Research Article

Green Synthesis Characterization and Thermotropic Behaviour of O-Linked Glycopyranosides of Phenolic Esters

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Focusing on green chemistry protocols, a series of carbohydrate derivatives (5a–l) have been synthesized by Fischer glycosylation of α -D-glucose, D-xylose, and α -maltose with several nonpolar phenolic ester aglycones (3a–d) derived from menthol by employing solid-supported Si-H⁺ as the catalyst. In order to study the extent of mesomorphism in target molecules, the thermotropic behaviour has been studied by using the thermoanalytic DSC/TGA technique and polarized optical microscope. Phase transitions in the DSC thermograms of 5a–l with two endothermic melting point peaks and various exothermic crystalline transitions exhibits the existence of mesophases. However, optical photomicrographs revealed that the new glycopyranosides formed smectic A phases. Moreover, all the compounds (3a–d and 5a–l) were confirmed by FTIR and ¹H NMR.

1. Introduction

Mesogens, the emerging scientific domain is thermodynamically stable, dimensionally ordered, flowing state of matter that exist between isotropic liquid and crystalline solid. They have been experiential for over hundred years but were first recognized systematically by Friedrich Reinitzer [1–3]. Glycosides are of special interest due to their role as thermotropic and lyotropic mesogens, surfactants, lubricants, solvents, drug delivery systems and membrane crystallizers in pharmaceuticals, food, biotechnology and material chemistry [4]. The existence of mesogens primarily depends upon the nature of glycone used as a hydrophilic part, hydrophobic aglycone part attached to the polar carbohydrate, ether or the ester linkage and the effect of any rigid spacer or unsaturation thus imparting the mesophase behaviour to the overall molecule [5].

According to literature guidelines, glycosylation reactions have been executed by employing various solvents such

as dichloromethane, tetrahydrofuran, toluene [6], dioxane [7, 8] and dimethylformamide [9, 10]. The variety of catalyst ranges from the organic catalyst such as N-iodosuccinimide, boron trifluoride etherate, 4-dimethylaminopyridine, pentamethyldiethylenetriamine, 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide to the metal catalyst including tin tetrachloride and indium [11–20]. However, their toxicity, prohibitive prices and increased waste disposal costs add up to serious drawbacks for the large-scale applications. The environmental concerns addressed elimination of toxic solvents and reagents in the chemical reactions and doing them “neat” goes a long way towards achieving the goals of green atom economic chemistry [21, 22].

Therefore, the aim of the present research deals with the solvent-free synthesis of twelve new glycosides by condensing α -D-glucose, D-xylose, and α -maltose to phenolic esters as candidates possessing phase transitions and mesogenic behaviour. Preparation of the solid-supported Si-H⁺ catalyst and its characterization are imperative features

of this work. First, direct condensation of mono-, di-, and trihydroxy phenolic acids with menthol was accomplished. Then, mesogenic nature of the molecule was achieved by chemical combination of hydrophobic esters and glycones by making some modifications in the reported glycosylation strategies.

2. Experimental

2.1. Materials and Methods. All reagents and solvents were of analytical grade with highest purity. L-Menthol, α -D-glucose, D-xylose, and α -maltose were purchased from Sigma-Aldrich and Merck. Melting points were determined with a Gallenkamp digital melting point apparatus with a maximum range of 360°C. Reaction progress was observed by TLC on silica gel 60F-254 sheets (Merck) visualized with the mineral light UV lamp (230 V~50/60 Hz). Silica gel mesh size 60–200 was used for catalyst preparation, while 230–400 mesh size was used for purification by column chromatography. Spectroanalytical techniques were used for the confirmation of chemical structures of all the products. FTIR spectra were scanned in a Shimadzu IR Tracer-100 FT-IR spectrometer. ^1H NMR spectra of all the compounds were recorded in ppm at 400 MHz in DMSO- d_6 on the Bruker NMR spectrometer. The thermal behaviour and the phase transitions were analyzed by DSC/TGA, SDT-Q600TA Instrument, USA, from 25°C to 600°C at 10°C/min heating rate (Exo Up). XRD patterns were recorded on D8 Discover diffractometer, Bruker, Germany. SEM micrographs were obtained using the ZEISS scanning electron microscope with the HDBSD detector. Optical textures were observed using the Polaroid Olympus camera-fitted optical microscope with a Mettler Toledo hot stage.

2.2. Preparation of Acid-Immobilized Silica Si-H^+ Catalyst. Si-H^+ catalyst was prepared by stirring silica gel (1 g), mesh size 60–200, in 2 ml dichloromethane for 15 min followed by addition of 0.75 ml (1.39 mol%) concentrated sulfuric acid (98%) dropwise in silica and further stirred for an hour. The mixture was gradually dried at 60, 100, and then 120°C in an oven to get free-flowing Si-H^+ catalyst.

2.3. Synthesis of Phenolic Ester Aglycones. Phenolic acids (1a–d) (1 mmol each), menthol (2) (0.468 g, 3 mmol) and Si-H^+ catalyst (0.294 g, 0.3 mole%) were stirred at 80–100°C for 2.5 hours. TLC assisted to observe reaction progress using 30% ethyl acetate and n-hexane as eluent. After reaction completion, the contents were dissolved in ethyl acetate, filtered and dried to isolate the product. The catalyst was washed with dichloromethane and dried in vacuum. The crude product was then subjected to column chromatography and eluted with ethyl acetate and n-hexane as the mobile phase to afford pure 3a–d.

2.3.1. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-Hydroxybenzoate (3a). Yield: 89%, pale yellow solid, mp: 145–148. FTIR: $\nu_{\text{max}} = 3340.71, 2954.95, 1735.32, 1446.61,$

1165.00 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): $\delta = 0.80$ (d, $J = 7.2$ Hz, 3H, H-7), 0.85 (d, $J = 7.4$ Hz, 3H, H-9), 0.87 (d, $J = 7.5$ Hz, 3H, H-10), 1.35–1.40 (m, 1H, H-4), 1.43–1.48 (m, 1H, H-8), 1.50–1.54 (m, 1H, H-1), 1.63–1.68 (m, 2H, H-2), 1.70–1.75 (m, 2H, H-5), 1.77–1.79 (m, 2H, H-6), 3.44 (dt, $J = 11$ Hz, 5 Hz, 1H, H-3), 6.72 (d, $J = 8.1$ Hz, 2H, H-1', H-5'), 7.88 (d, $J = 8$ Hz, 2H, H-2', H-4'), 9.58 (s, 1H, OH).

