First and Biomimetic Total Synthesis of a Member of the *C*-Glucosidic Subclass of Ellagitannins, 5-*O*-Desgalloylepipunicacortein A

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Supporting Information

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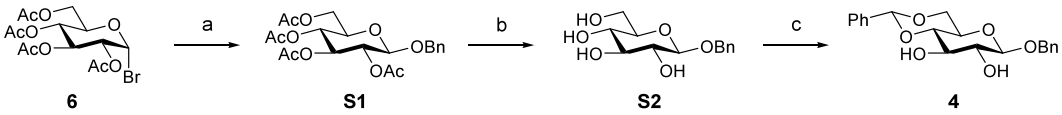
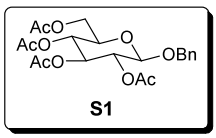
General Experimental Procedures. All moisture and oxygen sensitive reactions were carried out in flame-dried glassware under inert atmosphere with dry solvents. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purified immediately before use by filtration through activated alumina columns under nitrogen. Methanol (MeOH) was distilled from Mg under nitrogen prior to use. Acetone, ethanol (EtOH), ethyl acetate (EtOAc), petroleum ether (PET), cyclohexane and diethyl ether (Et_2O) were used as received. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. Evaporations were conducted under reduced pressure at temperatures less than 45 °C. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60 F_{254}), using UV light for visualization and a potassium permanganate solution and heat as the developing agent. A ferric chloride solution in HCl (0.5 M) was used to reveal catechol functions. In the case of polar compounds, reactions were monitored by reverse phase (RP) thin layer chromatography (TLC) carried out on E. Merck aluminum sheets (RP-18 F_{254}s), using UV light for visualization, or by HPLC on a reverse phase column (Pursuit C18, Varian), using MeCN/H_2O/0.1% HCOOH as the mobile phase (UV detection at 280 nm). Column chromatography was carried out under positive pressure using 40-63 μm silica gel (Merck) and the indicated solvents. Preparative HPLC was performed on a Varian semi-preparative LC system using a Varian Microsorb 100-8 C18 (41.4 × 250 mm) column. Melting points were recorded in open capillary tubes on a Buchi B-540 apparatus and are uncorrected. Optical rotations were determined on a Krüss P3001 digital polarimeter at 589 nm, and are given as $[\alpha]^{t°C}_{D}$ (concentration in g/100 mL solvent). IR spectra were recorded on a Bruker IFS55 FT-IR spectrometer. NMR spectra of samples in the indicated solvent were recorded on Bruker Avance 300 or 400 spectrometer and were calibrated using residual solvent as an internal reference. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, AB = AB quartet and br = broad singulet. Carbon multiplicities were determined by DEPT135 experiment. Diagnostic correlations were obtained by two-dimensional COSY, HSQC and HMBC experiments. CD spectra were measured on a JASCO J-815 using the wavelength range 495-230 nm, scanning at 1 nm intervals with an averaging time of 0.5 s at 20 °C in a 1 mm cell. The concentration of the solution used was 1 mg per 1 mL of CH_2Cl_2. Chemical ionization (CIMS) and electrospray (ESIMS) low and/or high resolution (HRMS) mass spectrometric analyses were obtained from the mass spectrometry laboratory at the Institut Européen de Chimie et Biologie (IECB), France. Elemental analyses were carried out at the Service Central d'Analyses du CNRS, Vernaison, France.



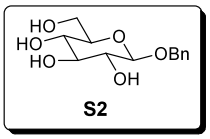
Scheme 1. Preparation of sugar derivative **4**: a) BnOH, Ag_2CO_3, I_2 (cat.), CH_2Cl_2, rt, 20 h; b) NaOMe, MeOH, rt, 3 h; c) PhCHO, $ZnCl_2$, rt, 16 h.

Benzyl-2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (S1).



According to the procedure described in the literature,[1] Ag_2CO_3 (2.01 g, 7.29 mmol, 3 eq) and a crystal of iodine were added to a solution of commercially available benzyl alcohol (1.31 g, 12.15 mmol, 5 eq) in dry CH_2Cl_2 (15 mL) and the mixture was stirred over 4 Å molecular sieves for 15 min. A solution of commercially available 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide **6** (1 g, 2.43 mmol, 1 eq) in dry CH_2Cl_2 (5 mL) (also stirred over 4 Å molecular sieves for 15 min) was then added dropwise. The reaction flask was shielded from light and stirred at room temperature under nitrogen for 20 h. The reaction mixture was diluted with EtOAc (20 mL), filtered through Celite®, and concentrated *in vacuo*. The crude material was purified by column chromatography (4:1 cyclohexane/EtOAc) to afford **S1** as a white solid (976 mg, 92%). m.p. 93-94 °C [lit.[2] m.p. 93.0-93.3 °C (EtOH)]; R_f = 0.05 (4:1 cyclohexane/EtOAc); $[\alpha]^{21}_D$ = –52.0 (c = 1, $CHCl_3$) [lit.[2] $[\alpha]^{25}_D$ = –51.0 (c = 1, $CHCl_3$)]; IR (NaCl) ν_{max} 1752, 1369, 1221 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 3H), 1,98 (s, 3H), 2.00 (s, 3H), 2.09 (s, 3H), 3.63-3.69 (m, 1H), 4.15 (dd, *J* = 2.4, 12.2 Hz, 1H), 4.26 (dd, *J* = 4.7, 12.3 Hz, 1H), 4.54 (d, *J* = 7.8 Hz, 1H), 4.61 and 4.88 (AB, J_{AB} = 12.3 Hz, 2H), 5.02-5.19 (m, 3H), 7.25-7.36 (m, 5H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.4, 170.0, 169.2, 169.0, 136.6, 128.3, 127.8, 127.6, 99.2, 72.7, 71.7, 71.2, 70.6, 68.4, 61.8, 20.5, 20.4, 20.4; CIMS *m/z* (%): 457 (100) $[M+NH_4]^+$, 331 (54).

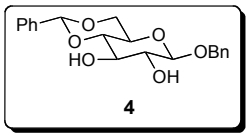
Benzyl-α-D-glucopyranoside (S2).



