α/β-Stereo- and Diastereoselective Glycosylation with *n*-Pentenyl Glycoside Donors, Promoted by *N*-Iodosuccinimide and Catalyzed by Chiral Brønsted Acid

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Supporting information

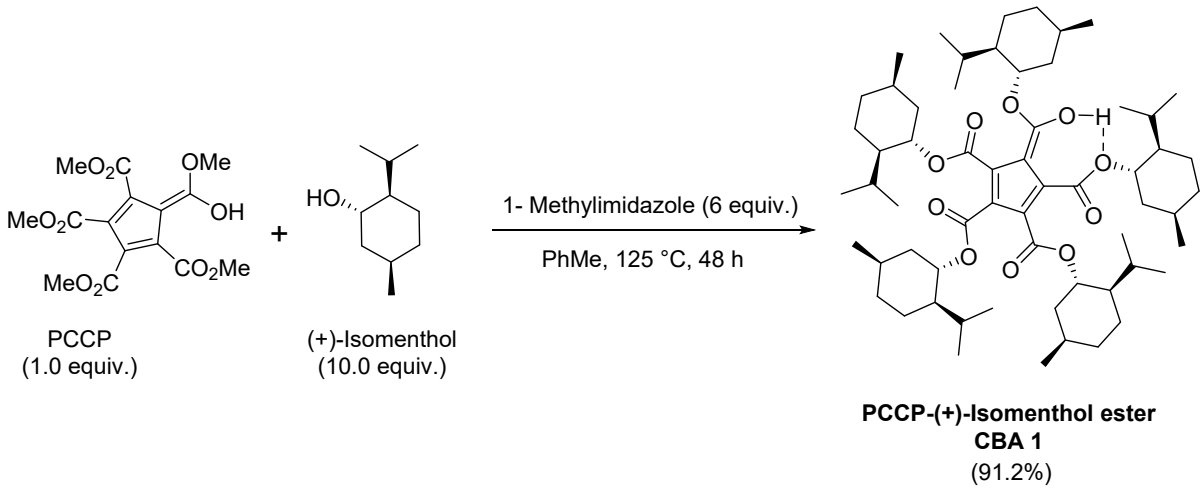
1. General materials and methods

All chemicals were commercially available of the best grade and are used without further purification. Freshly distilled dichloromethane (DCM) over calcium hydride was used for the glycosylation reactions. Thin layer chromatography (TLC) was performed on TLC silica gel 60 F_{254} aluminium sheets purchased from Merck Pvt. Ltd. Silica gel column chromatography (CC) of 100-200 mesh was performed using mixtures of hexane-ethyl acetate (EtOAc), methanol (MeOH)-DCM. Reactions were monitored by TLC; compounds were visualized by a short wavelength UV lamp and by charring the TLC plate after spraying with 15% sulphuric acid in methanol. NMR spectra were recorded with Bruker Ascend^{TM} spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C{^{1}H} NMR) instruments. The chemical shifts δ are given in ppm and referenced to the internal standard TMS. ^{1}H NMR coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), etc. Mass spectra were recorded on ESI-

HRMS from Thermo Scientific Exactive mass spectrometer equipped with the orbitrap analyzer. Diastereomeric ratios were examined with analytical High-Performance Liquid Chromatography (HPLC) consisting of a Shimadzu LC-20AD system controller, CHIRALPAK AD-H (PartNo.19325, Particle size 5 μM) (4.6mm ϕ x 250 mmL) column, column oven (CTO-20A), an autosampler injector (SIL-20AC HT), and a diode array detector (SPD-M20A). The isocratic mobile phase was a mixture of *n*-hexane and 2-propanol (97:3) with a run time of 20 min, a flow rate of 0.5 mL/min, and monitored by UV (200-400 nm). The solution of glycosides (1 mg/mL) in hexane:2-propanol (9:1) was filtered through a 0.22 μM PTFE filter, and injected into the HPLC system with a volume of 10 μL. The column was maintained at a temperature of 25 °C and LC Lab solutions software was used for data acquisition and analysis.

2. Synthesis of CBA 1, CBA 3 & CBA 4

1,2,3,4,5-Pentacarbomethoxycyclopentadiene (300 mg, 0.842 mmol, 1.0 equiv.), (+)-isomenthol (1.316 g, 10.0 equiv.), and 1-methylimidazole (0.403 mL, 5.052 mmol, 6.0 equiv.) were dissolved in toluene (10.0 mL). The reaction was heated in an ace pressure tube at a temperature of 125 ºC (Scheme S1). The reaction mixture was cooled after 48 h to room temperature and concentrated. The crude mixture was purified by CC using a gradient combination of MeOH/DCM (2 → 5%). The purified material was subsequently acidified with 3 M HCl (3 x 10 mL), dried with anhydrous Na_2SO_4, and concentrated in a vacuum to yield a black syrupy liquid, then it was dissolved in a small amount of hexane (10 mL), stirred with 200 mg of activated charcoal for 20 min, and filtered through celite-545® to yield a white solid (750.57 mg, 91.2% yield). The structure of the molecule was confirmed with ^{1}H NMR, ^{13}C NMR, and ESI-HRMS analysis.



Scheme S1: Synthesis of CBA **1** from PCCP and (+)-isomenthol.

CBA 1: ^{1}H NMR ($CDCl_3$): δ 20.29 (s, 1H, OH), 5.19 (m, 5H, OCH), 1.85 – 1.26 (m, 48H), 0.95 (m 48H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 171.9, 166.5, 162.8, 134.0, 118.7, 106.6, 78.6, 73.4, 72.5, 46.2, 45.6, 43.1, 36.2, 34.3, 30.1, 29.7, 29.1, 27.7, 26.8, 26.2, 25.9, 22.6, 22.4, 21.2, 21.1, 20.9, 20.0, 19.4, 18.2, 17.6 ppm. ESI-HRMS calculated for $C_{60}H_{95}O_{10}$ $[M-H]^-$: 975.6925; found m/z 975.6929.

Similarly, the other two chiral Brønsted acids CBA **3** and CBA **4** were synthesized.

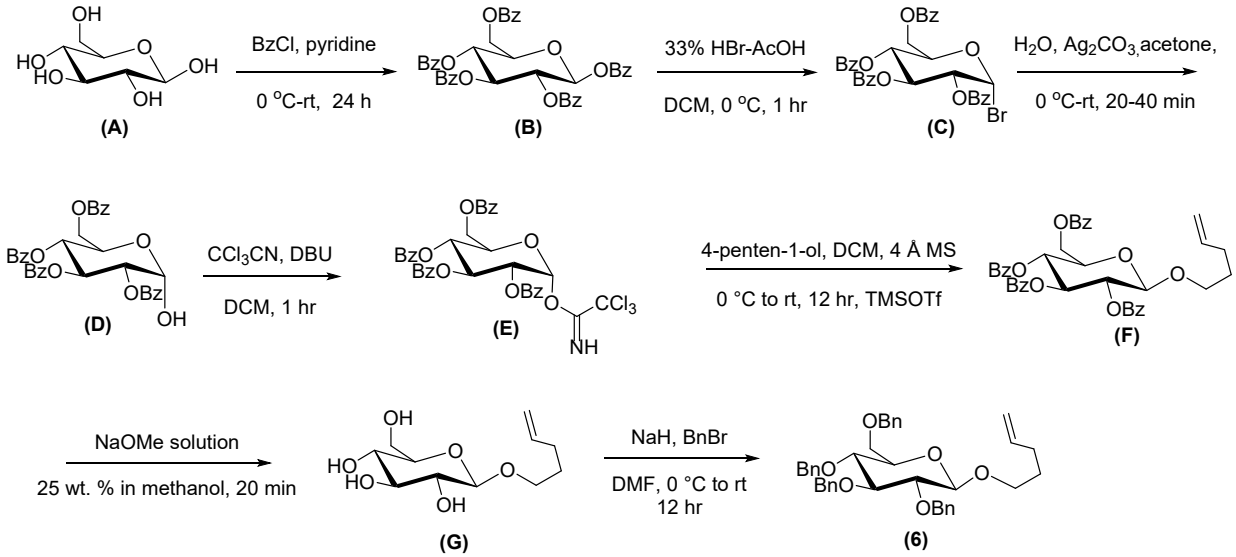
CBA 3: ^{1}H NMR ($CDCl_3$): δ 20.16 (s, 1H), 4.97 (m, 4H), 3.65 – 3.37 (m, 1H), 1.97 – 1.60 (m, 18H), 1.49 – 1.84 (m, 22H), 0.75 – 0.60 (m, 50H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 171.6, 167.7, 163.3, 133.0, 125.0, 107.0, 78.7, 69.6, 53.8, 52.3, 51.7, 45.9, 35.8, 31.9, 31.7, 30.9, 29.7, 29.3, 27.4, 26.0, 22.7, 20.9, 20.0, 18.3, 14.1. ESI-HRMS: calculated for $C_{60}H_{95}O_{10}$ $[M-H]^-$: 975.6925, found m/z 975.6940.

CBA 4: ^{1}H NMR ($CDCl_3$): δ 4.77 (s, 5H), 2.21 (m, 3H), 2.03 (m, 5H), 1.65 (d, J = 11.0 Hz, 9H), 1.56 – 1.38 (m, 7H), 1.32 (m, 7H), 1.13 – 0.90 (m, 25H), 0.83 (d, J = 6.1 Hz, 17H), 0.79 (d, J = 5.6 Hz, 17H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 168.00, 116.99, 77.28, 77.03, 76.77, 74.35, 46.36, 38.83, 34.28, 31.70, 25.33, 23.18, 22.66, 21.13, 16.71. ESI-HRMS calculated for $C_{60}H_{95}O_{10}$ $[M-H]^-$: 975.6925, found m/z 975.6939.

3. Procedure for the synthesis of glycosyl donors 6, 7, and 8

D-Glucose (5.0 g, 0.03 mol) was dissolved in pyridine (30 mL) and cooled to 0 °C. Benzoyl chloride (19.33 mL, 0.17 mol) was slowly added to the mixture with constant stirring and kept the reaction at room temperature for 24 h. After completion of the reaction, as indicated by TLC, the excess benzoyl chloride in the reaction mixture was quenched with ice-cold water. The resulting solid residue was dissolved in DCM and treated with 2 N HCl, saturated aqueous $NaHCO_3$, washed with water, dried with anhydrous Na_2SO_4, and concentrated to afford crude pentabenzoate of D-glucose **B** in 83% yield. The product **B** (5 g, 0.01 mol) was dissolved in freshly distilled DCM (30 mL), cooled to 0 °C and 33% HBr/AcOH (27.77 mL, 0.464 mol) was slowly added to the reaction mixture and stirred at room temperature for 1 h. After the complete consumption of **B**, the mixture was quenched with ice-cold water, and the organic layer was washed with water and saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated to obtain crude 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl

bromide **C** in 92% yield, which was directly used for the next step without further purification. To the solution of **C** (5 g, 0.01 mol) in acetone (20 mL) at 0 °C in an ice bath, 0.5 mL of water was added, followed by the addition of Ag_2CO_3 (1.672 g, 0.01 mol) portion-wise to the mixture. After completion of the reaction, as indicated by TLC, the mixture was filtered, concentrated, and purified by CC with EtOAc:hexane (3:7) and obtained **D** in 85% yield. Compound **D** (4.028 g, 0.01 mol) and trichloroacetonitrile (2.37 mL, 0.024 mol) were dissolved in freshly distilled DCM (15 mL), and then DBU (103 µL) was added to the mixture at 0 °C. After 1 h, the reaction mixture was washed with water, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude mixture thus obtained was further subjected to silica gel CC using 30% EtOAc in hexane as eluent, which resulted in **E** as a white crystalline solid. Thus, the obtained **E** (4.568 g, 0.006 mol) was further treated with 4-penten-1-ol (765 µL, 0.01 mol) in freshly distilled DCM (5 mL), and cooled to 0 °C, 4 Å powdered MS was added followed by the addition TMSOTf (15 mol%) in DCM after 10 min and stirred the reaction mixture at room temperature for 12 h. After complete consumption of the starting material, powdered MS was filtered off and the mixture was extracted with DCM. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Compound **F** was obtained as a white crystalline solid after CC using 20% EtOAC in hexane as the mobile phase. Debenzoylation of **F** was carried out by treatment with NaOMe solution in 25 wt% in MeOH, which resulted in the formation of **G**. Compound **G** was further purified by CC with a gradient of polarities from EtOAc to EtOAc-methanol (10%). The resultant **G** (1.120 g, 0.0045 mol) was dissolved in dry DMF (20 mL) and sodium hydride (1.08 g of 60% dispersion in oil, 0.045 mol) was slowly added to the reaction mixture in an ice bath and allowed to stir at room temperature for 20 min. Benzyl bromide (2.95 mL, 0.025 mol) was added portion-wise to the reaction mixture and continued to stir for 12 h. The excess sodium hydride and benzyl bromide were quenched by the slow addition of water, and the mixture was extracted with DCM. The organic layer was washed with water, and brine and dried with anhydrous Na_2SO_4. The product, *n*-pentenyl glucoside **6** was obtained as a colourless oil in 72% yield by CC using the mobile phase 10% EtOAc in hexane. The overall reactions are summarised in the following scheme (Scheme S2).



Scheme S2: Synthesis of the glycosyl donor **6** from D-glucose

Compound 6: ^{1}H NMR ($CDCl_3$): δ 7.30 (m, 18H), 7.16 (m, 2H), 5.88 – 5.74 (m, 1H), 5.05 – 4.90 (m, 4H), 4.80 (dd, J_1 = 14.7 Hz, J_2 = 11.0 Hz, 2H), 4.72 (d, J = 11.0 Hz, 1H), 4.57 (m, 3H), 4.38 (d, J = 7.8 Hz, 1H, C1), 4.01 – 3.92 (m, 1H), 3.74 (d, J = 10.6 Hz, 1H), 3.69 – 3.61 (m, 2H), 3.56 (m, 2H), 3.45 (t, J = 8.4 Hz, 2H), 2.22 – 2.12 (m, 2H), 1.76 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.7, 138.5, 138.3, 138.2, 138.1, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 127.6, 114.9, 103.7, 84.8, 82.3, 78.0, 75.7, 75.0, 74.9, 74.8, 73.5, 69.4, 69.1, 30.3, 29.0.

Similarly, the glycosyl donors **7** and **8** were synthesized from D-mannose and D-galactose, respectively.

Compound 7: ^{1}H NMR ($CDCl_3$): δ 7.44 – 7.28 (m, 20H), 5.91 – 5.77 (m, 1H), 5.09 – 4.96 (m, 3H), 4.91 (t, J = 4.3 Hz, 1H), 4.79 (m, 2H), 4.67 (m, 2H), 4.64 – 4.58 (m, 1H), 4.58 – 4.47 (m, 3H), 4.42 – 4.32 (m, 1H), 4.10 (m, 1H), 4.05 – 3.99 (m, 1H), 3.94 (s, 1H), 3.89 – 3.84 (m, 1H), 3.75 (m, 1H), 3.70 (m, 1H), 3.64 (m, 1H), 3.60 – 3.55 (m, 1H), 3.41 – 3.32 (m, 1H), 2.16 (m, 2H), 1.72 (m, 2H).^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.9, 138.7, 138.6, 138.3, 138.2, 138.0, 137.7, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 114.8, 114.8, 104.0, 100.0, 84.2, 82.3, 81.1, 80.4, 79.7, 79.6, 75.3, 74.5, 73.6, 73.5, 73.4, 73.4, 73.1, 72.4, 72.3, 70.4, 69.4, 68.9, 67.3, 30.4, 30.3, 29.0, 28.7.

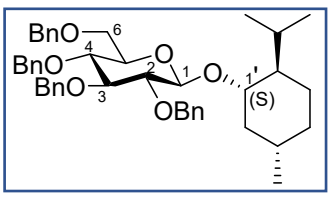
Compound 8: ^{1}H NMR ($CDCl_3$): δ 7.27 (m, 20H), 5.80 (dd, J_1 = 16.5 Hz, J_2 = 7.6 Hz, 1H), 5.03 (s, 1H), 5.00 – 4.93 (m, 1H), 4.72 (d, J = 11.7 Hz, 1H), 4.58 – 4.44 (m, 6H), 4.30 (d, J = 11.7 Hz, 1H), 4.12 (d, J = 6.9 Hz, 1H), 4.03 – 3.97 (m, 2H), 3.78 (s, 1H), 3.70 (m, 3H), 3.44

– 3.35 (m, 1H), 2.10 (d, J = 6.8 Hz, 2H), 1.65 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.5, 138.3, 138.2, 137.9, 137.7, 128.4, 128.4, 128.3, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 114.8, 106.0, 88.6, 82.7, 80.7, 76.3, 73.4, 73.3, 72.0, 71.9, 71.0, 66.9, 30.3, 28.8 ppm.

4. General procedure for chiral Brønsted acid-mediated glycosylation with racemic substrates

N-Pentenyl glycosides (**6/7/8**) (100 mg, 0.164 mmol, 1.0 equiv.) and acceptor **± 5/ ± 12/ ± 13 / ± 14** (2.0 equiv.) were azeotroped together with freshly distilled toluene (3 mL) thrice on rotavapour and dried under high vacuum. The resulting dry syrup was redissolved in freshly distilled DCM (9 mL) and cooled to 0 °C. *N*-Iodosuccinimide (NIS) (92.39 mg, 0.4107 mmol, 2.5 equiv.) and powdered 4 Å molecular sieves were added, stirred for 10 minute and then CBA **1** (10 mol%) in DCM was added, and the reaction mixture was slowly warmed to room temperature. After 16 h, the reaction mixture was quenched with 10% aqueous $Na_2S_2O_3$ and saturated $NaHCO_3$ solutions, filtered and washed with DCM. The organic layer was washed with water, brine and dried with anhydrous Na_2SO_4. The crude residue was further subjected to CC using EtOAc-hexane as the mobile phase affording the corresponding diastereomeric mixture. The diastereomeric ratio was determined by computing the area percentage of both the peaks in the HPLC chromatogram and by comparison with the retention times of respective glycosides of each individual enantiomer and / or from integration of the anomeric protons in ^1H NMR spectra, identified by their respective chemical shifts of the glycosides with pure enantiomers and HMQC spectra.

4.1. (β, 1*S*)-9

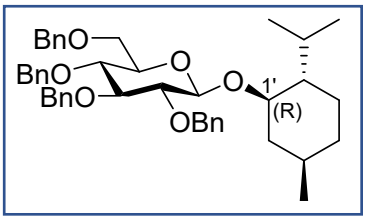


^1H NMR ($CDCl_3$): δ 7.34 - 7.27 (m, 20H, ArH), 4.91 (m, 2H, $ArCH_2$), 4.80 and 4.60 (m, 2H, $ArCH_2$), 4.71 (s, 2H, $ArCH_2$), 4.46 (m, 2H, $ArCH_2$), 4.41 - 4.34 (m, 2H), 4.32 (d, J = 7.5 Hz, 1H, H_1), 3.87 (m, 1H, H_3), 3.75 – 3.69 (m, 1H, H_2), 3.59 (m, 2H, H_4 & H_5), 3.52 (m, 2H, H_6), 3.35 (td, J_1 = 10.5 Hz, J_2 = 4.4 Hz, 1H, H_1'), 2.41 – 2.32 (m, 1H), 2.21 (d, J = 12.4 Hz, 1H),

1.76 – 1.69 (m, 1H), 1.44 (m, 1H), 1.10 (m, 2H), 0.99 (d, J = 6.7 Hz, 2H), 0.98 – 0.92 (m, 3H), 0.87 (d, J = 6.5 Hz, 3H), 0.80 (d, J = 6.9 Hz, 3H), 0.66 (d, J = 6.9 Hz, 3H).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.9, 138.7, 138.5, 138.1, 128.4, 128.4, 128.2, 128.1, 127.9, 127.8, 127.6, 104.8 (anomeric), 82.9, 81.3, 79.8, 75.3, 74.4, 73.6, 73.4, 73.0, 69.4, 48.7, 43.6, 34.3, 31.8, 29.7, 24.6, 22.8, 22.3, 21.3, 15.9.

ESI-HRMS calculated for $C_{44}H_{54}NaO_6$ $[M+Na]^+$: 701.3818; observed: 701.3836

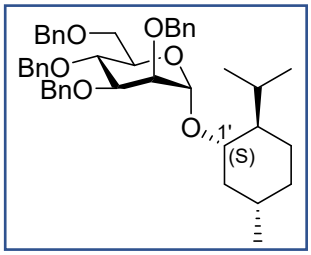
4.2. (β, 1*R*)-**9**



^1H NMR ($CDCl_3$): δ 7.38 – 7.26 (m, 20H, ArH), 4.93 (t, J = 10.7 Hz, 2H, $ArCH_2$), 4.73 and 4.61 (m, 4H, $ArCH_2$), 4.44 (m, 2H, $ArCH_2$), 4.39 (m, 1H, H_1, merged), 3.85 (m, 1H, H_3), 3.78 – 3.70 (m, 1H, H_2), 3.55 (m, 2H, H_4 & H_5), 3.53 – 3.47 (m, 2H, H_6), 3.43 (td, J_1 = 10.5 Hz, J_2 = 4.1 Hz, 1H, H_1'), 2.35 (m, 1H), 2.12 (d, J = 11.7 Hz, 1H), 2.04 (s, 2H), 1.70 – 1.62 (m, 3H), 0.96 (m, 2H), 0.88 (d, J = 5.8 Hz, 6H), 0.75 (d, J = 6.8 Hz, 3H).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.9, 138.8, 138.7, 138.0, 128.4, 128.3, 128.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.5, 101.6 (anomeric), 82.7, 79.5, 78.4, 75.2, 74.5, 74.0, 73.6, 73.2, 69.3, 48.1, 41.2, 34.5, 31.5, 29.7, 24.9, 23.1, 22.2, 21.2, 15.7.

ESI-HRMS calculated for $C_{44}H_{54}NaO_6$ $[M+Na]^+$: 701.3818; observed: 701.3839

4.3. (α, 1*S*)-**10**

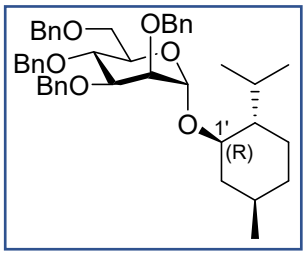


^1H NMR ($CDCl_3$): δ 7.25 (m, 18H, ArH), 7.14 (m, 2H, ArH), 5.10 (d, J = 4.5 Hz, 1H, H_1), 4.69 – 4.60 and 4.55 (m, 4H, $ArCH_2$), 4.88 – 4.33 (m, 4H, $ArCH_2$), 4.23 (t, J = 7.7 Hz, 1H, H_3), 3.94 (dd, J_1 = 7.5 Hz, J_2 = 4.7 Hz, 1H, H_2), 3.81 (dd, J_1 = 7.7 Hz, J_2 = 5.4 Hz, 1H, H_4),

3.68 (dd, J_1 = 10.8 Hz, J_2 = 5.3 Hz, 1H, H_5), 3.62 (dd, J_1 = 10.2, J_2 = 4.4 Hz, 1H, H_6), 3.55 (dd, J_1 = 10.2, J_2 = 6.3 Hz, 1H, H_6), 3.38 (td, J_1 = 10.6 Hz, J_2 = 4.2 Hz, 1H, H_1'), 2.36 (m, 1H), 1.96 (d, J = 8.9 Hz, 1H), 1.63 – 1.56 (m, 2H), 1.27 – 1.21 (m, 3H), 0.94 – 0.88 (m, 1H), 0.85 (d, J = 6.5 Hz, 3H), 0.83 – 0.74 (m, 4H), 0.71 (d, J = 7.1 Hz, 3H), 0.66 (d, J = 6.8 Hz, 3H).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.9, 138.4, 138.4, 137.8, 128.5, 128.5, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 127.9, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 96.9 (anomeric), 83.4, 80.3, 79.4, 78.7, 73.3, 72.8, 72.4, 72.3, 70.4, 47.7, 40.6, 34.4, 31.5, 31.0, 29.7, 24.5, 23.0, 22.4, 21.2, 16.1.

ESI-HRMS calculated for $C_{44}H_{54}NaO_6$ $[M+Na]^+$: 701.3818; observed: 701.3823

4.4. (α, 1*R*)-**10**

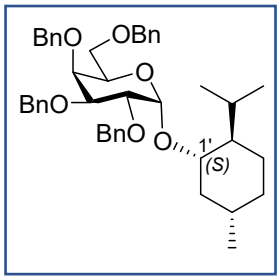


^1H NMR ($CDCl_3$): δ 7.27 (m,18H, ArH), 7.09 (m, 2H, ArH), 4.92 (app s, 1H, H_1), 4.76 (m, 2H, $ArCH_2$), 4.60 (d, J = 13.5 Hz, 4H, $ArCH_2$), 4.44 (d, J = 11.4 Hz, 2H, $ArCH_2$), 3.97 (t, J = 9.4 Hz, 1H, H_3), 3.79 (dd, J_1 = 9.5 Hz, J_2 = 2.9 Hz, 1H, H_2), 3.74 (m, 1H, H_4), 3.64 – 3.58 (m, 2H, H_5 & H_6), 3.60 (m, 1H, H_6), 3.34 (td, J_1 = 10.6 Hz, J_2 = 4.1 Hz, 1H, H_1'), 2.07 (dd, J_1 = 16.6 Hz, J_2 = 9.3 Hz, 1H), 1.75 (d, J = 12.0 Hz, 1H), 1.21 (s, 2H), 1.07 (dd, J_1 = 22.7 Hz, J_2 = 11.7 Hz, 1H), 0.85 (t, J = 9.2 Hz, 2H), 0.82 (s, 2H), 0.78 (d, J = 7.0 Hz, 3H), 0.72 (m, 2H), 0.64 (d, J = 6.9 Hz, 3H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.7, 138.5, 138.5, 138.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 94.6 (anomeric), 80.3, 75.8, 75.4, 75.2, 75.0, 73.5, 72.9, 72.4, 72.2, 69.2, 47.9, 39.7, 34.5, 31.3, 25.2, 22.8, 22.3, 21.2, 15.4.

ESI-HRMS calculated for $C_{44}H_{54}NaO_6$ $[M+Na]^+$: 701.3818; observed: 701.3833

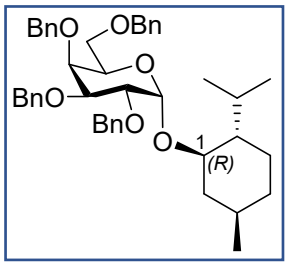
4.5. (α, 1*S*)-**11**



^{1}H NMR ($CDCl_3$): δ 7.31 – 7.20 (m, 18H, ArH), 7.14 (m, 2H, ArH), 5.09 (d, J = 3.4 Hz, 1H, H_1), 4.72 (m, 2H, $ArCH_2$), 4.61 and 4.51 (m, 2H, $ArCH_2$), 4.46 (s, 2H, $ArCH_2$), 4.44 – 4.39 (m, 2H, $ArCH_2$), 4.30 (t, J = 7.5 Hz, 1H, H_3), 4.01 (dd, J_1 = 7.4 Hz, J_2 = 4.8 Hz, H_2), 3.91 – 3.85 (m, 1H, H_4), 3.75 (dd, J_1 = 10.7 Hz, J_2 = 5.4 Hz, 1H, H_5) 3.69 (dd, J_1 = 10.2 Hz, J_2 = 4.5 Hz, 1H, H_6), 3.63 – 3.59 (m, 1H, H_6), 3.45 (td, J_1 = 10.6 Hz, J_2 = 3.9 Hz, 1H, H_1'), 2.39 – 2.33 (m, 1H), 2.14 (d, J = 12.8 Hz, 1H), 1.96 (d, J = 11.9 Hz, 1H), 1.55 (m, 2H), 1.22 (m, 3H), 0.85 (d, J = 6.0 Hz, 3H), 0.80 (m, 3H), 0.71 (d, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.9, 138.3, 137.8, 128.4, 128.3, 128.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.3, 96.9 (anomeric), 83.4, 80.3, 79.4, 78.7, 73.3, 72.8, 72.4, 72.2, 70.4, 47.7, 40.6, 34.4, 31.5, 24.5, 22.9, 22.4, 21.1, 16.1.

ESI-HRMS calculated for $C_{44}H_{54}NaO_6$ [M+Na]$^+$: 701.3818; observed: 701.3834

4.6. (α, 1*R*)-**11**



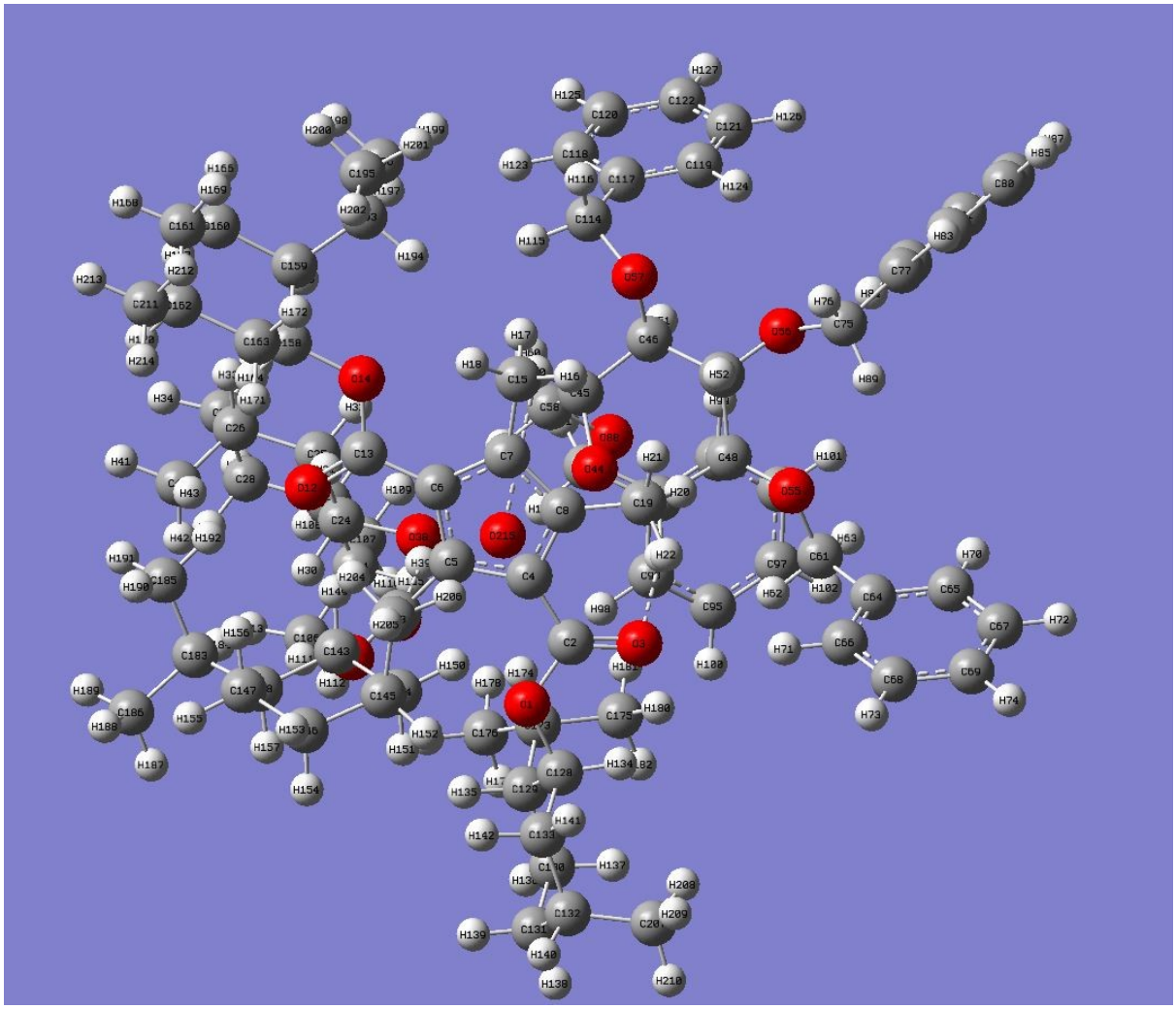
^{1}H NMR ($CDCl_3$): δ 7.25 (m, 17H, ArH), 7.14 (m, 3H, ArH), 5.06 (d, J = 4.0 Hz, 1H, H_1), 4.64 (m, 4H, $ArCH_2$), 4.46 – 4.36 (m, 4H, $ArCH_2$), 4.22 (t, J = 7.2 Hz, 1H, H_3), 3.96 (m, 1H, H_2), 3.86 (t, J = 6.7 Hz, 1H, H_4), 3.75 – 3.70 (m, 1H, H_5), 3.64 (dd, J_1 = 10.4 Hz, J_2 = 3.2 Hz, 1H, H_6), 3.52 (dd, J_1 = 10.2 Hz, J_2 = 6.4 Hz, 1H, H_6), 3.25 (td, J_1 = 10.5 Hz, J_2 = 4.1 Hz, 1H, H_1'), 2.31 – 2.21 (m, 2H), 1.53 (d, J = 12.0 Hz, 2H), 1.22 (m, 3H), 1.02 (m, 1H), 0.95 – 0.88 (m, 1H), 0.88 – 0.83 (m, 2H), 0.78 (d, J = 6.9 Hz, 3H), 0.73 (s, 3H), 0.66 (d, J = 6.9 Hz, 3H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.1, 138.3, 137.8, 128.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 127.2, 101.8 (anomeric), 84.0, 81.5, 80.9, 80.1, 80.0, 73.4, 72.9, 72.4, 72.3, 70.7, 48.4, 43.6, 34.3, 31.7, 24.9, 22.9, 22.3, 21.1, 15.9.

