magnetic Resonance Spectroscopy
RT	Room Temperature
sat	Saturated
TLC	Thin-Layer Chromatography
TOF	Time of Flight
µl	Microliters

List of Chemical Abbreviations

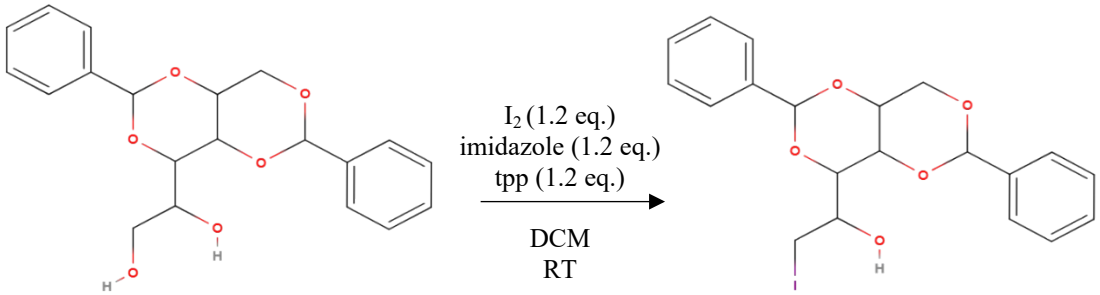
ACN	acetonitrile
DBS	1,3:2,4-dibenzylidene-D-sorbitol
DCM	dichloromethane
DMF	N, N-dimethylformamide
EtOH	ethanol
MeOH	methanol
pyr	pyridine
tpp	triphenylphosphine

Synthesis of DBS Derivatives

Reactions were performed using oven-dried glassware under dry nitrogen atmospheres with solvents dried over phosphorous pentoxide for dichloromethane and sodium for tetrahydrofuran before distillation. All other reagents from commercial suppliers are used as received. 1,3:2,4-Dibenzylidene-D-sorbitol (DBS) (BOC Sciences, New York, USA) was used as the precursor to synthesize 6-iodo-1,3:2,4-dibenzylidene-D-sorbitol (6-I-DBS), 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol (6-Br-DBS), and 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol (6-Cl-DBS). Chemicals required for synthesis included acetonitrile (≥99 %), dichloromethane (≥99.5 %) and methanol (≥99.5 %), from Fisher Scientific (ON, Canada), triphenylphosphine, imidazole, iodine, carbon tetrabromide and carbon tetrachloride, from Sigma-Aldrich (ON, CAN); and ethyl alcohol (95%) from Commercial Alcohols (ON, CAN).

^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker Avance spectrometer in $CDCl_3$ (internal standard, for ^{1}H, residual $CHCl_3$ δ 7.24; for ^{13}C $CDCl_3$ δ 77.0), or DMSO-d_6 (internal standard, for ^{1}H residual CD_2HSOCD_3 δ 2.49; for ^{13}C DMSO-d_6 δ 39.0). Chemical shifts (ppm) and coupling constants (J, Hz) were obtained from first-order analyses of 1D spectra and assignments of proton and carbon resonances were based on 2D ^{1}H-^{1}H and ^{13}C-^{1}H correlation experiments (Supplemental Figures S1-S12). Abbreviations for ^{1}H NMR data: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), triplet of doublets (td) and multiplet (m). TLC was performed on aluminum plates, precoated with silica gel 60 (250 μm) containing a fluorescent indicator; they were visualized under a UV lamp at 254 nm and were charred with a 10% solution of H_2SO_4 in EtOH. Compounds were purified by flash chromatography on Silica Gel 60 (230-400 mesh) (SiliCycle, QC, CA) and optical rotations were measured at 23 °C, on an Autopol III polarimeter (Rudolph Research, NJ, USA) and are reported as $[\alpha]_D$ (c in grams per 100 mL, solvent). Mass spectra were obtained under electrospray ionization (ESI) on a high-resolution mass spectrometer equipped with a TOF or an Orbitrap analyzer.