According to the procedure described in the literature,[2] a catalytic amount of sodium methoxide was added to a stirred solution of **S1** (2.87 g, 6.55 mmol) in dry MeOH (40 mL). TLC analysis indicated after 3 h complete conversion of the starting material. The solution was then neutralized with Dowex® 50X8-400 ion-exchange resin (H^+ form), filtered, and concentrated *in vacuo* to leave **S2** in pure form as white crystals (1.77 g, quantitative yield). m.p. 104 °C [lit.[2] m.p. 105-106 °C ($CHCl_3$-PET)]; R_f = 0.34 (5% acetone in EtOAc); $[\alpha]^{21}_D$ = –56.3 (c = 0.9, MeOH) [lit.[3] $[\alpha]^{20}_D$ = –55.5 (c = 0.885, MeOH)]; IR (KBr) ν_{max}

3500, 3427, 3060, 2931, 2884, 1496, 1455, 1414, 1380, 1369, 1317, 1280, 1240, 1209, 1156, 1106, 1083, 1048, 1032, 990 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 3.20-3.33 (m, 4H), 3.66 (dd, *J* = 5.2, 11.8 Hz, 1H), 3.86 (d, *J* = 11.7 Hz, 1H), 4.32 (d, *J* = 7.5 Hz, 1H), 4.63 and 4.89 (AB, J_{AB} = 11.8 Hz, 2H), 7.20-7.39 (m, 5H); ^{13}C-NMR (75 MHz, CD_3OD) δ 139.0, 129.2, 129.2, 128.6, 103.2, 78.0, 77.9, 75.1, 71.7, 71.6, 62.8; CIMS *m/z* (%): 288 (100) $[M+NH_4]^+$, 270 (82) $[M+H]^+$, 180 (89), 108 (68), 120 (73), 91 (27).

Benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (4).



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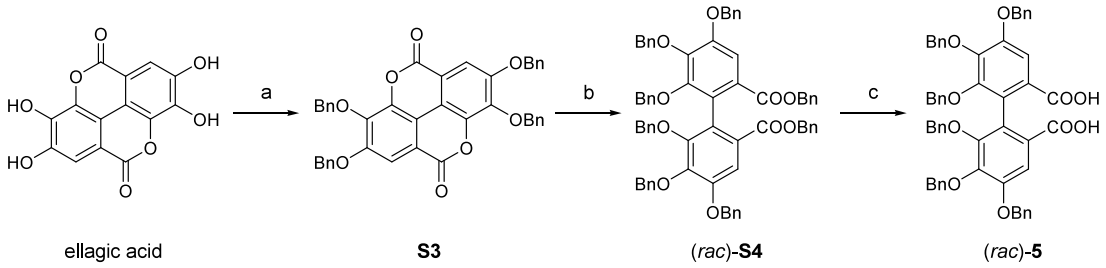
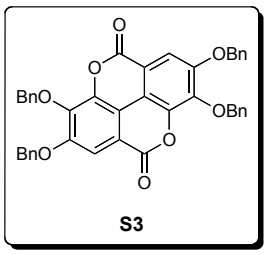
According to the procedure described in the literature,[4] zinc chloride (13.8 g, 0.10 mol, 5.3 eq) was added under nitrogen to a suspension of **S2** (5.13 g, 19 mmol, 1 eq) in 50 mL of freshly distilled benzaldehyde and the mixture was stirred at room temperature for 16 h. The reaction mixture was then diluted with ice, and the crude product was extracted with EtOAc (3 × 50 mL). The combined extracts were washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue, containing an excess of benzaldehyde, was purified by column chromatography (10:0 → 9:1 CH_2Cl_2/acetone) to yield **4** as a white solid (6.1 g, 90%). m.p. 158.5 °C; R_f = 0.10 (3:2 cyclohexane/EtOAc); $[\alpha]^{24}_D$ = –61.0 (*c* = 1.2, $CHCl_3$); IR (neat) ν_{max} 3434, 3063, 3031, 2917, 2874, 1455, 1380, 1094, 1027, 1002 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.46 (dt, *J* = 4.8, 9.5 Hz, 1H), 3.53-3.60 (m, 2H), 3.78-3.85 (m, 2H), 4.37 (dd, *J* = 4.8, 10.5 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.64 and 4.94 (AB, J_{AB} = 11.5 Hz, 2H), 5.54 (s, 1H), 7.32-7.51 (m, 10H); ^{13}C-NMR (75 MHz, DMSO-d_6) δ 137.9, 137.8, 128.8, 128.2, 128.0, 127.6, 127.5, 126.4, 103.0, 100.7, 80.6, 74.4, 72.9, 70.2, 68.0, 65.9; ESIMS *m/z* (%): 739 (100) $[2M+Na]^+$.



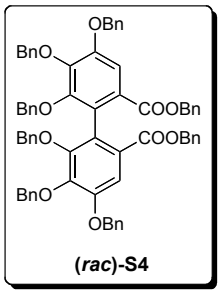
Scheme 2. Preparation of hexabenzyloxydiphenic acid (*rac*)-**5**. a) BnCl, K_2CO_3, NaI, acetophenone, 140 °C, 18 h; b) KOH, NaI, BnCl, 145 °C, 4 h; c) KOH, acetone/MeOH/H_2O (5:5:0.3), reflux, 3 h.

Tetrabenzylellagic acid (S3).



Adapted from the method of Kashiwada *et al*.[5] To a mixture of commercially available ellagic acid (20.0 g, 66 mmol, 1.0 eq), NaI (4.0 g, 27 mmol, 0.4 eq) and anhydrous powdered K_2CO_3 (76.8 g, 556 mmol, 8.4 eq) in 260 mL of acetophenone was added freshly distilled benzyl chloride (41 mL, 351 mmol, 5.3 eq). After stirring for 18 h at 140 °C, inorganic salts and unreacted ellagic acid were removed by filtration. Tetrabenzyl ellagic acid was crystallized from the filtrate by addition of cyclohexane. A large amount of cyclohexane was added until complete precipitation occurred. Compound **S3** was obtained as a white solid (22.0 g, 50%). m.p. 265-266 °C (acetophenone-cyclohexane) [lit.[15] m.p. 267 °C (1,4-dioxane)]; R_f = 0.60 (4:1 cyclohexane/EtOAc); IR (KBr) ν_{max} 2939, 2854, 1746, 1606, 1495, 1457, 1410, 1360, 1317, 1258, 1179, 1094 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 5.37 (s, 8H), 7.34-7.67 (m, 22H), 11.08 (s, 3H, due to lactone ring opening).

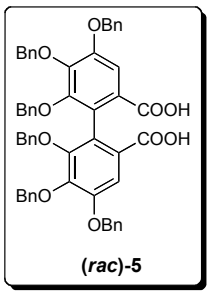
Dibenzyl 2,2',3,3',4,4'-hexabenzyloxy-diphenyl-6,6'-dicarboxylate [(*rac*)-S4].



