Supporting Information

Bio-inspired Synthesis and Bioactivities of Phenylpropanoid Glycosides Crenatosides

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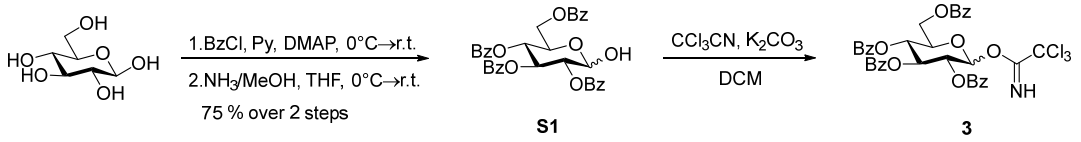
General Information

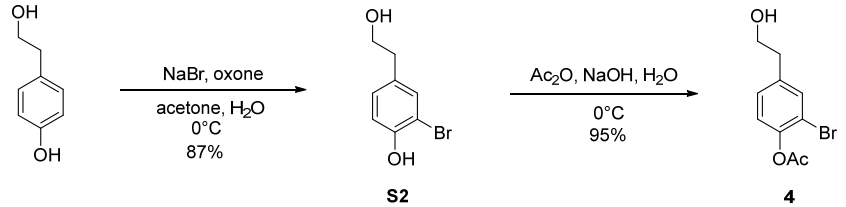
All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) was distilled immediately before use from sodium. Methylene chloride (CH_2Cl_2), *N*,*N*-dimethylformamide (DMF), and toluene were dried with activated Linde types 4 Å molecular sieves and stored under an argon atmosphere. Methanol (MeOH) was dried with activated Linde types 3 Å molecular sieves and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Adamas-beta®. Reactions were monitored by thin layer chromatography (TLC) carried out on MilliporeSigma glass TLC plates (silica gel 60 coated with F254, 250 μm) using UV light for visualization and/or by staining with EtOH/H_2SO_4 (10 %, v/v). Flash column chromatography was performed on silica gel 60 (40−64 μm, Fluka). Reversed phase chromatography was conducted using YMC*GEL ODS-A 12nm S-50 μm and monitored using Merck Silica gel 60 RP-18 F254 precoated aluminium sheets. NMR spectra were measured on an Agilent 500 or 600 MHz NMR spectrometer at 25 °C. ^{1}H and ^{13}C NMR signals were calibrated to the residual proton and carbon resonance of the solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3OD: δ_H = 3.31 ppm, δ_C = 49.00 ppm). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra were recorded with Shimadzu Biotech Axima Performance FTMS, maXis 4G FTMS, Thermo Scientific Q Exactive HF Orbitrap-FTMS, or Agilent-TOF/LC-MS 1260-6230 FTMS. Optical rotations were measured on an Anton Paar MCP5500 polarimeter.

Compound 3:



To a solution of anhydrous glucose (20.5 g, 114 mmol) in 250 mL pyridine was added DMAP (1.2 g, 10 mmol) and benzoyl chloride (90 mL, 776 mmol) under ice bath. The reaction was basically complete after 5 h at room temperature. Then methanol was added dropwise to quench the reaction. The mixture was concentrated in vacuo and diluted with CH_2Cl_2, washed successively with 1 M HCl aqueous solution, saturated $NaHCO_3$ solution and brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to get the product. The above product was dissolved in 400 mL THF, and 30% (w/v) ammonia-methanol solution (170 mL) was added under the ice bath. After 36 h, the reaction was basically complete. The reaction mixture was concentrated under vacuum and purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1 to 2:1) to give compound **S1**[1] (51.0 g, 75% over two steps) as a white solid. To a solution of compound **S1** (6.1 g, 10.2 mmol) in 60 mL CH_2Cl_2 was added CCl_3CN (10.3mL, 102 mmol), K_2CO_3 (8.5 g, 61.2 mmol). After stirring at room temperature for 2 h, the reaction was basically complete. Then K_2CO_3 was filtered through a Celite bed, and the filtrate was concentrated under vacuum. The residue was further concentrated under vacuum and azeotropically dried with toluene twice to give donor **3** as a yellow syrup, which was directly used for the next step.

Compound 4:



To a solution of commercially available 4-hydroxyphenethyl alcohol (13.8 g, 100 mmol) in acetone (150 mL) was added sodium bromide (12.3 g, 120 mmol). Then

oxone (61.4 g, 100 mmol) dissolved in water (250 mL) was added dropwise at 0 °C. After stirring at 0 °C for 2 h, TLC indicated the reaction was complete. Then, sodium thiosulfate ($Na_2S_2O_3$) was added to quench the reaction. The mixture was extracted with EtOAc and washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone = 9:1) to afford compound **S2**[2] (18.8 g, 87%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 2.1 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.95 (d, J = 8.2 Hz, 1H), 3.82 (t, J = 6.5 Hz, 2H), 2.78 (t, J = 6.5 Hz, 2H).

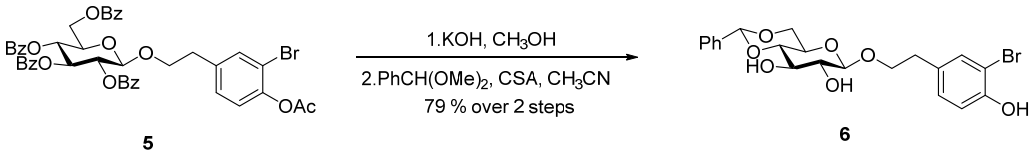
To a solution of the white solid **S2** (12.8 g, 59.3 mmol) in water (50 mL) was added sodium hydroxide (2.4 g, 59.3 mmol). Then acetic anhydride (6.7 ml, 71.2 mmol) was added dropwise at 0 °C. After stirring at room temperature for 1 h, TLC indicated the reaction was complete. Then HCl was added dropwise to quench the reaction. The mixture was extracted with EtOAc and washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone= 9:1) to afford compound **4** (8.0 g, 95%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 2.1 Hz, 1H), 7.19 (dd, J = 8.2, 2.1 Hz, 1H), 7.06 (d, J = 8.2 Hz, 1H), 3.85 (t, J = 6.5 Hz, 2H), 2.83 (t, J = 6.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.92, 146.89, 138.53, 133.84, 129.30, 123.71, 116.26, 63.37, 38.34, 20.94.

Compound 5:

Donor **3** (4.5 g, 5.8 mmol) and acceptor **4** (1143 mg, 4.4 mmol) were dissolved in dry CH_2Cl_2 (30 mL) under argon. Powdered freshly activated 4 Å molecular sieves (3.0 g) were added, and the mixture was stirred for 0.5 hour at ambient temperature. TMSOTf (80 μL, 443 μmol) was added at 0 °C. The reaction was basically complete after 2 h. Triethylamine was added to quench the reaction. The reaction mixture was filtered through a Celite bed, and the filtrate was concentrated under vacuum. The

residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1 to 6:1) to give **5** (3.5 g, 93%) as a white foam: $[\alpha]_D^{25} = 23.8$ (*c* 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 2H), 7.91 (m, 4H), 7.82 (m, 2H), 7.59 – 7.47 (m, 3H), 7.46 – 7.27 (m, 10H), 7.02 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.89 (m, 1H), 5.68 (m, 1H), 5.55 (m, 1H), 4.84 (d, *J* = 7.9, 1H), 4.65 (dd, *J* = 12.1, 3.0 Hz, 1H), 4.50 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.14 (m, 2H), 3.72 (m, 1H), 2.83 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.71, 166.27, 165.90, 165.30, 165.15, 146.59, 138.06, 129.96, 129.92, 129.87, 129.84, 129.63, 129.23, 129.16, 128.84, 128.82, 128.54, 128.52, 128.43, 123.36, 115.89, 101.26, 72.90, 72.37, 71.81, 70.28, 69.77, 63.18, 35.21, 20.91; $C_{44}H_{41}O_{12}NBr$ $[M + NH_4]^+$ 854.1807, found 854.1802.

Compound 6:

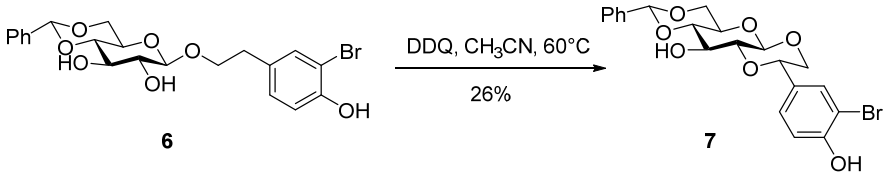


5 **6**

Compound **5** (16.8 g, 20.1 mmol) was dissolved in 100 mL methanol, KOH (5.6 g, 100.5 mmol) was added, and the mixture was stirred at room temperature overnight. Then quenched with HCl and concentrated under vacuum. The mixture was concentrated under vacuum and azeotropically dried with toluene twice to give the crude product, which can be directly used for the next step. Then, the crude product was dissolved in 100 mL acetonitrile, added CSA (1.6 g, 8.1 mmol), $PhCH(OMe)_2$ (6 mL, 40.2mmol). After stirring at room temperature overnight, the reaction mixture was quenched with triethylamine and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1 to 1:1) to give **6** (6.1 g, 79% over 2 steps) as a white solid: $[\alpha]_D^{25} = -19.8$ (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.40 – 7.36 (m, 3H), δ 7.34 (d, *J* = 2.0 Hz, 1H), 7.07 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 5.53 (s, 1H), 4.39 (d, *J* = 7.7 Hz, 1H), 4.34 (dd, *J* = 10.5, 4.9 Hz, 1H), 4.10 (m, 1H), 3.80 (m, 2H), 3.72 (m, 1H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.50 (dd, *J* = 9.0, 7.8 Hz, 1H), 3.45 (m, 1H), 2.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.04, 137.02, 132.30, 131.99, 129.80, 129.47, 128.51, 126.40, 116.17,

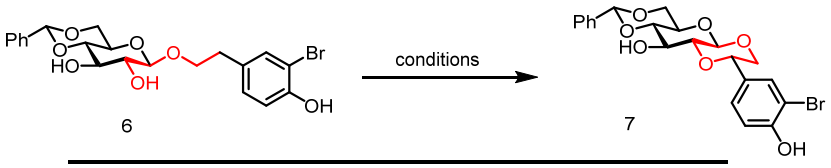
110.22, 103.35, 102.09, 80.65, 74.69, 73.22, 70.98, 68.78, 66.58, 35.03; HR-ESI-MS (*m/z*) calcd for $C_{21}H_{24}O_7Br$ $[M + H]^+$ 467.0700, found 467.0691.

Compound 7:



Compound **6** (47.0 mg, 0.1 mmol) was dissolved in dry CH_2Cl_2 (2 mL). Powdered freshly activated 4 Å molecular sieves (0.2 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. Then, 2,3-dichloro-5,6-dicyano-4-benzoquinone (27 mg, 120 μmol) was added, and the mixture was stirred for 2 h at 40 °C in heating mantle. Then the reaction solution was cooled to room temperature and filtered through a Celite bed. The filtrate was washed with saturated $NaHCO_3$ thrice. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford glycoside **7** (12.6 mg, 26%) as a white solid: $[\alpha]_D^{25}$ = 25.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.51 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.35 (m, 3H), 7.21 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.62 (s, 1H), 4.64 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.60 (d, *J* = 7.7 Hz, 1H), 4.33 (dd, *J* = 10.3, 4.7 Hz, 1H), 4.02 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.91 (t, *J* = 9.1 Hz, 1H), 3.85 (t, *J* = 10.1 Hz, 1H), 3.72 – 3.58 (m, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 154.09, 137.59, 131.06, 129.45, 128.57, 127.64, 126.68, 126.12, 115.58, 109.34, 101.80, 98.74, 81.50, 80.65, 76.72, 71.55, 70.30, 68.20, 68.07; HR-ESI-MS (*m/z*) calcd for $C_{21}H_{22}O_7Br$ $[M + H]^+$ 465.0542, found 465.0543.

Table S1 The reaction conditions examined for conversion of compound **6** to compound **7**. [a]

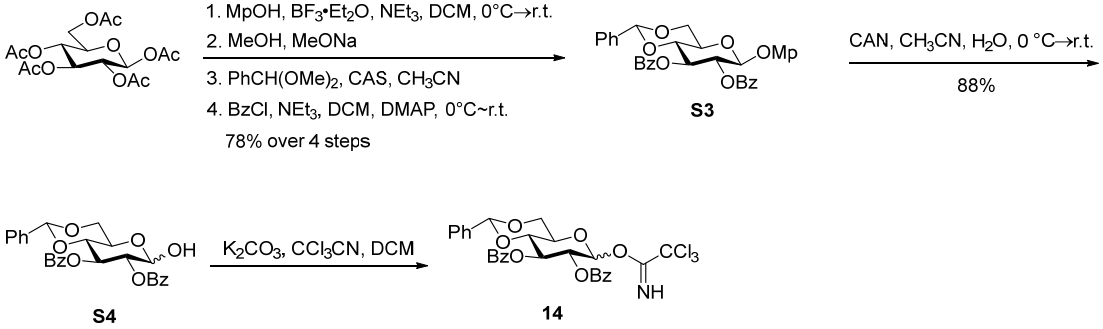


6 7

entry	conditions	results
1	CH_3OH, c=0.02, DDQ 1.2eq, r.t., 4Å MS, 6h	N.D.
2	CH_3CH_2OH, c=0.02, DDQ 1.2eq, r.t., 4Å MS, 6h	N.D.
3	CH_2Cl_2, c=0.02, DDQ 1.2eq, r.t., 4Å MS, 6h	23%
4	CH_2ClCH_2Cl, c=0.02, DDQ 1.2eq, r.t.,4Å MS, 6h	<23%
5	$C_6H_5CH_3$, c=0.02, DDQ 1.2eq, r.t., 4Å MS, 6h	<23%
6	CH_3CN, c=0.02, DDQ 1.2eq, r.t., 4Å MS, 6h	24%
7	CH_3CN, c=0.02, DDQ 1.2eq, -78°C, 4Å MS, 12h	<23%
8	CH_3CN, c=0.02, DDQ 1.2eq, -40°C, 4Å MS, 12h	<23%
9	CH_3CN, c=0.02, DDQ 1.2eq, 40°C, 4Å MS, 3h	25%
10	CH_3CN, c=0.02, DDQ 1.2eq, 70°C, 4Å MS, 2h	26%
11	CH_2ClCH_2Cl, c=0.02, $Ce(NH_4)_2(NO_3)_6$ 1.2eq, r.t.,4Å MS, 2h	N.D.
12	CH_2ClCH_2Cl, c=0.02, $PhI(OAc)_2$ 1.2eq, r.t.,4Å MS, 2h	N.D.

[a] The oxidative cyclization reaction was performed at a 0.02 mmol scale.

Compound 14:



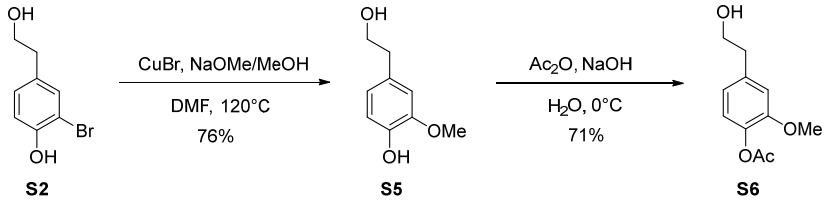
β-D-Galactose pentaacetate (39.0 g, 100.0 mmol) was dissolved in CH_2Cl_2 (300.0 mL), 4-methoxyphenol (17.4 g, 140.0 mmol) and NEt_3 (7.0 ml, 50.0 mmol) were added successively. To the reaction mixture, $BF_3 \cdot Et_2O$ (30.0 mL, 240.0 mmol) was added dropwise at 0 °C. After stirring at room temperature for 12 h, TLC indicated the reaction was complete. Then saturated aqueous $NaHCO_3$ was added dropwise at 0 °C followed

with vigorously stirring for 10 min to quench the reaction. The mixture was extracted with dichloromethane and washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was dissolved in MeOH (400 mL) and MeONa (2.7 g, 50 mmol) was added. After stirring at room temperature for 3 h, the reaction was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered. And the filtrate was concentrated under vacuum. The residue was dissolved in dry MeCN (400 mL), $PhCH(OMe)_2$ (30.0 mL, 200.0 mmol) and CSA (4.7 g, 20.0 mmol) were successively added. After stirring at room temperature for 12 h, the mixture was quenched with NEt_3 and concentrated under vacuum. The residue was dissolved in CH_2Cl_2 (500 mL), DMAP (4.9 g, 40.0 mmol) and NEt_3 (80.0 mL, 600.0 mmol) were added. Benzoyl chloride (25.5 mL, 220.0 mmol) was added to the reaction mixture slowly at 0 °C. After stirring at room temperature for 11 h, TLC indicated the reaction was complete. The mixture was diluted with dichloromethane, washed with $NaHCO_3$ and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered. And the filtrate was concentrated under vacuum. The residue was purified by recrystallization (chloroform/hexane) to afford **S3**[3] (45 g, 78% over 4 steps) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 4H), 7.57 – 7.48 (m, 2H), 7.46 – 7.36 (m, 6H), 7.32 (m, 3H), 6.98 – 6.90 (m, 2H), 6.84 – 6.76 (m, 2H), 5.84 (t, *J* = 9.5 Hz, 1H), 5.71 (dd, *J* = 9.4, 7.7 Hz, 1H), 5.58 (s, 1H), 5.25 (d, *J* = 7.7 Hz, 1H), 4.47 (dd, *J* = 10.6, 4.9 Hz, 1H), 4.04 (t, *J* = 9.5 Hz, 1H), 3.94 (t, *J* = 10.3 Hz, 1H), δ 3.79 (td, *J* = 9.7, 4.9 Hz, 1H), 3.75 (s, 3H).

The white solid **S3** (20.0 g, 34.3 mmol) was dissolved in CH_3CN (400 mL), and the reaction mixture was cooled down to 0 °C. Ammonium cerium (IV) nitrate (56.4 g, 102.9 mmol) was dissolved in CH_3CN (400 mL) and water (100 mL). Then the CAN solution was added to the reaction mixture. After stirring at room temperature for 2 h, TLC indicated the reaction was complete. The mixture was diluted with ethyl acetate, successively washed with $Na_2S_2O_3$ and $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 6:1 to 4:1) to afford **S4** (14.4 g, 88%) as a yellow solid. To a solution of the solid **S4** (14.4 g, 30.2 mmol) in

CH_2Cl_2 (100 mL) and acetone (50 mL) were added K_2CO_3 (26.0 g, 181.2 mmol) and trichloroacetonitrile (31 mL, 302.0 mmol). After stirring at room temperature for 12 h under argon, the mixture was filtered through a Celite bed using EtOAc. The filtrate was concentrated under vacuum to give donor **14** as a yellow syrup, which was pure enough for the next step.

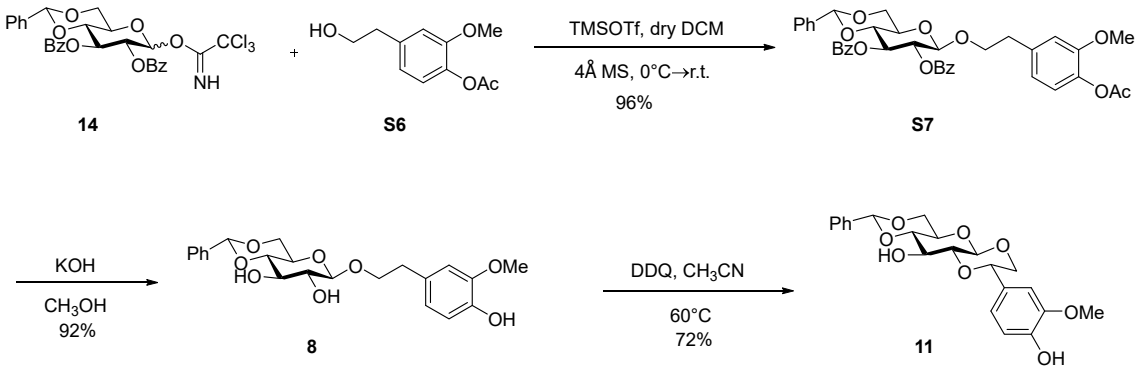
Compounds 8 and 11:



CuBr (11.3 g, 79.7 mmol) was dissolved in DMF (20 mL), 25% w/v sodium methylate methanol solution (160 mL) was added and the mixture was heated to 100 ℃. After the solution turned blue, compound **S2** (15.8 g, 72.4 mmol) dissolved in 20 mL DMF was added. After stirring at 100 ℃ for 3 h, the reaction was basically complete. The reaction was quenched with 2 M HCl, and then extracted with ethyl acetate. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1) to afford compound **S5**[4] (9.26 g, 76 %) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 – 6.85 (m, 1H), 6.72 (m, 2H), 3.88 (s, 3H), 3.83 (t, J = 6.5 Hz, 2H), 2.80 (t, J = 6.5 Hz, 2H).

Then compound **S5** (9.3 g, 55 mmol) was dissolved in aqueous solution (150 mL) of sodium hydroxide (2.6 g, 66 mmol), and then acetic anhydride (6.2 mL, 66 mmol) was slowly added under ice bath. After 2 h, the reaction was basically complete, the reaction was quenched with 2 M HCl and saturated aqueous $NaHCO_3$ in sequence. Then the mixture was extracted with dichloromethane and washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone = 2:1) to afford light yellow liquid **S6**[4] (8.2 g, 71%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 1.9 Hz, 1H), 6.80 (dd, J = 8.0, 1.9 Hz, 1H), 3.85 (t, J =

6.5 Hz, 2H), 3.82 (s, 3H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.43, 151.10, 137.71, 122.86, 121.22, 113.34, 63.65, 55.98, 39.24, 20.83.



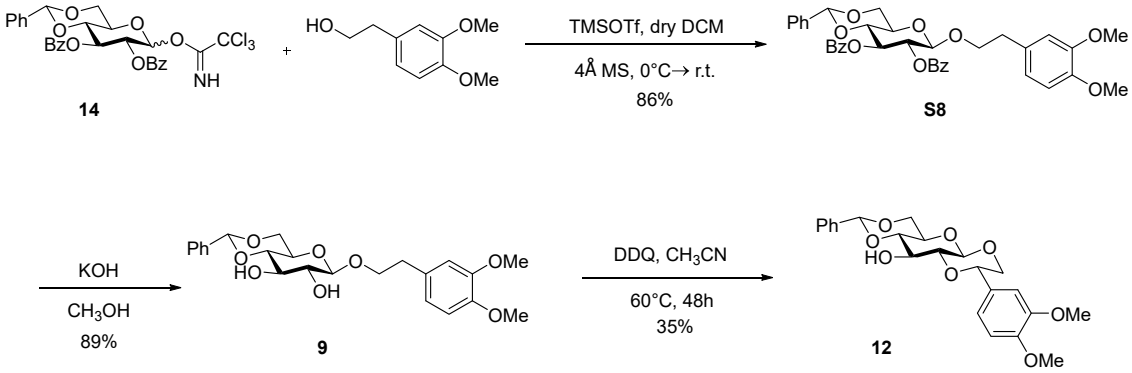
Glycosyl donor **14** (16.0 g, 25.8 mmol) and acceptor **S6** (5.0 g, 19.0 mmol) were dissolved in dry CH_2Cl_2 (250 mL). Powdered freshly activated 4 Å molecular sieves (16.0 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. Then, the mixture was cooled to 0 °C and TMSOTf (1 mL, 5.7 mmol) was added. After stirring at 0 °C for 2 h, the mixture was quenched with triethyl amine. The reaction mixture was filtered through a Celite bed, and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 8:1 to 4:1) to afford **S7** (12.2 g, 96%) as a white foam: $[\alpha]_D^{25}$ = 7.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.93 – 7.90 (m, 2H), 7.54 – 7.46 (m, 2H), 7.43 – 7.39 (m, 3H), 7.39 – 7.35 (m, 3H), 7.31 (m, 3H), 6.74 (d, *J* = 1.8 Hz, 1H), 6.72 – 6.69 (m, 1H), 6.66 (dd, *J* = 8.1, 1.8 Hz, 1H), 5.77 (t, *J* = 9.5 Hz, 1H), 5.54 (s, 1H), 5.49 (dd, *J* = 9.3, 7.7 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.43 (dd, *J* = 10.5, 4.9 Hz, 1H), 4.12 (m, *J* = 9.6, 6.8 Hz, 1H), 3.93 (t, *J* = 9.5 Hz, 1H), 3.87 (t, *J* = 10.3 Hz, 1H), 3.76 (s, 3H), 3.75 – 3.72 (m, 1H), 3.72 – 3.66 (m, 1H), 2.82 (t, *J* = 6.9 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.80, 138.20, 137.28, 136.88, 133.31, 133.25, 129.94, 129.89, 129.51, 129.37, 129.18, 128.51, 128.44, 128.34, 126.25, 122.52, 121.03, 113.26, 101.74, 101.61, 78.91, 72.54, 72.19, 70.95, 68.79, 66.76, 55.88, 36.13, 20.82; HR-ESI-MS (*m/z*) calcd for $C_{38}H_{36}O_{11}Na[M + Na]^+$ 691.2150, found 691.2159.

To a solution of **S7** (12.0 g, 18 mmol) in MeOH (200 mL) was added KOH (3.2 g, 57 mmol). After stirring at room temperature for 3 h, the reaction was neutralized with

DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford **8** (7.3 g, 92%) as a white solid: $[\alpha]_D^{25}$ = -28.8 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.37 (m, 3H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.75 – 6.69 (m, 2H), 5.53 (s, 1H), 4.39 (d, *J* = 7.7 Hz, 1H), 4.34 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.13 (m, 1H), 3.88 (s, 3H), 3.83 – 3.76 (m, 2H), 3.73 (m, 1H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.49 (dd, *J* = 9.2, 7.9 Hz, 1H), 3.47 – 3.42 (m, 1H), 2.89 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.60, 137.02, 130.10, 129.46, 128.51, 126.39, 121.61, 114.52, 111.56, 103.40, 102.08, 80.68, 74.71, 73.19, 71.49, 68.79, 66.58, 56.04, 35.88; HR-ESI-MS (*m/z*) calcd for $C_{22}H_{27}O_8$ $[M + H]^+$ 419.1700, found 419.1700, $C_{22}H_{26}O_8Na$ $[M + Na]^+$ 441.1520, found 441.1522.

Compound **8** (0.1 g, 0.2 mmol) was dissolved in dry MeCN (5 mL). Powdered freshly activated 4 Å molecular sieves (0.5 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. 2,3-dichloro-5,6-dicyano-4-benzoquinone (65 mg, 286 μmol) was added, then the mixture was stirred for 2 h at 60 °C in heating mantle. Then the reaction solution was cooled to room temperature and filtered through a Celite bed. The filtrate was washed with saturated aqueous $NaHCO_3$ thrice. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford glycoside **11** (72 mg, 72%) as a white solid: $[\alpha]_D^{25}$ = 41.9 (*c* 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.44 (m, 2H), 7.38 (m, 3H), 6.93 – 6.79 (m, 3H), 5.57 (s, 1H), 4.67 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.56 (d, *J* = 7.7 Hz, 1H), 4.41 (dd, *J* = 10.5, 3.8 Hz, 1H), 4.11 – 3.97 (m, 2H), 3.91 (s, 3H), 3.88 – 3.80 (m, 1H), 3.74 (dd, *J* = 12.2, 10.7 Hz, 1H), 3.70 – 3.63 (m, 2H), 3.47 (dd, *J* = 9.4, 7.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.71, 146.09, 136.90, 129.49, 128.50, 128.17, 126.42, 120.08, 114.55, 109.35, 102.31, 98.72, 81.38, 80.41, 78.21, 72.19, 70.92, 68.60, 68.36, 56.14, 29.36; HR-ESI-MS (*m/z*) calcd for $C_{24}H_{27}O_9$ $[M + H]^+$ 459.1650, found 459.1647.

Compounds 9 and 12:



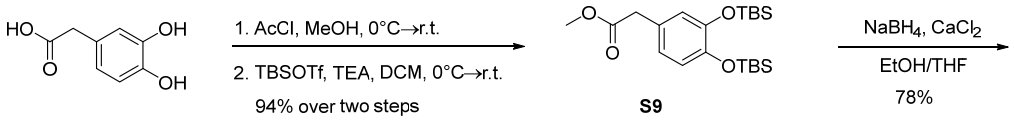
Glycosyl donor **14** (5.7 g, 9.2 mmol) and 2-(3,4-dimethoxyphenyl)ethanol (4.0 g, 19.0 mmol) were dissolved in dry CH_2Cl_2 (120 mL). Powdered freshly activated 4 Å molecular sieves (4.0 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. Then the mixture was cooled to 0 °C and TMSOTf (0.4 mL, 2.1 mmol) was added. After stirring at 0 °C for 2 h, the mixture was neutralized with NEt_3. The reaction mixture was filtered through a Celite bed, and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 8:1 to 4:1) to afford **S8** (3.9 g, 86%) as a white foam: $[\alpha]_D^{25} = 15.6$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.93 – 7.86 (m, 2H), 7.50 (m, 2H), 7.41 (m, 2H), 7.37 (q, *J* = 7.4 Hz, 4H), 7.31 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.64 (d, *J* = 1.9 Hz, 1H), 6.62 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.76 (t, *J* = 9.5 Hz, 1H), 5.53 (s, 1H), 5.48 (dd, *J* = 9.4, 7.8 Hz, 1H), 4.81 (d, *J* = 7.8 Hz, 1H), 4.43 (dd, *J* = 10.6, 4.9 Hz, 1H), 4.12 (m, 1H), 3.93 (t, *J* = 9.5 Hz, 1H), 3.87 (t, *J* = 10.3 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.70 (m, 2H), 2.78 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.75, 165.28, 148.71, 147.49, 136.88, 133.25, 130.89, 129.94, 129.88, 129.52, 129.43, 129.18, 128.44, 128.35, 126.24, 120.80, 112.25, 111.02, 101.74, 101.62, 78.94, 72.54, 72.21, 71.29, 68.82, 66.76, 55.85, 35.72; HR-ESI-MS (*m/z*) calcd for $C_{37}H_{37}O_{10}$ $[M + H]^+$ 641.2381, found 641.2377, $C_{37}H_{36}O_{10}Na$ $[M + Na]^+$ 663.2201, found 663.2200.

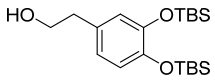
To a solution of **S8** (3.9 g, 6.0 mmol) in MeOH (50 mL) was added KOH (0.7 g, 12.2 mmol mmol). After stirring at room temperature for 3 h, the reaction was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by silica gel column

chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford **9** (2.3 g, 89%) as a white solid: $[\alpha]_D^{25}$ = -28.5 (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.36 (m, 3H), 6.83 – 6.71 (m, 3H), 5.53 (s, 1H), 4.40 (d, *J* = 7.7 Hz, 1H), 4.34 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.14 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.79 (d, *J* = 9.5 Hz, 2H), 3.75 (dd, *J* = 10.2, 2.9 Hz, 1H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.52 – 3.47 (m, 1H), 3.47 – 3.42 (m, 1H), δ 2.91 (td, *J* = 7.1, 2.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.05, 147.81, 137.02, 130.77, 129.45, 128.50, 126.39, 120.89, 112.27, 111.37, 103.38, 102.07, 80.67, 74.69, 73.19, 71.37, 68.78, 66.57, 56.05, 56.00, 35.78; HR-ESI-MS (*m/z*) calcd for $C_{23}H_{28}O_8Na$ $[M + Na]^+$ 455.1676, found 455.1682.

Compound **9** (0.1 g, 0.2 mmol) was dissolved in dry MeCN (10 mL). Powdered freshly activated 4 Å molecular sieves (1.0 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. 2,3-Dichloro-5,6-dicyano-4-benzoquinone (0.1 mg, 0.4 mmol) was added, then the mixture was stirred for 2 h at 60 °C in heating mantle. Then the reaction solution was cooled to room temperature and filtered through a Celite bed. The filtrate was washed with saturated $NaHCO_3$ thrice. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford **12** (35 mg, 35%) as a white solid: $[\alpha]_D^{25}$ = 47.6 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.42 – 7.34 (m, 3H), 6.95 – 6.81 (m, 3H), 5.58 (s, 1H), 4.70 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.58 (d, *J* = 7.7 Hz, 1H), 4.42 (dd, *J* = 10.5, 3.9 Hz, 1H), 4.09 – 3.97 (m, 2H), 3.91 (s, 3H), 3.87 (m, 4H), 3.76 (dd, *J* = 12.2, 10.7 Hz, 1H), 3.72 – 3.62 (m, 2H), 3.48 (dd, *J* = 9.3, 7.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.45, 149.22, 136.92, 129.49, 128.81, 128.50, 126.42, 126.38, 119.40, 111.24, 109.99, 102.33, 98.75, 81.41, 80.44, 78.15, 72.18, 70.94, 68.62, 68.39, 56.12, 56.08; HR-ESI-MS (*m/z*) calcd for $C_{23}H_{28}O_8Na$ $[M + Na]^+$ 455.1676, found 455.1682.

Compound 15:





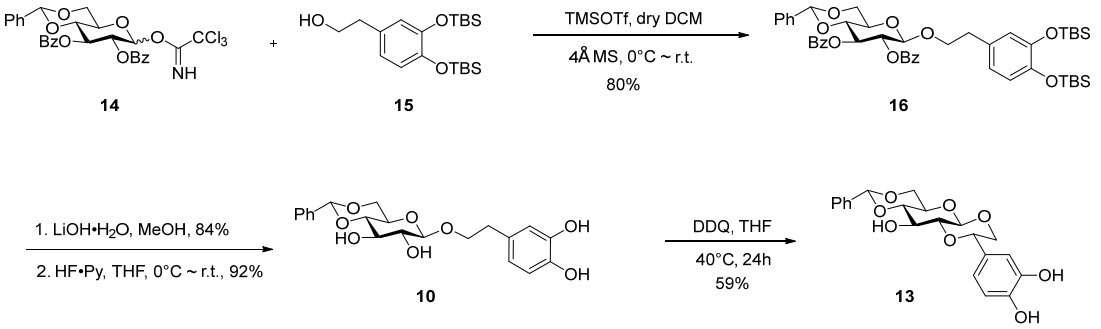
15

To a solution of 3,4-dihydroxyphenylacetic acid (17.0 g, 101 mmol) in methanol (120 mL) was added the acetyl chloride (17.5 mL, 242 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature until TLC indicated the reaction was complete. The mixture was concentrated under vacuum and washed with saturated brine and extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was dissolved in CH_2Cl_2 (30 mL), then triethylamine (113 mL, 808 mmol) and TBSOTf (93 mL, 404 mmol) were added at 0 °C in sequence. After stirring at room temperature for 3 h, TLC indicated the reaction was complete. The mixture was washed with saturated $NaHCO_3$ and saturated brine, then extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 100:1) to afford **S9**[5] (39 g, 94% over 2 steps) as a yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, J = 2.2 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 6.70 (dd, J = 8.1, 2.2 Hz, 1H), 3.67 (s, 3H), 3.49 (s, 2H), 0.98 (d, J = 2.0 Hz, 18H), 0.19 (d, J = 3.7 Hz, 12H).

Compound **S9** (10.0 g, 24.3 mmol) was dissolved in 100 mL ethanol and 50 mL tetrahydrofuran, calcium chloride (4.0 g, 36.5 mmol) was added, and then sodium borohydride (1.9 g, 48.7 mmol) was slowly added. After stirring at room temperature for 30 h, the reaction was basically complete. Ammonium chloride was added to quench the reaction, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 50:1 to 20:1) to afford **15** (7.24 g, 78%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (d, J = 8.0 Hz, 1H), 6.69 (d, J = 2.2 Hz, 1H), 6.65 (dd, J = 8.1, 2.2 Hz, 1H), 3.79

(t, J = 6.5 Hz, 2H), 2.74 (t, J = 6.5 Hz, 2H), 0.98 (d, J = 1.7, 18H), δ 0.19 (d, J = 0.9 Hz, 1H).

Compounds 10, 13, and 16:



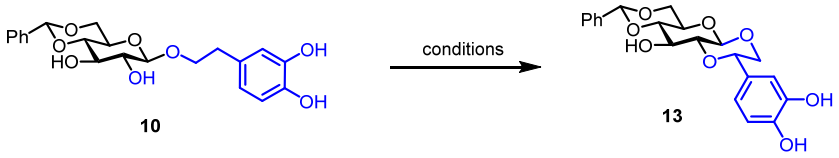
Glycosyl donor **14** (21.3 g, 34.43 mmol) and **15** (12 g, 31.3 mmol) were dissolved in dry CH_2Cl_2 (200 mL). Powdered freshly activated 4 Å molecular sieves (10.0 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. Then the mixture was cooled to 0 °C and TMSOTf (1.6 mL, 9.39 mmol) was added. After stirring at 0 °C for 2 h, the mixture was neutralized with triethyl amine. The reaction mixture was filtered through a Celite bed, and the filtrate was concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 8:1 to 4:1) to afford **16** (21.1 g, 80%) as a white foam: $[\alpha]_D^{25}$ = 21.3 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (m, 4H), 7.55 – 7.47 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 (m, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.32 (dd, J = 5.2, 2.0 Hz, 3H), 6.61 (s, 1H), 6.54 (d, J = 1.2 Hz, 2H), 5.78 (t, J = 9.5 Hz, 1H), 5.55 (s, 1H), 5.50 (dd, J = 9.4, 7.8 Hz, 1H), 4.83 (d, J = 7.8 Hz, 1H), 4.43 (dd, J = 10.6, 4.9 Hz, 1H), 4.04 (m, 1H), 3.94 (t, J = 9.5 Hz, 1H), 3.89 (t, J = 10.3 Hz, 1H), 3.74 – 3.61 (m, 2H), 2.72 (t, J = 7.4 Hz, 2H), 0.98 (s, 9H), 0.97 (s, 9H), 0.17 (d, J = 3.3 Hz, 6H), 0.15 (d, J = 1.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.75, 165.32, 146.62, 145.37, 136.88, 133.33, 133.23, 131.12, 129.94, 129.92, 129.50, 129.43, 129.16, 128.51, 128.43, 128.33, 126.23, 121.88, 121.77, 120.97, 101.69, 101.57, 78.91, 72.55, 72.22, 71.40, 68.80, 66.71, 35.49, 26.07, 26.06, 18.54, 18.53, -3.94, -3.98, -3.99, -4.02; HR-ESI-MS (*m/z*) calcd for $C_{47}H_{60}O_{10}Si_2Na$ $[M + Na]^+$ 863.3617, found 863.3620.

To a solution of **16** (20 g, 23.7 mmol) in CH_2Cl_2 (380 mL) and MeOH (95 mL) was added LiOH (0.1 g, 2.38 mmol). Another LiOH (0.1 g, 2.38 mmol) was added respectively at 1 h, 2 h, 3 h of the reaction. After stirring at room temperature for 24 h, the reaction was basically complete. Then neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography to give 12.6 g product (84 %). Then solve it in THF (200 mL) in plastic bottle and HF·py (20.0 mL, 201.79 mmol) was added dropwise at 0 °C. After stirring at room temperature for 10 h, TLC indicated the reaction was complete. Then $NaHCO_3$ was added dropwise at 0 °C to quench the reaction, and extracted with EtOAc. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone = 2:1 to 1:1) to afford **10** (7.4 g, 92%) as a white solid: $[\alpha]_D^{25}$ = -24.1 (*c* 0.2, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.55 – 7.46 (m, 2H), 7.34 (dd, *J* = 5.0, 2.0 Hz, 3H), 6.71 – 6.64 (m, 2H), 6.55 (dd, *J* = 8.1, 2.1 Hz, 1H), 5.57 (s, 1H), 4.43 (d, *J* = 7.8 Hz, 1H), 4.28 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.96 (ddd, *J* = 9.7, 8.4, 6.6 Hz, 1H), 3.76 (t, *J* = 9.4 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.63 (t, *J* = 8.8 Hz, 1H), 3.50 – 3.42 (m, 2H), δ 3.30 – 3.27 (m, 1H), 2.78 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 146.16, 144.71, 139.14, 131.34, 129.92, 129.03, 127.52, 121.20, 117.06, 116.29, 105.04, 102.92, 82.29, 75.95, 74.65, 72.45, 69.73, 67.59, 36.64; HR-ESI-MS (*m/z*) calcd for $C_{18}H_{28}O_9K$ $[M + K]^+$ 427.1365, found 427.1370.

To a solution of compound **10** (2.4 g, 5.9 mmol) in dry THF (300 mL) were added powdered freshly activated 4 Å molecular sieves (4.0 g), and the mixture was stirred at room temperature for 30 minutes under argon. 2,3-Dichloro-5,6-dicyano-4-benzoquinone (1.6 g, 7.1 mmol) was added, then the mixture was stirred for 2 h at 40 °C in heating mantle. Then the reaction solution was cooled to room temperature and filtered through a Celite bed using EtOAc. The filtrate was washed with saturated $NaHCO_3$ thrice. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ acetone = 2:1 to 1:1) to afford **13** (1.4 g, 59%) as a white solid: $[\alpha]_D^{25}$ = 31.0 (*c* 0.6, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.56 – 7.47

(m, 2H), 7.35 (dd, J = 5.1, 2.0 Hz, 3H), 6.85 (d, J = 1.5 Hz, 1H), 6.73 (d, J = 1.7 Hz, 2H), 5.61 (s, 1H), 4.66 – 4.49 (m, 2H), 4.32 (dd, J = 10.3, 4.6 Hz, 1H), 3.97 (dd, J = 12.0, 3.0 Hz, 1H), 3.91 – 3.80 (m, 2H), 3.73 – 3.56 (m, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 146.46, 146.22, 138.81, 130.02, 129.65, 129.07 (d, J = 3.2 Hz), 127.48, 119.46, 116.18, 115.03, 103.09, 100.05, 82.74, 81.87, 79.02, 73.01, 71.62, 69.44, 69.36; HR-ESI-MS (*m/z*) calcd for $C_{21}H_{23}O_8$ $[M + H]^+$ 403.1387, found 403.1395.

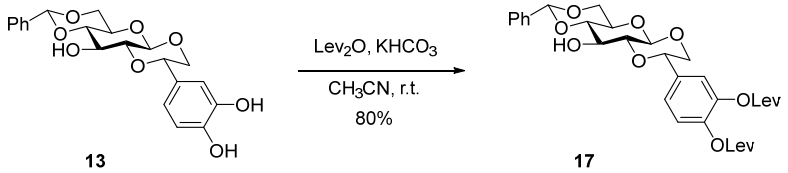
Table S2 The reaction conditions optimization for conversion of compound **10** to compound **13**.[a]



entry	conditions	results
1	DDQ 1.2eq, CH_3CN c=0.02, r.t.	decompose
2	DDQ 1.2eq, DMF,c=0.02, r.t.	decompose
3	DDQ 1.2eq, DCE, c=0.02, r.t.	decompose
4	DDQ 1.2eq, Toluene, c=0.02, r.t.	decompose
5	DDQ 1.2eq, CH_3OH, c=0.02, r.t.	~10%
6	DDQ 1.2eq, DCM, c=0.02, r.t.	~10%
7	DDQ 1.2eq, EA, c=0.02, r.t.	~20%
8	DDQ 1.2eq, CH_3NO_2, c=0.02, r.t.	~20%
9	DDQ 1.2eq, Acetone ,c=0.02, r.t.	~50%
10	DDQ 1.2eq, THF, c=0.02, r.t.	~50%
11[b]	DDQ 1.2eq, THF, c=0.02, 40°C	63%

[a] The oxidative cyclization reaction was performed at a 0.02 mmol scale. [b] The oxidative cyclization reaction was run on a 0.2 mmol scale.

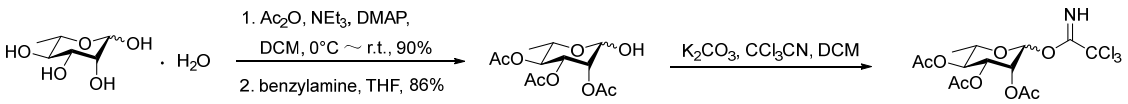
Compound 17:



To a solution of **13** (100 mg, 248 μmol) in anhydrous CH_3CN (4 mL) was added $KHCO_3$ (124 mg, 1.2 mmol) at room temperature, and the mixture was stirred for 30

minutes. Then Lev_2O (0.1 ml, 546 μmol) was added dropwise.[6] After stirring at room temperature for 2 h, TLC indicated the reaction was complete. The reaction mixture was diluted with CH_2Cl_2, then washed with saturated $NaHCO_3$ and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford **17** (120 mg, 80%) as a white solid: $[\alpha]_D^{25} = 34.4$ (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.37 (m, 3H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 1H), 5.57 (s, 1H), 4.74 (dd, *J* = 10.7, 2.9 Hz, 1H), 4.53 (d, *J* = 7.7 Hz, 1H), 4.50 – 4.29 (m, 1H), 4.08 (dd, *J* = 12.2, 3.0 Hz, 1H), 4.00 (t, *J* = 8.7 Hz, 1H), 3.85 (t, *J* = 9.8 Hz, 1H), 3.73 – 3.60 (m, 3H), 3.46 (dd, *J* = 9.3, 7.8 Hz, 1H), 2.87 (m, 8H), 2.21 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.53, 206.48, 170.55, 170.54, 142.43, 142.35, 136.92, 135.18, 129.46, 128.48, 126.42, 124.81, 123.70, 121.80, 102.29, 98.63, 81.35, 80.33, 71.97, 70.82, 68.57, 68.38, 37.82, 29.97, 27.81; HR-ESI-MS (*m/z*) calcd for $C_{31}H_{38}O_{12}N$ $[M + NH_4]^+$ 616.2389, found 616.2392.

Compound 18:

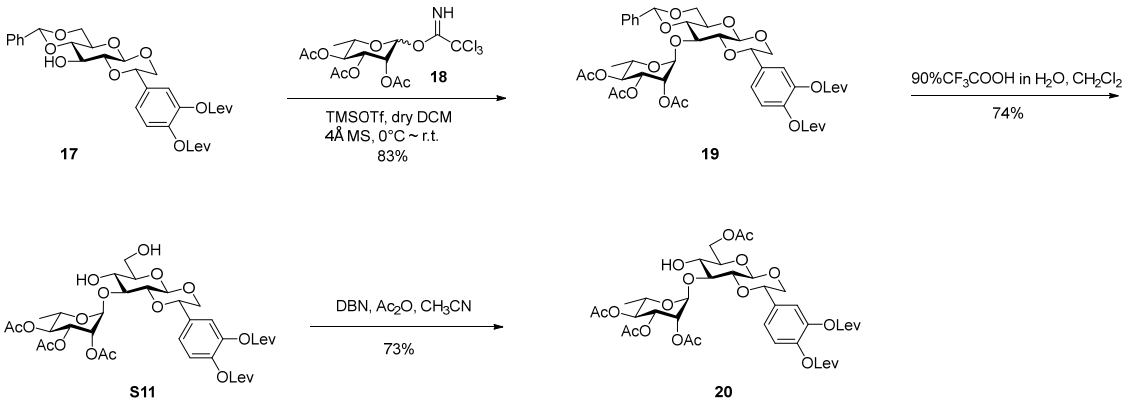


To a solution of L-rhamnose-monohydrate (16.4 g, 100 mmol) in 600 mL dichloromethane was added DMAP (1.23 g, 10 mmol), triethylamine (126 mL, 900 mmol) and acetic anhydride (60.4 mL, 600 mmol) under ice bath. After stirring at room temperature overnight, the reaction was basically complete. Then the mixture was concentrated under vacuum, and washed with $NaHCO_3$, extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone = 3:1) to give the product (30 g, 90 %). Then the above product (22.7 g, 68.3 mmol) was dissolved in 200 mL THF, and benzylamine (11 mL, 102.5 mmol) was added. The reaction was basically complete after stirring at room temperature overnight, then quenched with HCl and extracted with CH_2Cl_2. The organic phase was dried over

anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4: 1) to gvie **S10**[7] (17 g, 86%) as a yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.26 (dd, *J* = 3.5, 1.9 Hz, 1H), 5.15 (d, *J* = 1.8 Hz, 1H), 5.07 (t, *J* = 10.0 Hz, 1H), 4.16 – 4.08 (m, 1H), 2.15 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.21 (d, *J* = 6.3 Hz, 3H).

To a solution of compound **S10** (2.7 g, 9.1 mmol) in CH_2Cl_2 (50 mL) was added K_2CO_3 (7.6 g, 54.6 mmol) and trichloroacetonitrile (13.2 mL, 91 mmol). After stirring at room temperature overnight, the reaction was basically complete. Then K_2CO_3 was filtered through a Celite bed. The filtrate was concentrated under vacuum and azeotropically dried with toluene twice to give compound **18** as a yellow syrup, which can be directly used for the next step.

Compounds 19 and 20:



Glycosyl donor **18** (100 mg, 217 μmol)) and acceptor **17** (100 mg, 167 μmol)) were dissolved in anhydrous dichloromethane (4 mL). Powdered freshly activated 4 Å molecular sieves (0.2 g) were added, and the mixture was stirred at room temperature for 30 minutes under argon. Then the mixture was cooled to 0 °C, and TMSOTf (15 μL, 83.5 μmol) was added. After stirring at 0 °C for 2 h, TLC indicated the reaction was complete. The reaction mixture was returned to room temperature and filtered through a Celite bed. The filtrate was washed with saturated $NaHCO_3$ and brine, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1 to 3:1) to afford **19** (0.12 g, 83%) as a

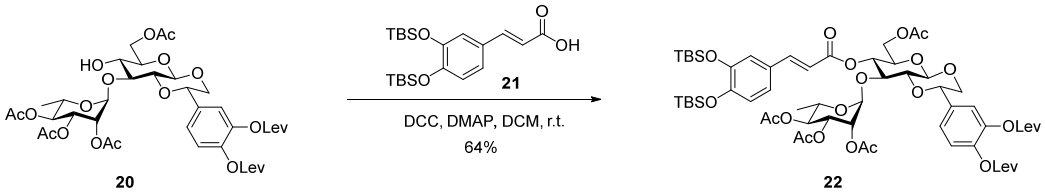
white foam: $[\alpha]_D^{25}$ = 1.9 (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.33 (m, 3H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 1.9 Hz, 1H), 5.59 (s, 1H), 5.31 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.24 (dd, *J* = 10.0, 3.5 Hz, 1H), 5.07 (d, *J* = 1.7 Hz, 1H), 4.95 (t, *J* = 10.0 Hz, 1H), 4.74 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.41 (dd, *J* = 10.5, 4.7 Hz, 1H), 4.23 (m, 1H), 4.12 – 4.06 (m, 2H), 3.86 (t, *J* = 10.2 Hz, 1H), 3.74 (t, *J* = 9.3 Hz, 1H), 3.69 – 3.59 (m, 2H), 3.56 (dd, *J* = 9.3, 7.8 Hz, 1H), 2.87 (m, 8H), 2.21 (s, 3H), 2.20 (s, 3H), 2.06 (s, 3H), 1.93 (s, 3H), 1.93 (s, 3H), 0.92 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.41, 206.34, 170.56, 170.42, 170.30, 170.03, 169.96, 142.30, 142.14, 137.06, 135.18, 129.17, 128.15, 126.31, 124.40, 123.67, 121.12, 101.91, 98.73, 97.72, 81.24, 79.40, 76.45, 73.37, 72.03, 70.98, 69.35, 69.31, 68.77, 68.58, 66.16, 37.83, 37.81, 29.96, 27.83, 27.81, 20.99, 20.86, 16.98; HR-ESI-MS (*m/z*) calcd for $C_{43}H_{50}O_{19}Na$ $[M + Na]^+$ 893.2839, found 893.2841.

To a solution of **19** (600 mg, 688 μmol) in dichloromethane (4 mL) was added 90% trifluoroacetic acid in water (0.43 ml, 3.4 mmol). After stirring at room temperature for 10 h, TLC indicated the reaction was complete. Then $NaHCO_3$ was added dropwise to quench the reaction, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone = 2:1 to 1:1) to afford product **S11** (396 mg, 74%) as a white foam: $[\alpha]_D^{25}$ = 26.9 (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.13 – 7.10 (m, 2H), 5.31 (dd, *J* = 9.9, 3.4 Hz, 1H), 5.28 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.14 (d, *J* = 1.8 Hz, 1H), 5.02 (t, *J* = 9.9 Hz, 1H), 4.71 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.43 (d, *J* = 7.8 Hz, 1H), 4.20 (m, 1H), 4.06 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.96 (dd, *J* = 12.1, 3.2 Hz, 1H), 3.87 (dd, *J* = 12.1, 4.2 Hz, 1H), 3.81 (t, *J* = 9.0 Hz, 1H), 3.76 (t, *J* = 9.0 Hz, 1H), 3.58 (dd, *J* = 12.2, 10.6 Hz, 1H), 3.54 (dd, *J* = 8.5, 4.6 Hz, 1H), 3.44 (dd, *J* = 9.3, 7.8 Hz, 1H), 2.86 (m, 8H), 2.21 (s, 3H), 2.20 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H), 1.22 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.41, 206.38, 170.51, 170.41, 170.31, 170.10, 169.92, 142.24, 142.06, 135.34, 124.39, 123.59, 121.13, 98.17, 97.86, 79.53, 79.31, 76.06, 71.67, 71.28, 69.69, 69.34, 68.89, 67.08, 62.11, 37.81, 37.79, 29.93, 29.91, 27.81, 27.78, 20.88, 20.86,

20.79, 17.55; HR-ESI-MS (*m/z*) calcd for $C_{36}H_{50}O_{19}N$ $[M + NH_4]^+$ 800.2972, found 800.2981, $C_{36}H_{46}O_{19}Na$ $[M + Na]^+$ 805.2526, found 805.2528.

To a solution of **S11** (390 mg, 498 μmol) in anhydrous CH_3CN (10 mL) were added 1,5-diazabicyclo[4.3.0]non-5-ene (12 μL, 0.1 mmol) and acetic anhydride (52 μL, 548 μmol) dropwise.[8] After stirring at room temperature for 24 h, TLC indicated the reaction was complete. The reaction mixture was then concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ acetone = 3:1 to 2:1) to afford **20** (300 mg, 73%) as a white foam: $[\alpha]_D^{25}$ = 9.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 1.9 Hz, 1H), 5.33 – 5.26 (m, 2H), 5.12 (d, *J* = 1.7 Hz, 1H), 5.02 (t, *J* = 9.8 Hz, 1H), 4.71 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.54 (dd, *J* = 12.3, 4.2 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.37 – 4.32 (m, 1H), 4.27 – 4.19 (m, 1H), 4.07 (dd, *J* = 12.2, 2.9 Hz, 1H), 3.82 (t, *J* = 9.1 Hz, 1H), 3.68 – 3.53 (m, 3H), 3.44 (dd, *J* = 9.5, 7.8 Hz, 1H), 2.93 – 2.81 (m, 8H), 2.21 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.22 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.44, 206.39, 172.03, 170.54, 170.44, 170.30, 170.14, 169.95, 142.28, 142.11, 135.32, 124.41, 123.63, 121.15, 98.26, 97.89, 79.62, 78.52, 76.13, 75.87, 71.66, 71.22, 69.62, 68.99, 67.02, 63.07, 37.84, 37.81, 29.97, 29.95, 27.84, 27.81, 21.05, 20.93, 20.89, 20.82, 17.52; HR-ESI-MS (*m/z*) calcd for $C_{38}H_{48}O_{20}Na$ $[M + Na]^+$ 847.2631, found 847.2635.

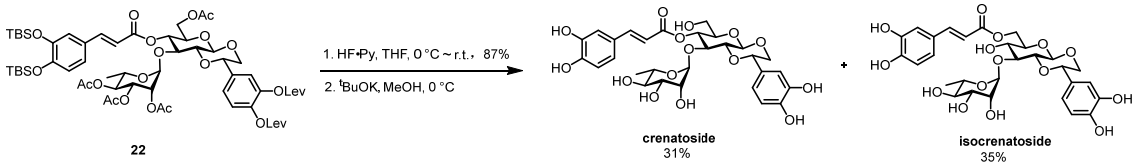
Compound 22:



To a solution of compound **20** (200 mg, 242 μmol) in anhydrous CH_2Cl_2 (5 mL) were added *tert*-butyldimethylsilyl protected caffeic acid **21** (200 mg, 485 μmol), dicyclohexylcarbodiimide (100 mg, 485 μmol), and 4-dimethylaminopyridine (29 mg, 242 μmol) in sequence. After stirring at room temperature for 10 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was

washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford **22** (190 mg, 64%) as a white foam: $[\alpha]_D^{25}$ = -28.6 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 15.8 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.08 (s, 1H), 7.00 (s, 2H), 6.81 (d, *J* = 6.8 Hz, 1H), 6.19 (d, *J* = 16.0 Hz, 1H), 5.28 (d, *J* = 11.3 Hz, 2H), 5.14 (s, 1H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.91 (t, *J* = 10.0 Hz, 1H), 4.75 (d, *J* = 10.4 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.21 (s, 2H), 4.09 (d, *J* = 10.2 Hz, 2H), 3.95 – 3.79 (m, 2H), 3.61 (t, *J* = 10.0 Hz, 2H), 2.85 (s, 8H), 2.20 (d, *J* = 4.5 Hz, 6H), 2.09 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.64 (s, 3H), 1.07 (d, *J* = 6.1 Hz, 3H), 0.97 (d, *J* = 3.4 Hz, 18H), 0.19 (d, *J* = 3.8 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.36, 206.31, 170.86, 170.45, 170.36, 170.03, 169.73, 165.41, 150.06, 147.41, 146.67, 142.25, 142.12, 135.07, 127.64, 124.43, 123.58, 122.55, 121.28, 121.07, 120.53, 113.93, 98.10, 97.58, 80.05, 76.12, 75.79, 73.83, 71.57, 70.67, 69.33, 68.91, 68.43, 66.79, 62.43, 37.77, 37.76, 29.90, 29.88, 27.78, 27.75, 25.93, 25.90, 20.87, 20.74, 20.68, 20.41, 18.56, 18.49, 17.52, -4.02; HR-ESI-MS (*m/z*) calcd for $C_{59}H_{86}O_{23}Si_2N$ $[M + NH_4]^+$ 1232.5124, found 1232.5129.