Synthesis of 1,3:2,4-dibenzylidene-6-iodo-D-sorbitol

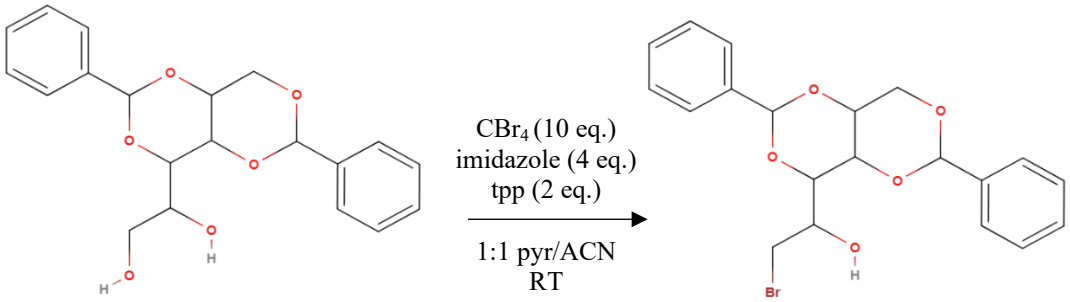


DBS (85%) 6-I-DBS

To a mixture of iodine (850 mg, 1.2 equiv), imidazole (228 mg, 1.2 equiv) and triphenylphosphine (878 mg, 1.2 equiv) in DCM (30 ml) was added DBS (1g, 2.79 mmol) at RT. The reaction was sealed under a nitrogen atmosphere and stirred vigorously for 5 hr at RT. Progress of the reaction was followed by TLC (1:50 MeOH/DCM). The crude product, obtained, was washed with EtOH (3 x 35 ml), filtered and concentrated by removing solvent on a rotary evaporator. 1,3:2,4-Dibenzylidene-6-iodo-D-sorbitol (6-I-DBS) was obtained in a white solid in a yield of 85% (1.1 g, 2.37 mmol).

$[\alpha]^{22}_{D}$ = +27.83 (c 1.0, CH_3CN). ^{1}H NMR (DMSO, 400 MHz, 298 K) (Figure S1) δ_H: 7.4-7.5 and 7.3-7.4 (2m, 4H and 6H, aromatics), 5.6 (d, 2H, 2CHPh), 5.5 (d, 1H, OH), 4.1 (m, 3H, H-1a, H-1b, H-3), 3.9 (d, 1H, H-2), 3.7 (dd, 1H, *J* = 1.46, 8.73 Hz, H-4), 3.5 (m, 1H, H-5), 3.4 (m, 2H, H-6a, H-6b). ^{13}C NMR (DMSO, 100 MHz, 298 K) (Figure S2) δ_C: 139.0, 138.6, 129.1, 129.0, 128.5, 128.4, 126.6, 126.5 (aromatics), 99.8 (2CHPh), 81.0 (C-4), 70.3 (C-2), 69.6 (C-1), 68.5 (C-3), 65.3 (C-5), 16.3 (C-6). HR-MS (ESI): m/z calculated for $C_{20}H_{21}O_5I$ $[M]^+$ = 469.05064, found = 469.05040.

Synthesis of 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol

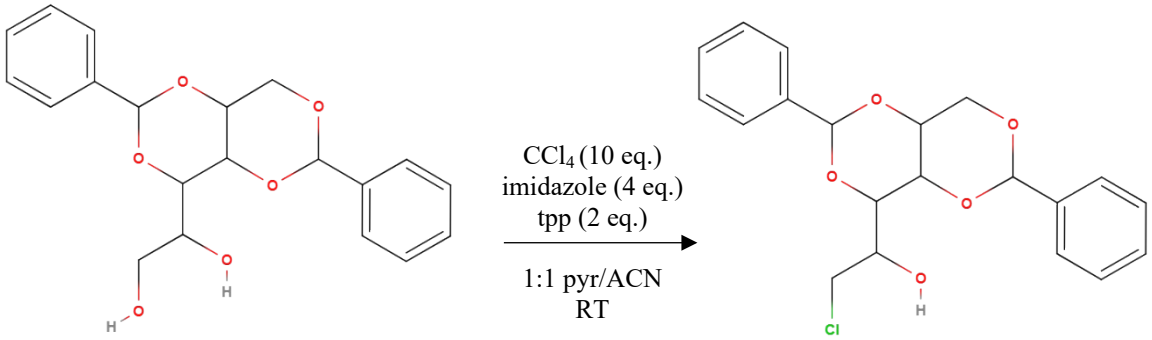


DBS (63%) 6-Br-DBS

DBS (1g, 2.79 mmol) was added to a mixture of carbon tetrabromide (9.3 g, 10 equiv), imidazole (763 mg, 4 equiv) and triphenylphosphine (1.5 g, 2 equiv) in 1:1 pyridine/acetonitrile (20 ml) at RT. The reaction mixture was sealed under a nitrogen atmosphere and stirred vigorously for 5 hr at RT. Progress of the reaction was followed by TLC (1:50 MeOH/DCM) and quenched by adding MeOH (250 µl) and stirring for 10 min. The reaction mixture was diluted with toluene (6 x 50 ml), reduced to residue on a rotary evaporator and dried under vacuum. The residue, 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol (6-Br-DBS), was passed twice a through a silica column using (1:50 MeOH/DCM) to yield 63% (738 mg, 1.75 mmol) of product.