Adapted from the method of Schmidt *et al*.[6] In a dry round-bottom flask, a mixture of **S3** (5.3 g, 8 mmol, 1 eq), KOH (11.5 g, 205 mmol, 25 eq), NaI (0.6 g, 4 mmol, 0.5 eq) and benzyl chloride (40 mL) was heated at 145 °C for 4 h under an argon atmosphere. The reaction mixture was then quenched with H_2O (100 mL) and extracted with EtOAc (3 × 100 mL). The organic layer was washed with brine (100 mL), dried over $MgSO_4$, filtered and evaporated. The resulting mixture was distilled at 120 °C under high vacuum using a Kugelrohr apparatus and the residue was purified by column chromatography (9:1 → 8:2 PET/EtOAc) to give (*rac*)-**S4** as a colorless syrup (7.4 g, 87%). R_f = 0.46 (9:1 cyclohexane/EtOAc); IR (neat) ν_{max} 3032, 1712, 1458, 1371, 1326, 1096, 1019, 977 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.70 and 4.80 (AB, J_{AB} = 11.2 Hz, 4H), 4.88 and 4.91 (AB, J_{AB} = 11.0 Hz, 4H), 4.99 and 5.03 (AB, J_{AB} = 12.3 Hz, 4H), 5.17 (br, 4H), 6.83-7.54 (m, 42H); ^{13}C-NMR

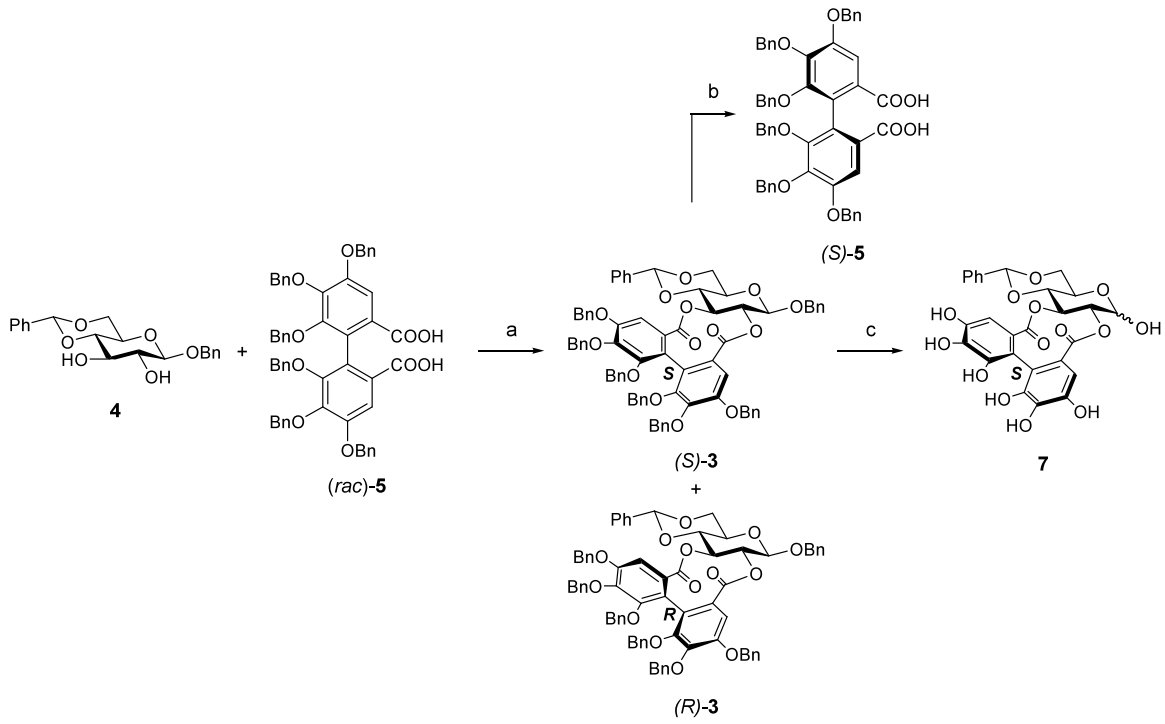
(75 MHz, $CDCl_3$) δ 166.2, 151.5, 150.8, 145.5, 137.6, 137.2, 136.6, 135.5, 128.5, 128.4, 128.2, 128.2, 128.2, 128.0, 127.9, 127.8, 127.5, 127.5, 127.3, 127.3, 125.4, 111.1, 75.1, 74.3, 70.8, 66.6; ESIMS *m/z* (%): 1060 (57) $[M+H]^+$, 1059 (100), 952 (36), 951 (66).

2,2',3,3',4,4'-hexabenzyloxydiphenyl-6,6'-dicarboxylic acid [(*rac*)-5].



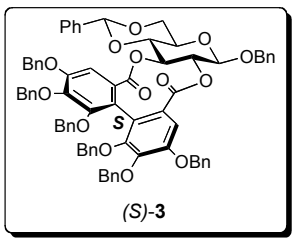
(*rac*)-5

Adapted from the method of Schmidt *et al*.[6] To a solution of (*rac*)-**S4** (12.3 g, 12 mmol, 1 eq) in a 5:5:0.3 mixture of acetone/MeOH/H_2O (187 mL) was added KOH (14.6 g, 260 mmol, 22 eq). The suspension was stirred at 75 °C for 4 h, after which time the volume of solvents was reduced to 1/3 by evaporation. The resulting mixture was then diluted with H_2O (250 ml), acidified to pH 1 with concentrated HCl (3 mL) and extracted with EtOAc (4 × 200 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, filtered and evaporated. The oily residue was dissolved in a small amount of EtOAc and (*rac*)-**5** was crystallized as a white solid (1.94 g) by adding cyclohexane. The mother liquor was then evaporated and purified by column chromatography, eluting with cyclohexane/EtOAc (1:1) to remove apolar impurities, then with EtOAc/acetone/AcOH (10:10:0.1 → 0:10:0.1) to afford 4.70 g of (*rac*)-**5** as a white solid (6.64 g, 63%). m.p. 185-186 °C (cyclohexane) [lit.[6] m.p. 187 °C (PET)]; R_f = 0.53 (98:2 EtOAc/acetone); IR (neat) ν_{max} 3032, 1685, 1584, 1454, 1410, 1363, 1322, 1097 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.74 (d, *J* = 11.1 Hz, 2H), 4.94-5.02 (m, 6H), 5.16 and 5.24 (AB, J_{AB} = 11.2 Hz, 4H), 6.81-7.63 (m, 32H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 172.1, 151.6, 151.0, 146.3, 137.7, 137.2, 136.6, 128.9, 128.6, 128.6, 128.2, 128.1, 127.9, 127.8, 127.3, 123.6, 112.0, 75.2, 74.5, 71.0; ESIMS *m/z* (%): 901 (100) $[M+Na]^+$.