Crenatoside (1) and Isocrenatoside (2):



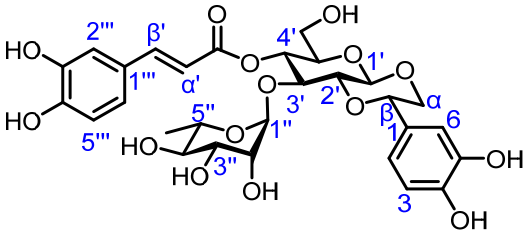
To a solution of compound **22** (120 mg, 98 μmol) in THF (3.3 mL) in a plastic bottle was added HF·py (0.3 mL, 3 mmol) dropwise at 0 °C. After stirring at room temperature for 10 h, TLC indicated the reaction was complete. Then saturated aqueous $NaHCO_3$ was added dropwise at 0 °C to quench the reaction, and the mixture was extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography to give the product (86 mg, 87 %). The above product (80 mg, 81 μmol) was added into MeOH (4 mL), and potassium *tert*-butoxide (12 % in THF, 1 mol/L, 40

μL, 41 μmol) was added dropwise at 0 °C. Then, potassium *tert*-butoxide (40 μL, 41 μmol) was added at 1 h, 2 h, 3 h, and 4 h, respectively. After 12 h, the reaction was basically complete. The mixture was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford crenatoside **1** (15.3 mg, 31%) as a yellow solid and isocrenatoside **2** (17.8 mg, 35%) as a yellow solid.

Crenatoside (**1**): $[\alpha]_D^{25}$ = -32.9 (*c* 0.3, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.62 (d, *J* = 15.8 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 6.97 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 5.17 (d, *J* = 1.7 Hz, 1H), 5.13 – 5.07 (m, 1H), 4.61 (dd, *J* = 10.6, 3.0 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.14 (t, *J* = 9.4 Hz, 1H), 3.99 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.77 (m, 2H), 3.71 – 3.63 (m, 2H), 3.61 – 3.55 (m, 2H), 3.52 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.46 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.27 (t, *J* = 9.5 Hz, 1H), 1.12 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 167.98, 149.85, 148.27, 146.84, 146.43, 146.38, 129.83, 127.65, 123.27, 118.91, 116.50, 116.24, 115.28, 114.50, 114.46, 102.21, 99.06, 81.95, 78.45, 77.83, 77.43, 73.58, 72.97, 72.09, 71.96, 70.41, 70.17, 62.10, 18.32; HR-ESI-MS (*m/z*) calcd for $C_{29}H_{34}O_{15}Na$ $[M + Na]^+$ 645.1790, found 645.1799.

Isocrenatoside (**2**): $[\alpha]_D^{25}$ = 20.6 (*c* 0.7, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.59 (d, *J* = 15.8 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 6.96 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.56 (m, 2H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.37 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.03 (m, 1H), 3.96 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.85 (t, *J* = 9.2 Hz, 1H), 3.82 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.78 (m, 1H), 3.70 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.62 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.58 – 3.53 (m, 1H), 3.39 – 3.37 (m, 1H), 3.36 – 3.34 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 169.03, 149.66, 147.31, 146.81, 146.80, 146.39, 146.34, 129.91, 127.68, 123.07, 118.96, 116.51, 116.21, 115.14, 114.73, 114.55, 101.84, 99.07, 81.92, 78.74, 78.37, 77.29, 73.97, 72.94, 72.13, 72.04, 70.23, 69.83, 64.48, 17.93; HR-ESI-MS (*m/z*) calcd for $C_{29}H_{34}O_{15}Na$ $[M + Na]^+$ 645.1790, found 645.1785.

Table S3 Comparison of ^{1}H NMR spectra between crenatoside and the synthetic **1**.



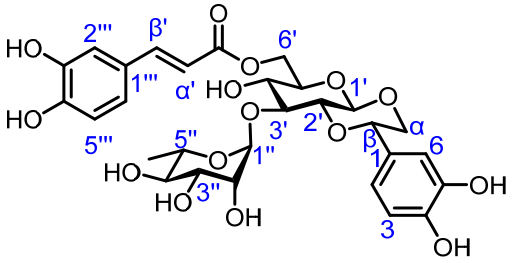
1 (crenatoside)

Position	Natural product[9]	Synthetic 1	Δδ (N.−S.)
phenylethanol moiety			
2	6.83 d (1.8)	6.83 d (2)	0.00
5	6.74 d (8.4)	6.73 d (8.1)	0.01
6	6.69 dd (1.8/8.4)	6.69 dd (2/8.2)	0.00
β	4.59 dd (3/10.5)	4.61 dd (3/10.6)	-0.02
α	3.98 dd (3/12.5) 3.63	3.99 dd (2.9/12.1) 3.64	-0.01
α-glucose			
1′	4.54 d (7.8)	4.56 d (7.8)	-0.02
2′	3.45 dd (7.8/9.5)	3.46 dd (7.8/9.6)	-0.01
3′	4.13 t (9.5)	4.14 t (9.4)	-0.01
4′	5.08 t (9.5)	5.1 t (9.4)	-0.02
5′	3.76	3.77	-0.01
6′	3.67/3.56	3.66/3.57	0.01/-0.01
L-rhamnose			
1″	5.15 d (1.8)	5.17 d (1.7)	-0.02
2″	3.77	3.77	0.00
3″	3.51 dd (3.5/10)	3.52 dd (3.3/9.6)	-0.01
4″	3.26 t (10)	3.27 t (9.5)	-0.01
5″	3.59	3.59	0.00
6″	1.10 d (6.5)	1.12 d (6.2)	-0.02
Caffeoyl moiety			
2‴	7.06 d (2)	7.07 d (2.1)	-0.01
5‴	6.78 d (8.5)	6.79 d (8.2)	-0.01
6‴	6.97 dd (2/8.5)	6.97 dd (2.1/8.2)	0.00
β'	7.61 d (16)	7.62 d (15.8)	-0.01
α'	6.28 d (16)	6.28 d (15.9)	0.00

Table S4 Comparison of ^{13}C NMR spectra between crenatoside[9] and the synthetic **1**.

Position	Natural product[9]	Synthetic product	Δδ(N.−S.)
phenylethanol moiety			
1	129.85	129.83	0.02
2	114.52	114.5	0.02
3	146.87	149.85	**-2.98**
4	146.87	146.84	0.03
5	116.27	116.24	0.03
6	118.96	118.91	0.05
β	78.97	78.45	**0.52**
α	73.00	72.97	0.03
α-glucose			
1′	99.08	99.06	0.02
2′	81.97	81.95	0.02
3′	77.46	77.43	0.03
4′	70.2	70.17	0.03
5′	77.88	77.83	0.05
6′	62.14	62.10	0.04
L-rhamnose			
1″	102.22	102.21	0.01
2″	72.14	72.09	0.05
3″	72.03	71.96	0.07
4″	73.63	73.58	0.05
5″	70.46	70.41	0.05
6″	18.38	18.32	0.06
Caffeoyl moiety			
1‴	127.71	127.65	0.06
2‴	115.31	115.28	0.03
3‴	146.43	146.43	0.00
4‴	146.43	146.38	0.05
5‴	116.53	116.5	0.03
6‴	123.32	123.27	0.05
β'	148.29	148.27	0.02
α'	114.52	114.46	0.06
C=O	168.02	167.98	0.04

Table S5 Comparison of ^{1}H NMR spectrum between isocrenatoside[10] and the synthetic **2**.



2 (isocrenatoside)

Position	Natural product[10]	Synthetic product	Δδ(N.−S.)
phenylethanol moiety			
2	6.81 d (1.5)	6.82 d (2.0)	-0.01
5	6.73 d (8.0)	6.73 d (8.1)	0.00
6	6.67 dd (2.0/8.0)	6.68 dd (2.0/8.2)	-0.01
β	4.56	4.56	0.00
α	3.95 dd (2.5/12.0) 3.62	3.96 dd (3.0/12.0) 3.62	-0.01/0.00
α-glucose			
1′	4.48 d (8.0)	4.49 d (7.8)	-0.01
2′	3.37	3.37	0.00
3′	3.83	3.85	-0.02
4′	3.55	3.55	0.00
5′	4.00	4.03	-0.03
6′	4.36/4.54	4.37/4.56	-0.01/-0.02
L-rhamnose			
1″	5.19 d (1.0)	5.20 d (1.7)	-0.01
2″	3.81	3.82	-0.01
3″	3.69 dd (3.5/9.5)	3.70 dd (3.4/9.5)	-0.01
4″	3.35	3.35	0.00
5″	4.00	3.96	-0.04
6″	1.25 d (6.0)	1.25 d (6.2)	0.00
Caffeoyl moiety			
2‴	7.05 d (2.0)	7.06 d (2.1)	-0.01
5‴	6.78 d (8.5)	6.79 d (8.2)	-0.01
6‴	6.96 dd (1.5/8.0)	6.96 dd (2.1/8.2)	0.00

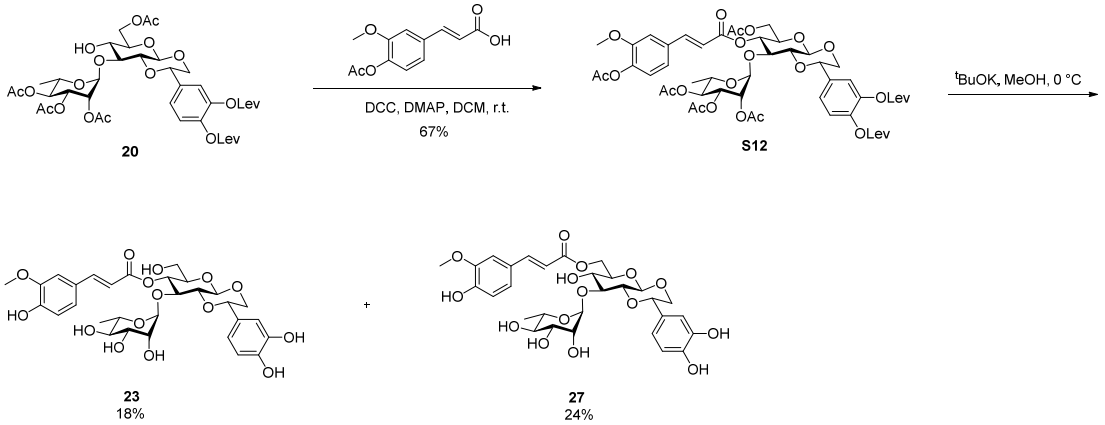
β'	7.58 d (15.5)	7.59 d (15.8)	-0.01
α'	6.30 d (16.0)	6.31 d (15.8)	-0.01

Table S6 Comparison of ^{13}C NMR spectrum between isocrenatoside[10] and the synthetic **2**.

Position	Natural product[10]	Synthetic product	Δδ(N.−S.)
phenylethanol moiety			
1	129.9	129.9	0.0
2	114.8	114.7	0.1
3	146.4	146.3	0.1
4	146.5	146.4	0.1
5	116.3	116.2	0.1
6	119.0	119.0	0.0
β	78.4	78.3	0.1
α	73.0	73.0	0.0
α-glucose			
1′	99.1	99.1	0.0
2′	82.0	81.9	0.1
3′	78.8	78.7	0.1
4′	70.3	70.2	0.1
5′	77.4	77.3	0.1
6′	64.6	64.5	0.1
L-rhamnose			
1″	101.9	101.8	0.1
2″	72.2	72.1	0.1
3″	72.1	72.0	0.1
4″	74.0	74.0	0.0
5″	69.9	69.8	0.1
6″	18.0	17.9	0.1
Caffeoyl moiety			
1‴	127.7	127.7	0.0
2‴	115.2	115.1	0.1
3‴	146.9	146.8	0.1
4‴	149.7	149.7	0.0
5‴	116.6	116.5	0.1

6'''	123.1	123.1	0.0
β'	147.4	147.3	0.1
α'	114.6	114.6	0.0
C=O	169.1	169.0	0.1

Compounds 23 and 27:



To a solution of compound **20** (80 mg, 97 μmol) in anhydrous CH_2Cl_2 (3.2 mL) was added 3-methoxy-4-acetoxy-cinnamic acid (46.4 mg, 194 μmol), dicyclohexylcarbodiimide (40 mg, 194 μmol), 4-dimethylaminopyridine (11.8 mg, 97 μmol) in sequence. After stirring at room temperature for 7 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S12** (68 mg, 67%) as a white foam: $[\alpha]_D^{25}$ = -25.9 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 15.9 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.15 – 7.11 (m, 2H), 7.10 (s, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 5.30 (t, *J* = 9.7 Hz, 1H), 5.27 (m, 1H), 5.14 (d, *J* = 1.7 Hz, 1H), 5.10 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.93 (t, *J* = 10.0 Hz, 1H), 4.77 (m, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.23 (m, 2H), 4.14 – 4.04 (m, 2H), 3.88 (d, *J* = 6.9 Hz, 1H), 3.86 (s, 3H), 3.83 (dd, *J* = 10.0, 6.3 Hz, 1H). 3.71 – 3.57 (m, 2H), 2.87 (dd, *J* = 8.3, 4.0 Hz, 8H), 2.32 (s, 3H), 2.21 (s, 3H), 2.22 (s, 3H), 2.11 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H), 1.09 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.39, 206.34, 170.95, 170.53, 170.44, 170.14, 169.85, 169.80, 168.74, 165.09, 151.73, 146.09, 142.35, 142.23, 142.06, 135.11, 133.04, 129.18, 128.37,

125.44, 124.52, 123.68, 123.60, 121.33, 121.15, 116.78, 111.59, 98.34, 97.72, 79.99, 76.27, 73.90, 71.71, 70.75, 69.52, 68.90, 68.82, 67.05, 62.49, 56.11, 37.87, 37.85, 30.00, 29.98, 27.87, 27.84, 21.60, 20.97, 20.83, 20.77, 20.48, 17.64; HR-ESI-MS (*m/z*) calcd for $C_{50}H_{62}O_{24}N$ $[M + NH_4]^+$ 1060.3656, found 1060.3661, $C_{50}H_{58}O_{24}Na$ $[M + Na]^+$ 1065.3210, found 1065.1210.

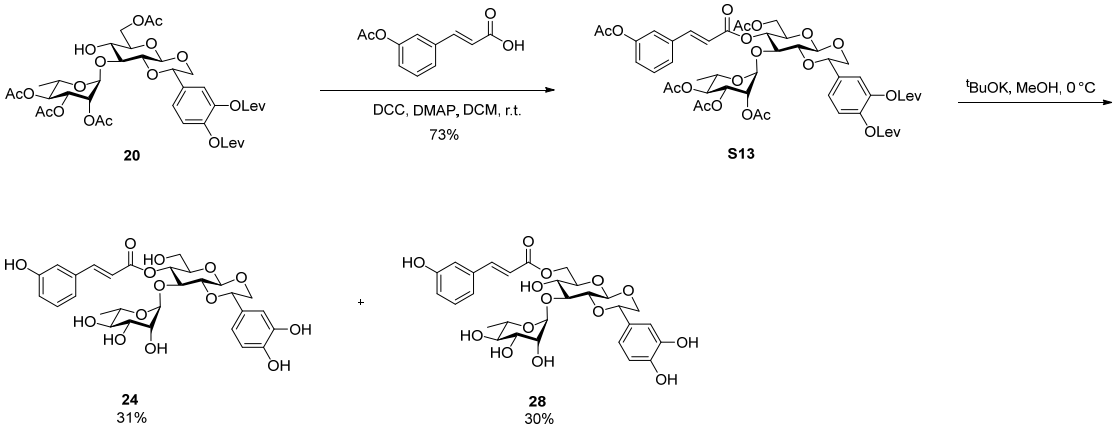
To a solution of the compound **S12** (36 mg, 35 μmol) in MeOH (1.7 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 17 μL, 17 μmol) dropwise at 0 °C. Then, potassium *tert*-butoxide (17 μL, 17 μmol) was added at 1 h, 2 h, 3 h, 5 h, 7 h, 9 h respectively. After 12 h, the reaction was basically complete. Then the mixture was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **23** (4.2 mg, 18%) as a white solid and **27** (5.7 mg, 24%) as a white solid.

23: $[\alpha]_D^{25}$ = -63.9 (*c* 0.2, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.68 (d, *J* = 15.8 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.84 – 6.82 (m, 2H), 6.75 – 6.60 (m, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 5.19 (d, *J* = 1.7 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 4.61 (dd, *J* = 10.4, 2.9 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.14 (t, *J* = 9.4 Hz, 1H), 3.99 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.90 (s, 3H), 3.78 (m, 2H), 3.67 (m, 2H), 3.60 (m, 2H), 3.52 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.47 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.27 (t, *J* = 9.6 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 167.96, 150.86, 149.39, 148.15, 146.44, 146.39, 129.83, 127.67, 124.45, 118.91, 116.48, 116.24, 114.90, 114.51, 111.80, 102.15, 99.08, 81.98, 78.46, 77.85, 77.23, 73.57, 72.98, 72.09, 71.98, 70.39, 70.23, 62.12, 56.44, 18.29; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{15}Na$ $[M + Na]^+$ 659.1946, found 659.1948.

27: $[\alpha]_D^{25}$ = 23.1 (*c* 0.5, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.65 (d, *J* = 15.9 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.1 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.60 – 4.54 (m, 2H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.38 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.03 (m, 1H), 3.96 (dd, *J* = 12.0, 2.9 Hz, 1H), 3.90 (s, 3H), 3.85 (t, *J* = 9.2 Hz, 1H), 3.82 (dd, *J* = 3.3, 1.7 Hz, 1H), 3.77 (m, 1H), 3.70 (dd, *J* = 9.5, 3.4 Hz,

1H), 3.62 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.57 (dd, *J* = 10.0, 8.8 Hz, 1H), 3.40 – 3.33 (m, 2H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.99, 150.69, 149.40, 147.18, 146.41, 146.37, 129.92, 127.69, 124.23, 118.96, 116.48, 116.21, 115.15, 114.55, 111.70, 101.86, 99.10, 81.94, 78.76, 78.39, 77.30, 73.97, 72.96, 72.15, 72.05, 70.22, 69.84, 64.48, 56.46, 17.94; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{15}Na$ $[M + Na]^+$ 659.1946, found 659.1939.

Compounds 24 and 28:



To a solution of compound **20** (80 mg, 97 μmol) in anhydrous CH_2Cl_2 (3.2 mL) were added 3-acetoxy cinnamic acid (40 mg, 194 μmol), dicyclohexylcarbodiimide (40 mg, 194 μmol), 4-dimethylaminopyridine (11.8 mg, 97 μmol) in sequence. After stirring at room temperature for 7 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S13** (72 mg, 73%) as a white foam: $[\alpha]_D^{25}$ = -14.4 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.40 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.10 (s, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.30 (t, *J* = 9.6 Hz, 1H), 5.27 (m, 1H), 5.14 (s, 1H), 5.09 (dd, *J* = 10.2, 3.5 Hz, 1H), 4.92 (t, *J* = 10.0 Hz, 1H), 4.76 (m, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.23 (s, 2H), 4.15 – 4.04 (m, 2H), 3.89 (m, 1H), 3.82 (m, 1H), 3.63 (dd, *J* = 15.2, 8.0 Hz, 2H), 2.92 – 2.81 (m, 8H), 2.31 (s, 3H), 2.22 (s, 3H), 2.21 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H), 1.65 (s, 3H), 1.09 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 206.43, 206.38, 170.90, 170.51, 170.42, 170.15, 169.82, 169.18, 164.92, 151.30, 145.68, 142.29, 142.16, 135.60, 135.07, 130.14, 125.75, 124.47, 124.07, 123.64, 121.11, 117.61, 98.18, 97.64, 79.98, 76.19, 75.93, 73.79, 71.64, 70.66, 69.44, 68.86, 68.78, 67.00, 62.39, 37.82, 37.80, 29.95, 29.93, 27.82, 27.79, 21.18, 20.91, 20.79, 20.71, 20.37, 17.55; HR-ESI-MS (*m/z*) calcd for $C_{49}H_{60}O_{23}N$ $[M + NH_4]^+$ 1030.3551, found 1030.3546.

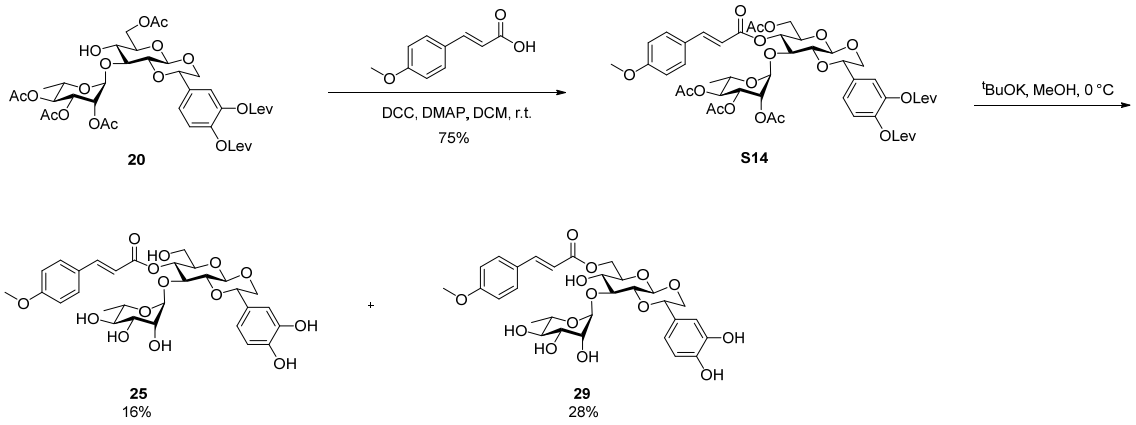
To a solution of the compound **S13** (49 mg, 0.0484 mmol) in MeOH (2.4 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 24 μL, 24 μmol) dropwise at 0 °C. Then, another potassium *tert*-butoxide (24 μL, 24 μmol) was added at 1 h, 2 h, 3 h, 5 h, 7 h respectively. After 12 h, the reaction was basically complete. Then neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **24** (9.3 mg, 31%) as a white solid and **28** (8.7 mg, 30%) as a white solid.

24: $[\alpha]_D^{25}$ = -12.8 (*c* 0.5, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.12 – 7.06 (m, 1H), 7.02 (t, *J* = 2.1 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 5.13 (t, *J* = 9.6 Hz, 1H), 4.61 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.15 (t, *J* = 9.4 Hz, 1H), 4.00 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.81 – 3.77 (m, 2H), 3.68 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.66 – 3.62 (m, 1H), 3.61 – 3.56 (m, 2H), 3.52 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.47 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.27 (t, *J* = 9.6 Hz, 1H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 167.39, 159.11, 147.78, 146.45, 146.40, 136.93, 131.04, 129.82, 129.78, 126.97, 121.05, 118.93, 118.90, 118.14, 116.23, 115.42, 114.50, 102.20, 99.06, 81.94, 78.47, 77.73, 77.35, 73.56, 72.98, 72.08, 71.96, 70.41, 62.07, 18.29; HR-ESI-MS (*m/z*) calcd for $C_{29}H_{38}O_{14}$ $[M + H]^+$ 624.2287, found 624.2282, $C_{29}H_{34}O_{14}Na$ $[M + Na]^+$ 629.1841, found 629.1836.

28: $[\alpha]_D^{25}$ = -2.4 (*c* 0.4, CH_3OH); ^1H NMR (600 MHz, CD_3OD) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.08 (m, 1H), 7.02 (t, *J* = 2.0 Hz, 1H), 6.84 (m, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.60 – 4.54 (m, 2H), 4.50 (d, *J* = 7.8 Hz, 1H),

4.39 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.03 (m, 1H), 3.96 (dd, *J* = 12.0, 2.9 Hz, 1H), 3.87 – 3.83 (m, 1H), 3.82 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.78 (m, 1H), 3.70 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.63 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.56 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.39 – 3.34 (m, 2H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.41, 159.11, 146.84, 146.43, 146.39, 136.97, 131.06, 129.91, 120.91, 118.95, 118.81, 118.35, 116.20, 115.28, 114.55, 101.87, 99.10, 81.95, 78.73, 78.41, 77.25, 73.98, 72.97, 72.15, 72.06, 70.24, 69.84, 64.67, 17.93; HR-ESI-MS (*m/z*) calcd for $C_{29}H_{34}O_{14}Na$ $[M + Na]^+$ 629.1841, found 629.1835.

Compounds 25 and 29:



To a solution of compound **20** (35 mg, 0.097 mmol) in anhydrous CH_2Cl_2 (3.2 mL) was added 4-methoxycinnamic acid (40 mg, 194 μmol), dicyclohexylcarbodiimide (40 mg, 194 μmol), 4-dimethylaminopyridine (11.8 mg, 97 μmol) in sequence. After stirring at room temperature, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S14** (81 mg, 75%) as a white foam: $[\alpha]_D^{25}$ = -33.0 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.9 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.17 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 1.9 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.28 (d, *J* = 15.9 Hz, 1H), 5.33 – 5.25 (m, 2H), 5.14 (d, *J* = 1.8 Hz, 1H), 5.09 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.91 (t, *J* = 10.0 Hz, 1H), 4.76 (dd, *J* = 10.4, 2.9 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.29 –

4.18 (m, 2H), 4.14 – 4.04 (m, 2H), 3.92 – 3.87 (m, 1H), 3.86 (d, *J* = 5.8 Hz, 1H), 3.83 (s, 3H), 3.65 – 3.58 (m, 2H), 2.86 (m, 8H), 2.21 (s, 3H), 2.20 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H), 1.65 (s, 3H), 1.07 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.40, 206.34, 170.90, 170.39, 170.08, 169.78, 165.47, 161.90, 146.41, 142.26, 142.13, 135.09, 129.98, 126.79, 124.45, 123.60, 121.08, 114.56, 97.61, 80.01, 76.15, 76.05, 73.87, 69.38, 68.91, 66.86, 62.46, 55.51, 37.79, 29.92, 29.90, 27.80, 20.90, 20.75, 20.70, 20.42, 17.56; HR-ESI-MS (*m/z*) calcd for $C_{48}H_{60}O_{22}N$ $[M + NH_4]^+$ 1002.3601, found 1002.3596.

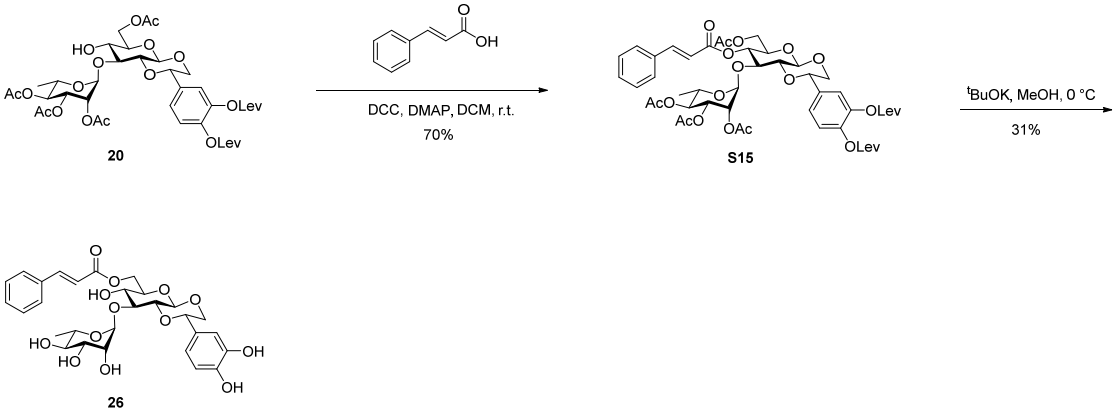
To a solution of the compound **S14** (60 mg, 60 μmol) in MeOH (3 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 30 μL, 30 μmol) dropwise at 0 °C. Then, another potassium *tert*-butoxide (30 μL, 30 μmol) was added at 1 h, 2 h, 3 h, 5 h respectively. After 6 h, the reaction was basically complete. Then the mixture was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **25** (6.1 mg, 16%) as a white solid and **29** (10.6 mg, 28%) as a white solid.

25: $[\alpha]_D^{25}$ = -28.3 (*c* 0.3, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.72 (d, *J* = 15.9 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 1.9 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 5.11 (t, *J* = 9.6 Hz, 1H), 4.61 (m, 1H), 4.56 (d, *J* = 7.8 Hz, 1H), 4.14 (t, *J* = 9.4 Hz, 1H), 4.01 – 3.95 (m, 2H), 3.84 (s, 3H), 3.77 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.67 (m, 2H), 3.61 – 3.56 (m, 2H), 3.52 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.46 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.26 (t, *J* = 9.5 Hz, 1H), 1.10 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 167.80, 163.38, 147.47, 146.44, 146.40, 131.23, 131.07, 129.83, 128.29, 118.91, 116.24, 115.54, 115.46, 114.50, 102.18, 99.07, 81.96, 78.46, 77.81, 77.34, 73.57, 72.98, 72.09, 71.97, 70.39, 70.27, 62.10, 55.90, 18.28; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{37}O_{14}$ $[M + H]^+$ 621.2178, found 621.2181, $C_{30}H_{36}O_{14}Na$ $[M + Na]^+$ 643.1997, found 643.2001.

29: $[\alpha]_D^{25}$ = 19.6 (*c* 0.5, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.69 (d, *J* = 15.9 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.73

(d, J = 8.1 Hz, 1H), 6.68 (dd, J = 8.1, 2.0 Hz, 1H), 6.43 (d, J = 15.9 Hz, 1H), 5.20 (d, J = 1.7 Hz, 1H), 4.56 (dd, J = 12.2, 2.1 Hz, 2H), 4.49 (d, J = 7.8 Hz, 1H), 4.38 (dd, J = 12.0, 5.6 Hz, 1H), 4.03 (m, 1H), 3.96 (dd, J = 12.0, 2.9 Hz, 1H), 3.86 (d, J = 9.1 Hz, 1H), 3.82 (s, 3H), 3.78 (m, 1H), 3.70 (dd, J = 9.6, 3.4 Hz, 1H), 3.62 (dd, J = 12.1, 10.6 Hz, 1H), 3.56 (dd, J = 9.9, 8.8 Hz, 1H), 3.42 – 3.36 (m, 2H), 1.25 (d, J = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.82, 163.25, 146.52, 146.41, 146.37, 131.07, 129.92, 128.31, 118.95, 116.21, 115.78, 115.45, 114.55, 101.86, 99.09, 81.94, 78.75, 78.39, 77.28, 73.97, 72.96, 72.15, 72.05, 70.23, 69.84, 64.55, 55.89, 17.93; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{37}O_{14}$ $[M + H]^+$ 621.2178, found 621.2173, $C_{30}H_{36}O_{14}Na$ $[M + Na]^+$ 643.1997, found 643.1993.

Compound 26:

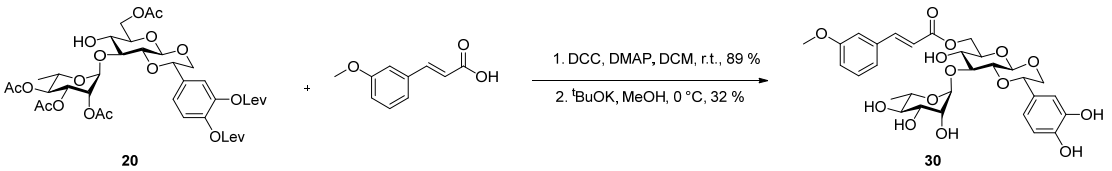


To a solution of compound **20** (75 mg, 90 μmol) in anhydrous CH_2Cl_2 (3 mL) were added *trans*-cinnamic acid (27 mg, 0.18 μmol), dicyclohexylcarbodiimide (37.2 mg, 180 μmol), 4-dimethylaminopyridine (11 mg, 90 μmol) in sequence. After stirring at room temperature for 20 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S15** (60 mg, 70%) as a white foam: $[\alpha]_D^{25}$ = -22.0 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 16.0 Hz, 1H), 7.52 (dd, J = 6.8, 2.9 Hz, 2H), 7.39 (dd, J = 5.2, 1.8 Hz, 3H), 7.18 (dd, J = 8.5, 2.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 5.31 (t, J = 9.7 Hz, 1H), 5.27 (dd, J = 3.5, 1.8 Hz, 1H), 5.14 (d, J = 1.8

Hz, 1H), 5.09 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.91 (t, *J* = 10.0 Hz, 1H), 4.76 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.23 (t, *J* = 3.4 Hz, 2H), 4.14 – 4.04 (m, 2H), 3.90 (m, 1H), 3.83 (m, 1H), 3.62 (m, 2H), 2.91 – 2.83 (m, 8H), 2.21 (s, 3H), 2.22 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H), 1.88 (s, 3H), 1.61 (s, 3H), 1.08 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.41, 206.35, 170.96, 170.54, 170.44, 170.13, 169.81, 169.80, 165.20, 146.82, 142.33, 142.21, 135.12, 134.12, 131.00, 129.20, 128.31, 124.52, 123.68, 121.15, 116.57, 98.25, 97.69, 80.07, 76.24, 76.00, 73.89, 71.70, 70.76, 69.44, 68.92, 68.72, 66.97, 62.48, 37.85, 30.00, 27.85, 20.97, 20.84, 20.77, 20.39, 17.61; HR-ESI-MS (*m/z*) calcd for $C_{47}H_{58}O_{21}N$ $[M + NH_4]^+$ 972.3496, found 972.3501, $C_{47}H_{54}O_{21}Na$ $[M + Na]^+$ 977.3050, found 977.3055.

To a solution of the compound **S15** (45 mg, 47 μmol) in MeOH (2.4 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 23 μL, 23 μmol) dropwise at 0 °C. Then, another potassium *tert*-butoxide (23 μL, 24 μmol) was added at 1 h, 2 h, 3 h respectively. After 12 h, the reaction was basically complete. Then the mixture was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **26** (8.7 mg, 31%) as a white solid: $[\alpha]_D^{25}$ = 9.2 (*c* 0.3, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.44 – 7.38 (m, 3H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.57 (m, 2H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.40 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.03 (m, 1H), 3.96 (dd, *J* = 12.0, 2.9 Hz, 1H), 3.85 (t, *J* = 9.2 Hz, 1H), 3.82 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.79 (m, 1H), 3.70 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.62 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.57 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.39 – 3.34 (m, 2H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.38, 146.66, 146.43, 146.38, 135.72, 131.60, 130.05, 129.91, 129.30, 118.95, 118.55, 116.20, 114.55, 101.87, 99.10, 81.95, 78.74, 78.40, 77.25, 73.97, 72.97, 72.15, 72.06, 70.24, 69.85, 64.68, 17.93; HR-ESI-MS (*m/z*) calcd for $C_{29}H_{38}O_{13}N$ $[M + NH_4]^+$ 608.2338, found 608.2336, $C_{29}H_{34}O_{13}Na$ $[M + NH_4]^+$ 613.1892, found 613.1893.

Compound 30:

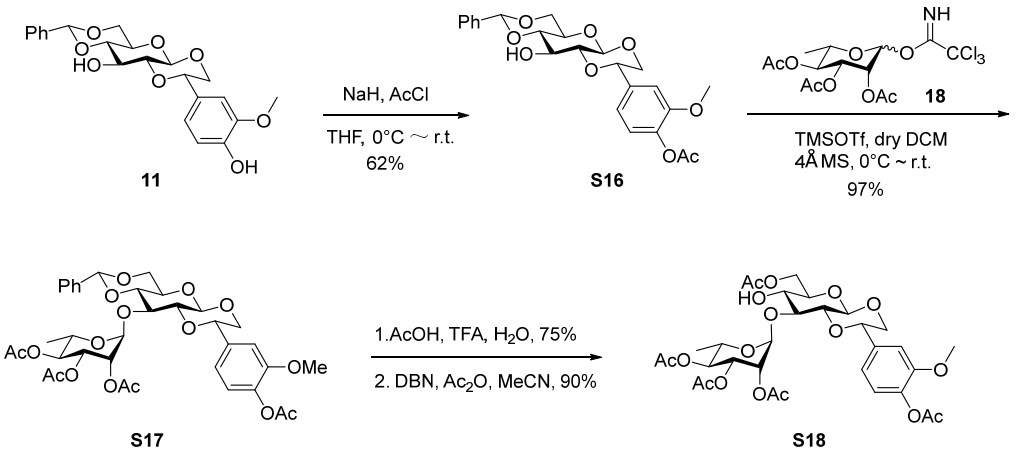


20 30

To a solution of compound **20** (50 mg, 60 μmol) in anhydrous CH_2Cl_2 (1.6 mL) was added 3-methoxycinnamic acid (21.3 mg, 120 μmol), dicyclohexylcarbodiimide (24.7 mg, 120 μmol), 4-dimethylaminopyridine (3.6 mg, 30 μmol) in sequence. After stirring at room temperature for 10 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford the product (55.5 mg, 89 %) as a white foam. To a solution of the above product (55 mg, 53 μmol) in MeOH (2.7 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 26 μL, 26 μmol) dropwise at 0 °C. Then, another potassium *tert*-butoxide (26 μL, 26 μmol) was added at 1 h, 2 h, 3 h respectively. After 7 h, the reaction was basically complete. Then the mixture was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **30** (10.3 mg, 32%) as a white solid: $[\alpha]_D^{25}$ = 17.0 (*c* 0.3, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.17 (t, *J* = 2.0 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.68 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.60 – 4.54 (m, 2H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.40 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.03 (m, 1H), 3.96 (dd, *J* = 12.0, 2.9 Hz, 1H), 3.86 (d, *J* = 9.1 Hz, 1H), 3.83 (s, 3H), 3.82 – 3.81 (m, 1H), 3.78 (m, 1H), 3.70 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.62 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.57 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.39 – 3.34 (m, 2H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.36, 161.58, 146.62, 146.47, 146.42, 137.06, 131.04, 129.87, 121.88, 118.93, 118.81, 117.57, 116.20, 114.55, 114.01, 101.87, 99.09, 81.94, 78.75, 78.41,

77.24, 73.97, 72.97, 72.14, 72.06, 70.22, 69.84, 64.68, 55.82, 17.93. HR-ESI-MS (*m/z*) calcd for $C_{30}H_{35}O_{14}$ $[M - H]^-$ 619.2032, found 619.2039.

Compounds 31 and 38:



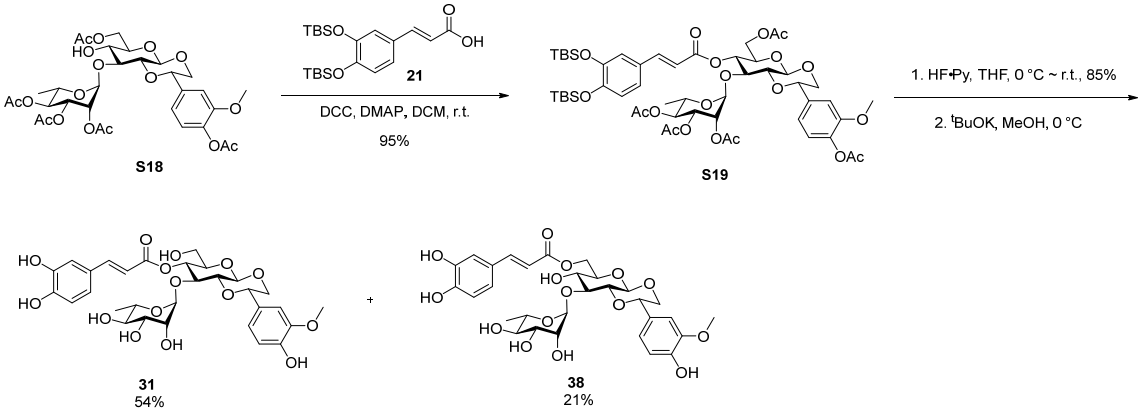
To a solution of **11** (1.2 g, 2.8 mmol) in anhydrous THF (55 mL) was added NaH (120 mg, 60 % dispersion in mineral oil, 3.0 mmol) at 0 °C and stirred for 30 minutes. Then AcCl (0.21 ml, 3.0 mmol) was added dropwise over the course of 5 minutes.[11] The reaction mixture was stirred at room temperature for 3 h, then quenched with saturated NH_4Cl, extracted with CH_2Cl_2, and washed with saturated brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone = 9:1 to 6:1) to afford **S16** (780 mg, 62%) as a white foam: $[\alpha]_D^{25} = 41.9$ (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.2, 2.5 Hz, 2H), 7.38 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.94 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.58 (s, 1H), 4.75 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.58 (d, *J* = 7.7 Hz, 1H), 4.43 (dd, *J* = 10.5, 3.8 Hz, 1H), 4.09 (dd, *J* = 12.3, 2.9 Hz, 1H), 4.05 (t, *J* = 8.9 Hz, 1H), 3.86 (m, 4H), 3.74 (dd, *J* = 12.2, 10.6 Hz, 1H), 3.71 – 3.64 (m, 2H), 3.49 (dd, *J* = 9.3, 7.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.06, 151.36, 140.01, 136.89, 135.16, 129.51, 128.51, 126.41, 123.03, 119.10, 110.86, 102.33, 98.71, 81.41, 80.37, 77.98, 72.19, 70.92, 68.60, 68.38, 56.13, 20.79; HR-ESI-MS (*m/z*) calcd for $C_{24}H_{27}O_9$ $[M + H]^+$ 459.1650, found 459.1647.

Glycosyl donor **18** (750 mg, 1.6 mmol) and acceptor **S16** (1020 mg, 2.4 mmol)

were dissolved in anhydrous dichloromethane (60 mL). Powdered freshly activated 4 Å molecular sieves (4.0 g) were added and the mixture was stirred at room temperature for 30 minutes under argon. Then the mixture was cooled to 0 °C and TMSOTf (90 μL, 0.48 mmol) was added. After stirring at 0 °C for 2 h, the reaction mixture was returned to room temperature and filtered through a Celite bed. The filtrate was washed with saturated $NaHCO_3$, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4:1 to 3:1) to afford **S17** (1160 mg, 97%) as a white foam: $[\alpha]_D^{25}$ = -1.3 (*c* 2.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.37 – 7.31 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.88 (m, 2H), 5.60 (s, 1H), 5.32 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.24 (dd, *J* = 10.1, 3.5 Hz, 1H), 5.09 (d, *J* = 1.8 Hz, 1H), 4.95 (t, *J* = 10.0 Hz, 1H), 4.74 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.54 (d, *J* = 7.8 Hz, 1H), 4.43 (dd, *J* = 10.5, 4.7 Hz, 1H), 4.24 (m, 1H), 4.16 – 4.06 (m, 2H), 3.88 (t, *J* = 10.3 Hz, 1H), 3.83 (s, 3H), 3.76 (t, *J* = 9.3 Hz, 1H), 3.71 – 3.63 (m, 2H), 3.58 (dd, *J* = 9.3, 7.8 Hz, 1H), 2.31 (s, 3H), 2.10 – 2.01 (s, 3H), 1.93 (d, *J* = 0.7 Hz, 6H), 0.92 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.35, 170.06, 170.03, 169.10, 151.20, 139.70, 135.31, 129.21, 128.19, 126.34, 122.96, 118.51, 110.41, 101.96, 98.85, 97.74, 81.29, 79.47, 73.38, 72.29, 70.96, 69.45, 69.37, 68.83, 66.23, 56.08, 21.02, 20.89, 20.82, 17.01; HR-ESI-MS (*m/z*) calcd for $C_{36}H_{42}O_{16}Na$ [M + Na]$^+$ 753.2365, found 753.2370.

To a solution of **S17** (1.1 g, 1.5 mmol) in acetic acid (50 mL) and water (12.5 mL) was added trifluoroacetic acid (3 mL, 26.3 mmol). After stirring at room temperature for 10 h, TLC indicated the reaction was complete. Then $NaHCO_3$ was added dropwise to quench the reaction, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 1:1) to afford product (720 mg, 75 %) as a white solid. To a solution of above product (700 mg, 1.1 mmol) in anhydrous CH_3CN (21 mL) was added 1,5-diazabicyclo[4.3.0]non-5-ene (27 μL, 218 μmol) and acetic anhydride (0.11ml, 1.2 mmol) in sequence.[12] After stirring at room temperature for 24 h, TLC indicated the reaction was complete. The reaction was then

concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1 to 1:1) to afford **S18** (680 mg, 90%) as a white foam: $[\alpha]_D^{25}$ = 11.7 (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.85 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.35 – 5.25 (m, 2H), 5.16 (d, *J* = 1.7 Hz, 1H), 5.02 (t, *J* = 9.8 Hz, 1H), 4.69 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.49 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.36 (dd, *J* = 12.2, 2.1 Hz, 1H), 4.22 (m, 1H), 4.08 (dd, *J* = 12.1, 3.0 Hz, 1H), 3.82 (m, 4H), 3.64 – 3.61 (m, 1H), 3.60 – 3.51 (m, 2H), 3.44 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.29 (s, 3H), 2.14 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H), 1.21 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.96, 170.34, 170.11, 169.96, 169.09, 151.18, 139.58, 135.40, 122.84, 118.33, 110.37, 98.19, 97.92, 79.53, 78.56, 76.70, 75.82, 71.81, 71.13, 69.64, 69.04, 69.01, 67.02, 63.14, 56.03, 21.04, 20.92, 20.89, 20.80, 20.76, 17.51; $C_{31}H_{44}O_{17}N$ $[M + NH_4]^+$ 702.2604, found 702.2607; $C_{31}H_{40}O_{17}Na$ $[M + Na]^+$ 707.2158, found 707.2158.



To a solution of compound **S18** (100 mg, 146 μmol) in anhydrous CH_2Cl_2 (4 mL) was added *tert*-butyldimethylsilyl protected caffeic acid **21** (120 mg, 292 μmol), dicyclohexylcarbodiimide (60 mg, 292 μmol), 4-dimethylaminopyridine (17 mg, 146 μmol) in sequence. After stirring at room temperature for 10 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S19** (148 mg, 95%) as a white foam: $[\alpha]_D^{25}$ = -32.9 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.09 – 6.95 (m, 3H), 6.90 – 6.84 (m, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H), 5.37 – 5.25 (m, 2H),

5.19 (d, J = 1.8 Hz, 1H), 5.08 (dd, J = 10.2, 3.4 Hz, 1H), 4.91 (t, J = 10.0 Hz, 1H), 4.75 (dd, J = 10.6, 2.9 Hz, 1H), 4.49 (d, J = 7.8 Hz, 1H), 4.29 – 4.18 (m, 2H), 4.15 – 4.08 (m, 2H), 3.91 (m, 1H), 3.88 – 3.83 (m, 1H), 3.83 (s, 3H), 3.70 – 3.57 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.88 (s, 3H), 1.63 (s, 3H), 1.09 (d, J = 6.3 Hz, 3H), 0.98 (d, J = 6.2 Hz, 18H), 0.23 – 0.16 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.97, 170.11, 169.80, 169.07, 165.46, 151.17, 150.14, 147.48, 146.76, 139.68, 135.22, 127.70, 122.92, 122.58, 121.35, 120.63, 118.44, 113.98, 110.45, 98.05, 97.73, 80.10, 75.61, 73.92, 71.87, 70.69, 69.44, 68.99, 68.51, 66.85, 62.53, 56.05, 25.99, 25.97, 20.97, 20.84, 20.80, 20.76, 20.47, 18.64, 18.57, 17.58, -3.91, -3.93, -3.96, -3.99; HR-ESI-MS (*m/z*) calcd for $C_{52}H_{78}O_{20}Si_2N$ $[M + NH_4]^+$ 1092.4650, found 1092.4646.

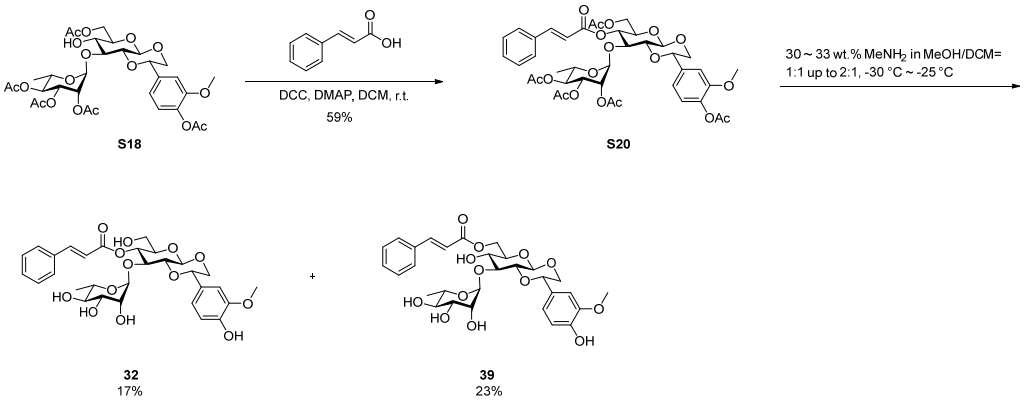
To a solution of compound **S19** (148 mg, 0.139 mmol) in THF (5 mL) in plastic bottle was added HF·py (0.5 mL, 5 mmol) dropwise at 0 °C. After stirring at room temperature for 10 h, TLC indicated the reaction was complete. Then, saturated aqueous $NaHCO_3$ was added dropwise at 0°C to quench the reaction, and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/acetone, 2:1 to 1:1) to afford colorless liquid (100 mg, 85 %). To a solution of the colorless liquid (77 mg, 90 μmol) in MeOH (4.5 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 45 μL, 45 μmol) dropwise at 0 °C. Then, another potassium tert-butoxide (45 μL, 45 μmol) was added at 1 h, 2 h, 3 h respectively. After 11 h, the reaction was basically complete. Then neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **31** (31.4 mg, 54%) as a yellow solid and **38** (12 mg, 21%) as a yellow solid.

31: $[\alpha]_D^{25}$ = -34.0 (*c* 0.8, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.62 (d, J = 15.8 Hz, 1H), 7.07 (d, J = 2.1 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.88 – 6.75 (m, 3H), 6.28 (d, J = 15.8 Hz, 1H), 5.18 (d, J = 1.7 Hz, 1H), 5.11 (t, J = 9.6 Hz, 1H), 4.68 (dd, J = 10.5, 2.9 Hz, 1H), 4.58 (d, J = 7.7 Hz, 1H), 4.15 (t, J = 9.4 Hz, 1H), 4.04 (dd, J = 12.1, 2.9 Hz, 1H), 3.86 (s, 3H), 3.78 (m, 2H), 3.67 (m, 2H), 3.59 (m, 2H), 3.52 (dd, J = 9.6, 3.2 Hz, 1H), 3.48 (dd, J = 9.6, 7.8 Hz, 1H), 3.27 (t, J = 9.5 Hz, 1H), 1.12 (d, J = 6.2 Hz, 3H);

^{13}C NMR (125 MHz, CD_3OD) δ 167.98, 149.89, 149.02, 148.27, 147.60, 146.86, 129.78, 127.61, 123.28, 120.04, 116.50, 116.09, 115.25, 114.42, 110.94, 102.34, 99.02, 81.97, 78.46, 77.85, 77.52, 73.58, 72.87, 72.11, 72.00, 70.43, 70.16, 62.10, 56.46, 18.32; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{15}Na$ $[M + Na]^+$ 659.1946, found 659.1954.

38: $[\alpha]_D^{25} = 27.5$ (*c* 0.7, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.59 (d, *J* = 15.9 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 6.96 (dd, *J* = 8.0, 2.0 Hz, 2H), 6.82 – 6.74 (m, 3H), 6.32 (d, *J* = 15.9 Hz, 1H), 5.21 (d, *J* = 1.7 Hz, 1H), 4.63 (dd, *J* = 10.5, 2.8 Hz, 1H), 4.56 (dd, *J* = 12.1, 2.0 Hz, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.37 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.06 – 4.02 (m, 1H), 4.00 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.87 (d, *J* = 9.2 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 1H), 3.78 (m, 1H), 3.70 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.65 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.56 (t, *J* = 9.4 Hz, 1H), 3.41 – 3.35 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 169.03, 149.66, 148.97, 147.56, 147.31, 146.80, 129.85, 127.67, 123.08, 120.12, 116.52, 116.07, 115.15, 114.73, 110.98, 101.93, 99.02, 81.93, 78.78, 78.39, 77.29, 73.95, 72.82, 72.14, 72.08, 70.23, 69.84, 64.48, 56.45, 17.91; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{15}Na$ $[M + Na]^+$ 659.1946, found 659.1955.

Compounds 32 and 39:



To a solution of compound **S18** (0.1 g, 146 μmol) in anhydrous CH_2Cl_2 (4 mL) was added *trans*-cinnamic acid (43 mg, 292 μmol), dicyclohexylcarbodiimide (75 mg, 365 μmol), 4-dimethylaminopyridine (27 mg, 219 μmol) in sequence. After stirring at room temperature for 24 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel

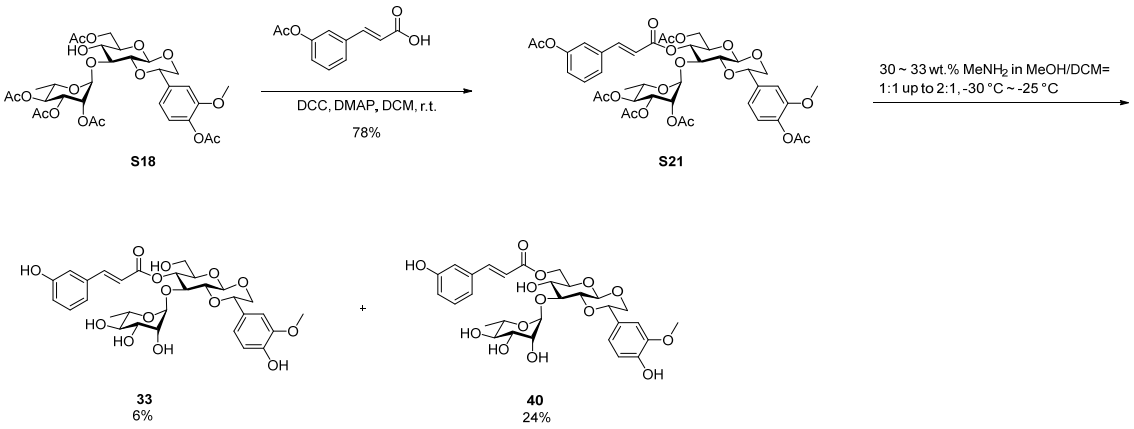
column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S20** (70 mg, 59%) as a white foam: $[\alpha]_D^{25}$ = -28.8 (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.0, 1H), 7.52 (m, 2H), 7.39 (m, 3H), 7.03 – 6.95 (m, 1H), 6.92 – 6.82 (m, 2H), 6.43 (d, *J* = 16.0, 1H), 5.35 – 5.29 (m, 1H), 5.28 (m, 1H), 5.20 (d, *J* = 1.8 Hz, 1H), 5.08 (m, 1H), 4.91 (td, *J* = 10.1, 1.8 Hz, 1H), 4.75 (dd, *J* = 10.5, 2.8 Hz, 1H), 4.49 (d, *J* = 7.9, 1H), 4.24 (m, 2H), 4.18 – 4.03 (m, 2H), 3.95 – 3.89 (m, 1H), 3.83 (m, 4H), 3.65 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.58 (s, 3H), 1.09 (d, *J* = 6.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.96, 170.11, 169.81, 169.79, 169.07, 165.18, 151.17, 146.83, 139.67, 135.18, 134.09, 131.00, 129.19, 128.29, 122.91, 118.42, 116.52, 110.43, 98.06, 97.74, 80.03, 75.67, 73.87, 71.88, 70.68, 69.46, 68.92, 68.71, 66.93, 62.48, 56.05, 20.97, 20.84, 20.80, 20.75, 20.33, 17.58; HR-ESI-MS (*m/z*) calcd for $C_{40}H_{46}O_{18}Na$ $[M + Na]^+$ 837.2576, found 837.2674.

To a solution of compound **S20** (60 mg, 73 μmol) in CH_2Cl_2 (4 mL) was added methylamine (30 ~ 33 wt % solution in absolute methanol, 4 mL) dropwise at -30 °C. After 10 h, additional methylamine solution (4 mL) was added to the mixture. After stirring at -25 °C for another 9 h, TLC indicated the reaction was complete. Then, the mixture was concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **32** (7.3 mg, 17%) as a yellow solid and **39** (10.2 mg, 23%) as a yellow solid.

32: $[\alpha]_D^{25}$ = -16.0 (*c* 0.4, CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.46 – 7.39 (m, 3H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.82 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.15 (t, *J* = 9.6 Hz, 1H), 4.69 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.59 (d, *J* = 7.7 Hz, 1H), 4.18 (t, *J* = 9.4 Hz, 1H), 4.05 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.87 (s, 3H), 3.80 (m, 2H), 3.68 (t, *J* = 11.3 Hz, 2H), 3.63 – 3.56 (m, 2H), 3.55 – 3.46 (m, 2H), 3.27 (t, *J* = 9.6 Hz, 1H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 167.35, 149.02, 147.61, 135.68, 131.73, 130.05, 129.77, 129.43, 120.04, 118.34, 116.08, 110.92, 102.30, 99.02, 81.97, 78.47, 77.74, 77.37, 73.53, 72.88, 72.09, 71.99, 70.42, 62.06, 56.44, 18.26; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{13}Na$ $[M + Na]^+$ 627.2048, found 627.2052.