$[\alpha]^{22}_D$ = +29.13 (c 1.0, CH_3CN). ^1H NMR (CD_3OD, 400 MHz, 298 K) (Figure S5) δ_H: 7.51-7.59 and 7.3-7.4 (2m, 4H and 6H, aromatics), 5.6 (d, 2H, 2CHPh), 4.4 (dd, 1H, J = 1.4, 12.6 Hz, H-1a), 4.2 (m, 1H, H-5), 4.1 (m, 2H, H-1b, H-3), 3.9 (dd, 1H, J = 1.9, 8.5 Hz, H-4), 3.8 (m, 1H, H-2), 3.7 (m, 2H, H-6a, H-6b), 2.3 (d, 1H, OH). ^{13}C NMR (CD_3OD, 100 MHz, 298 K) (Figure S6) δ_C: 137.8, 137.5, 129.16, 129.10, 128.26, 128.23, 126.46, 126.41 (aromatics), 100.9, 100.8 (2CHPh), 78.9 (C-4), 70.3 (C-2), 70.0 (C-1), 68.6 (C-3), 67.1 (C-5), 38.2 (C-6). HR-MS (ESI): m/z calculated for $C_{20}H_{21}O_5Br$ $[M]^+$ = 421.06451 and 423.06451, found = 421.06448 and 423.06231.

Synthesis of 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol



DBS (69%) 6-Cl-DBS

DBS (1g, 2.79 mmol) was added to a mixture of carbon tetrachloride (2.7 ml, 10 equiv), imidazole (763 mg, 4 equiv) and triphenylphosphine (1.5 g, 2 equiv) in 1:1 pyridine/acetonitrile (20 ml) at RT. The reaction mixture was sealed under a nitrogen atmosphere and stirred vigorously for 4-5 hr at RT. Progress of the reaction was followed by TLC (1:50 MeOH/DCM) and quenched by adding MeOH (250 µl) and stirring for 10 min. The reaction mixture was diluted with toluene (6 x 50 ml), reduced to residue on a rotary evaporator and dried under vacuum. The residue, 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol (6-Br-DBS), was passed through a silica column using (1:50 MeOH/DCM) to yield 724 mg (69%, 1.92 mmol) of 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol (6-Cl-DBS).

$[\alpha]^{22}_{D}$ = +32.13 (c 1.0, CH_3CN). 1H NMR (CD_3OD, 400 MHz, 298 K) (Figure S9) δ_H: 7.51-7.59 and 7.3-7.4 (2m, 4H and 6H, aromatics), 5.6 (d, 2H, 2CHPh), 4.4 (dd, 1H, J = 1.4, 12.6 Hz, H-1a), 4.3 (m, 1H, H-5), 4.1 (m, 2H, H-1b, H-3), 3.9 (dd, 1H, J = 1.9, 8.6 Hz, H-4), 3.8 (m, 3H, H-6a, H-6b, H-2), 2.3 (d, 1H, OH). ^{13}C NMR (CD_3OD, 100 MHz, 298 K) (Figure S10) δ_C: 137.9, 137.5, 129.16, 129.10, 128.26, 128.22, 126.46, 126.40 (aromatics), 100.9, 100.8 (2CHPh), 78.0 (C-4), 70.4 (C-2), 70.0 (C-1), 68.7 (C-3), 67.6 (C-5), 47.8 (C-6). HR-MS (ESI): m/z calculated for $C_{20}H_{21}O_5Cl$ $[M]^+$ = 377.11503, found = 377.11485.