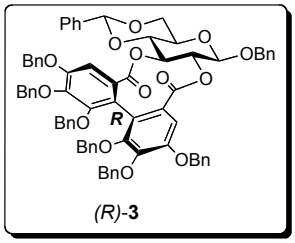
Scheme 3. Bis-esterification of the HHDP unit (*rac)*-**5** on the sugar derivative **4**. a) DCC, DMAP, CH_2Cl_2, rt, 18 h; b) *t*-BuOK, H_2O, THF, rt, 12 h; c) H_2, Pd/C, THF, rt, 24 h.

Compounds (*S*)- and (*R*)-3. To a solution of **4** (410 mg, 1.15 mmol, 1 eq), racemic diacid (*rac*)-**5** (1.11 g, 1.26 mmol, 1.1 eq) and DMAP (309 mg, 2.53 mmol, 2.2 eq) in dry CH_2Cl_2 (10 mL) at 0 °C was added DCC (1.04 g, 5.05 mmol, 4.4 eq). The solution was purged with nitrogen and stirred at room temperature for 18 h. The mixture was then filtered through Celite®. The filter cake was washed with CH_2Cl_2 and the combined filtrates were evaporated. After addition of cold EtOAc, the excess of DCU was removed by filtration (this manipulation was repeated 5 times). The resulting crude product was purified by column chromatography (90:10:0 → 100:0:0 → 95:0:5 CH_2Cl_2/PET/Et_2O) to obtain pure (*S*)-**3** as a pale yellow foam (485 mg, 35%) and a more polar fraction containing (*R*)-**3** (yellow foam, 535 mg). The determination of the absolute configuration of (*S*)-**3** was accomplished by subjecting this compound to hydrolysis under Gassman conditions (*i.e.*, *t*-BuOK in dry THF, plus a trace of water),[7] and by comparing the CD spectrum of the resulting hexabenzyloxydiphenic acid **5** (*vide infra*) to those reported for biarylic (*S*)-atropoisomers.[8]



(*S*)-**3**: m.p. 91-92 °C; R_f = 0.75 (4:1 CH_2Cl_2/PET); $[\alpha]^{21}_D$ = –73.1 (c = 0.52, $CHCl_3$); IR (neat) ν_{max} 3430, 1752, 1590, 1452, 1368, 1332, 1186, 1094, 1007, 748, 697 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.56-3.64 (m, 1H), 3.90-3.99 (m, 2H), 4.46 (dd, *J* = 4.6, 10.5 Hz, 1H), 4.63-5.22 (m, 16H),

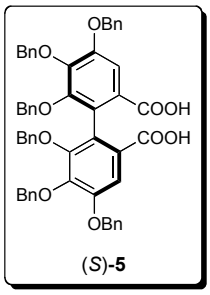
5.42 (t, J = 9.6 Hz, 1H), 5.62 (s, 1H), 6.83 (s, 1H), 6.98-7.54 (m, 41H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 168.3, 167.4, 152.7, 152.6, 152.6, 152.5, 144.5, 137.6, 137.5, 137.5, 136.8, 136.8, 136.4, 136.4, 129.4, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.5, 126.4, 122.3, 122.2, 107.2, 106.9, 101.7, 99.1, 77.4, 75.9, 75.8, 75.5, 75.5, 75.3, 75.3, 71.3, 70.8, 68.6, 67.2; ESIMS m/z (%): 1223 (20) $[M+Na]^+$, 477 (100); HRMS (ESI-TOF) calcd for $C_{76}H_{64}O_{14}Na$ $[M+Na]^+$ 1223.4194, found 1223.4402.



(R)-**3**

(*R*)-**3**: This compound could not be isolated as a pure fraction. Only assignable peaks from the mixture are listed here. R_f = 0.45 (4:1 CH_2Cl_2/PET); IR (neat) ν_{max} 3436, 1719, 1591, 1456, 1364, 1332, 1197, 1094, 1025, 741, 697 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.45-3.53 (m, 1H), 3.61-3.67 (m, 1H), 3.86 (t, J = 10.1 Hz, 1H), 4.38-4.45 (m, 1H), 4.62-5.16 (m, 17H), 5.52 (s, 1H), 6.81-7.52 (m, 42H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 167.5, 167.0, 152.6, 152.6, 152.1, 152.0, 145.5, 144.8, 137.4, 137.2, 136.7, 136.6, 136.2, 136.1, 129.2, 128.5, 128.5, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 127.5, 126.2, 124.9, 124.7, 101.4, 99.6, 77.6, 75.3, 75.2, 75.2, 75.1, 71.4, 70.9, 70.8, 68.3, 66.7; ESIMS m/z (%): 1223 (11) $[M+Na]^+$, 723 (100).

2,2',3,3',4,4'-hexabenzyloxy-(*S*)-diphenyl-6,6'-dicarboxylic acid [(*S*)-5].

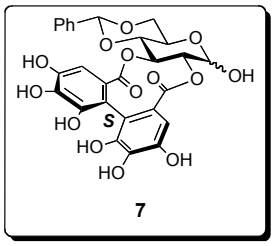


(*S*)-**5**

According to the procedure described in the literature,[7] to a solution of potassium *tert*-butoxide (28.5 mg, 0.27 mmol, 6.3 eq) and H_2O (4,8 μL, 0.27 mmol, 6.3 eq) in THF (10 mL), which was stirred at room temperature for 3 min, was added (*S*)-**3** (50 mg, 0.042 mmol, 1 eq) and the mixture was stirred for 16 h at room temperature. The reaction mixture was then diluted with CH_2Cl_2 (3 mL) and a 1 M aqueous solution of HCl (3 mL) was added. This mixture was stirred for 30 min, separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, filtered and evapoated. The resulting crude solid was recrystallized from Et_2O:hexane (1:1) to give (*S*)-**5** as a white solid (26 mg, 69%). m.p. 185-186 °C (lit.[6] m.p. 187 °C); R_f = 0.24 (15:1 CH_2Cl_2:MeOH); $[\alpha]^{22}_D$ = –30.3 (c = 1, CH_2Cl_2); CD (CH_2Cl_2) 233 nm, +109.7, 264 nm, –36.7, 282 nm, +8.8, 303 nm, –10.7; IR (neat) ν_{max} 3032, 1685, 1584, 1454, 1410, 1363, 1322, 1097 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.74 (d, J = 11.3 Hz, 2H), 4.93-5.02 (m, 6H), 5.16 and 5.24 (AB, J_{AB} = 11.4 Hz, 4H), 6.80-7.63 (m, 32H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ

172.2, 151.5, 151.0, 146.3, 137.7, 137.2, 136.5, 129.0, 128.6, 128.5, 128.2, 128.1, 127.9, 127.8, 127.3, 123.6, 112.1, 75.2, 74.5, 71.0; ESIMS *m/z* (%): 901 (100) $[M+Na]^+$.