39: $[\alpha]_D^{25}$ = 32.0 (*c* 0.5, CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.62 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.44 – 7.37 (m, 3H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.81 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 5.21 (d, *J* = 1.7 Hz, 1H), 4.64 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.58 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.40 (dd, *J* = 12.1, 5.7 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.91 – 3.86 (m, 1H), δ 3.86 (s, 3H), 3.82 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.81 – 3.77 (m, 1H), 3.70 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.66 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.57 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.39 (dd, *J* = 9.6, 8.2 Hz, 2H), 1.26 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 168.36, 148.99, 147.59, 146.65, 135.71, 131.60, 130.05, 129.86, 129.31, 120.12, 118.55, 116.06, 110.97, 101.95, 99.05, 81.98, 78.74, 78.43, 77.25, 73.95, 72.86, 72.15, 72.08, 70.22, 69.85, 64.69, 56.43, 17.93; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{13}Na$ $[M + Na]^+$ 627.2048, found 627.2045.

Compounds 33 and 40:



To a solution of compound **S18** (100 mg, 146 μmol) in anhydrous CH_2Cl_2 (3 mL) was added 3-acetoxy cinnamic acid (60 mg, 292 μmol), dicyclohexylcarbodiimide (75 mg, 365 μmol), 4-dimethylaminopyridine (27 mg, 219 μmol) in sequence. After stirring at room temperature for 18 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S21** (100 mg, 78%) as a white foam: $[\alpha]_D^{25}$ = -25.5 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.74

(d, J = 16.0 Hz, 1H), 7.40 (m, 2H), 7.27 (s, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 10.2 Hz, 2H), 6.42 (dd, J = 16.0, 1.0 Hz, 1H), 5.34 – 5.29 (m, 1H), 5.27 (m, 1H), 5.19 (s, 1H), 5.11 – 5.02 (m, 1H), 4.92 (t, J = 10.0 Hz, 1H), 4.75 (d, J = 10.3 Hz, 1H), 4.49 (d, J = 7.8 Hz, 1H), 4.23 (d, J = 4.0 Hz, 2H), 4.16 – 4.02 (m, 2H), 3.91 (m, 1H), 3.83 (m, 4H), 3.71 – 3.58 (m, 2H), δ 2.31 (s, 1H), 2.30 (s, 1H), 2.10 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.62 (s, 3H), 1.09 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.93, 170.16, 169.81, 169.21, 169.07, 164.93, 151.31, 151.18, 145.72, 139.68, 135.64, 135.17, 130.16, 125.77, 124.09, 122.91, 121.14, 118.41, 117.62, 110.43, 98.05, 97.74, 79.98, 75.66, 73.83, 71.88, 70.64, 69.50, 68.88, 68.82, 67.01, 62.43, 56.05, 21.22, 20.96, 20.84, 20.79, 20.74, 20.36, 17.57; HR-ESI-MS (*m/z*) calcd for $C_{42}H_{48}O_{20}Na$ $[M + Na]^+$ 895.2631, found 895.2627.

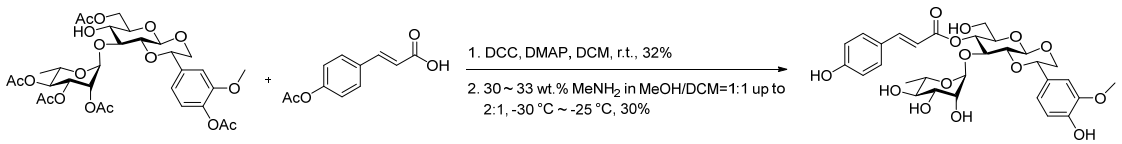
To a solution of compound **S21** (100 mg, 115 μmol) in CH_2Cl_2 (5 mL) was added methylamine (30 ~ 33 wt % solution in absolute methanol, 5 mL) dropwise at -30 °C. To the stirring mixture were added additional methylamine solution (5 mL) after 5 h. After stirring at -25 °C for another 5 h, TLC indicated the reaction was complete. Then, the mixture was concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **33** (3.9 mg, 6%) as a white solid and **40** (16.6 mg, 24%) as a white solid.

33: $[\alpha]_D^{25}$ = -22.8 (*c* 0.4, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.68 (d, J = 16.0 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.03 (t, J = 2.0 Hz, 1H), 6.98 (d, J = 1.9 Hz, 1H), 6.85 (dd, J = 7.9, 2.4 Hz, 1H), 6.82 (dd, J = 8.2, 1.9 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), δ 6.48 (d, J = 16.0 Hz, 1H), 5.18 (d, J = 1.8 Hz, 1H), 5.14 (t, J = 9.6 Hz, 1H), 4.69 (dd, J = 10.5, 2.9 Hz, 1H), 4.59 (d, J = 7.7 Hz, 1H), 4.17 (t, J = 9.4 Hz, 1H), 4.05 (dd, J = 12.1, 2.9 Hz, 1H), 3.87 (s, 3H), 3.82 – 3.77 (m, 2H), 3.72 – 3.65 (m, 2H), 3.58 (m, 2H), 3.52 (dd, J = 9.5, 3.3 Hz, 1H), 3.49 (dd, J = 9.6, 7.8 Hz, 1H), 3.27 (t, J = 9.6 Hz, 1H), 1.12 (d, J = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 167.41, 159.09, 149.03, 147.79, 147.61, 136.91, 131.05, 129.77, 121.06, 120.05, 118.94, 118.12, 116.10, 115.43, 110.95, 102.33, 99.01, 81.95, 78.46, 77.74, 77.47, 73.55, 72.87, 72.09,

72.00, 70.43, 70.40, 62.07, 56.47, 18.29; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{14}Na$ [M + Na]$^+$ 643.1997, found 643.2000.

40: $[\alpha]_D^{25}$ = 11.3 (*c* 0.2, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.86 – 6.83 (m, 1H), 6.81 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.21 (d, *J* = 1.7 Hz, 1H), 4.64 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.57 (d, *J* = 2.0 Hz, 2H), 4.53 (d, *J* = 7.8 Hz, 1H), 4.39 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.86 (s, 4H), 3.82 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.79 (ddd, *J* = 9.9, 5.7, 2.0 Hz, 1H), 3.71 – 3.69 (m, 1H), 3.68 – 3.64 (m, 1H), 3.57 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.41 – 3.37 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.41, 159.11, 149.02, 146.84, 136.97, 131.07, 129.87, 120.92, 120.14, 118.81, 118.36, 116.08, 115.29, 111.02, 101.97, 99.06, 81.99, 78.78, 78.45, 77.28, 73.97, 72.87, 72.16, 72.10, 70.24, 69.87, 64.67, 56.45, 17.92; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{14}Na$ [M + Na]$^+$ 643.1997, found 643.1993.

Compound 34:

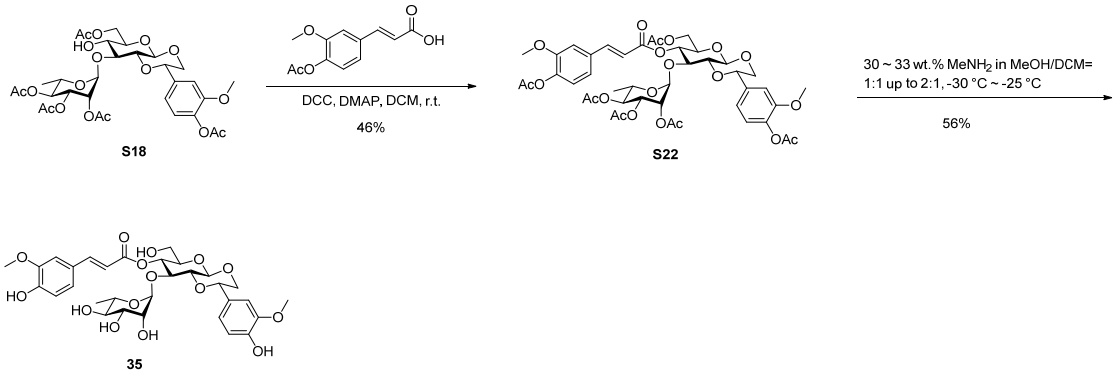


S18 34

To a solution of compound **S18** (0.1 g, 0.146 mmol) in anhydrous DCM (3 mL), and the 4-acetoxy cinnamic acid (60 mg, 0.292 mmol), Dicyclohexylcarbodiimide (75 mg, 0.365 mmol), 4-Dimethylaminopyridine (75 mg, 0.365 mmol), were added in sequence. After stirring at room temperature for 18 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford the product (40 mg, 32 %) as a white foam. To a solution of the above product (20 mg, 0.0229 mmol) in DCM (2 mL) and the 2 ml methylamine (30 ~ 33 wt% solution in absolute methanol) was added dropwise at -30 °C. To the stirring mixture were added additional 2 ml methylamine after 6 h After stirring at -25 °C for another 12 h,

TLC indicated the reaction was complete. Then concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **34** (4.3 mg, 30%): $[\alpha]_D^{25}$ = -25.4 (*c* 0.1650, CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ 7.69 (d, *J* = 15.9 Hz, 1H), 7.52 – 7.46 (m, 2H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.81 (m, 3H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 5.11 (t, *J* = 9.6 Hz, 1H), 4.69 (dd, *J* = 10.4, 2.9 Hz, 1H), 4.59 (d, *J* = 7.8 Hz, 1H), 4.16 (t, *J* = 9.4 Hz, 1H), 4.05 (dd, *J* = 12.1, 2.9 Hz, 1H), 3.87 (s, 3H), 3.78 (m, 2H), 3.68 (m, 3H), 3.62 – 3.56 (m, 2H), 3.52 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.48 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.26 (t, *J* = 9.5 Hz, 1H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 168.07, 162.33, 149.05, 148.03, 147.65, 134.34, 131.44, 129.77, 126.70, 120.06, 117.11, 117.06, 116.10, 114.16, 110.95, 102.31, 99.04, 81.99, 78.48, 77.88, 77.46, 73.58, 72.88, 72.12, 72.01, 70.42, 70.17, 62.11, 56.46, 18.28; HR-ESI-MS (*m/z*) calcd for $C_{30}H_{36}O_{14}Na$ $[M + Na]^+$ 643.1997, found 643.1990.

Compound 35:

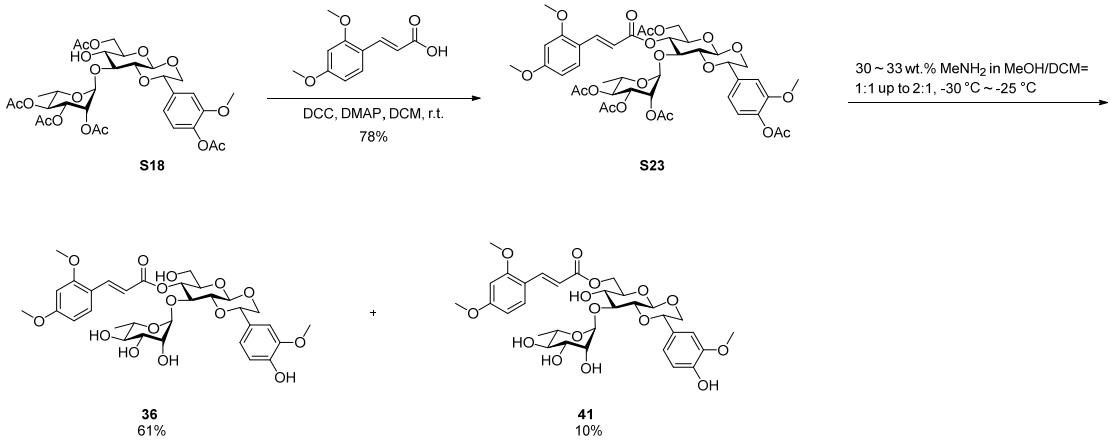


To a solution of compound **S18** (100 mg, 146 μmol) in anhydrous CH_2Cl_2 (3 mL) was added 3-methoxy-4-acetoxy-cinnamic acid (60 mg, 292 μmol), dicyclohexylcarbodiimide (75 mg, 365 μmol), 4-dimethylaminopyridine (27 mg, 219 μmol) in sequence. After stirring at room temperature for 18 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S22** (60 mg, 46%) as a white foam: $[\alpha]_D^{25}$ = -26.7 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 15.9 Hz, 1H), 7.12 (dd, *J* = 8.1, 1.8 Hz, 1H),

7.10 (d, *J* = 1.9 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 15.9 Hz, 1H), 5.31 (t, *J* = 9.5 Hz, 1H), 5.27 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.09 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.92 (t, *J* = 10.0 Hz, 1H), 4.75 (dd, *J* = 10.6, 2.9 Hz, 1H), 4.49 (d, *J* = 7.7 Hz, 1H), 4.24 (t, *J* = 3.4 Hz, 2H), 4.17 – 4.06 (m, 2H), 3.95 – 3.89 (m, 1H), 3.85 (s, 3H), 3.83 (m, 4H), 3.69 – 3.60 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 2.11 (s, 3H), 1.98 (s, 3H), 1.88 (s, 3H), 1.65 (s, 3H), 1.10 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.96, 170.12, 169.84, 169.79, 169.07, 168.75, 165.07, 151.69, 151.17, 146.10, 142.01, 139.67, 135.16, 133.01, 123.57, 122.91, 121.28, 118.41, 116.71, 111.55, 110.41, 98.13, 97.75, 79.94, 76.81, 75.88, 73.85, 71.88, 70.65, 69.51, 68.87, 68.78, 67.00, 62.47, 56.07, 56.04, 20.97, 20.83, 20.79, 20.76, 20.43, 17.60; HR-ESI-MS (*m/z*) calcd for $C_{43}H_{50}O_{21}Na$ $[M + Na]^+$ 925.2737, found 925.2728.

To a solution of compound **S22** (30 mg, 33 μmol) in CH_2Cl_2 (3 mL) was added methylamine (30 ~ 33 wt % solution in absolute methanol, 3 mL) dropwise at -30 °C. After 6 h, additional methylamine solution (3 mL) were added. After stirring at -25 °C for another 12 h, TLC indicated the reaction was complete. Then, the mixture was concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **35** (12 mg, 56%) as a white solid: $[\alpha]_D^{25}$ = -35.4 (*c* 0.5, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.68 (d, *J* = 15.9 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.82 (dd, *J* = 8.1, 2.4 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.11 (t, *J* = 9.0 Hz,1H), 4.68 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.16 (t, *J* = 9.4 Hz, 1H), 4.05 (dd, *J* = 12.1, 3.0 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.80 – 3.75 (m, 2H), 3.68 (m, 2H), 3.64 – 3.57 (m, 2H), 3.52 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.49 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.27 (t, *J* = 9.5 Hz, 1H), 1.13 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 166.59, 149.71, 148.06, 147.64, 146.80, 146.23, 128.38, 126.13, 118.66, 115.14, 114.70, 113.38, 110.38, 109.56, 100.88, 97.65, 80.60, 77.07, 76.48, 75.94, 72.17, 71.48, 70.72, 70.63, 69.01, 68.82, 60.73, 55.07, 55.03, 16.89; HR-ESI-MS (*m/z*) calcd for $C_{31}H_{38}O_{15}Na$ $[M + Na]^+$ 673.2103, found 673.2105.

Compounds 36 and 41:



To a solution of compound **S18** (100 mg, 146 μmol) in anhydrous CH_2Cl_2 (3 mL) was added 2,4-dimethoxycinnamic acid (61 mg, 292 μmol), dicyclohexylcarbodiimide (75 mg, 365 μmol), 4-dimethylaminopyridine (27 mg, 219 μmol) in sequence. After stirring at room temperature for 18 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S23** (100 mg, 78%) as a white foam: $[\alpha]_D^{25}$ = -45.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 16.1 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.88 (m, 2H), 6.49 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.46 – 6.41 (m, 2H), 5.38 – 5.25 (m, 2H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.09 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.90 (t, *J* = 10.0 Hz, 1H), 4.75 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.49 (d, *J* = 7.9 Hz, 1H), 4.29 – 4.17 (m, 2H), 4.16 – 4.06 (m, 2H), 3.93 – 3.88 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.70 – 3.54 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H), 1.88 (s, 3H), 1.67 (s, 3H), 1.08 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.96, 170.22, 169.82, 169.77, 169.06, 166.10, 163.26, 160.22, 151.15, 142.08, 139.67, 135.25, 131.11, 122.89, 118.45, 116.25, 114.42, 110.47, 105.49, 98.53, 98.15, 97.71, 80.11, 75.90, 73.97, 71.85, 70.75, 69.42, 69.07, 68.42, 66.80, 62.64, 56.05, 55.62, 55.51, 20.96, 20.81, 20.77, 20.75, 20.40, 17.46; $C_{42}H_{51}O_{20}$ $[M + H]^+$ 875.2968, found 875.2968; $C_{42}H_{54}O_{20}N$ $[M + NH_4]^+$ 892.3234, found 892.3237; $C_{42}H_{50}O_{20}Na$ $[M + Na]^+$ 897.2788, found 897.2792.

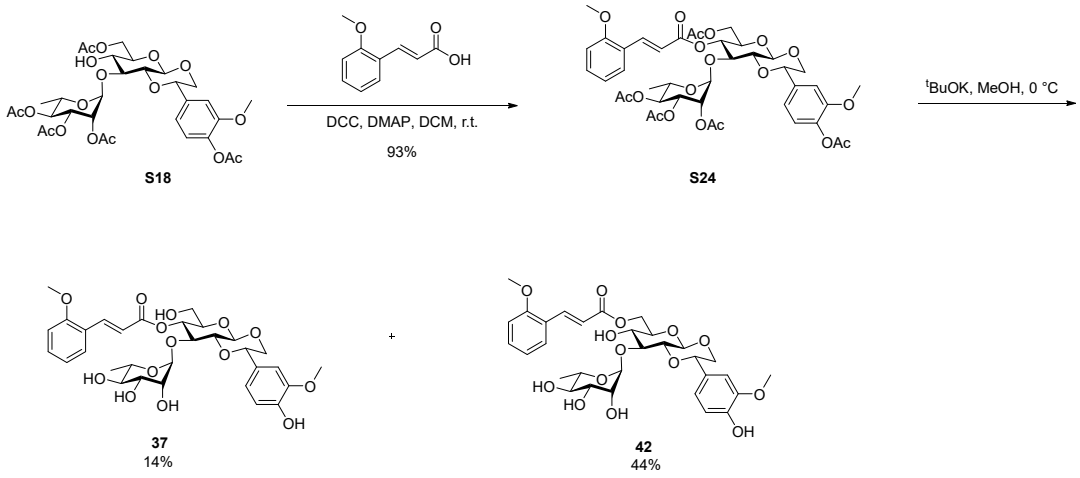
To a solution of compound **S23** (45 mg, 51 μmol) in CH_2Cl_2 (3 mL) was added methylamine (30 ~ 33 wt % solution in absolute methanol, 3 mL) dropwise at -30 °C.

After 6 h, additional methylamine solution (3 mL) was added. After stirring at -25 ℃ for another 12 h, TLC indicated the reaction was complete. Then the mixture was concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **36** (21 mg, 61%) and **41** (3.5 mg, 10%) as a white solid.

36: $[\alpha]_D^{25}$ = -34.6 (*c* 0.1, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.96 (d, *J* = 16.1 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 6.98 (d, *J* = 1.9 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 2H), 6.47 (d, *J* = 16.1 Hz, 1H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 4.69 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.58 (d, *J* = 2.2 Hz, 1H), 4.16 (t, *J* = 9.4 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.80 – 3.76 (m, 2H), 3.71 – 3.65 (m, 2H), 3.62 – 3.56 (m, 2H), 3.52 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.48 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.26 (t, *J* = 9.6 Hz, 1H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.49, 164.98, 161.61, 149.04, 147.62, 143.03, 131.80, 129.81, 120.06, 117.20, 116.10, 115.38, 110.96, 107.05, 102.35, 99.18, 99.04, 82.01, 78.48, 77.92, 77.49, 73.60, 72.88, 72.13, 72.02, 70.41, 70.13, 62.14, 56.47, 56.12, 56.01, 18.20; HR-ESI-MS (*m/z*) calcd for $C_{32}H_{41}O_{15}$ $[M + H]^+$ 665.2440, found 665.6432，$C_{32}H_{40}O_{15}Na$ $[M + Na]^+$ 687.2254, found 687.2259.

41: $[\alpha]_D^{25}$ = 12.4 (*c* 0.2, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 7.94 (d, *J* = 16.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.81 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.58 (m, 2H), 6.50 (d, *J* = 16.1 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.64 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.59 (s, 1H), 4.55 (dd, *J* = 12.0, 2.1 Hz, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.37 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.07 – 3.98 (m, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.82 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.78 (m, 1H), 3.71 – 3.68 (m, 1H), 3.68 – 3.64 (m, 1H), 3.56 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.41 – 3.35 (m, 2H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 169.53, 164.81, 161.52, 149.02, 147.63, 142.13, 131.60, 129.88, 120.14, 117.25, 116.08, 115.71, 111.02, 106.99, 101.96, 99.21, 99.06, 82.00, 78.81, 78.45, 77.36, 73.98, 72.86, 72.17, 72.11, 70.26, 69.87, 64.45, 56.45, 56.14, 55.99, 17.92; HR-ESI-MS (*m/z*) calcd for $C_{32}H_{41}O_{15}$ $[M + H]^+$ 665.2440, found 665.6445，$C_{32}H_{40}O_{15}Na$ $[M + Na]^+$ 687.2259, found 687.2264.

Compounds 37 and 42:



To a solution of compound **S18** (70 mg, 102 μmol) in anhydrous CH_2Cl_2 (3.4 mL) was added 2-methoxycinnamic acid (36.4 mg, 204 μmol), dicyclohexylcarbodiimide (42.2 mg, 204 μmol), 4-dimethylaminopyridine (12.4 mg, 102 μmol) in sequence. After stirring at room temperature for 20 h, TLC indicated the reaction was complete. The mixture was diluted with CH_2Cl_2. The organic phase was washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 3:1 to 2:1) to afford **S24** (81 mg, 93%) as a white foam: $[\alpha]_D^{25}$ = -37.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 16.1 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 4.3, 2.6 Hz, 2H), 6.55 (d, *J* = 16.1 Hz, 1H), 5.38 – 5.27 (m, 2H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.09 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.91 (t, *J* = 10.0 Hz, 1H), 4.81 – 4.70 (m, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.28 – 4.18 (m, 2H), 4.17 – 4.06 (m, 2H), 3.92 (m, 1H), 3.89 (m, 4H), 3.83 (s, 3H), 3.71 – 3.61 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.88 (s, 3H), 1.64 (s, 3H), 1.08 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.89, 170.14, 169.74, 169.72, 169.00, 165.66, 158.62, 151.12, 142.06, 139.64, 135.19, 132.16, 129.42, 122.92, 122.86, 120.88, 118.40, 117.15, 111.29, 110.41, 98.11, 97.68, 80.07, 76.78, 75.76, 73.86, 71.82, 70.68, 69.38, 68.99, 68.58, 66.82, 62.56, 56.01, 55.48, 20.93, 20.79, 20.75, 20.72, 20.30, 17.42; HR-ESI-MS (*m/z*) calcd for $C_{41}H_{52}O_{19}N$ $[M + NH_4]^+$ 862.3128, found 862.3131.

To a solution of the compound **S24** (60 mg, 71 μmol) in MeOH (3.5 mL) was added potassium *tert*-butoxide (12 % in THF, 1 mol/L, 35 μL, 35 μmol) dropwise at

0 °C. Then, another potassium *tert*-butoxide (35 μL, 35 μmol) was added at 1 h, 2 h, 3 h respectively. After 11 h, the reaction was basically complete. Then, the mixture was neutralized with DOWEX 50W X8(H) cationic exchange resin, filtered, and concentrated under vacuum. The residue was purified by C18 column chromatography (H_2O/MeOH = 2:1 to 1:1) to afford **37** (6.5 mg, 14%) as a white solid and **42** (19.8 mg, 44%) as a white solid.

37: $[\alpha]_D^{25}$ = -14.9 (*c* 0.3, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.04 (d, *J* = 16.1 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 (m, 1H), 7.06 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.82 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 16.1 Hz, 1H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.13 (t, *J* = 9.0 Hz, 1H), 4.69 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 4.18 (t, *J* = 9.4 Hz, 1H), 4.06 – 4.03 (m, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.82 – 3.76 (m, 2H), 3.68 (m, 2H), 3.61 – 3.56 (m, 2H), 3.52 (dd, *J* = 9.6, 3.3 Hz, 1H), 3.49 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.26 (t, *J* = 9.6 Hz, 1H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 167.96, 159.99, 149.04, 147.62, 142.91, 133.27, 130.16, 129.80, 124.16, 121.87, 120.06, 118.40, 116.10, 112.48, 110.96, 102.33, 99.03, 81.99, 78.48, 77.82, 77.44, 73.58, 72.88, 72.12, 72.01, 70.42, 70.31, 62.10, 56.47, 56.10, 18.19; HR-ESI-MS (*m/z*) calcd for $C_{31}H_{38}O_{14}Na$ $[M + Na]^+$ 657.2154, found 657.2158.

42: $[\alpha]_D^{25}$ = 22.6 (*c* 0.5, CH_3OH); ^{1}H NMR (600 MHz, CD_3OD) δ 8.01 (d, *J* = 16.1 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.39 (m, 1H), 7.04 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.98 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.81 – 6.78 (m, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 5.20 (d, *J* = 1.7 Hz, 1H), 4.63 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.59 – 4.56 (m, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.39 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.05 – 4.02 (m, 1H), 4.00 (dd, *J* = 12.0, 2.9 Hz, 1H), 3.91 (s, 3H), 3.88 – 3.86 (m, 1H), 3.85 (s, 3H), 3.82 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.80 – 3.78 (m, 1H), 3.70 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.65 (dd, *J* = 12.0, 10.5 Hz, 1H), 3.57 (dd, *J* = 10.0, 8.8 Hz, 1H), 3.41 – 3.37 (m, 1H), 3.37 – 3.34 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.99, 159.91, 149.00, 147.59, 142.02, 133.10, 129.99, 129.87, 124.21, 121.87, 120.13, 118.67, 116.08, 112.47, 111.00, 101.95, 99.03, 81.97, 78.80, 78.41, 77.29, 73.96, 72.84, 72.16, 72.09, 70.25, 69.86, 64.60, 56.45, 56.12, 17.93; HR-ESI-MS (*m/z*) calcd for $C_{31}H_{38}O_{14}Na$ $[M + Na]^+$

657.2154, found 657.2155.

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Biological Activities Assays

Anti-inflammatory Activity Assay

For anti-inflammatory activity testing, mouse macrophage cell line RAW264.7 cells (1

× 10^5 cells) were incubated in DMEM medium containing 10 % FBS, 100 μg/mL streptomycin and 100 U/mL penicillin. Then the cells were incubated with the compounds and LPS (1 μg/mL) for 24 h. Cell culture supernatants were assayed using the mouse TNF-α ELISA kit.

LPS-Induced B Cell Proliferation Assay

Fresh splenocytes (5 × 10^5 cells) were cultured in 96-well plates for 48 h with or without compounds, and B cell activation was induced by stimulation with LPS (10 μg/mL). At 40 h, the cells were treated with 0.5 μCi/well of [^{3}H] thymidine for 8 h. The cells were then harvested on glass fiber filters, and the incorporated radioactivity was counted using the β scintillation counter.

Cell Viability Assay.

The Splenocytes (1 × 10^6 cells) were incubated with or without compounds for 48 h. Then, 20 μL of CCK-8 stock solution was added and incubated for 8 h. Finally, cell viability was determined by measuring absorbance values at 450 nm (650 nm calibration) using a microplate reader.

Table S7. Anti-inflammatory activity of crenatoside (**1**), isocreteoside (**2**), and their analogues **23-42** at 20 μM.

Compound	Concentration (μM)	TNF-α Inhibition %
1	20	9.84
2	20	27.97
23	20	31.24
24	20	36.44
25	20	32.9
26	20	53.39
27	20	45.51
28	20	27.76
29	20	16.22
30	20	0

31	20	33.6
32	20	29.31
33	20	39.77
34	20	36.44
35	20	30.76
36	20	29.47
37	20	40.31
38	20	25.93
39	20	37.68
40	20	0
41	20	27.54
42	20	23.36

Note: TNF-α is the most typical cytokine related to inflammation. It plays an important role in host defense by regulating immune and inflammatory responses.

Table S8. The immunosuppressive activity of crenatoside (**1**), isocreteoside (**2**), and their analogues **23**-**42** on B cell proliferation at 10 μM.

Compound	Concentration (μM)	B cell proliferation inhibition %
1	10	31.9
2	10	30.3
23	10	30.8
24	10	34.4
25	10	23.2
26	10	31.5
27	10	33.3
28	10	34.0
29	10	32.9
30	10	26.5
31	10	42.9
32	10	32.2
33	10	21.9
34	10	34.6
35	10	29.6

36	10	47.9
37	10	19.5
38	10	29.3
39	10	33.9
40	10	28.0
41	10	40.7
42	10	37.0

Note: LPS is a glycolipid complex unique to bacteria that can activate the body's immune system, which can promote the proliferation of B cells.

Table S9. The immunosuppressive activity of compounds **23**-**42**.

Compounds	**Cytotoxicity CC_{50} (μM)**	**Proliferation Responses of B Cells To LPS Stimulation IC_{50} (μM)**	**SI**
26	65.41	35.39	1.85
27	72.04	36.16	1.99
36	46.86	19.91	2.35
41	25.08	21.5	1.17
42	30.46	26.18	1.16

Note: a. CC_{50}: Half of the cell toxic concentration. b. SI: The therapeutic index, which is equal to the ratio of CC_{50} to IC_{50}.

NMR Spectra

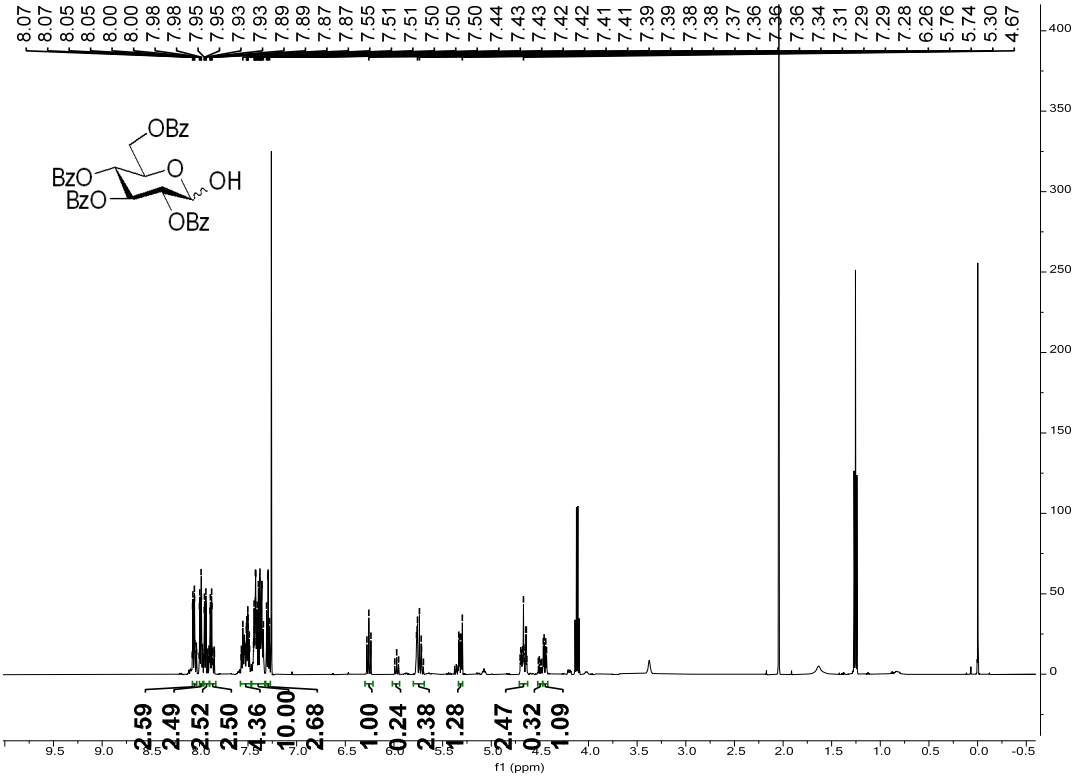

Figure S1 ^{1}H NMR spectrum of compound **S1** ($CDCl_3$, 500 MHz)

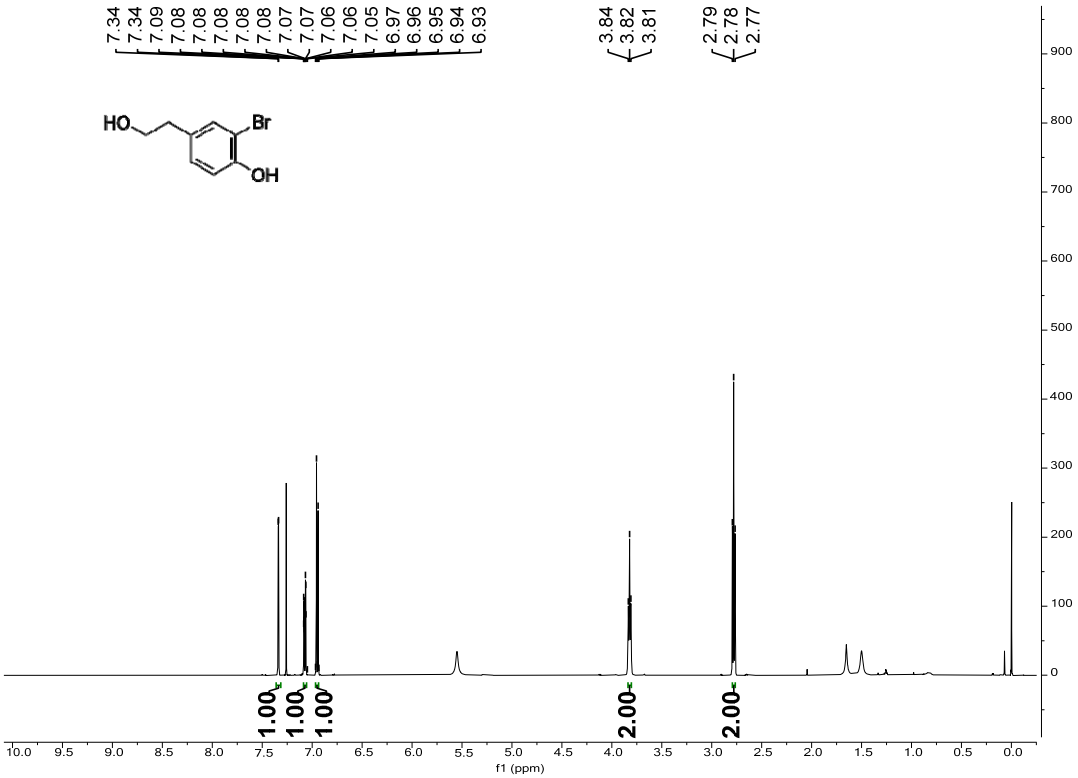

Figure S2 ^{1}H NMR spectrum of compound **S2** ($CDCl_3$, 500 MHz)

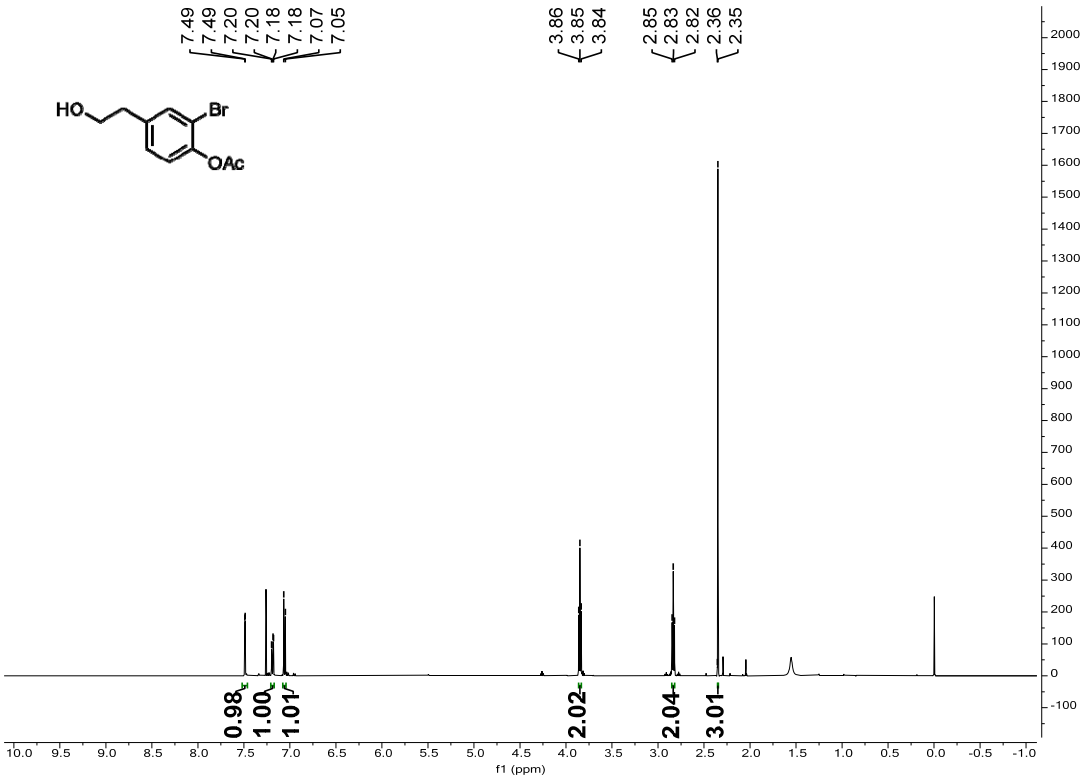

Figure S3 ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 500 MHz)

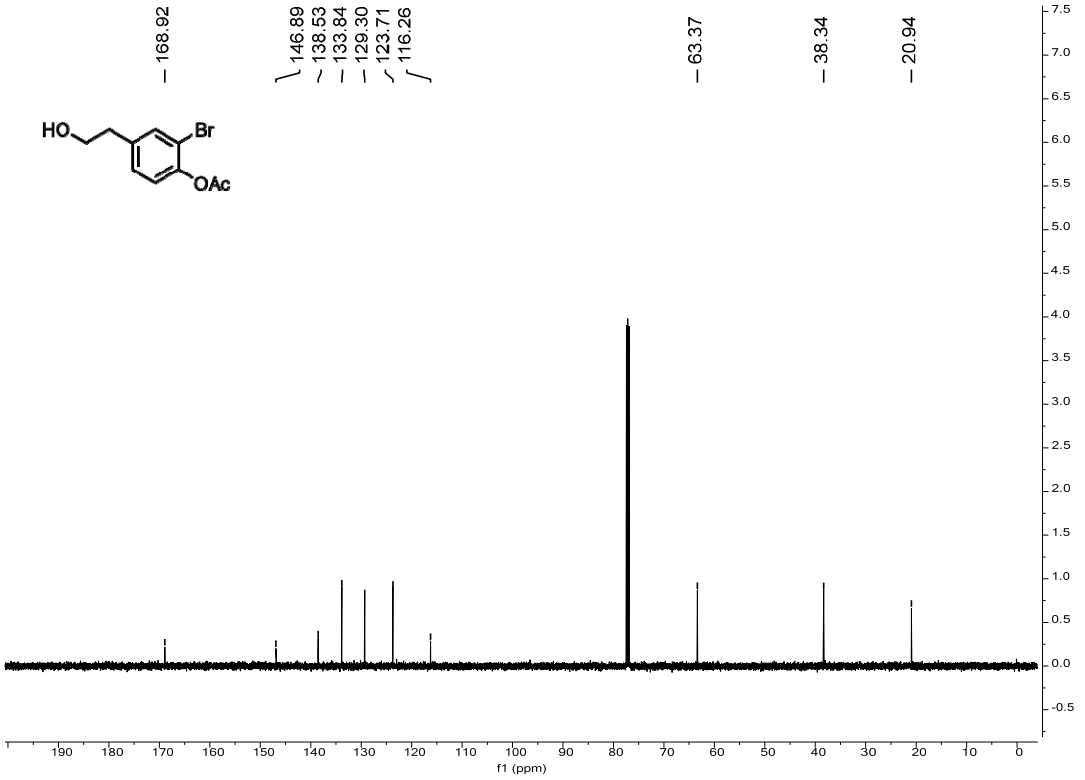

Figure S4 ^{13}C NMR spectrum of compound **4** ($CDCl_3$, 125 MHz)

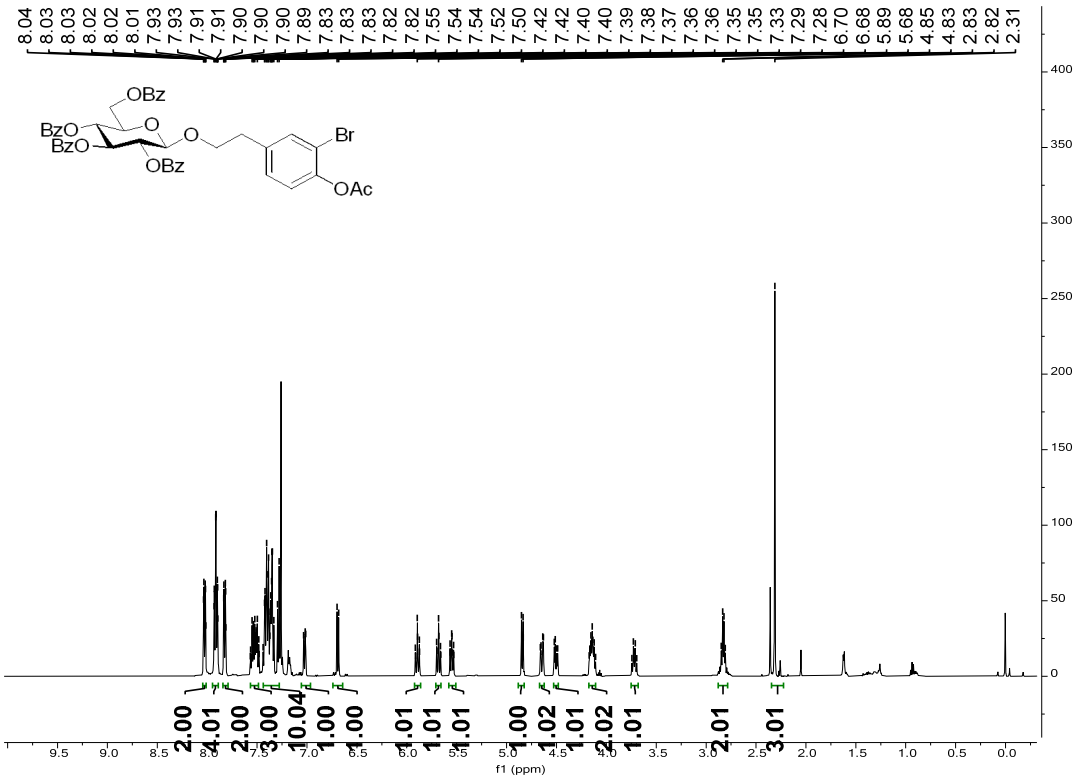

Figure S7 ^{1}H NMR spectrum of compound **5** ($CDCl_3$, 500 MHz)

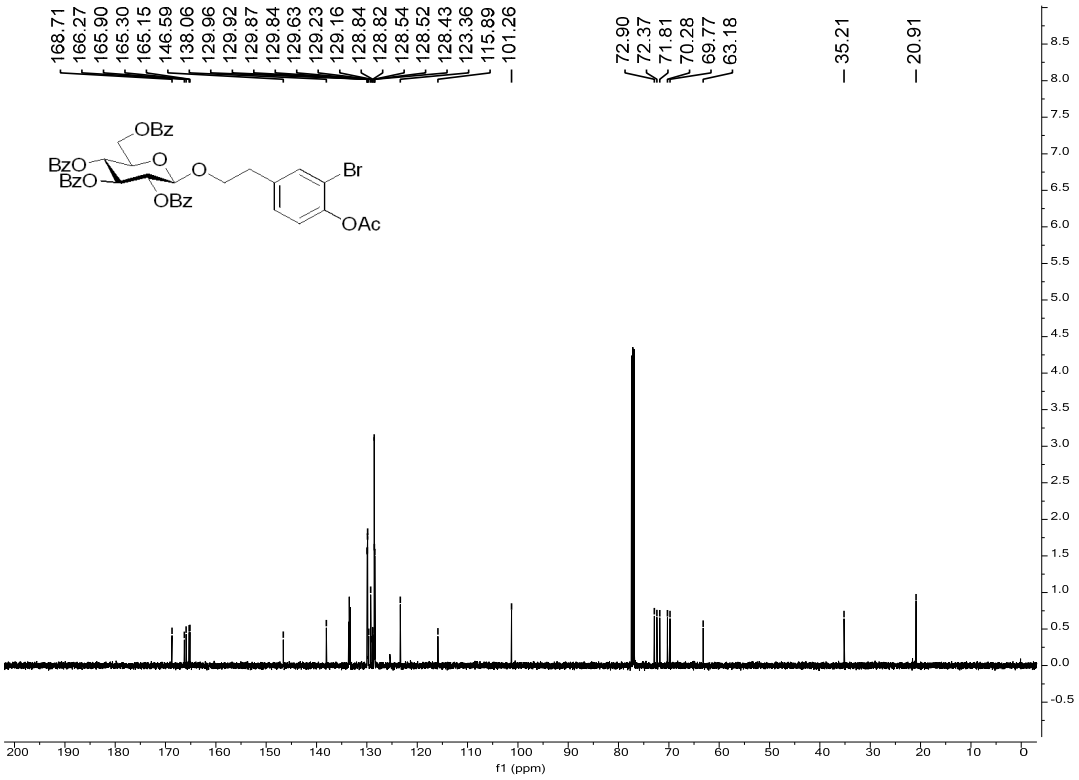

Figure S8 ^{13}C NMR spectrum of compound **5** ($CDCl_3$, 125 MHz)

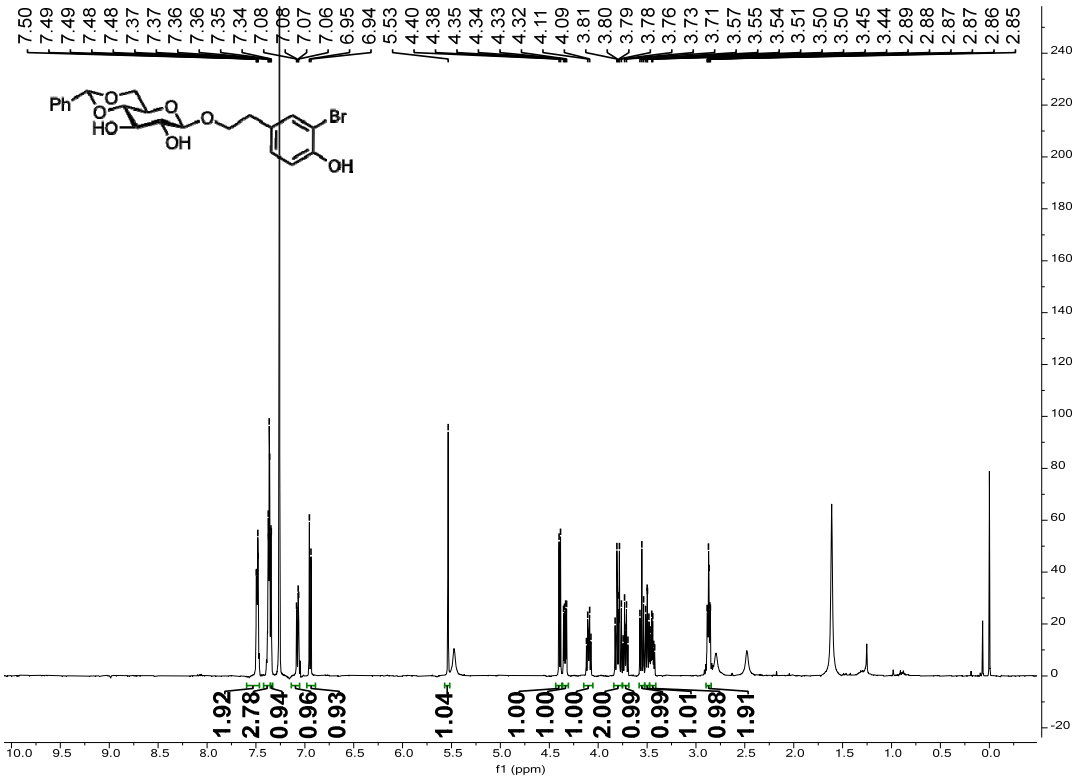

Figure S9 ^{1}H NMR spectrum of compound **6** ($CDCl_3$, 500 MHz)

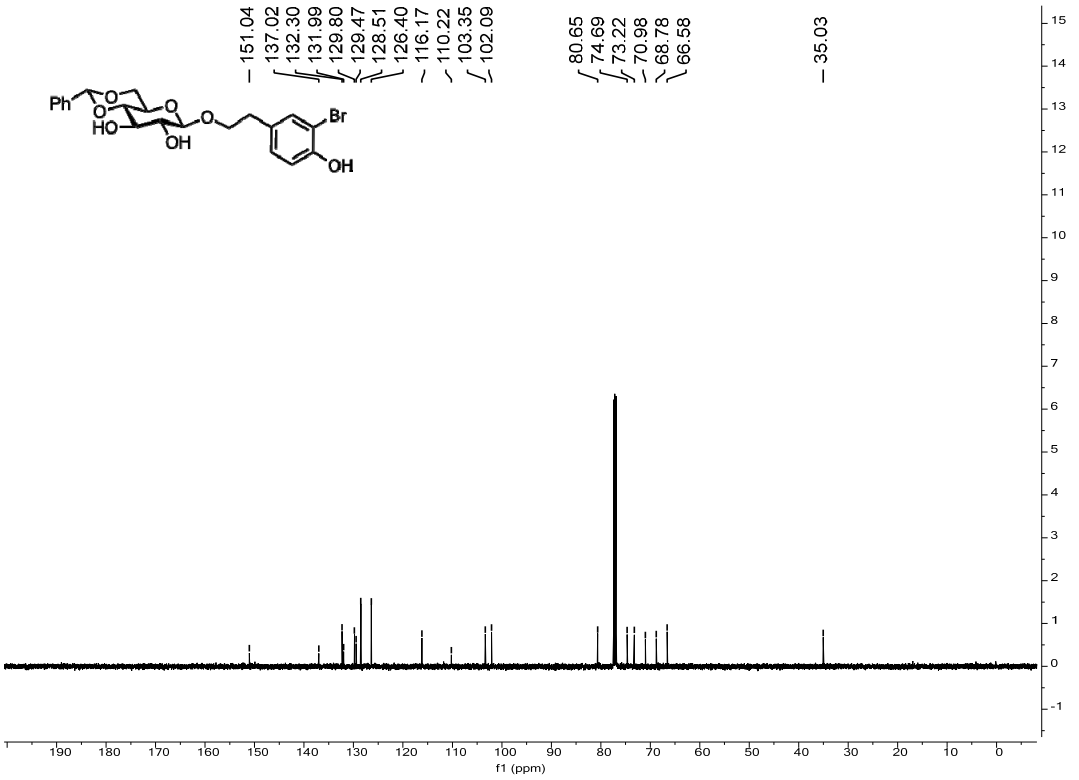

Figure S10 ^{13}C NMR spectrum of compound **6** ($CDCl_3$, 125 MHz)

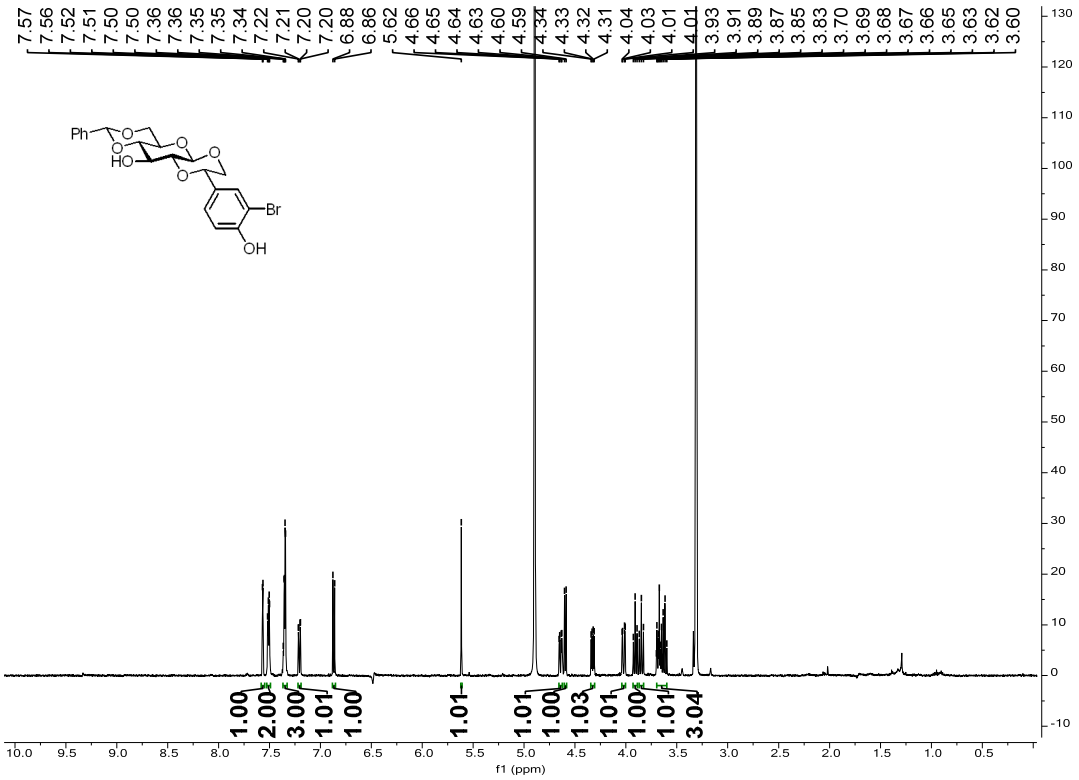

Figure S11 ^{1}H NMR spectrum of compound **7** (CD_3OD, 500 MHz)

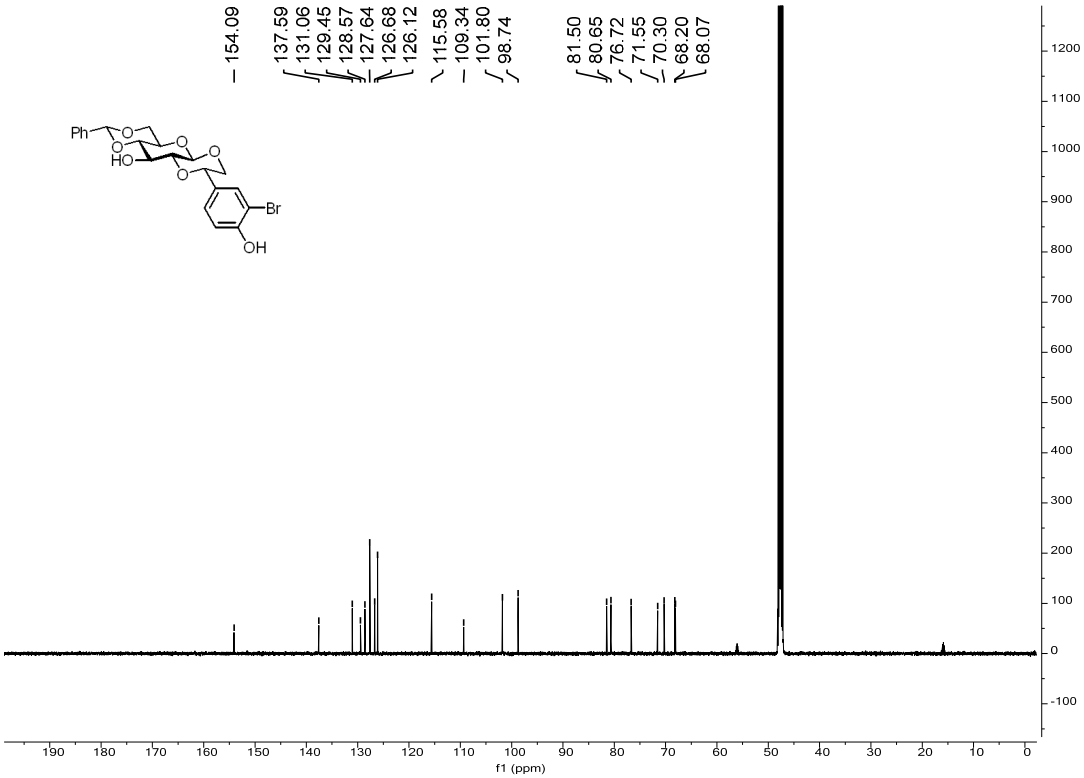

Figure S12 ^{13}C NMR spectrum of compound **7** (CD_3OD, 125 MHz)