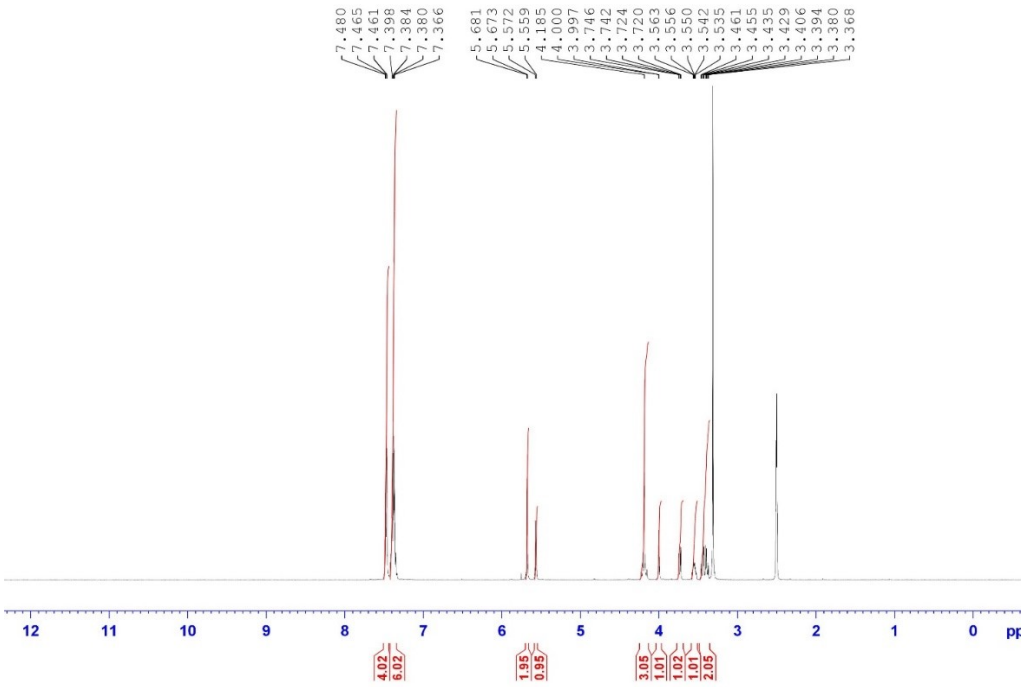


Figure S1: ^{1}H-NMR of 1,3:2,4-dibenzylidene-6-iodo-D-sorbitol; 400MHz, 298 K, $CDCl_3$.

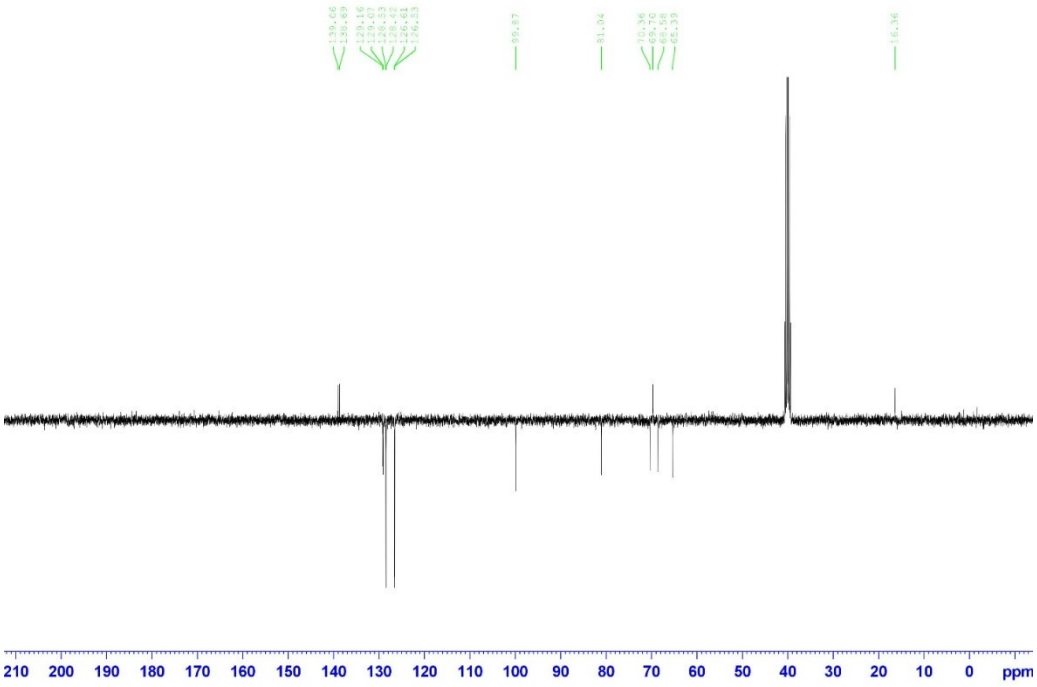


Figure S2: ^{13}C-NMR of 1,3:2,4-dibenzylidene-6-iodo-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