Compound 7



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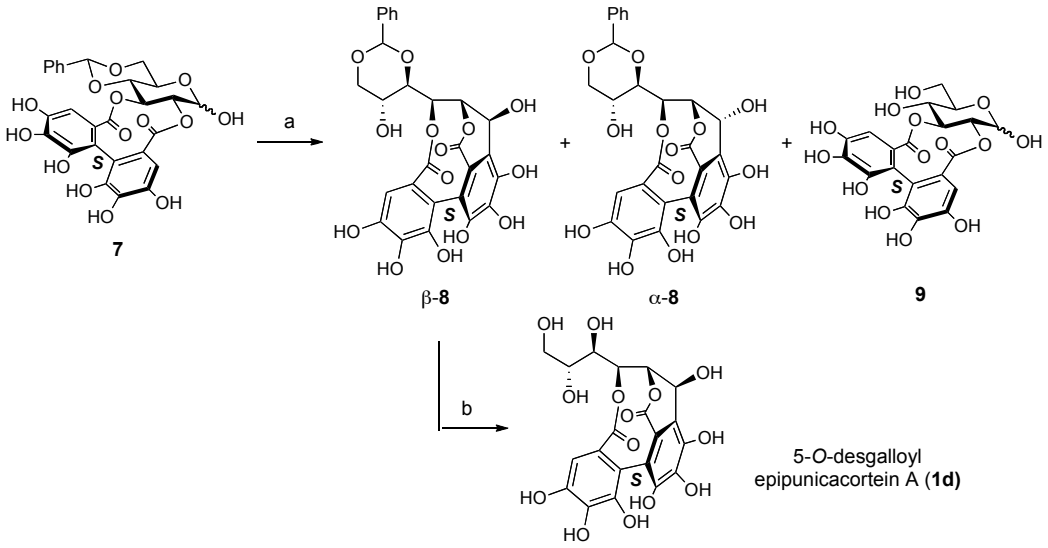
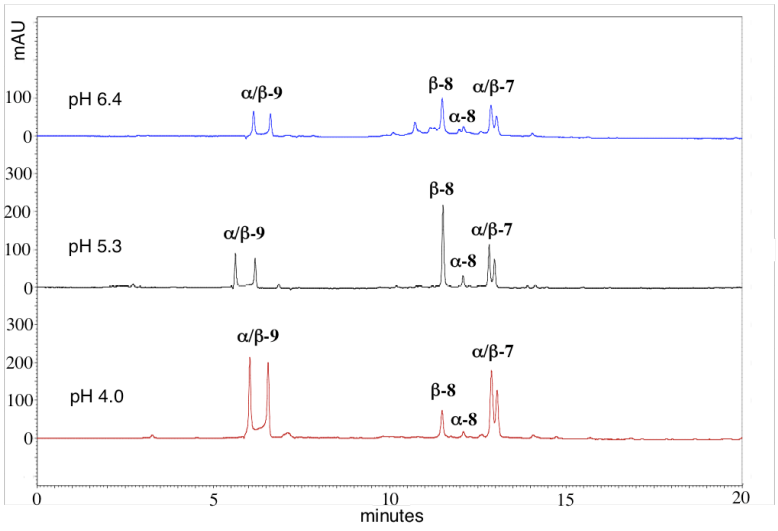
A solution of (*S*)-**3** (1.99 g, 1.66 mmol) and 10% Pd/C (800 mg) in anhydrous THF (100 mL) was purged 3 times with H_2. The mixture was stirred at room temperature under H_2 for 24 h, filtered through Celite®. The filter cake was then washed with THF (100 mL). Evaporation of the filtrates gave **7** as a brown foam (947 mg, quantitative yield) and as an inseparable mixture of α- and β-anomers (α/β = 1:1 from ^{1}H NMR). m.p. 210.5 °C with decomposition; R_f = 0.38 (RP-TLC, 30:70:0.1 H_2O/MeOH/HCOOH); R_t = 12.9, 13.1 min (Pursuit 5 C-18, 250 × 4.6 mm; solvent A: H_2O + 0.1% HCOOH, solvent B: MeCN + 0.1% HCOOH; method: gradient 0→100% of B in 20 min; flow: 1 mL/min; UV detection: 280 nm); IR (neat) ν_{max} 3751, 3496, 3281, 2930, 1743, 1620, 1452, 1361, 1324, 1190 cm^{-1}; ^{1}H-NMR (300 MHz, acetone-d_6) δ 3.61-4.34 (m, 8H$_{\alpha,\beta}$), 4.83 (dd, *J* = 8.1, 9.3 Hz, 1H$_\beta$), 5.05 (dd, *J* = 3.6, 9.3 Hz, 1H$_\alpha$), 5.14 (d, *J* = 8.1 Hz, 1H$_\beta$), 5.27 (dd, *J* = 9.3, 9.8 Hz, 1H$_\beta$), 5.46 (d, *J* = 3.6 Hz, 1H$_\alpha$), 5.52 (t, *J* = 9.6 Hz, 1H$_\alpha$), 5.72 (s, 1H$_\alpha$), 5.72 (s, 1H$_\beta$), 6.56 (s, 1H), 6.56 (s, 1H), 6.59 (s, 1H), 6.59 (s, 1H), 7.35-7.53 (m, 10H$_{\alpha,\beta}$); ^{13}C-NMR (75 MHz, acetone-d_6) δ 169.3, 169.3, 169.0, 168.9, 145.2, 145.2, 144.4, 144.4, 144.4, 144.3, 138.7, 138.7, 136.4, 136.3, 136.3, 136.2, 129.8, 128.9, 127.3, 127.3, 127.0, 126.9, 126.8, 126.7, 114.6, 114.5, 114.5, 114.4, 107.7, 107.4, 107.4, 107.3, 102.4, 102.2, 95.6, 92.4, 79.2, 78.5, 78.5, 76.6, 75.7, 74.3, 69.5, 69.2, 67.7, 63.7; ESIMS *m/z* (%): 1139 (16) $[2M-H]^-$, 569 (100) $[M-H]^-$; HRMS (ESI-TOF) calcd for $C_{27}H_{21}O_{14}$ $[M-H]^-$ 569.0931, found 569.0947.