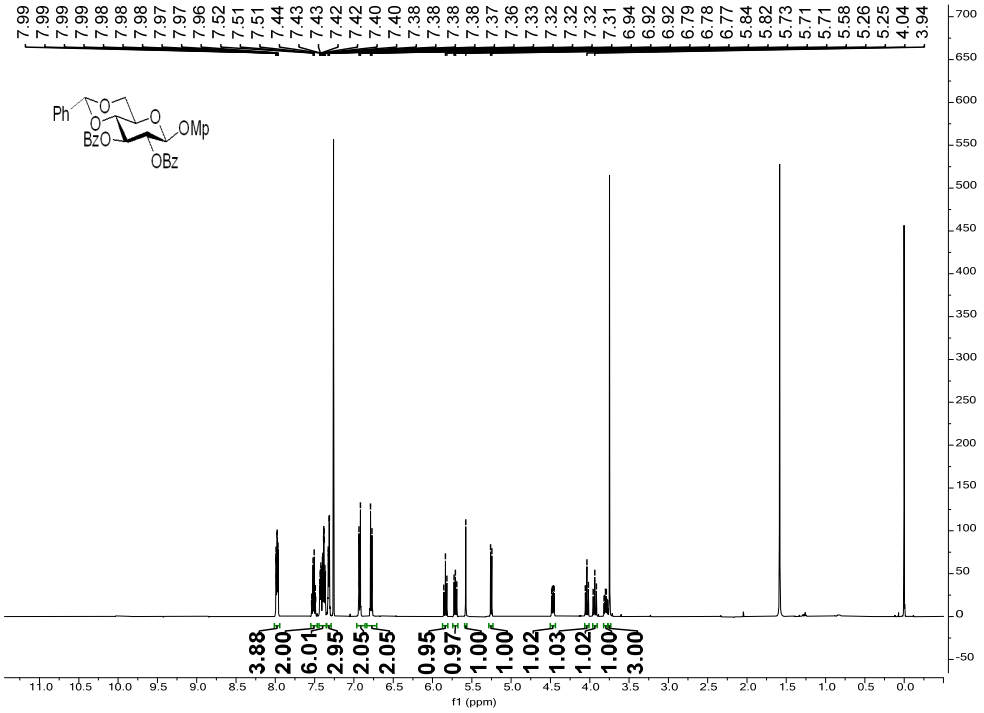

Figure S13 ^{1}H NMR spectrum of compound **S3** ($CDCl_3$, 500 MHz)

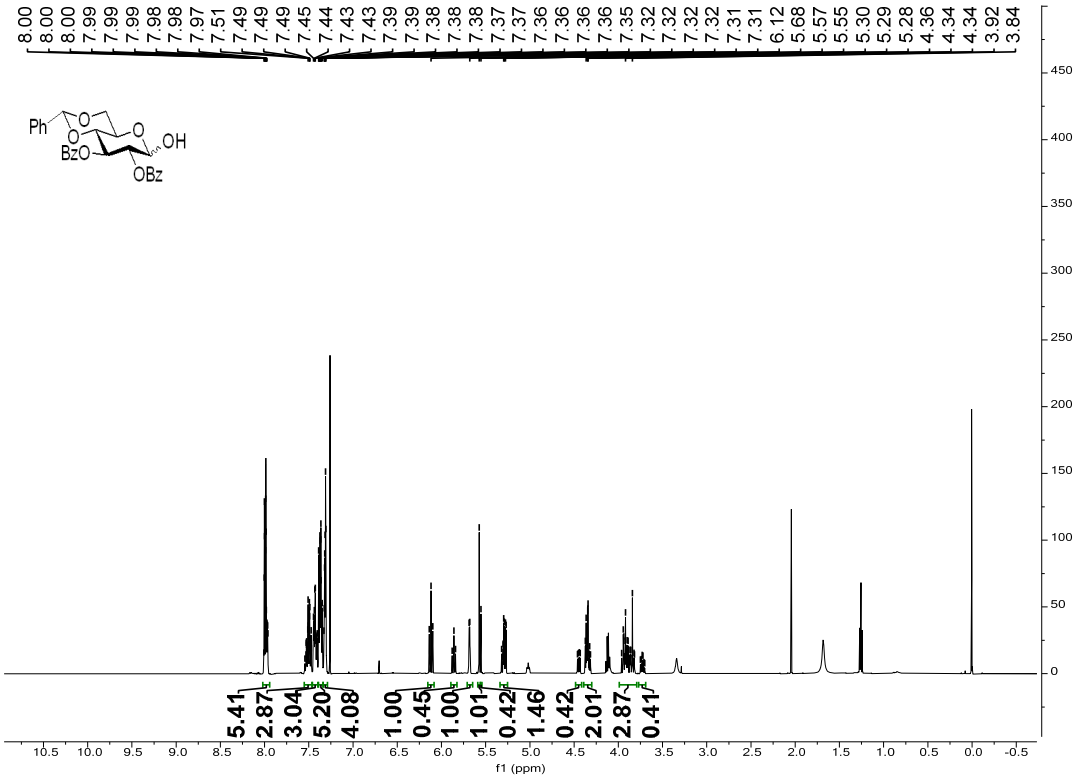

Figure S14 ^{1}H NMR spectrum of compound **S4** ($CDCl_3$, 500 MHz)

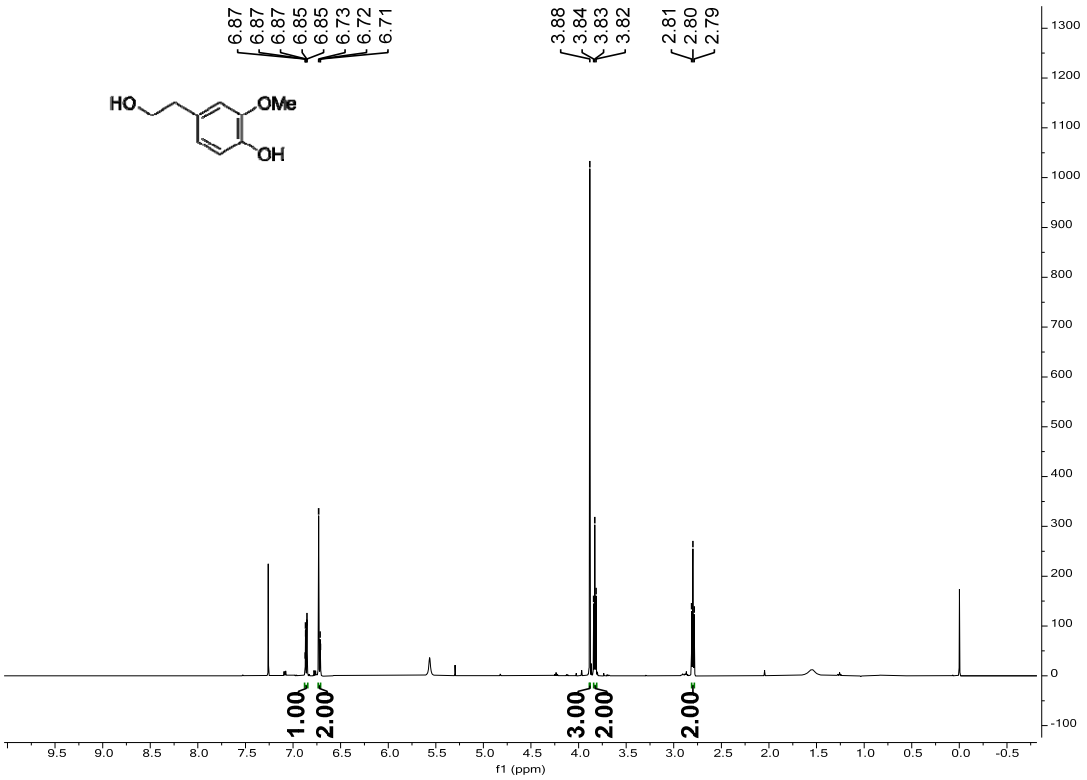

Figure S15 ^{1}H NMR spectrum of compound **S5** ($CDCl_3$, 500 MHz)

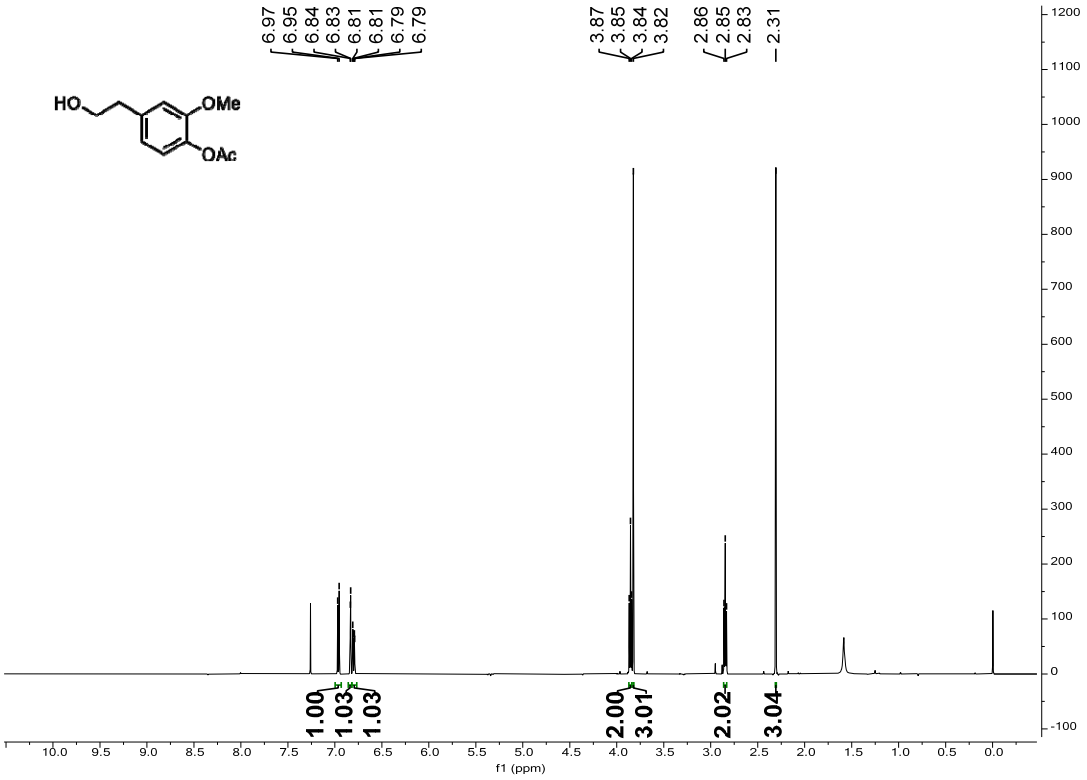

Figure S16 ^{1}H NMR spectrum of compound **S6** ($CDCl_3$, 500 MHz)

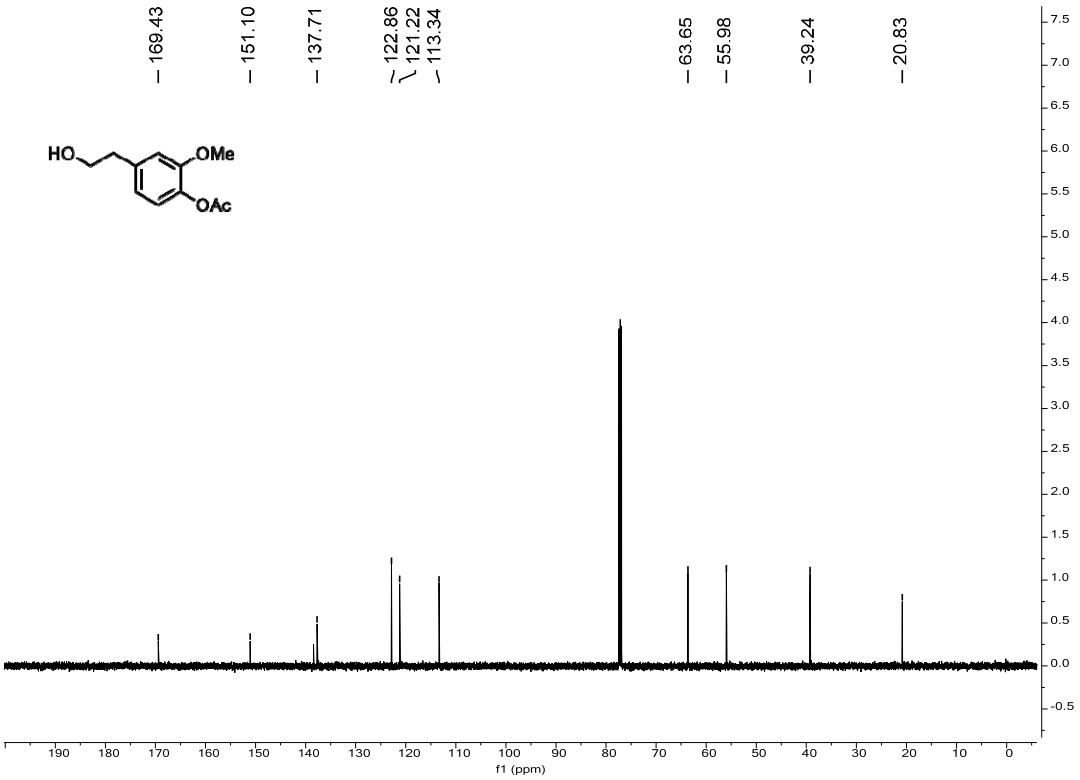

Figure S17 ^{13}C NMR spectrum of compound **S6** ($CDCl_3$, 125 MHz)

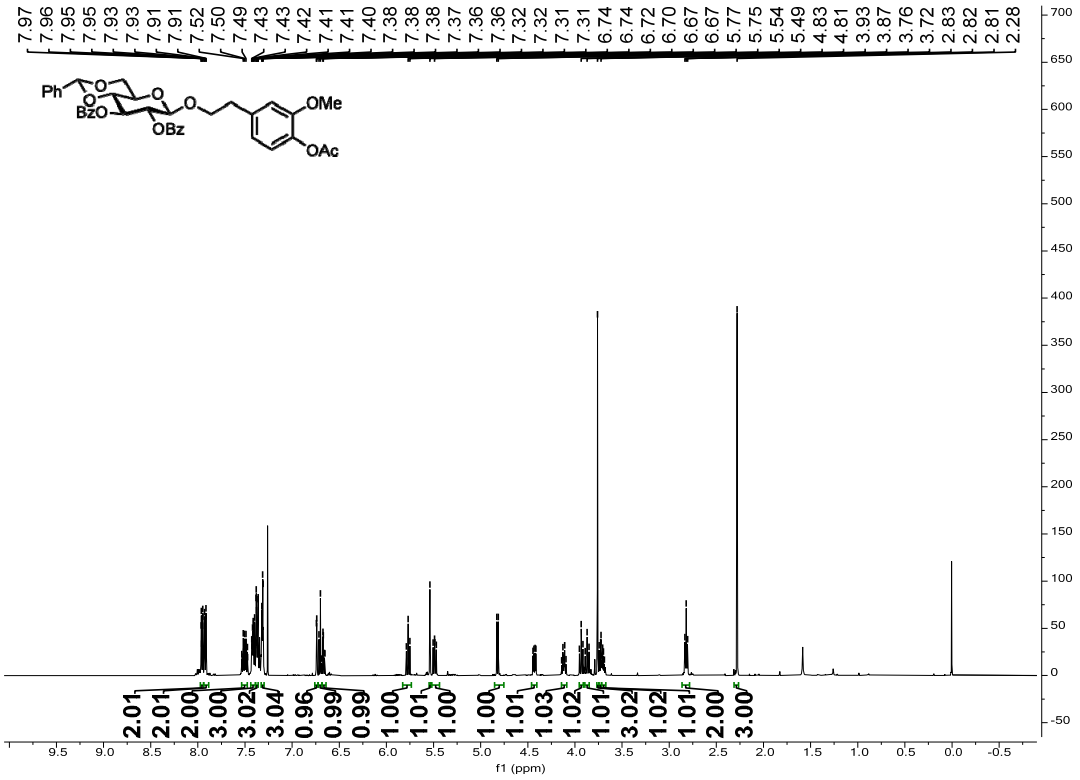

Figure S18 ^{1}H NMR spectrum of compound **S7** ($CDCl_3$, 500 MHz)

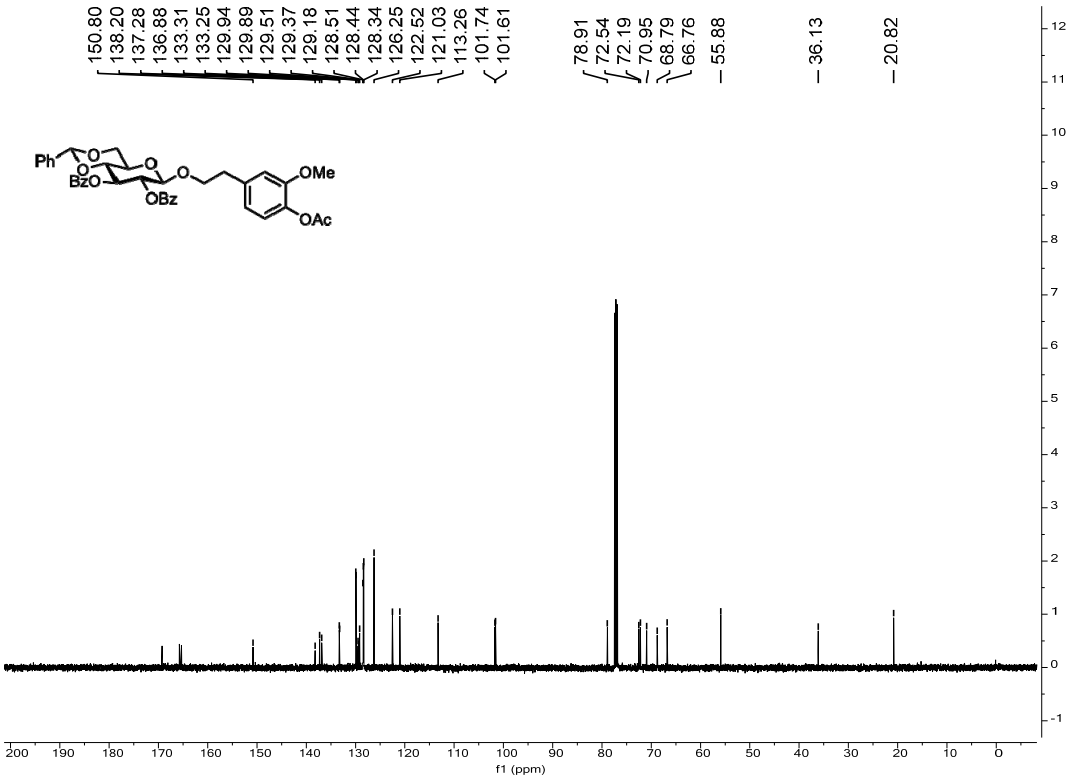

Figure S19 ^{13}C NMR spectrum of compound **S7** ($CDCl_3$, 125 MHz)

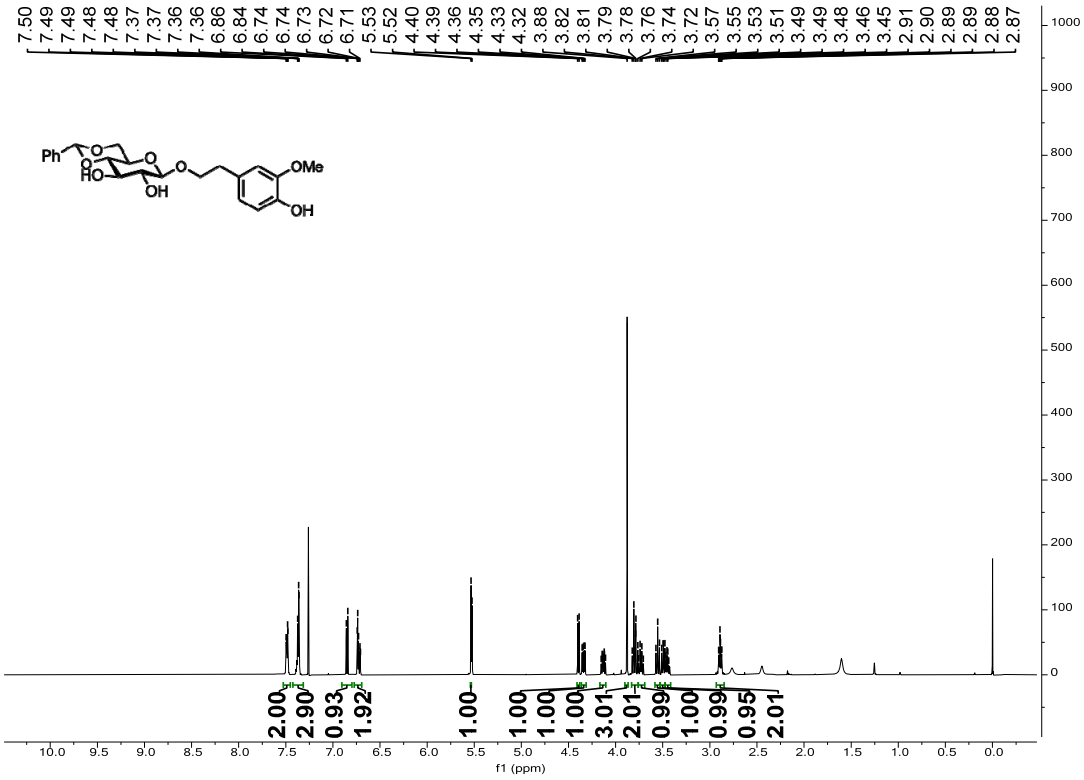

Figure S20 ^{1}H NMR spectrum of compound **8** ($CDCl_3$, 500 MHz)

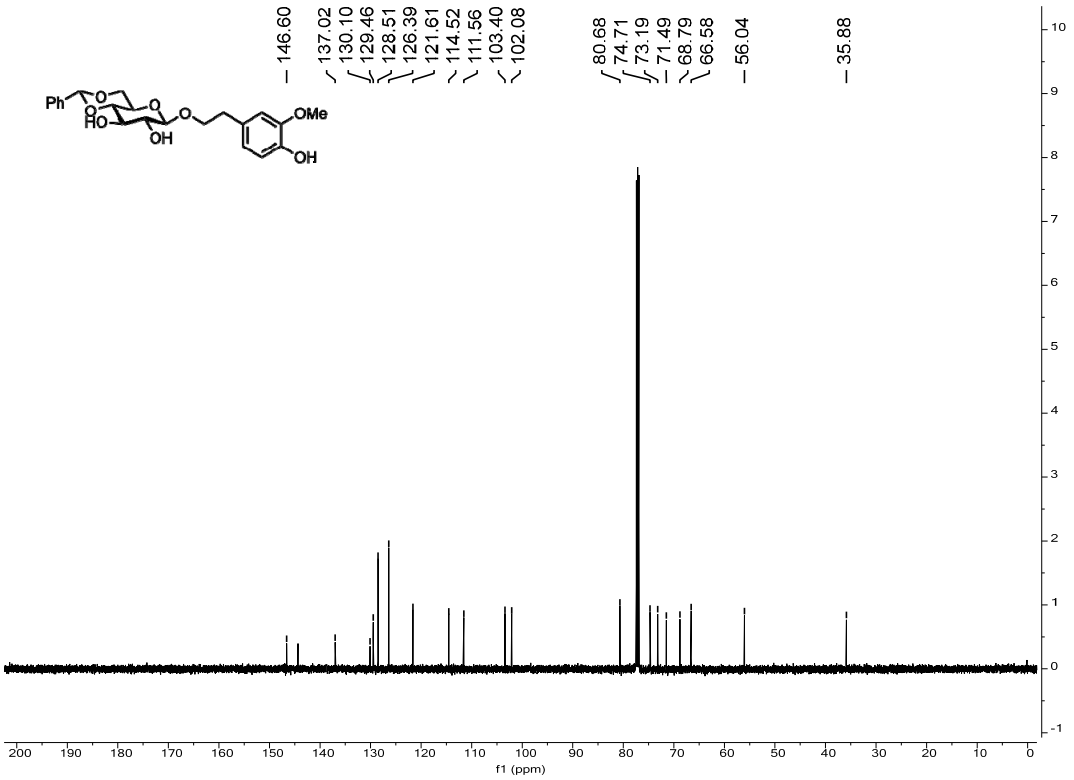

Figure S21 ^{13}C NMR spectrum of compound **8** ($CDCl_3$, 125 MHz)

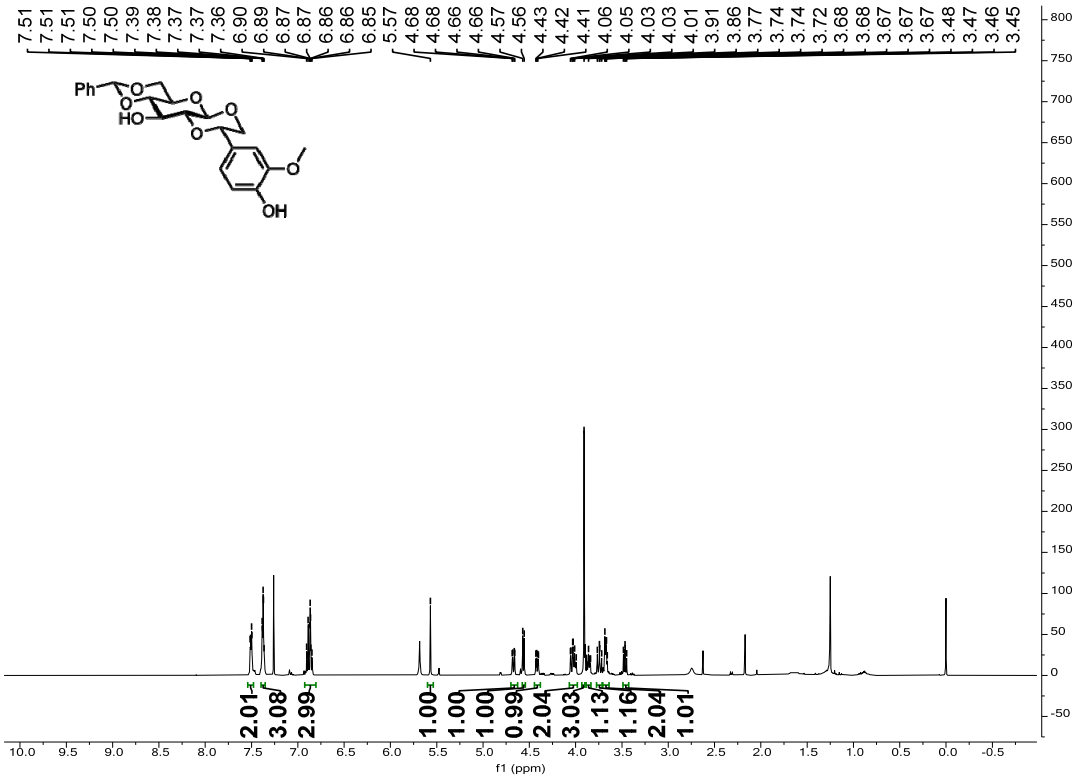

Figure S22 ^{1}H NMR spectrum of compound **11** ($CDCl_3$, 500 MHz)

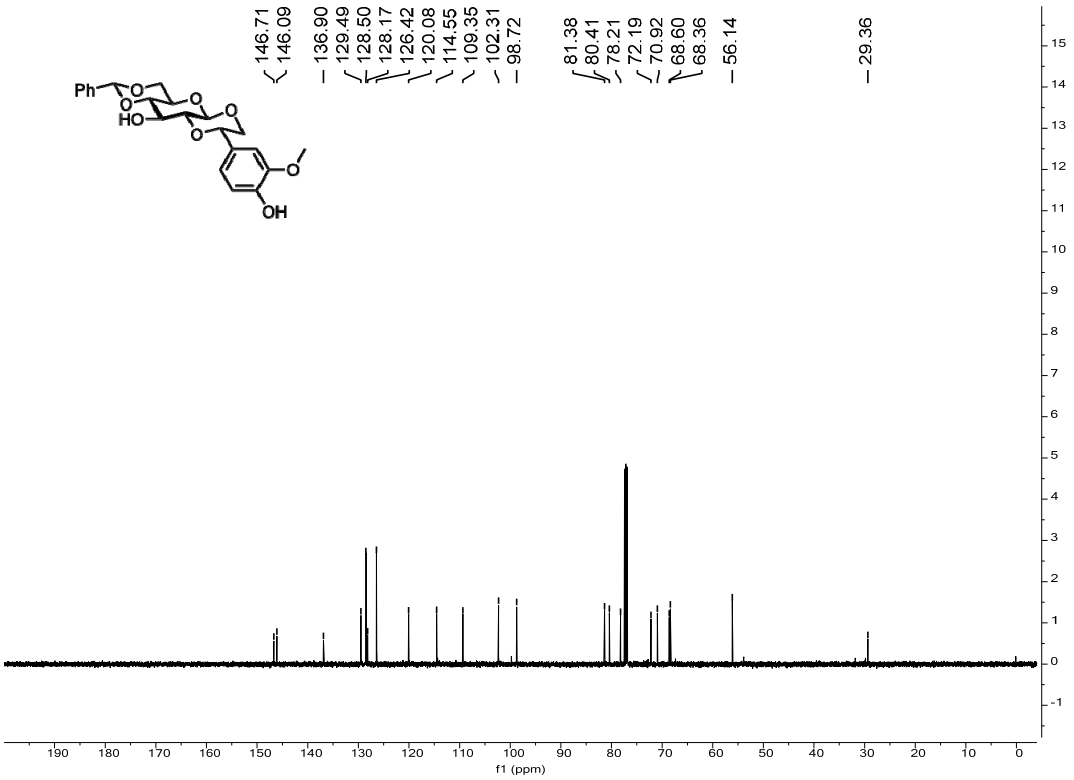

Figure S23 ^{13}C NMR spectrum of compound **11** ($CDCl_3$, 125 MHz)

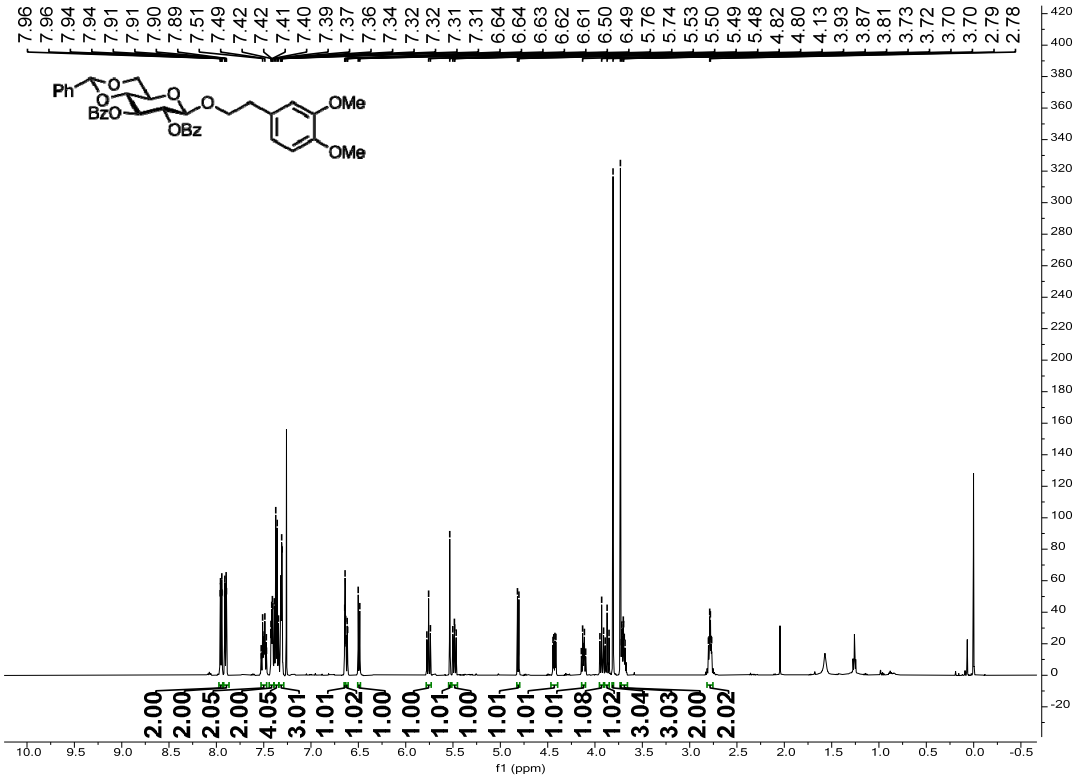

Figure S24 ^{1}H NMR spectrum of compound **S8** ($CDCl_3$, 500 MHz)

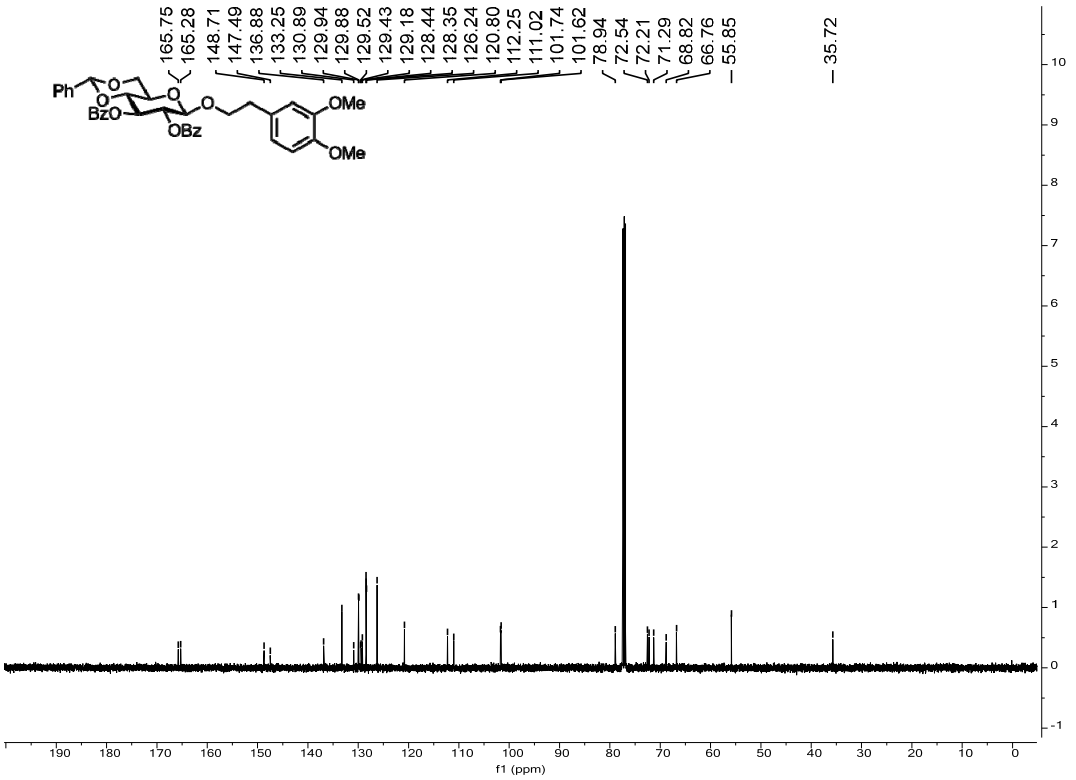

Figure S25 ^{13}C NMR spectrum of compound **S8** ($CDCl_3$, 125 MHz)

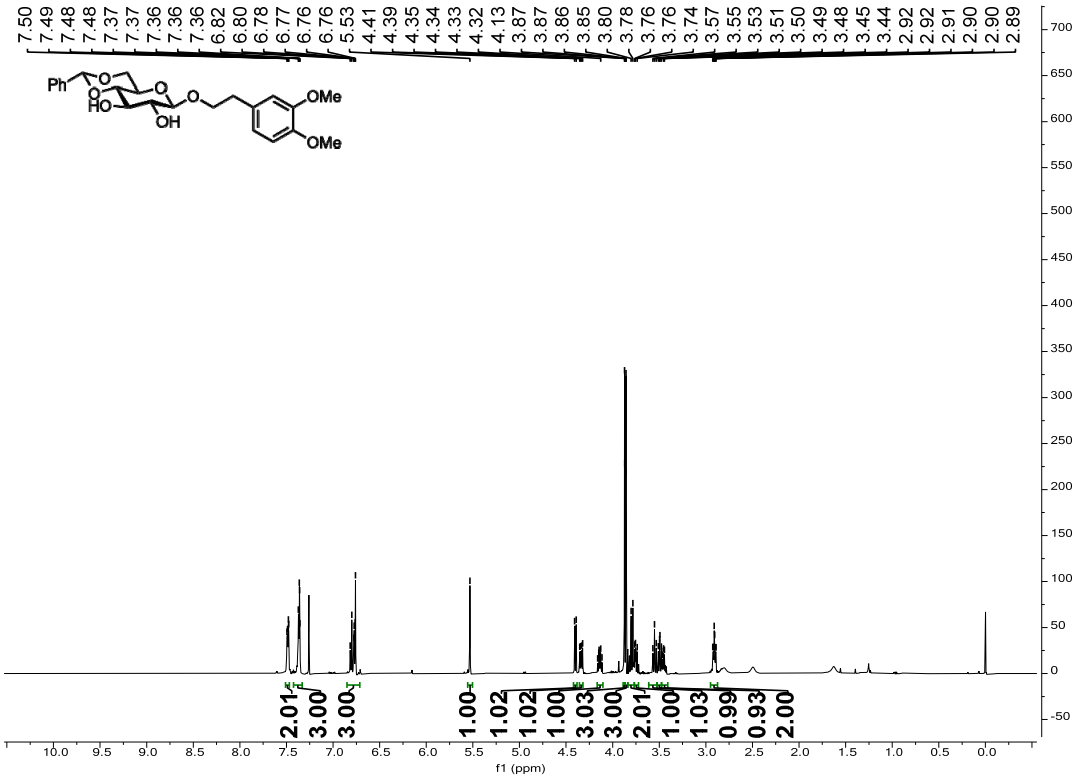

Figure S26 ^{1}H NMR spectrum of compound **9** ($CDCl_3$, 500 MHz)

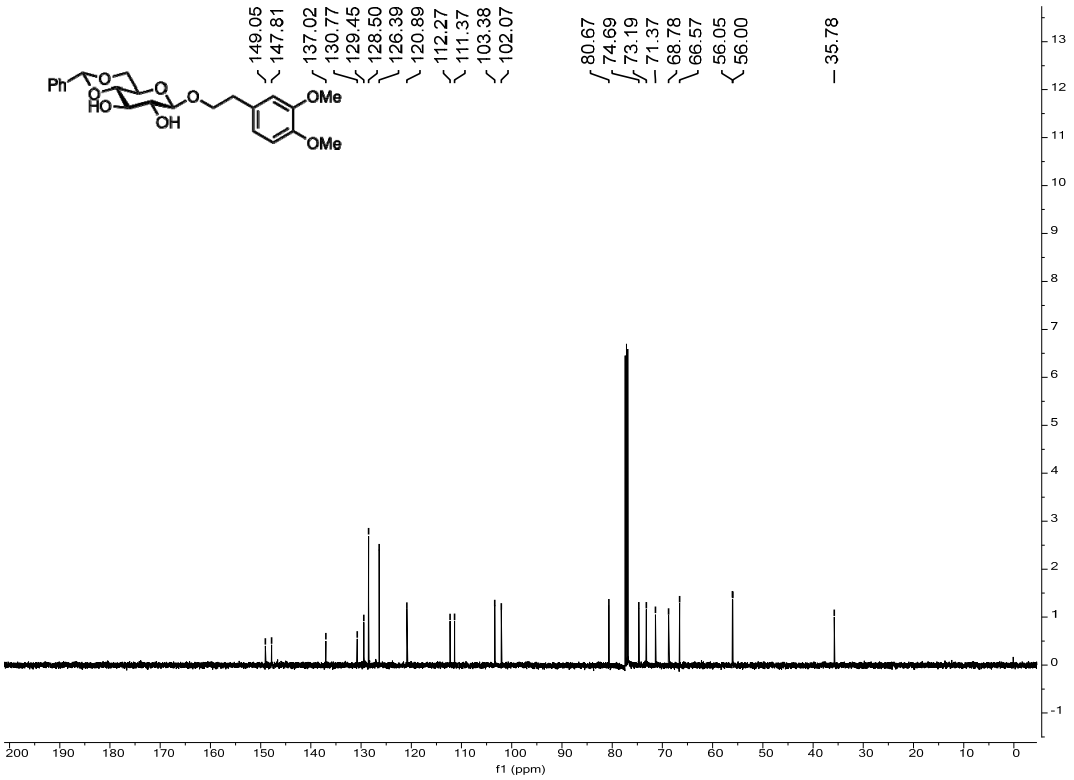

Figure S27 ^{13}C NMR spectrum of compound **9** ($CDCl_3$, 125 MHz)

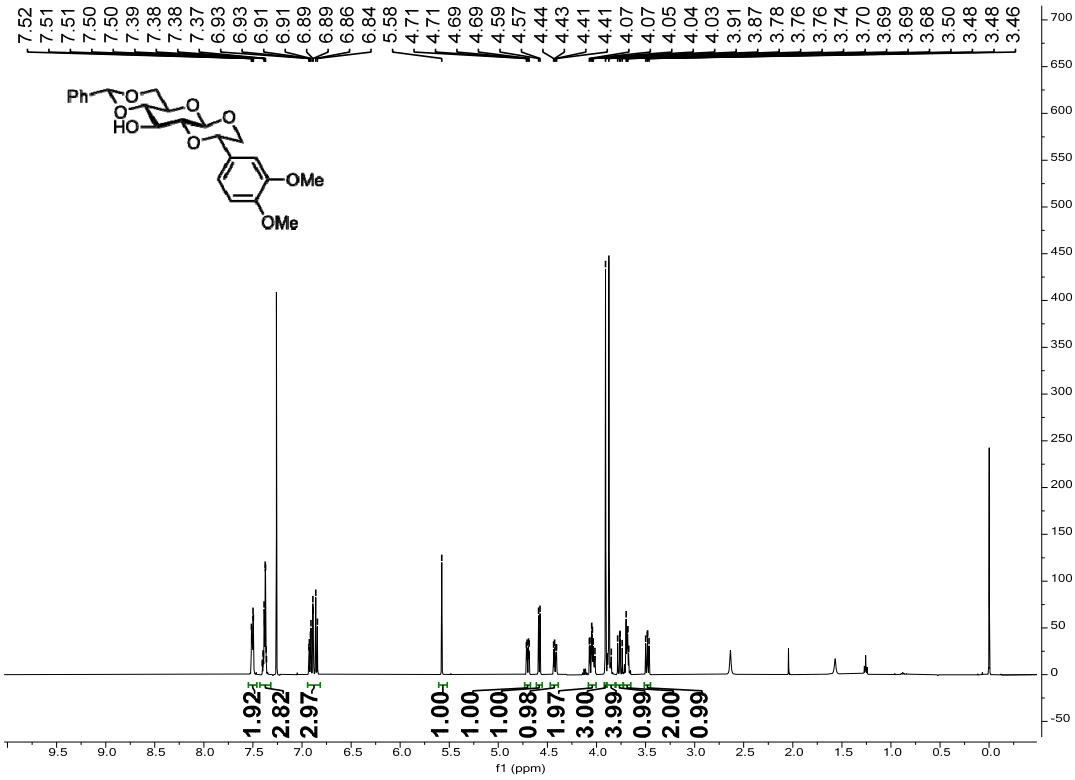

Figure S28 ^{1}H NMR spectrum of compound **12** ($CDCl_3$, 500 MHz)

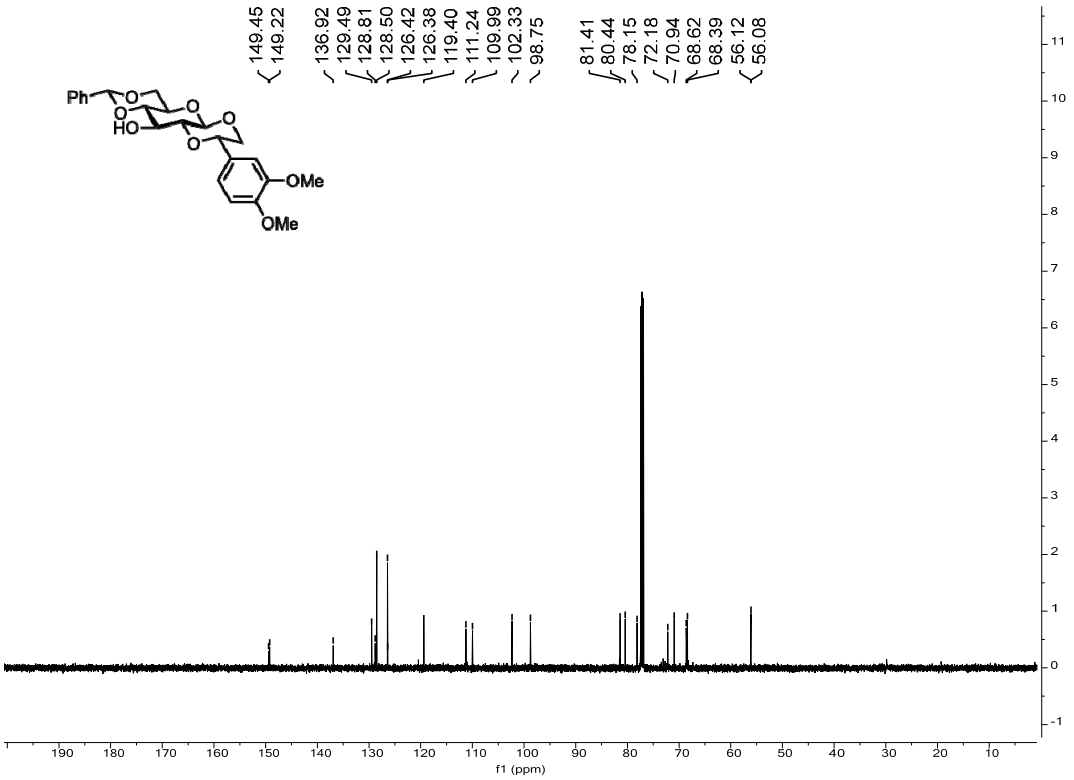

Figure S29 ^{13}C NMR spectrum of compound **12** ($CDCl_3$, 125 MHz)

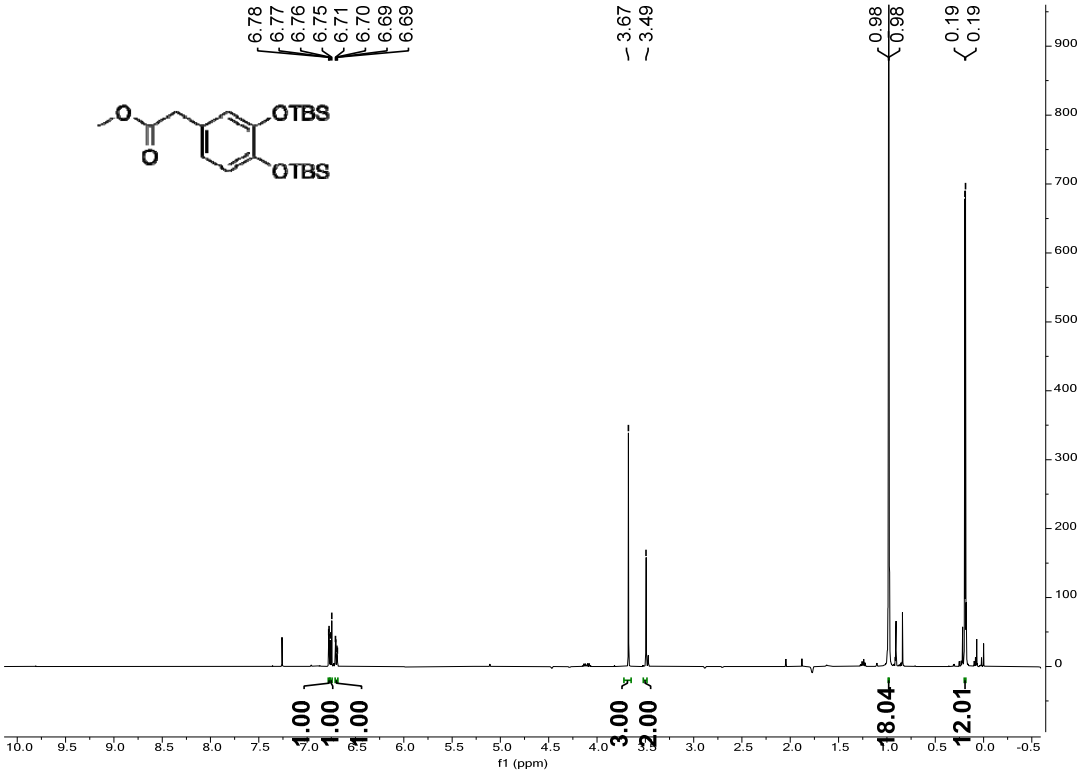

Figure S30 ^{1}H NMR spectrum of compound **S9** ($CDCl_3$, 500 MHz)

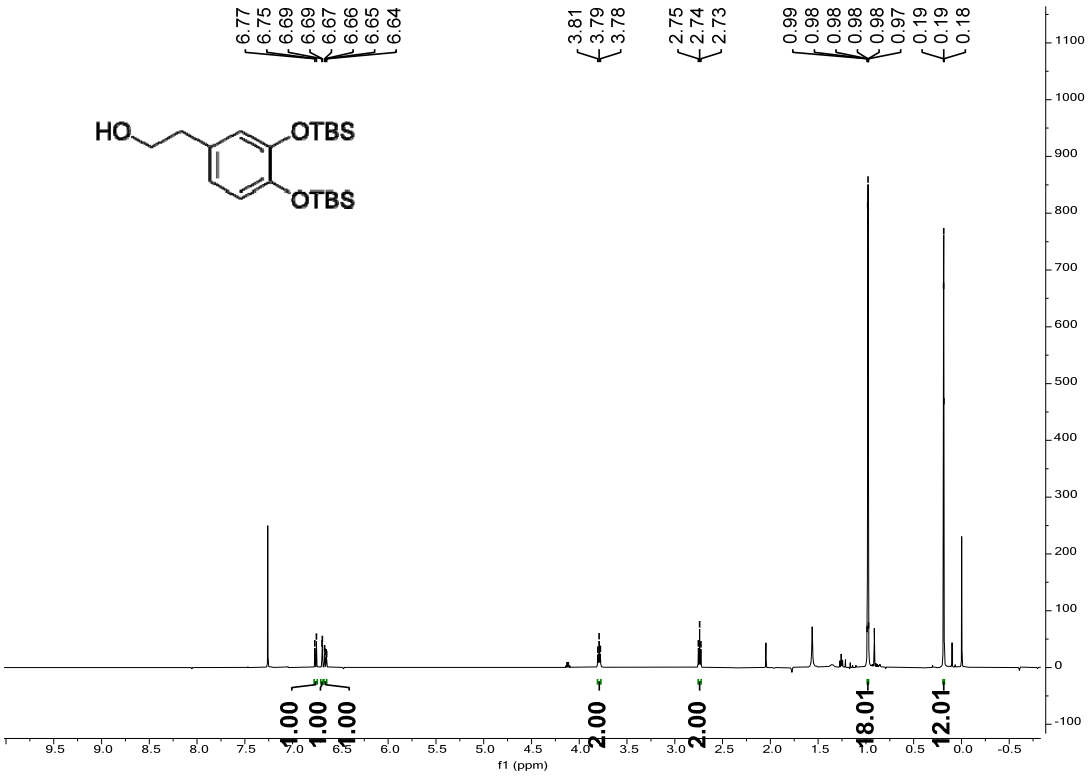

Figure S31 ^{1}H NMR spectrum of compound **15** ($CDCl_3$, 500 MHz)

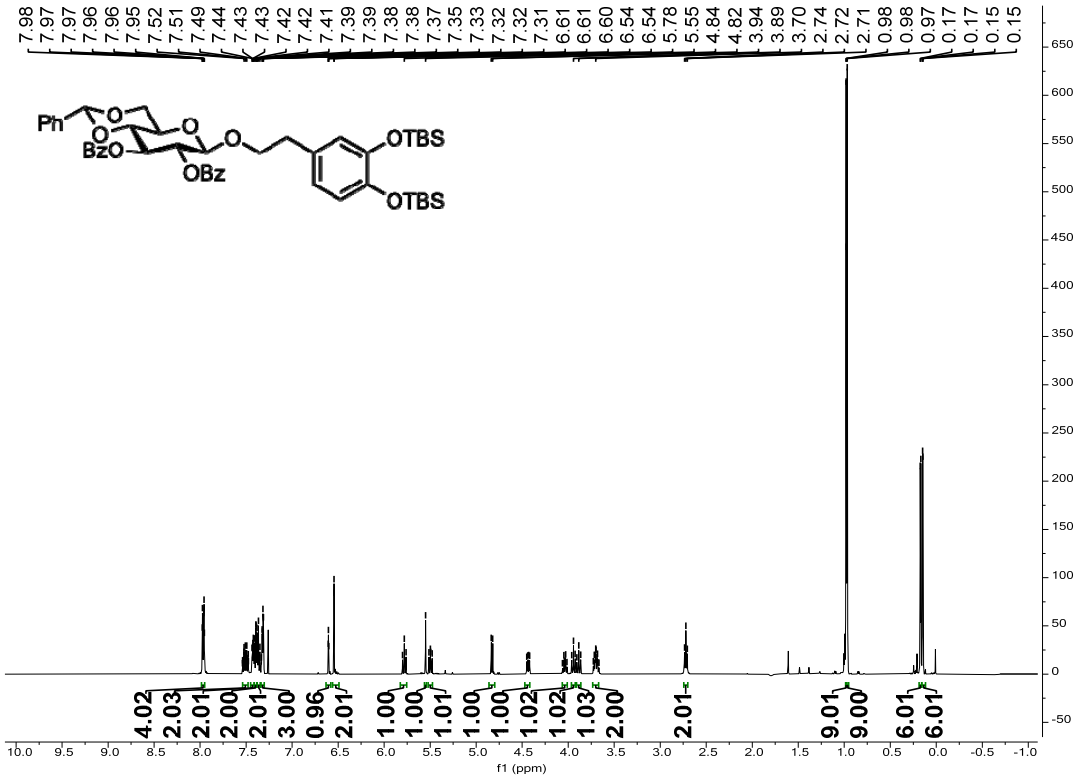

Figure S32 ^{1}H NMR spectrum of compound **16** ($CDCl_3$, 500 MHz)

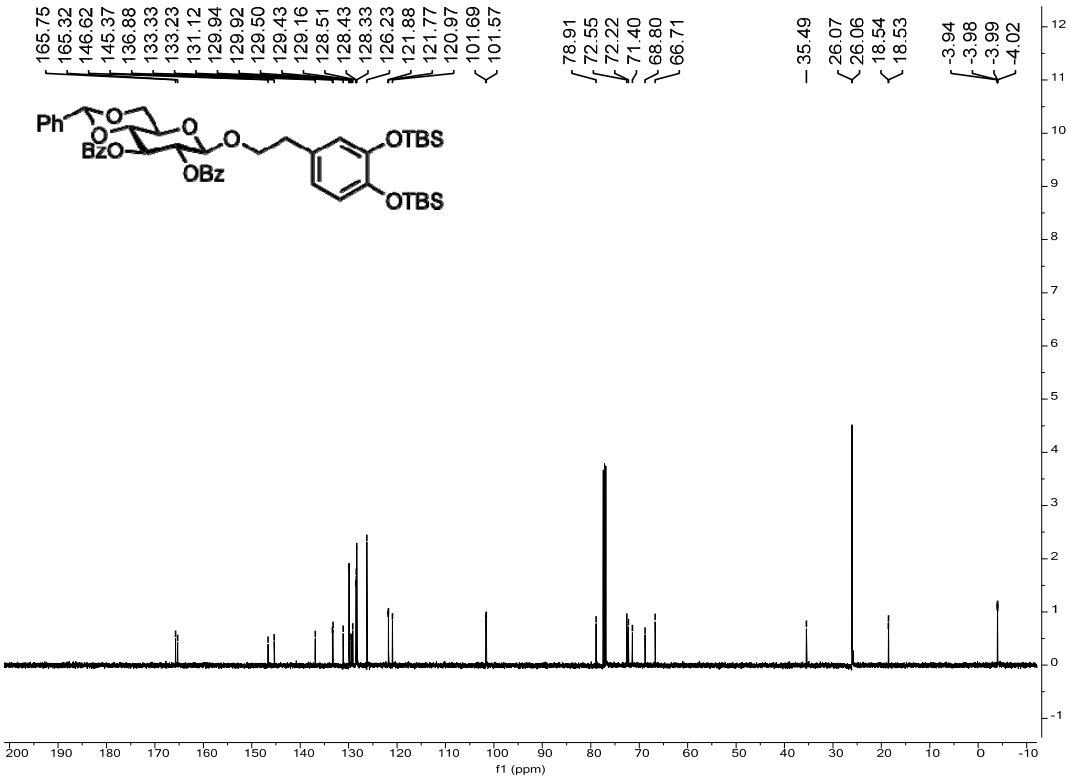

Figure S33 ^{13}C NMR spectrum of compound **16** ($CDCl_3$, 125 MHz)

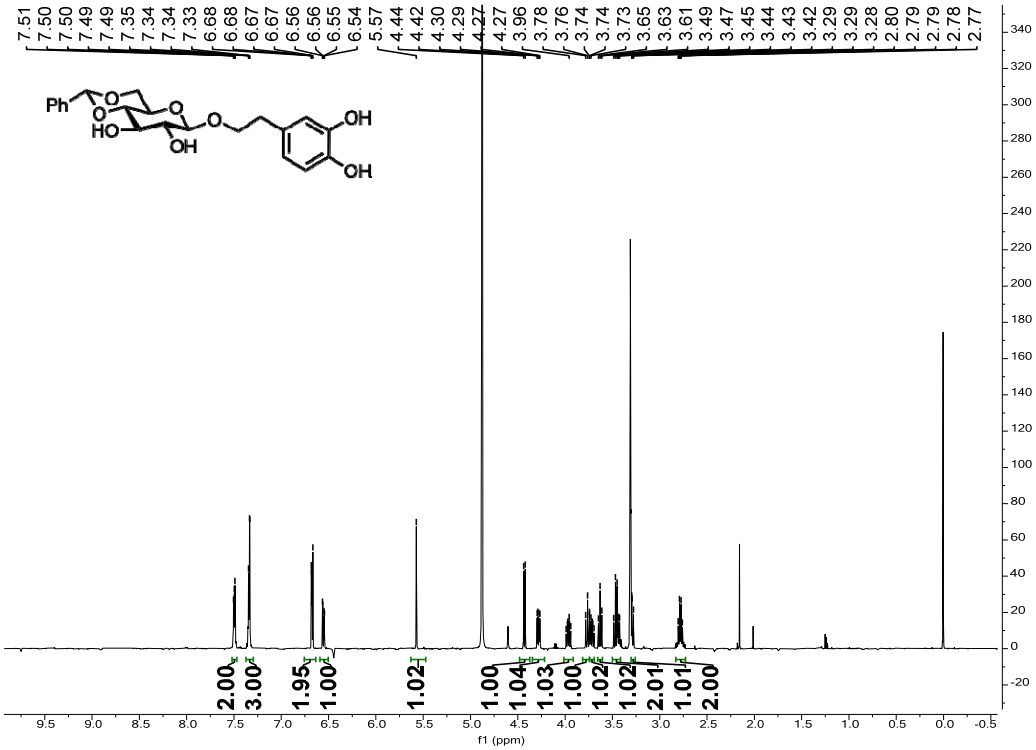

Figure S34 ^{1}H NMR spectrum of compound **10** ($CDCl_3$, 500 MHz)