ESI-HRMS calculated for $C_{44}H_{54}NaO_6$ [M+Na]$^+$: 701.3818; observed: 701.3833

Computational methods

Model construction

Here we adopt the Gauss View 5.0 [5] program package to establish the atomistic model for the catalyst (CBA **1**), oxocarbenium intermediate and the acceptor systems (± **5**). A model containing cyclopentadienyl ring as the core for the catalyst, and an oxocarbenium based core for the intermediate were constructed. Based the above approximation we have developed a model system having 215 atoms and 726 electrons, which is further used for the interaction studies. The developed model was optimized via Density functional theory (DFT) calculation,[1,2] which was carried out using Gaussian-09 software by minimizing the total energy without symmetry constrain. The electronic structure and bonding interaction existed in the proposed transition state were studied by using Becke three-parameter Lee−Yang−Parr hybrid functional (B3LYP) method. Calculation were performed for the optimized structures of CBA-**1**, oxocarbenium ion, and menthol using 6-31G* basis set and B3LYP/6-31g (d,p) level of theory. The optimized structure of the materials was visualized using Gauss view version 5.0. HOMO and LUMO energy levels were also evaluated.



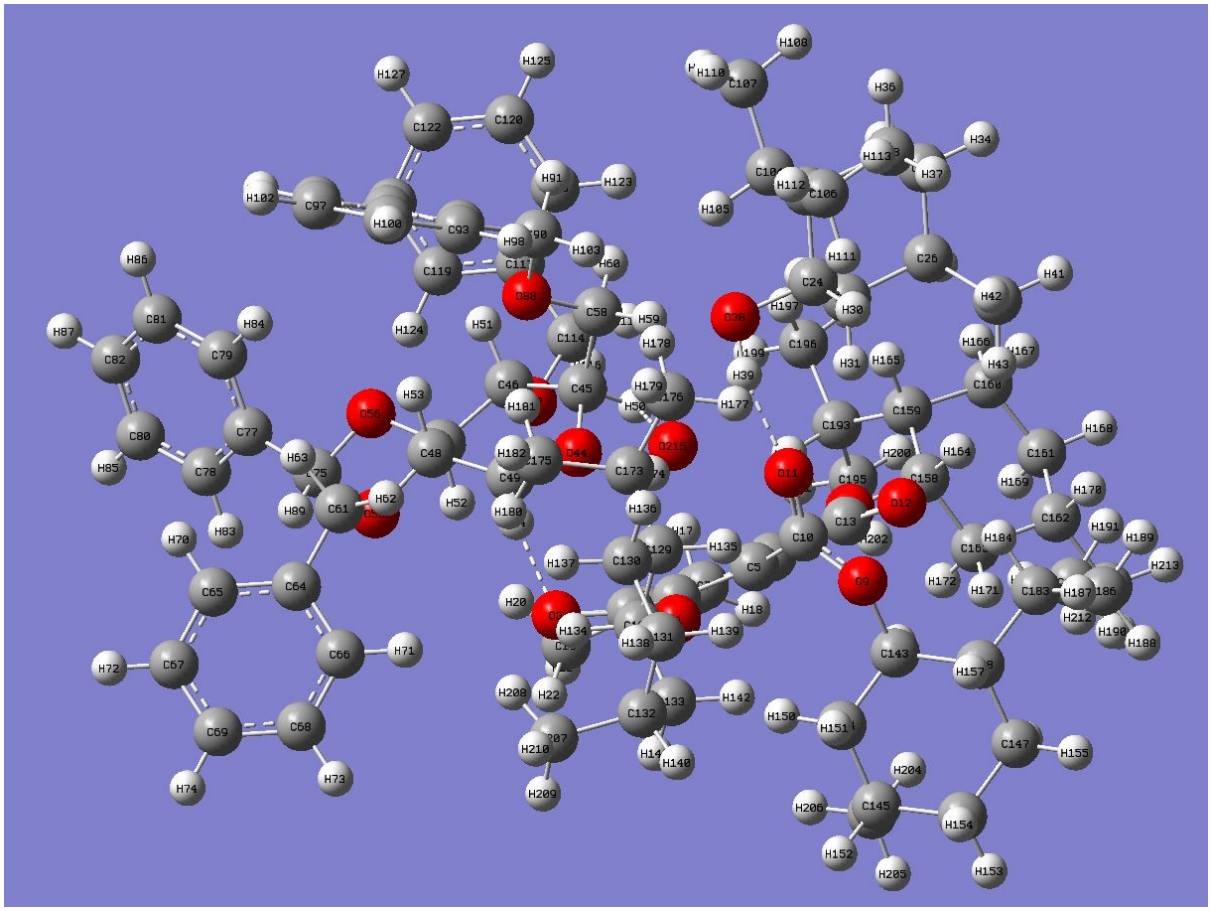


Figure S1: B3LYP/6-31 g(d,p) optimised model for the transition state in two different orientations.

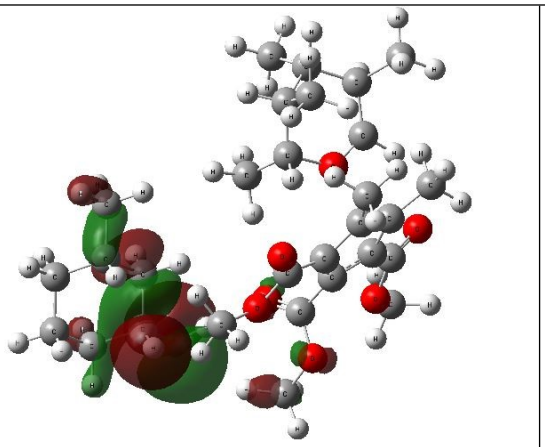
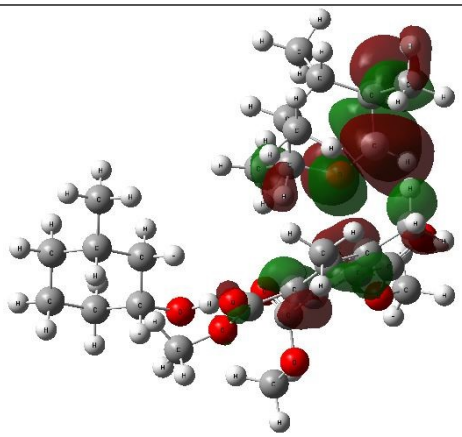
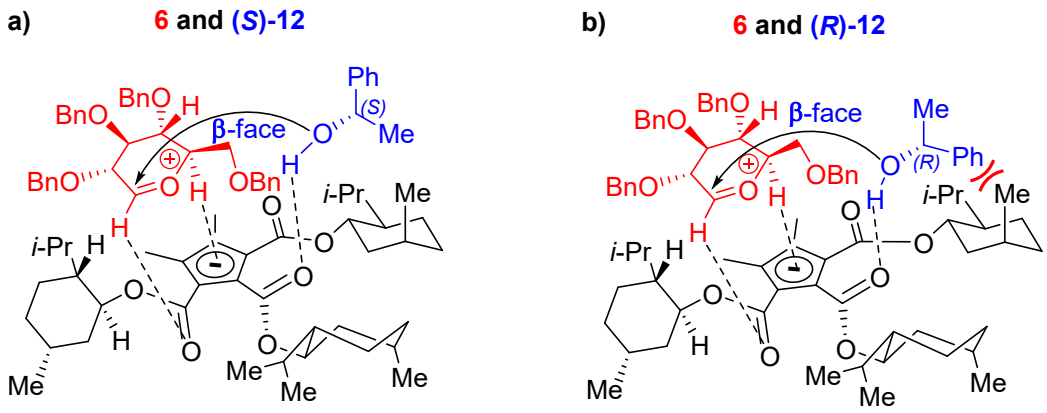
	
HOMO	**LUMO**

Table S1: HOMO, LUMO energy levels for the transition state

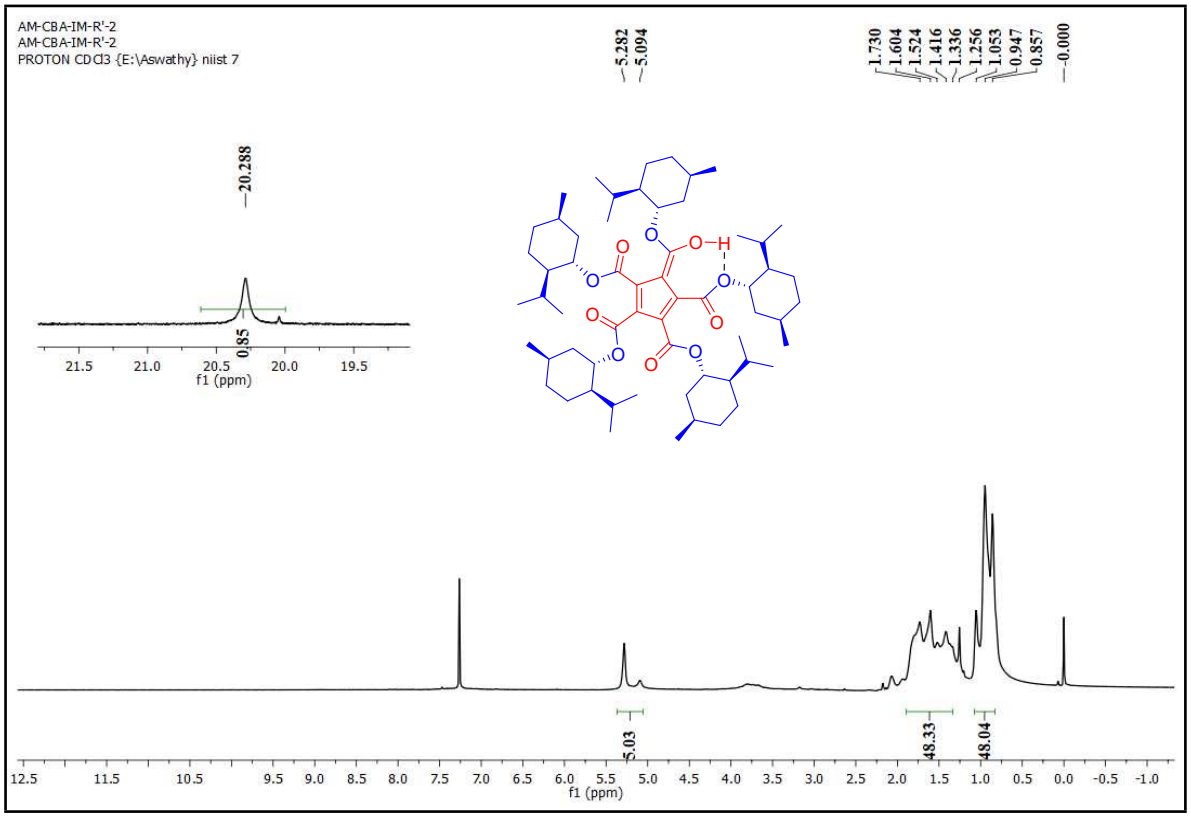
Mechanistic rationale for the stereo and diasterocontrol in glycosylation of **12** with CBA **1**

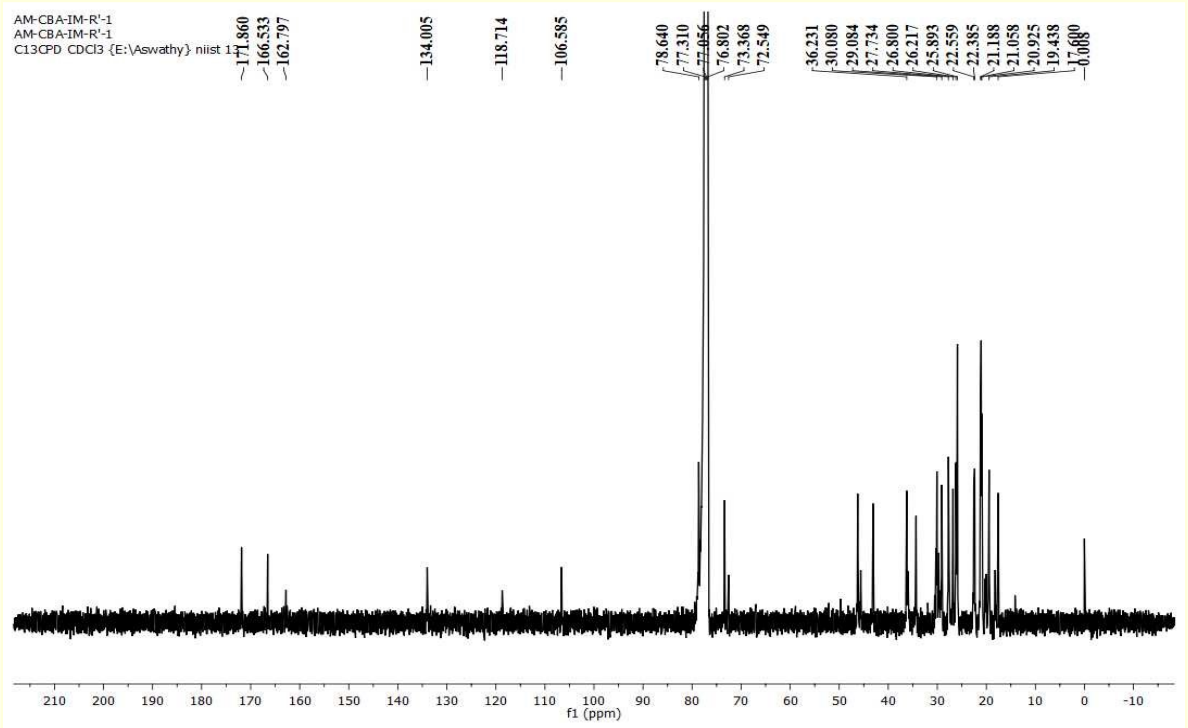


Scheme S3: Rationale for the stereo and diastereocontrol in glycosylation of **12** with CBA **1.**

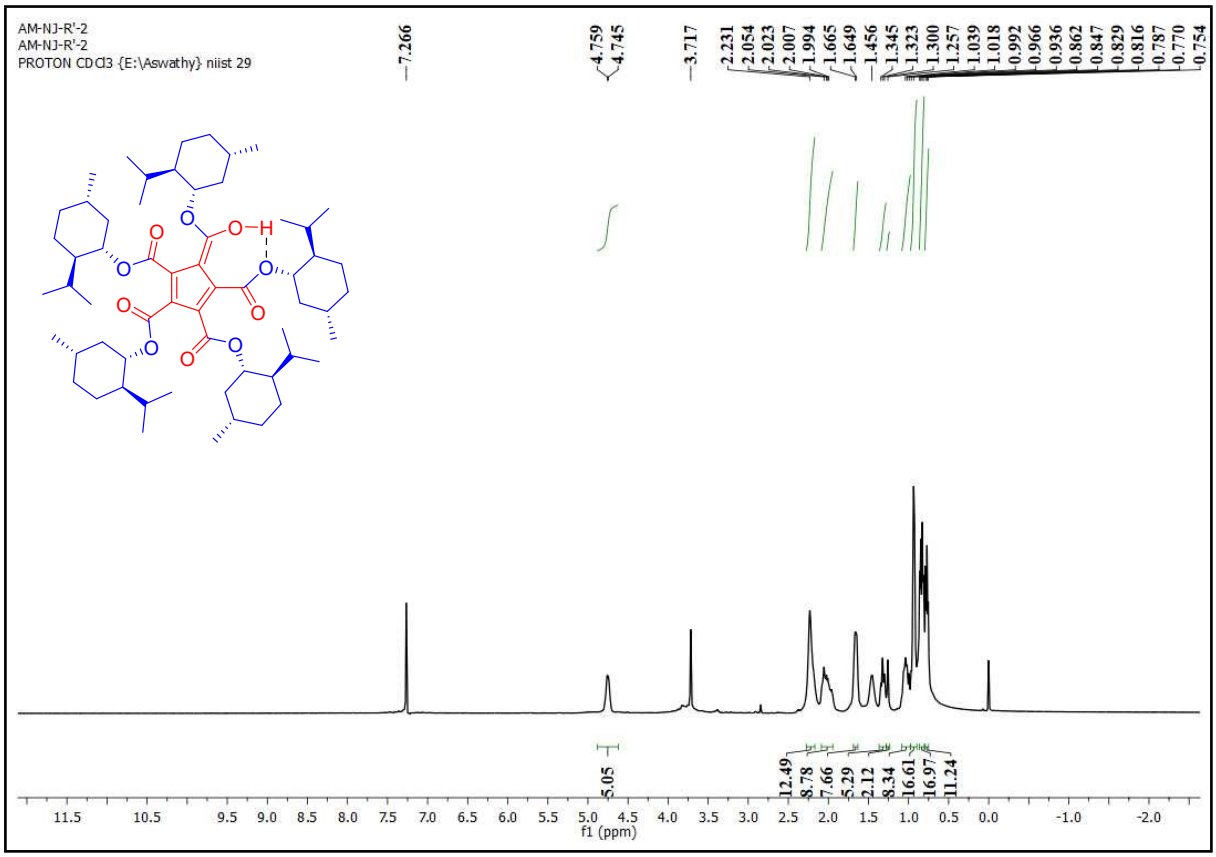
5. NMR SPECTRA

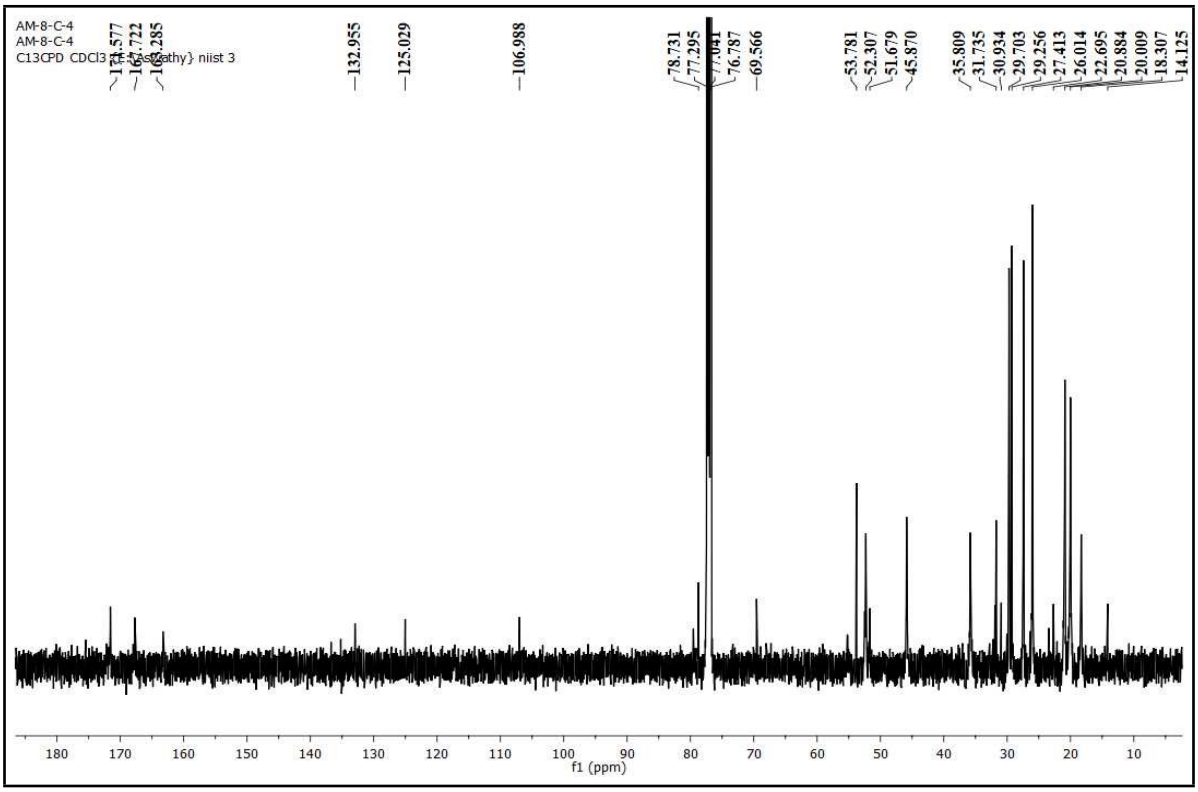
^{1}H (500 MHz, $CDCl_3$) & ^{13}C NMR (125 MHz, $CDCl_3$) of CBA **1**



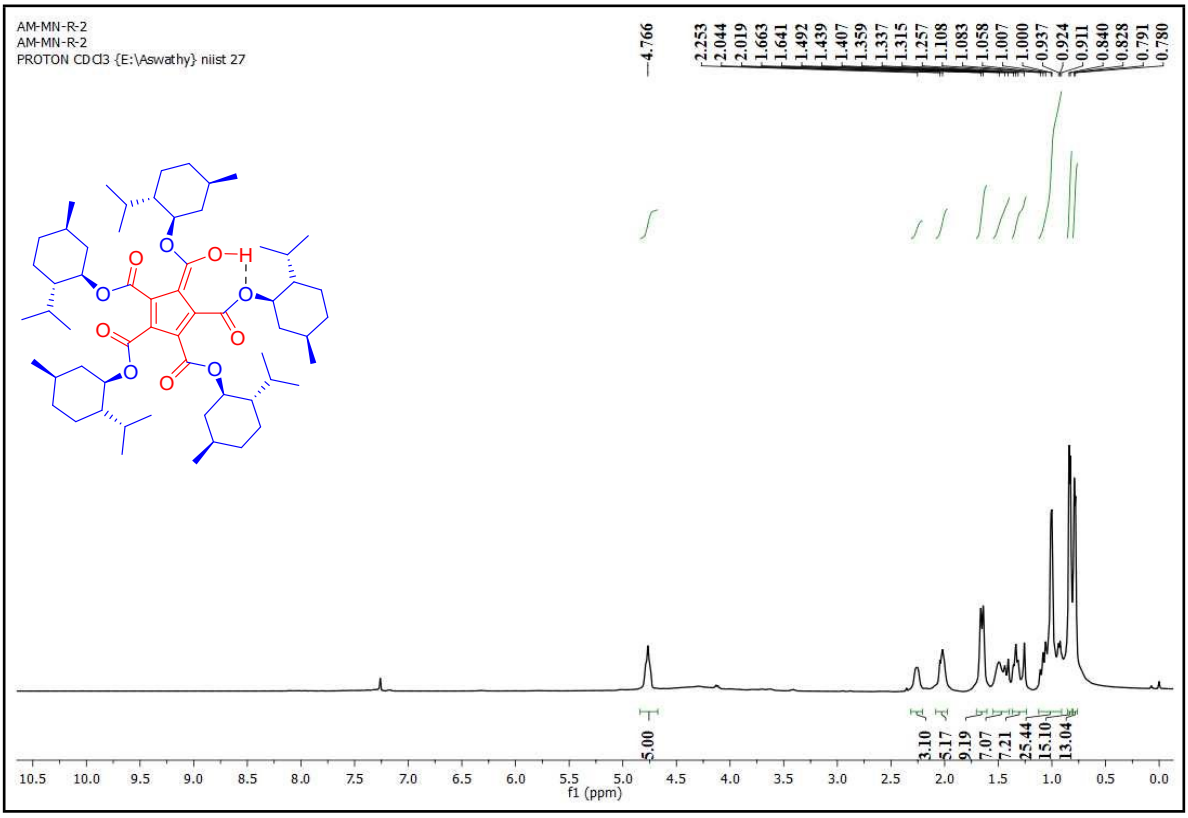


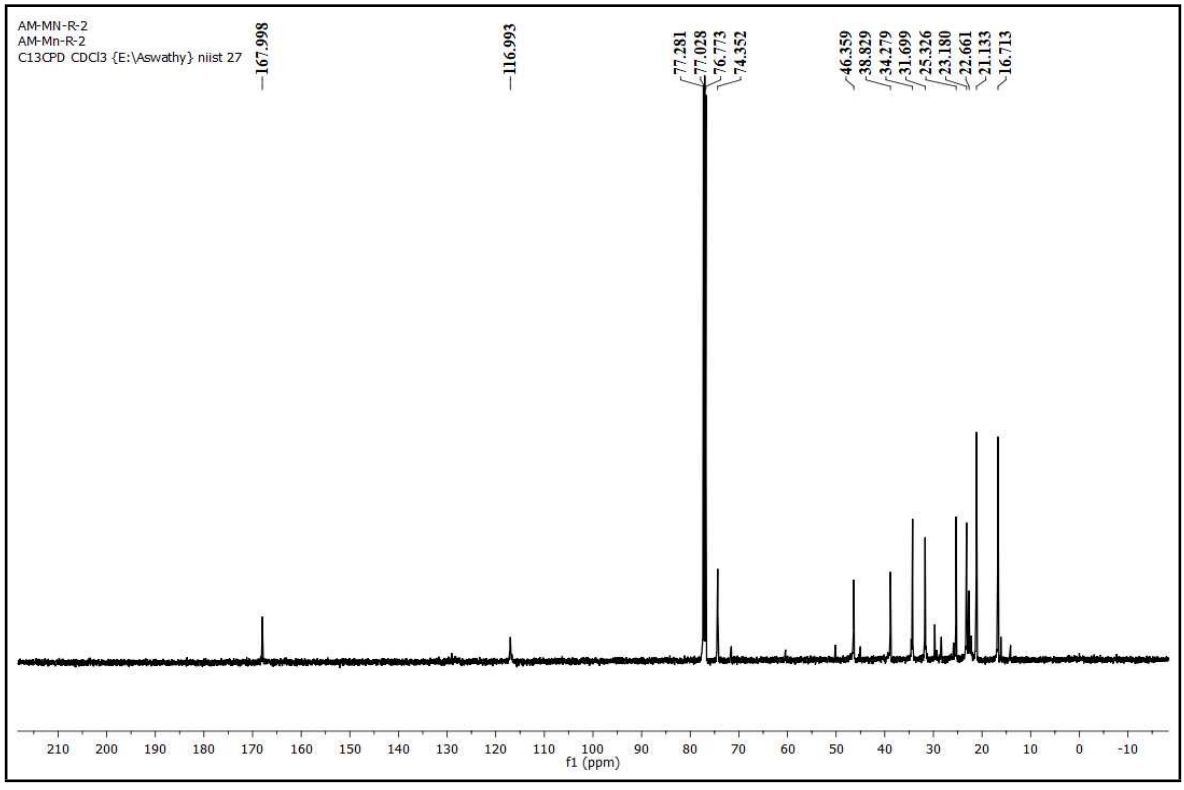
^{1}H (500 MHz, $CDCl_3$) & ^{13}C NMR (125 MHz, $CDCl_3$) of CBA **3**