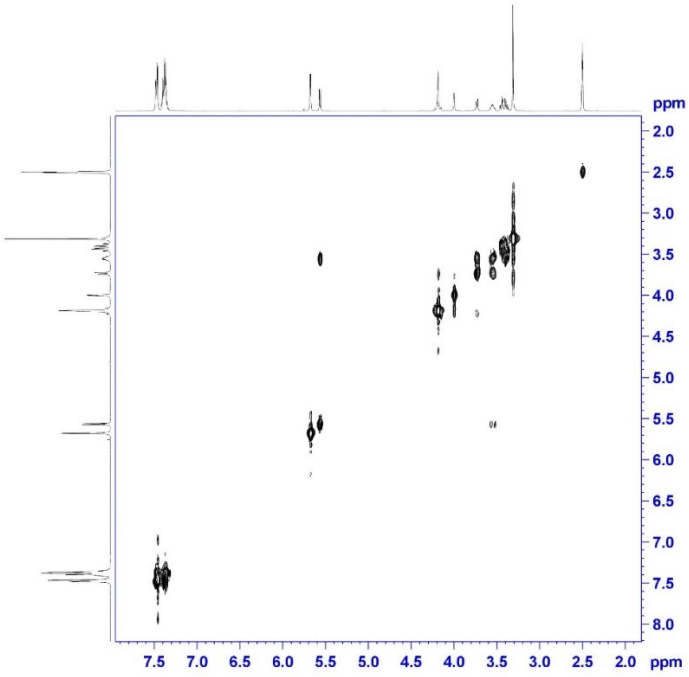


Figure S3: COSY of 1,3:2,4-dibenzylidene-6-iodo-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

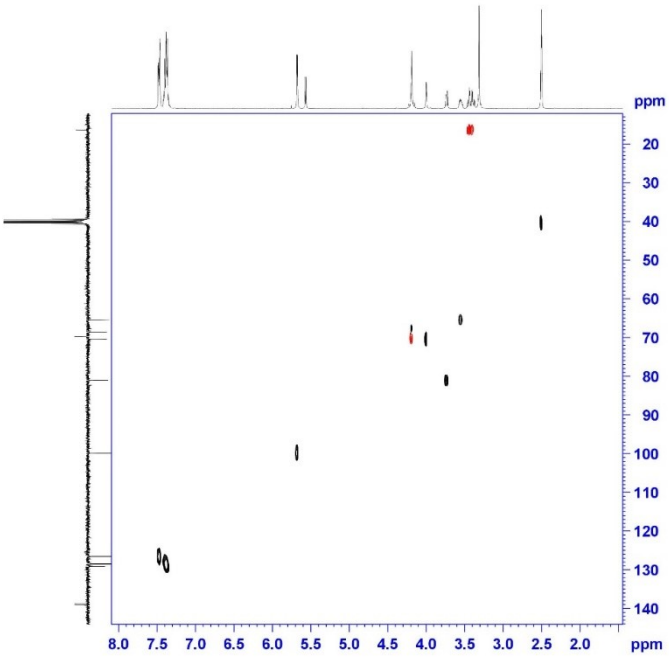


Figure S4: HSQC of 1,3:2,4-dibenzylidene-6-iodo-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