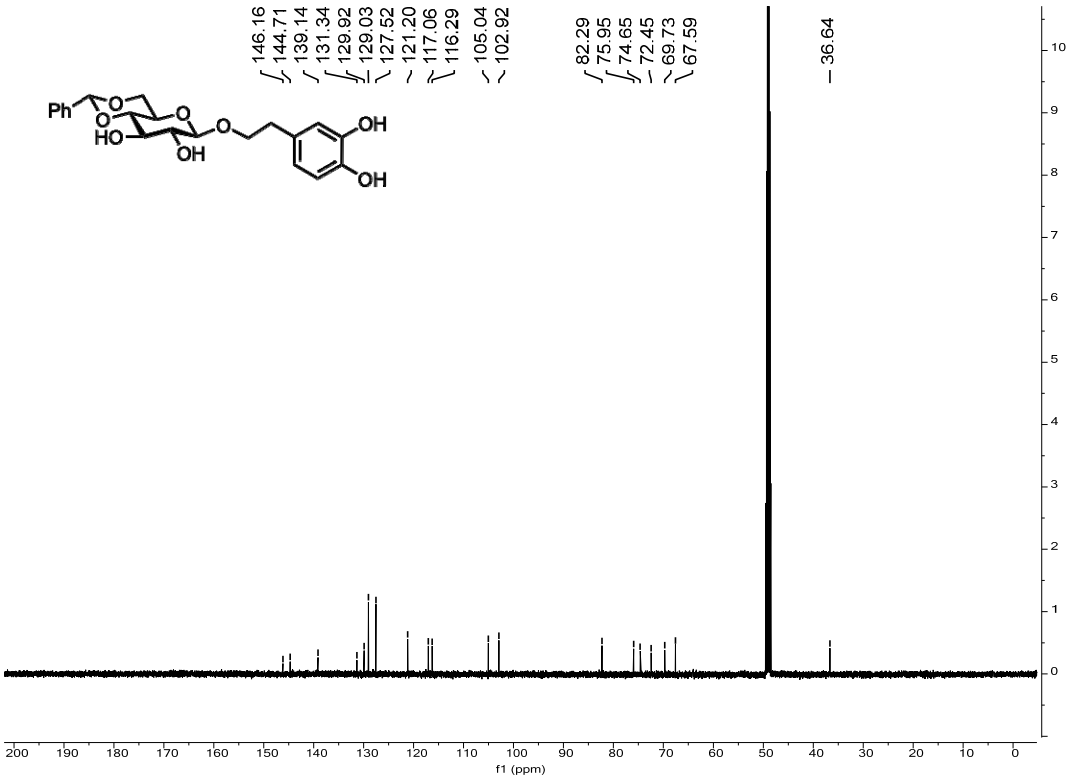

Figure S35 ^{13}C NMR spectrum of compound **10** ($CDCl_3$, 125 MHz)

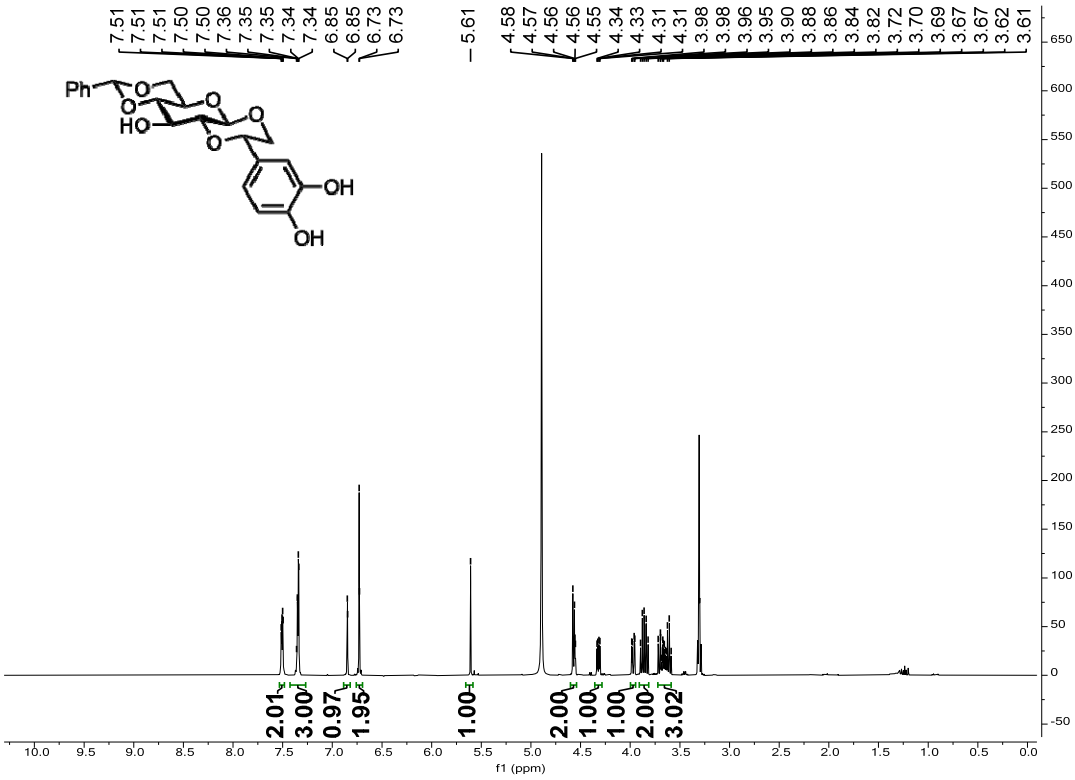

Figure S36 ^{1}H NMR spectrum of compound **13** ($CDCl_3$, 500 MHz)

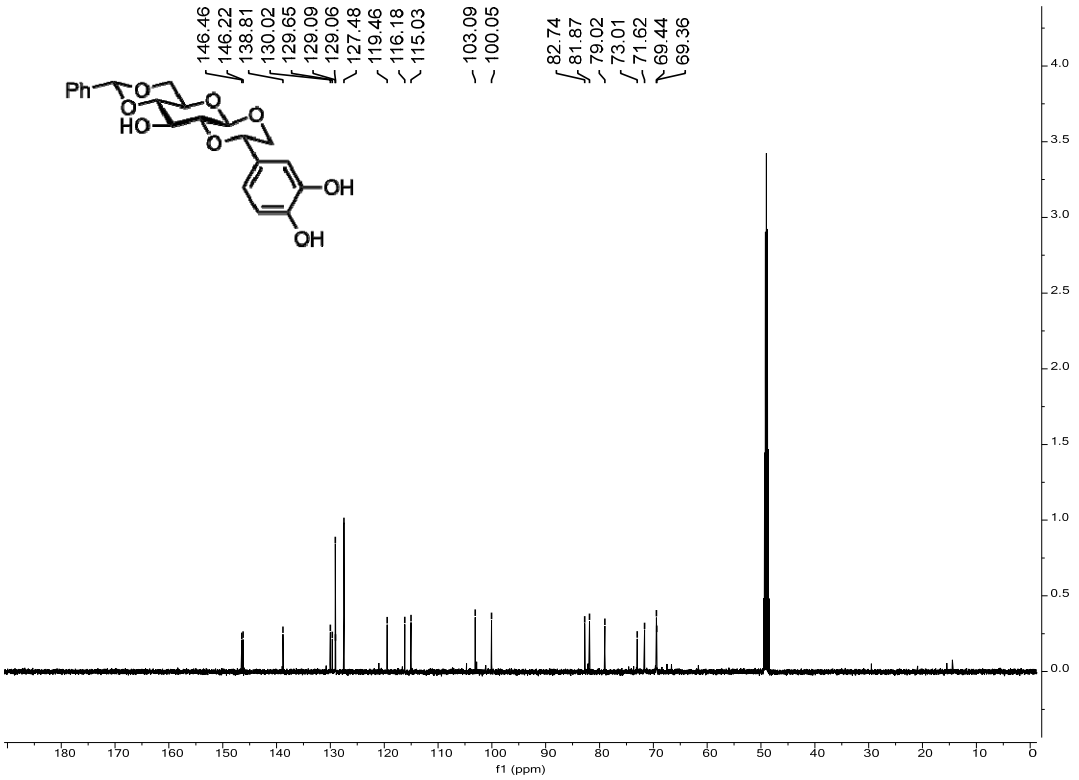

Figure S37 ^{13}C NMR spectrum of compound **13** ($CDCl_3$, 125 MHz)

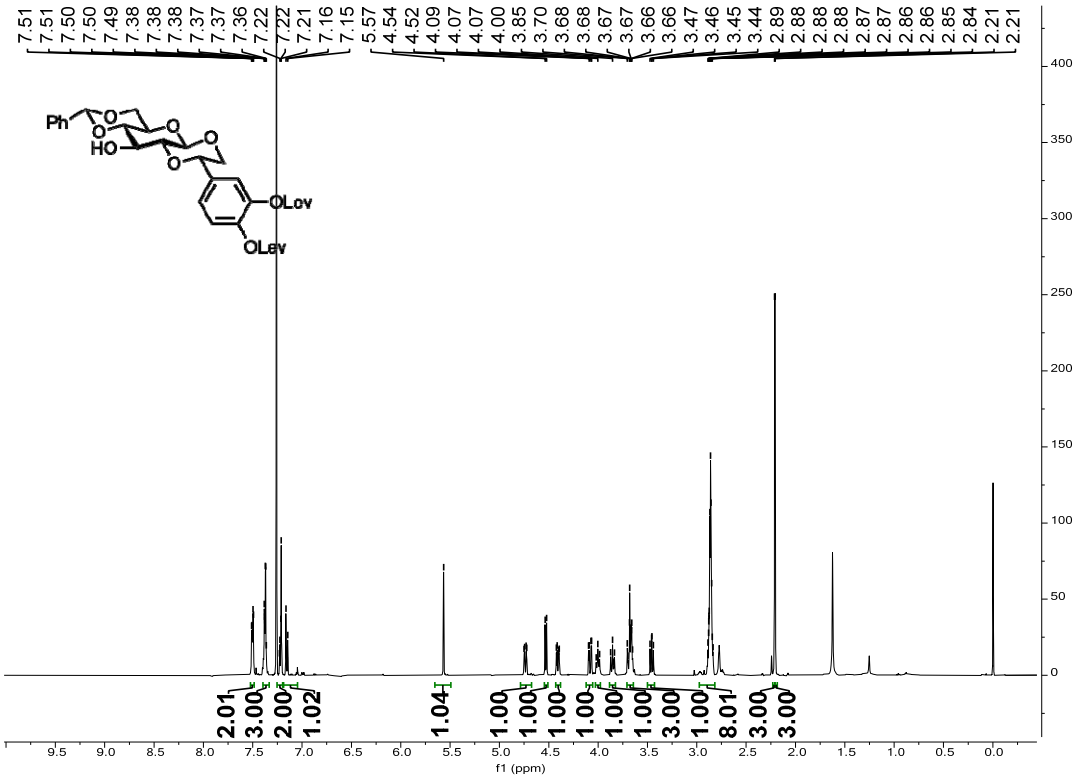

Figure S38 ^{1}H NMR spectrum of compound **17** ($CDCl_3$, 500 MHz)

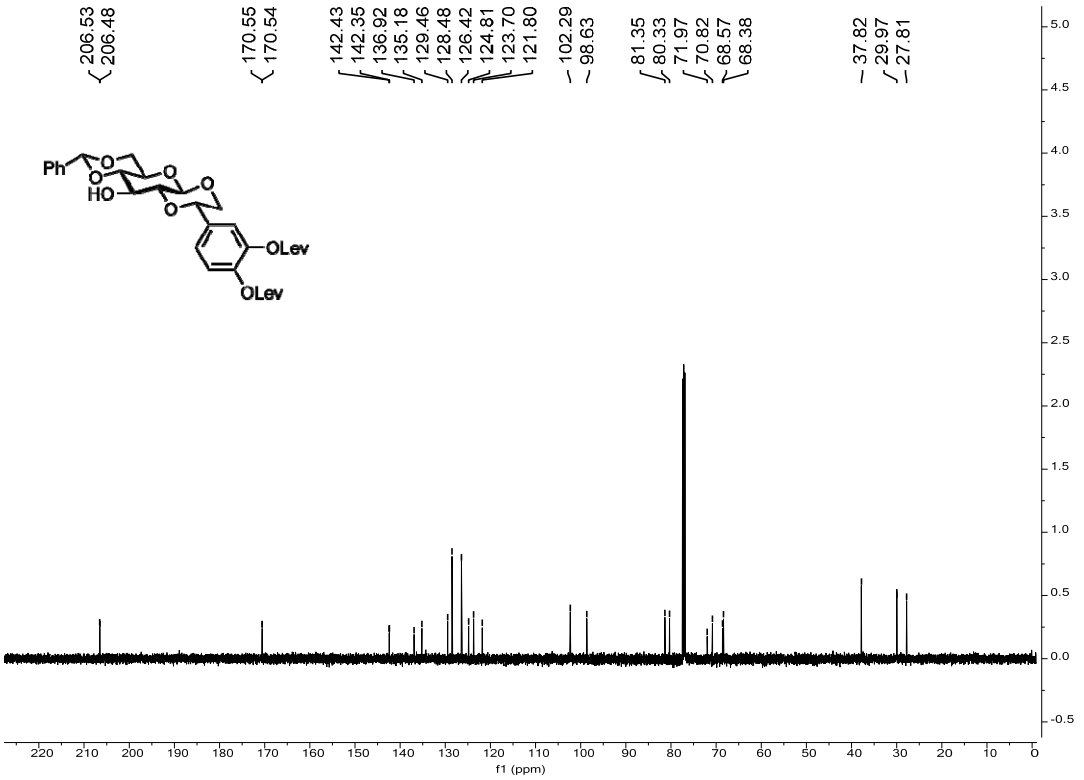

Figure S39 ^{13}C NMR spectrum of compound **17** ($CDCl_3$, 125 MHz)

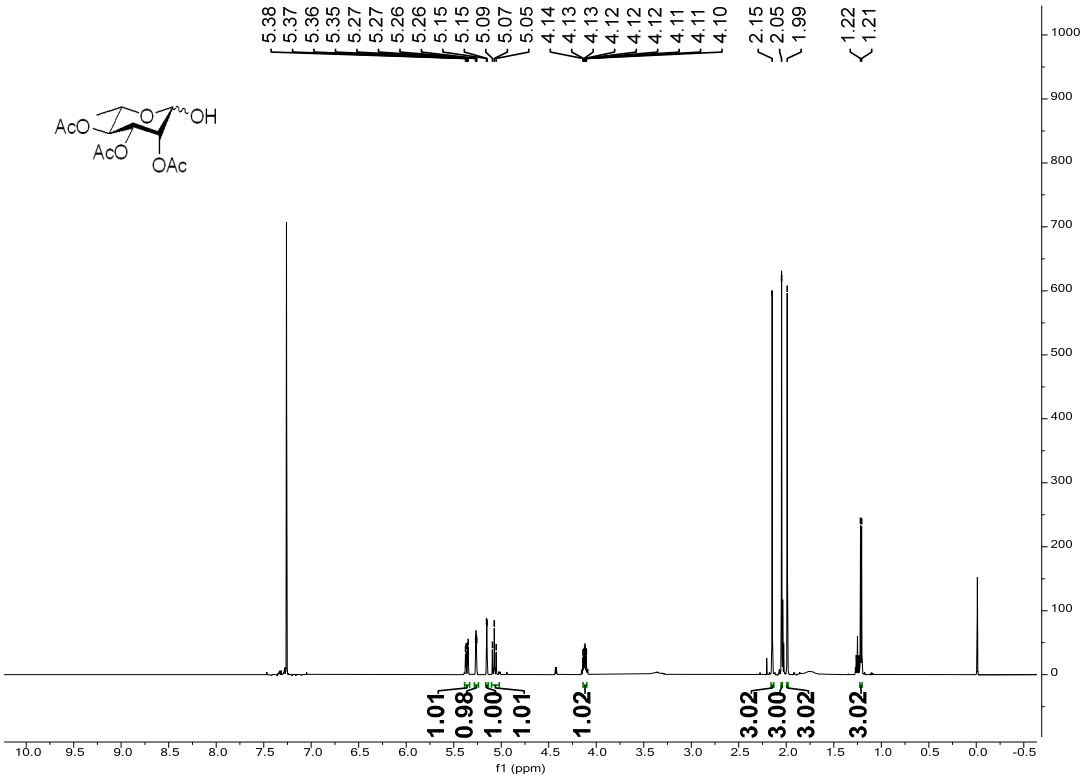

Figure S40 ^{1}H NMR spectrum of compound **S10** ($CDCl_3$, 500 MHz)

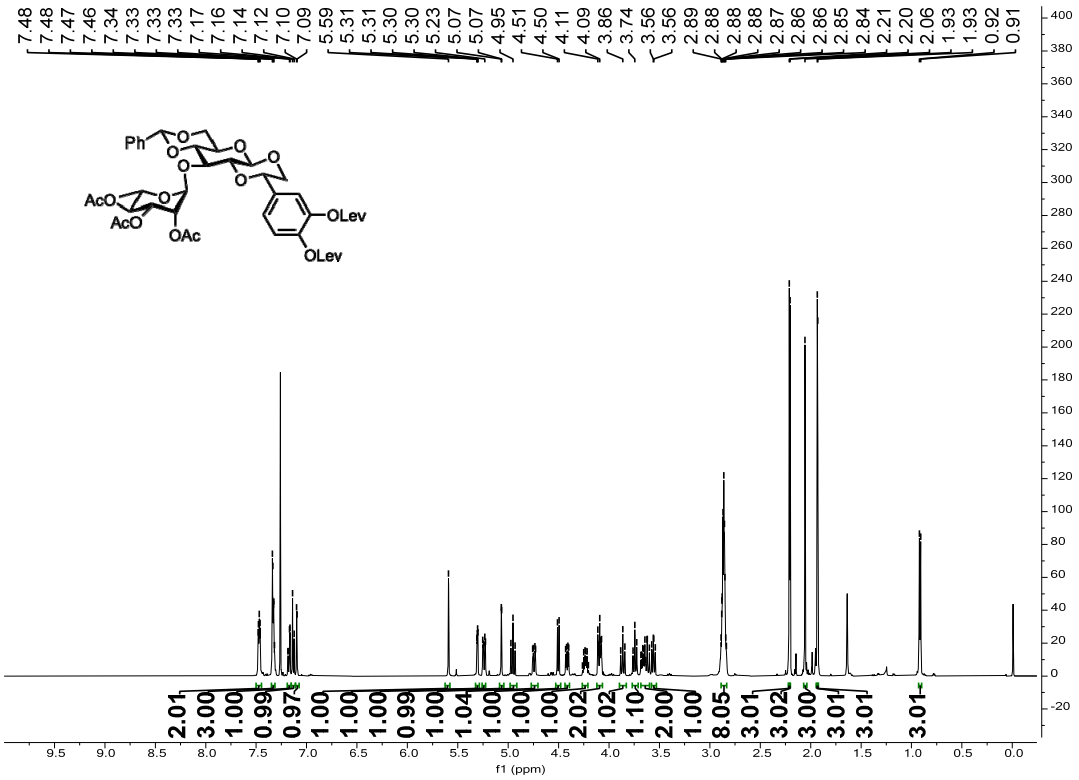

Figure S41 ^{1}H NMR spectrum of compound **19** ($CDCl_3$, 500 MHz)

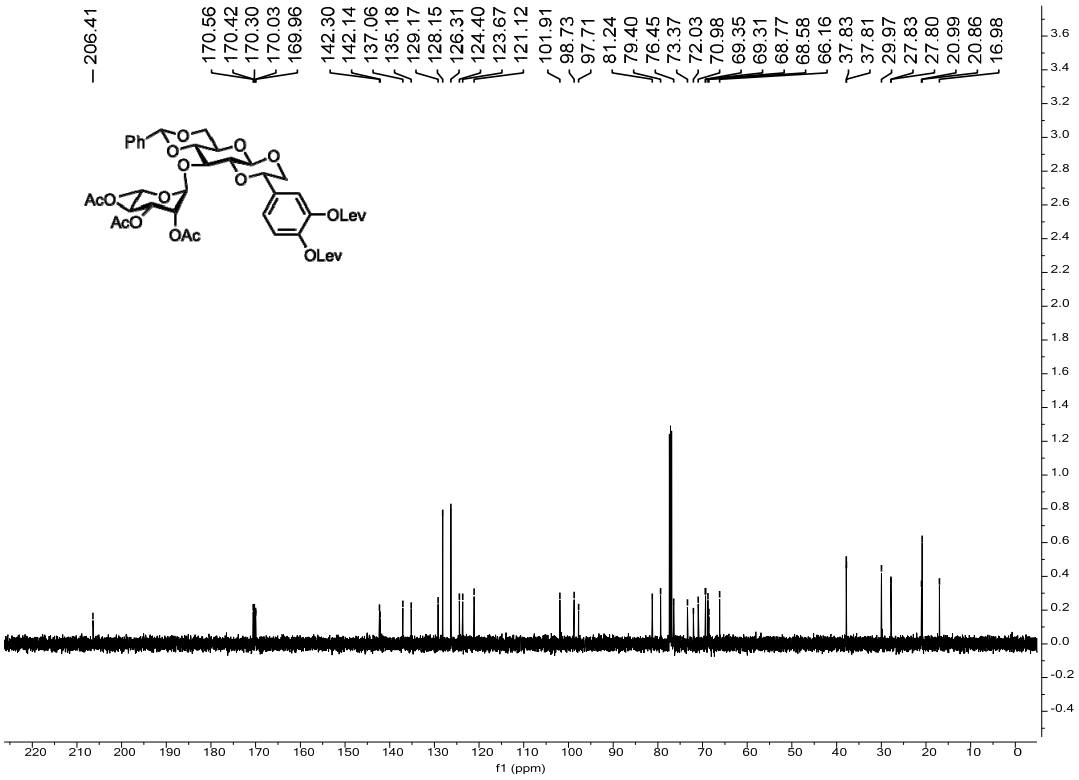

Figure S42 ^{13}C NMR spectrum of compound **19** ($CDCl_3$, 125 MHz)

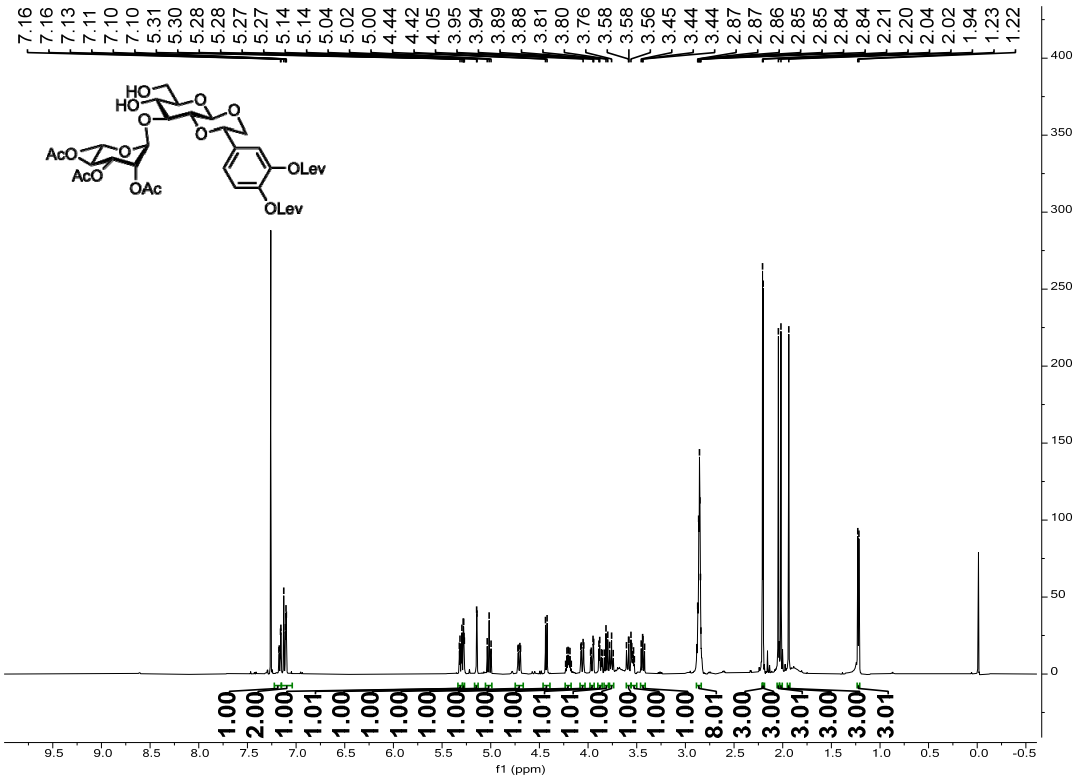

Figure S43 ^{1}H NMR spectrum of compound **S11** ($CDCl_3$, 500 MHz)

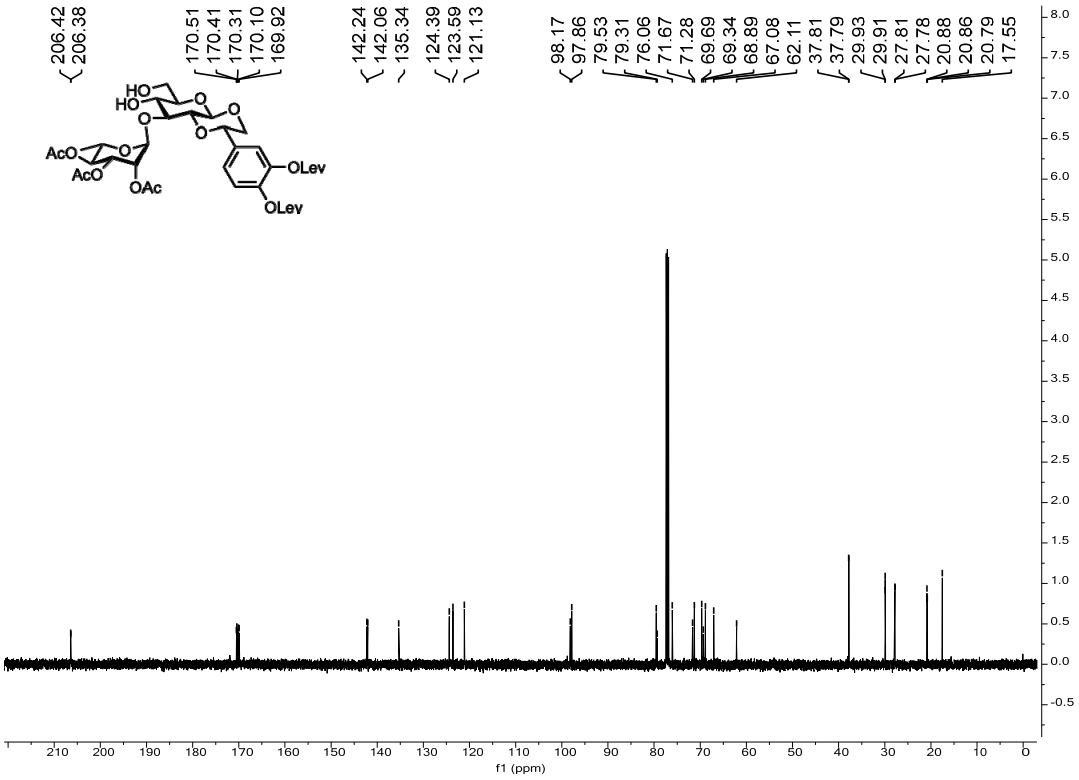

Figure S44 ^{13}C NMR spectrum of compound **S11** ($CDCl_3$, 125 MHz)

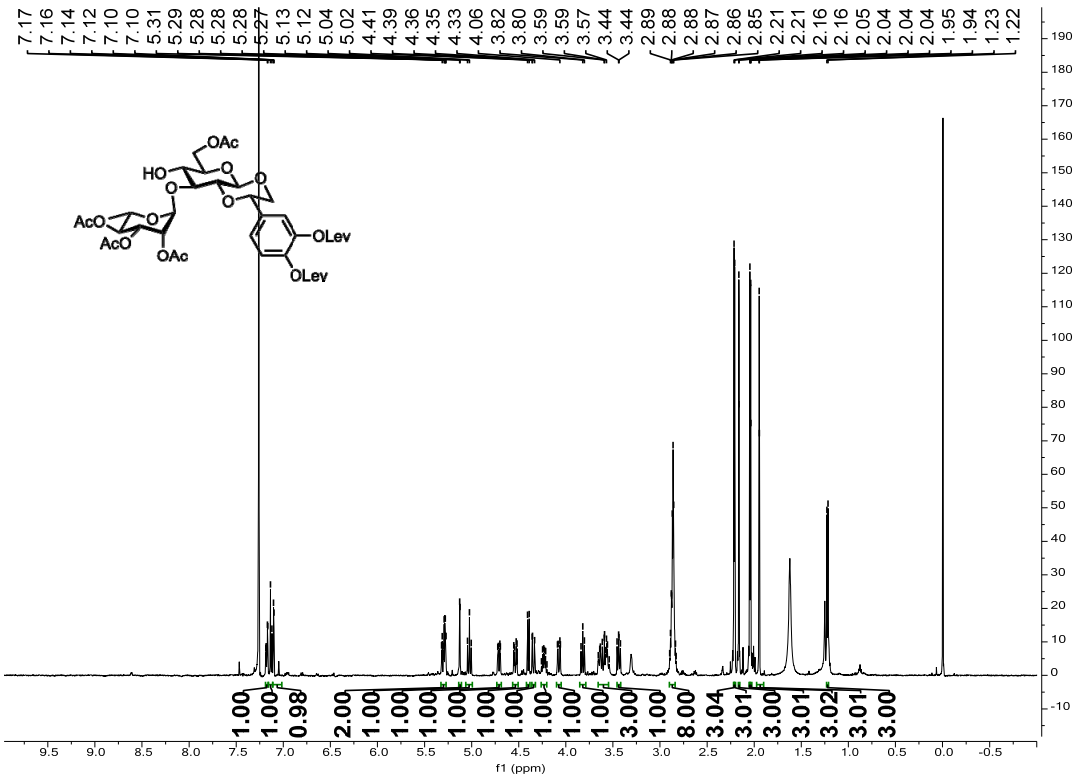

Figure S45 ^{1}H NMR spectrum of compound **20** ($CDCl_3$, 500 MHz)

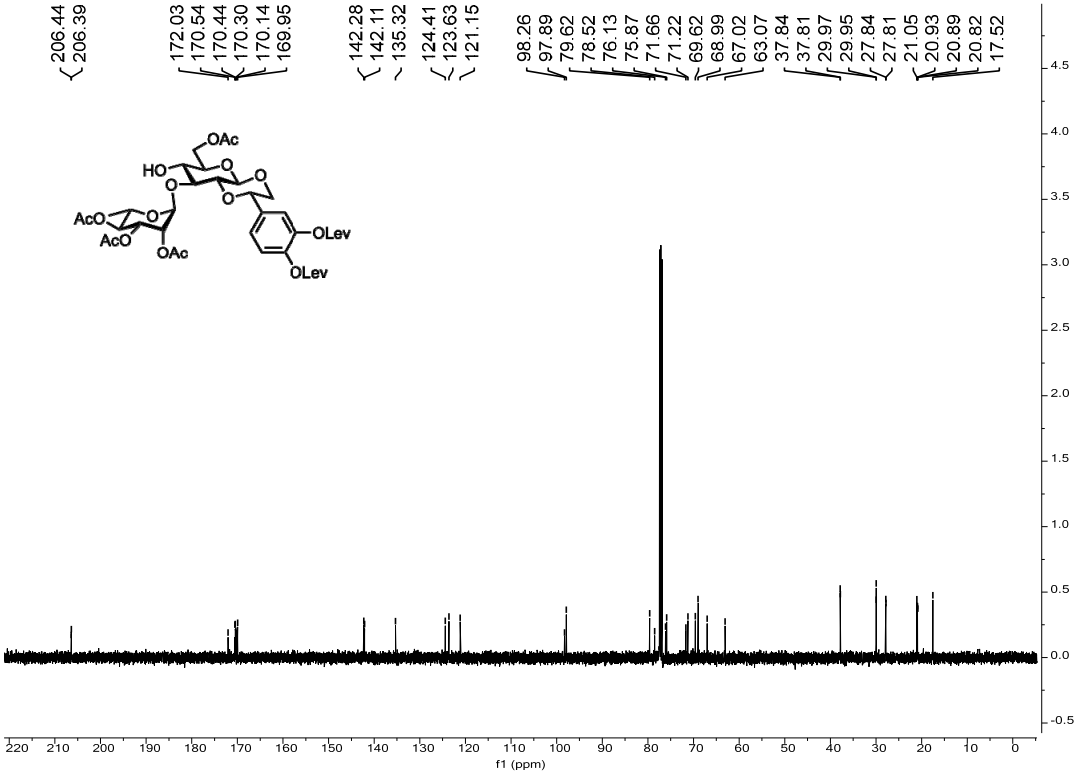

Figure S46 ^{13}C NMR spectrum of compound **20** ($CDCl_3$, 125 MHz)

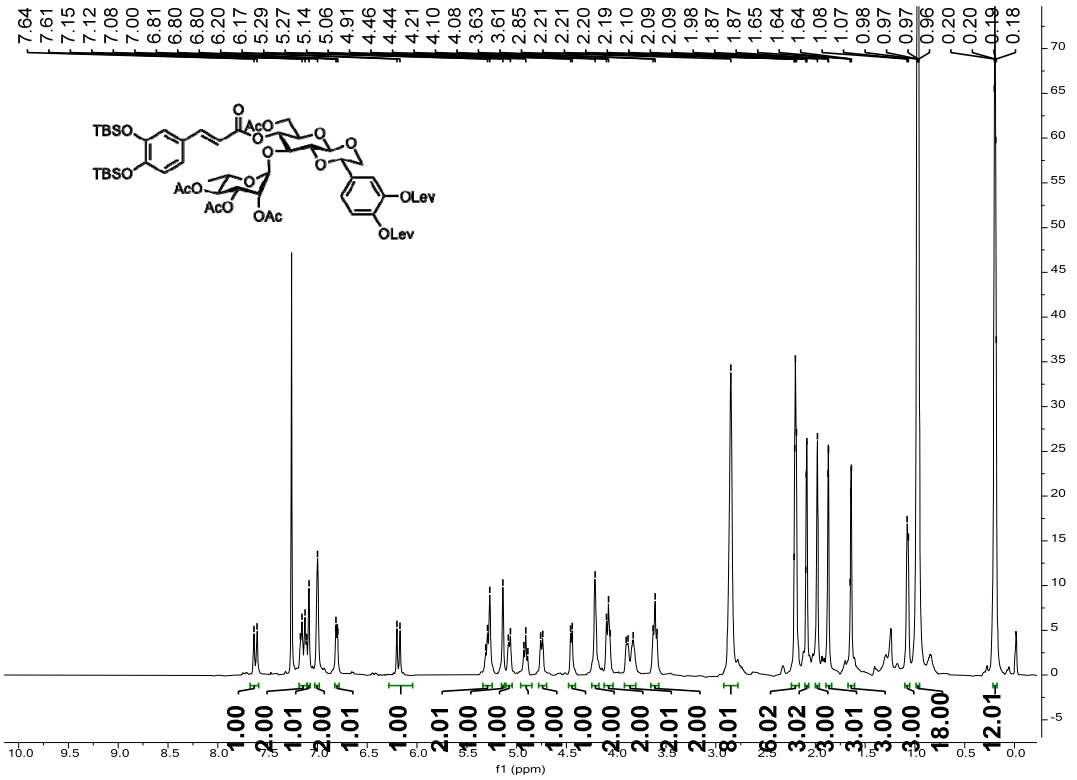

Figure S47 ^{1}H NMR spectrum of compound **22** ($CDCl_3$, 500 MHz)

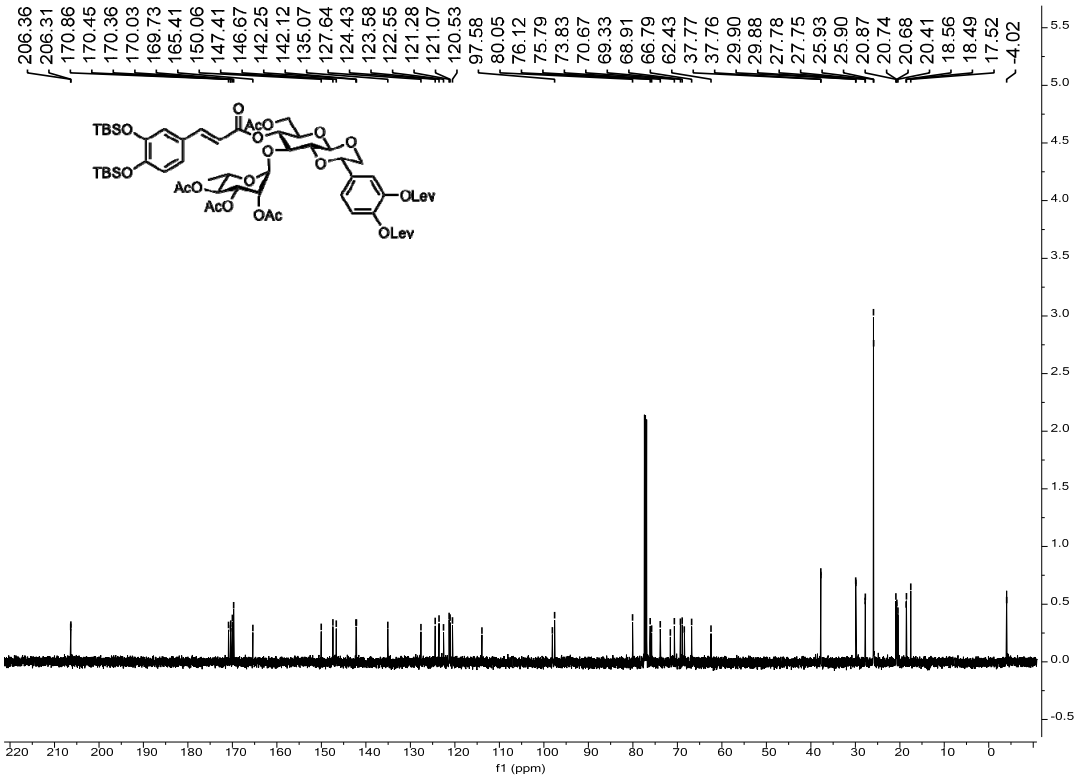

Figure S48 ^{13}C NMR spectrum of compound **22** ($CDCl_3$, 125 MHz)

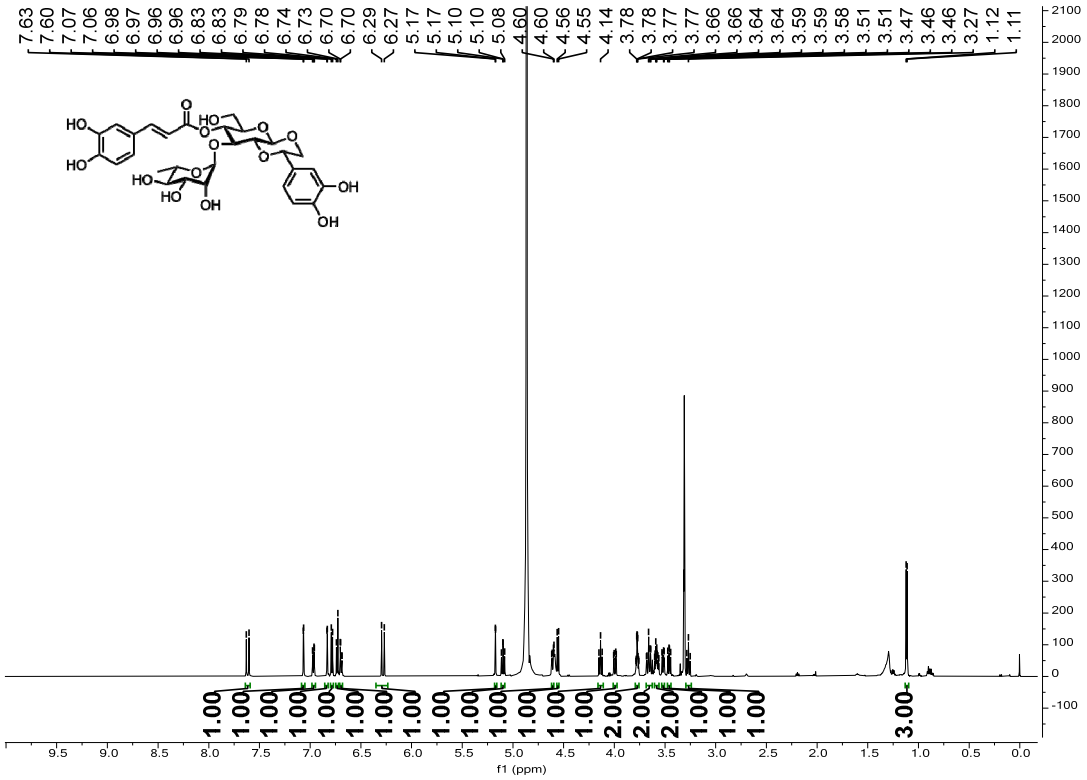

Figure S49 ^{1}H NMR spectrum of **crenatoside** (CD_3OD, 600 MHz)

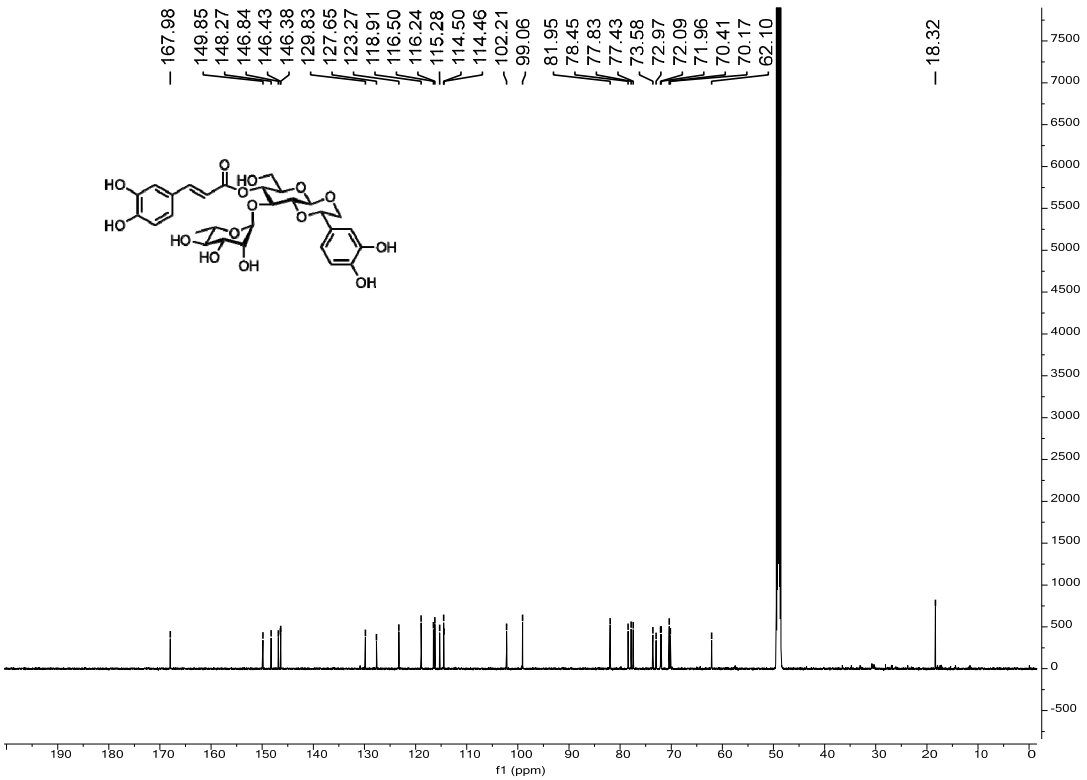

Figure S50 ^{13}C NMR spectrum of **crenatoside** (CD_3OD, 150 MHz)

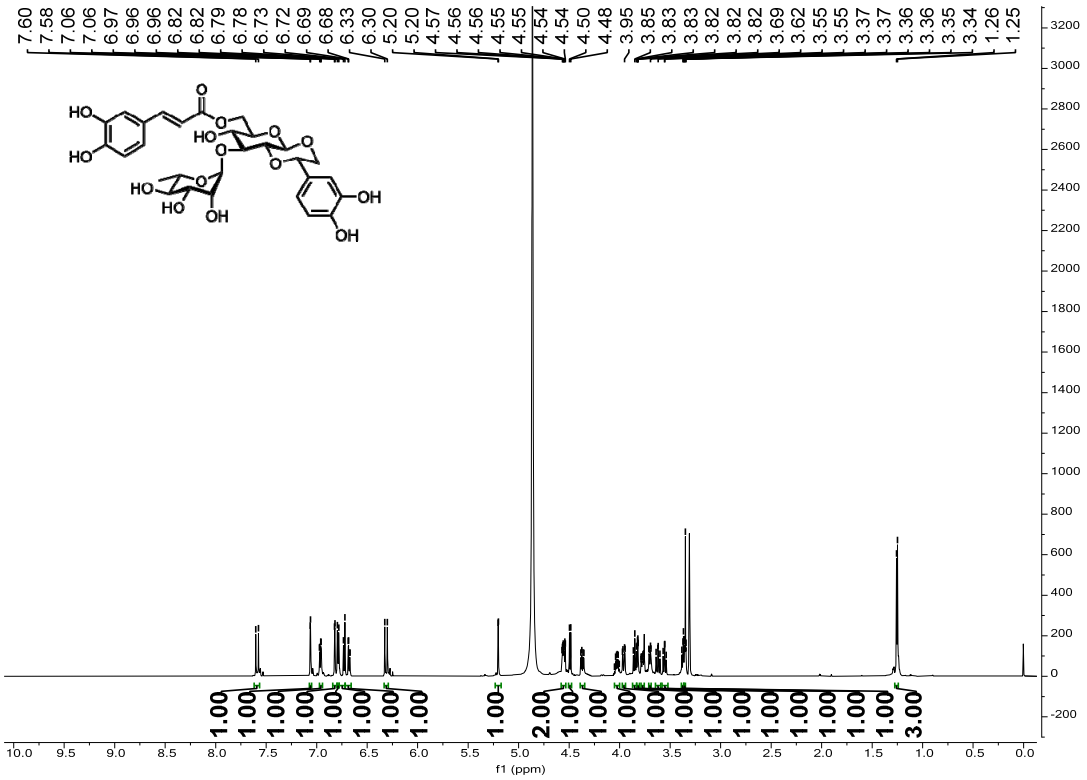

Figure S51 ^{1}H NMR spectrum of **isocrenatoside** (CD_3OD, 600 MHz)

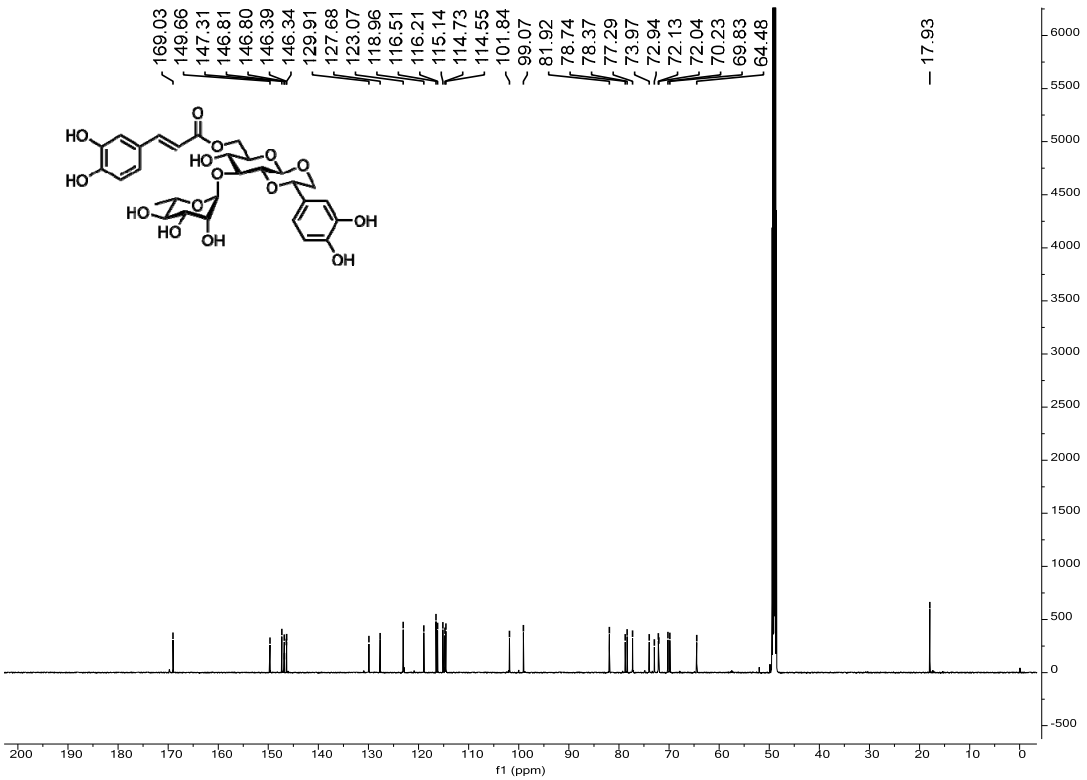

Figure S52 ^{13}C NMR spectrum of **isocrenatoside** (CD_3OD, 150 MHz)

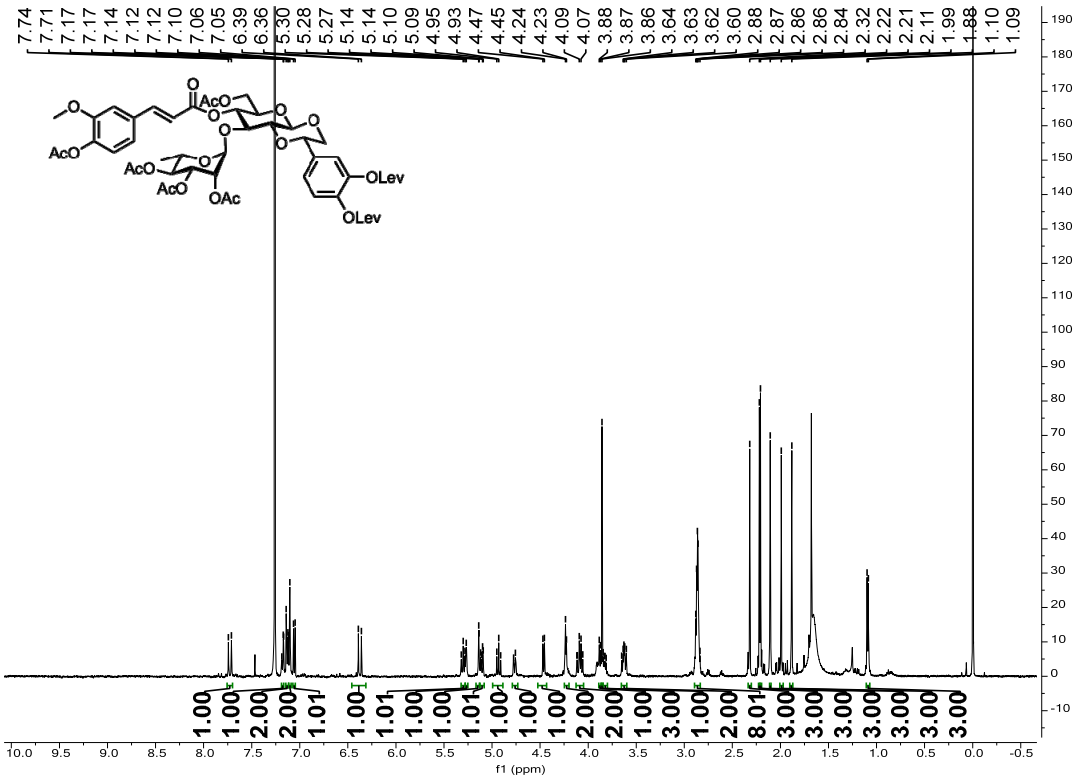

Figure S53 ^{1}H NMR spectrum of compound **S12** ($CDCl_3$, 500 MHz)

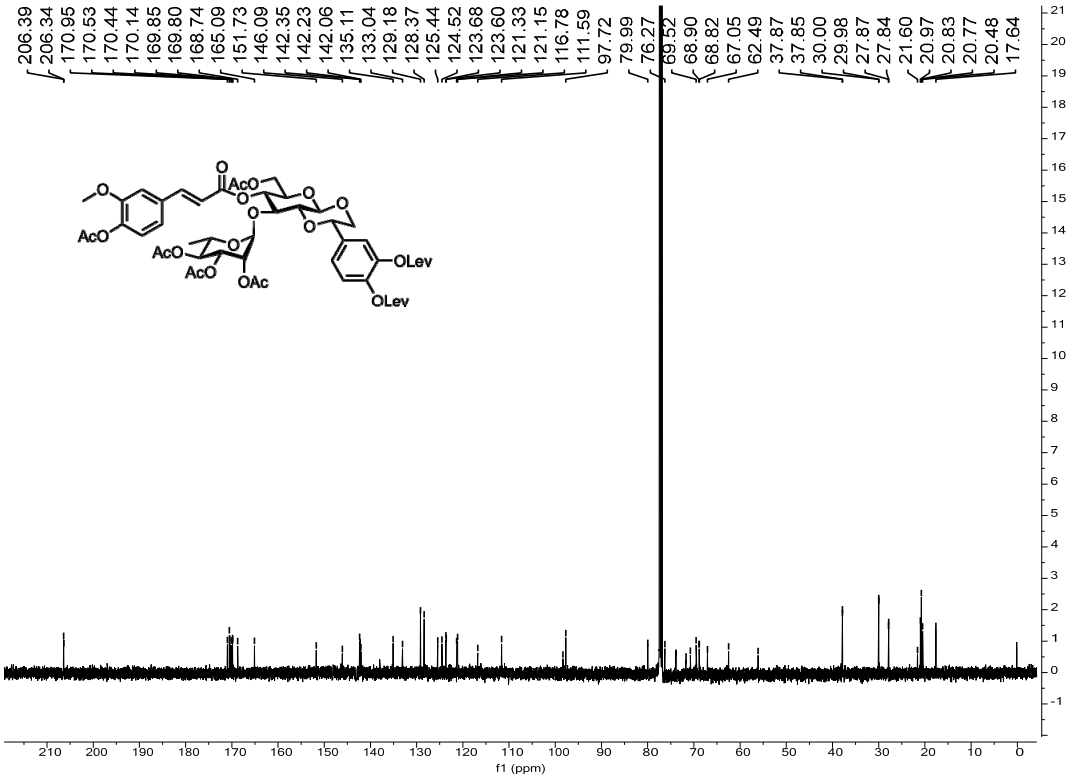

Figure S54 ^{13}C NMR spectrum of compound **S12** ($CDCl_3$, 125 MHz)

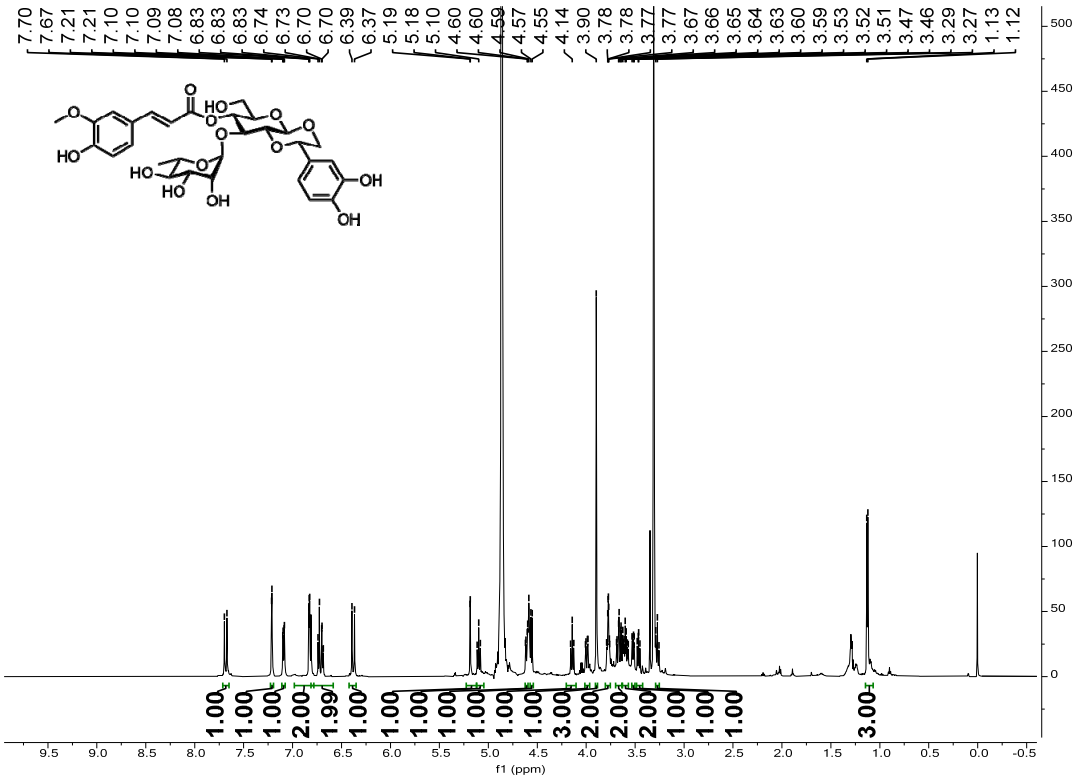

Figure S55 ^{1}H NMR spectrum of compound **23** (CD_3OD, 600 MHz)