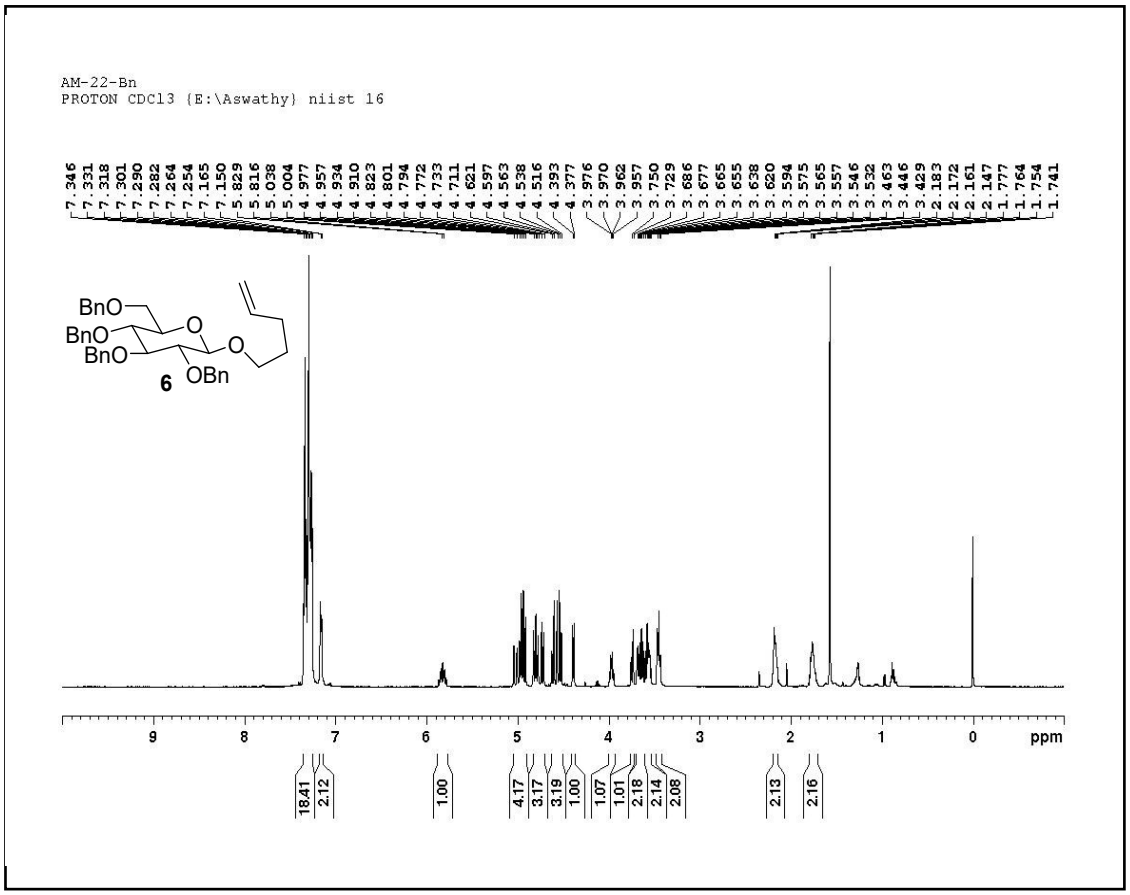


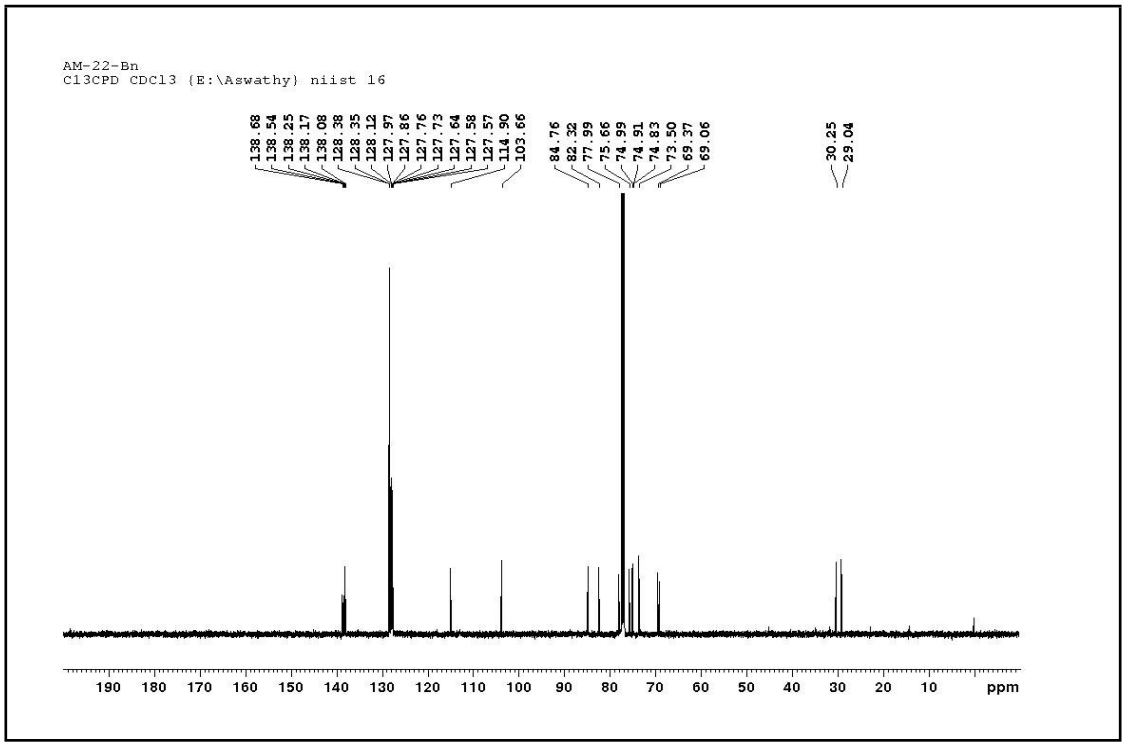
^{1}H (500 MHz, $CDCl_3$) & ^{13}C NMR (125 MHz, $CDCl_3$) of CBA **4**



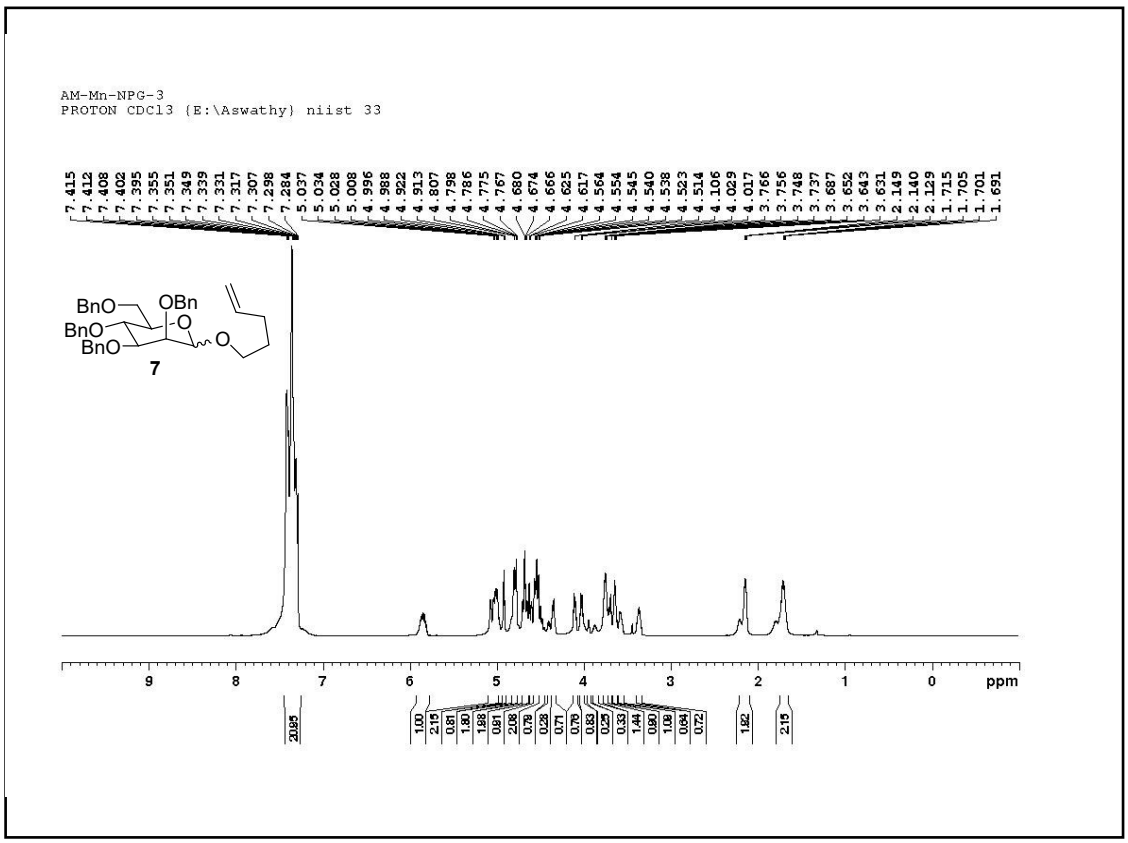


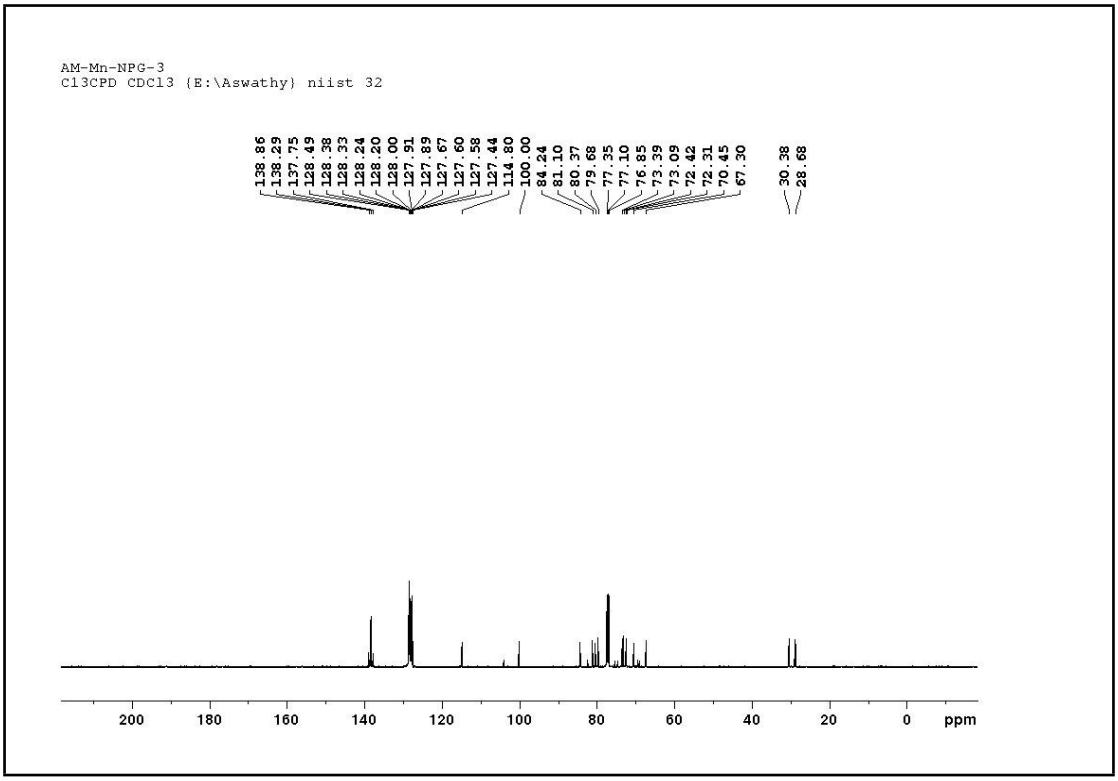
^{1}H (500 MHz, $CDCl_3$) & ^{13}C NMR (125 MHz, $CDCl_3$) of **6**



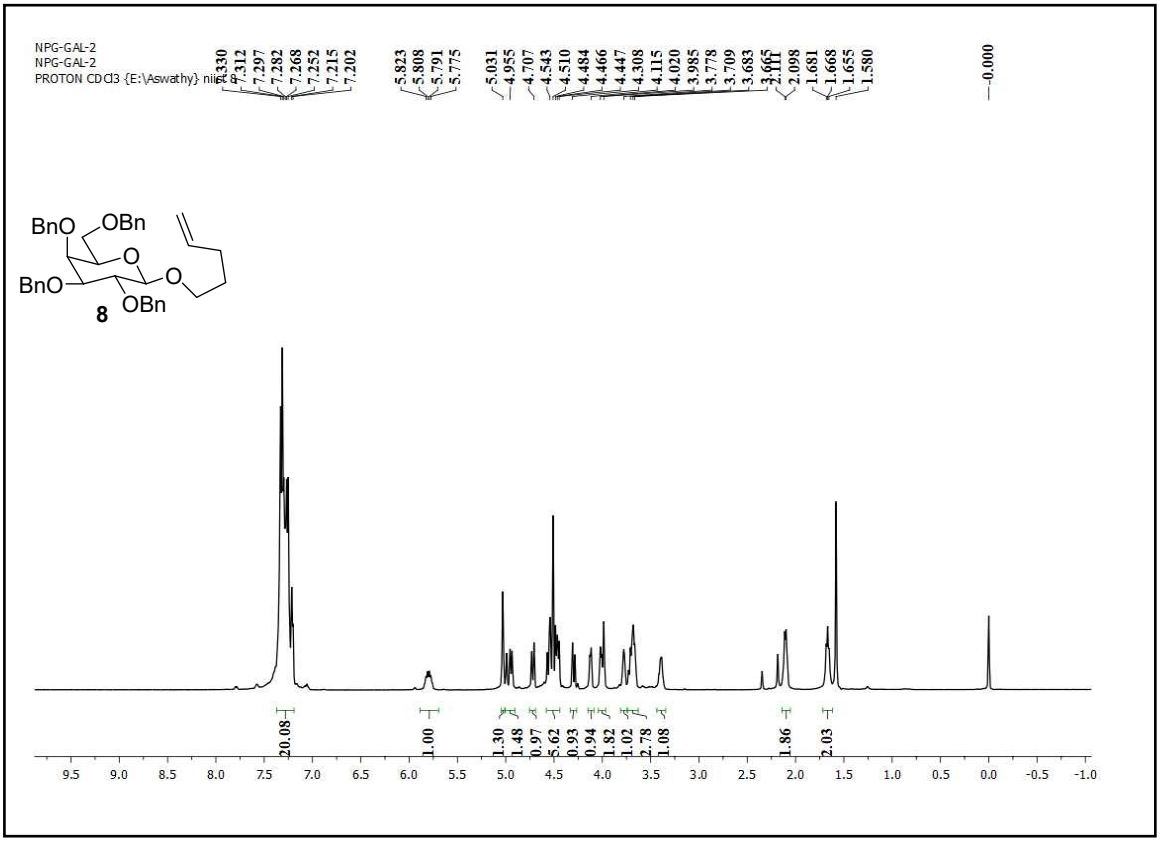


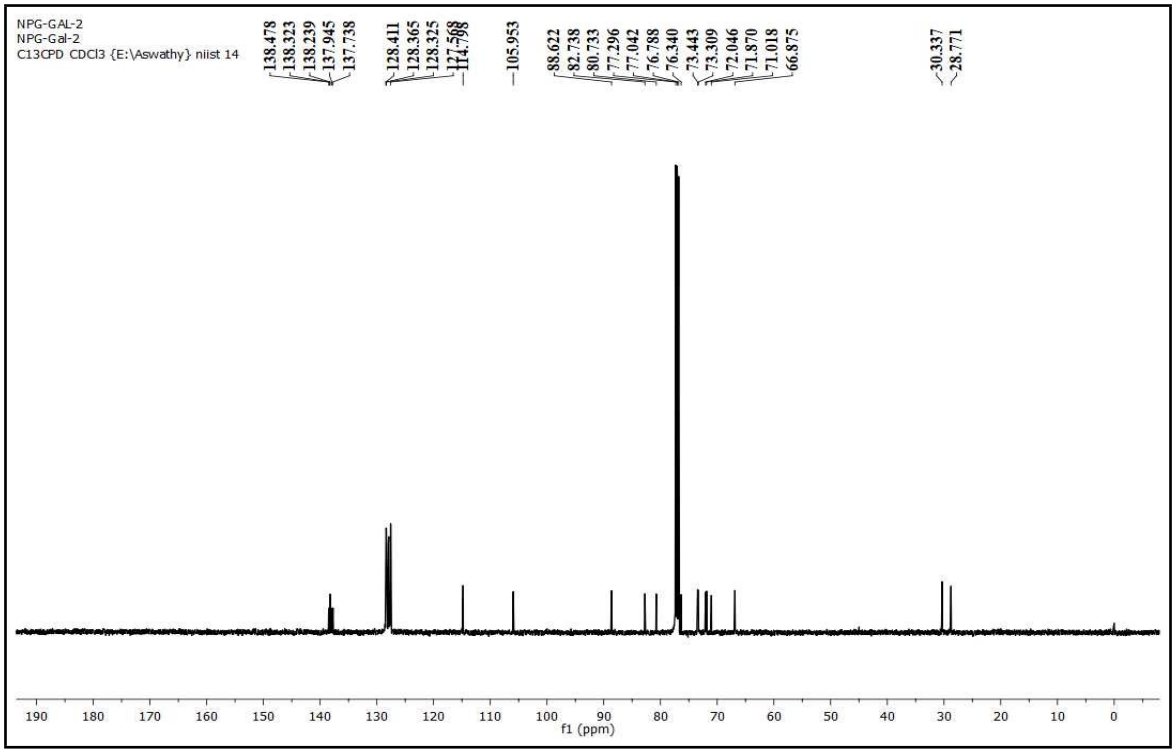
^{1}H (500 MHz, $CDCl_3$) & ^{13}C NMR (125 MHz, $CDCl_3$) of **7**



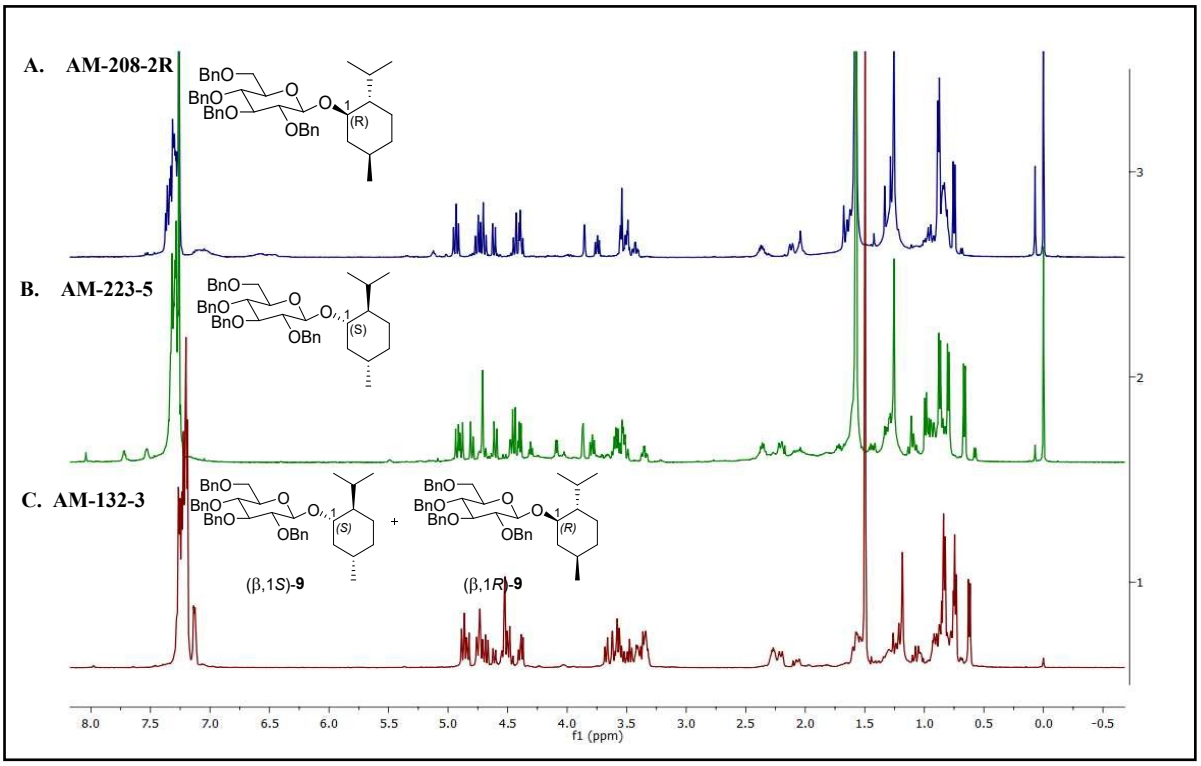


^{1}H (500 MHz, $CDCl_3$) & ^{13}C NMR (125 MHz, $CDCl_3$) of **8**

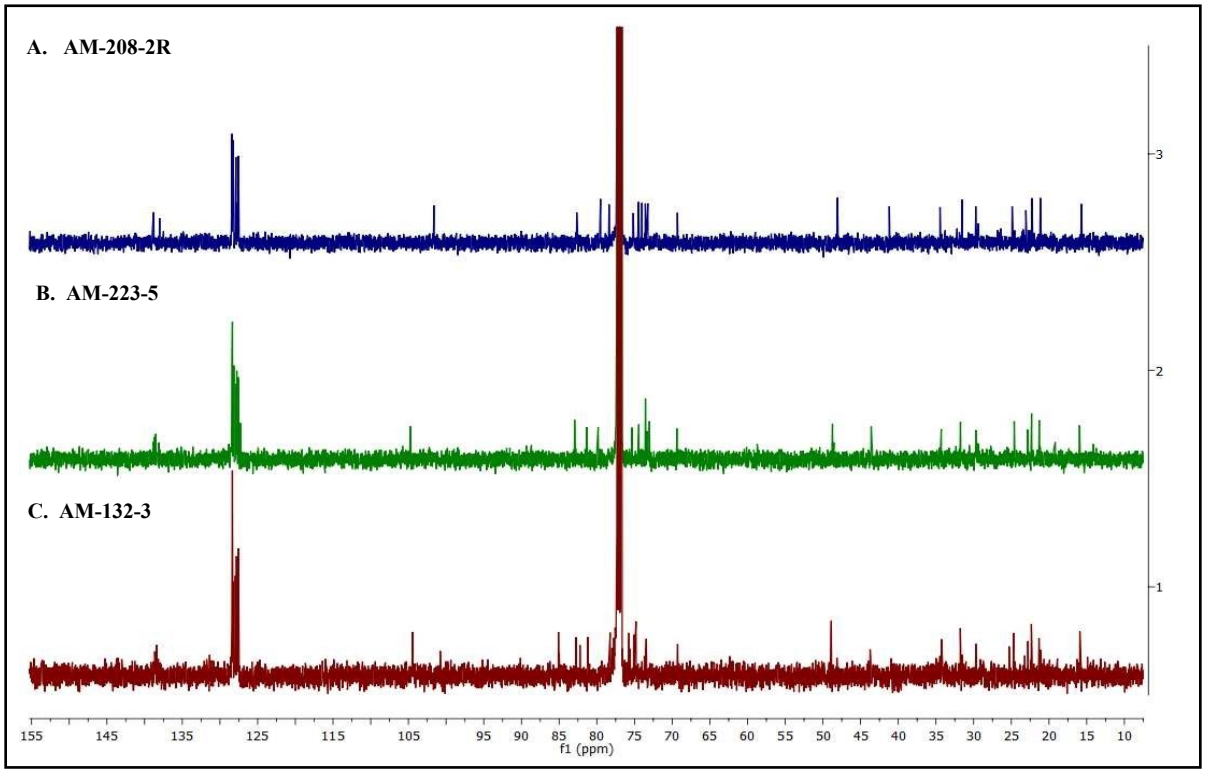




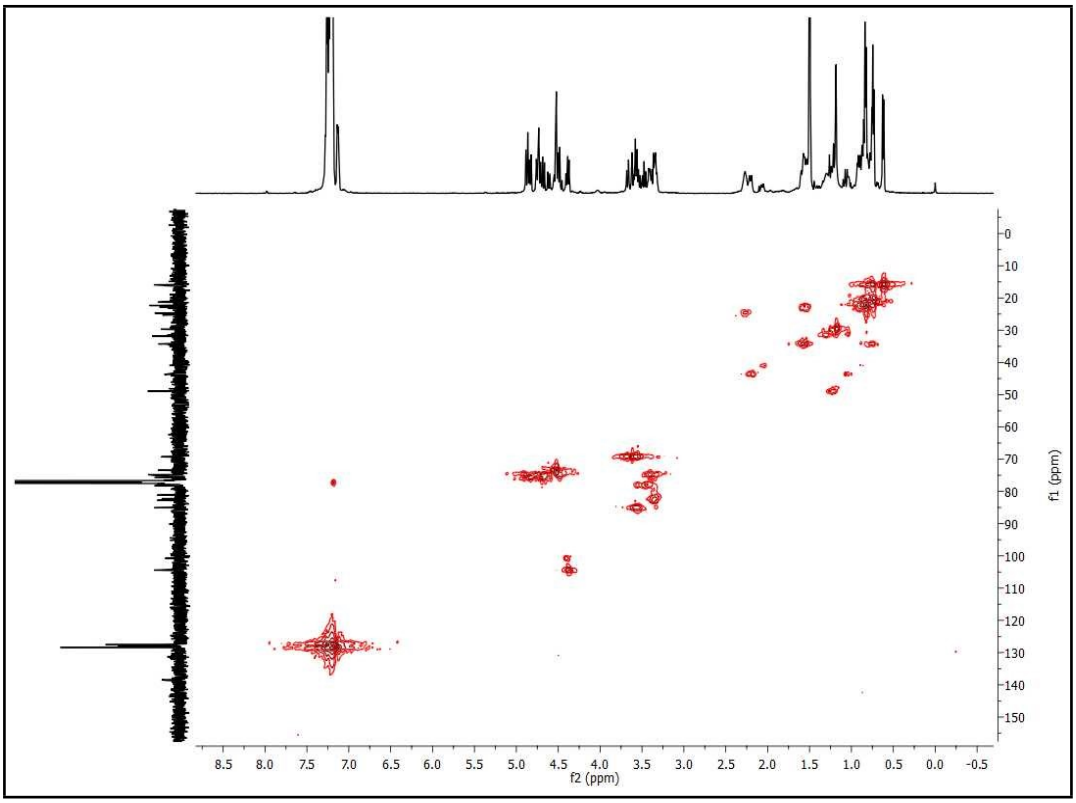
^{1}H NMR ((500 MHz, $CDCl_3$) of glycosides **(A)** (β, 1*R*)-**9 (B)** (β, 1*S*)-**9 (C)** mixture of (β, 1*S*)-**9** and (β, 1*R*)-**9**



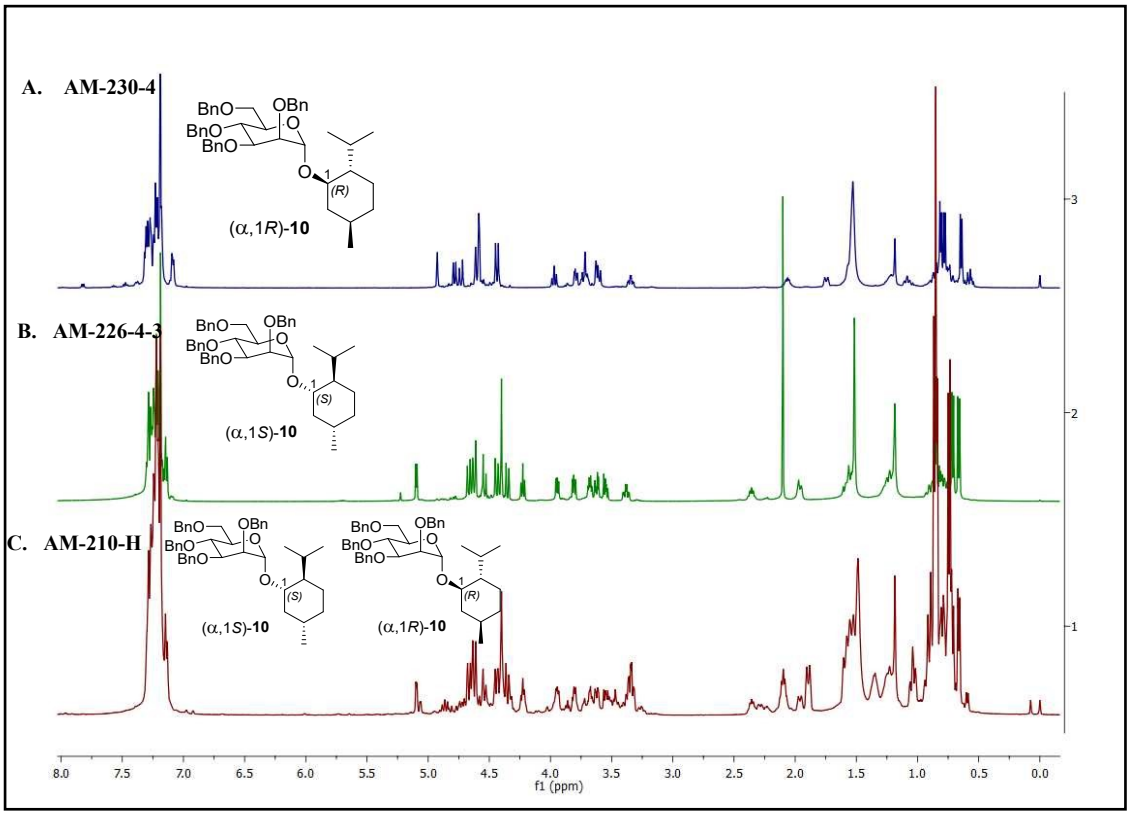
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides **(A)** (β, 1*R*)-**9 (B)** (β, 1*S*)-**9 (C)** mixture of (β, 1*S*)-**9** and (β, 1*R*)-**9**



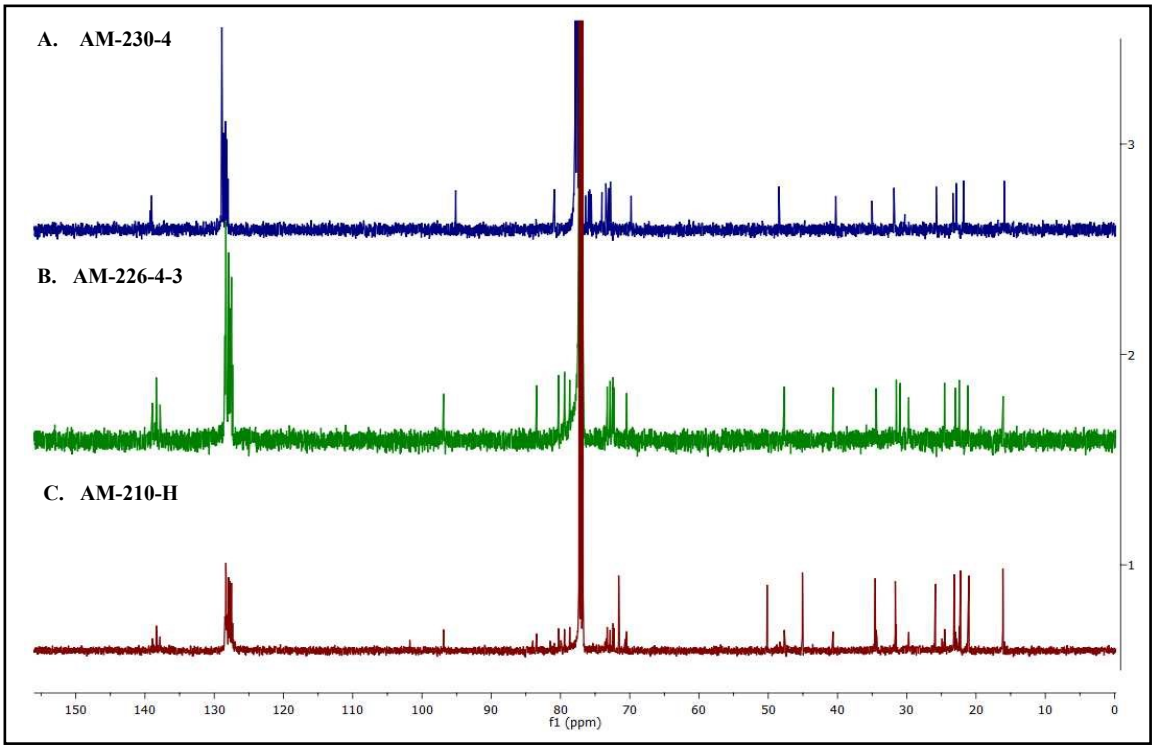
HMQC of diastereomeric mixture of (β, 1*S*)-**9** and (β, 1*R*)-**9**