2.3.2. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-Hydroxy-3-methoxybenzoate (3b). Yield: 93%, white crystalline solid, mp: 130–135. FTIR: $\nu_{\text{max}} = 3371.57, 2966.52, 1731.27, 1440.33, 1161.15\text{ cm}^{-1}$. ^1H NMR (400 MHz, DMSO- d_6): $\delta = 0.81$ (d, $J = 7.2$ Hz, 3H, H-7), 0.84 (d, $J = 7.3$ Hz, 3H, H-9), 0.87 (d, $J = 7.5$ Hz, 3H, H-10), 1.34–1.38 (m, 1H, H-4), 1.43–1.46 (m, 1H, H-8), 1.51–1.54 (m, 1H, H-1), 1.64–1.67 (m, 2H, H-2), 1.70–1.74 (m, 2H, H-5), 1.76–1.79 (m, 2H, H-6), 3.43 (dt, $J = 11$ Hz, 4.9 Hz, 1H, H-3), 3.77 (s, 3H, OCH₃), 7.11 (d, $J = 8$ Hz, 1H, H-4'), 7.43 (dd, $J = 8$ Hz, 3 Hz, 1H, H-5'), 7.54 (d, $J = 2$ Hz, 1H, H-1'), 9.50 (s, 1H, OH).

2.3.3. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-Hydroxy-3,5-dimethoxybenzoate (3c). Yield: 82%, brown crystalline solid, mp: 108–110. FTIR: $\nu_{\text{max}} = 3336.85, 2954.95, 1734.05, 1458.18, 1118.71\text{ cm}^{-1}$. ^1H NMR (400 MHz, DMSO- d_6): $\delta = 0.79$ (d, $J = 7.2$ Hz, 3H, H-7), 0.83 (d, $J = 7.4$ Hz, 3H, H-9), 0.87 (d, $J = 7.4$ Hz, 3H, H-10), 1.33–1.37 (m, 1H, H-4), 1.43–1.45 (m, 1H, H-8), 1.52–1.57 (m, 1H, H-1), 1.62–1.65 (m, 2H, H-2), 1.71–1.74 (m, 2H, H-5), 1.76–1.78 (m, 2H, H-6), 3.45 (dt, $J = 11$ Hz, 5 Hz, 1H, H-3), 3.70 (s, 6H, O-CH₃), 6.92 (d, $J = 2.5$ Hz, 2H, H-1', H-5'), 8.56 (s, 1H, OH).

2.3.4. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl (E)-3-(4-Hydroxy-3-methoxyphenyl) Acrylate (3d). Yield: 96%, pale yellow amorphous solid, mp: 245–250. FTIR: $\nu_{\text{max}} = 3610.74, 2962.66, 671.23\text{--}956.69, 1728.93, 1427.32, 1180.44, 956.69, 671.23\text{ cm}^{-1}$. ^1H NMR (400 MHz, DMSO- d_6): $\delta = 0.82$ (d, $J = 7.2$ Hz, 3H, H-7), 0.84 (d, $J = 7.5$ Hz, 3H, H-9), 0.86 (d, $J = 7.4$ Hz, 3H, H-10), 1.34–1.35 (m, 1H, H-4), 1.43–1.47 (m, 1H, H-8), 1.53–1.57 (m, 1H, H-1), 1.62–1.64 (m, 2H, H-2), 1.70–1.74 (m, 2H, H-5), 1.77–1.79 (m, 2H, H-6), 3.47 (dt, $J = \text{Hz, Hz, 1H, H-3}$), 3.72 (s, 3H, O-CH₃), 6.32 (d, $J = 11.5$ Hz, 1H, H-8'), 6.95 (d, $J = 8$ Hz, 1H, H-4'), 7.10 (dd, $J = 8.3$ Hz, 2.5 Hz, 1H, 5'), 7.19 (d, $J = 2$ Hz, 1H, H-1'), 7.75 (d, $J = 11.2$ Hz, 1H, H-7'), 9.42 (s, 1H, OH).

2.4. Synthesis of O-Glycopyranosides. Phenolic esters (3a–d) (2 mmol) were treated with saccharides (4a–c) (1 mmol) separately in the presence of Si-H^+ catalyst (0.098 g, 0.1 mole %) at 80–100°C. The reaction was monitored by TLC using dichloromethane and methanol (5:7) as eluent. Product spots were confirmed by spraying 2% ceric sulphate in 2N H₂SO₄ followed by heating. The reaction contents were dissolved in methanol and filtered. After drying the filtrate, it was purified by column chromatography using gradient dichloromethane and methanol as the mobile phase to afford

the amorphous products (5a–d). The catalyst was separated as the residue, washed, and dried under vacuum.

2.4.1. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-(((2R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)benzoate (5a). Yield: 80%, pale yellow. FTIR: $\nu_{\max}$ = 3340.71, 2927.94, 1735.05, 1562.34, 1441.89, 1158.42, 540.37 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.81 (d, J = 7.3 Hz, 3H, H-7), 0.84 (d, J = 7.5 Hz, 3H, H-9), 0.86 (d, J = 7.5 Hz, 3H, H-10), 1.34–1.37 (m, 1H, H-4), 1.41–1.47 (m, 1H, H-8), 1.52–1.56 (m, 1H, H-1), 1.63–1.67 (m, 2H, H-2), 1.71–1.74 (m, 2H, H-5), 1.76–1.79 (m, 2H, H-6), 3.07 (dd, J = 7.5 Hz, 3.4 Hz, 1H, H-2''), 3.12–3.18 (m, 1H, H-3''), 3.24–3.31 (m, 1H, H-4''), 3.45 (dt, J = 11 Hz, 4.5 Hz, 1H, H-3), 3.48–3.50 (m, 1H, H-5''), 3.95 (dd, J = 14.5 Hz, 3 Hz, 2H, H-6''), 4.15 (d, J = 7.4 Hz, 1H, H-1''), 6.71 (d, J = 8.3 Hz, 2H, H-1', H-5'), 7.88 (d, J = 8.5 Hz, 2H, H-2', H-4'), 9.55 (s, 4H, OH).