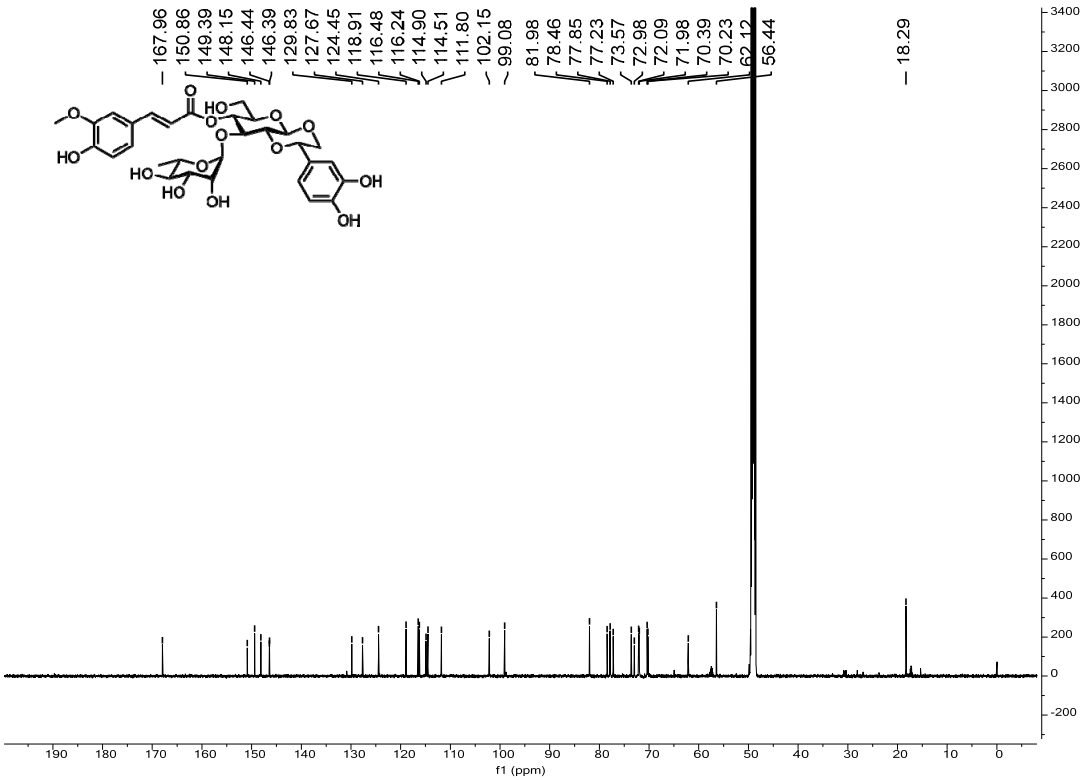

Figure S56 ^{13}C NMR spectrum of compound **23** (CD_3OD, 150 MHz)

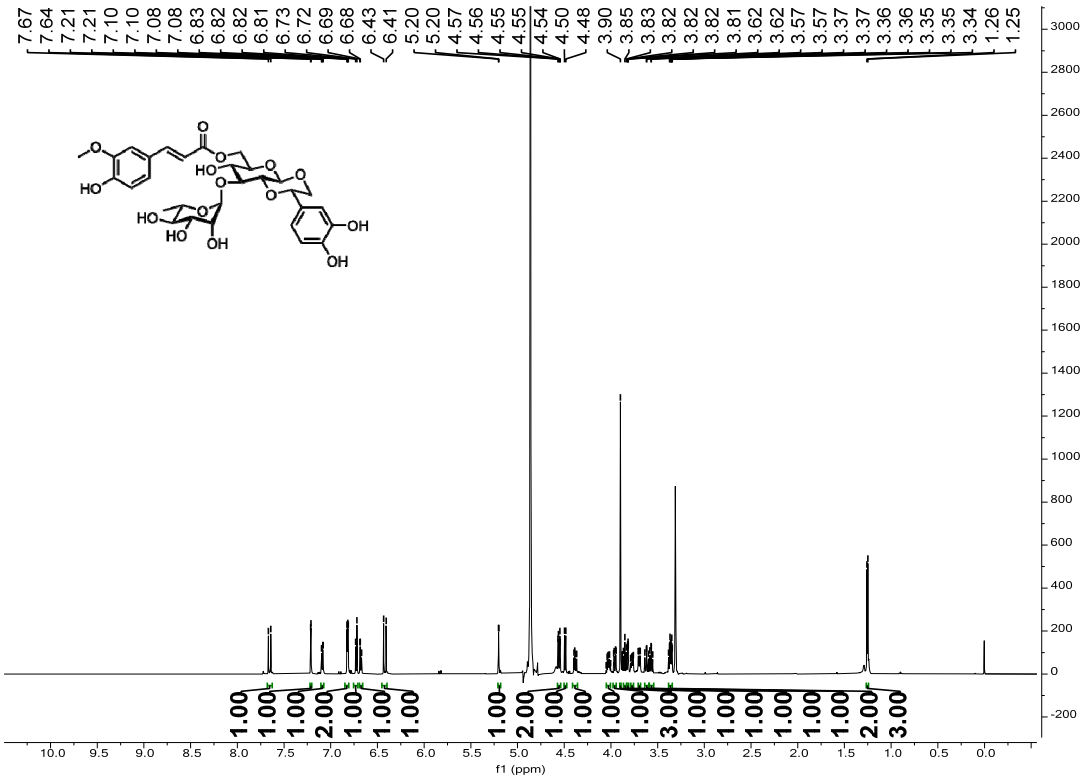

Figure S57 ^{1}H NMR spectrum of compound **27** (CD_3OD, 600 MHz)

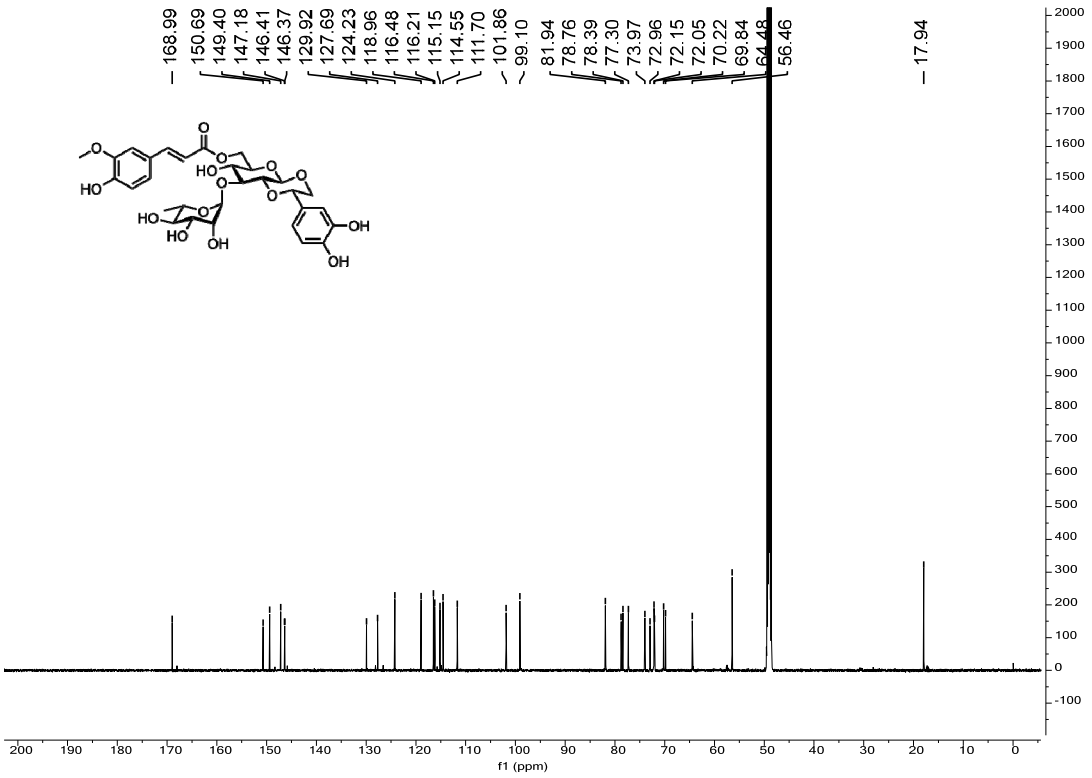

Figure S58 ^{13}C NMR spectrum of compound **27** (CD_3OD, 150 MHz)

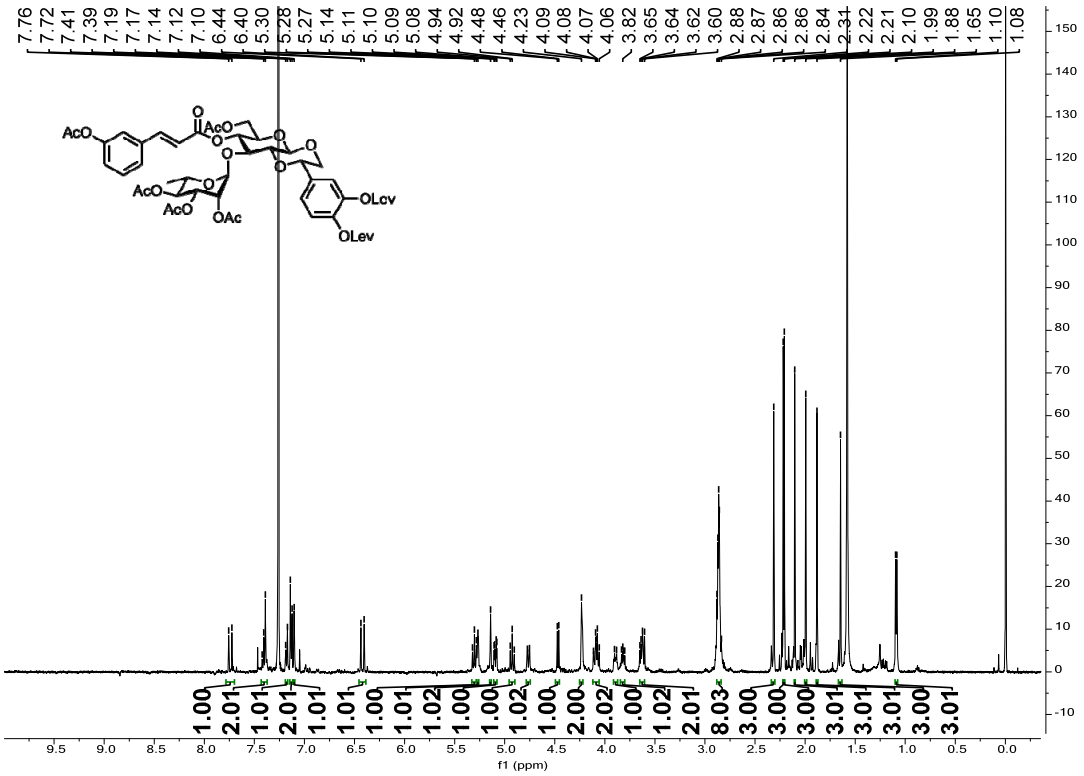

Figure S59 ^{1}H NMR spectrum of compound **S13** ($CDCl_3$, 500 MHz)

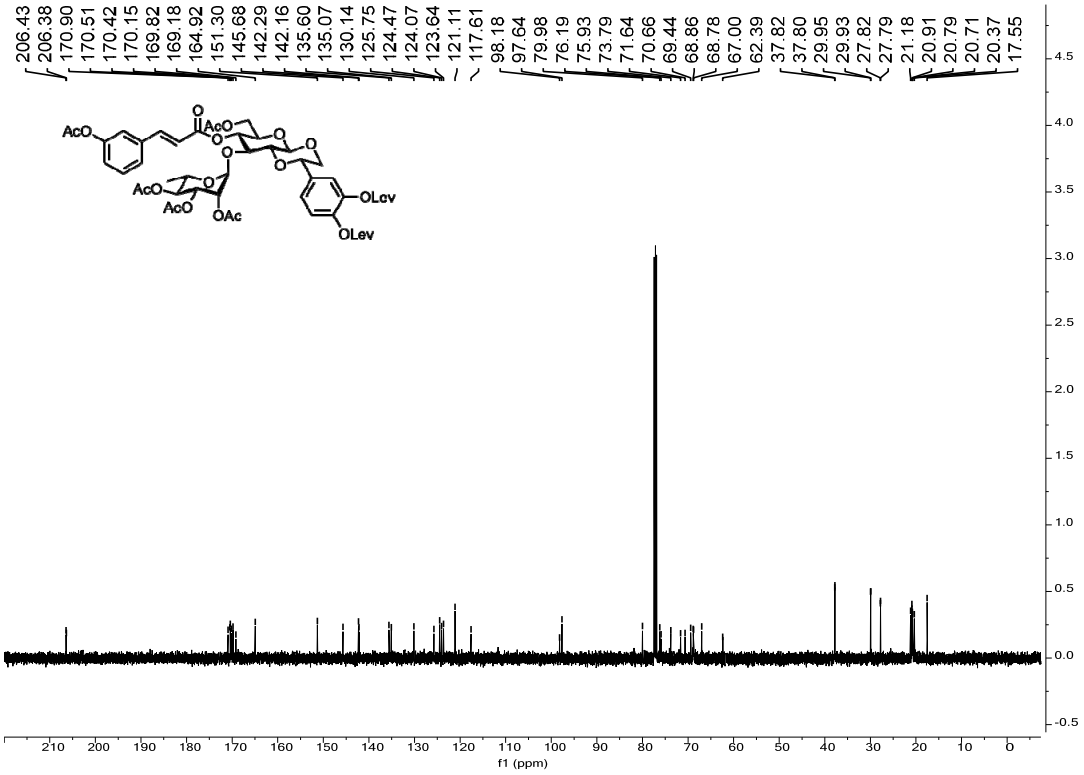

Figure S60 ^{13}C NMR spectrum of compound **S13** ($CDCl_3$, 125 MHz)

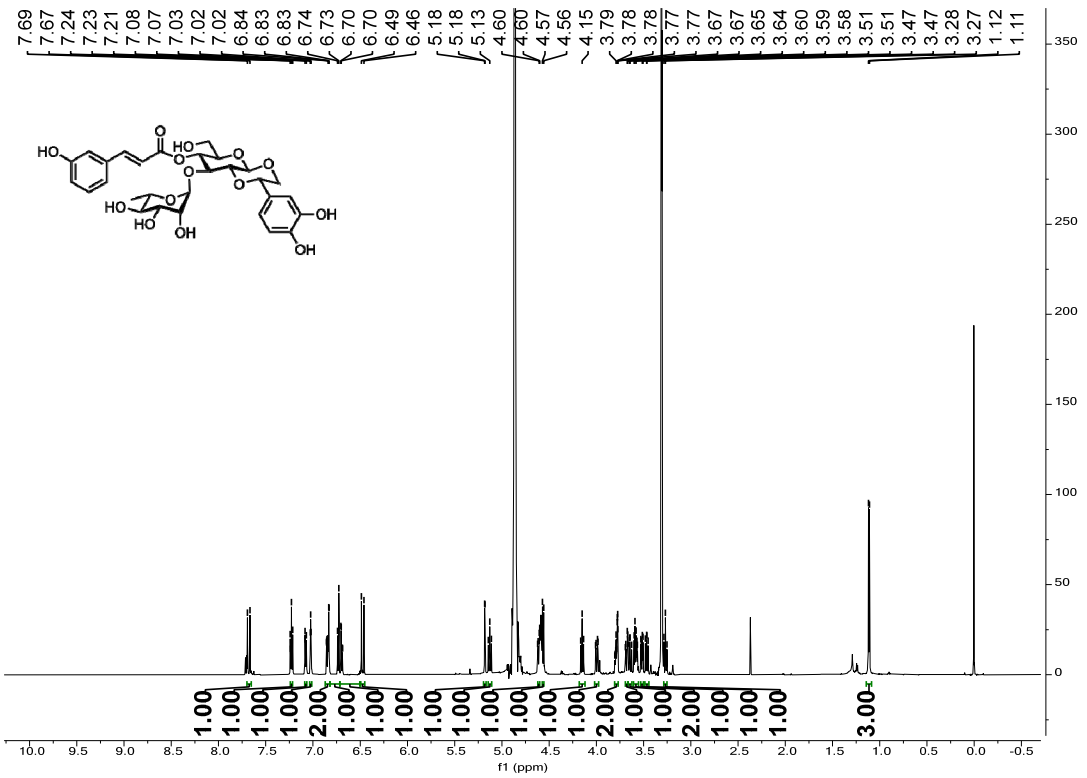

Figure S61 ^{1}H NMR spectrum of compound **24** (CD_3OD, 600 MHz)

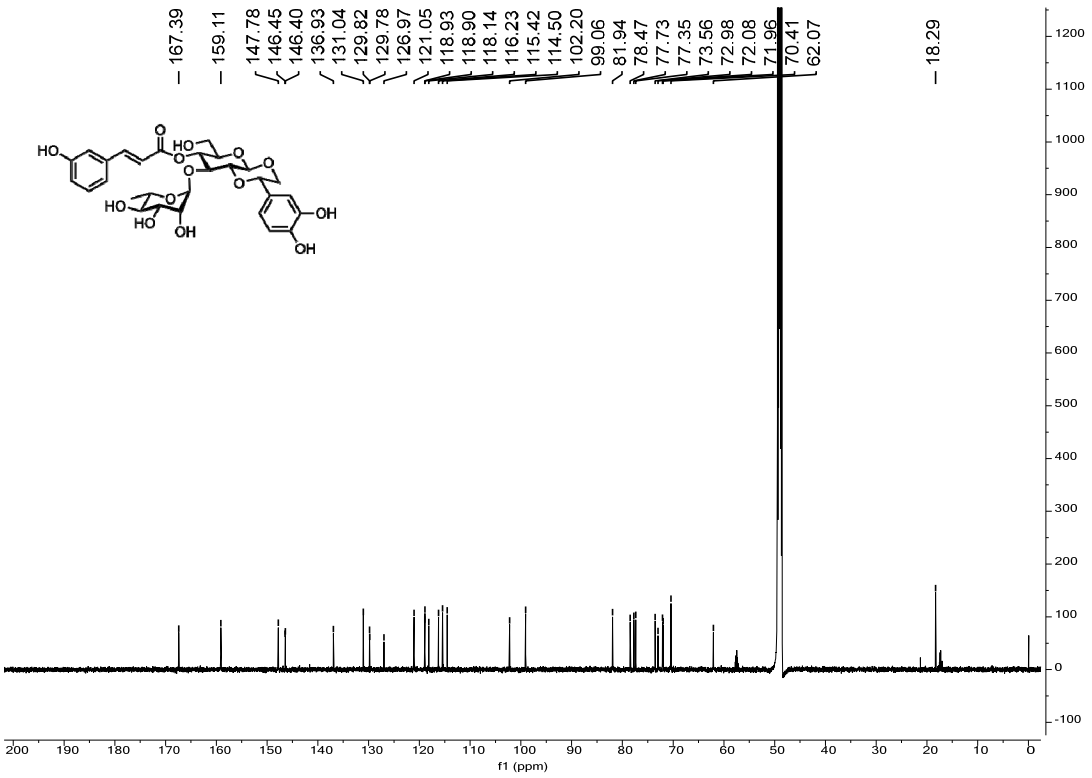

Figure S62 ^{13}C NMR spectrum of compound **24** (CD_3OD, 150 MHz)

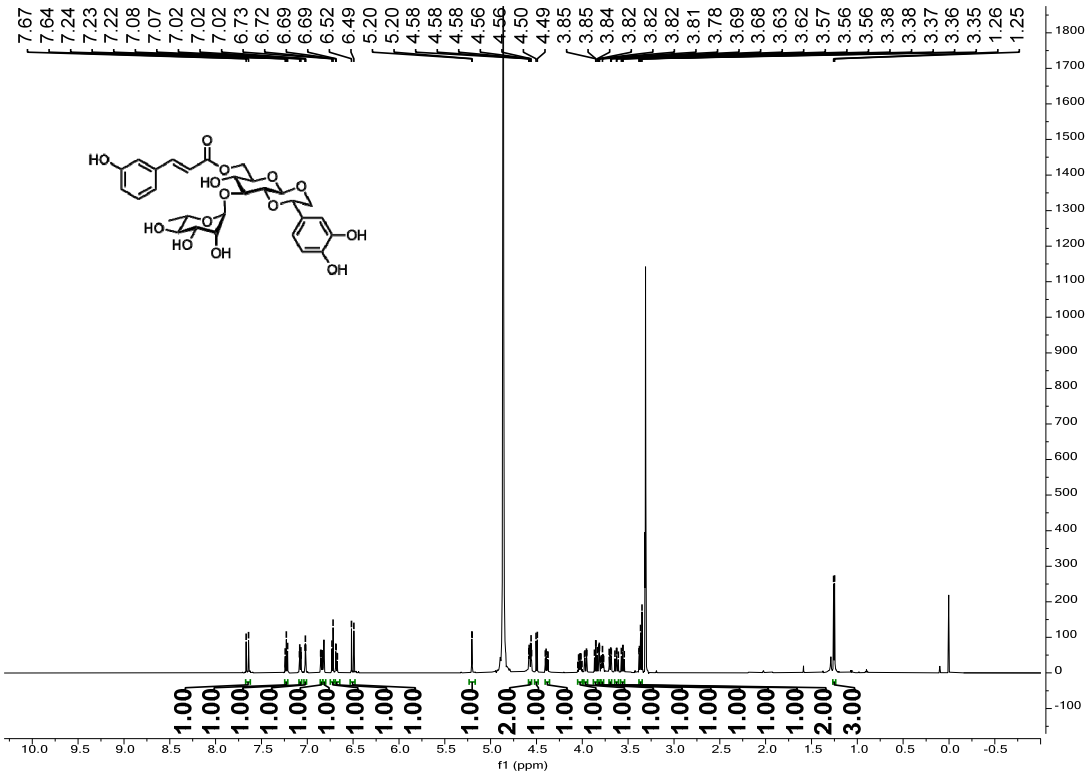

Figure S63 ^{1}H NMR spectrum of compound **28** (CD_3OD, 600 MHz)

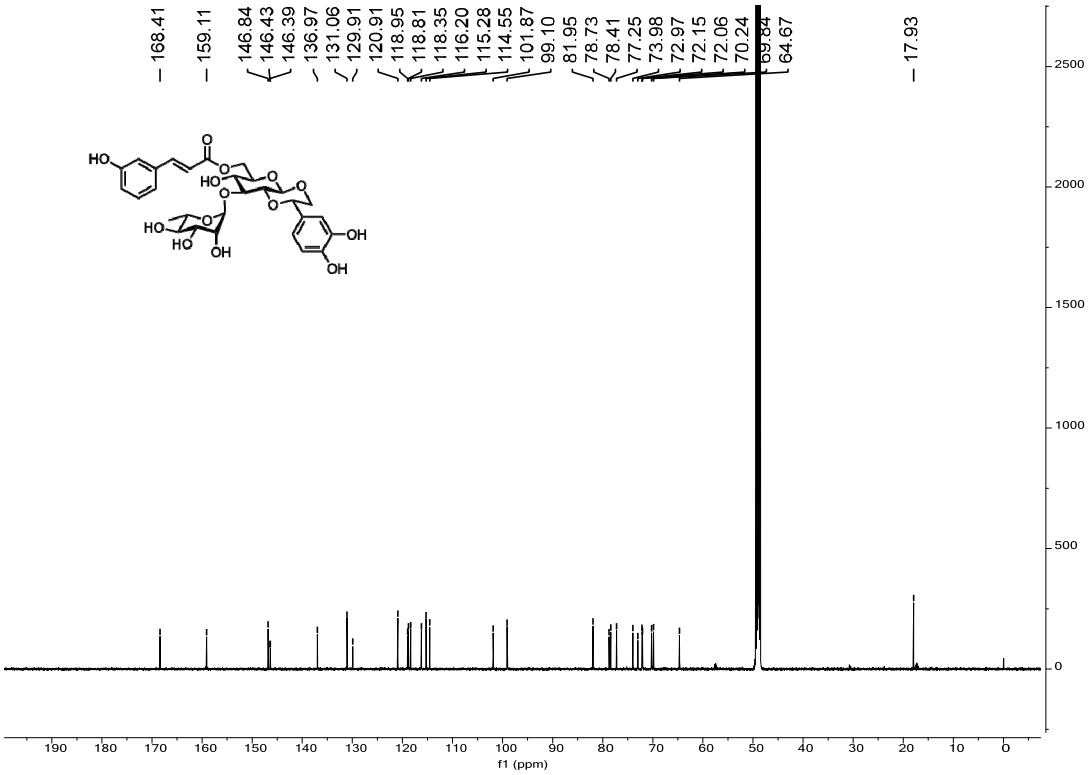

Figure S64 ^{13}C NMR spectrum of compound **28** (CD_3OD, 150 MHz)

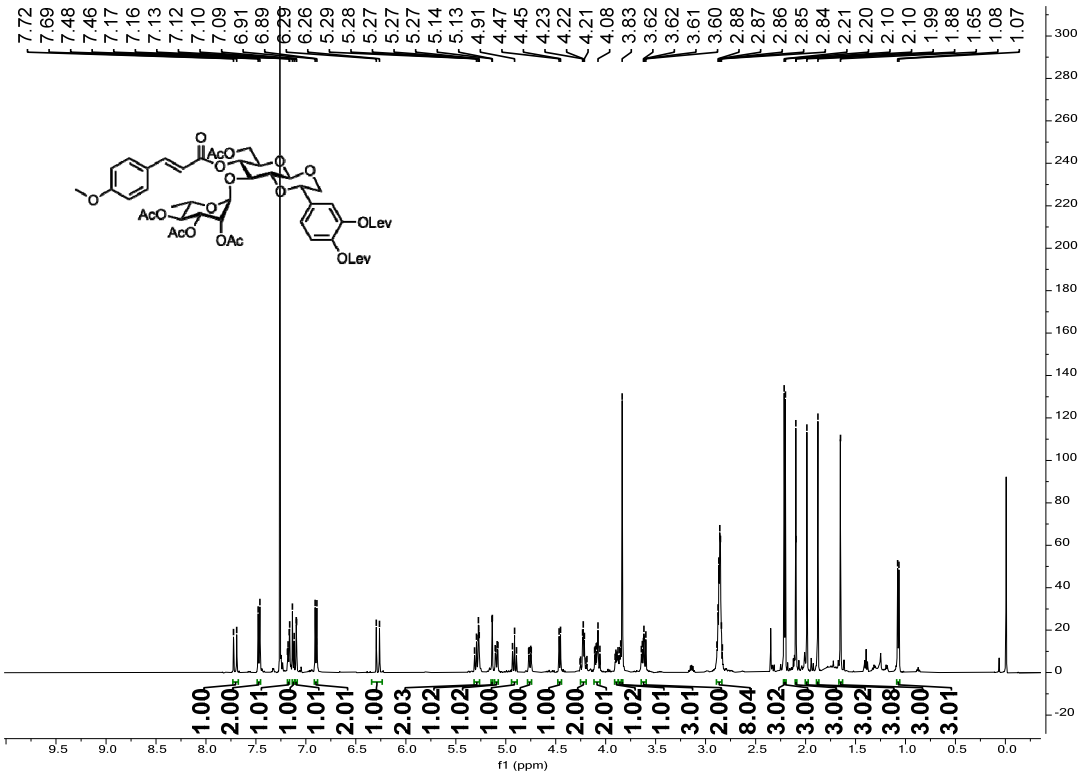

Figure S65 ^{1}H NMR spectrum of compound **S14** ($CDCl_3$, 500 MHz)

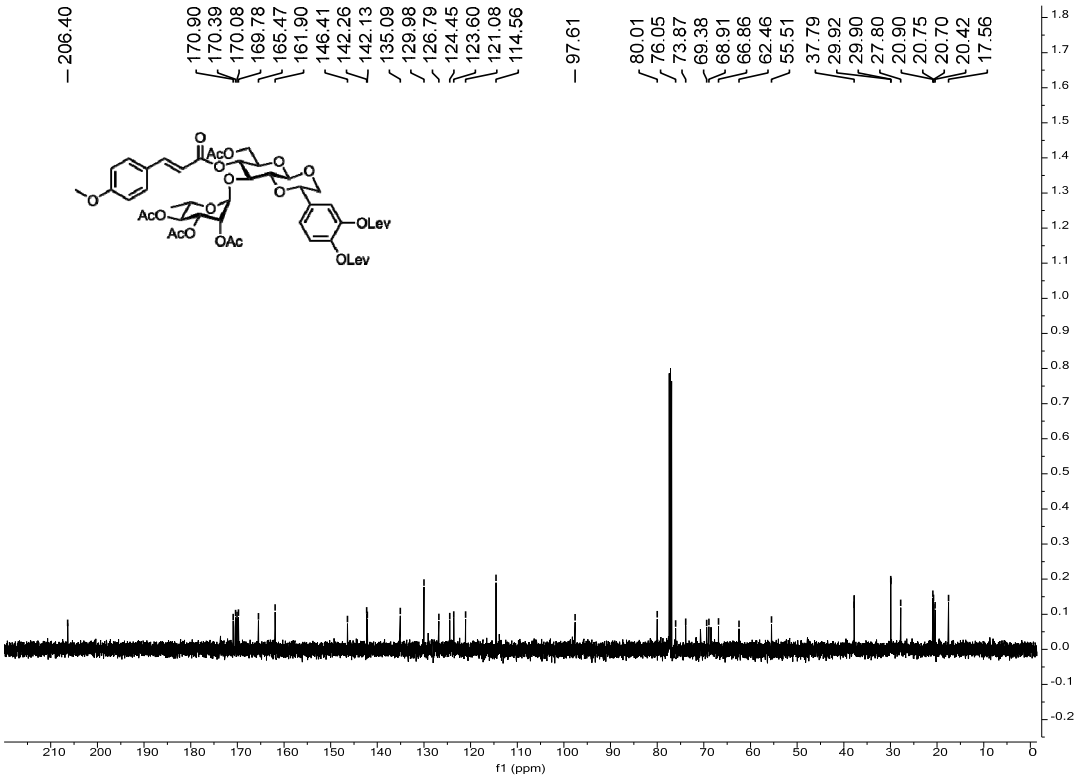

Figure S66 ^{13}C NMR spectrum of compound **S14** ($CDCl_3$, 125 MHz)

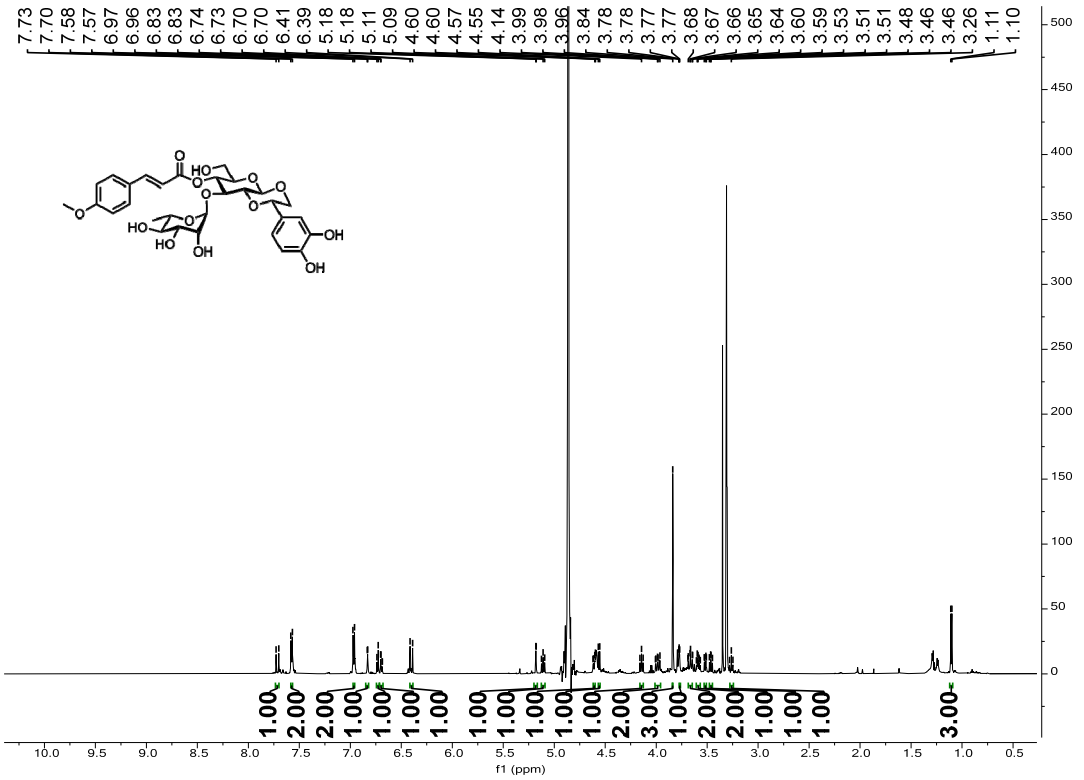

Figure S67 ^{1}H NMR spectrum of compound **25** (CD_3OD, 600 MHz)

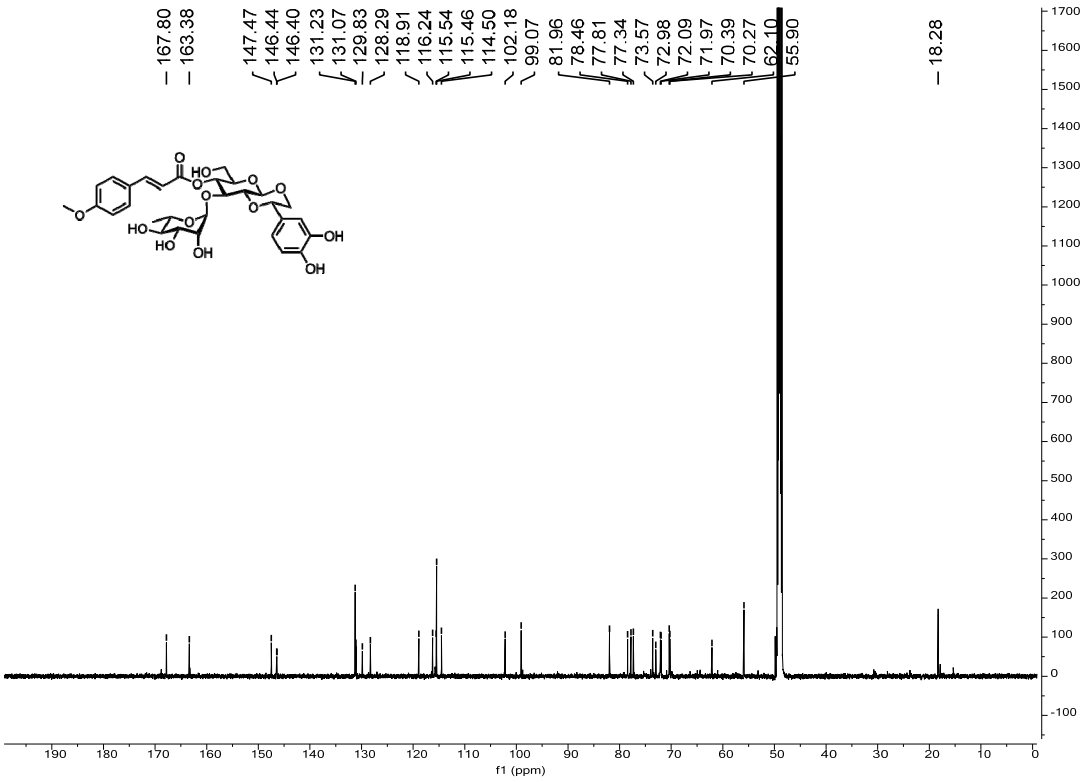

Figure S68 ^{13}C NMR spectrum of compound **25** (CD_3OD, 150 MHz)

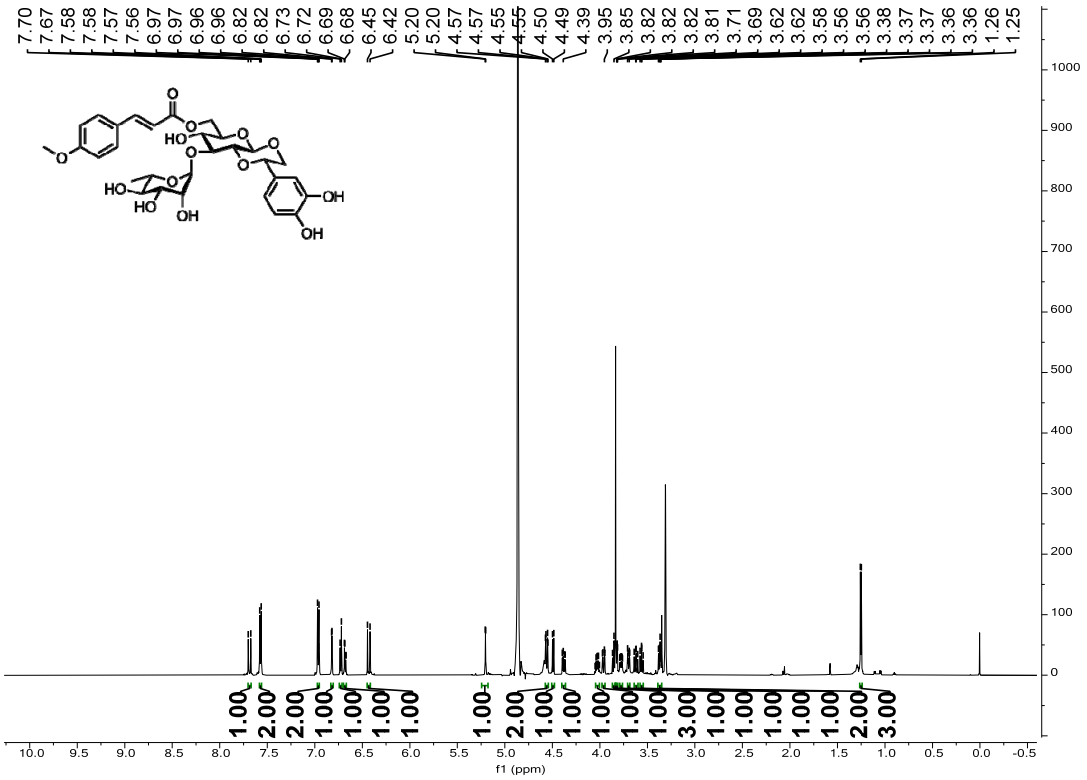

Figure S69 ^{1}H NMR spectrum of compound **29** (CD_3OD, 600 MHz)

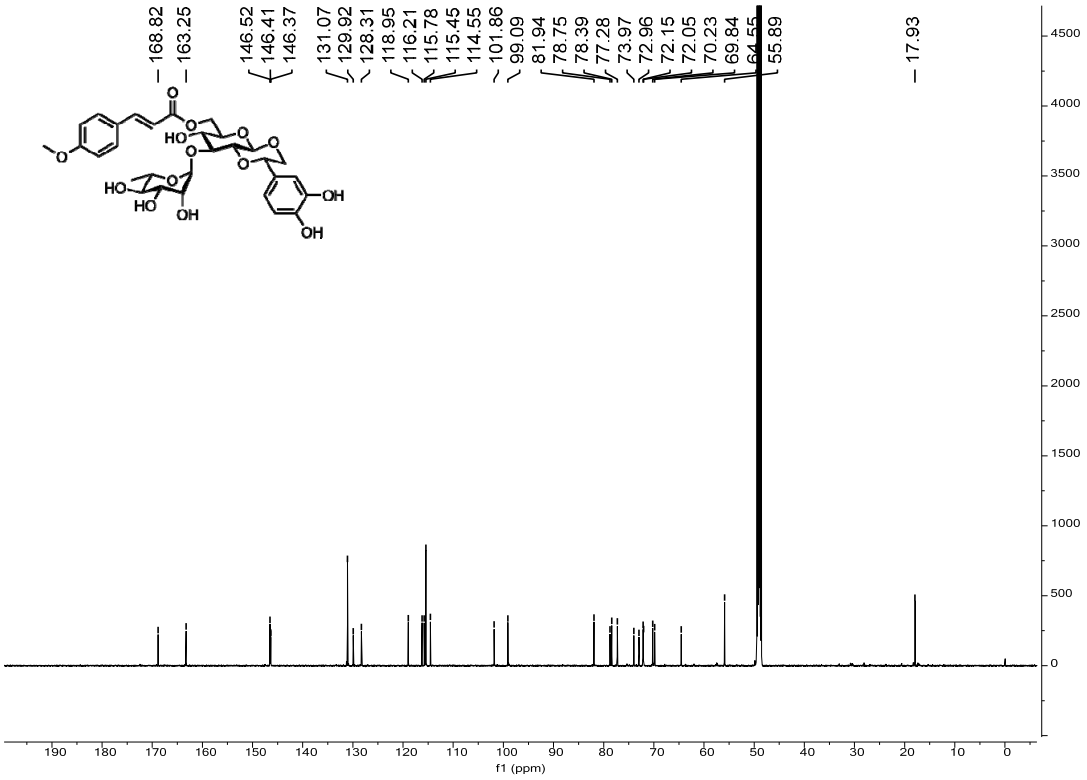

Figure S70 ^{13}C NMR spectrum of compound **29** (CD_3OD, 150 MHz)

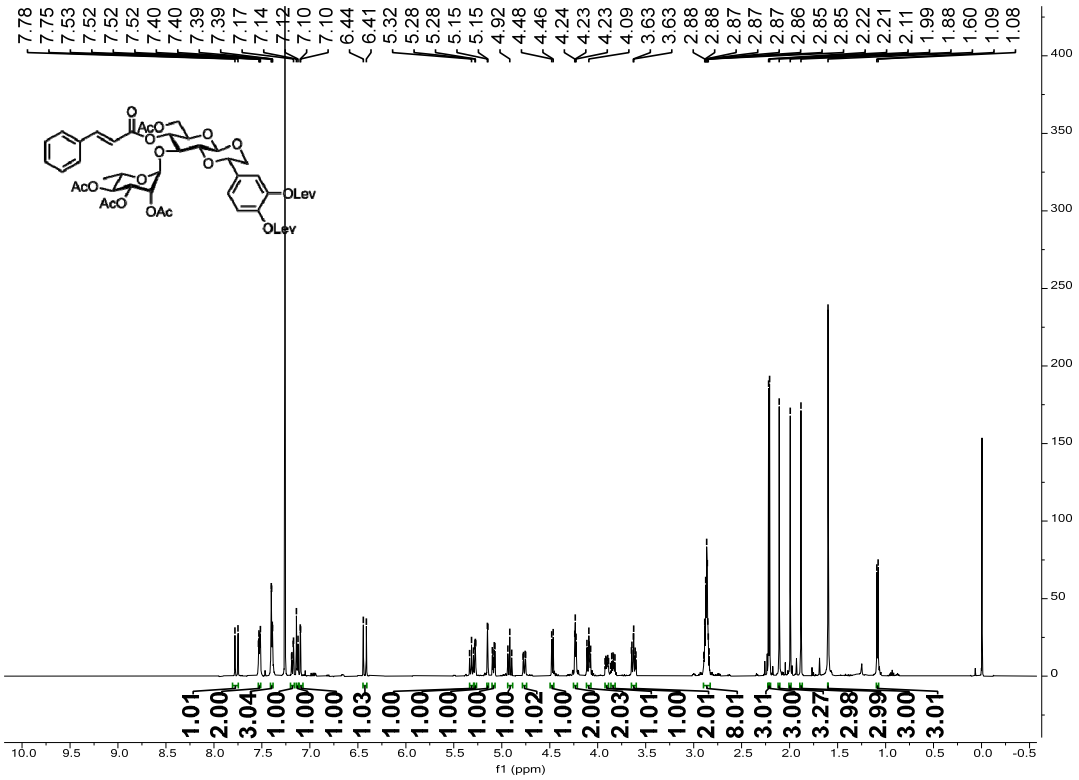

Figure S71 ^{1}H NMR spectrum of compound **S15** ($CDCl_3$, 500 MHz)

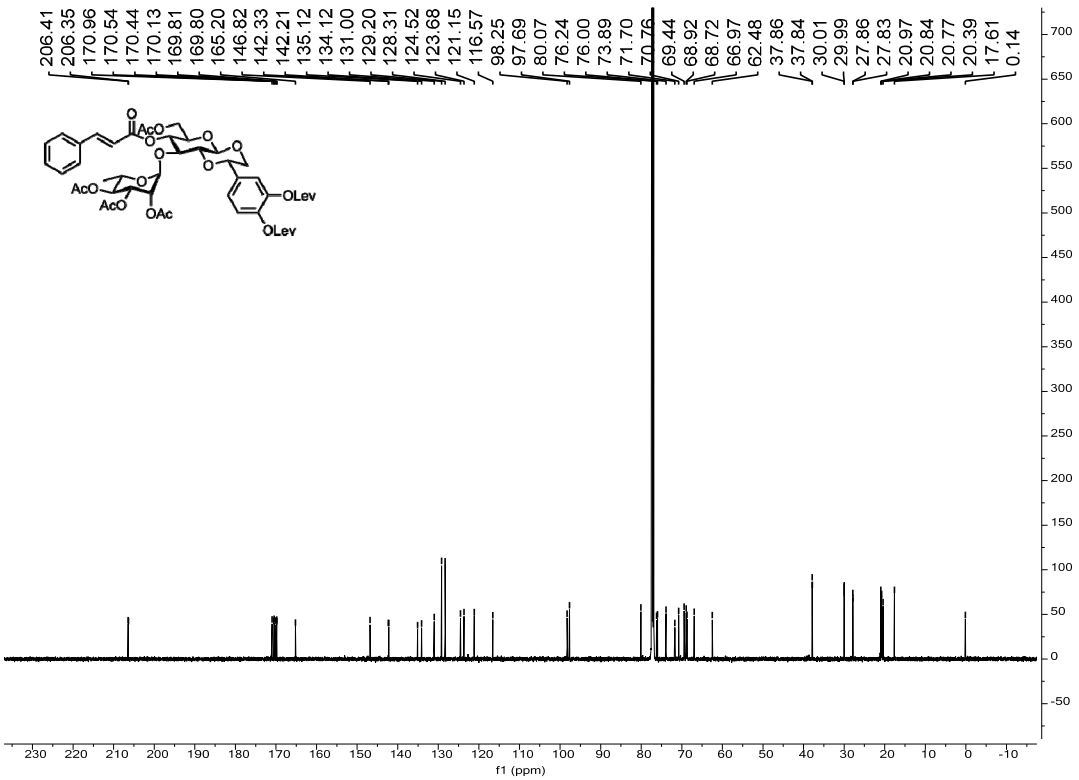

Figure S72 ^{13}C NMR spectrum of compound **S15** ($CDCl_3$, 125 MHz)

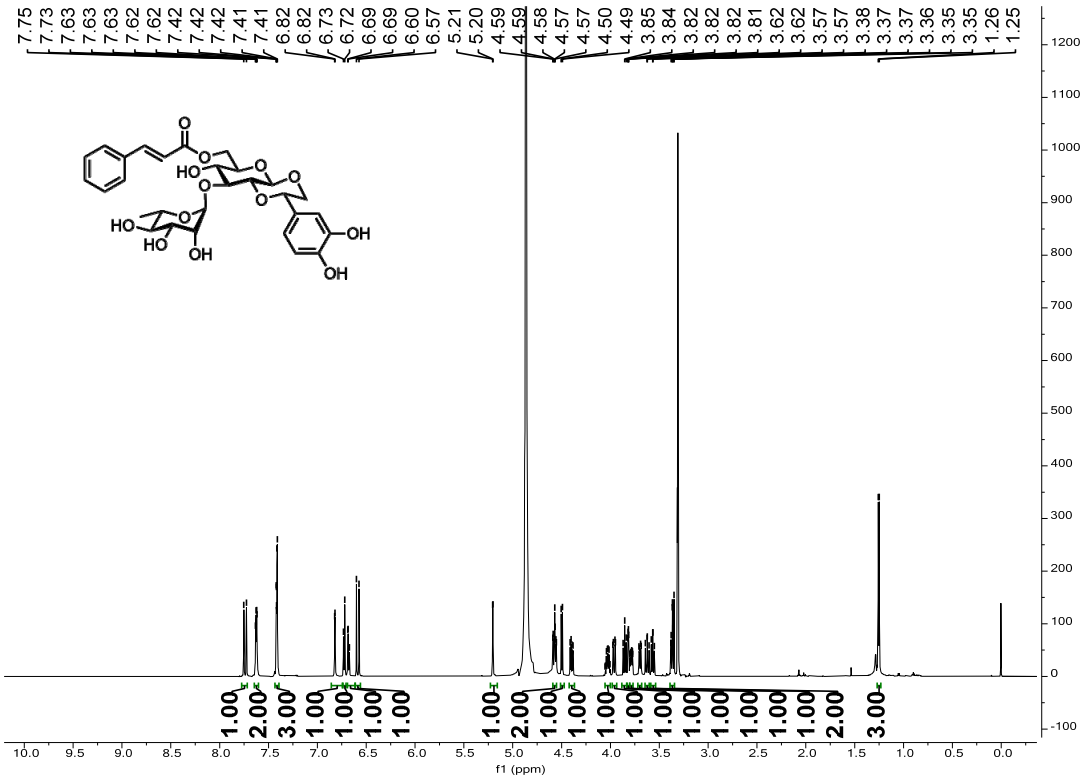

Figure S73 ^{1}H NMR spectrum of compound **26** (CD_3OD, 600 MHz)

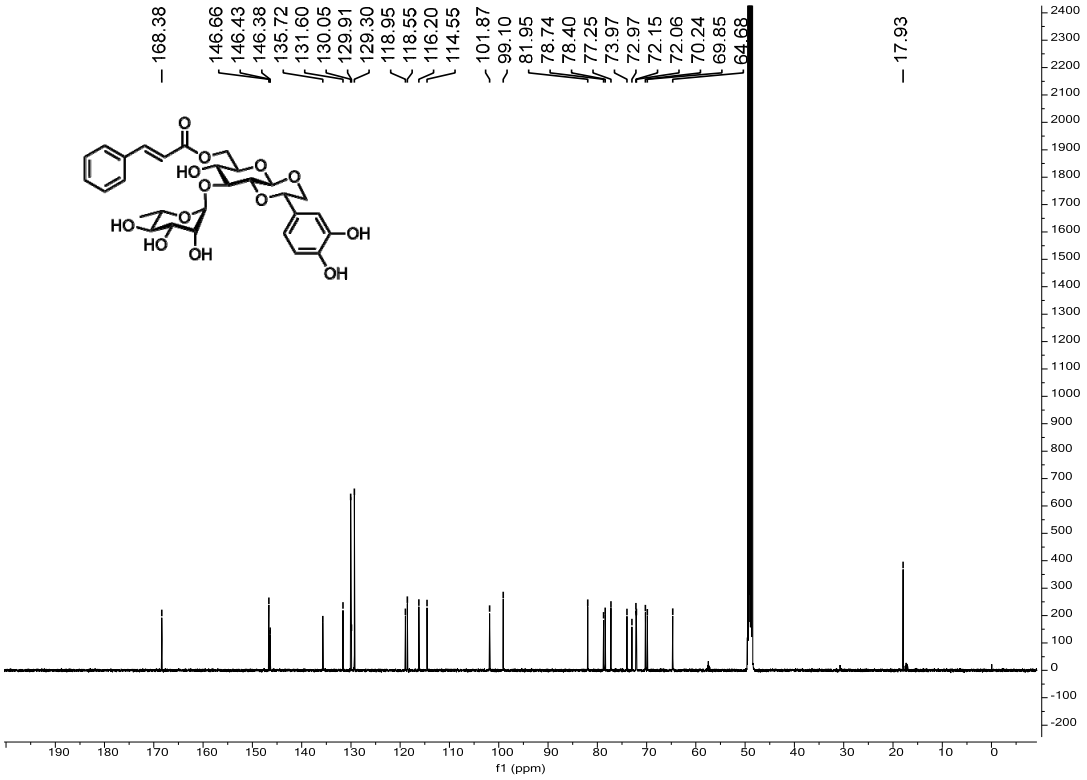

Figure S74 ^{13}C NMR spectrum of compound **26** (CD_3OD, 150 MHz)

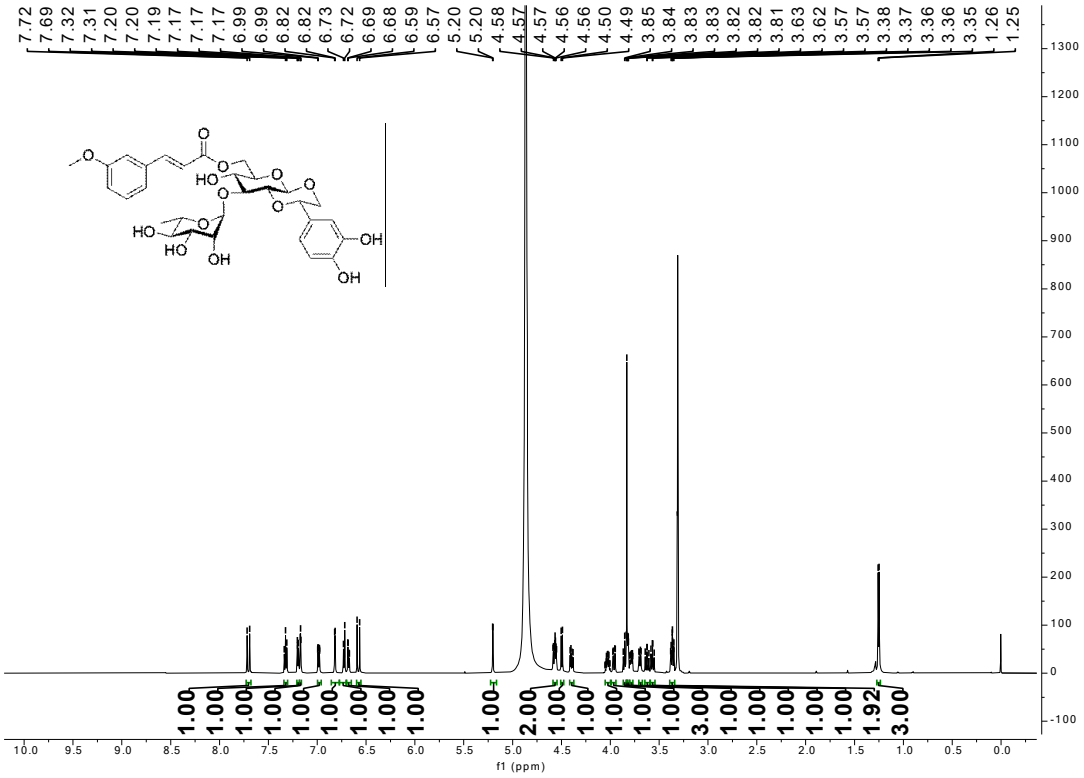

Figure S75 ^{1}H NMR spectrum of compound **30** (CD_3OD, 600 MHz)

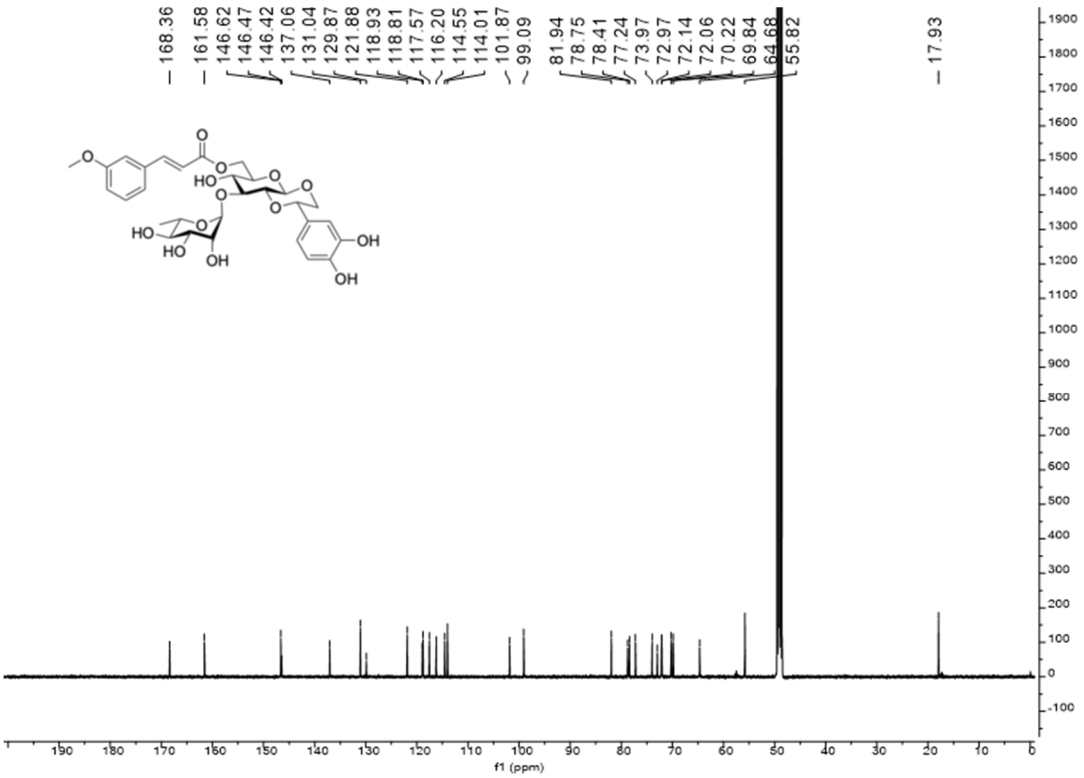

Figure S76 ^{13}C NMR spectrum of compound **30** (CD_3OD, 150 MHz)