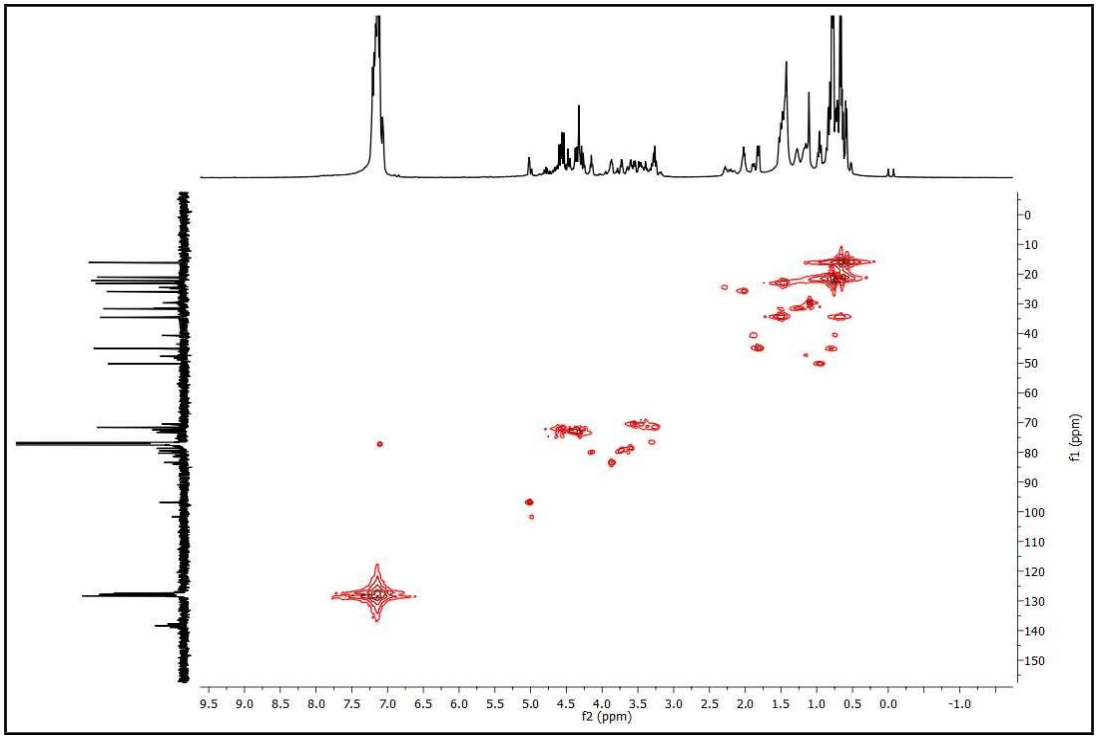
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides **(A)** (α,1*R*)-**10 (B)** (α,1*S*)-**10 (C)** mixture of (α, 1*S*)-**10** and (α, 1*R*)-**10**



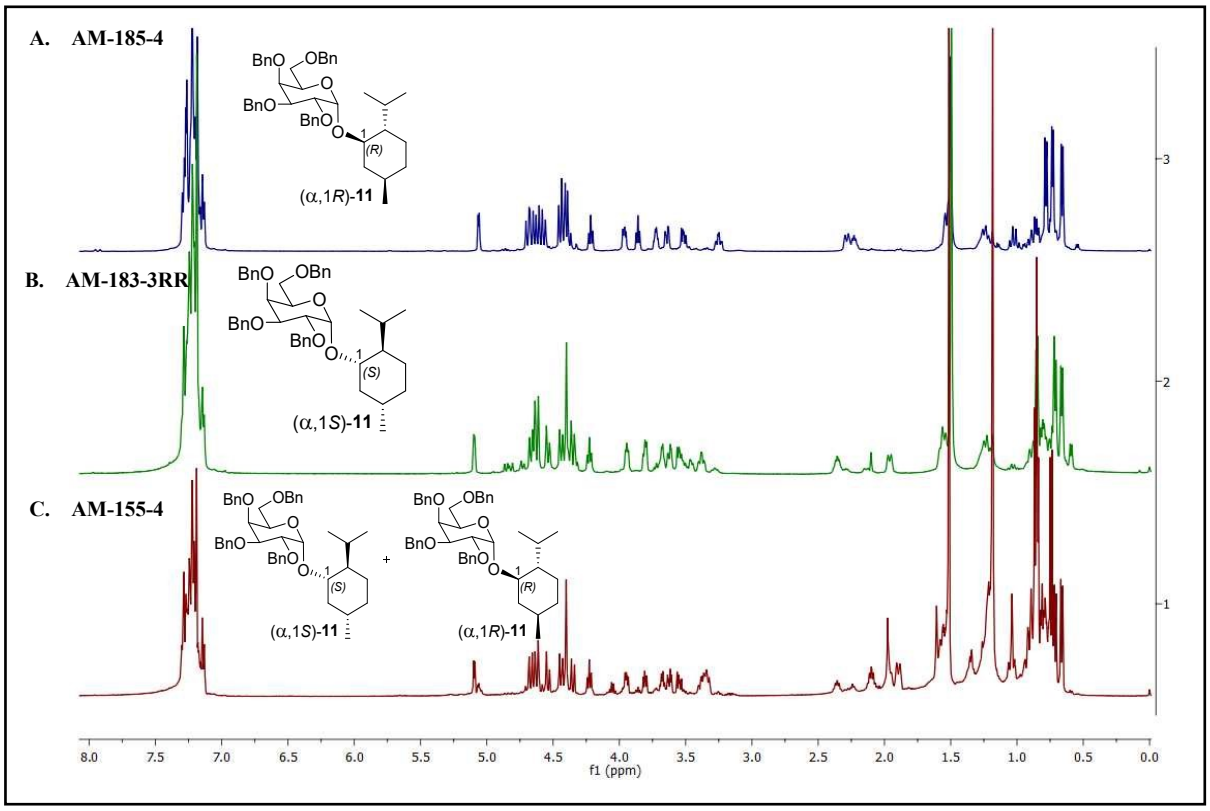
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides **(A)** (α,1*R*)-**10 (B)** (α,1*S*)-**10 (C)** mixture of (α, 1*S*)-**10** and (α, 1*R*)-**10**



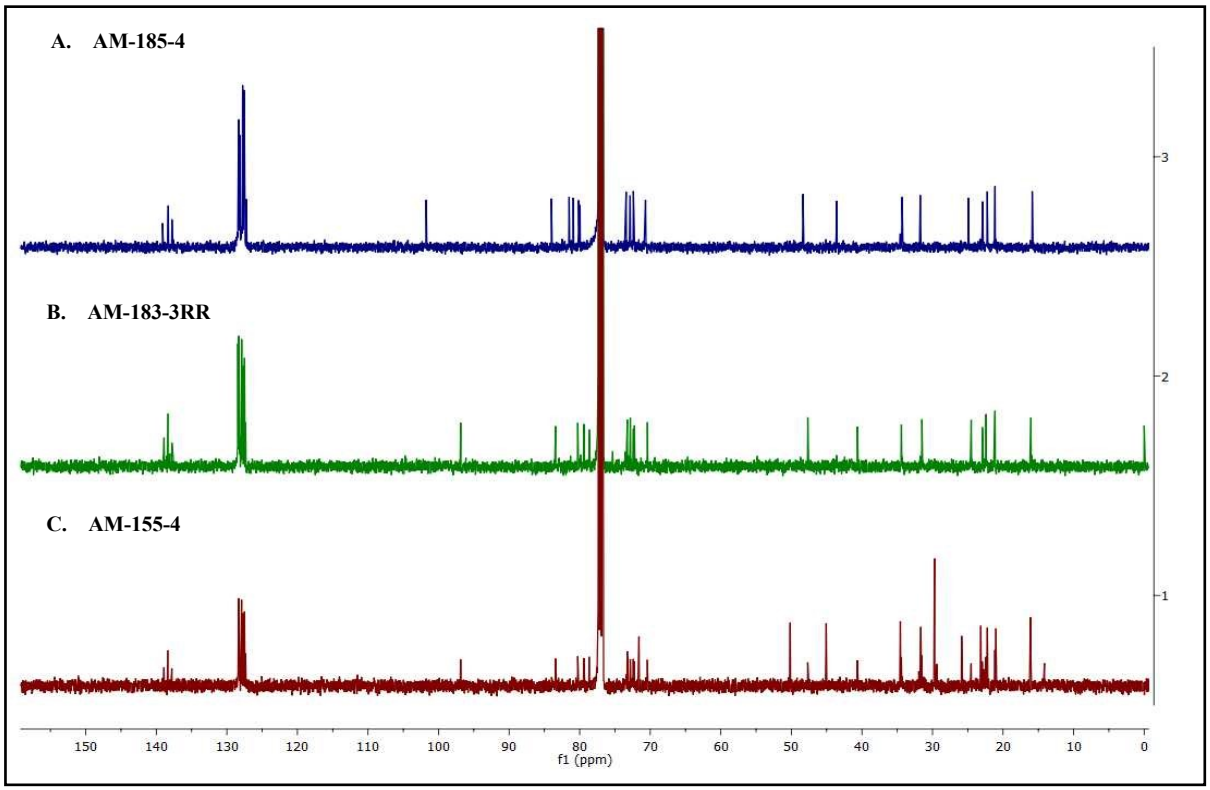
HMQC of diastereomeric mixture of (α, 1*S*)-**10** and (α, 1*R*)-**10**



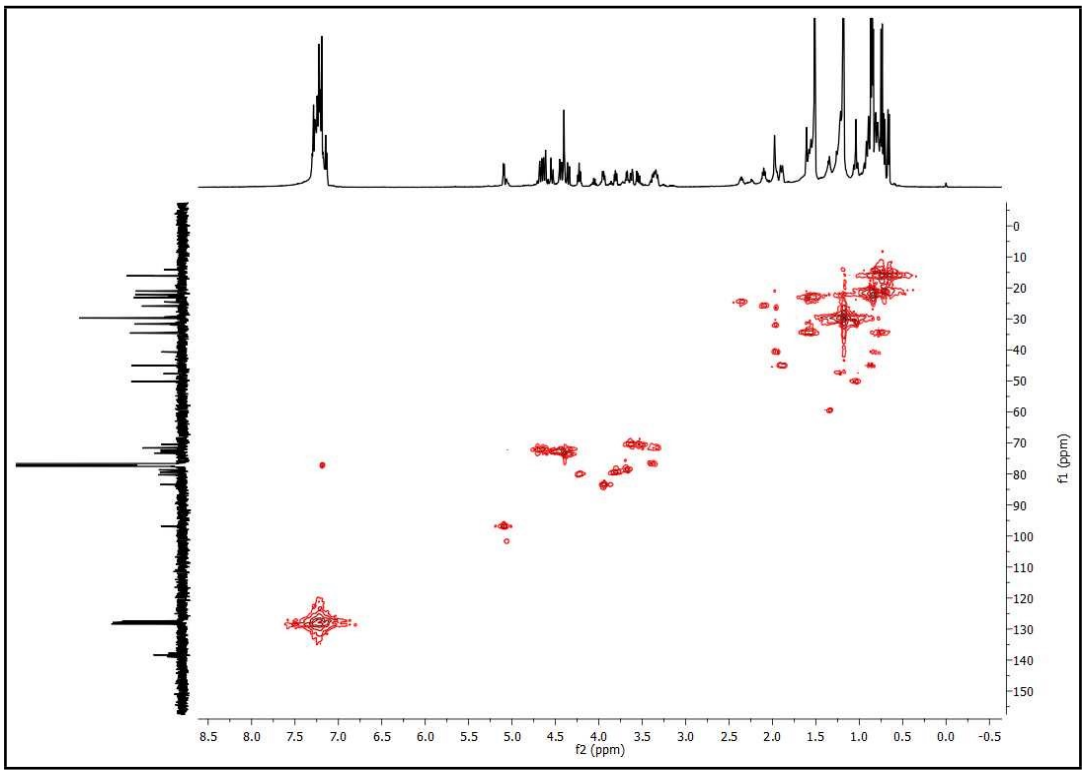
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides **(A)** (α, 1*R*)-**11 (B)** (α, 1*S*)-**11 (C)** mixture of (α, 1*S*)-**11** and (α, 1*R*)-**11** catalysed by CBA **1**



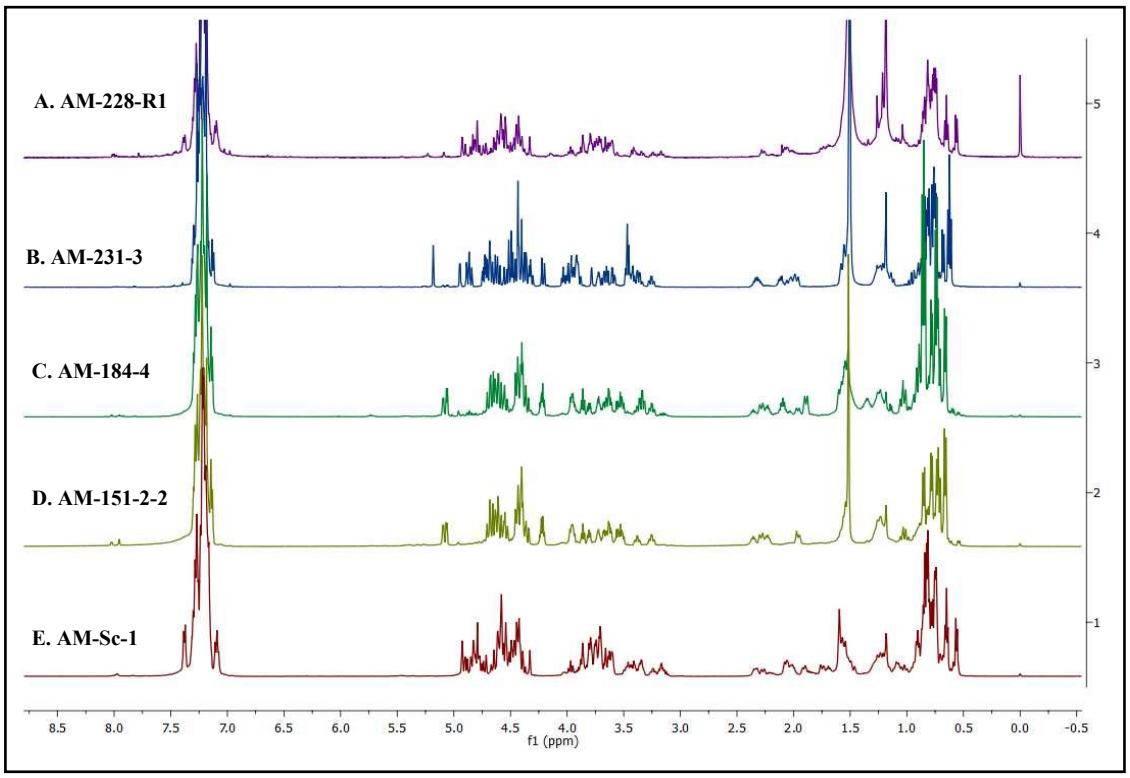
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides **(A)** (α, 1*R*)-**11 (B)** (α, 1*S*)-**11 (C)** mixture of (α, 1*S*)-**11** and (α, 1*R*)-**11** catalysed by CBA **1**



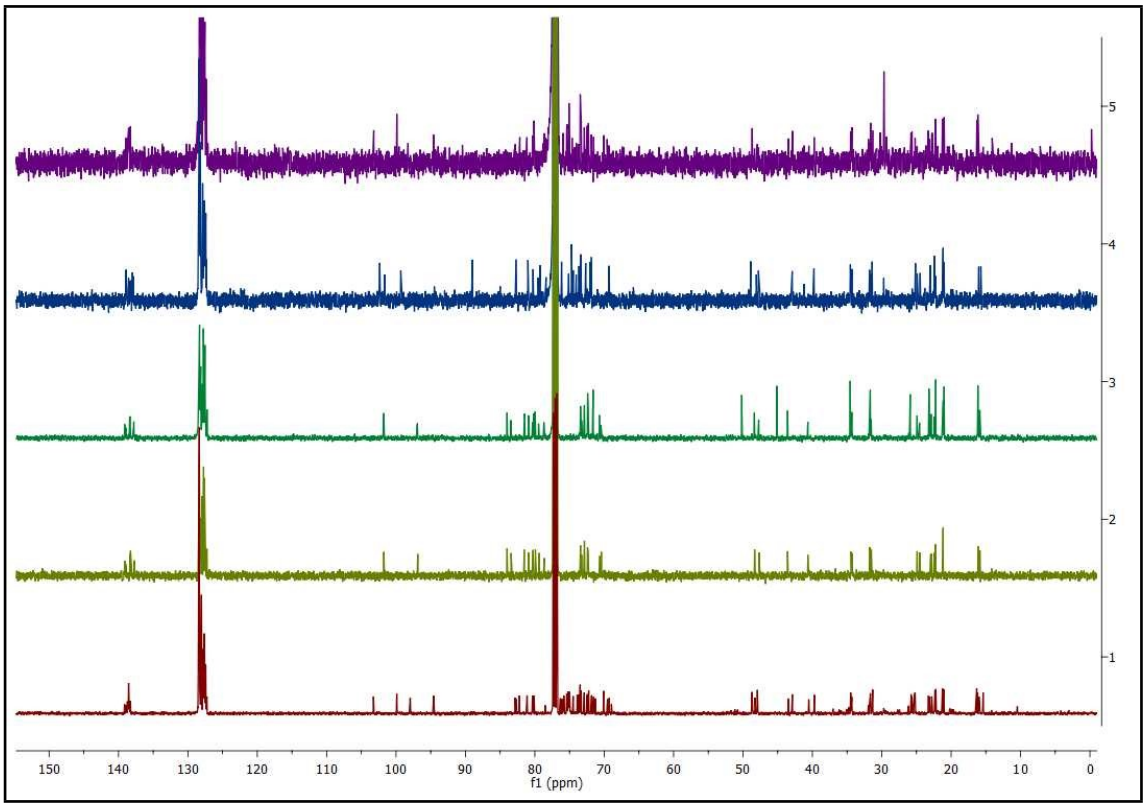
HMQC of diastereomeric mixture of (α, 1*S*)-**11** and (α, 1*R*)-**11** catalysed by CBA **1**



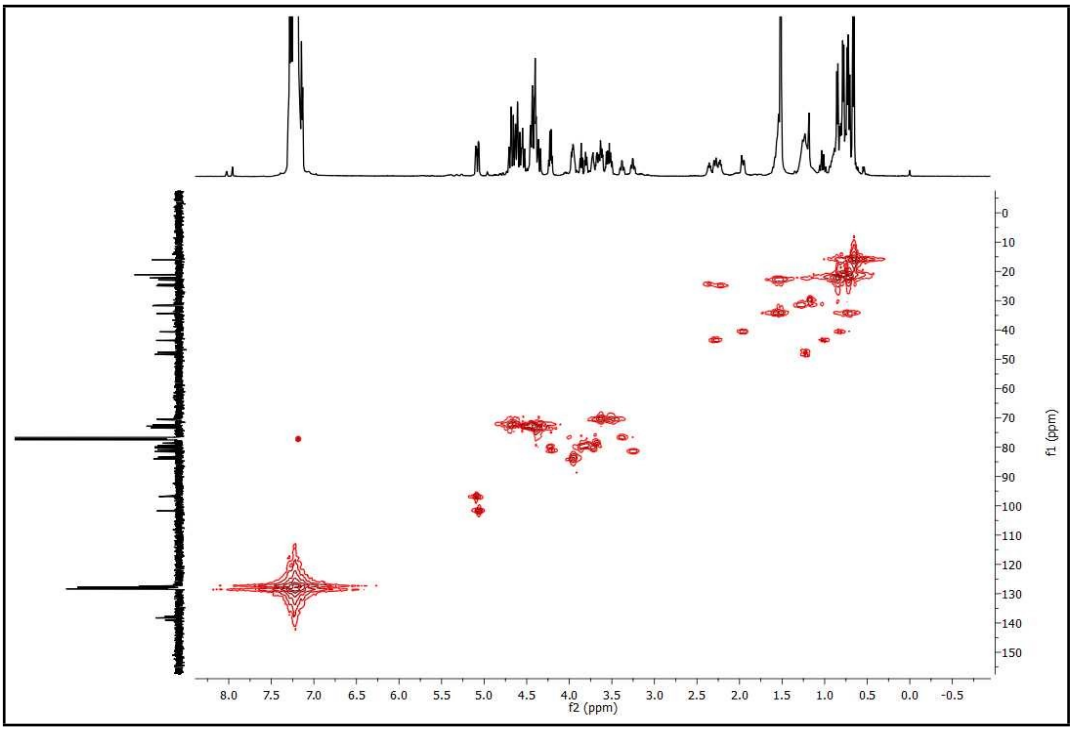
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides catalysed by **(A)** PCCP **(B)** CF_3SO_3H **(C)** (*R*)-2 **(D)** (*S*)-2 **(E)** $Sc(OTf)_3$ (entries 4-8, Table 1)



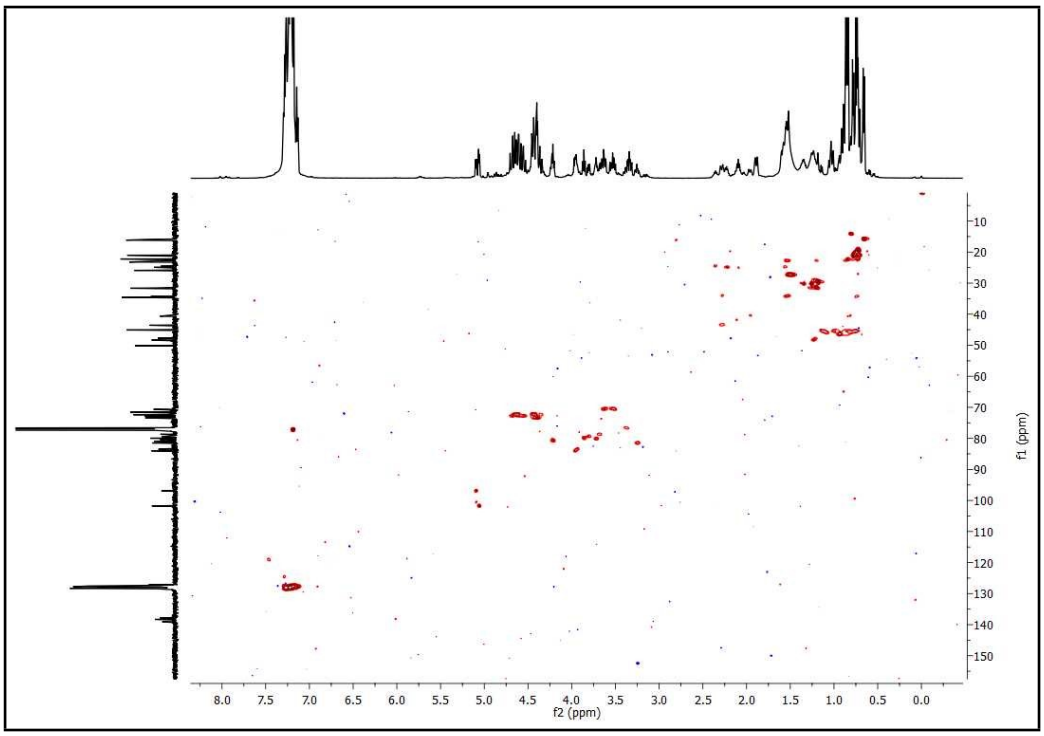
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides catalysed by **(A)** PCCP **(B)** CF_3SO_3H **(C)** (*R*)-2 **(D)** (*S*)-2 **(E)** $Sc(OTf)_3$ (entries 4-8, Table 1)



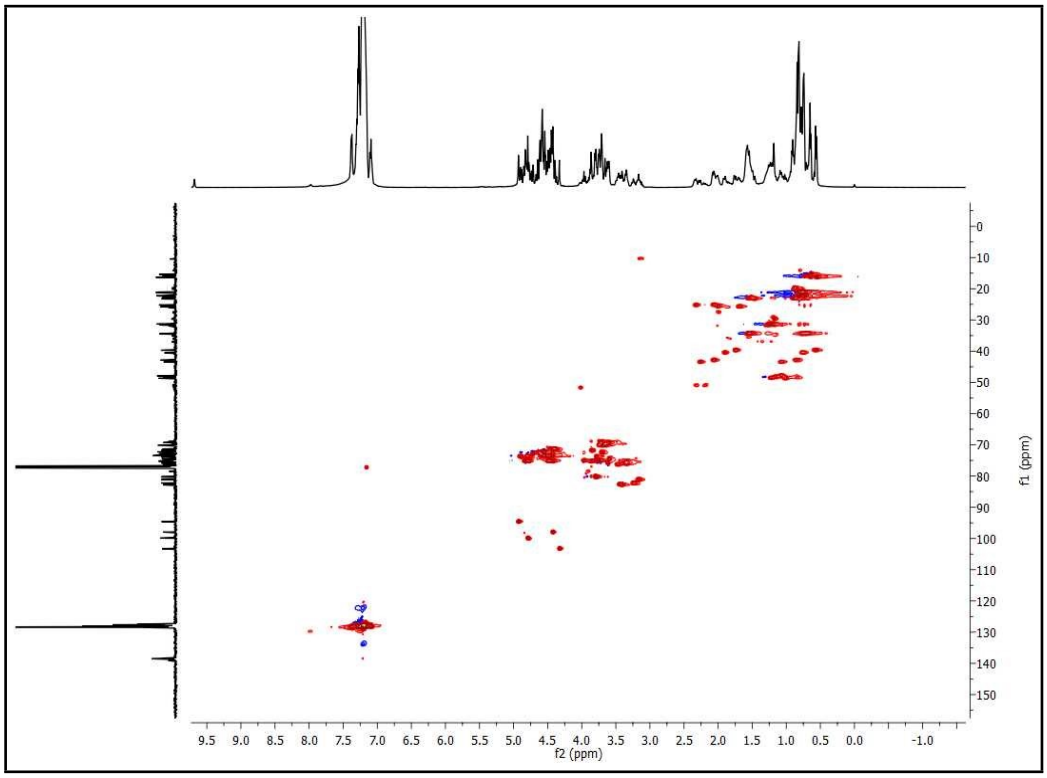
HMQC of diastereomeric mixture of (α, 1*S*)-**11** and (α, 1*R*)-**11** catalysed by (*S*)-**2**



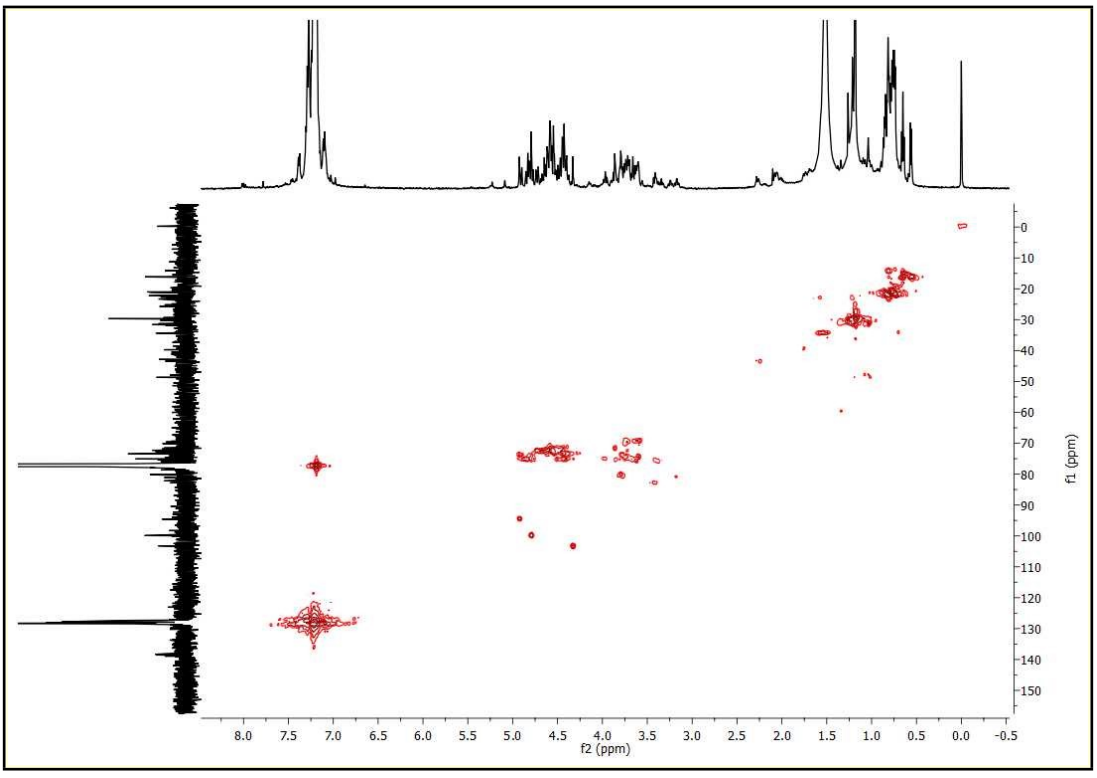
HSQC of diastereomeric mixture of (α, 1*S*)-**11** and (α, 1*R*)-**11** catalysed by (*R*)-**2**



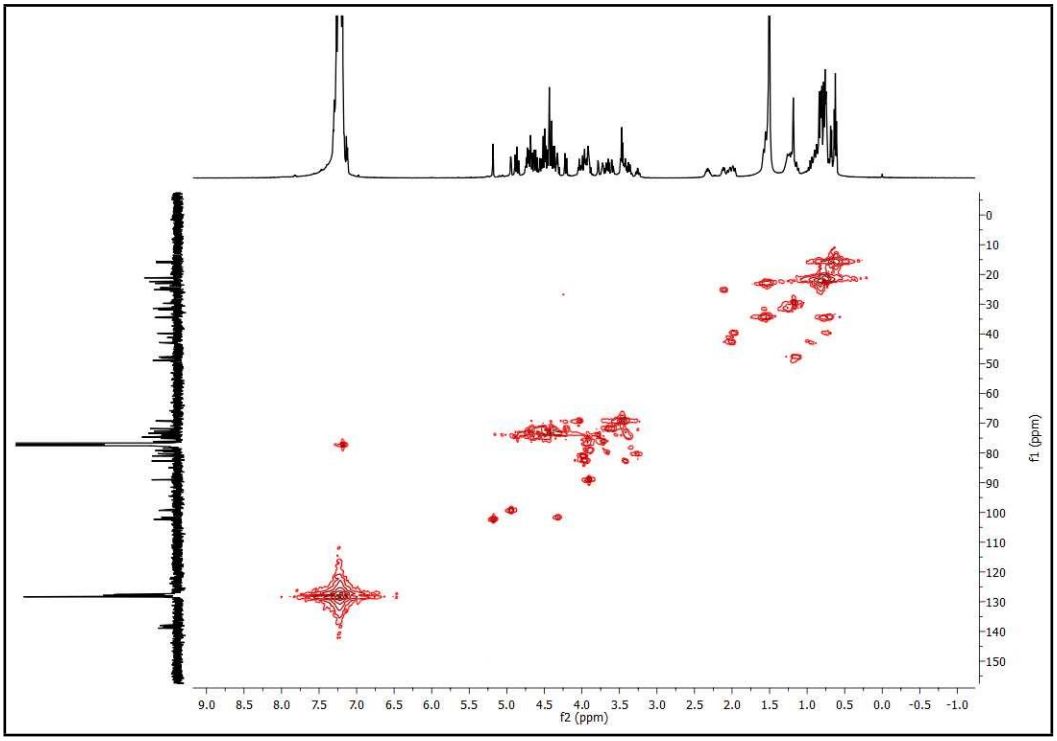
HSQC of stereoisomeric mixture of **11** catalysed by $Sc(OTf)_3$