2.4.2. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-(((2R,3R,4S,5R)-3,4,5-Trihydroxytetrahydro-2H-pyran-2-yl)oxy)benzoate (5b). Yield: 85%, pale yellow. FTIR: $\nu_{\max}$ = 3339.14, 2920.23, 1735.27, 1564.63, 1442.01, 1147.85, 555.50 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.82 (d, J = 7.5 Hz, 3H, H-7), 0.84 (d, J = 7.4 Hz, 3H, H-9), 0.87 (d, J = 7.5 Hz, 3H, H-10), 1.32–1.35 (m, 1H, H-4), 1.43–1.47 (m, 1H, H-8), 1.51–1.55 (m, 1H, H-1), 1.61–1.64 (m, 2H, H-2), 1.72–1.73 (m, 2H, H-5), 1.75–1.80 (m, 2H, H-6), 3.10 (dd, J = 7.5 Hz, 3.5 Hz, 1H, H-2''), 3.17–3.20 (m, 1H, H-3''), 3.23–3.27 (m, 1H, H-4''), 3.34 (dt, J = 11.5 Hz, 5 Hz, 1H, H-3), 4.05–4.10 (m, 2H, H-5''), 4.20 (d, J = 7.5 Hz, 1H, H-1''), 6.75 (d, J = 8 Hz, 2H, H-1', H-5'), 7.89 (d, J = 8.5 Hz, 2H, H-2', H-4'), 9.49 (s, 3H, OH).

2.4.3. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-(((2R,3R,4R,5S,6R)-3,4-Dihydroxy-6-(hydroxymethyl)-5-(((1S,2R,3S,4R,5R)-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexyl)oxy)tetrahydro-2H-pyran-2-yl)oxy)benzoate (5c). Yield: 84%, pale yellow gel-like. FTIR: $\nu_{\max}$ = 3335.99, 2927.94, 1736.07, 1562.03, 1438.94, 1147.06, 544.08 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.83 (d, J = 7.4 Hz, 3H, H-7), 0.85 (d, J = 7.5 Hz, 3H, H-9), 0.88 (d, J = 7.2 Hz, 3H, H-10), 1.30–1.35 (m, 1H, H-4), 1.41–1.44 (m, 1H, H-8), 1.52–1.54 (m, 1H, H-1), 1.62–1.65 (m, 2H, H-2), 1.73–1.77 (m, 2H, H-5), 1.79–1.82 (m, 2H, H-6), 3.06 (dd, J = 7.6 Hz, 3.5 Hz, 2H, H-2''), 3.12–3.17 (m, 2H, H-3''), 3.20–3.23 (m, 2H, H-4''), 3.45 (dt, J = 11.7 Hz, 5.5 Hz, 1H, H-3), 4.18–4.20 (m, 2H, H-5''), 4.23 (dd, J = 15 Hz, 3.2 Hz, 4H, H-6''), 4.53 (d, J = 7.6 Hz, 2H, H-1''), 6.73 (d, J = 8.3 Hz, 2H, H-1', H-5'), 7.86 (d, J = 7.6 Hz, 2H, H-2', H-4'), 9.57 (s, 7H, OH).

2.4.4. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 3-Methoxy-4-(((2R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)benzoate (5d). Yield: 82%, off-white. FTIR: $\nu_{\max}$ = 3309.85, 2927.94, 1730.22, 1564.43, 1420.60, 1109.56, 550.50 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.81 (d, J = 7.5 Hz, 3H, H-7), 0.85 (d, J = 7.6 Hz, 3H,

H-9), 0.88 (d, J = 7.2 Hz, 3H, H-10), 1.32–1.36 (m, 1H, H-4), 1.41–1.45 (m, 1H, H-8), 1.52–1.54 (m, 1H, H-1), 1.60–1.65 (m, 2H, H-2), 1.72–1.75 (m, 2H, H-5), 1.79–1.81 (m, 2H, H-6), 3.08 (dd, J = 7.5 Hz, 3.1 Hz, 1H, H-2''), 3.15–3.20 (m, 1H, H-3''), 3.22–3.25 (m, 1H, H-4''), 3.47 (dt, J = 10.6 Hz, 5 Hz, 1H, H-3), 3.77 (s, 3H, OCH₃), 4.06–4.11 (m, 1H, H-5''), 4.20 (dd, J = 15.1 Hz, 2.8 Hz, 2H, H-6''), 4.50 (d, J = 7.8 Hz, 1H, H-1''), 7.11 (d, J = 8 Hz, 1H, H-4'), 7.43 (dd, J = 8 Hz, 3 Hz, 1H, H-5'), 7.54 (d, J = 2 Hz, 1H, H-1'), 9.50 (s, 1H, OH).

2.4.5. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 3-Methoxy-4-(((2R,3R,4S,5R)-3,4,5-trihydroxytetrahydro-2H-pyran-2-yl)oxy)benzoate (5e). Yield: 71%, off-white. FTIR: $\nu_{\max}$ = 3370.67, 2966.50, 1730.08, 1560.35, 1431.49, 1109.14, 583.03 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.83 (d, J = 7.5 Hz, 3H, H-7), 0.85 (d, J = 7.4 Hz, 3H, H-9), 0.87 (d, J = 7.5 Hz, 3H, H-10), 1.31–1.34 (m, 1H, H-4), 1.42–1.47 (m, 1H, H-8), 1.50–1.53 (m, 1H, H-1), 1.62–1.64 (m, 2H, H-2), 1.69–1.73 (m, 2H, H-5), 1.78–1.80 (m, 2H, H-6), 3.10 (dd, J = 7.4 Hz, 3.5 Hz, 1H, H-2''), 3.18–3.24 (m, 1H, H-3''), 3.26–3.37 (m, 1H, H-4''), 3.49 (dt, J = 10.5 Hz, 4.9 Hz, 1H, H-3), 3.60 (s, 3H, OCH₃), 4.20–4.24 (m, 2H, H-5''), 4.43 (d, J = 7.2 Hz, 1H, H-1''), 7.15 (d, J = 8 Hz, 1H, H-4'), 7.45 (dd, J = 8.1 Hz, 3.5 Hz, 1H, H-5'), 7.51 (d, J = 2.1 Hz, 1H, H-1'), 9.34 (s, 3H, OH).