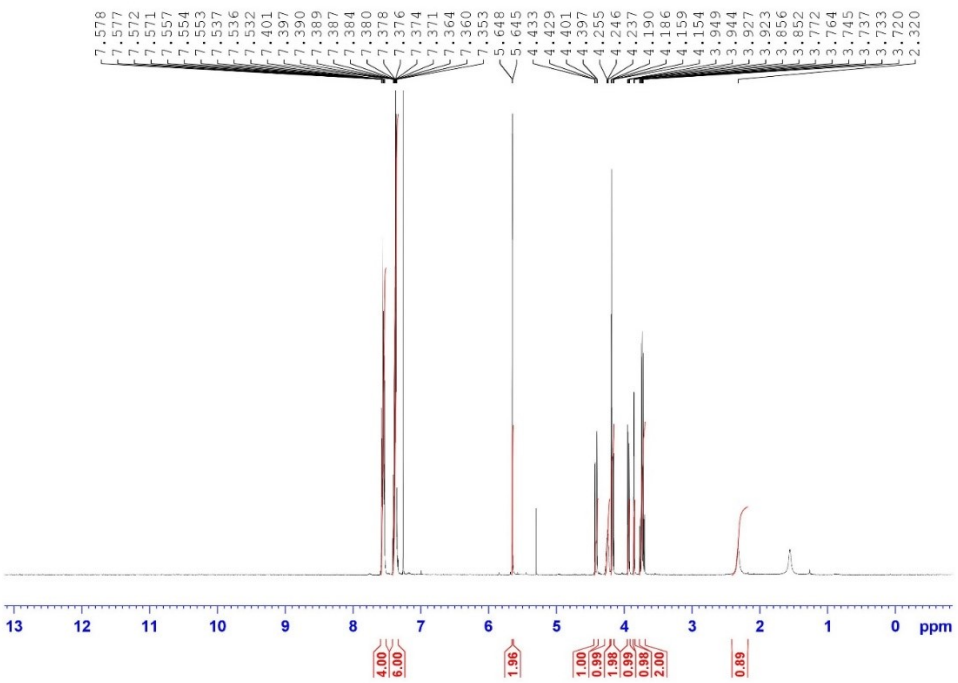


Figure S5: ^{1}H-NMR of 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol; 400MHz, 298 K, $CDCl_3$.