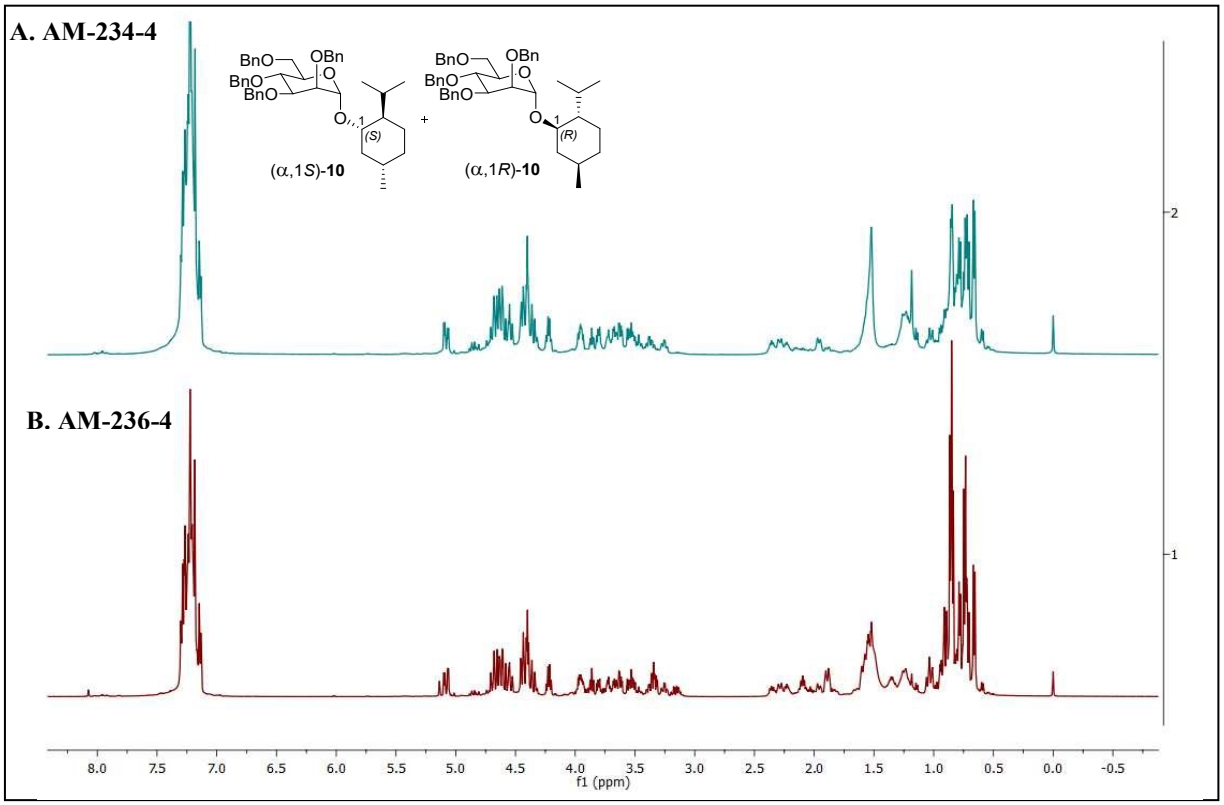
HSQC of stereoisomeric mixture of **11** catalysed by PCCP



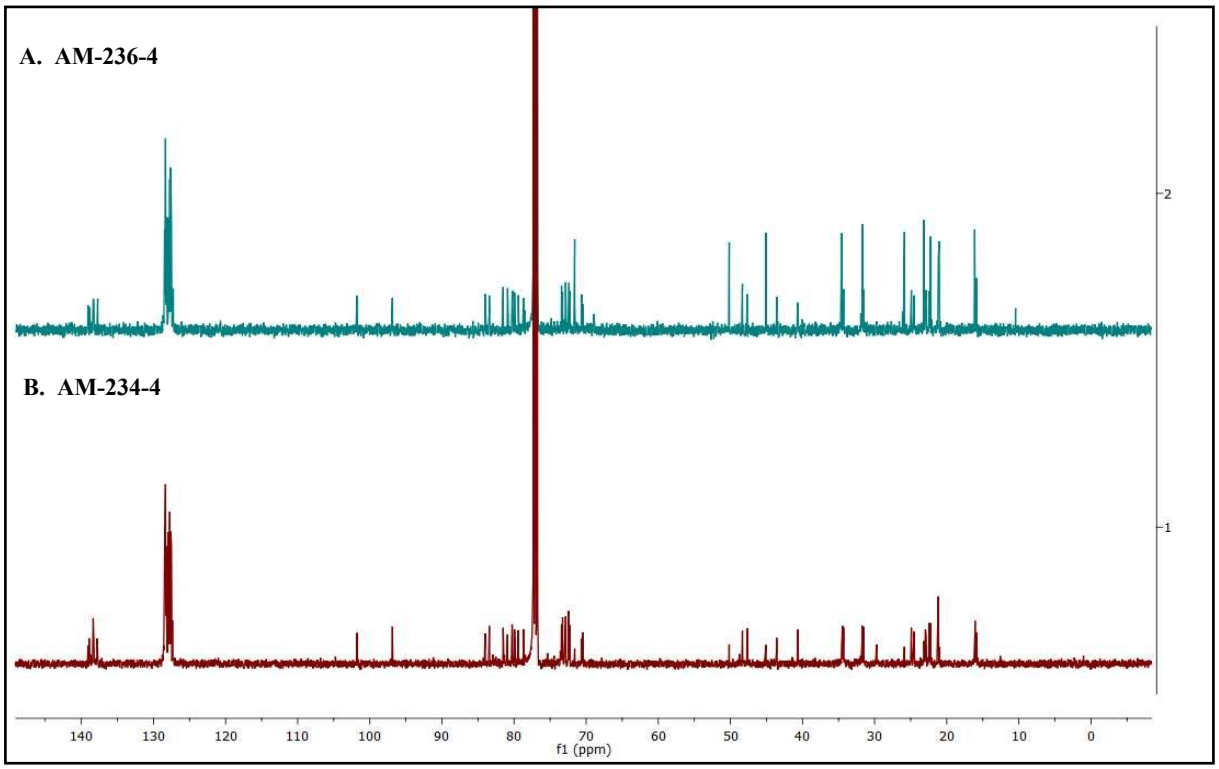
HSQC of stereoisomeric mixture of **11** catalysed by CF_3SO_3H



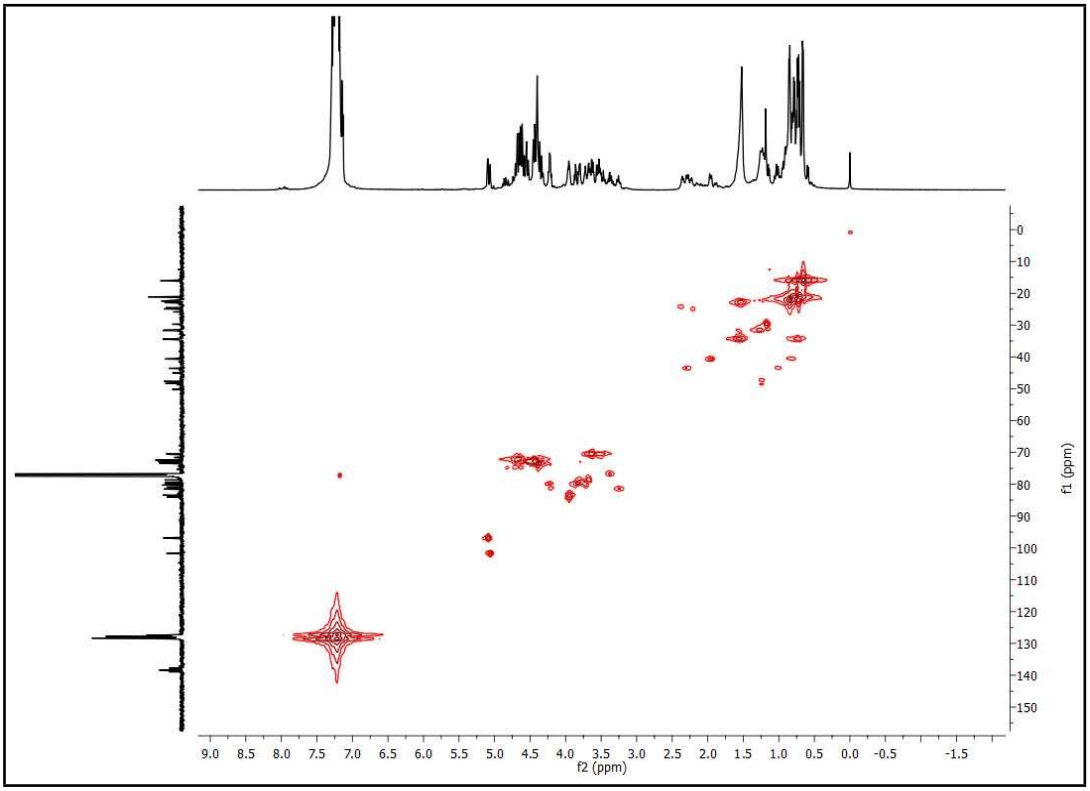
^{1}H NMR (500 MHz, $CDCl_3$) of diastereomeric mixture of (α, 1*S*)-**10** and (α, 1*R*)-**10** catalysed by **(A)** CBA **3** **(B)** CBA **4**



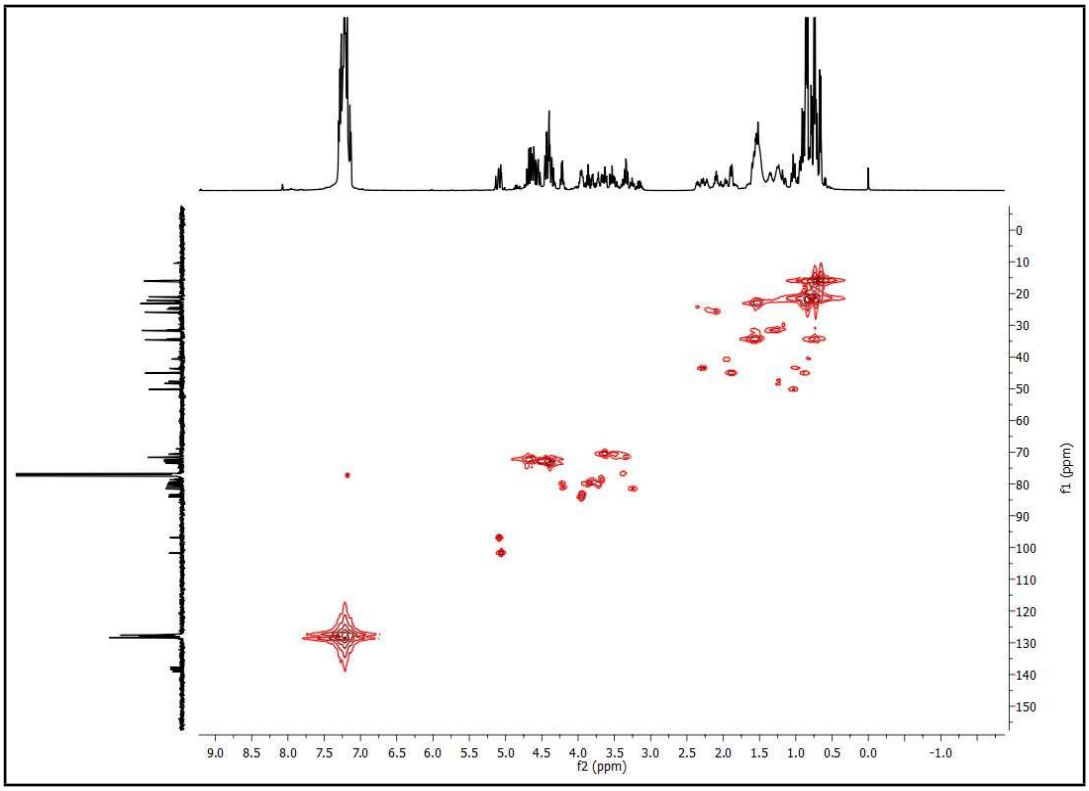
^{13}C NMR (125 MHz, $CDCl_3$) of diastereomeric mixture of (α, 1*S*)-**10** and (α, 1*R*)-**10** catalysed by **(A)** CBA **4** **(B)** CBA **3**



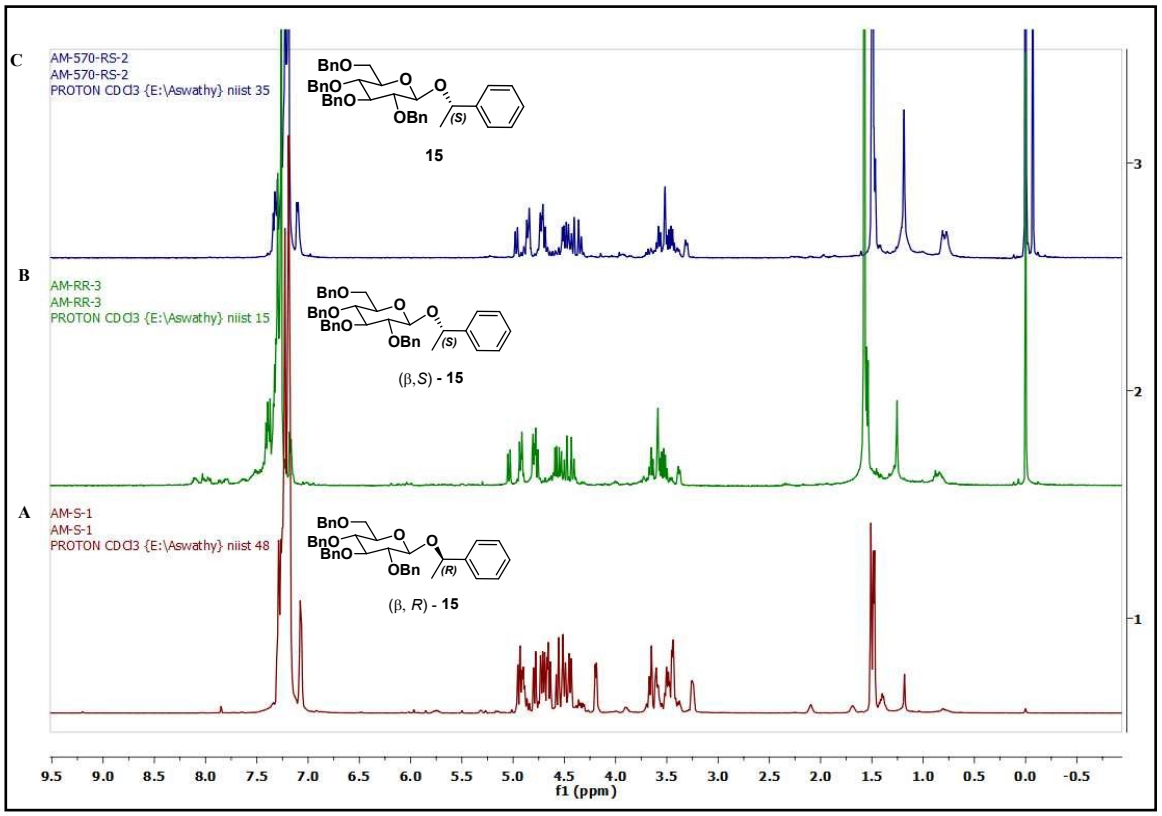
HMQC of diastereomeric mixture of (α, 1*S*)-**10** and (α**,** 1*R*)-**10** catalysed by CBA **3**



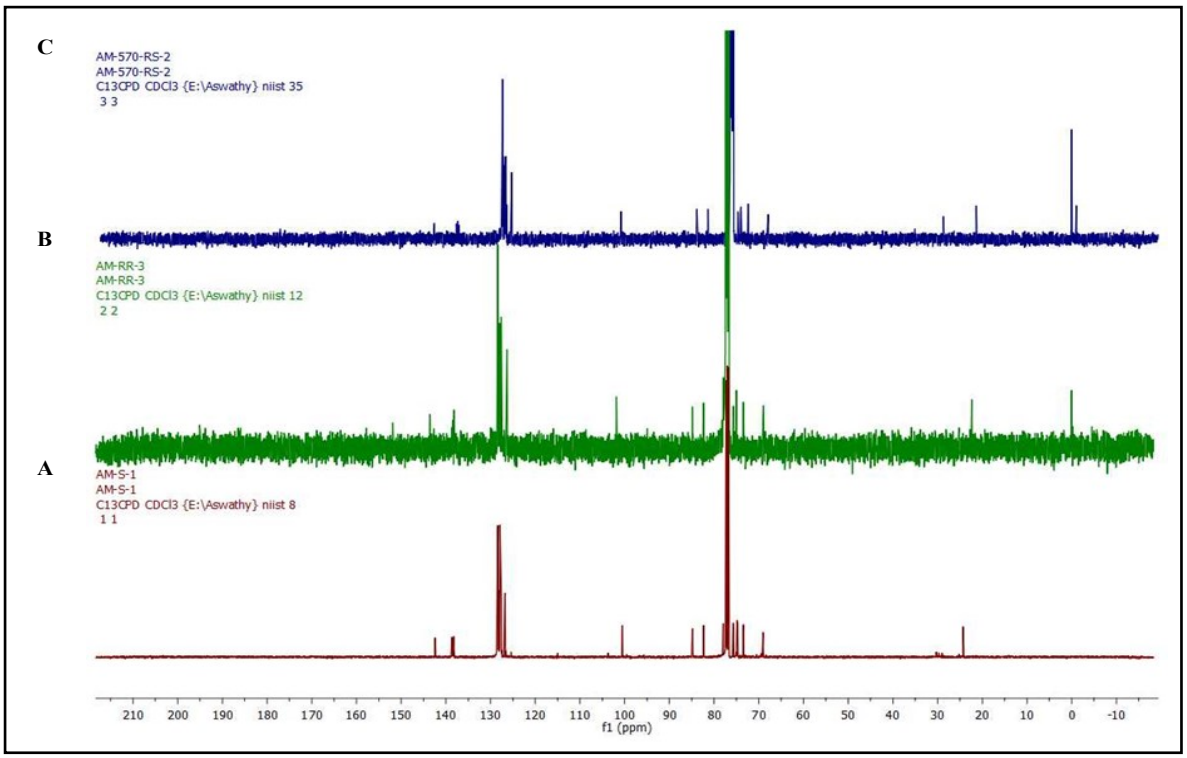
HMQC of diastereomeric mixture of (α, 1*S*)-**10** and (α**,** 1*R*)-**10** catalysed by CBA **4**



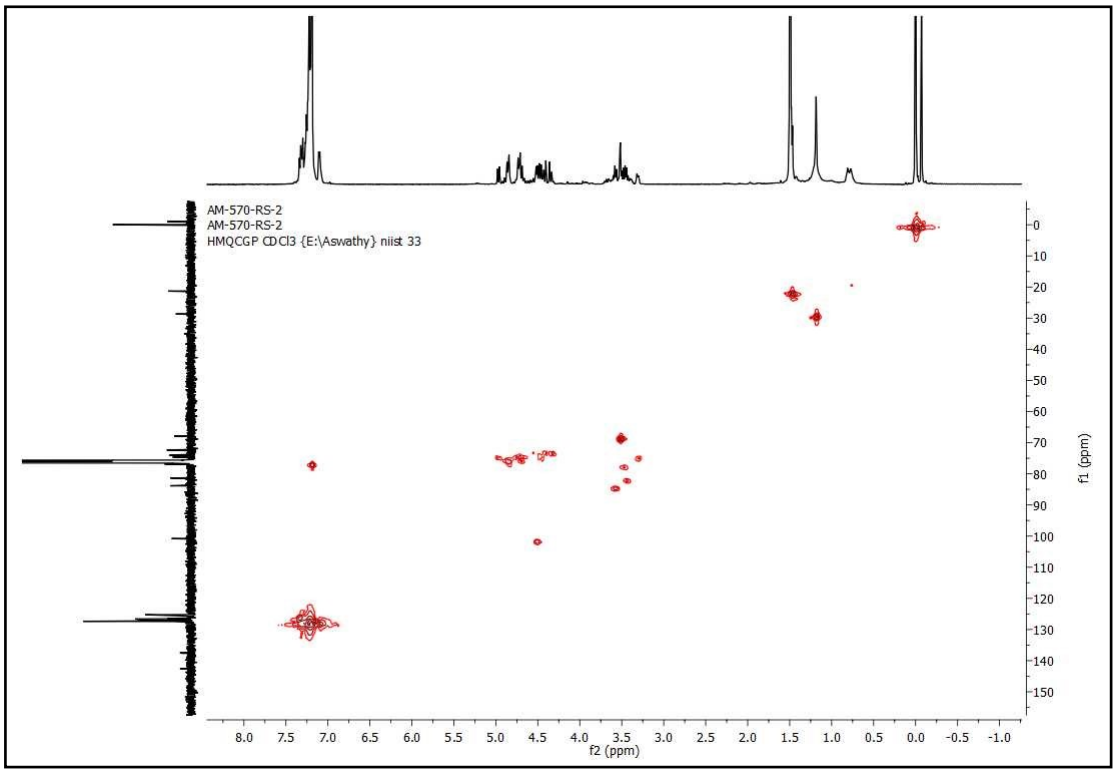
^{1}H NMR (500 MHz, $CDCl_3$) spectra of glycosides of **(A)** (β, *R*)-**15** **(B)** (β, *S*)-**15** **(C)** Compound **15**



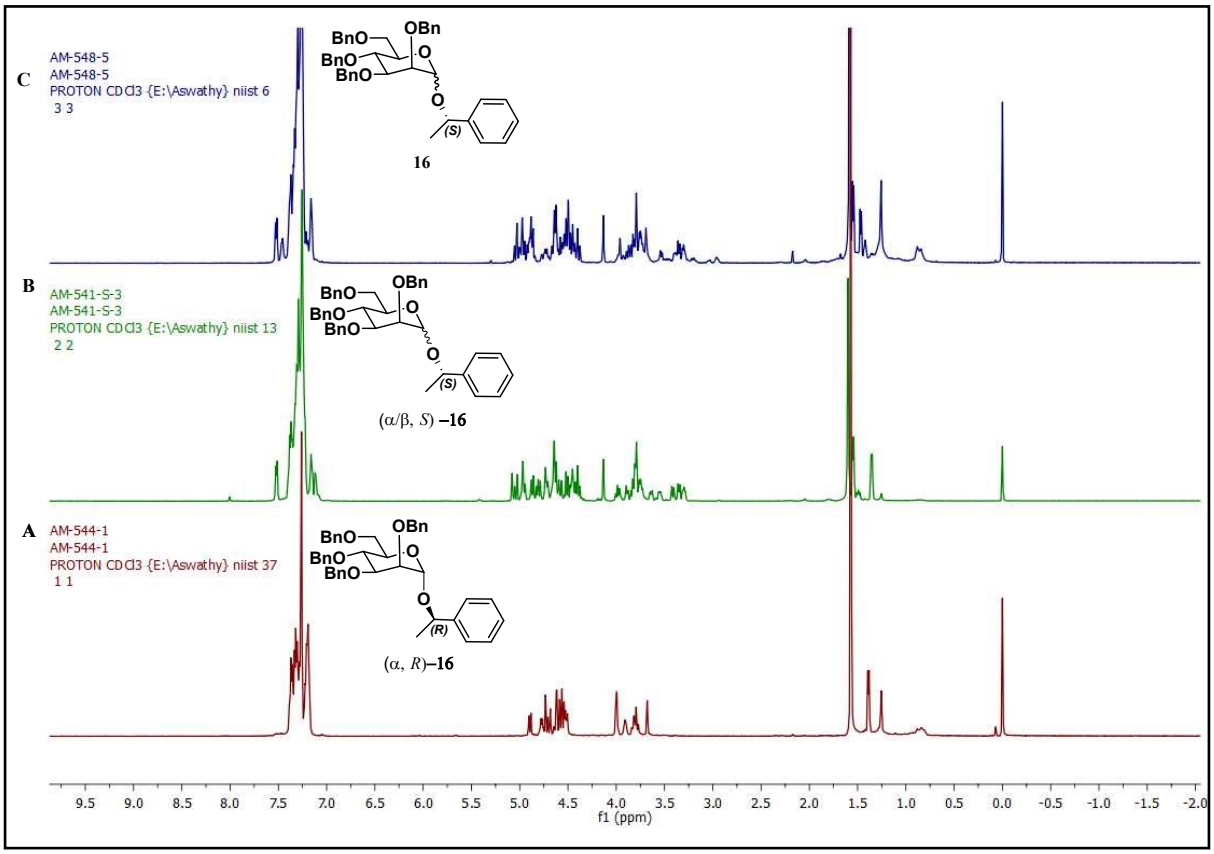
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (β, *R*)-**15** **(B)** (β, *S*)-**15** **(C)** Compound **15**



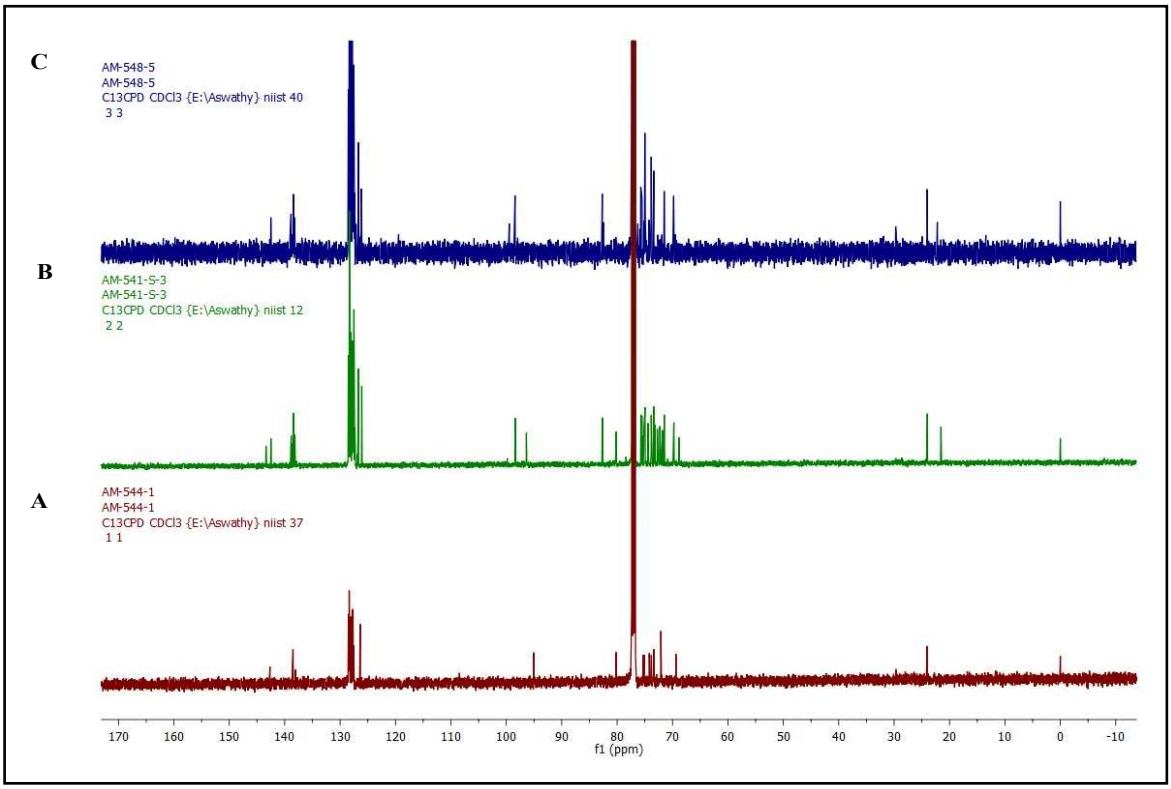
HMQC Spectra of compound **15**



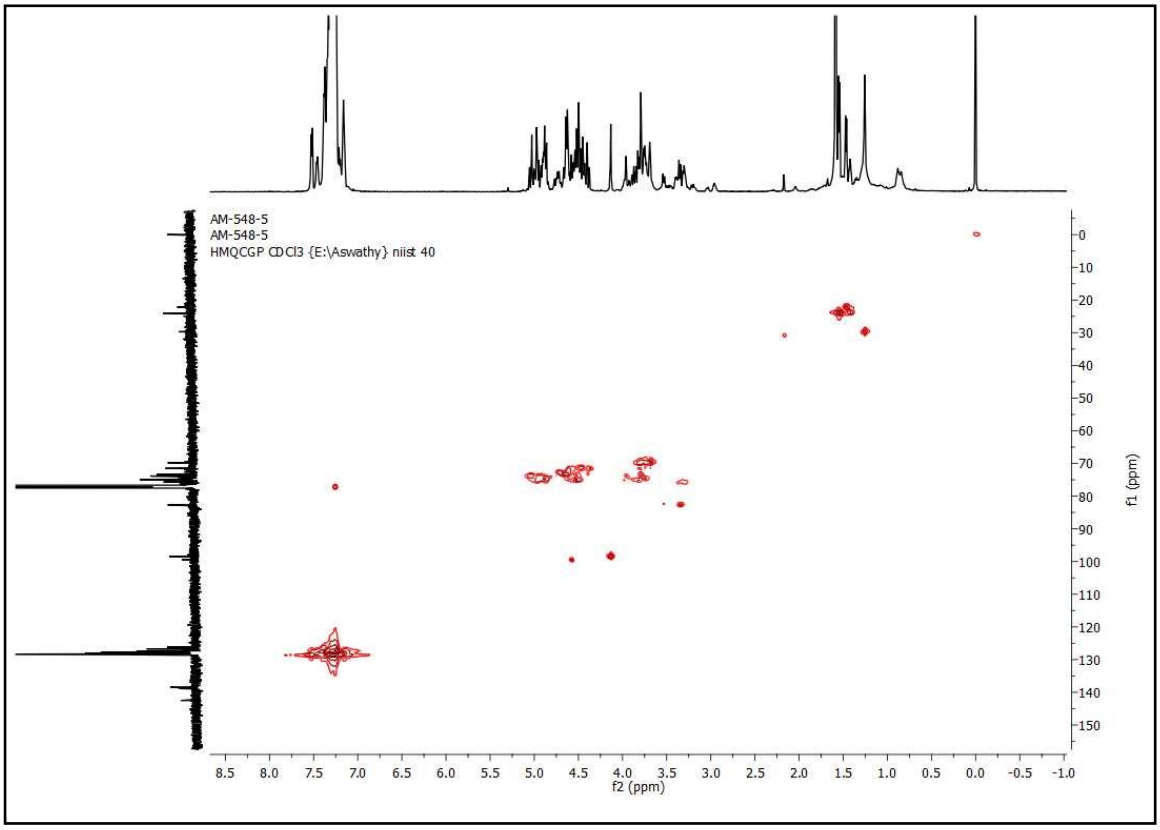
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**16 (B)** (α/β, *S*)-**16 (C)** Compound **16**