2.4.6. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-(((2R,3R,4R,5S,6R)-3,4-Dihydroxy-6-(hydroxymethyl)-5-(((1S,2R,3S,4R,5R)-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexyl)oxy)tetrahydro-2H-pyran-2-yl)oxy)-3-methoxybenzoate (5f). Yield: 80%, off-white. FTIR: $\nu_{\max}$ = 3378.09, 2967.95, 1729.87, 1560.40, 1430.97, 1111.00, 580.78 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.82 (d, J = 7.4 Hz, 3H, H-7), 0.85 (d, J = 7.5 Hz, 3H, H-9), 0.88 (d, J = 7.4 Hz, 3H, H-10), 1.32–1.34 (m, 1H, H-4), 1.41–1.45 (m, 1H, H-8), 1.51–1.55 (m, 1H, H-1), 1.60–1.63 (m, 2H, H-2), 1.65–1.68 (m, 2H, H-5), 1.73–1.76 (m, 2H, H-6), 3.13 (dd, J = 7.5 Hz, 3.1 Hz, 2H, H-2''), 3.15–3.18 (m, 2H, H-3''), 3.20–3.23 (m, 2H, H-4''), 3.50 (dt, J = 11.2 Hz, 5 Hz, 1H, H-3), 3.63 (s, 3H, OCH₃), 4.21–4.23 (m, 2H, H-5''), 4.27 (dd, J = 15.3 Hz, 3.5 Hz, 4H, H-6''), 4.57 (d, J = 7.4 Hz, 2H, H-1''), 7.19 (d, J = 8.2 Hz, 1H, H-4'), 7.32 (dd, J = 8 Hz, 4.5 Hz, 1H, H-5'), 7.53 (d, J = 2.5 Hz, 1H, H-1'), 9.61 (s, 7H, OH).

2.4.7. (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 3,5-Dimethoxy-4-(((2R,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)benzoate (5g). Yield: 74%, pale yellow, FTIR: $\nu_{\max}$ = 3335.85, 2957.35, 1734.93, 1562.30, 1451.98, 1118.41, 559.36 cm^{-1} . ^1H NMR (400 MHz, DMSO- d_6): δ = 0.81 (d, J = 7.2 Hz, 3H, H-7), 0.83 (d, J = 7.5 Hz, 3H, H-9), 0.85 (d, J = 7.4 Hz, 3H, H-10), 1.30–1.34 (m, 1H, H-4), 1.44–1.47 (m, 1H, H-8), 1.53–1.57 (m, 1H, H-1), 1.63–1.67 (m, 2H, H-2), 1.71–1.75 (m, 2H, H-5), 1.76–1.79 (m, 2H, H-6), 3.15 (dd, J = 7.4 Hz, 2.8 Hz, 1H, H-2''), 3.17–3.19 (m, 1H, H-3''), 3.21–3.25 (m, 1H, H-4''), 3.52 (dt, J = 12 Hz, 5 Hz, 1H, H-3), 3.65 (s, 6H,

O-CH₃), 4.18–4.22 (m, 1H, H-5''), 4.25 (dd, $J = 15$ Hz, 3.4 Hz, 2H, H-6''), 4.60 (d, $J = 8.1$ Hz, 1H, H-1''), 7.20 (d, $J = 2.5$ Hz, 2H, H-1', H-5'), 9.01 (s, 4H, OH).

2.4.8. (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 3,5-Dimethoxy-4-(((2*R*,3*R*,4*S*,5*R*)-3,4,5-trihydroxytetrahydro-2H-pyran-2-yl)oxy)benzoate (5h). Yield: 69%, pale yellow. FTIR: $\nu_{\max} = 3335.73, 2954.95, 1734.05, 1543.44, 1452.01, 1099.71, 559.41$ cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 0.82$ (d, $J = 7.4$ Hz, 3H, H-7), 0.85 (d, $J = 7.6$ Hz, 3H, H-9), 0.87 (d, $J = 7.2$ Hz, 3H, H-10), 1.32–1.35 (m, 1H, H-4), 1.43–1.47 (m, 1H, H-8), 1.52–1.55 (m, 1H, H-1), 1.62–1.65 (m, 2H, H-2), 1.72–1.74 (m, 2H, H-5), 1.76–1.79 (m, 2H, H-6), 3.18 (dd, $J = 7.6$ Hz, 3.6 Hz, 1H, H-2''), 3.20–3.24 (m, 1H, H-3''), 3.26–3.29 (m, 1H, H-4''), 3.49 (dt, $J = 11.6$ Hz, 5 Hz, 1H, H-3), 3.60 (s, 6H, O-CH₃), 4.17–4.21 (m, 2H, H-5''), 4.49 (d, $J = 7.9$ Hz, 1H, H-1''), 6.69 (d, $J = 2.7$ Hz, 2H, H-1', H-5'), 9.64 (s, 3H, OH).

2.4.9. (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 4-(((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-Dihydroxy-6-(hydroxymethyl)-5-(((1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexyl)oxy)tetrahydro-2H-pyran-2-yl)oxy)-3,5-dimethoxybenzoate (5i). Yield: 68%, gel-like. FTIR: $\nu_{\max} = 3336.05, 2954.02, 1735.01, 1548.08, 1451.76, 1120.71, 560.02$ cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 0.80$ (d, $J = 7.5$ Hz, 3H, H-7), 0.83 (d, $J = 7.4$ Hz, 3H, H-9), 0.85 (d, $J = 7.4$ Hz, 3H, H-10), 1.30–1.34 (m, 1H, H-4), 1.41–1.45 (m, 1H, H-8), 1.50–1.54 (m, 1H, H-1), 1.60–1.64 (m, 2H, H-2), 1.71–1.73 (m, 2H, H-5), 1.75–1.78 (m, 2H, H-6), 3.16 (dd, $J = 7.4$ Hz, 3.5 Hz, 2H, H-2''), 3.18–3.20 (m, 2H, H-3''), 3.26–3.29 (m, 2H, H-4''), 3.47 (dt, $J = 11.5$ Hz, 4.5 Hz, 1H, H-3), 3.73 (s, 6H, O-CH₃), 4.14–4.21 (m, 2H, H-5''), 4.23 (dd, $J = 15.3$ Hz, 4.3 Hz, 4H, H-6''), 4.48 (d, $J = 8$ Hz, 2H, H-1''), 6.71 (d, $J = 2.5$ Hz, 2H, H-1', H-5'), 9.51 (s, 7H, OH).