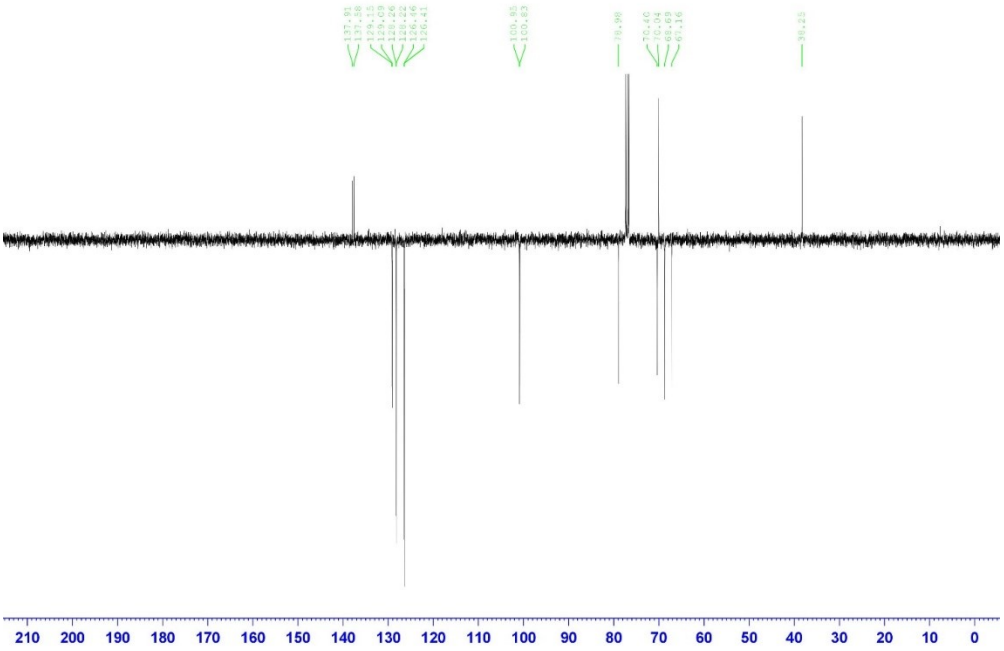


Figure S6: ^{13}C-NMR of 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

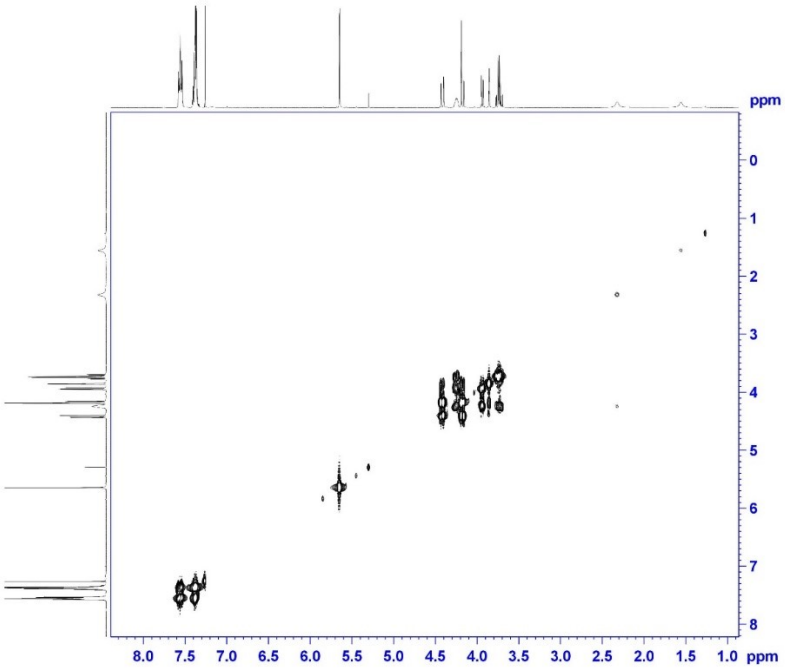


Figure S7: COSY of 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

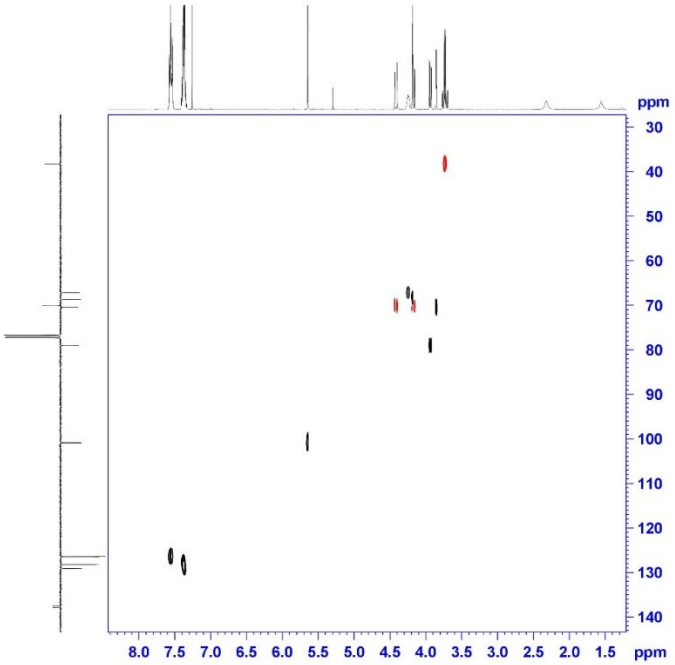


Figure S8: HSQC of 6-bromo-1,3:2,4-dibenzylidene-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

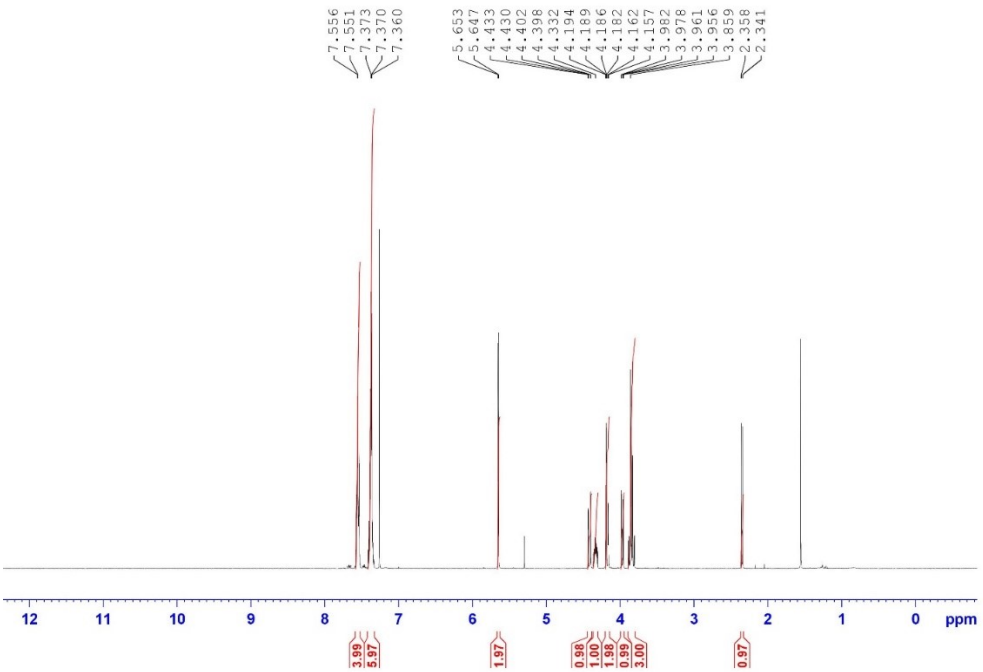


Figure S9: ^{1}H-NMR of 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol; 400MHz, 298 K, $CDCl_3$.