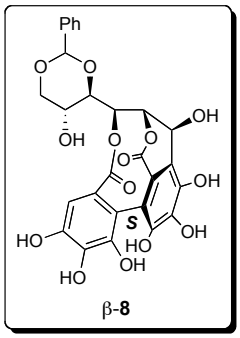


Scheme 4. Total synthesis of 5-*O*-desgalloylepipunicacortein A (**1d**). a) Phosphate buffer solution (0.2 M, pH 5.3), 65 °C, 48 h; b) H_2, $Pd(OH)_2/C$, THF, rt, 96 h.

Compound 8. Compound **7** (60 mg, 0.10 mmol) was dissolved in 9 mL of phosphate buffer solutions (0.2 M, pH 4.0, 5.3 or 6.4) and stirred at 65 °C for 48 hours. The reaction progress was monitored by analytic HPLC (see profile below). The reaction mixture run at pH 5.3 was then lyophilized and purified by preparative RP-HPLC (microsorb C-18, 41.4 × 250 mm; solvent A: H_2O + 0.1% HCOOH, solvent B: MeCN + 0.1% HCOOH; method: gradient 0→100% B in 25 min; flow: 20 mL/min; UV detection: 254 and 280 nm) to afford β-**8** as a pale yellow solid (19 mg, 32%), **9** (11 mg, 23%) and 16 mg (27%) of starting material **7**. The epimer α-**8** was only obtained as an impure fraction (4 mg, brown solid).

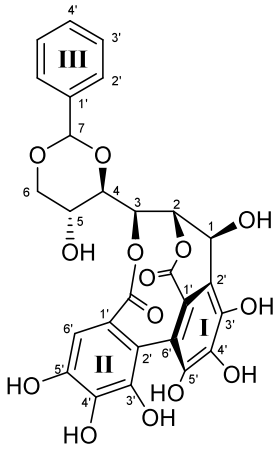


HPLC profiles after 48 hours of the *C*-glucosidation reactions of **7** into **8** run at different pH values. Column: Pursuit 5 C-18 (Varian), 250 × 4.6 mm; Solvent A: H_2O + 0.1% HCOOH, Solvent B: MeCN + 0.1% HCOOH; Method: gradient 0→100% of B in 20 min; Flow: 1 mL/min; UV detection: 280 nm.



β-**8**

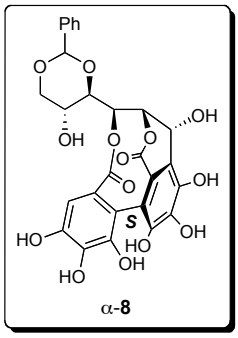
β-**8**: m.p. 179.3-180.5°C; R_f = 0.37 (RP-TLC, 30:20:0.1 H_2O/MeCN/HCOOH); R_t = 11.5 min (Pursuit 5 C-18, 250 × 4.6 mm; solvent A: H_2O + 0.1% HCOOH, solvent B: MeCN + 0.1% HCOOH; method: gradient 0→100% of B in 20 min; flow: 1 mL/min; UV detection: 280 nm); $[\alpha]^{21}_D$ = –56.5 (c = 0.23, MeOH); IR (neat) ν_{max} 3385, 1721, 1599, 1463, 1374, 1320, 1190, 1072 cm^{-1}; ^{1}H-NMR (300 MHz, acetone-d_6) δ 3.59-3.73 (m, 2H), 3.94 (dd, *J* = 2.6, 8.7 Hz, 1H), 4.21 (dd, *J* = 4.0, 9.4 Hz, 1H), 4.78 (t, *J* = 2.6 Hz, 1H), 4.86 (d, *J* = 1.7 Hz, 1H), 5.10 (br, 1H), 5.64 (s, 1H), 6.41 (s, 1H), 7.32-7.52 (m, 5H); ^{13}C-NMR (75 MHz, acetone-d_6) δ 171.1, 164.7, 146.5, 145.8, 144.3, 143.8, 139.1, 137.4, 134.8, 129.4, 128.8, 128.3, 127.1, 124.0, 118.8, 116.1, 115.4, 105.5, 101.7, 83.3, 80.0, 72.6, 71.5, 65.7, 62.4; ESIMS *m/z* (%): 1139 (10) $[2M-H]^-$, 569 (100) $[M-H]^-$; HRMS (ESI-TOF) calcd for $C_{27}H_{21}O_{14}$ $[M-H]^-$ 569.0931, found 569.0947.