2.4.10. (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (E)-3-(3-Methoxy-4-(((2*R*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)oxy)phenyl)acrylate (5j). Yield: 83%, pale yellow. FTIR: $\nu_{\max} = 3610.71, 2962.66, 1728.75, 1540.45, 1426.76, 1181.40, 906.69, 660.73, 540.57$ cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 0.79$ (d, $J = 7.4$ Hz, 3H, H-7), 0.82 (d, $J = 7.5$ Hz, 3H, H-9), 0.86 (d, $J = 7.6$ Hz, 3H, H-10), 1.33–1.37 (m, 1H, H-4), 1.41–1.45 (m, 1H, H-8), 1.50–1.56 (m, 1H, H-1), 1.62–1.65 (m, 2H, H-2), 1.73–1.75 (m, 2H, H-5), 1.76–1.78 (m, 2H, H-6), 3.19 (dd, $J = 7.3$ Hz, 3.1 Hz, 1H, H-2''), 3.20–3.23 (m, 1H, H-3''), 3.25–3.29 (m, 1H, H-4''), 3.44 (dt, $J = 11$ Hz, 5.5 Hz, 1H, H-3), 3.65 (s, 3H, O-CH₃), 4.22–4.24 (m, 1H, H-5''), 4.26 (dd, $J = 15.1$ Hz, 3.5 Hz, 2H, H-6''), 4.56 (d, $J = 7.2$ Hz, 1H, H-1''), 6.32 (d, $J = 11.5$ Hz, 1H, H-8'), 6.97 (d, $J = 7.8$ Hz, 1H, H-4'), 7.15 (dd, $J = 8.5$ Hz, 2.5 Hz, 1H, 5'), 7.29 (d, $J = 2.5$ Hz, 1H, H-1'), 7.60 (d, $J = 11.5$ Hz, 1H, H-7'), 9.48 (s, 4H, OH).

2.4.11. (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (E)-3-(3-Methoxy-4-(((2*R*,3*R*,4*S*,5*R*)-3,4,5-trihydroxytetrahydro-2H-pyran-2-yl)oxy)phenyl)acrylate (5k). Yield: 76%, pale

yellow. FTIR: $\nu_{\max} = 3611.04, 2960.40, 1728.93, 1543.50, 1427.32, 1176.44, 960.05, 676.23, 533.20$ cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 0.82$ (d, $J = 7.3$ Hz, 3H, H-7), 0.84 (d, $J = 7.2$ Hz, 3H, H-9), 0.87 (d, $J = 7.6$ Hz, 3H, H-10), 1.32–1.35 (m, 1H, H-4), 1.42–1.47 (m, 1H, H-8), 1.52–1.57 (m, 1H, H-1), 1.60–1.64 (m, 2H, H-2), 1.71–1.74 (m, 2H, H-5), 1.76–1.80 (m, 2H, H-6), 3.17 (dd, $J = 7.2$ Hz, 3.4 Hz, 1H, H-2''), 3.20–3.24 (m, 1H, H-3''), 3.26–3.30 (m, 1H, H-4''), 3.45 (dt, $J = 11.5$ Hz, 5.5 Hz, 1H, H-3), 3.57 (s, 3H, O-CH₃), 4.25–4.27 (m, 2H, H-5''), 4.51 (d, $J = 7.4$ Hz, 1H, H-1''), 6.29 (d, $J = 11$ Hz, 1H, H-8'), 6.95 (d, $J = 8$ Hz, 1H, H-4'), 7.20 (dd, $J = 8$ Hz, 3.1 Hz, 1H, 5'), 7.33 (d, $J = 2.3$ Hz, 1H, H-1'), 7.57 (d, $J = 11.5$ Hz, 1H, H-7'), 9.77 (s, 3H, OH).

2.4.12. (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (E)-3-(4-(((2*R*,3*R*,4*R*,5*S*,6*R*)-3,4-Dihydroxy-6-(hydroxymethyl)-5-(((1*S*,2*R*,3*S*,4*R*,5*R*)-2,3,4-trihydroxy-5-(hydroxymethyl)cyclohexyl)oxy)tetrahydro-2H-pyran-2-yl)oxy)-3-methoxyphenyl)acrylate (5l). Yield: 65%, yellow gel-like. FTIR: $\nu_{\max} = 3610.74, 2962.68, 1729.01, 1540.34, 1425.62, 1180.32, 956.79, 665.90, 541.45$ cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 0.81$ (d, $J = 7.5$ Hz, 3H, H-7), 0.83 (d, $J = 7.3$ Hz, 3H, H-9), 0.87 (d, $J = 7.5$ Hz, 3H, H-10), 1.30–1.34 (m, 1H, H-4), 1.41–1.45 (m, 1H, H-8), 1.53–1.55 (m, 1H, H-1), 1.62–1.66 (m, 2H, H-2), 1.72–1.75 (m, 2H, H-5), 1.79–1.82 (m, 2H, H-6), 3.12 (dd, $J = 7.4$ Hz, 3.6 Hz, 2H, H-2''), 3.24–3.27 (m, 2H, H-3''), 3.29–3.31 (m, 2H, H-4''), 3.49 (dt, $J = 11$ Hz, 4.5 Hz, 1H, H-3), 3.61 (s, 3H, O-CH₃), 4.15–4.20 (m, 2H, H-5''), 4.24 (dd, $J = 15.2$ Hz, 4.1 Hz, 4H, H-6''), 4.49 (d, $J = 8.1$ Hz, 2H, H-1''), 6.25 (d, $J = 10.6$ Hz, 1H, H-8'), 6.98 (d, $J = 8$ Hz, 1H, H-4'), 7.14 (dd, $J = 8.1$ Hz, 2 Hz, 1H, 5'), 7.31 (d, $J = 2.5$ Hz, 1H, H-1'), 7.49 (d, $J = 11$ Hz, 1H, H-7'), 9.48 (s, 7H, OH).