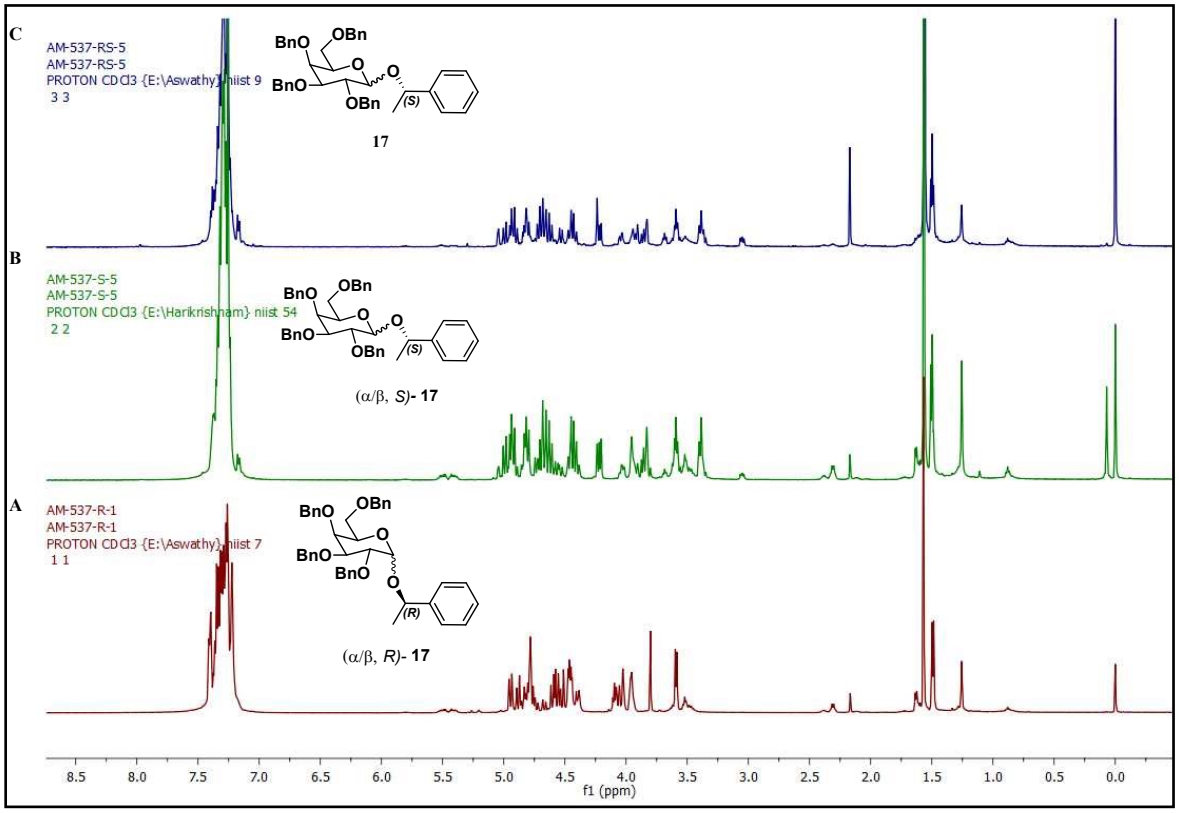
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**16 (B)** (α/β, *S*)-**16 (C)** Compound **16**



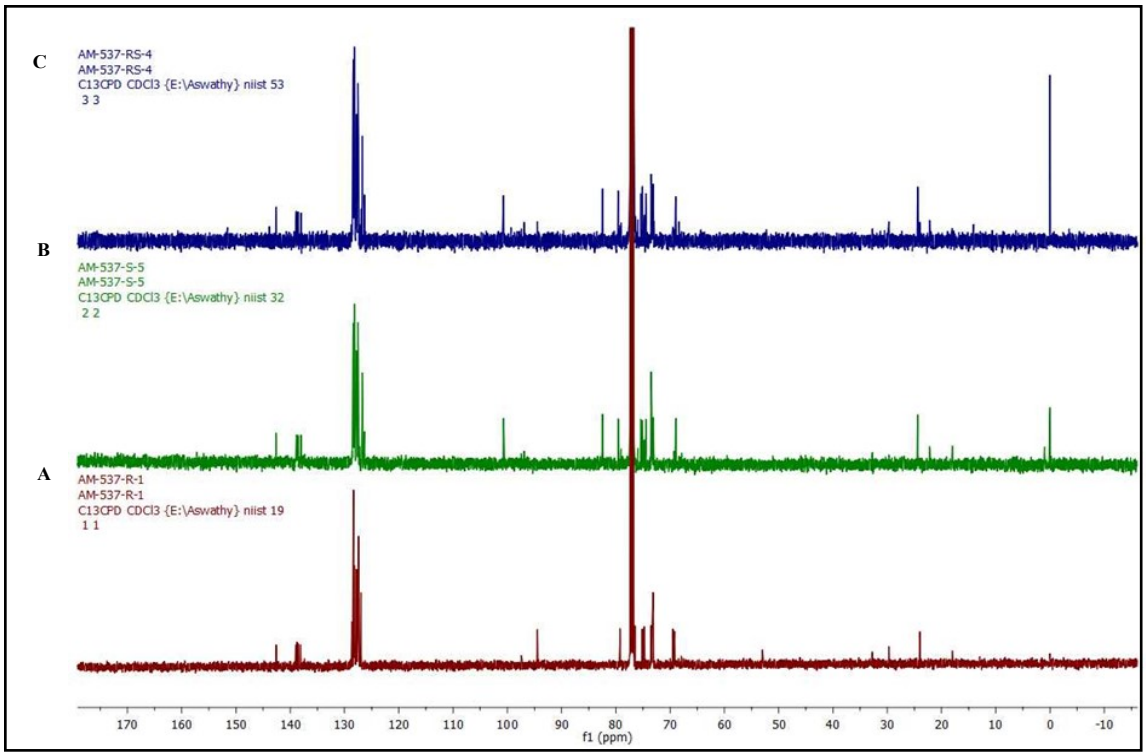
HMQC spectra of compound **16**



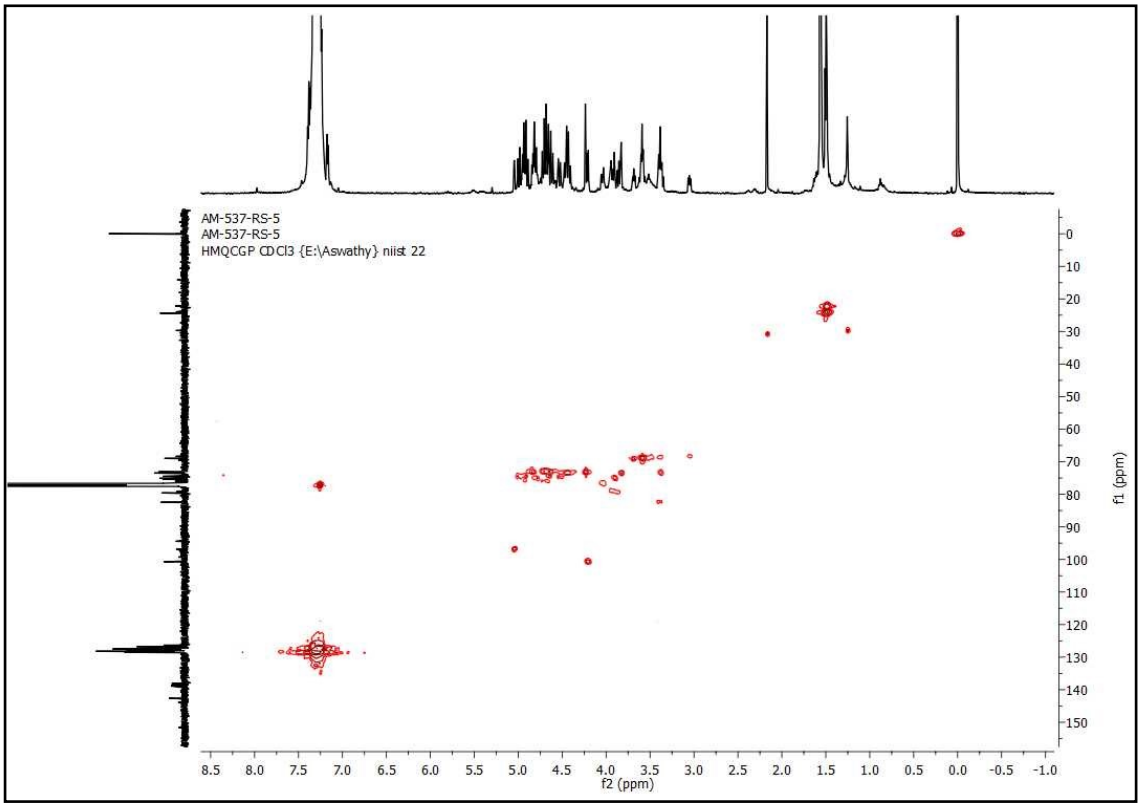
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**17 (B)** (α/β, *S*)-**17 (C)** Compound **17**



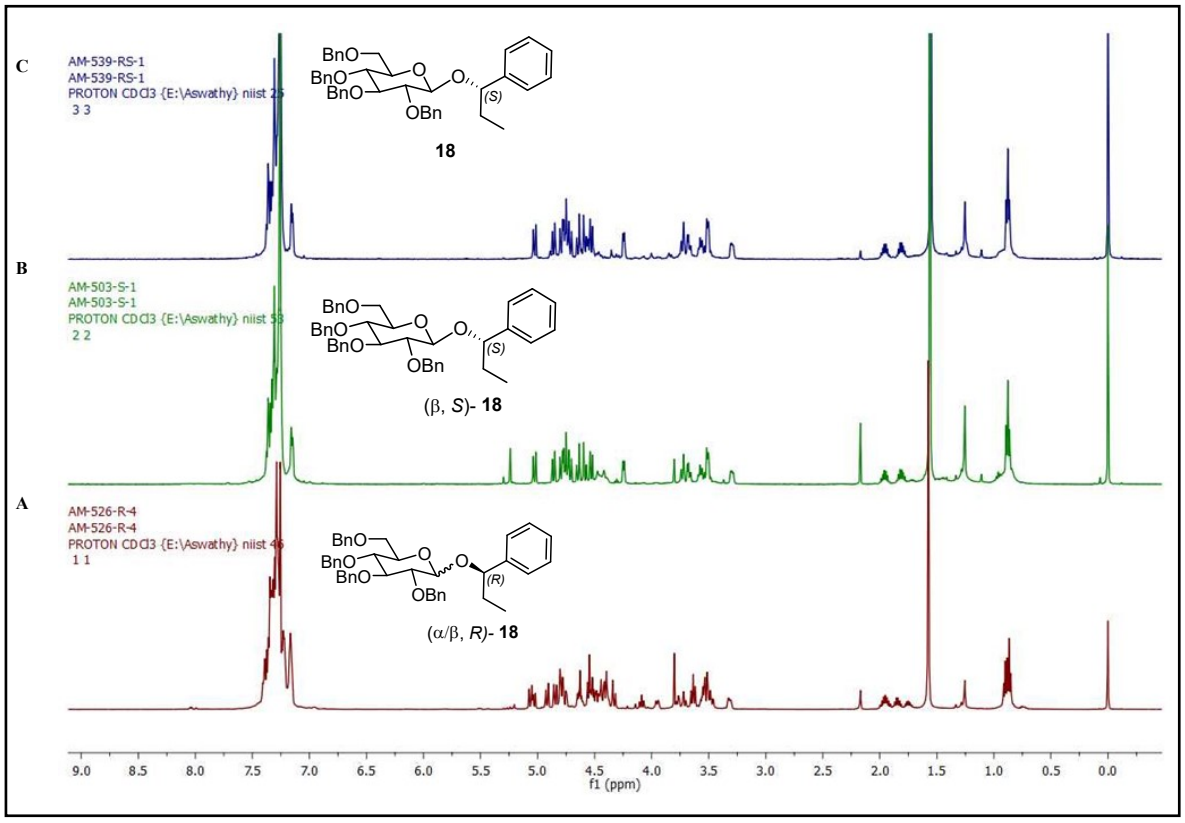
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**17 (B)** (α/β, *S*)-**17 (C)** Compound **17**



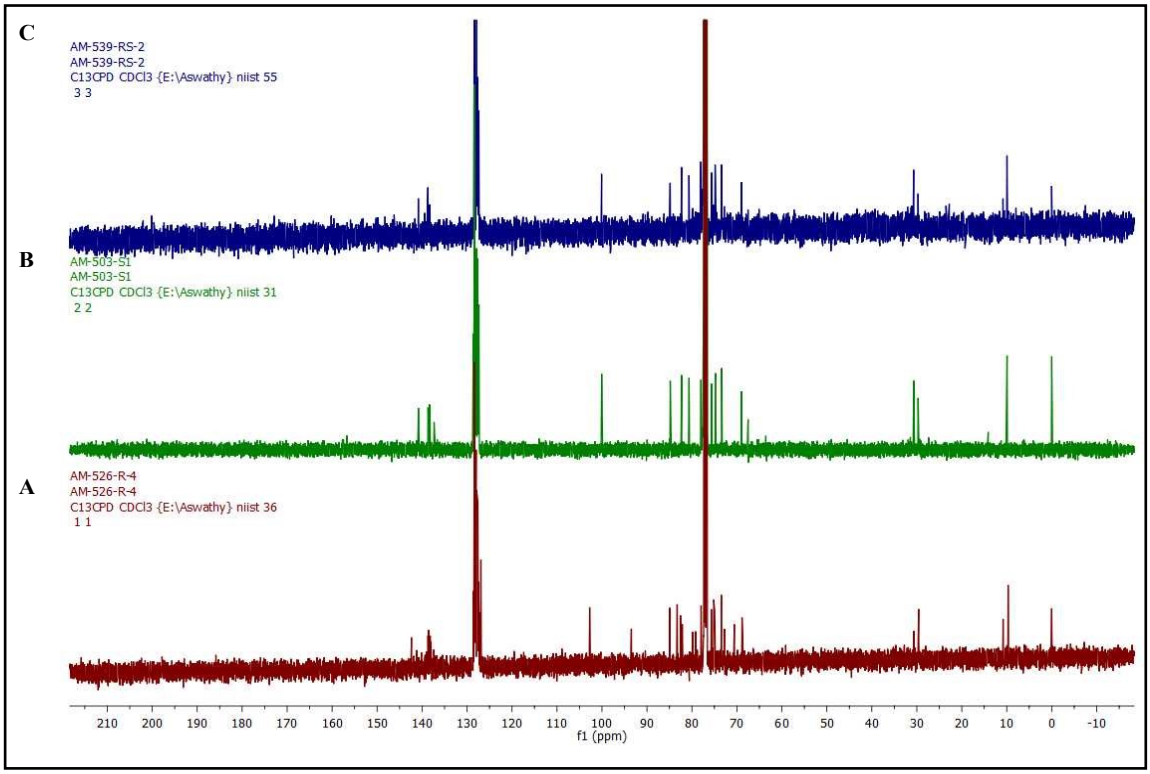
HMQC spectra of compound **17**



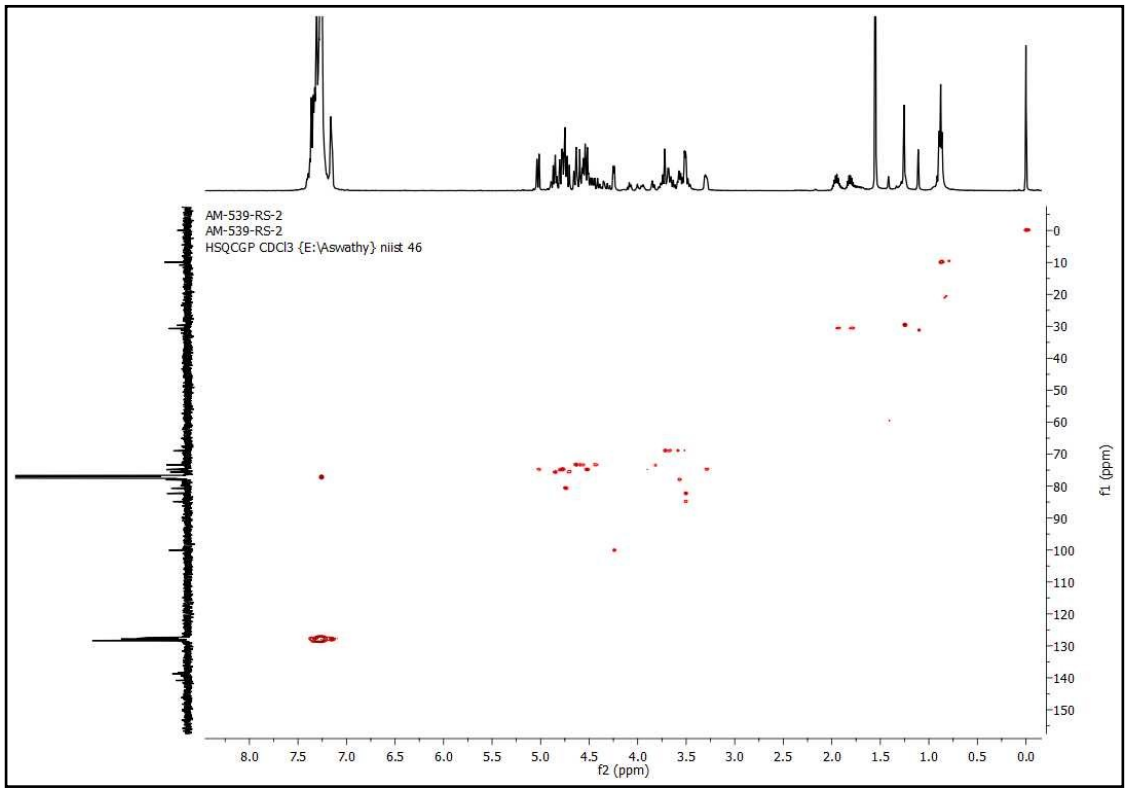
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**18 (B)** (β, *S*)-**18 (C)** Compound **18**



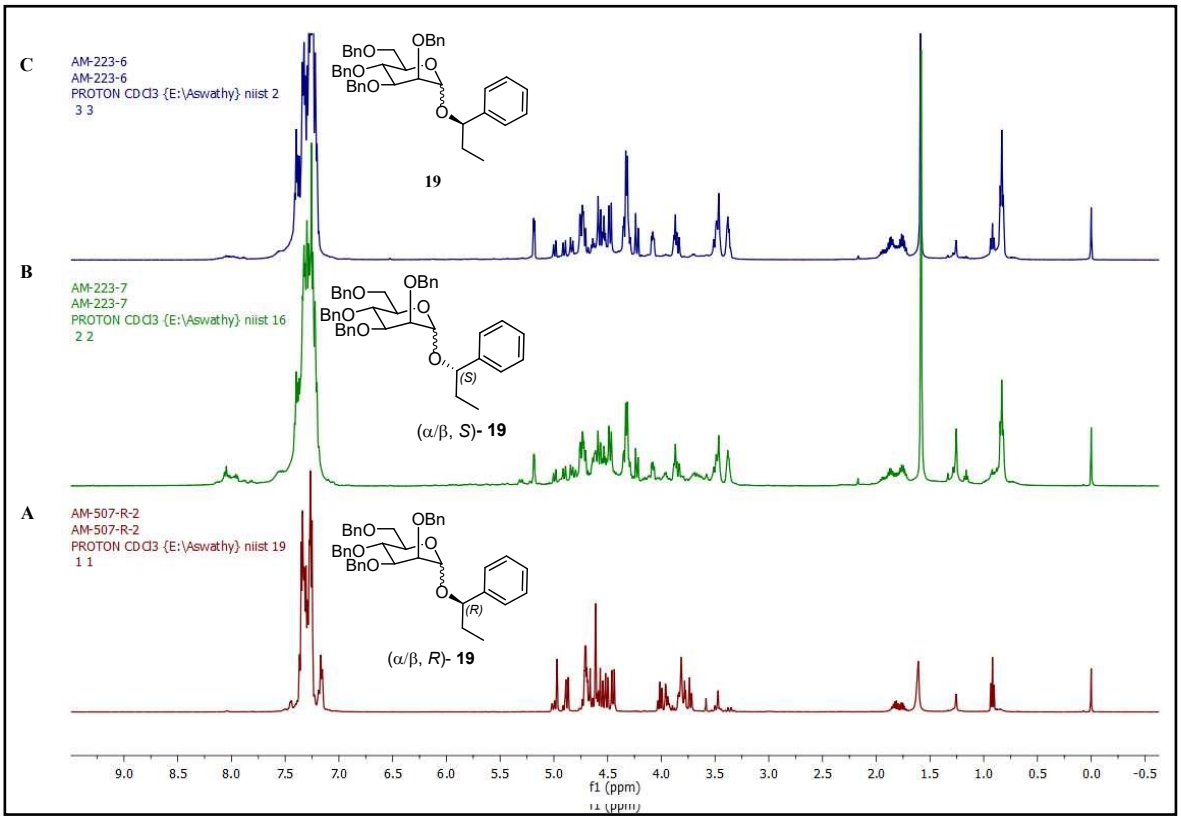
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**18 (B)** (β, *S*)-**18 (C)** Compound **18**



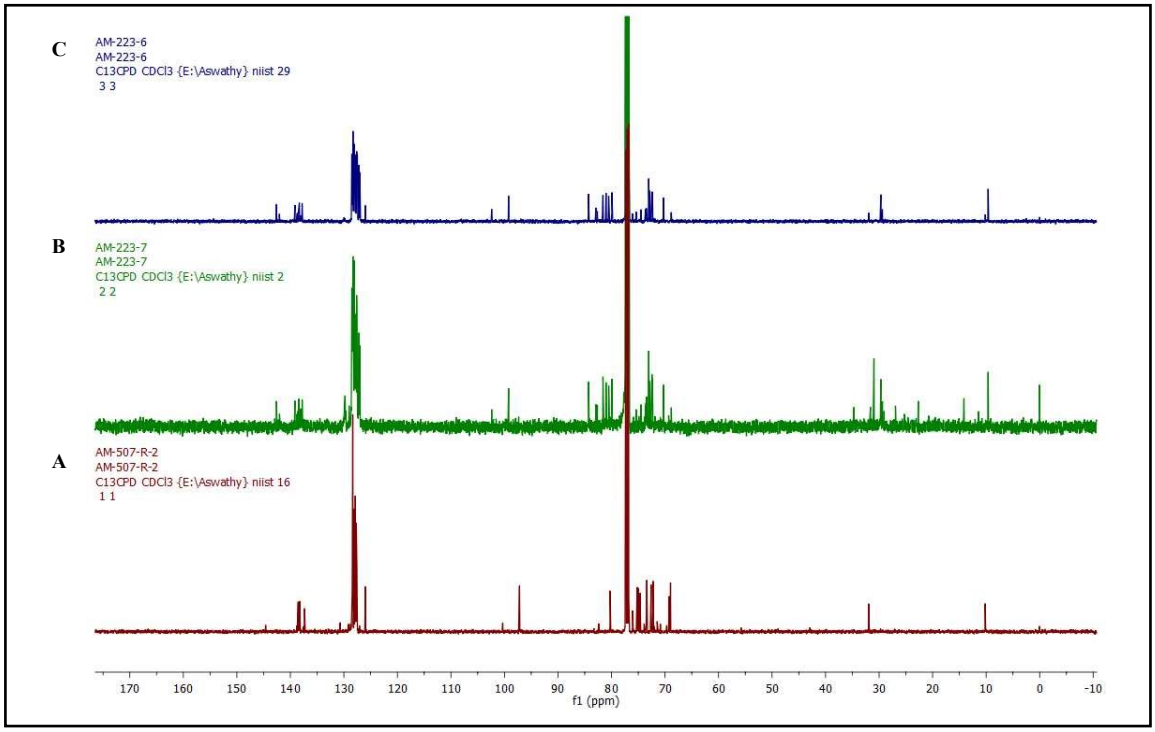
HSQC spectra of compound **18**



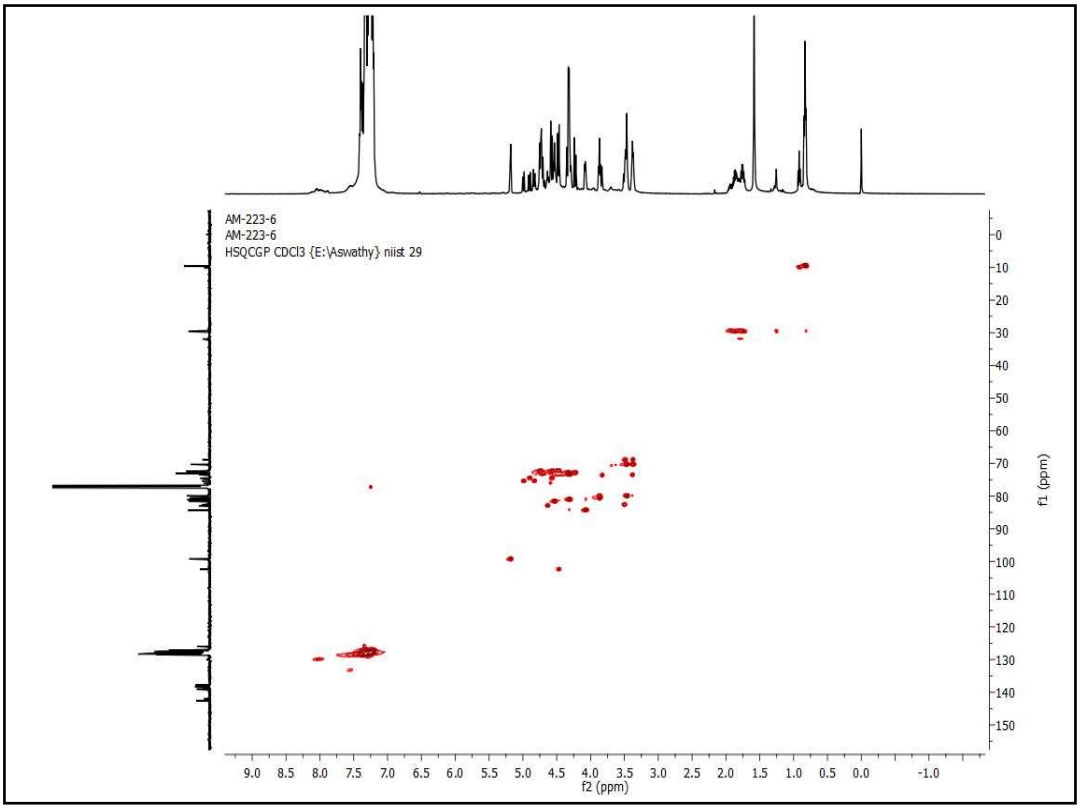
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**19 (B)** (α/β, *S*)-**19 (C)** Compound **19**



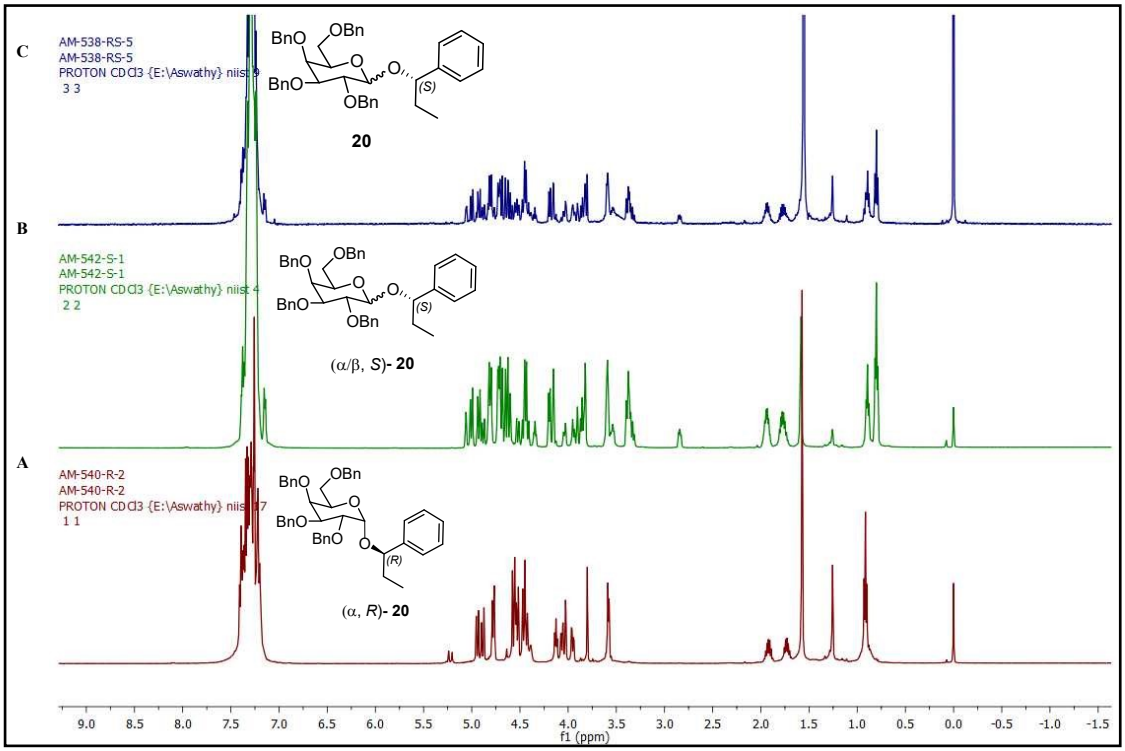
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**19 (B)** (α/β, *S*)-**19 (C)** Compound **19**