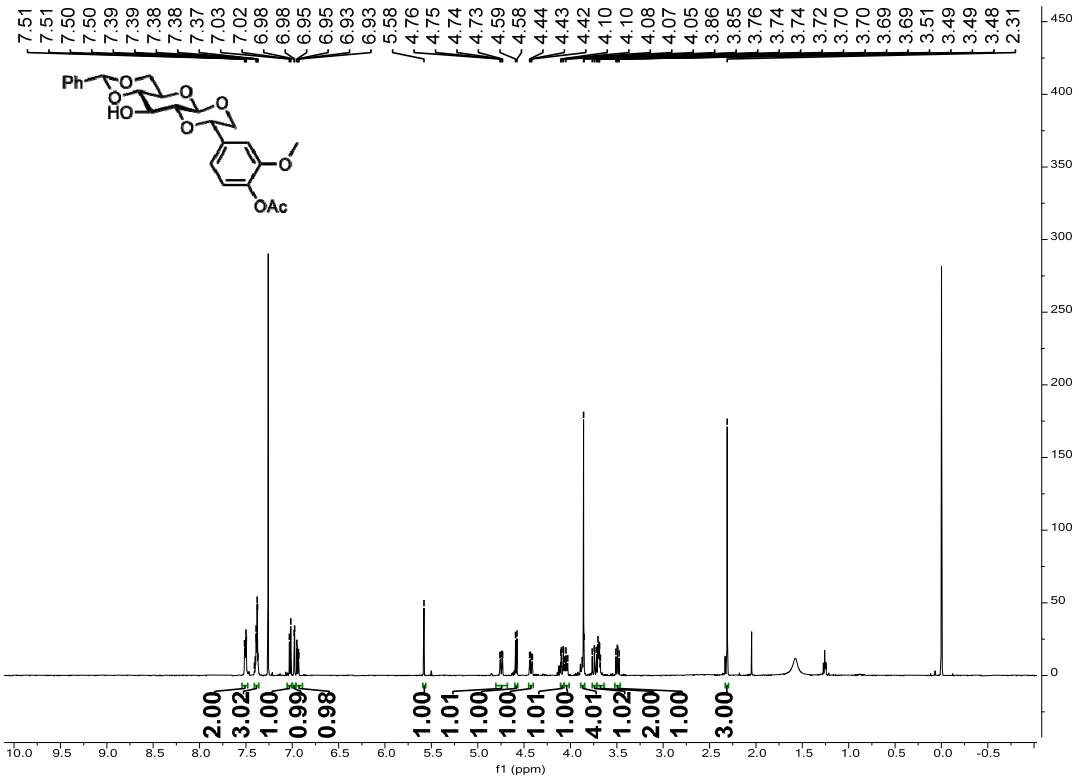

Figure S77 ^{1}H NMR spectrum of compound **S16** ($CDCl_3$, 500 MHz)

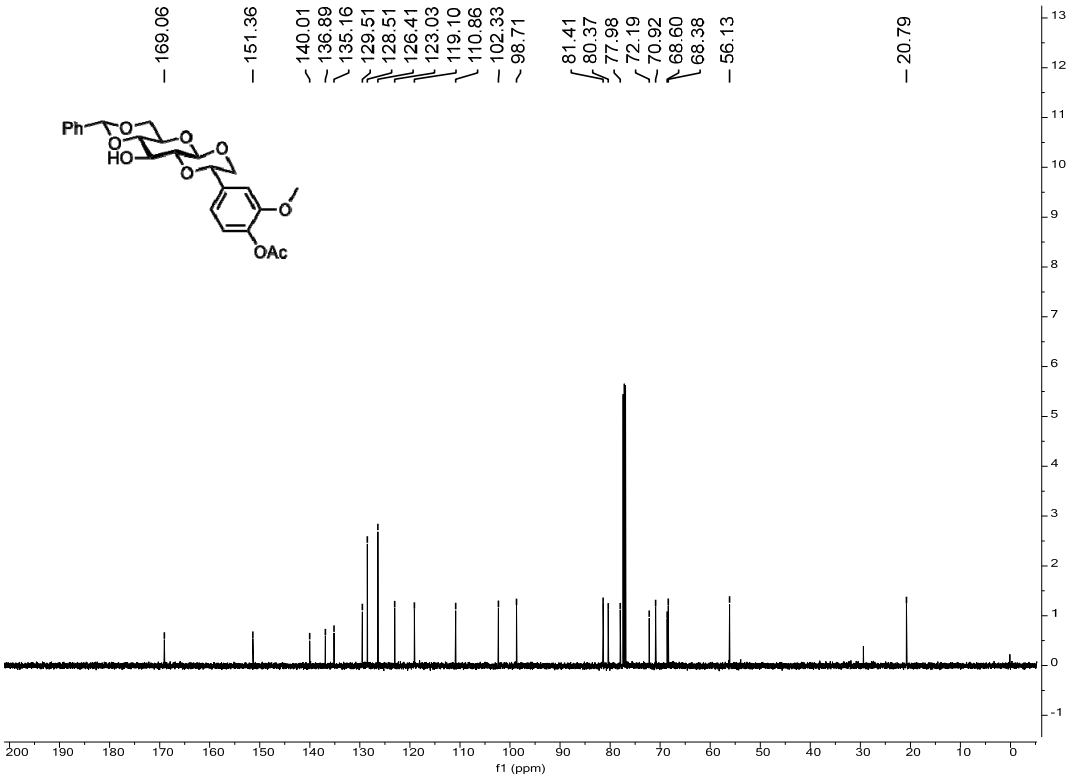

Figure S78 ^{13}C NMR spectrum of compound **S16** ($CDCl_3$, 125 MHz)

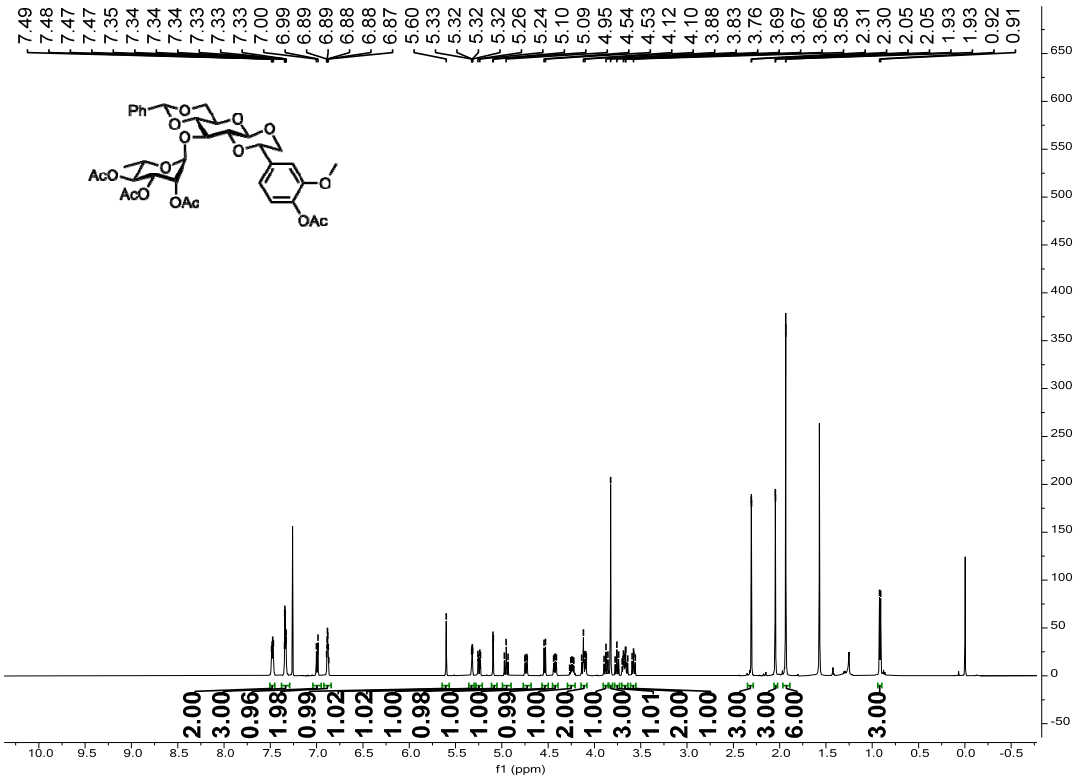

Figure S79 ^{1}H NMR spectrum of compound **S17** ($CDCl_3$, 500 MHz)

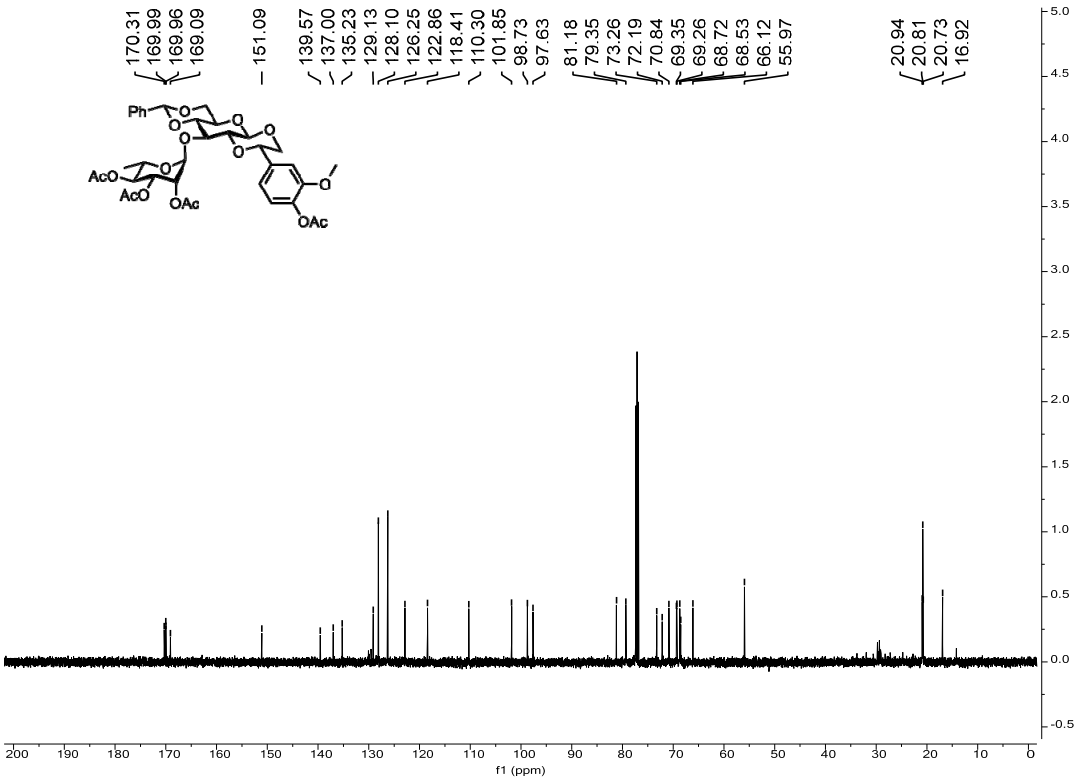

Figure S80 ^{13}C NMR spectrum of compound **S17** ($CDCl_3$, 125 MHz)

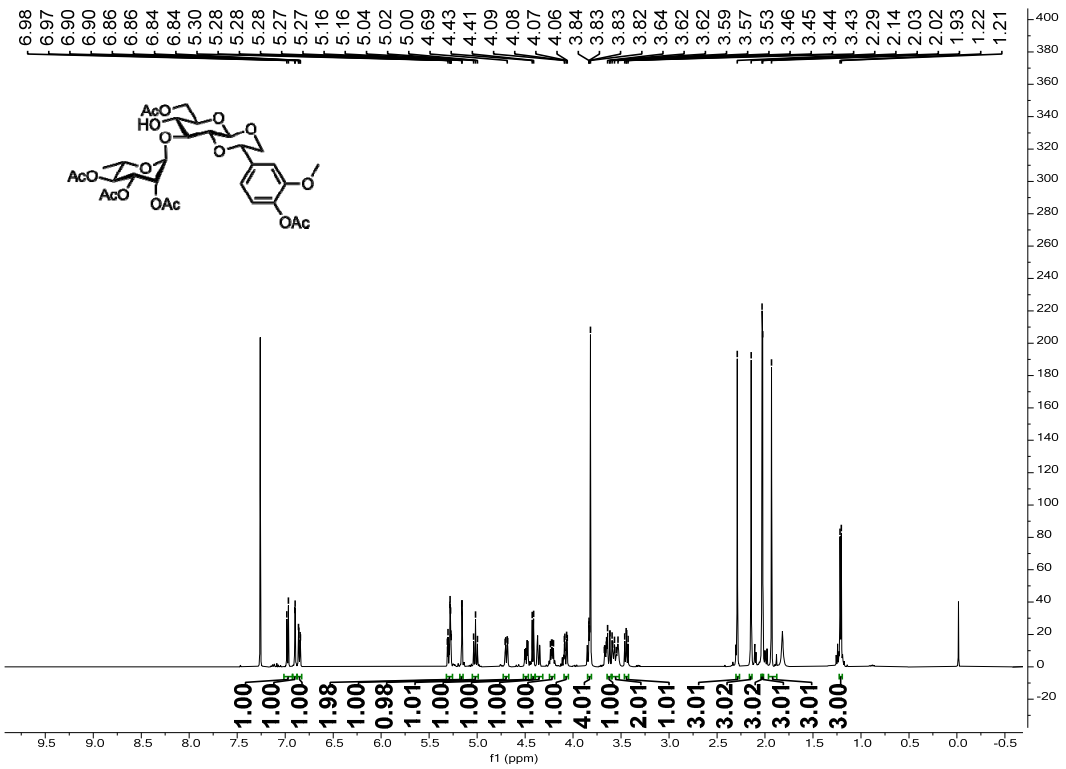

Figure S81 ^{1}H NMR spectrum of compound **S18** ($CDCl_3$, 500 MHz)

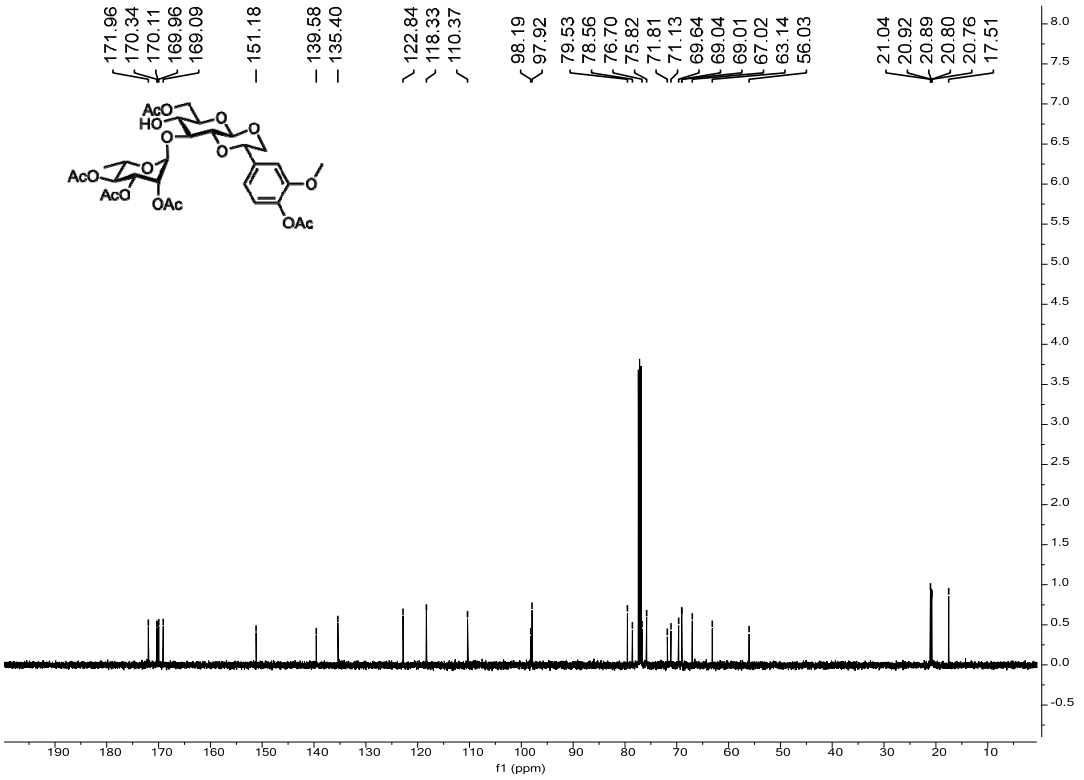

Figure S82 ^{13}C NMR spectrum of compound **S18** ($CDCl_3$, 125 MHz)

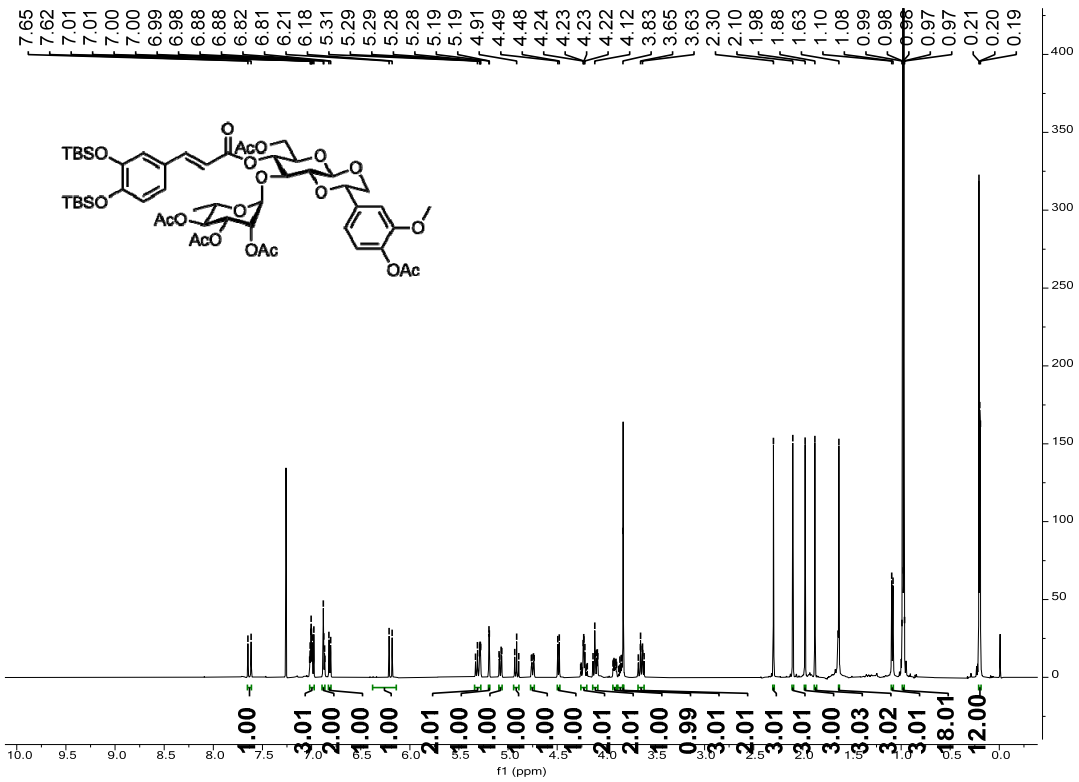

Figure S83 ^{1}H NMR spectrum of compound **S19** ($CDCl_3$, 500 MHz)

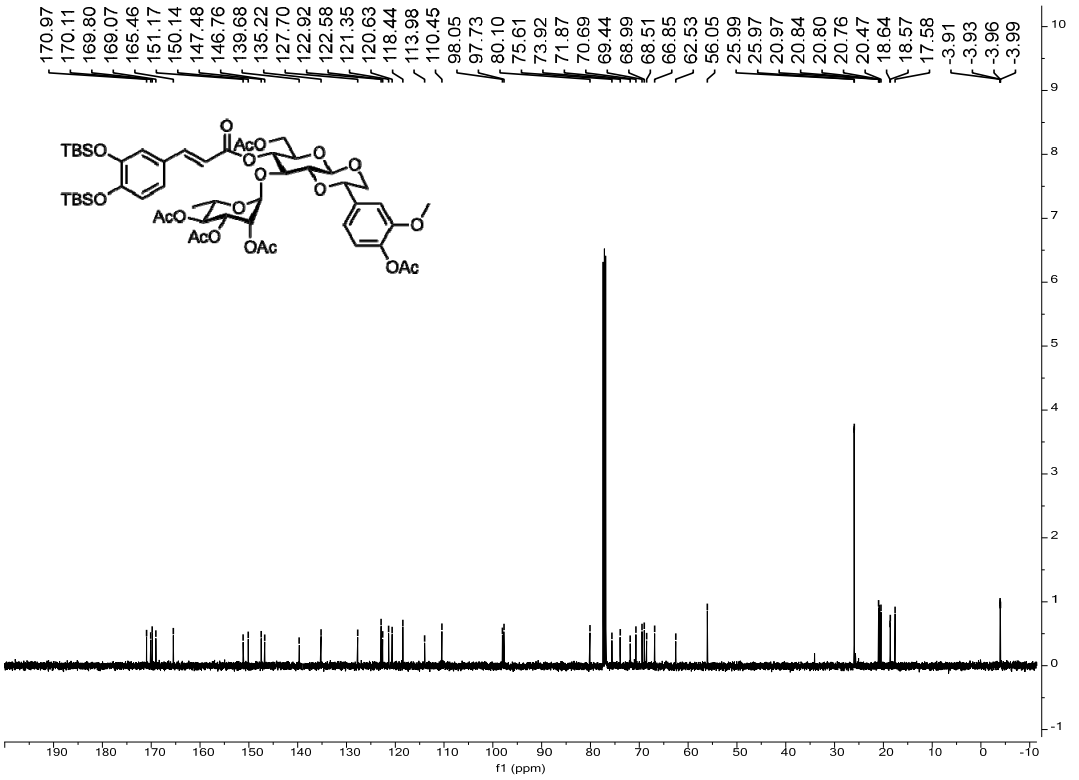

Figure S84 ^{13}C NMR spectrum of compound **S19** ($CDCl_3$, 125 MHz)

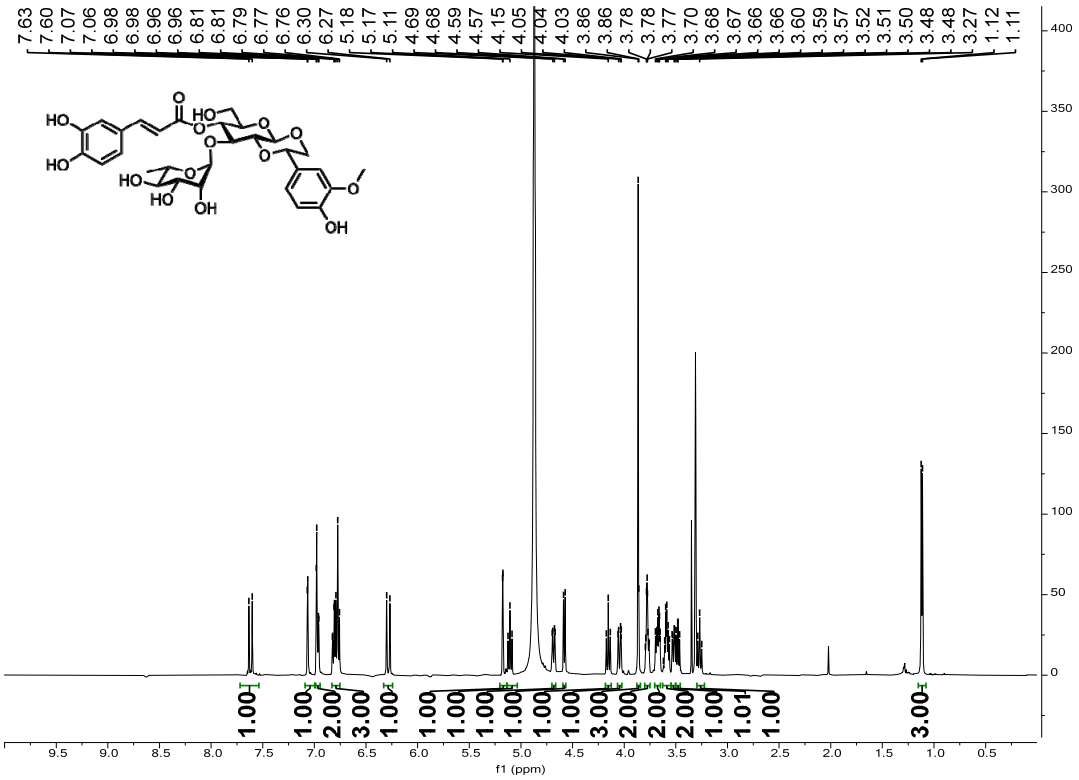

Figure S85 ^{1}H NMR spectrum of compound **31** (CD_3OD, 500 MHz)

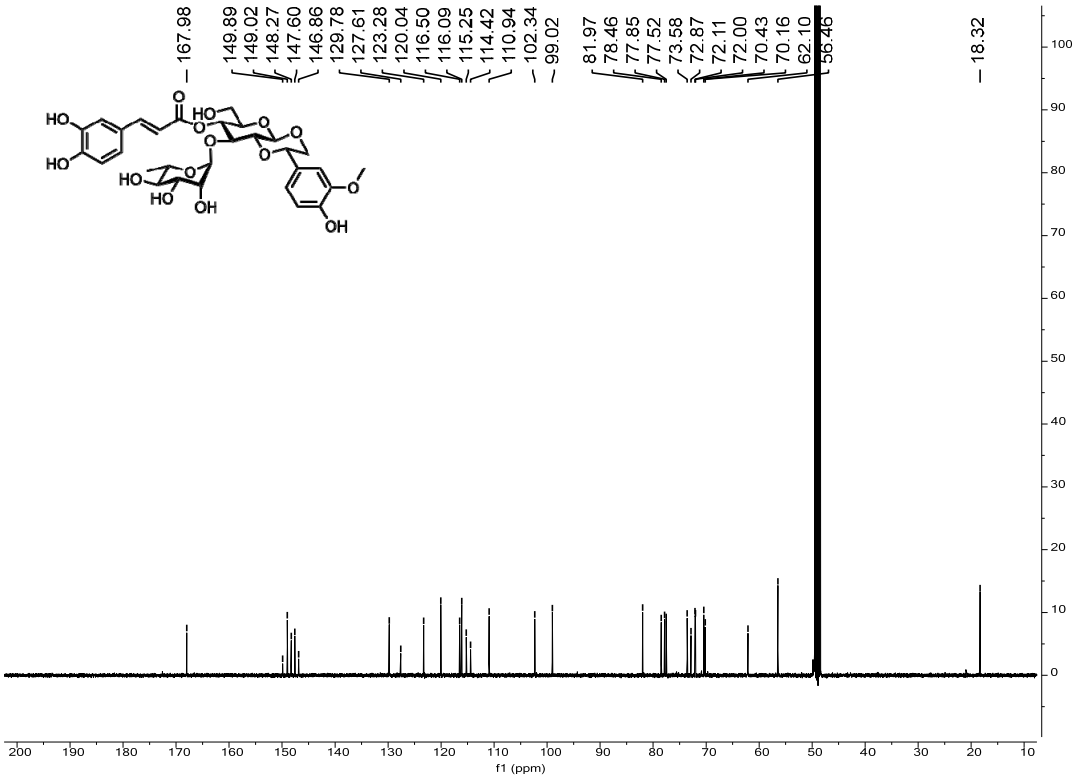

Figure S86 ^{13}C NMR spectrum of compound **31** (CD_3OD, 125 MHz)

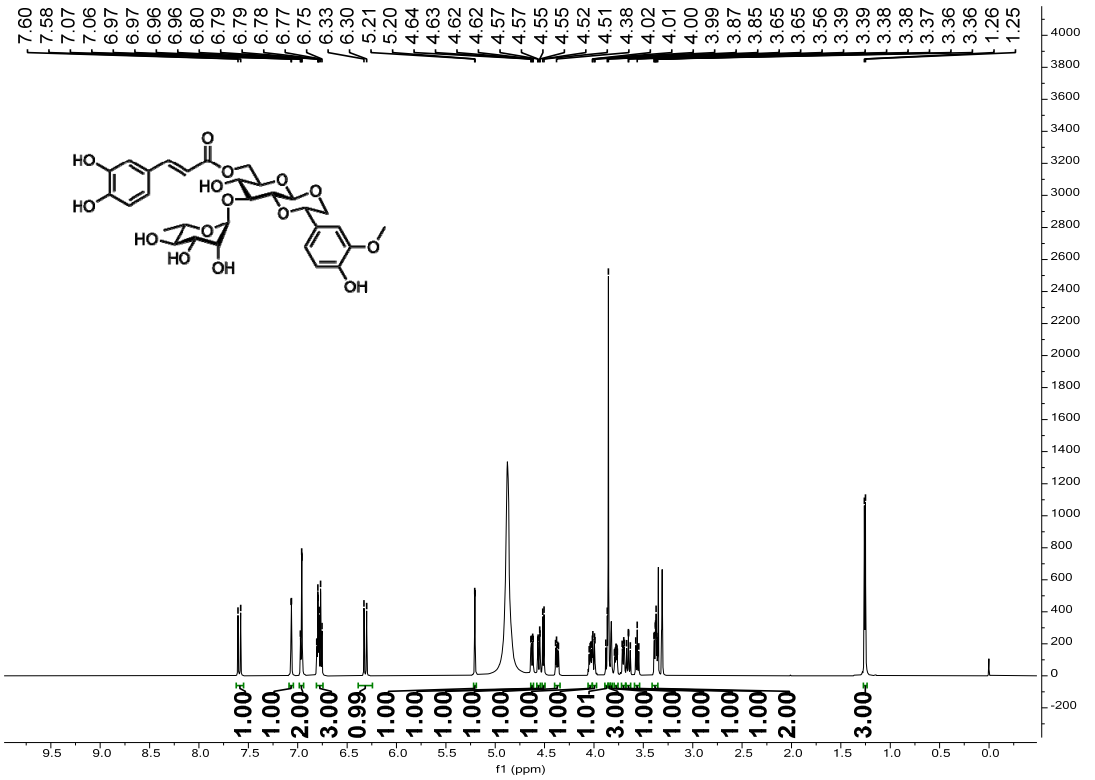

Figure S87 ^{1}H NMR spectrum of compound **38** (CD_3OD, 600 MHz)

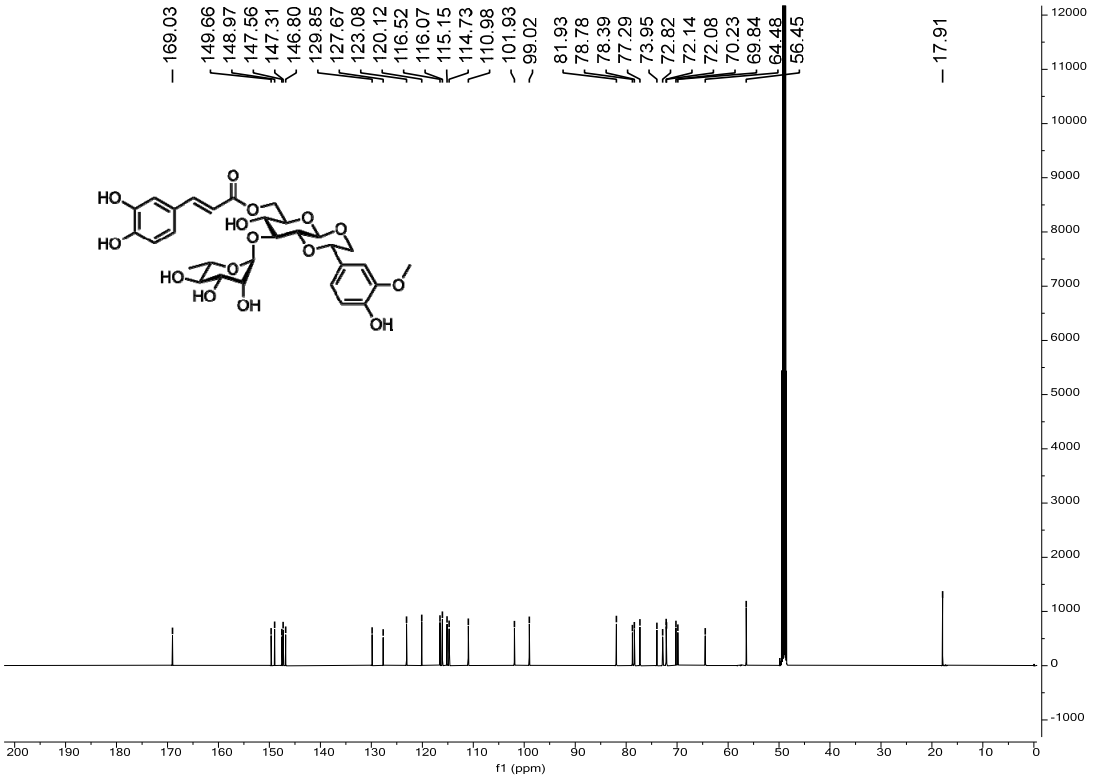

Figure S88 ^{13}C NMR spectrum of compound **38** (CD_3OD, 150 MHz)

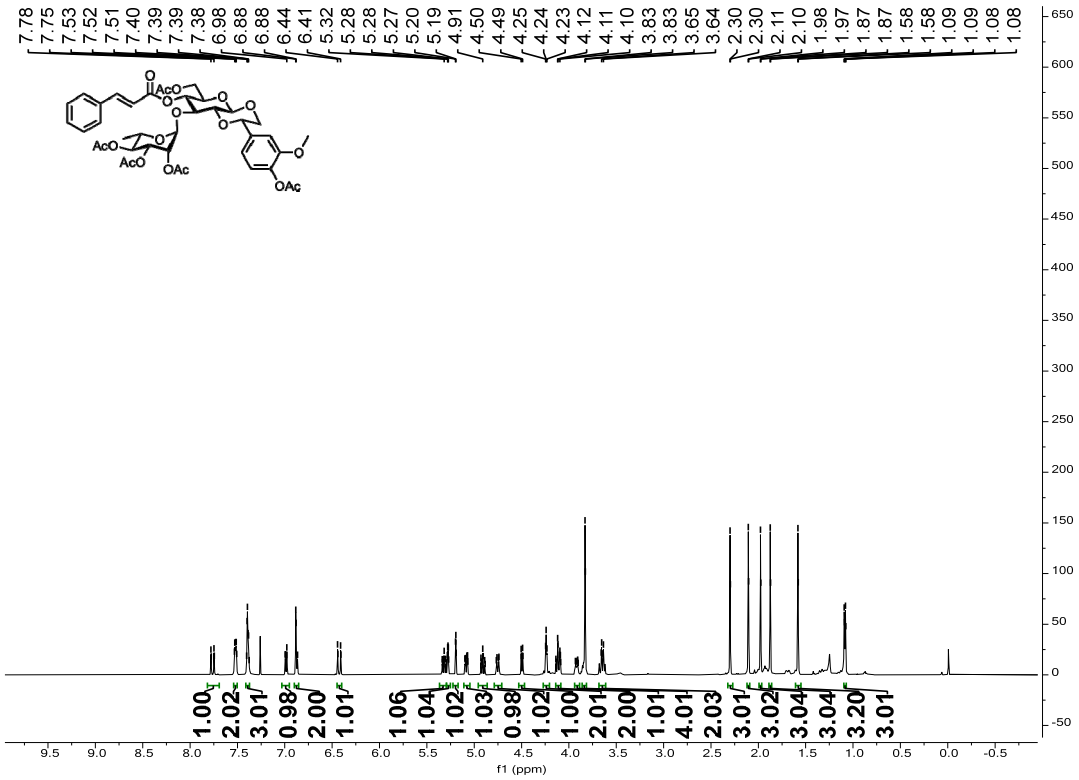

Figure S89 ^{1}H NMR spectrum of compound **S20** ($CDCl_3$, 500 MHz)

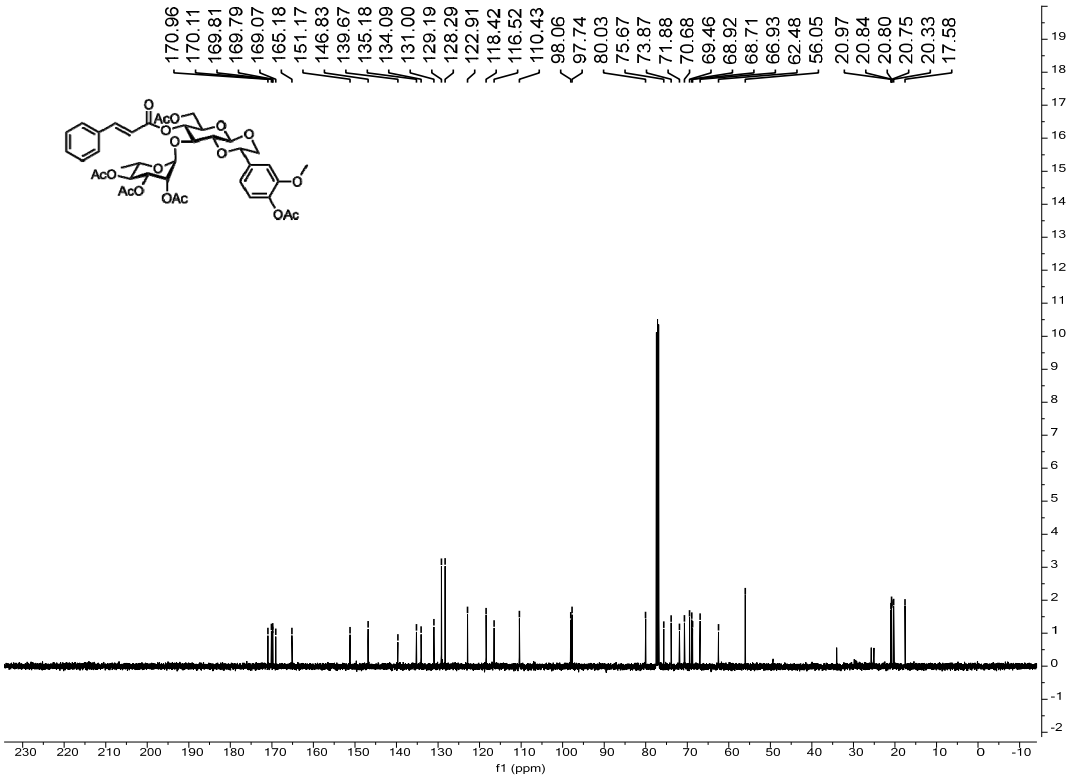

Figure S90 ^{13}C NMR spectrum of compound **S20** ($CDCl_3$, 125 MHz)

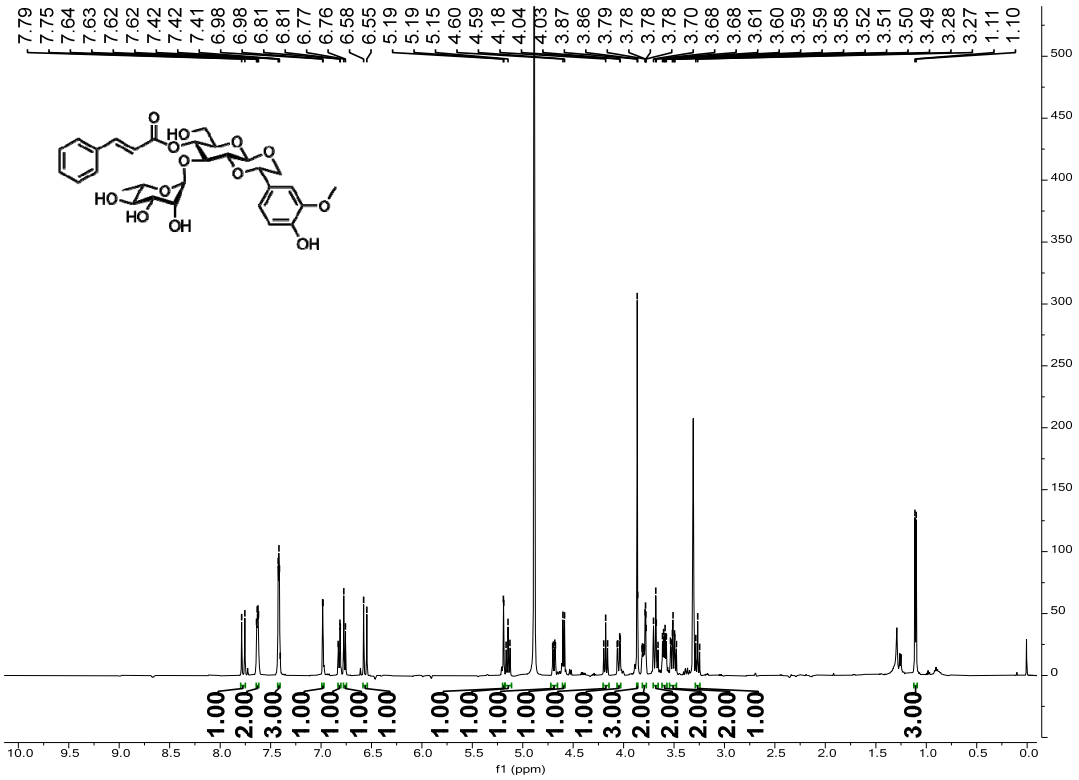

Figure S91 ^{1}H NMR spectrum of compound **32** (CD_3OD, 500 MHz)

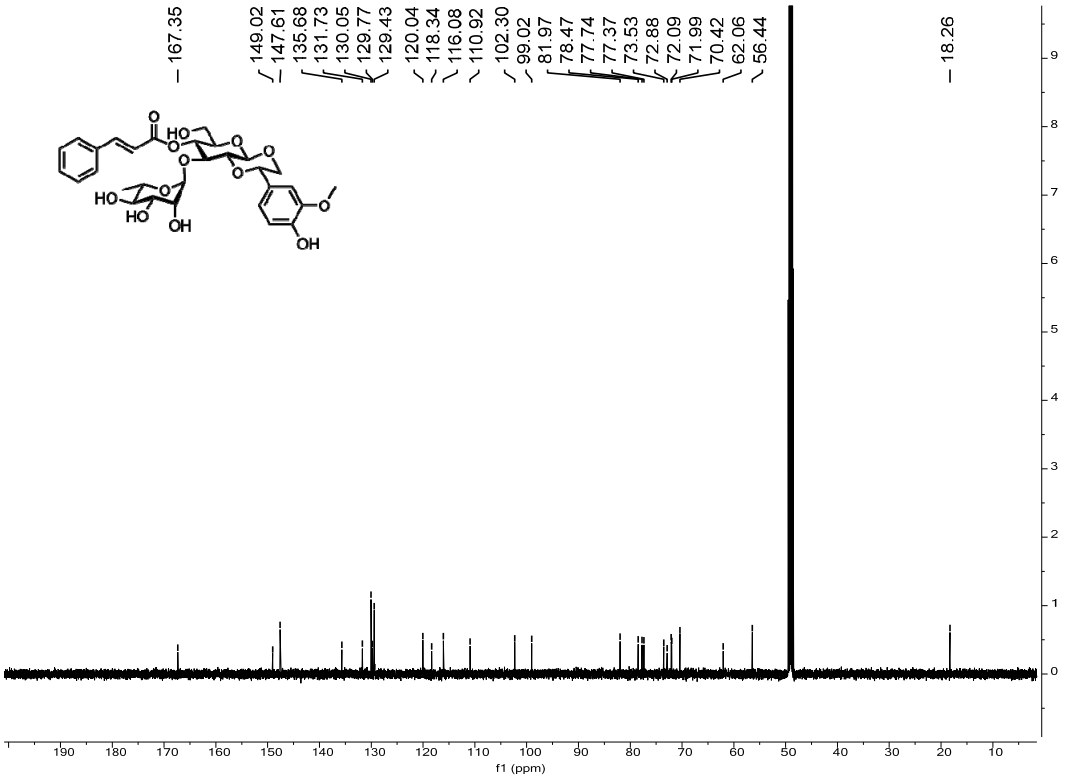

Figure S92 ^{13}C NMR spectrum of compound **32** (CD_3OD, 125 MHz)

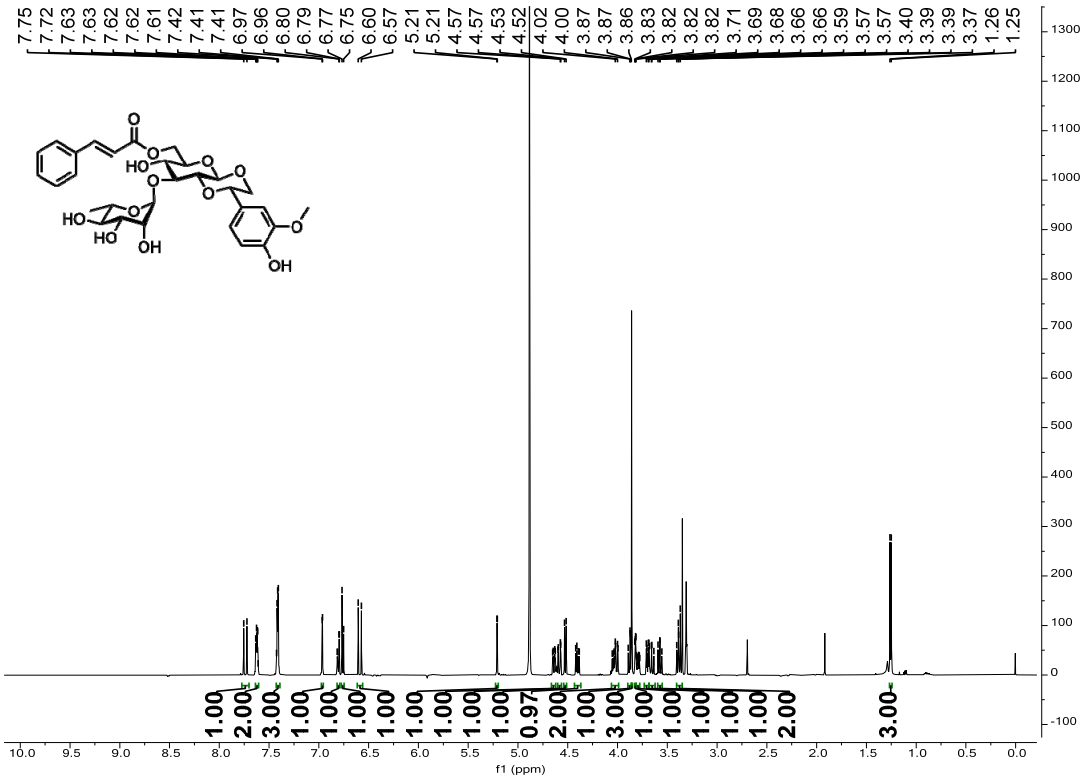

Figure S93 ^{1}H NMR spectrum of compound **39** (CD_3OD, 500 MHz)

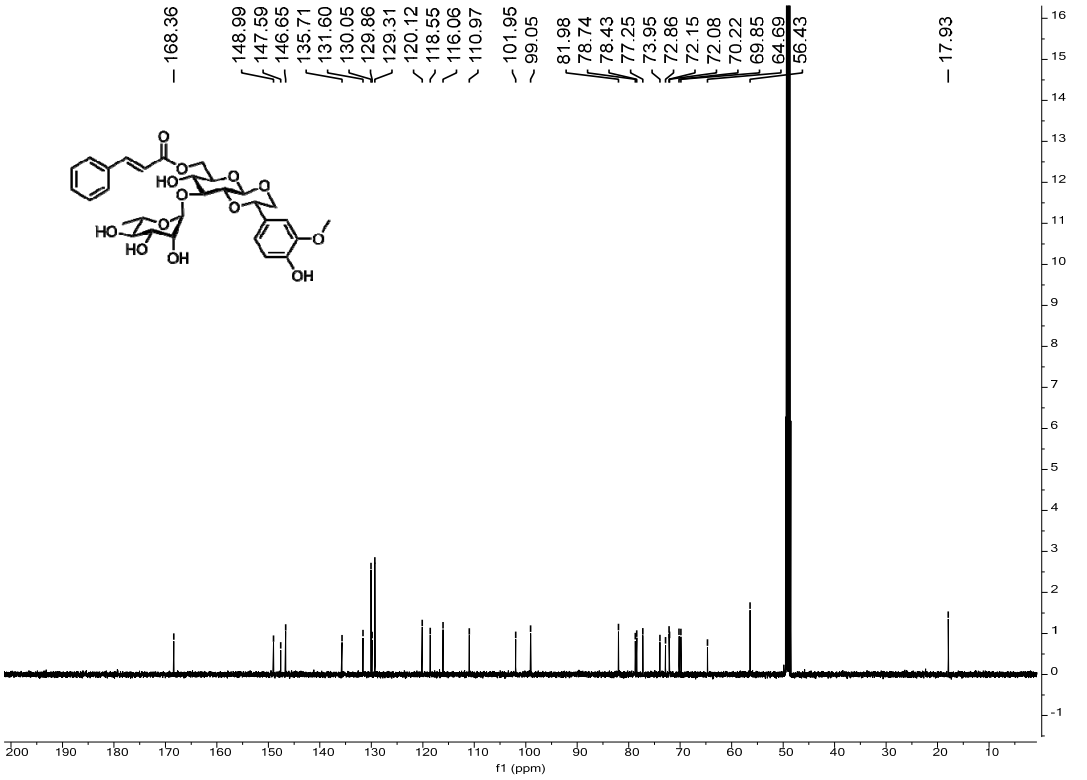

Figure S94 ^{13}C NMR spectrum of compound **39** (CD_3OD, 125 MHz)

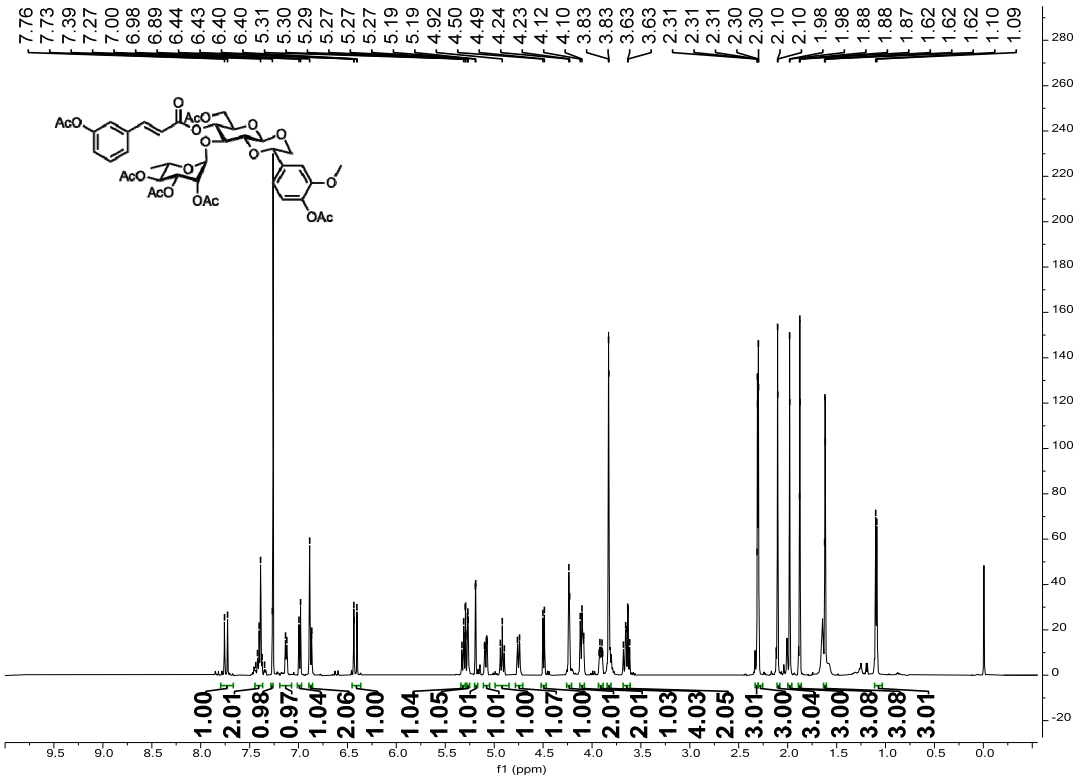

Figure S95 ^{1}H NMR spectrum of compound **S21** ($CDCl_3$, 500 MHz)

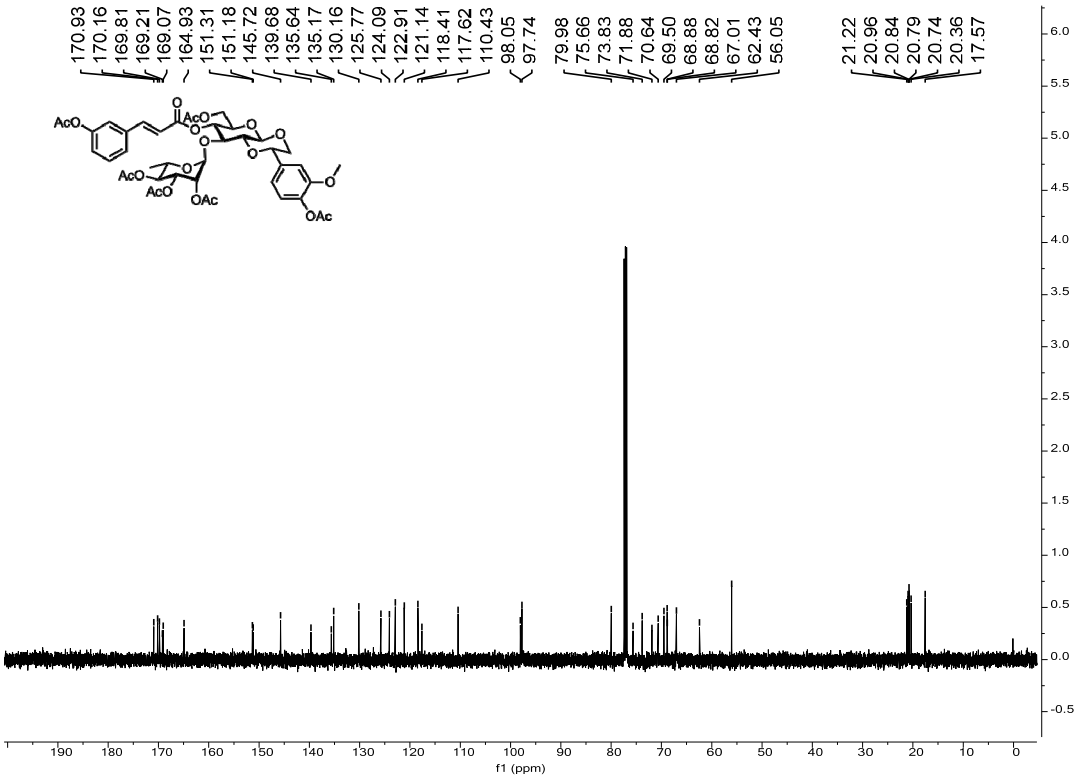

Figure S96 ^{13}C NMR spectrum of compound **S21** ($CDCl_3$, 125 MHz)

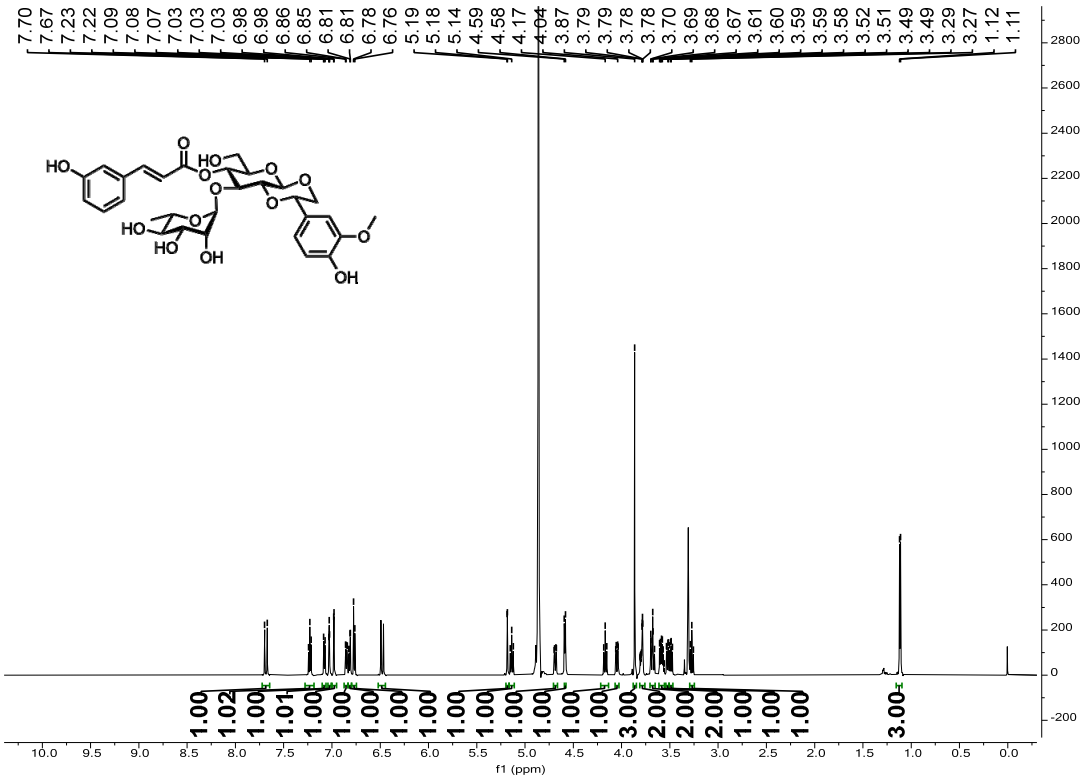

Figure S97 ^{1}H NMR spectrum of compound **33** (CD_3OD, 600 MHz)