3. Results and Discussion

3.1. Selection of the Catalyst and Synthesis. The mesoporous solid-supported catalysts with large surface area and greater pore volume have high organic functionality on their surface and have been employed in a variety of organic reactions as environmentally safe and less-damaging green substitutes to conventional reagents [23]. Therefore, to promote environmental friendly processes, solid-supported catalyst has been employed for Fischer esterification followed by glycosylation to carry out direct condensation. In the first step, the hydroxyl group of menthol (2) was condensed with the carboxylic group of phenolic acids (1a–d) to yield nonpolar phenolic ester aglycones (3a–d). Later, 3a–d were glycosylated with polar glycones (4a–c) at the anomeric carbon to yield glycosides (5a–l) in appreciable yields (Figure 1). To make quantitative discussion of the effect, the role of different catalysts (Table 1) was explored using menthol (2) and 4-hydroxybenzoic acid (1a) as model substrates to synthesize 3a. Reaction parameters such as ratio of silica and acid as the effective catalyst, amount of the catalyst, temperature and reactant ratio were optimized under solvent-free conditions.

Several acids such as sulfuric acid (H₂SO₄), sulfamic acid (SA), and *p*-toluenesulfonic acid (PTSA) were directly

FIGURE 1: Synthesis of O-glycopyranosides. Reagents and conditions: (i) 0.3 mole% Si-H⁺ catalyst, 1 mmole of 1a–d, 3 mmole of 2, 3–5 hours of stirring, and temp 80–100°C; (ii) 0.1 mole% Si-H⁺ catalyst, 2 mmole of 3a–d, 1 mmole of 4a–c, 3–7 hours of stirring, and temp 80–100°C.

TABLE 1: Optimization of the catalyst for the preparation of phenolic ester 3a using the direct condensation reaction.

Entry	Catalyst	Physical state	Time (hr)	Yield % (3a)
1	Conc. sulfuric acid (H ₂ SO ₄)	Viscous liquid	1.5	5
2	Paratoluenesulfonic acid (PTSA)	White solid	5.5	63
3	Sulfamic acid (SA)	White crystals	4.5	67
4	Bentonite-H ₂ SO ₄	Grey solid	2.5	71
5	Bentonite-PTSA	Grey solid	5.5	55
6	Bentonite-SA	Grey solid	5.5	60
7	Silica-H ₂ SO ₄ (Si-H ⁺)	Grey powder	2.5	86
8	Silica-PTSA	Grey powder	5.5	56
9	Silica-SA	White powder	4.5	54

Reagents and conditions: 4-hydroxybenzoic acid (1 mmole), menthol (3 mmole), 0.3 mole % catalyst, and temp 80°C.

employed for Fischer esterification. H₂SO₄ is an extremely strong oxidizing agent and dehydrates several organic compounds producing carbon in the form of graphite; the same was observed while using conc. sulfuric acid directly as the esterification catalyst. The reaction mixture turned to a solid black mass with a mere yield of 5%. To overcome dehydration and degradation of the reaction mixture, mesoporous solid acid catalysts, silica-H₂SO₄ (Si-H⁺), silica-SA, silica-PTSA, bentonite-H₂SO₄, bentonite-SA, and bentonite-PTSA, were designed (Table 1). The %yield indicated that most of them exhibit significantly improved esterification yields. Interestingly, Si-H⁺ catalyst, being a superior

proton source, affords the highest yield among these catalysts as one site is bonded with Si, while the other end is available to donate proton and carry out reactions under heterogeneous conditions. The silica gel alone did not show any considerable catalytic effects, but H₂SO₄ immobilization induced the catalytic activity. However, the mesoporous nature of silica showed enhanced catalytic effects in contrast to bentonite.

After catalyst selection, the concentration was another important factor that was responsible for appreciable yield of the product. For this purpose, different ratios of silica gel and sulfuric acid (1 : 0.25, 1 : 0.5, and 1 : 0.75) were explored

using 1 mmole of 4-hydroxybenzoic acid and 3 mmole of menthol at 80°C. The results showed that 1:0.75 was the best concentration for esterification on the basis of H₂SO₄ properties. In the next step, the same concentration was employed for glycosylation of 2 mmole of 3a and 1 mmole of α -D-glucose at 80°C to afford the corresponding glycosides; to our delight, we observed 1:0.75 was equally efficient for glycosylation reducing several steps of protection-deprotection of various functional groups as in traditional glycosylation (Table 2).

To access the catalytic performance of the selected Si-H⁺ catalyst (1:0.75), different mole% of the catalyst were utilized at 80°C. The best amount of the Si-H⁺ catalyst for 3a was found to be 0.3 mole% which gave greater yield in short time thus increasing catalyst loading to 0.3 mole% which actually increased the efficiency of the catalyst due to increased active sites. However, for 5a, any further increase in the amount from 0.1 mole% resulted in low yield which could be due to dehydration of the glycone (Table 3).

The effect of temperature was studied to locate an effective temperature range for the Si-H⁺ catalyst (1:0.75) since its selectivity and catalytic activity are temperature-dependent. The optimum temperature ranges from 70°C to 80°C with relatively enhanced yield at 80°C for most of the esters and glycosides. However, for the compound having steric hindrance, the temperature of 100°C was more favorable to carry out the reaction (Table 4).

Looking at the effect of reactant ratio showed that the increased amount of menthol in esterification and aglycone in glycosylation enhanced the %yield of the reaction by driving the equilibrium of the reaction towards the product and limiting the reverse reaction (Table 5). Solvent-free conditions were employed to carry out all the reactions.

Reaction conditions of 3a-d and 5a-l were optimized with the Si-H⁺ catalyst (1:0.75) that demonstrated excellent results according to TLC and FTIR monitoring. Physical data and reaction conditions of 3a-d and 5a-l are summarized in Tables 6 and 7, respectively.

3.2. Catalyst Characterization. The FTIR spectrum of untreated silica gel and Si-H⁺ catalyst (1:0.75) was recorded and compared. Catalyst (b) showed small absorption bands at 1400 cm⁻¹ that were assigned to the S=O stretching mode. This observation illustrated the immobilization of sulfuric acid on free terminal silanol (Si-OH) groups. This further ensured the exchange of HSO₄⁻ with H of the silanol group in silica gel [17]. This stretching was not observed in (a), thus explaining the proposed immobilization of sulfuric acid groups on the free terminal silanol (Si-OH) groups in the Si-H⁺ catalyst (Figure 2). Hence, it was inferred that the irregular tridimensional framework of the porous silica surface allows the insertion of proton due to the presence of siloxane (Si-O-Si) and silanol (Si-OH) groups (Figure 3).

A broad band (b) at 3400 cm⁻¹ was observed due to OH stretching that supported increased hydrogen bonding due

to sulfuric acid (Figure 2). The absorption frequency bands observed at 519 and 801 cm⁻¹ were assigned to bending and out-of-plane deformations of Si-O bonds which further endorsed successful modifications on the surface of silica, thus proving the formation of catalyst Si-H⁺ (Table 8).