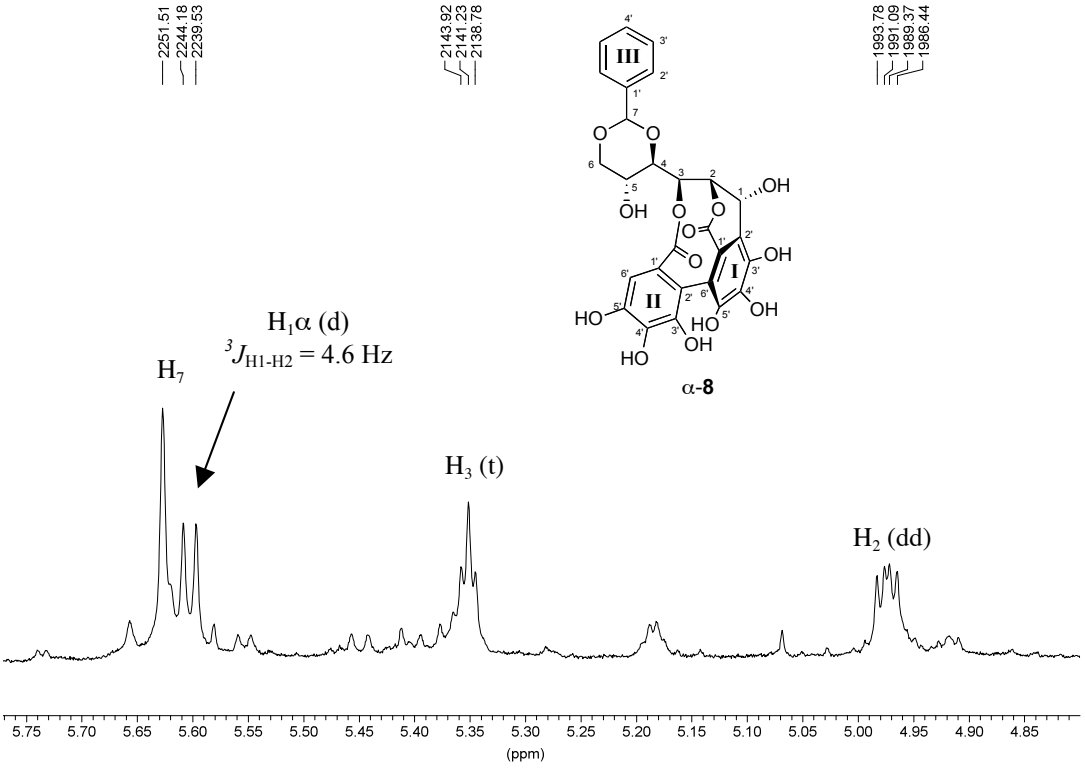
β-8

position	δ_H (mult., *J* in Hz)	δ_C (mult.)	HMQC[a]	HMBC[b]
		glucose		
1	4.86 (d, *1.7*)	65.6	C_1	H_2, H_3, C_2, $C_{1'I}$, $C_{2'I}$, $C_{3'I}$
2	5.10 (br)	80.0	C_2	H_1, C_1, C_4, $C_{2'I}$, C_I=O
3	4.78 (t, *2.6*)	72.5	C_3	H_4, C_1, C_{II}=O
4	3.94 (dd, *2.6*, *8.7*)	83.3	C_4	H_2, H_6, H_7, C_3, C_7
5	3.59-3.73 (m)	62.4	C_5	H_4, H_6, H_7
6	3.59-3.73 (m) 4.21 (dd, *4.0*, *9.4*)	71.5	C_6	H_7, C_4, C_5
		aromatics I and II		
$1'_I$		124.0		H_1
$1'_{II}$		128.7		
$2'_I$		118.8		H_1, H_2
$2'_{II}$		115.4 or 116.2		$H_{6'II}$
$3'_I$		144.3		H_1
$3'_{II}$		143.8		$H_{6'II}$
$4'_I$		139.1		
$4'_{II}$		139.1		
$5'_I$		146.5		
$5'_{II}$		145.7		$H_{6'II}$
$6'_I$		115.4 or 116.2		
$6'_{II}$	6.41 (s)	105.4	$C_{6'II}$	$C_{2'II}$, $C_{3'II}$, $C_{5'II}$
		benzylidene group		
7	5.64 (s)	101.7	C_7	$H_{2'III}$, $H_{3'III}$, $H_{4'III}$, H_4, C_4, C_5, C_6, $C_{1'III}$, $C_{2'III}$, C_{II}=O
$1'_{III}$		134.8		H_7
$2'_{III}$	7.32-7.52 (m)	128.2	$C_{2'III}$	H_7
$3'_{III}$	7.32-7.52 (m)	129.3	$C_{3'III}$	$H_{2'III}$, $H_{3'III}$, $H_{4'III}$
$4'_{III}$	7.32-7.52 (m)	129.4	$C_{4'III}$	$H_{2'III}$, $H_{3'III}$, $H_{4'III}$
		carbonyls		
C_I=O		164.6		H_2
C_{II}=O		171.0		H_3, H_7

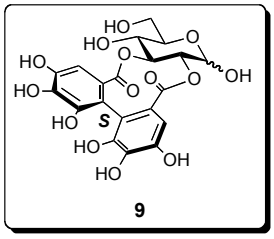
[a] Carbons correlate with the protons resonating at the ppm value indicated in the δ_H column.
[b] Indicated carbons and protons correlated with the protons or carbons at the position indicated in the left column.



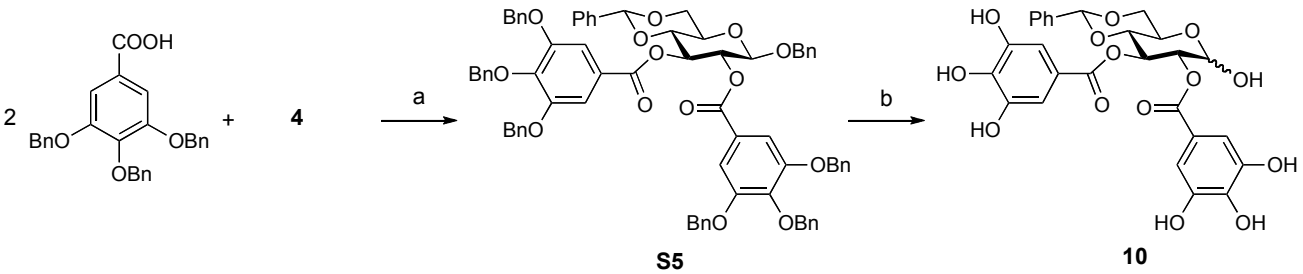
α-**8**: This compound could not be isolated as a pure fraction. Only assignable peaks from the mixture are listed here. ^{1}H NMR and COSY analyses of the mixture confirmed the presence of the α-epimer. The epimeric proton assigned at 5.60 ppm, with a coupling constant $^{3}J_{H1\text{-}H2}$ = 4.6 Hz, is characteristic of an α-epimer.[9] R_f = 0.52 (RP-TLC, 30:20:0.1 H_2O/MeCN/HCOOH, double elution); R_t = 12.1 min (Pursuit 5 C-18, 250 × 4.6 mm; solvent A: H_2O + 0.1% HCOOH, solvent B: MeCN + 0.1% HCOOH; method: gradient 0→100% of B in 20 min; flow: 1 mL/min; UV detection: 280 nm); ^{1}H-NMR (300 MHz, acetone-d_6) δ 3.60-3.81 (m, 3H), 4.21 (dd, J = 4.8, 10.1 Hz, 1H), 4.97 (dd, J = 2.7, 4.4 Hz, 1H), 5.35 (t, J = 2.6 Hz, 1H), 5.60 (d, J = 4.6 Hz, 1H), 5.63 (s, 1H), 6.43 (s, 1H), 7.31-7.54 (m, 5H); ^{13}C-NMR (75 MHz, acetone-d_6) δ 171.7, 170.1, 145.7, 138.8, 129.3, 128.7, 126.9, 116.7, 110.0, 105.0, 101.6, 84.5, 76.1, 71.2, 70.0, 68.0, 61.8; ESIMS m/z (%): 569 (100) $[M\text{-}H]^-$.