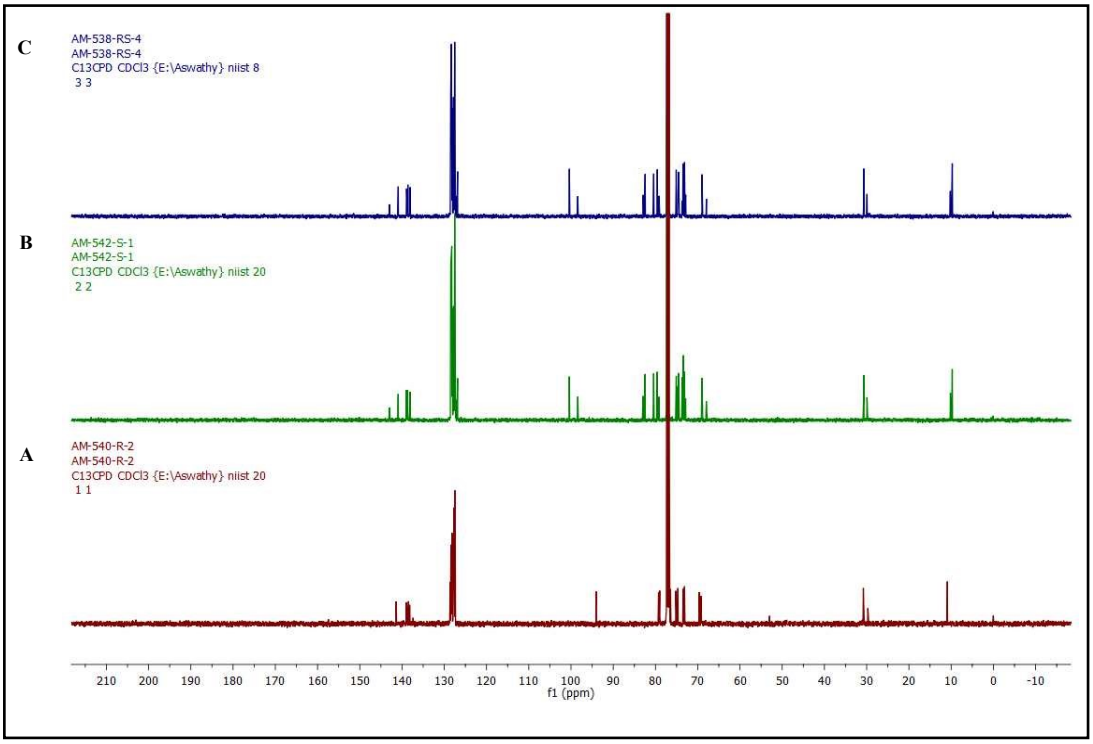
HSQC spectra compound **19**



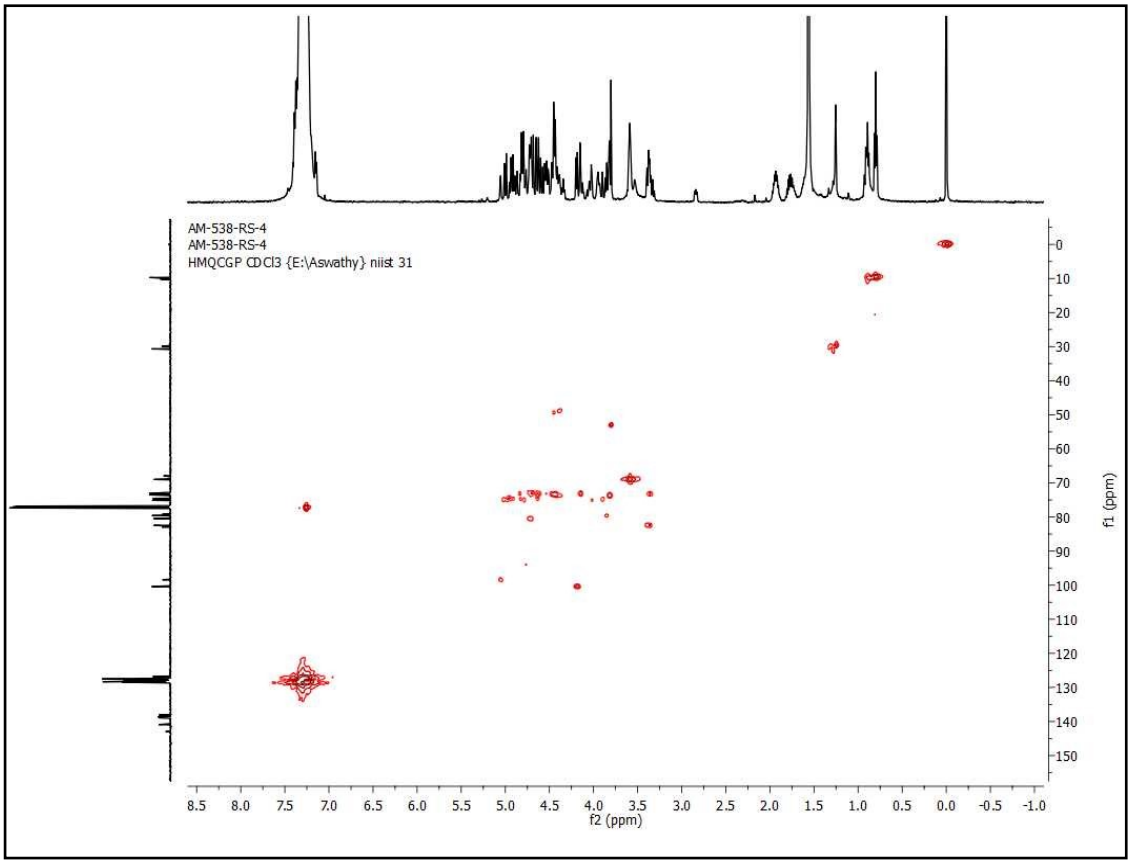
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**20 (B)** (α/β, *S*)-**20 (C)** Compound **20**



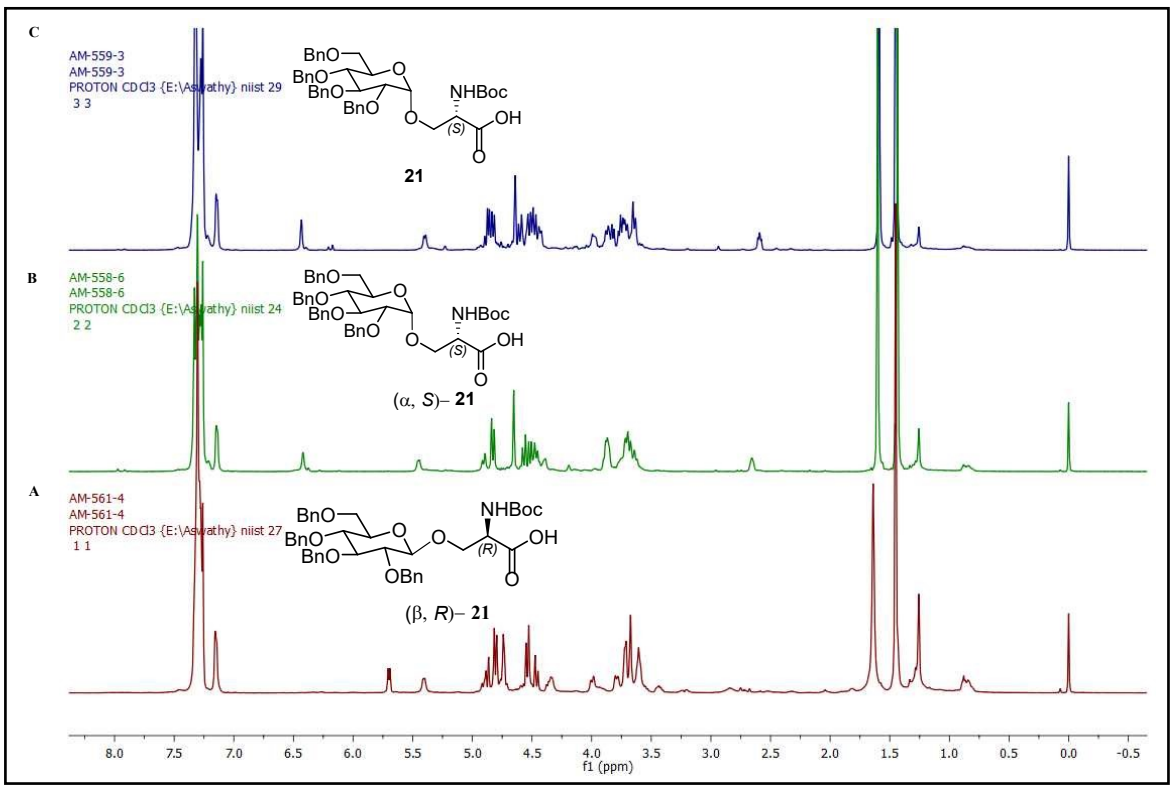
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**20 (B)** (α/β, *S*)-**20 (C)** Compound **20**



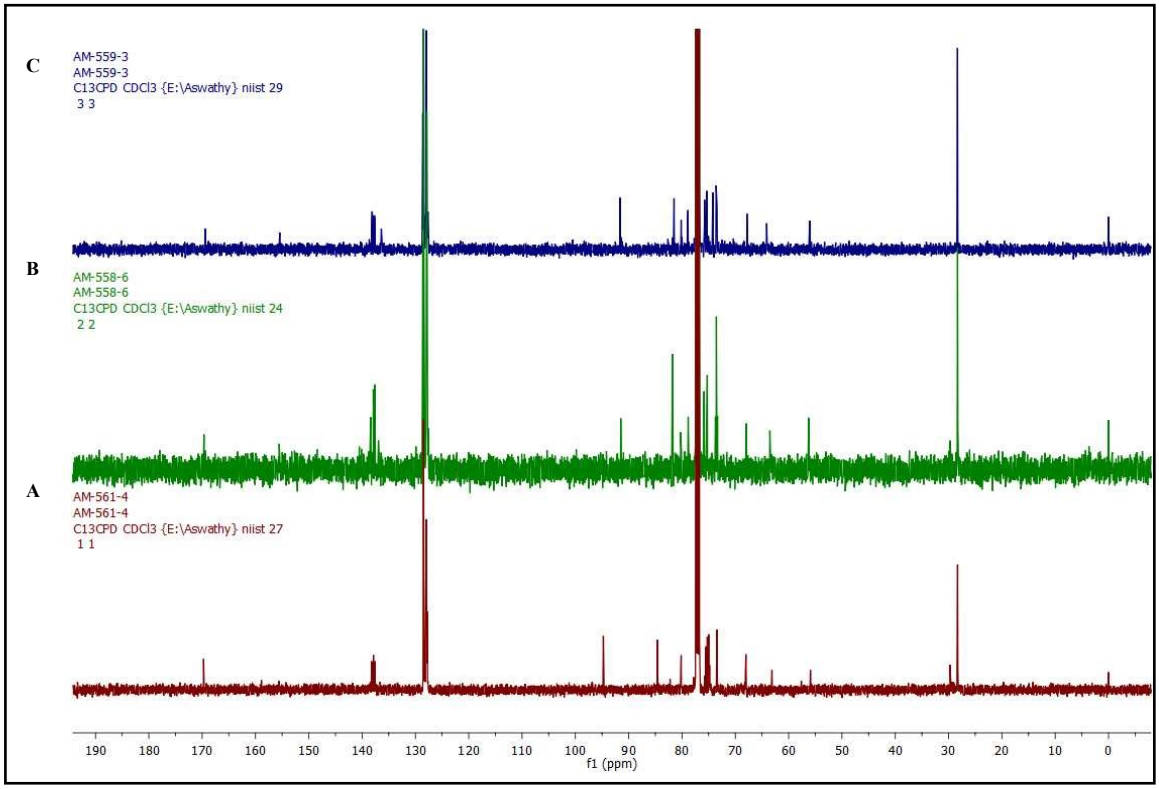
HMQC spectra of compound **20**



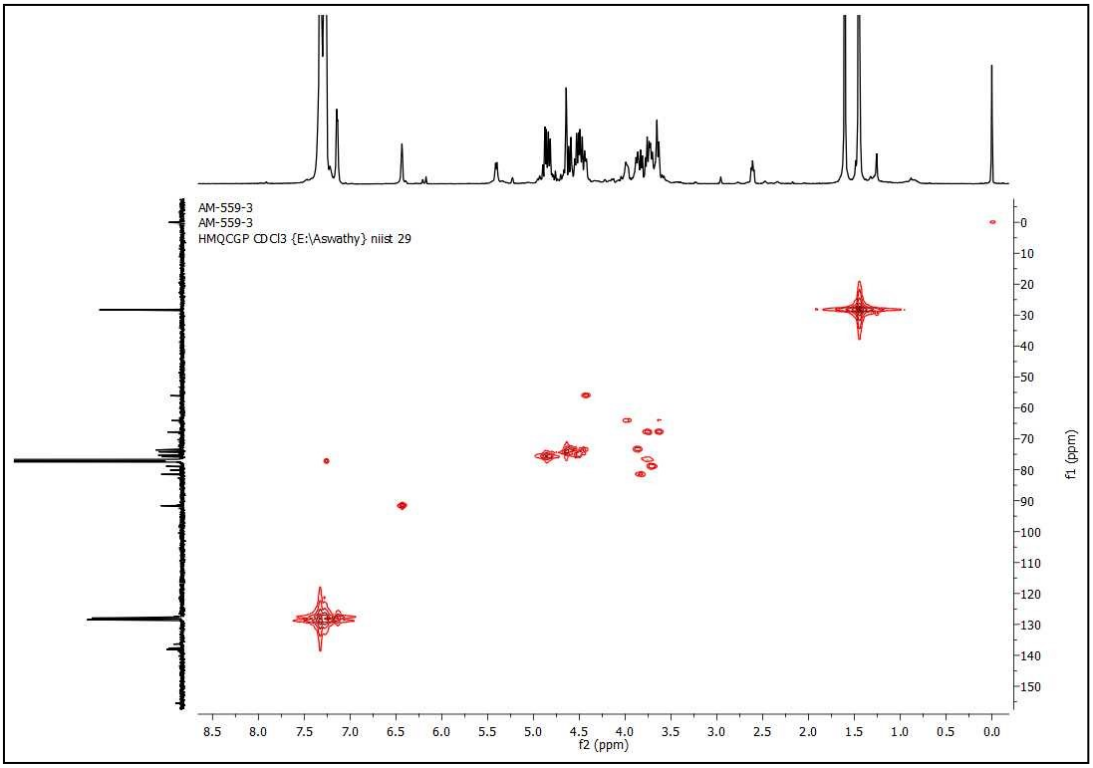
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (β, *R*)-**21 (B)** (α, *S*)-**21 (C)** Compound **21**



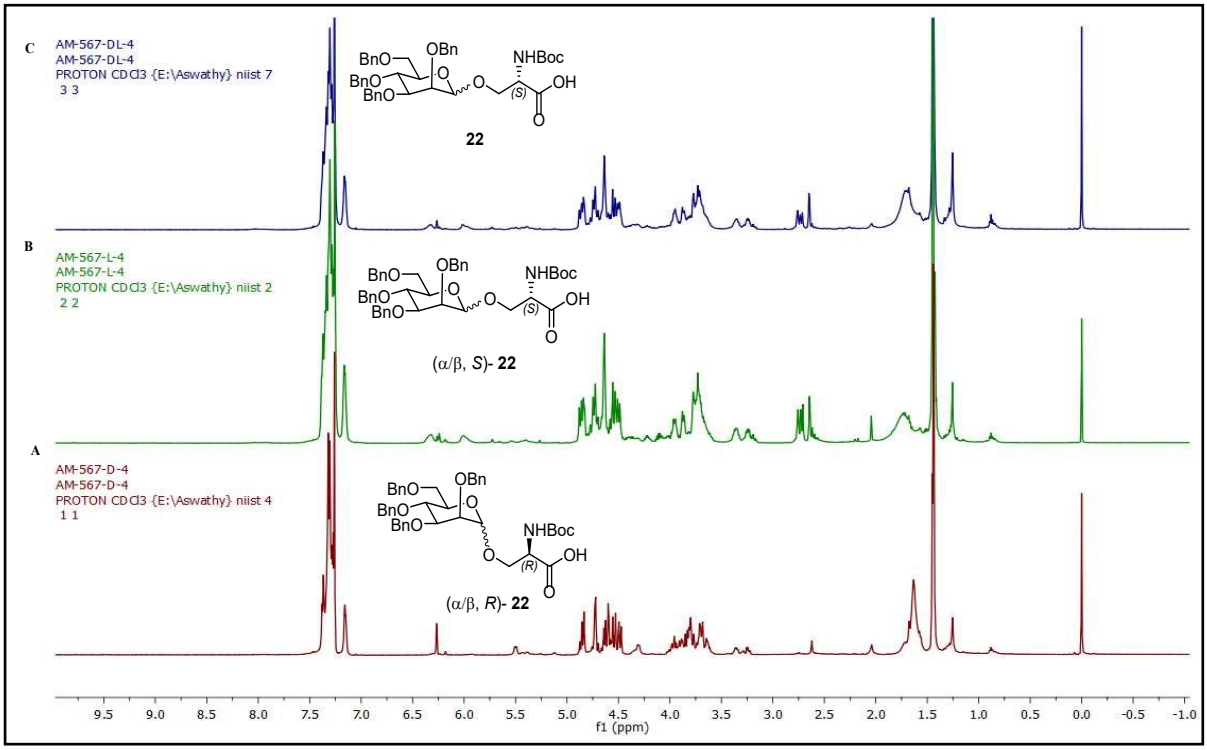
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**21 (B)** (α, *S*)-**21 (C)** Compound **21**



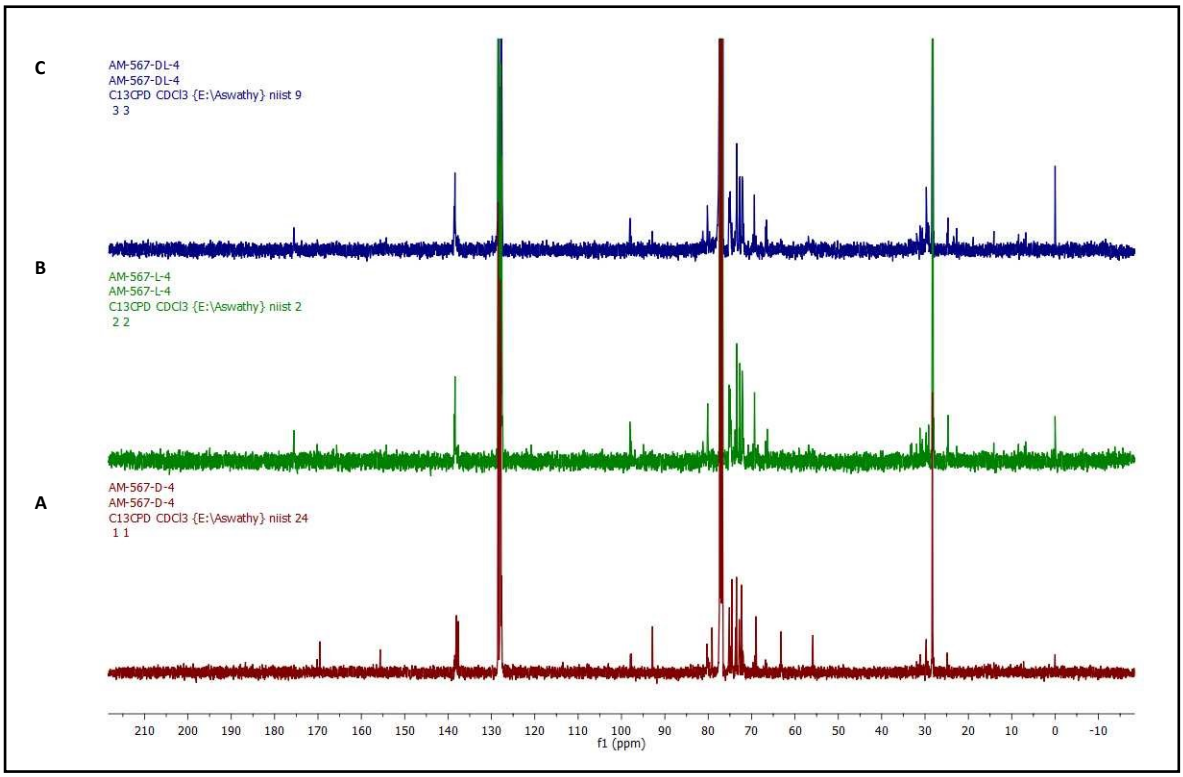
HMQC spectra of compound **21**



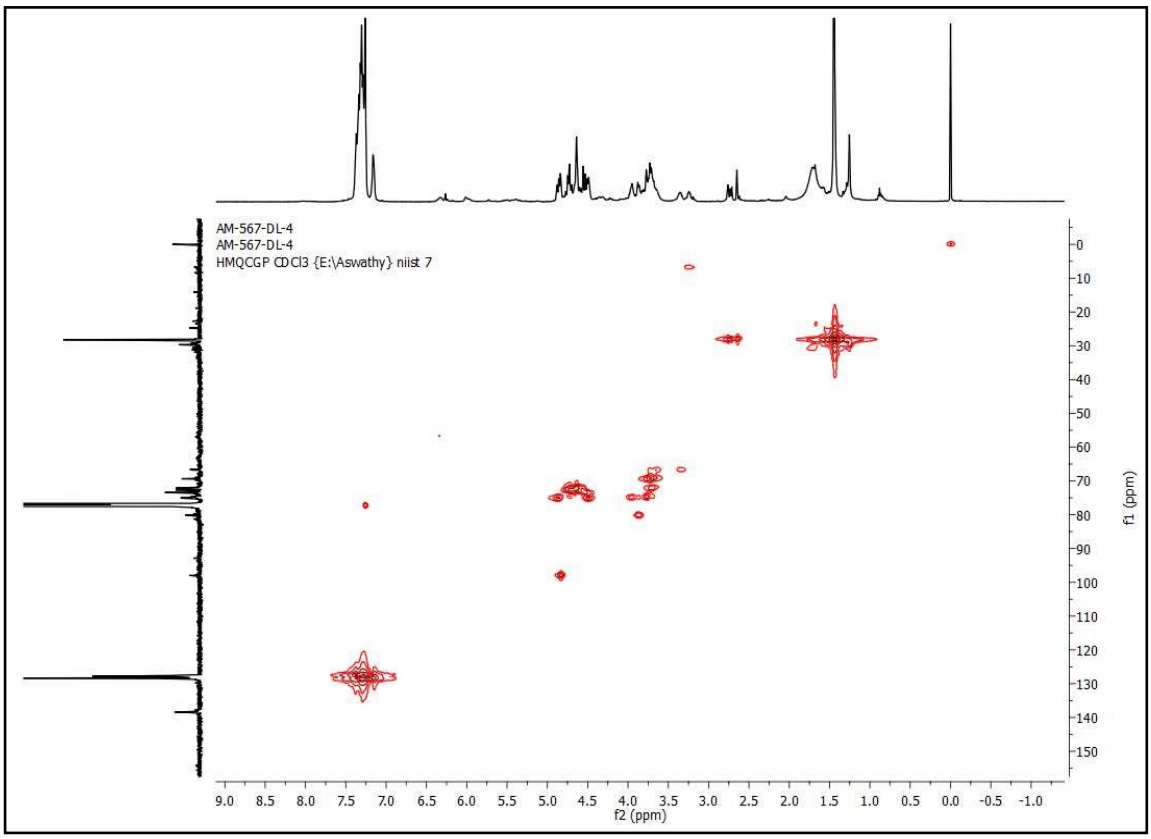
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**22 (B)** (α/β, *S*)-**22 (C)** Compound **22**



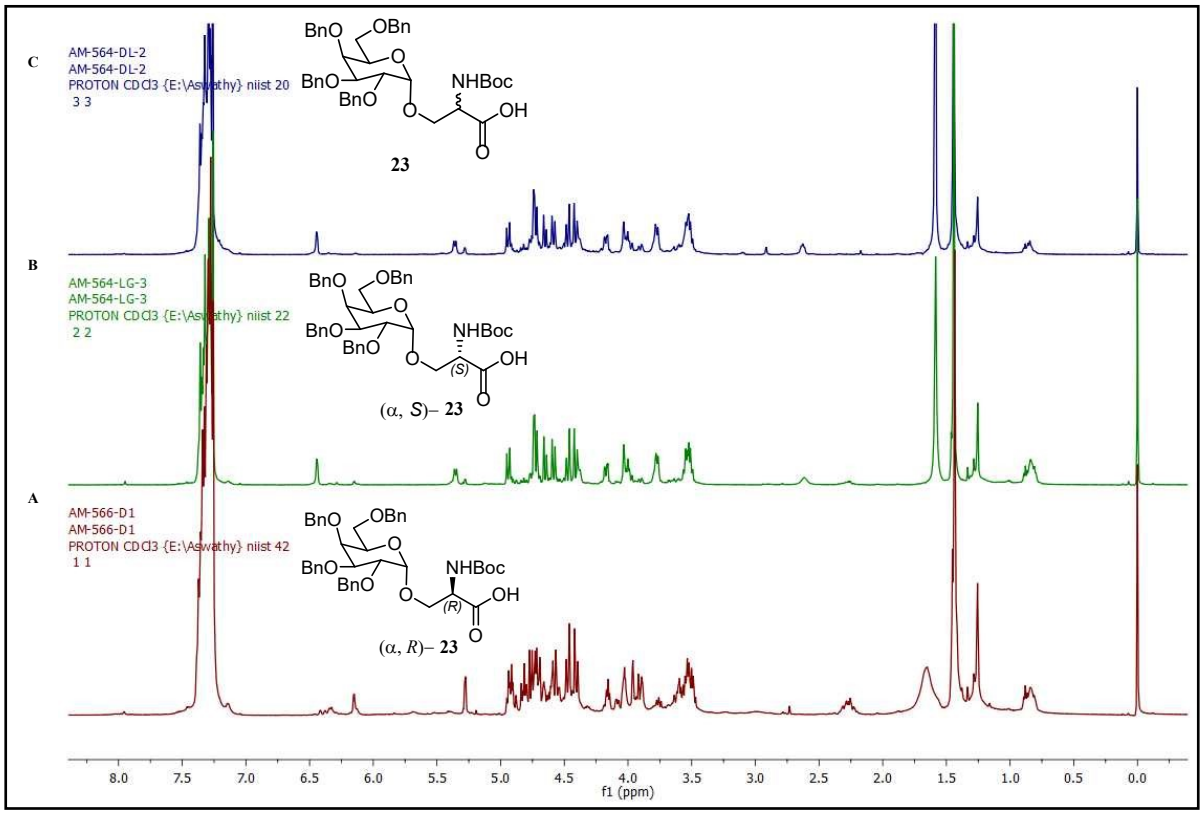
^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α/β, *R*)-**22 (B)** (α/β, *S*)-**22 (C)** Compound **22**



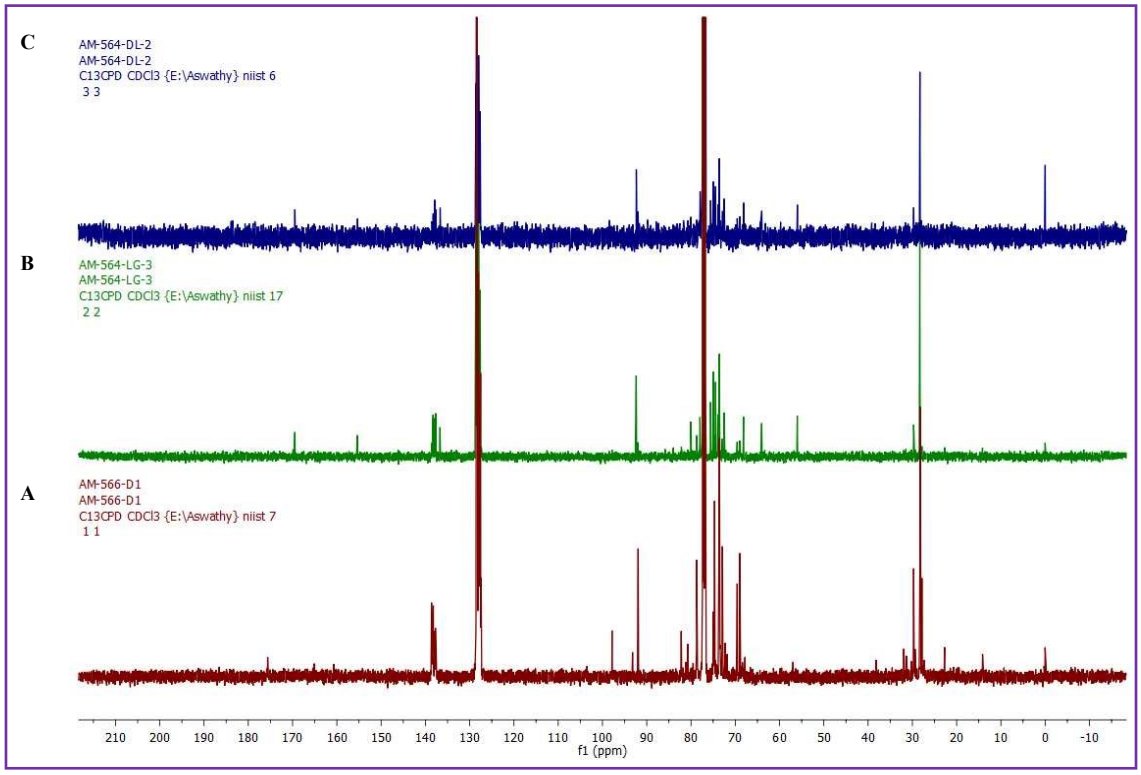
HMQC spectra of compound **22**



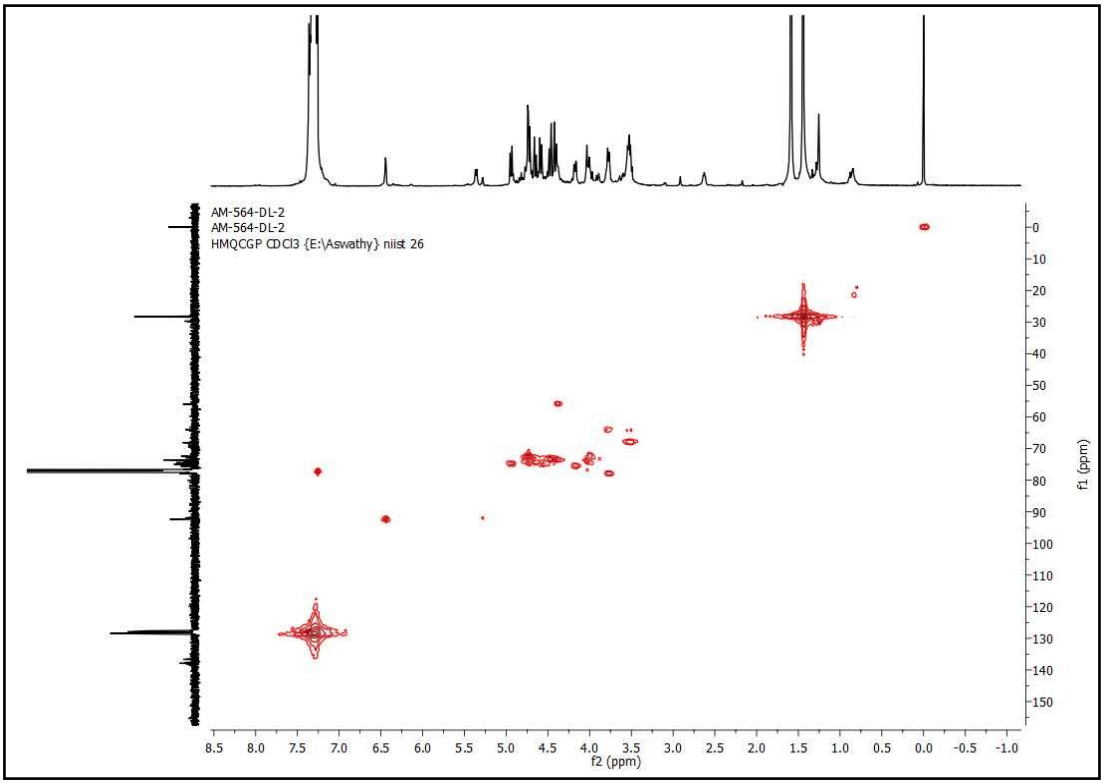
^{1}H NMR (500 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**23 (B)** (α, *S*)-**23 (C)** Compound **23**



^{13}C NMR (125 MHz, $CDCl_3$) of glycosides of **(A)** (α, *R*)-**23 (B)** (α, *S*)-**23 (C)** Compound **23**