The thermal stability of the Si-H⁺ catalyst (1:0.75) and silica was studied via differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) from ambient temperature to 800°C (Figure 4).

The TGA curve of the Si-H⁺ catalyst (Figure 4(b)) showed two gradual weight losses at 65°C and 240°C due to the loss of water molecules formed during the catalyst formation and the other from acid. The linear TGA curve after 350°C in the spectrum of the catalyst showed greater thermal stability as compared to starting material. The descending TGA thermal curve for silica gel (Figure 4(a)) exhibited abrupt weight loss at $\approx$ 100°C due to the removal of water of hydration. The DSC thermogram of silica gel (Figure 4(a)) showed a large endothermic peak at 100°C and a small peak at 770°C. The sharp endothermic peak of silica gel observed at 100°C shifted towards higher temperature at 130°C in the Si-H⁺ catalyst (Figure 4(b)) that supported the stability of the solid acid catalyst.

The powder XRD patterns of (a) Si-H⁺ catalyst and (b) silica gel were compared (Figure 5). The XRD pattern of both (a) and (b) exhibits one broad ($2\theta = 20-30^\circ$) and another relatively sharp ($2\theta = 03-04^\circ$) diffraction peak. The main difference between silica gel and Si-H⁺ catalyst exists in the emergence of another small diffraction peak in (a) at $2\theta = 11^\circ$. The increased intensity of diffraction peaks in the catalyst verified the proposed modification of silica by immobilization of sulfuric acid groups.

The surface morphology of the silica gel and Si-H⁺ catalyst was observed by SEM micrographs (Figure 6). These micrographs showed increased surface area and enhanced microporosity of the Si-H⁺ catalyst in Figure 6(b) as compared to the relatively smooth and regular-shaped silica gel particles (Figure 6(a)).

3.3. Characterization and Thermotropic Behaviour of Aglycones and O-Glycopyranosides. The structures of the nonpolar aglycones (3a-d) and the saccharide derivatives (5a-l) were confirmed by FTIR and ¹H NMR spectroscopy. FTIR spectra were scanned from 500 to 4000 cm⁻¹ under dry air at room temperature. A broad band extending from 3300 to 3600 cm⁻¹ was observed corresponding to the stretching vibration of the hydroxyl groups. A distinctive peak above 1700 cm⁻¹ in the FTIR spectrum confirmed the esterification of the menthol hydroxyl group. Absorption peak of $\approx$ 1100 cm⁻¹ was due to the existence of the ether (C-O-R) linkage between aglycone and saccharide. In ¹H NMR spectra, the peaks from 6.72 to 7.88 ppm confirmed the presence of aromatic C-H protons in 3a-d and 5a-l. Multiplets were observed at 1.60–1.97 ppm due to the methylene and methyl protons. A singlet at $\approx$ 9.50 ppm confirmed the presence of the hydroxyl proton.

The TGA and DSC curves for compounds 3a-d and 5a-l were studied within the varying temperature range of 0–500°C with a linear heating rate of 10°C/min. The

TABLE 2: Screening of catalyst concentration.

Entry	Ratio	3a		5a	
		Time (hr)	Yield (%)	Time (hr)	Yield (%)
1	1:0.25	5.5	77	8.5	54
2	1:0.5	2.5	80	6.5	72
3	1:0.75	2.5	89	6.25	80

TABLE 3: Screening of catalyst loading.

Entry	Amount (mole%)	3a		5a	
		Time (hr)	Yield (%)	Time (hr)	Yield (%)
1	0.1	5.5	55	6.5	80
2	0.2	4.5	62	6.5	72
3	0.3	2.5	87	6.5	67
4	0.4	2.5	71	6.25	62

TABLE 4: Screening of optimum temperature.

Entry	Temperature (°C)	3a		5a	
		Time (hr)	Yield (%)	Time (hr)	Yield (%)
1	50	6.5	54	9.5	34
2	80	2.5	89	7.5	81
3	100	2.25	83	6.25	80

TABLE 5: Screening of reactant ratio.

Entry	Reactant ratio	3a		5a	
		Time (hr)	Yield (%)	Time (hr)	Yield (%)
1	1:1	8.5	53	9.25	48
2	1:2	7.5	71	7.5	54
3	1:3	3.5	82	6.5	80
4	1:4	2.5	86	6.25	83

thermogram of 3a (Figure 7) exhibited a loss of mass at 200–400°C; this abrupt fall in the TGA curve was attributed to a change of state in the compound, i.e., ordered to disordered state. A glass transition (T_g) in the DSC thermogram of 3a (Figure 7) was generally observed at 131°C lower than the melting point transition (T_m) at 147°C. T_g is the gradual and reversible transition in amorphous and semicrystalline compounds from hard to viscous state as the temperature was increased, while T_m endothermic peak corresponds to the first-order phase transition. The onset of crystallization on the DSC curve of 3a was observed at 338°C with a crystallization exothermic peak at 412°C (Figure 7). The onset of crystallization for 3b, 3c, and 3d was 308, 341, and 237, respectively. The inclusion of methoxy groups in 3b and 3c decreases T_m , while the increased chain length in 3c causes an increase in T_m as compared with 3a. Phase transition temperatures observed for 3a–d compounds using DSC are stated in Table 9.

TGA curves of 5a showed several gradual weight loss events at 112–137°C, 150–187°C, and 200–250°C. The DSC

curve of 5a showed that it melted through the mesophases with two varying melting point transitions (Figure 8).

First, the hydrocarbon part melted at low temperature (T_m^1) at 75°C resulting in the loss of the three-dimensional framework of soft hydrocarbon crystals. However, the hard crystals that correspond to the carbohydrate part melted at a higher temperature (T_m^2) at 134°C and formed isotropic liquid. In between the two melting points, the mesophases appeared to be stable at 117°C in 5a. An exothermic peak at a lower temperature of 28°C is also related to the carbohydrate liquid crystals. With an onset of crystallization at 200°C, two exothermic crystalline peaks are observed at 219 and 283°C. The two melting point transitions in glycosides 5a–l supported the thermotropic mesophase behaviour including various crystal-to-crystal, crystal-to-mesophase and mesophase-to-mesophase transitions [5]. Phase transition temperatures supporting the mesogenic character of synthesized carbohydrate derivatives (5a–l) are stated in Table 10.