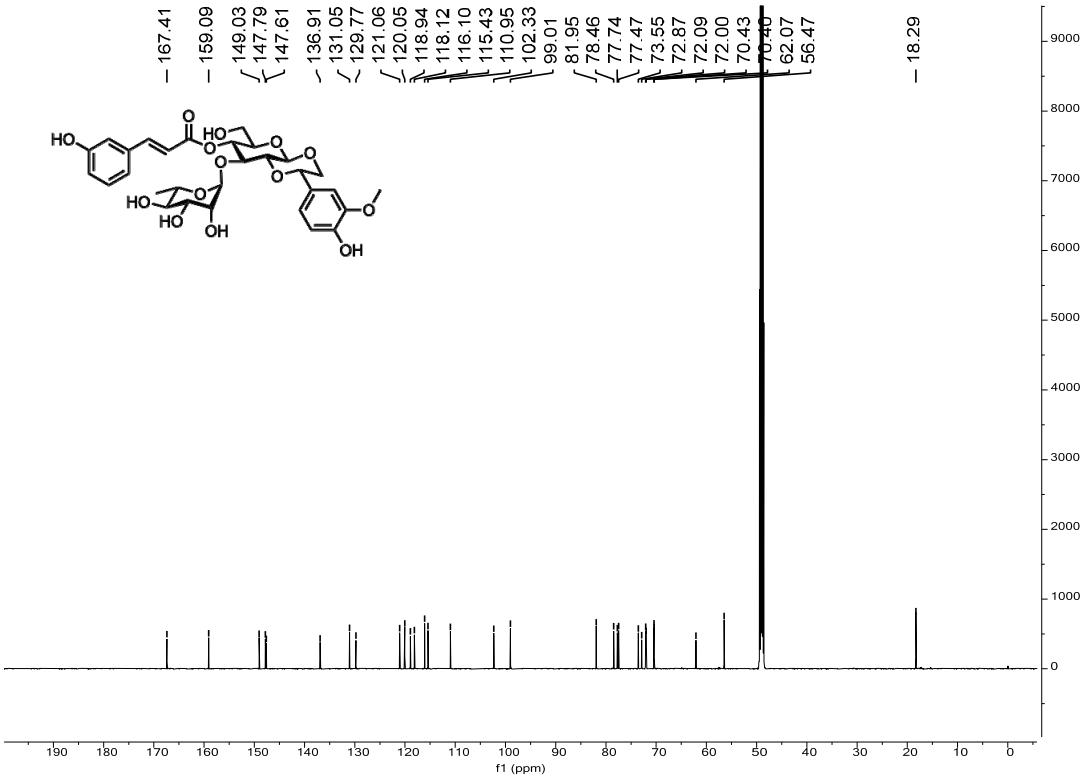

Figure S98 ^{13}C NMR spectrum of compound **33** (CD_3OD, 150 MHz)

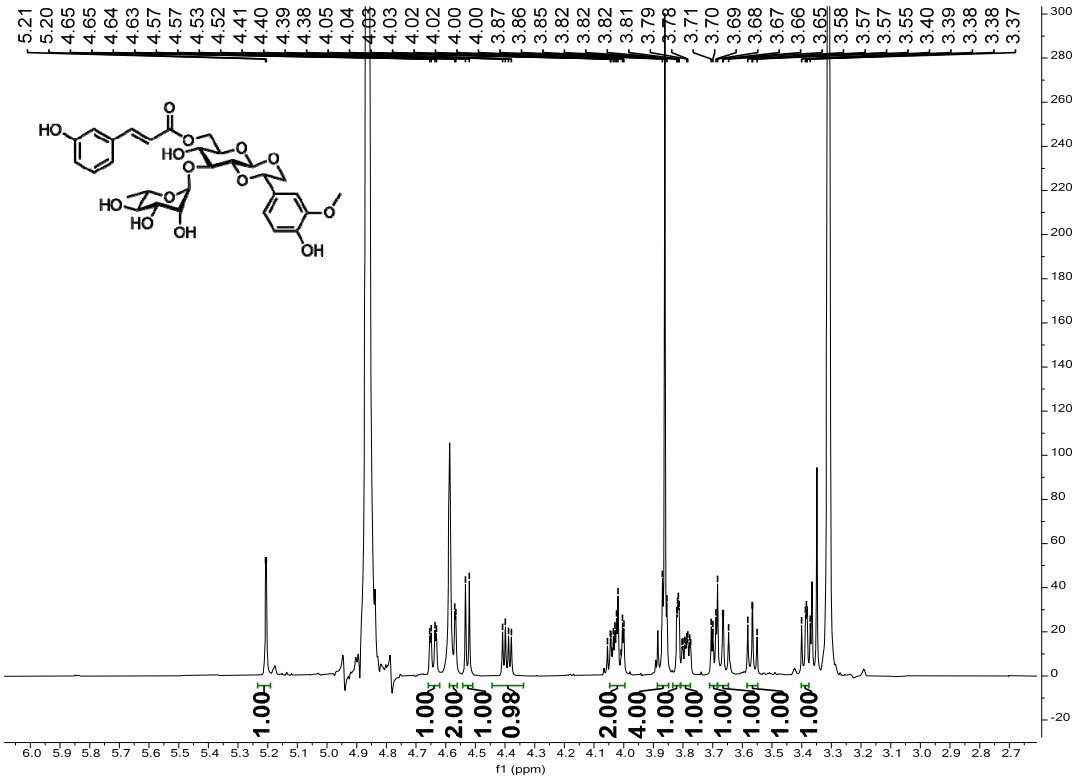

Figure S99 ^{1}H NMR spectrum of compound **40** (CD_3OD, 600 MHz)

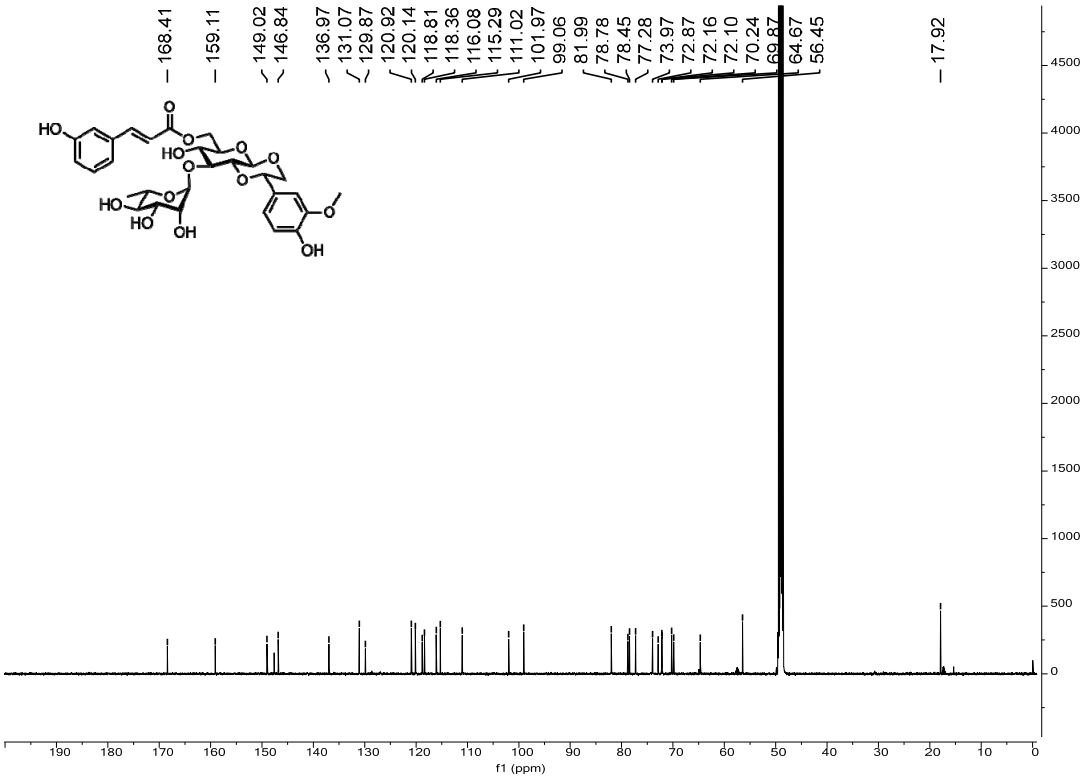

Figure S100 ^{13}C NMR spectrum of compound **40** (CD_3OD, 150 MHz)

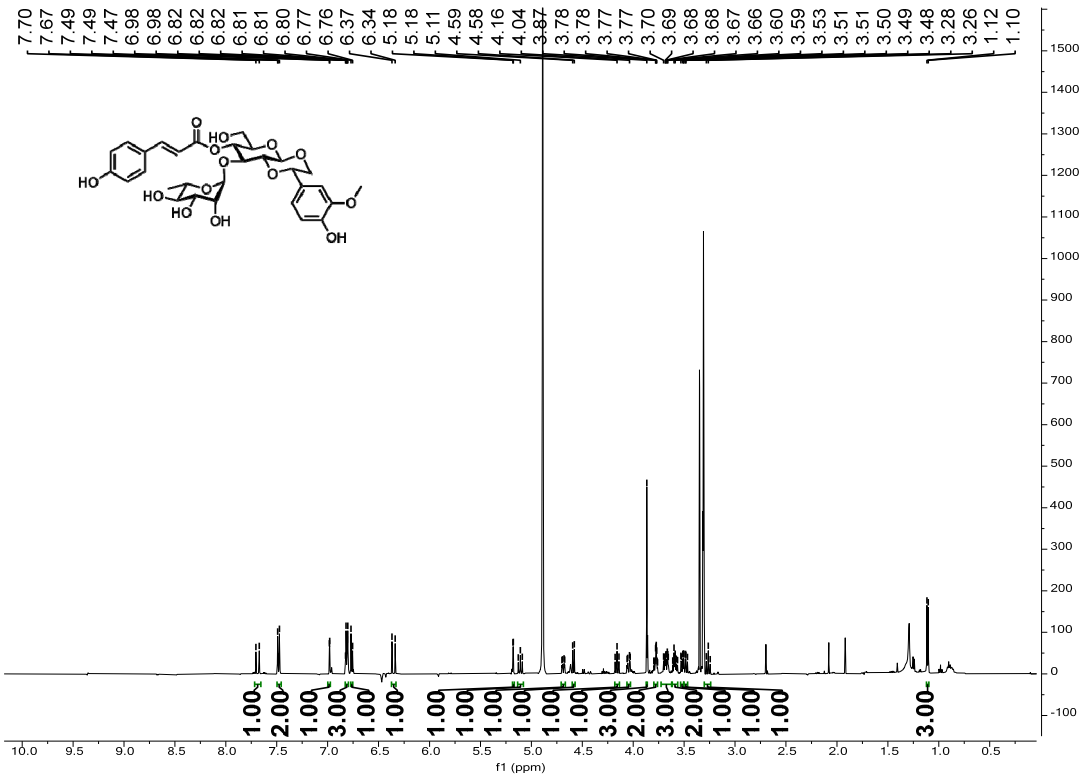

Figure S101 ^{1}H NMR spectrum of compound **34** (CD_3OD, 500 MHz)

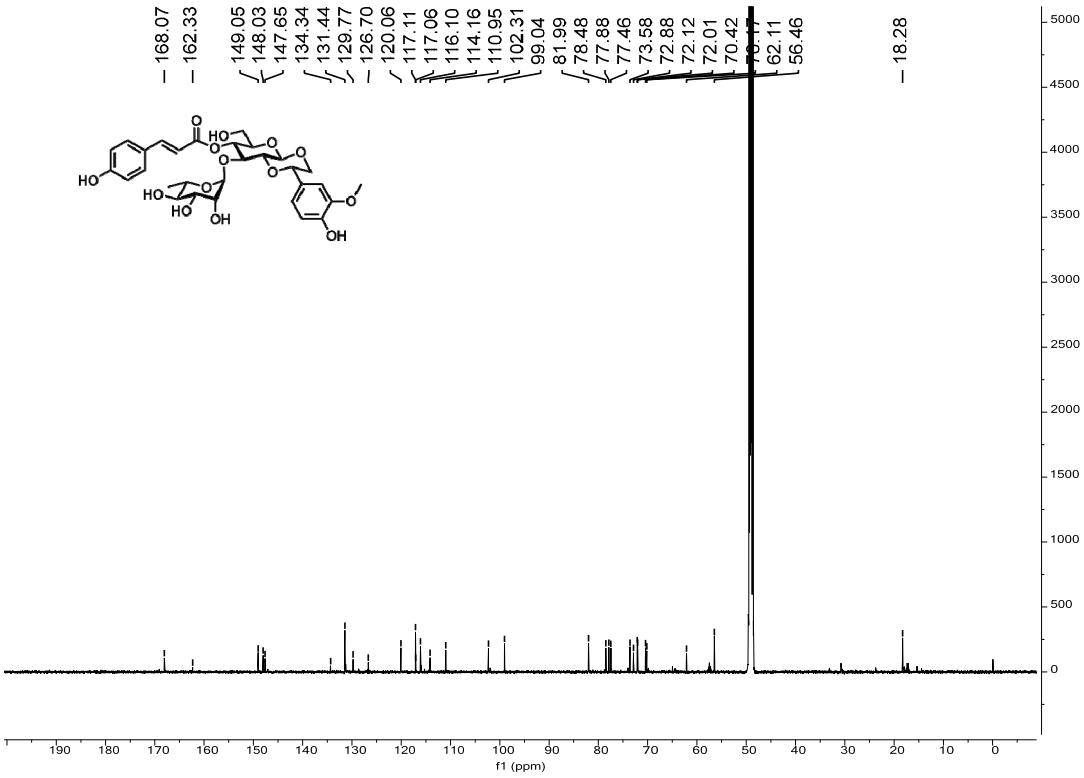

Figure S102 ^{13}C NMR spectrum of compound **34** (CD_3OD, 125 MHz)

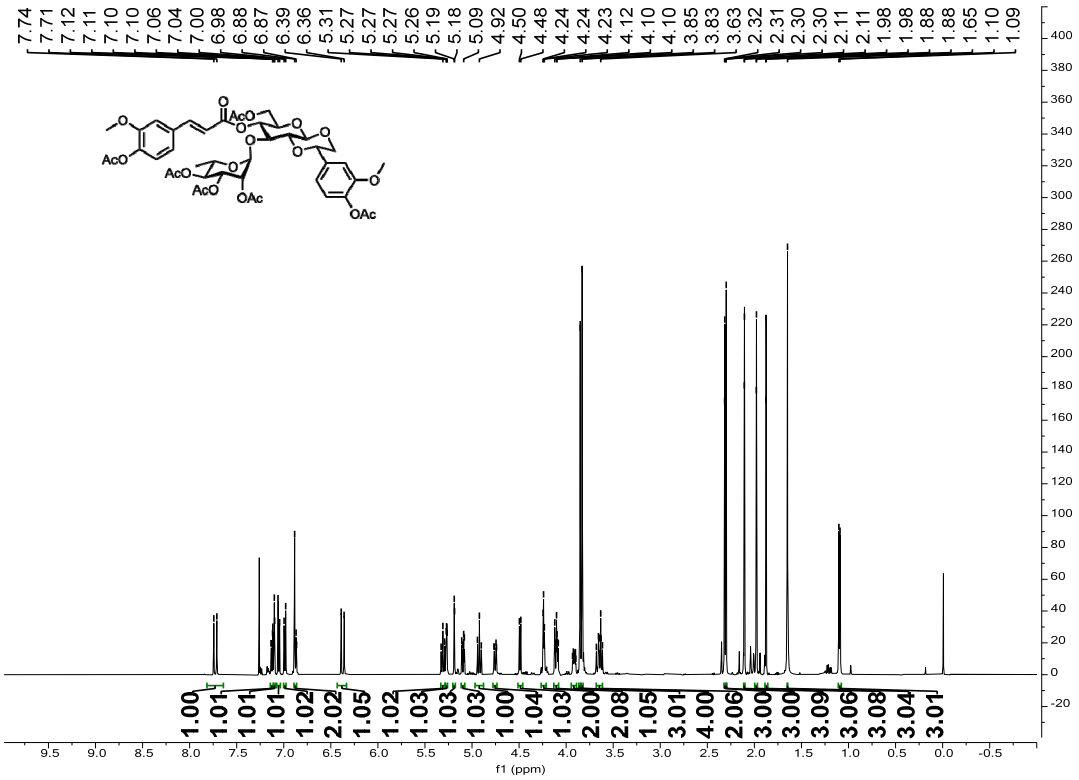

Figure S103 ^{1}H NMR spectrum of compound **S22** ($CDCl_3$, 500 MHz)

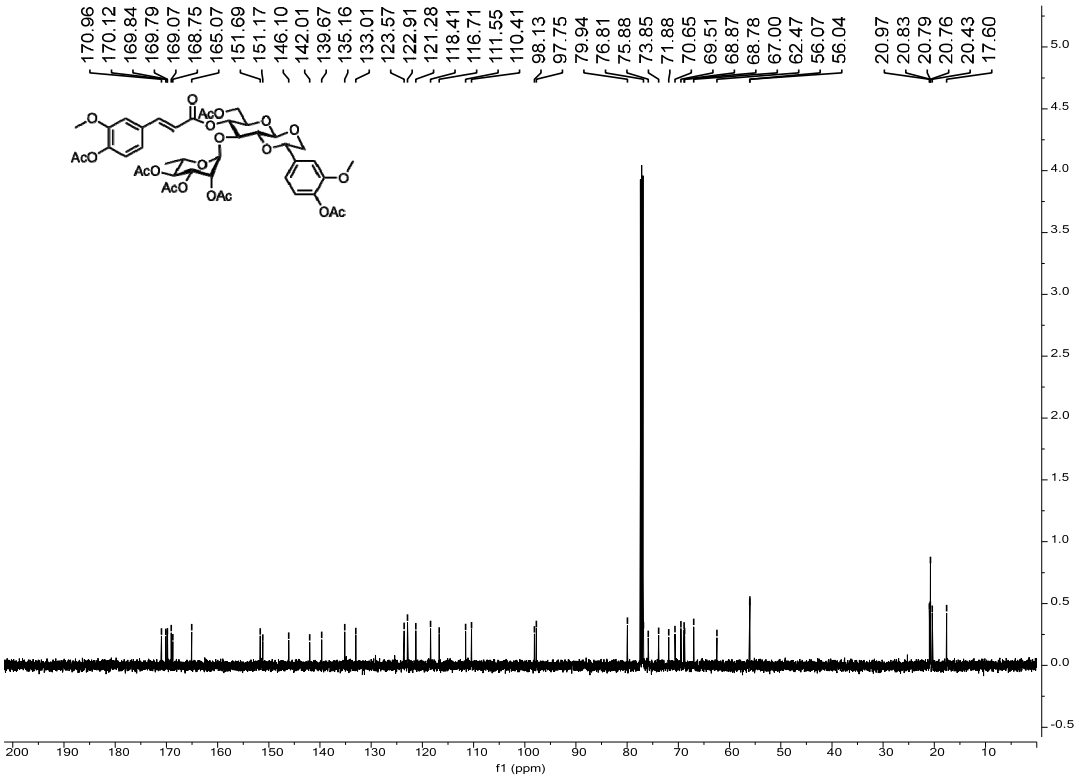

Figure S104 ^{13}C NMR spectrum of compound **S22** ($CDCl_3$, 125 MHz)

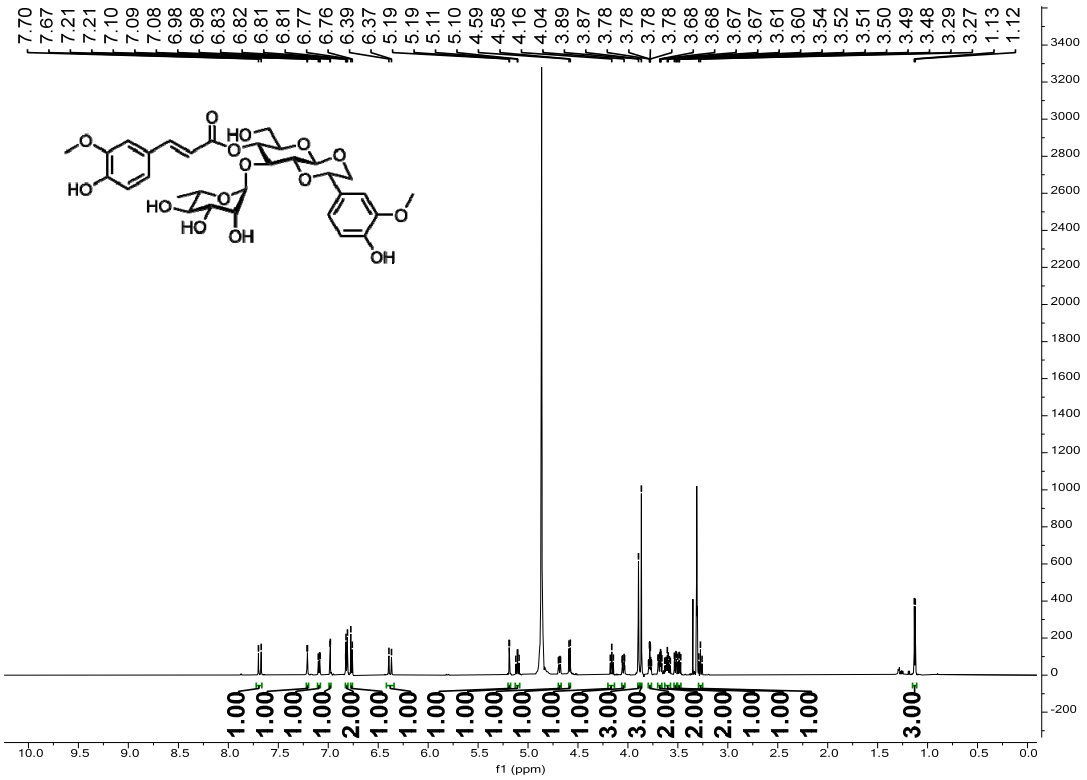

Figure S105 ^{1}H NMR spectrum of compound **35** (CD_3OD, 600 MHz)

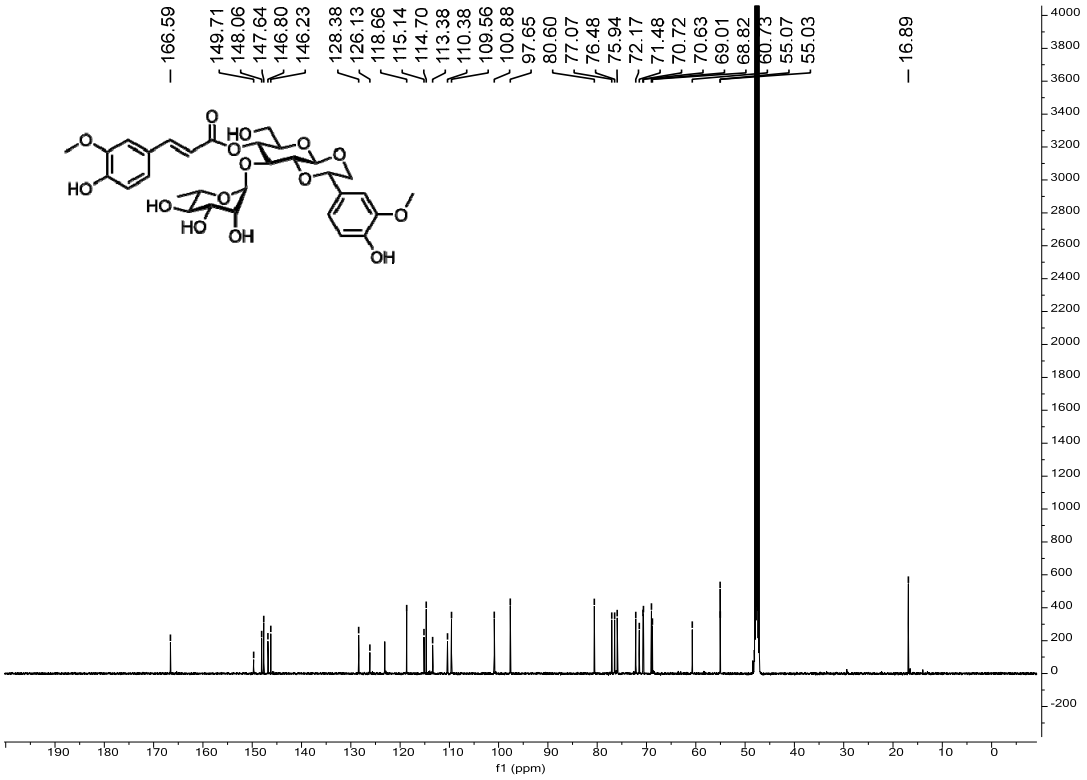

Figure S106 ^{13}C NMR spectrum of compound **35** (CD_3OD, 150 MHz)

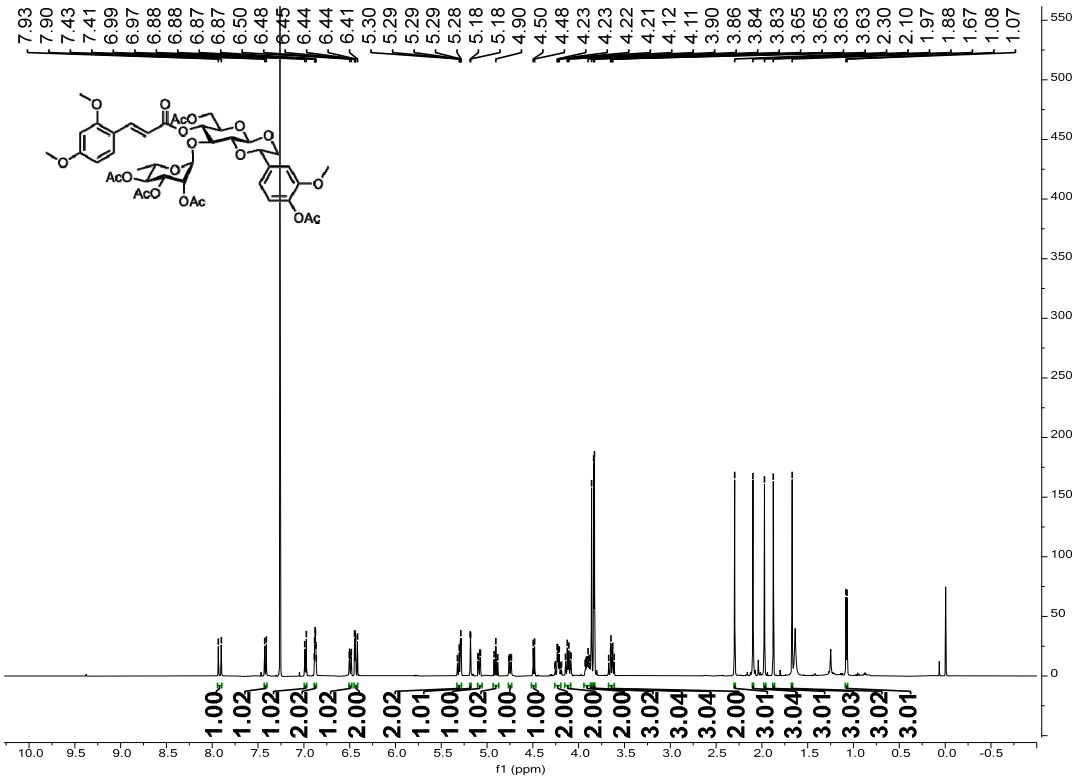

Figure S107 ^{1}H NMR spectrum of compound **S23** ($CDCl_3$, 500 MHz)

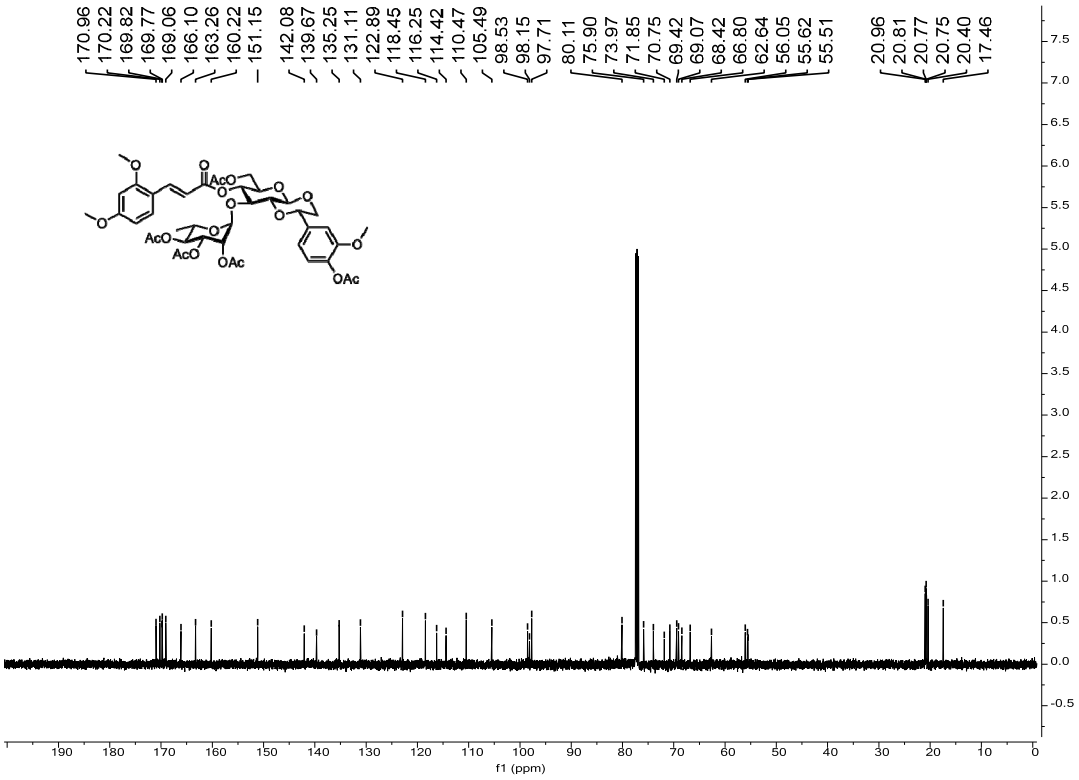

Figure S108 ^{13}C NMR spectrum of compound **S23** ($CDCl_3$, 125 MHz)

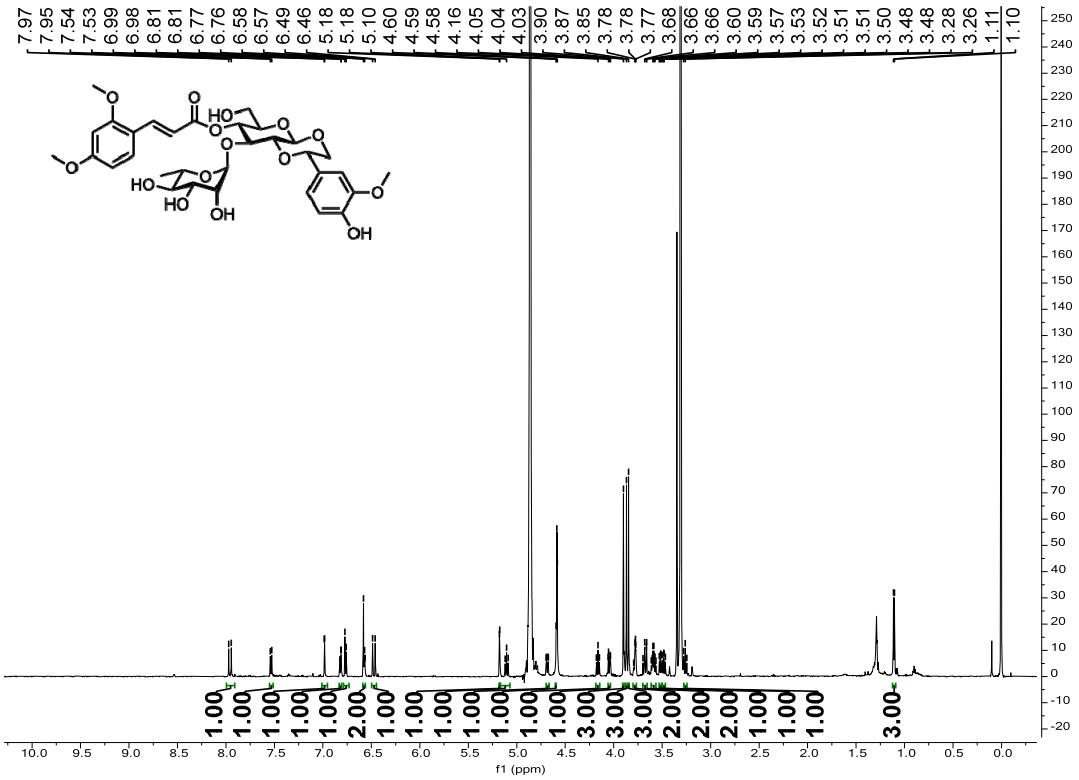

Figure S109 ^{1}H NMR spectrum of compound **36** (CD_3OD, 600 MHz)

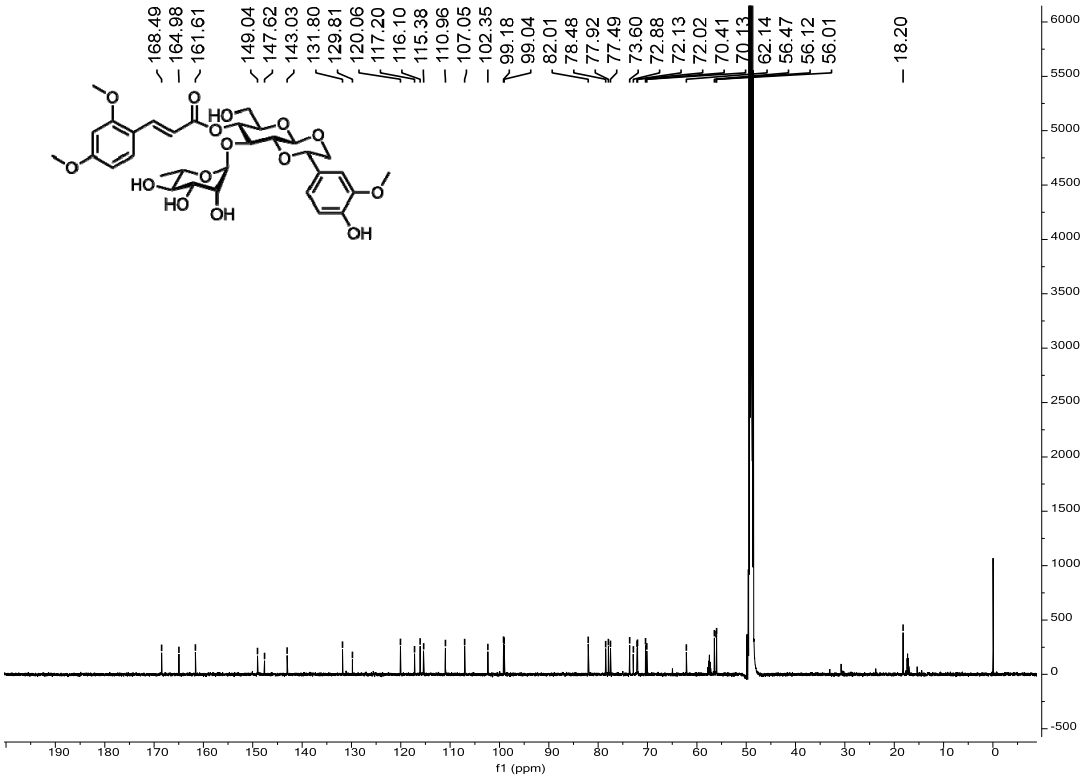

Figure S110 ^{13}C NMR spectrum of compound **36** (CD_3OD, 150 MHz)

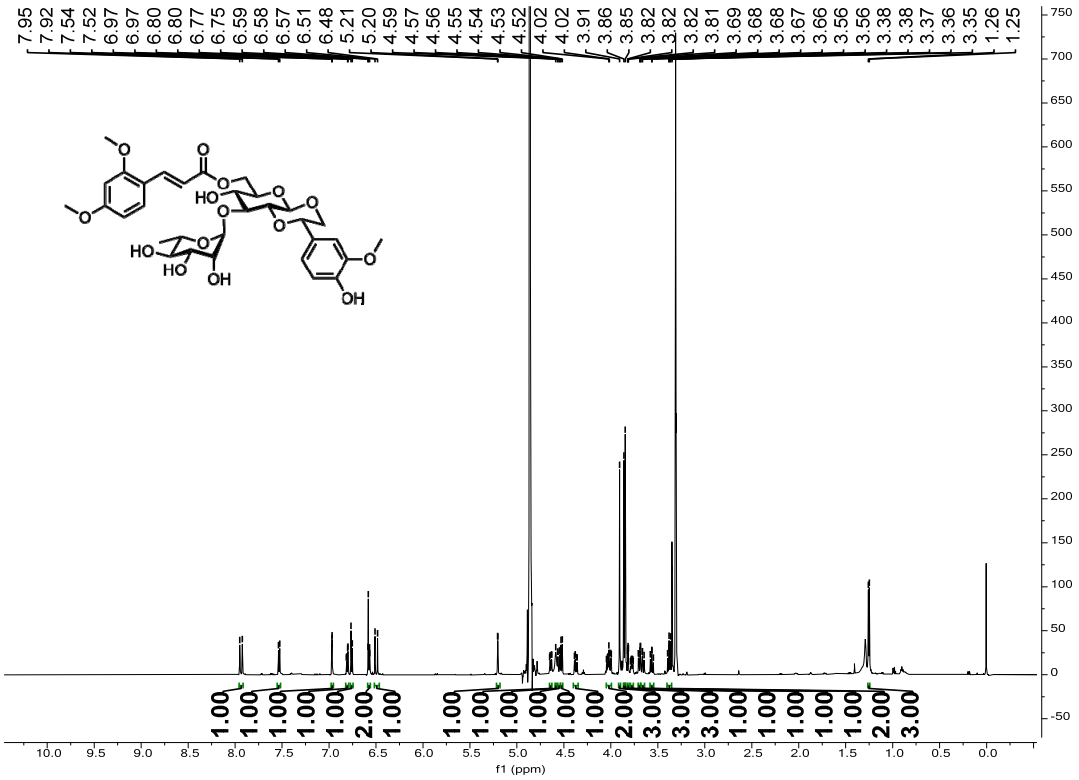

Figure S111 ^{1}H NMR spectrum of compound **41** (CD_3OD, 600 MHz)

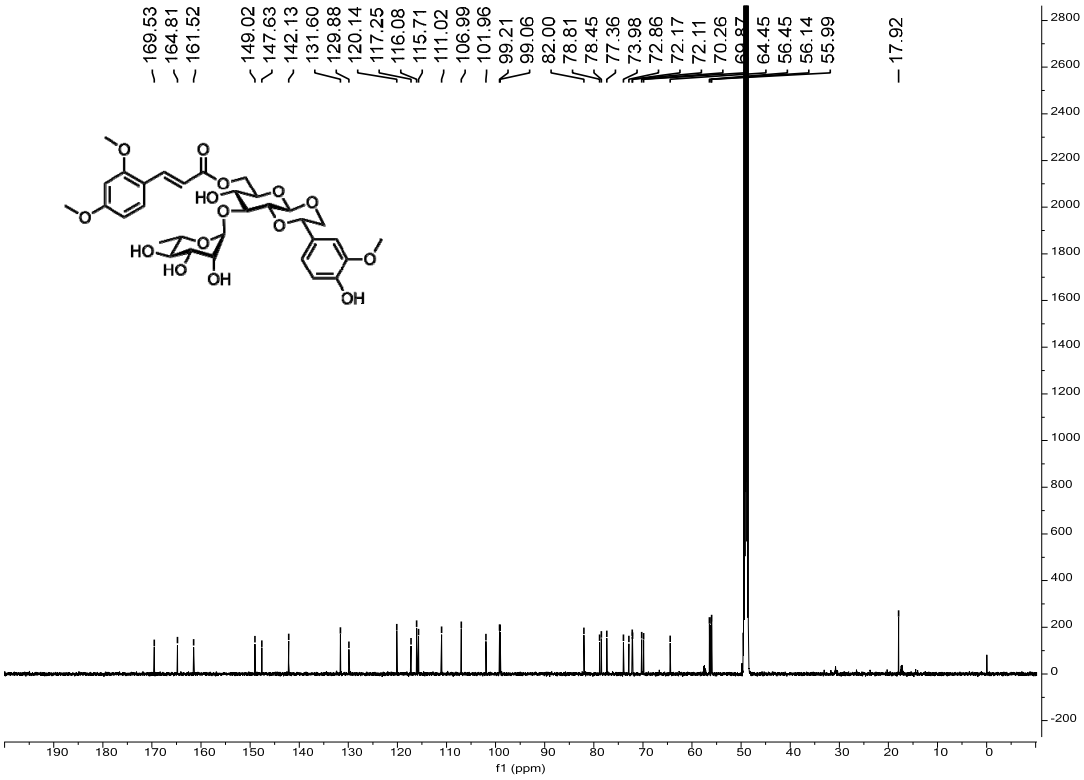

Figure S112 ^{13}C NMR spectrum of compound **41** (CD_3OD, 150 MHz)

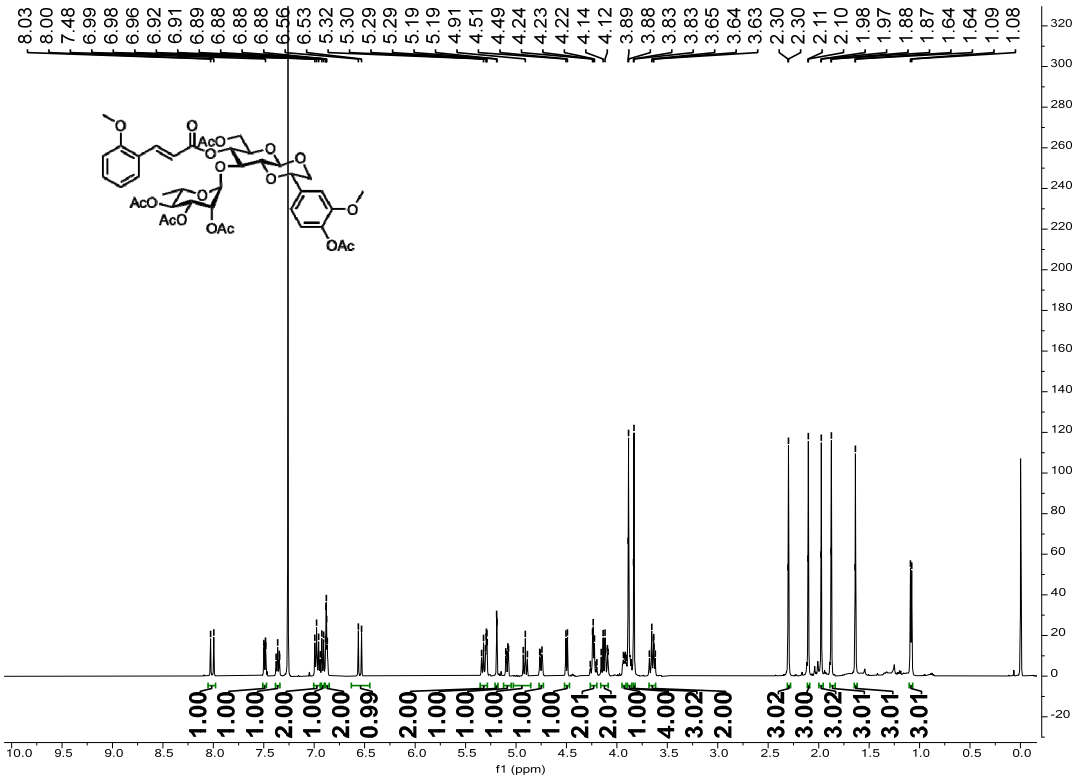

Figure S113 ^{1}H NMR spectrum of compound **S24** ($CDCl_3$, 500 MHz)

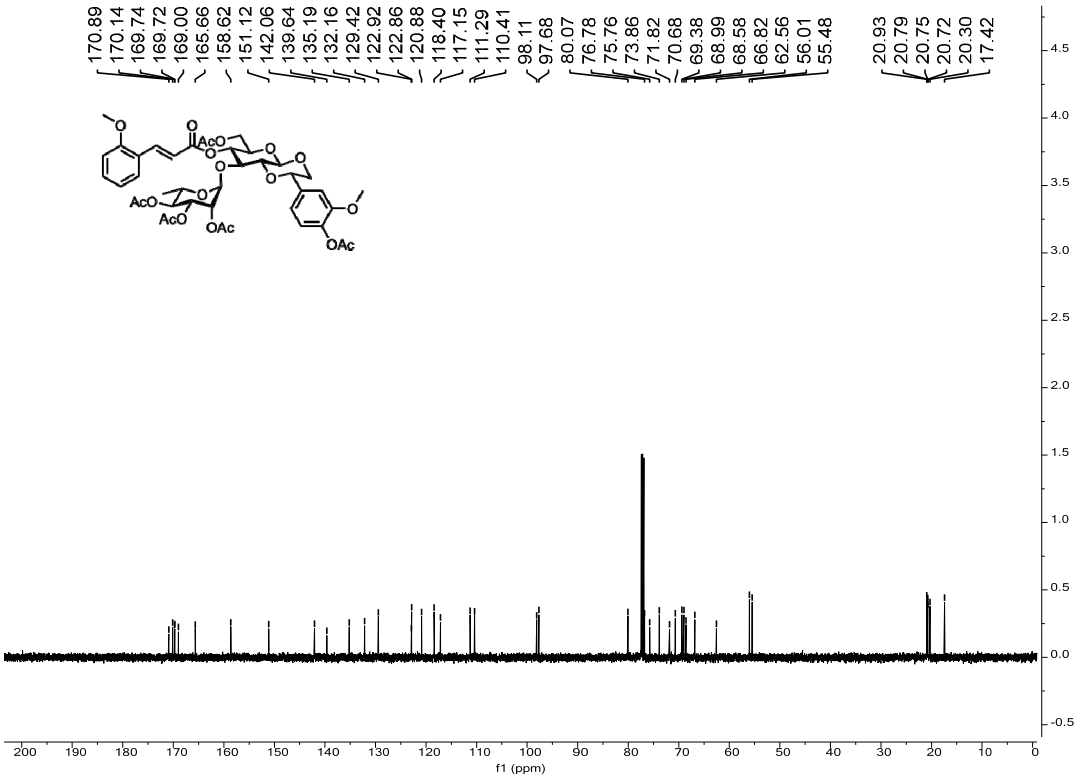

Figure S114 ^{13}C NMR spectrum of compound **S24** ($CDCl_3$, 125 MHz)

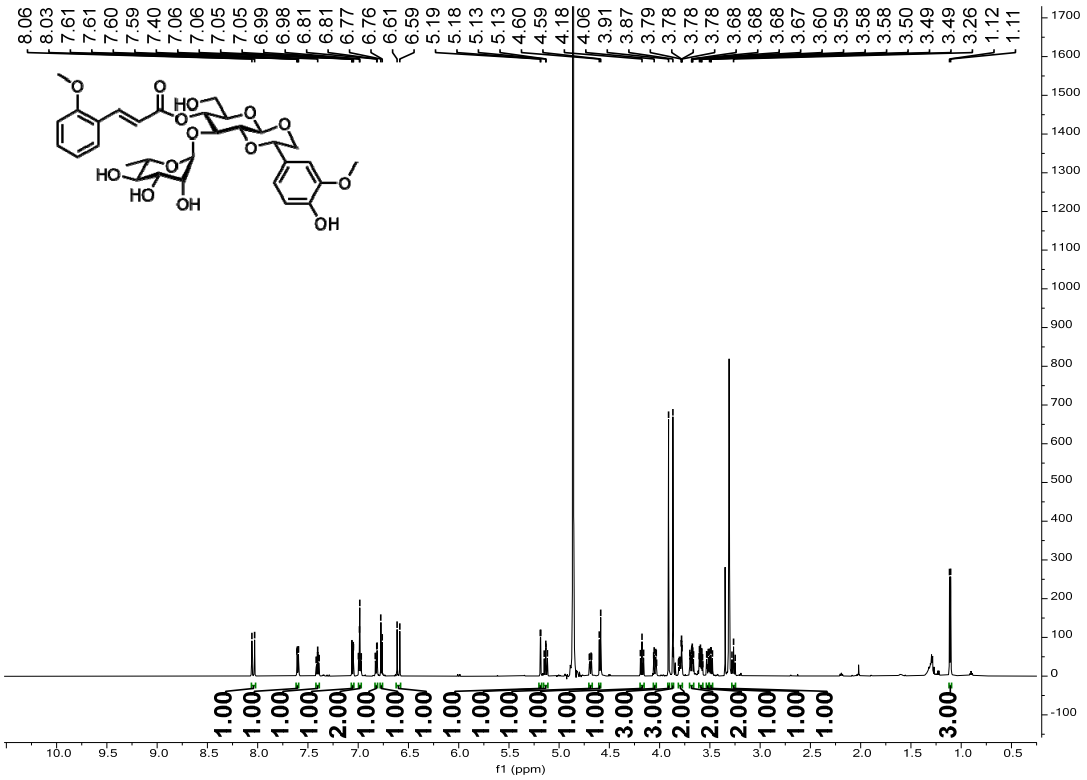

Figure S115 ^{1}H NMR spectrum of compound **37** (CD_3OD, 600 MHz)

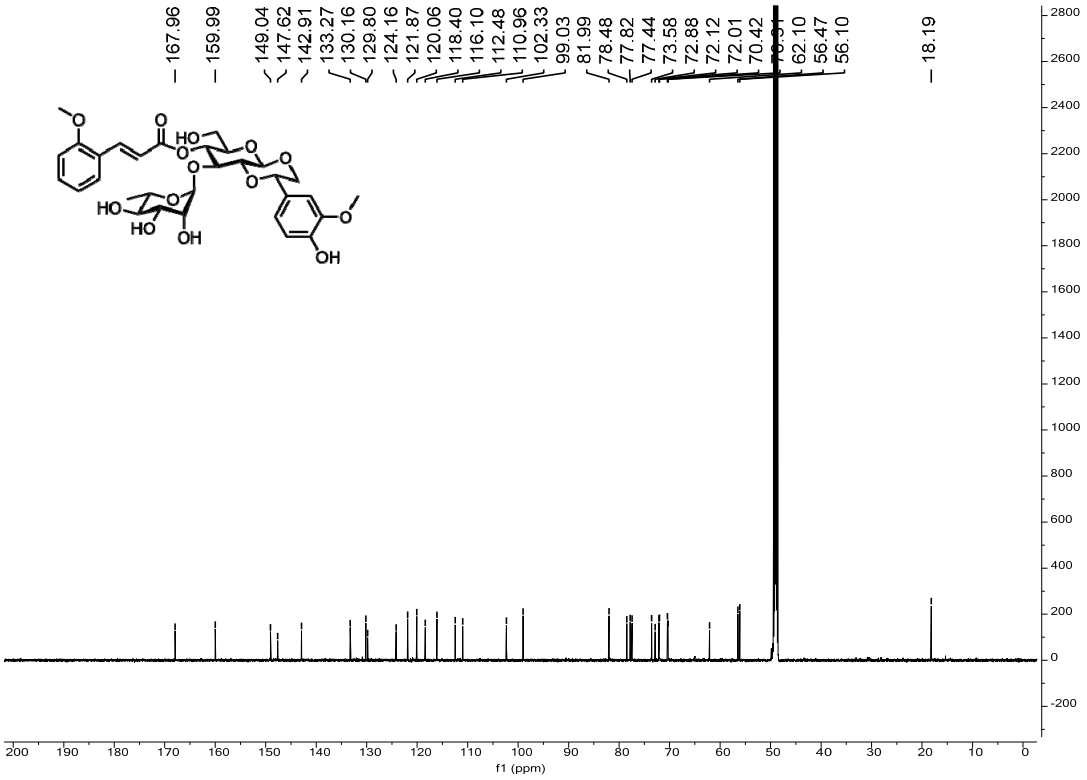

Figure S116 ^{13}C NMR spectrum of compound **37** (CD_3OD, 150 MHz)

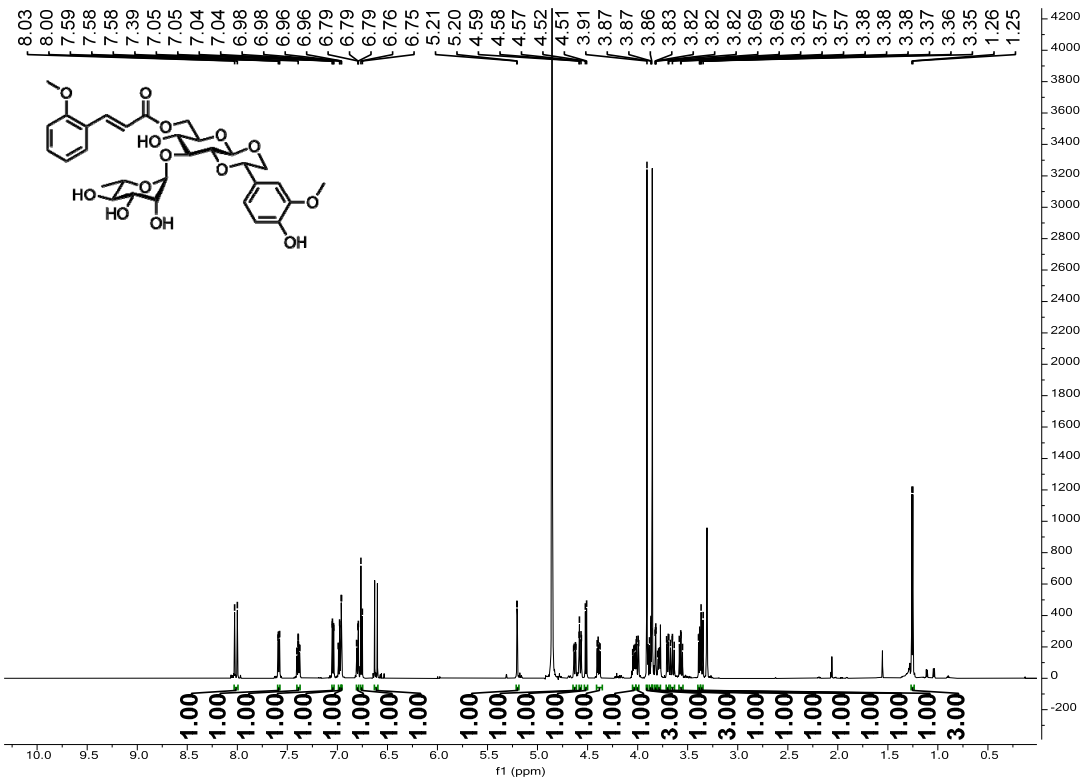

Figure S117 ^{1}H NMR spectrum of compound **42** (CD_3OD, 600 MHz)

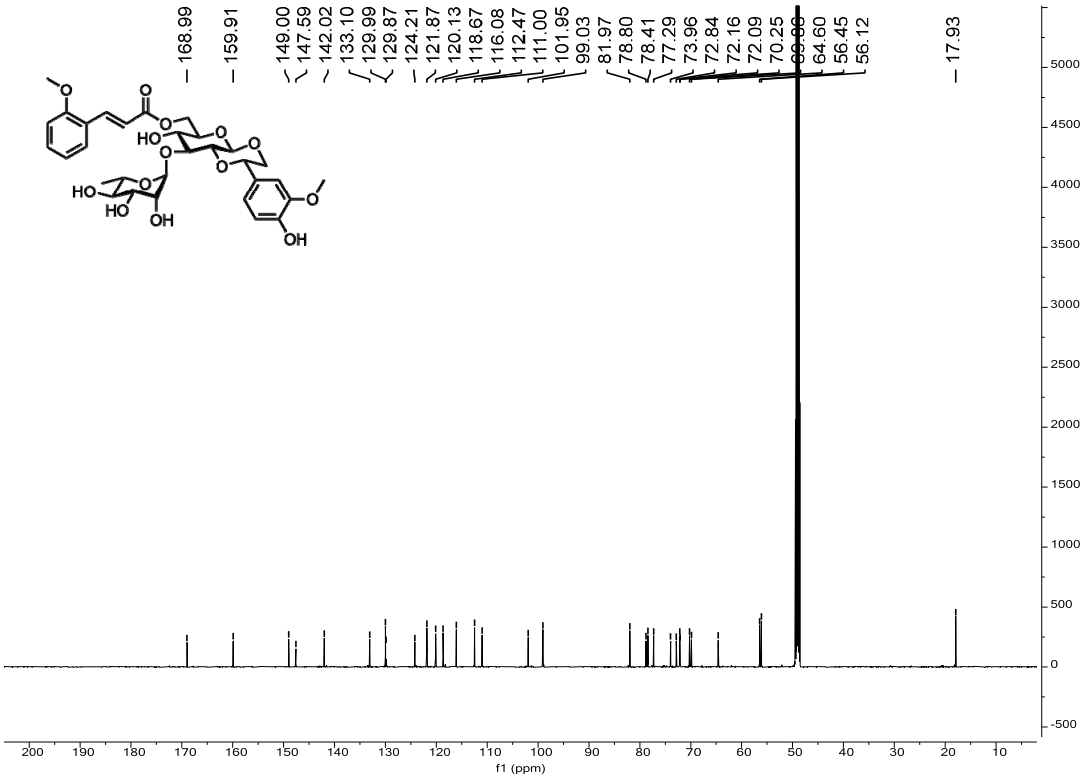

Figure S118 ^{13}C NMR spectrum of compound **42** (CD_3OD, 150 MHz)