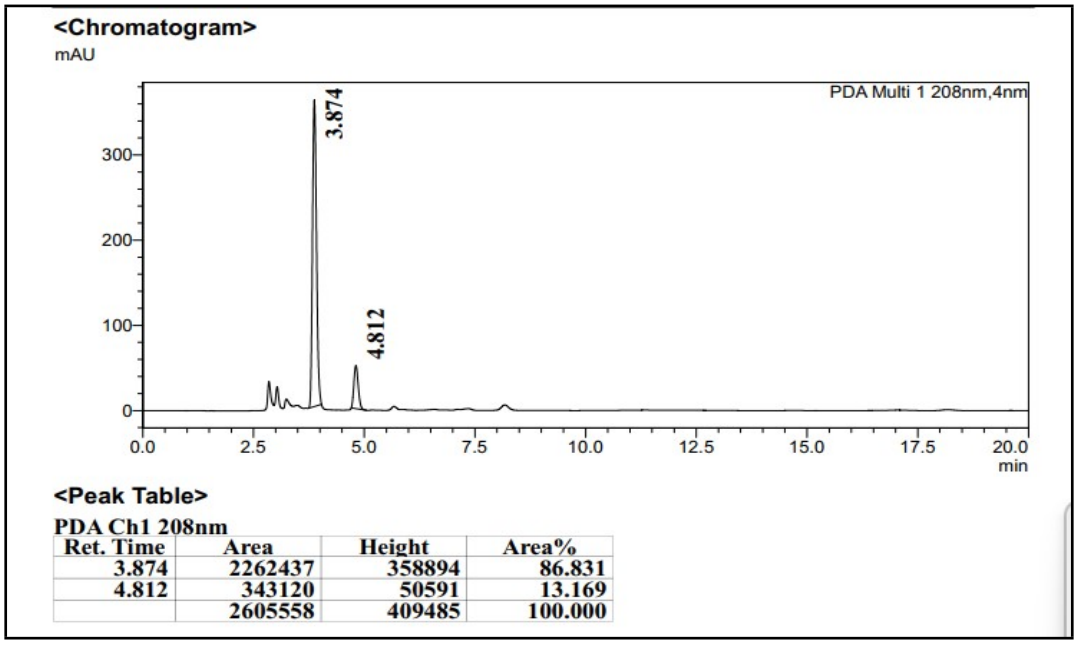


HMQC spectra of compound **23**


AM-564-DL-2
AM-564-DL-2
HMQCGP CDCl3 {E:\Aswathy} niist 26
f2 (ppm)
f1 (ppm)

6. HPLC Chromatograms

Diastereomeric mixture of (β, 1*S*)-**9** and (β, 1*R*)-**9**

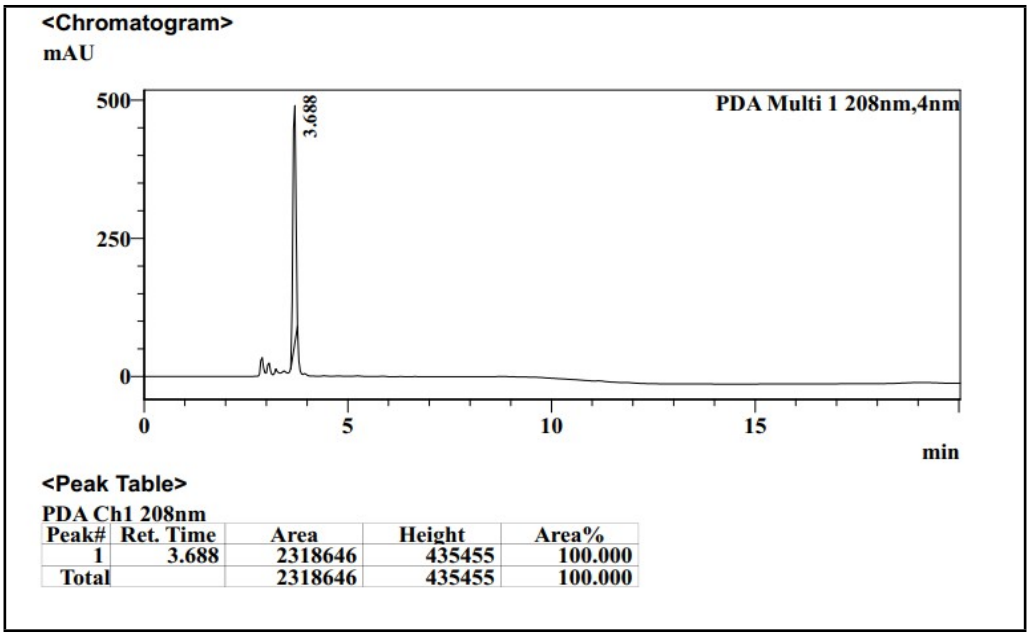


<Peak Table>

PDA Ch1 208nm

Ret. Time	Area	Height	Area%
3.874	2262437	358894	86.831
4.812	343120	50591	13.169
	2605558	409485	100.000

(β, 1*S*)-**9**

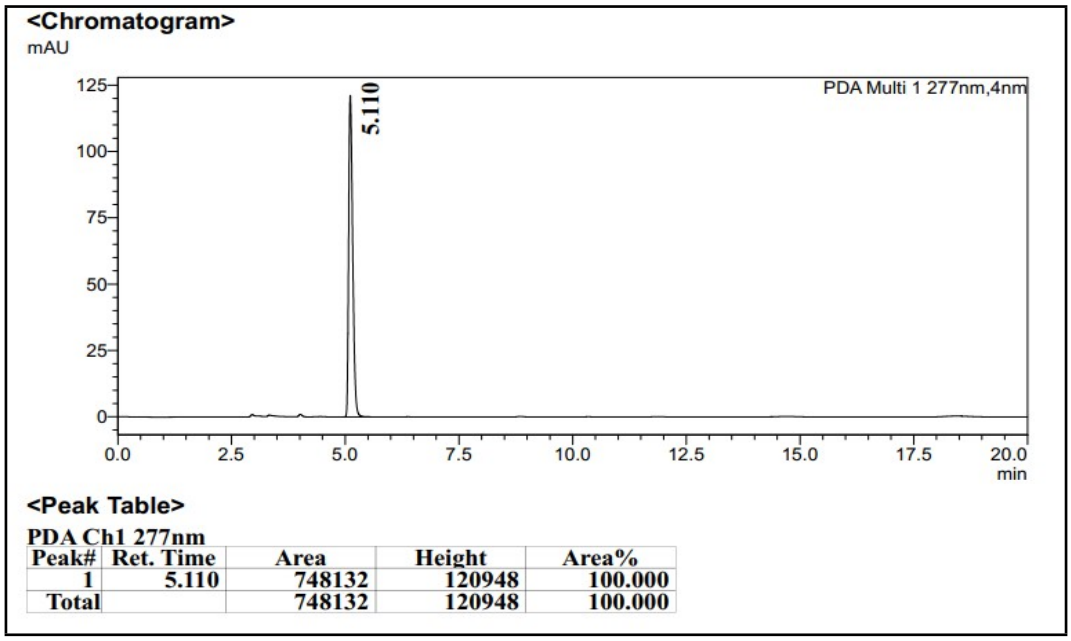


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	3.688	2318646	435455	100.000
Total		2318646	435455	100.000

(β, 1*R*)-**9**

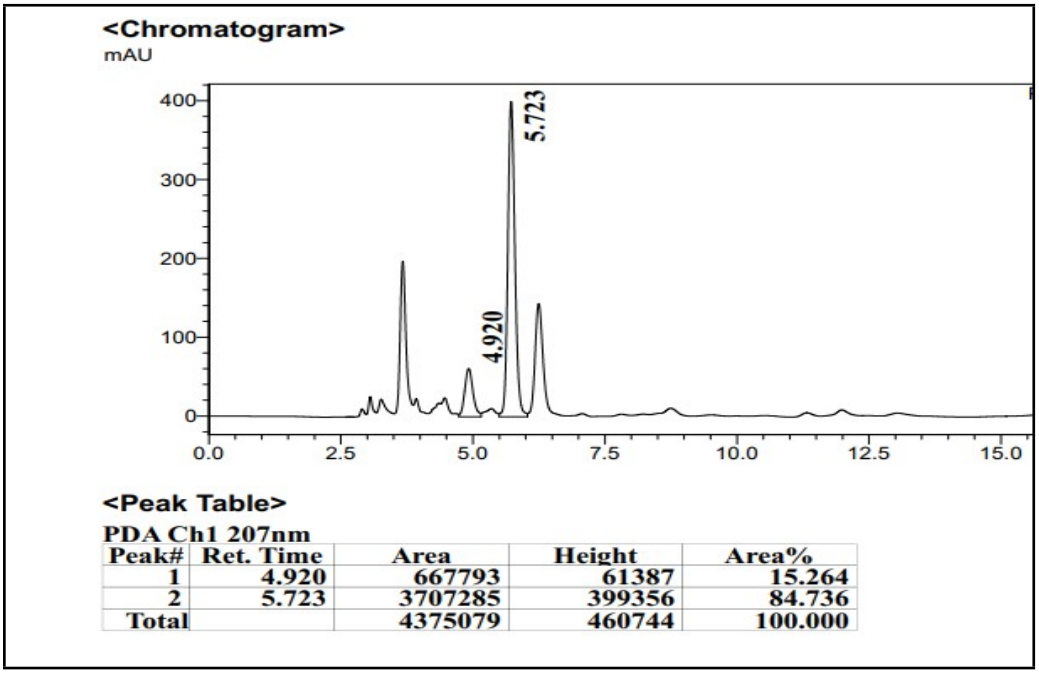


<Peak Table>

PDA Ch1 277nm

Peak#	Ret. Time	Area	Height	Area%
1	5.110	748132	120948	100.000
Total		748132	120948	100.000

Diastereomeric mixture of (α, 1*S*)-**10** and (*α*, 1*R*)-**10**

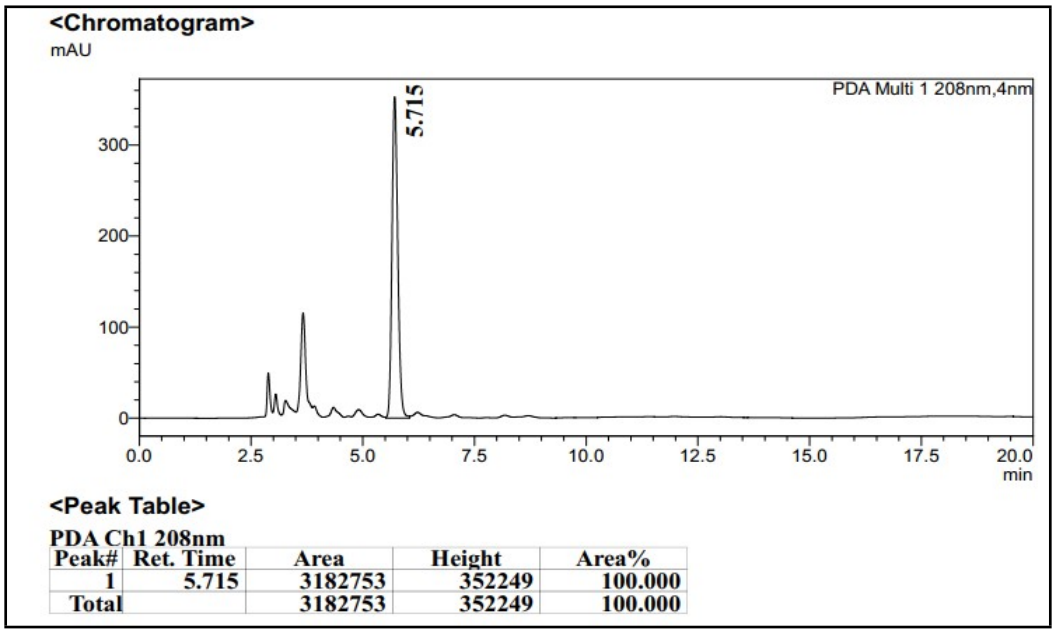


<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Area%
1	4.920	667793	61387	15.264
2	5.723	3707285	399356	84.736
Total		4375079	460744	100.000

(α, 1*S*)-**10**

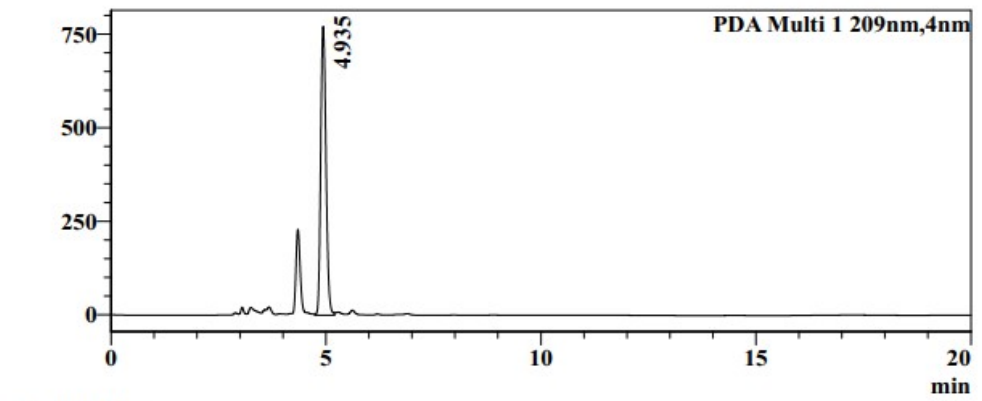


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	5.715	3182753	352249	100.000
Total		3182753	352249	100.000

(α, 1*R*)-**10**

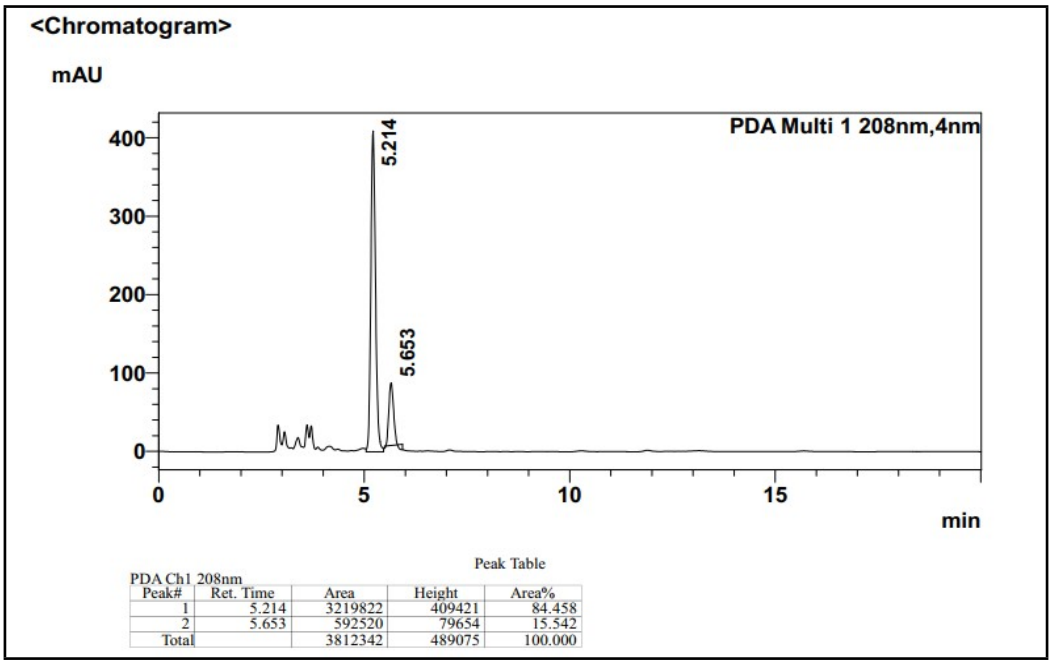


<Peak Table>

PDA Ch1 209nm

Peak#	Ret. Time	Area	Height	Area%
1	4.935	6589809	770542	100.000
Total		6589809	770542	100.000

Diastereomeric mixture of (*α*, 1*S*)-**11** and (*α*, 1*R*)-**11**

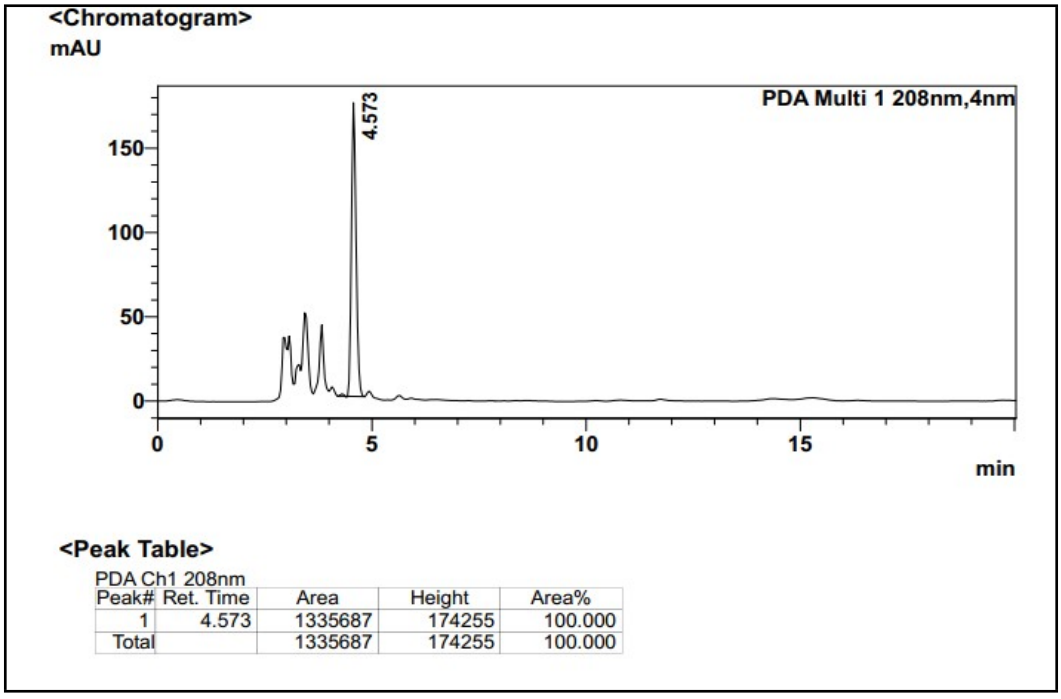


Peak Table

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	5.214	3219822	409421	84.458
2	5.653	592520	79654	15.542
Total		3812342	489075	100.000

(α, 1*S*)-**11**

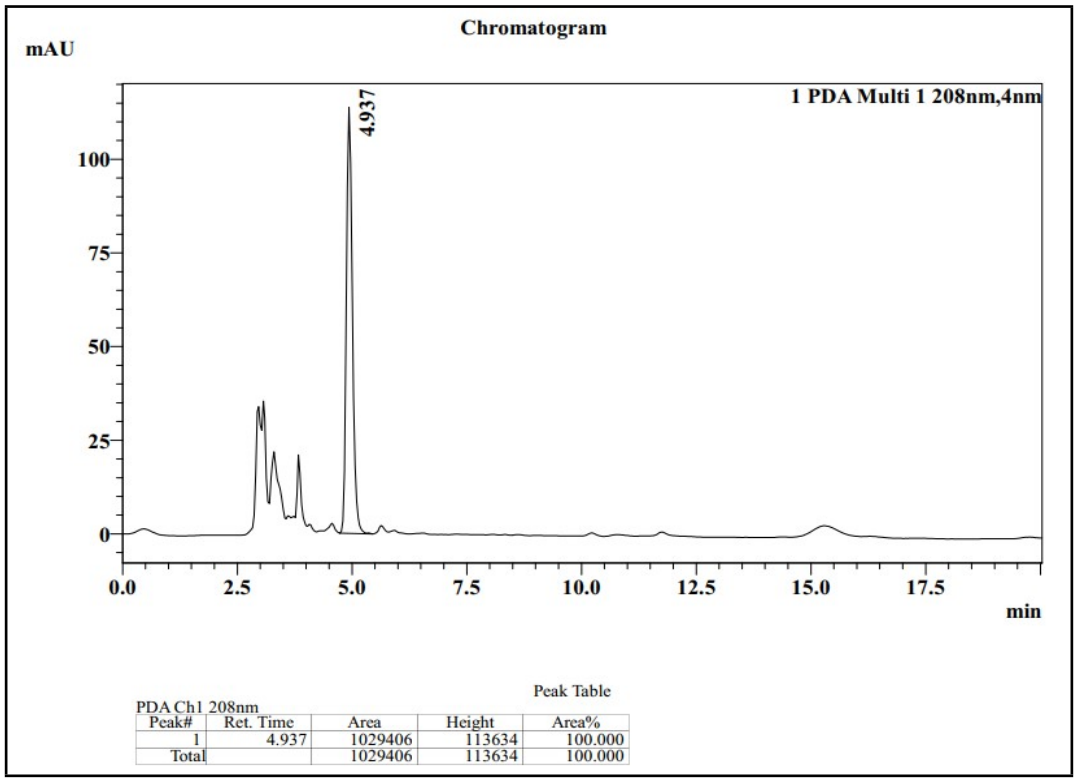


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	4.573	1335687	174255	100.000
Total		1335687	174255	100.000

(α, 1*R*)-**11**

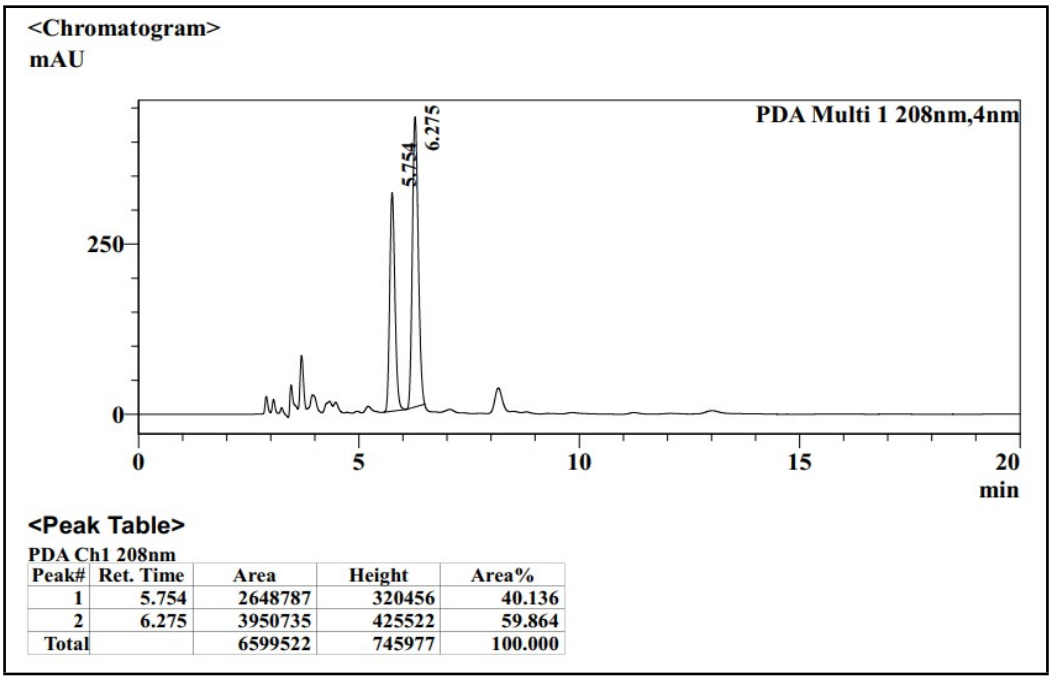


Peak Table

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	4.937	1029406	113634	100.000
Total		1029406	113634	100.000

Diastereomeric mixture of (α, 1*S*)-**11** and (α, 1*R*)-**11** catalysed by (*R*)-**2**

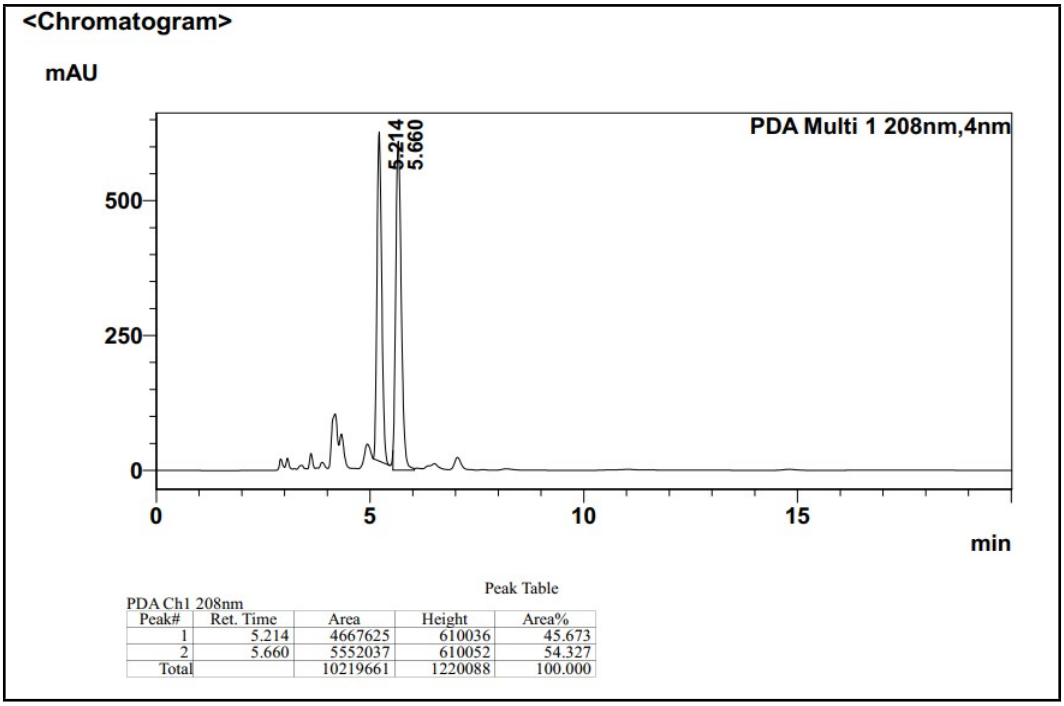


<Peak Table>

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	5.754	2648787	320456	40.136
2	6.275	3950735	425522	59.864
Total		6599522	745977	100.000

Diastereomeric mixture of (*α*, 1*S*)-**11** and (*α*, 1*R*)-**11** catalysed by (*S*)-**2**

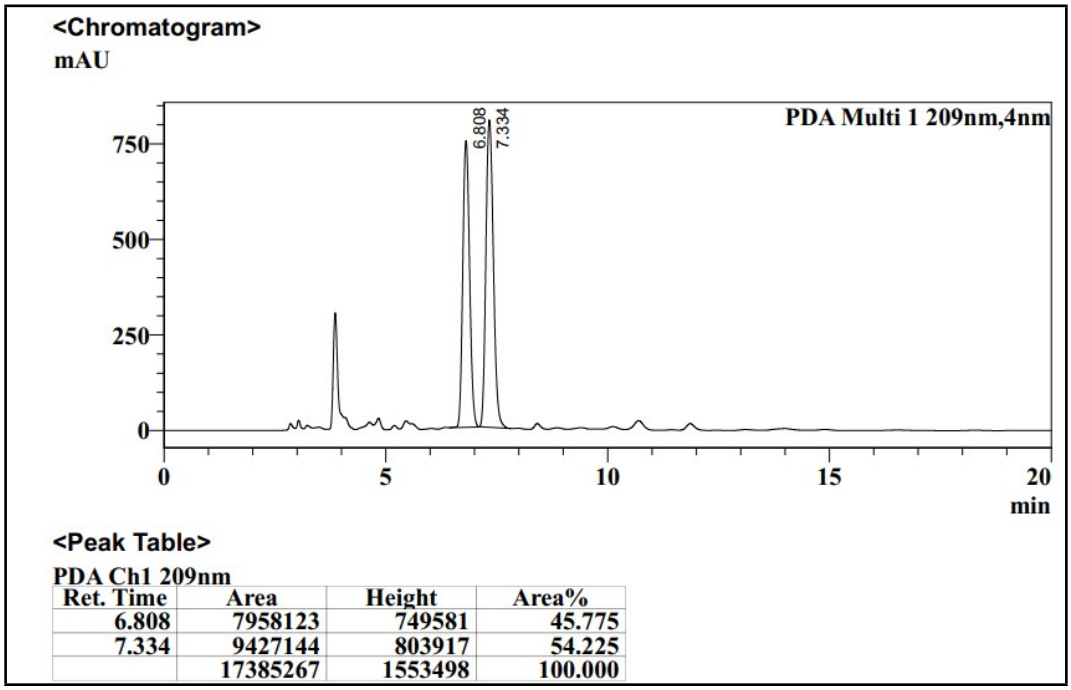


Peak Table

PDA Ch1 208nm

Peak#	Ret. Time	Area	Height	Area%
1	5.214	4667625	610036	45.673
2	5.660	5552037	610052	54.327
Total		10219661	1220088	100.000

Diastereomeric mixture of (*α*, 1*S*)-**10** and (*α*, 1*R*)-**10** catalysed by CBA **3**

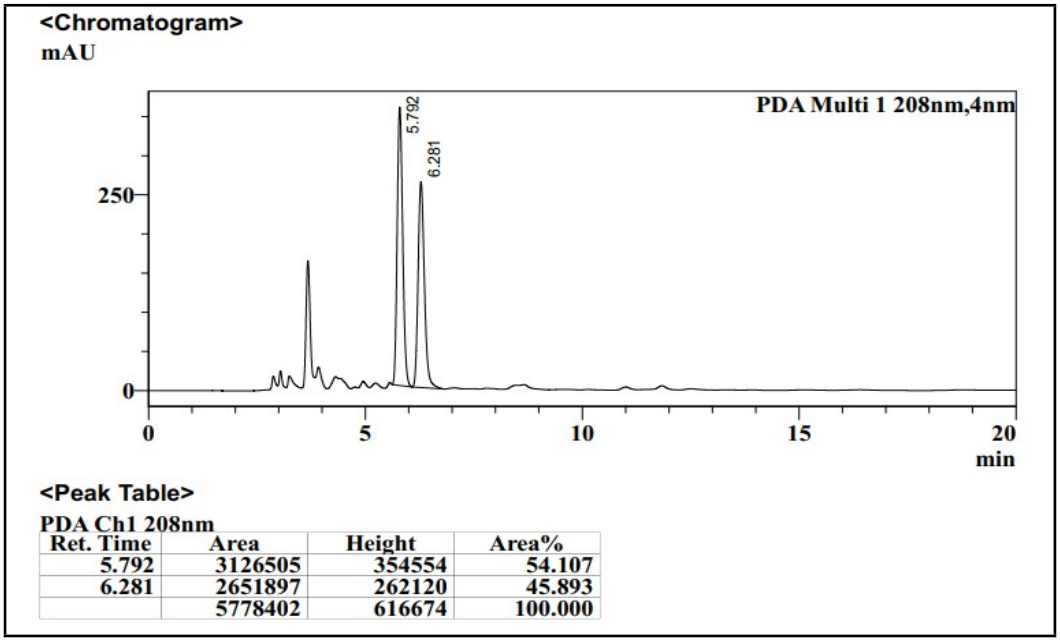


<Peak Table>

PDA Ch1 209nm

Ret. Time	Area	Height	Area%
6.808	7958123	749581	45.775
7.334	9427144	803917	54.225
	17385267	1553498	100.000

Diastereomeric mixture of (α, 1*S*)-**10** and (*α*, 1*R*)-**10** catalysed by CBA **4**



<Peak Table>

PDA Ch1 208nm

Ret. Time	Area	Height	Area%
5.792	3126505	354554	54.107
6.281	2651897	262120	45.893
	5778402	616674	100.000

References

1 W. K. P. Hohenberg, *Phys. Rev.*, 1964, **136**, B 864-B 871.

2 W. Kohn, L. J. Sham, *Phys. Rev.*, 1965, **140**, A 1133-A 1138.