The mesogenic textures of the amphiphilic glycopyranosides (5a–l) were observed by polarized optical microscopy under crossed polarizers. All the glycopyranosides showed the formation of thermotropic mesophases during heating and cooling of the pure samples. For compound 5a, the mesophase was observed between 80 and 130°C with a fan/focal-conical texture (Figure 9(a)) that is common for the smectic A (SmA) phases. In Figure 9(b), typical focal conics of the SmA phase were observed for compound 5b between 65 and 125°C, while Figure 9(c) shows fan-shaped focal-conical SmA phases of compound 5c between 70 and 150°C. Compound 5e showed SmA phase droplets (Figure 10(a)) at 110°C with phase transition temperature between 60 and 125°C. SmA phase of compound 5h with focal-conical defects (Figure 10(b)) was visible between 80 and 160°C. SmA phase focal-conical texture was also observed for compound 5k (Figure 10(c)) at 90°C. In addition to crystal-to-crystal transitions at lower temperature and existence of double melting points, the formation of smectic thermotropic phases supported the liquid crystalline nature of synthesized glycopyranosides.

TABLE 6: Summary of physical data and reaction conditions of nonpolar aglycones (3a–3d).

Product code	Product structure	Molecular formula	Time (hr)	Temperature, T (°C)	R_f value	Yield (%)
3a		$C_{17}H_{24}O_3$	2.5	80	0.75	89
3b		$C_{18}H_{26}O_4$	3	80	0.66	93
3c		$C_{19}H_{28}O_5$	4.5	100	0.57	82
3d		$C_{20}H_{28}O_4$	1.5	70	0.60	96

TABLE 7: Summary of physical data and reaction conditions of 5a–5l.

Product code	Compound structure	Molecular formula	Time (hr)	Temperature, T (°C)	R_f value	Yield (%)
5a		$C_{23}H_{34}O_8$	6.5	80	0.77	80
5b		$C_{22}H_{32}O_7$	6.25	80	0.68	85
5c		$C_{29}H_{44}O_{13}$	6.5	80	0.52	84
5d		$C_{24}H_{36}O_9$	8.5	90	0.86	82
5e		$C_{23}H_{34}O_8$	8.25	90	0.73	71

TABLE 7: Continued.

Product code	Compound structure	Molecular formula	Time (hr)	Temperature, T (°C)	R_f value	Yield (%)
5f		$C_{30}H_{46}O_{14}$	9.25	90	0.65	80
5g		$C_{25}H_{38}O_{10}$	9.5	100	0.89	74
5h		$C_{24}H_{36}O_9$	9.25	100	0.81	69
5i		$C_{31}H_{48}O_{15}$	9.5	100	0.73	68
5j		$C_{26}H_{38}O_9$	6.5	75	0.57	83
5k		$C_{25}H_{36}O_8$	6.5	80	0.61	76
5l		$C_{32}H_{48}O_{14}$	7.25	80	0.73	65

FIGURE 2: FTIR spectra of (a) silica gel and (b) $Si-H^+$ catalyst.

FIGURE 3: Proposed structure of the Si-H⁺ catalyst.

TABLE 8: Characteristic FTIR absorption bands of silica-supported acid catalysts.

Entry	Catalysts	FTIR bands, ν (cm ⁻¹)					
		Si-O	Si-O bending	Si-OH stretching	Si-O-Si	Si-OH	S=O
1	SiO ₂	519	801	967	1057	3250	—
2	SiO ₂ -H ₂ SO ₄	597	811	871	1054	3400	1400

FIGURE 4: DSC and TGA profiles of (a) silica gel and (b) Si-H⁺ catalyst. FIGURE 5: XRD patterns of (a) Si-H⁺ catalyst and (b) silica gel.

FIGURE 6: SEM photograph of (a) silica gel and (b) Si-H⁺ catalyst.

FIGURE 7: DSC and TGA thermogram of 3a.

TABLE 9: DSC transition temperatures of phenolic ester aglycones.

Product code	Melting point, T_m (°C)	Crystallization point, T_{Cr} (°C)	Glass transition temperature, T_g (°C)	Temperature range of TGA mass loss (°C)
3a	147	412	31	200–400
3b	131	387	112	200–325
3c	108	358	–	200–350
3d	256	387	218	200–300

FIGURE 8: DSC and TGA thermogram of 5a.

TABLE 10: DSC transition temperatures of O-glycopyranosides.

Product code	1 st melting point, T_m^1 (°C)	2 nd melting point, T_m^2 (°C)	Crystallization point, T_{Cr} (°C)	Glass transition temperature, T_g (°C)
5a	75	134	28, 117, 219, 283	—
5b	67	133	31, 225	100
5c	71	146	17, 250	106
5d	87	287	183, 221, 254	—
5e	63	125	112, 212	96
5f	125	275	33, 250, 334, 434	—
5g	95	102	33, 390	217
5h	85	167	145, 320, 375	—
5i	130	325	25, 265, 385	115
5j	87	150	30, 265, 410	130
5k	65	110	25, 220, 360	—
5l	75	166	35, 275	110

(a)

(b)

FIGURE 9: Continued.

(c)

FIGURE 9: Optical photomicrographs of (a) compound 5a (80°C, 40x), (b) compound 5b (89°C, 10x), and (c) compound 5c (75°C, 10x) showing mesophase textures.

(a)

(b)

(c)

FIGURE 10: Optical photomicrographs of (a) compound 5e (110°C, 10x), (b) compound 5h (85°C, 10x), and (c) compound 5k (90°C, 10x) showing mesophase textures.

4. Conclusion

In conclusion, a study of the mesogenic behaviour of O-glycopyranosides (5a–l), derived from various mono-saccharides and disaccharides, has shown that all the compounds have double melting point endothermic and crystalline exothermic peaks in DSC thermograms. The presence of the phenyl ring stabilizes the mesophases of the compounds and results in the formation of thermotropic phases. Optical textures of compounds 5a–c, 5e, 5h, and 5k displayed smectic A phases. These results for improved potentials of the solid-supported Si-H⁺ catalyst for glycosylation in solvent-free conditions will greatly contribute to the practical synthesis of glycosides in an environmentally acceptable manner and their use as thermotropic liquid crystals in various biomedical and material applications.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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