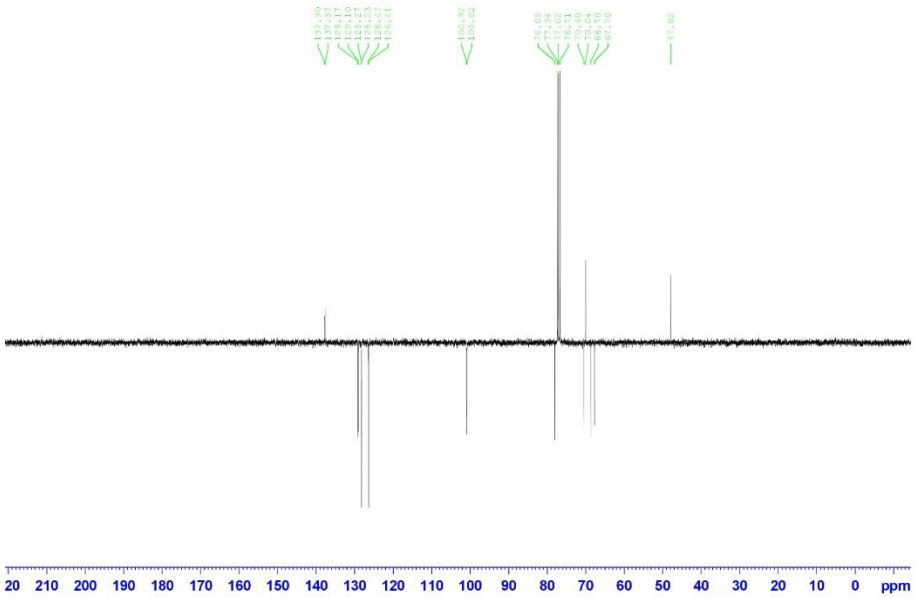


Figure S10: ^{13}C-NMR of 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

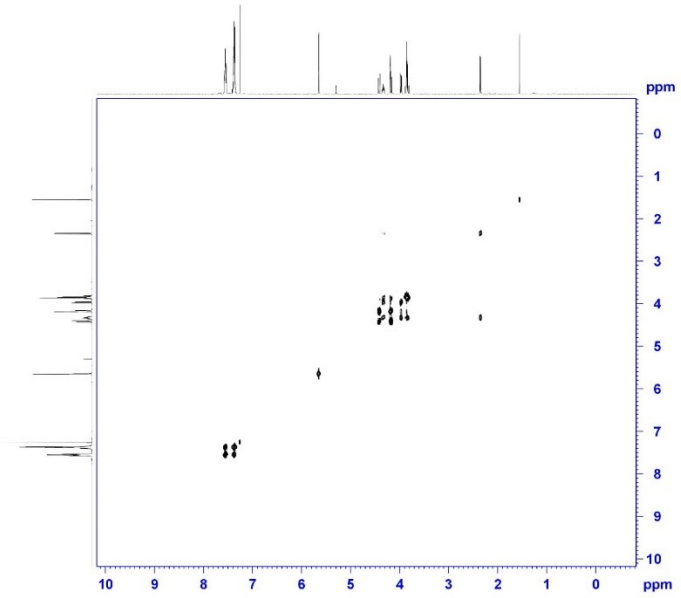


Figure S11: COSY of 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol; 100MHz, 298 K, $CDCl_3$.

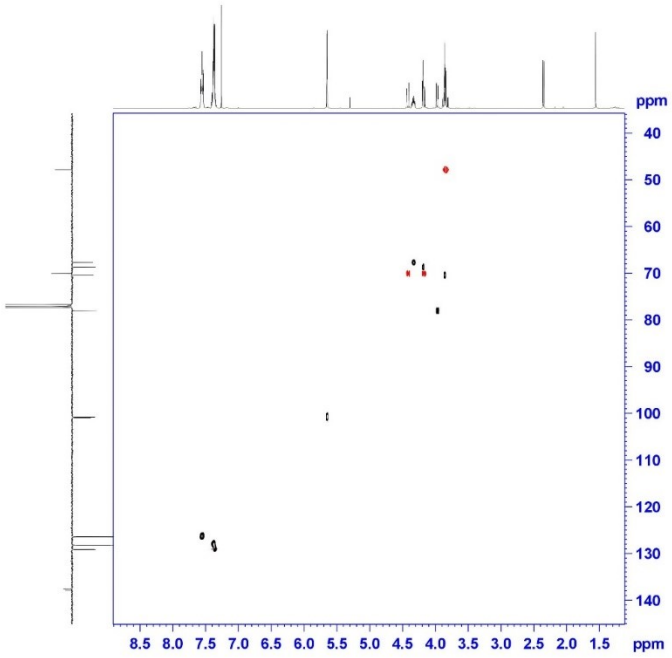


Figure S12: HSQC of 6-chloro-1,3:2,4-dibenzylidene-D-sorbitol; 100MHz, 298 K, $CDCl_3$.