Compound 9.

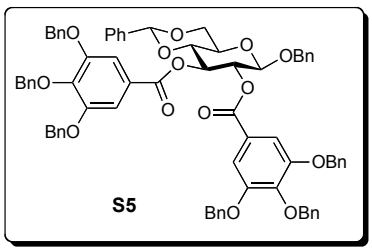


This compound was obtained as a mixture of α- and β- anomers (α/β = 1:1 from ^{1}H NMR). R_f = 0.98 (RP-TLC, 30:20:0.1 H_2O/MeCN/HCOOH); R_t = 6.1, 6.6 min (Pursuit 5 C-18, 250 × 4.6 mm; solvent A: H_2O + 0.1% HCOOH, solvent B: MeCN + 0.1% HCOOH; method: gradient 0→100% of B in 20 min; flow: 1 mL/min; UV detection: 280 nm); IR (neat) ν_{max} 3387, 2963, 2927, 2857, 1744, 1620, 1445, 1365, 1314, 1230, 1182, 1084, 1037 cm^{-1}; ^{1}H-NMR (300 MHz, acetone-d_6/D_2O 8:1) δ 3.47-3.98 (m, 8H$_{\alpha,\beta}$), 4.70 (dd, J = 9.6, 8.1 Hz, 1H$_\beta$), 4.91 (dd, J = 9.6, 3.6 Hz, 1H$_\alpha$), 4.98 (d, J = 8.1 Hz, 1H$_\beta$), 5.02 (t, J = 9.4 Hz, 1H$_\beta$), 5.38 (d, J = 2.5 Hz, 1H$_\alpha$), 5.39 (t, J = 9.3 Hz, 1H$_\alpha$), 6.58 (s, 2H), 6.68 (s, 1H), 6.68 (s, 1H); ^{13}C-NMR (75 MHz, acetone-d_6/D_2O 8:1) δ 169.6, 169.5, 169.1, 168.9, 145.1, 145.0, 144.9, 144.3, 144.2, 144.1, 136.1, 136.0, 127.6, 127.4, 127.1, 114.5, 114.5, 114.4, 107.7, 107.6, 107.3, 94.8, 91.5, 80.7, 78.3, 77.8, 77.8, 75.4, 73.0, 68.7, 68.4, 62.3, 62.2; ESIMS m/z (%): 481 (100) [M-H]$^-$; HRMS (ESI-TOF) calcd for $C_{20}H_{17}O_{14}$ [M-H]$^-$ 481.0618, found 481.0630.



Scheme 5. Esterification of 3,4,5-tribenzyloxybenzoic acid on the sugar derivative **4**. a) DCC, DMAP, CH_2Cl_2, rt, 18 h; b) H_2, Pd/C, THF, rt, 72 h.

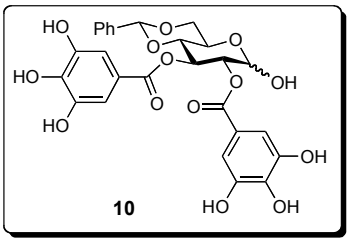
Benzyl 4,6-*O*-benzylidene-2,3-bis(3,4,5-tribenzyloxy)benzoyl-β-D-glucopyranoside (S5).



To a solution of **4** (2 g, 5.58 mmol, 1 eq) and 3,4,5-tribenzyloxybenzoic acid[10] (5.41 g, 12.28 mmol, 2.2 eq) in dry CH_2Cl_2 (60 mL) were added DMAP (1.5 g, 12.28 mmol, 2.2 eq) and DCC (5.07 g, 24.55 mmol, 4.4 eq). The solution was purged with nitrogen and stirred at rt for 18 h. The mixture was then filtered through Celite®. The filter cake was washed with CH_2Cl_2 and the combined filtrates were evaporated. After addition of cold EtOAc, the excess of DCU was removed by filtration (this manipulation was repeated 5 times). The resulting crude product was purified by column chromatography (9:1 → 1:0 CH_2Cl_2/PET) to give **S5** as a white solid (5.08 g, 76%). m.p. 174.5-175.5 °C; R_f = 0.55 (4:1 CH_2Cl_2/PET); $[\alpha]^{22}_D$ = +37.4 (c = 0.97,

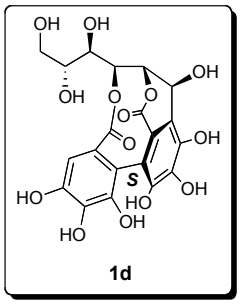
$CHCl_3$); IR (neat) ν_{max} 1723, 1588, 1427, 1332, 1201, 1099, 1000, 752, 734, 697 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.76 (dt, *J* = 4.8, 9.5 Hz, 1H), 3.95-4.05 (m, 2H), 4.54 (dd, *J* = 4.6, 10.3 Hz, 1H), 4.74 and 5.00 (AB, J_{AB} = 12.4 Hz, 2H), 4.90 (d, *J* = 7.7 Hz, 1H), 5.06-5.17 (m, 12H), 5.63 (t, *J* = 8.6 Hz, 1H), 5.63 (s, 1H), 5.80 (t, *J* = 9.5 Hz, 1H), 7.23-7.52 (m, 44H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 165.3, 164.8, 152.4, 152.4, 142.7, 137.4, 137.3, 136.7, 136.5, 136.5, 129.0, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.5, 127.5, 126.1, 124.4, 124.2, 109.3, 101.4, 100.0, 78.7, 75.0, 72.6, 72.4, 71.1, 70.8, 68.6, 66.6; ESIMS *m/z* (%): 1203 (100) $[M+H]^+$.

4,6-*O*-benzylidene-2,3-bis(3,4,5-trihydroxy)benzoyl-α,β-D-glucopyranose (10).



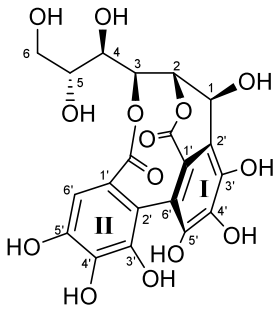
A solution of **S5** (4.7 g, 3.91 mmol) and 10% Pd/C (1 g) in 200 mL of anhydrous THF was purged 3 times with H_2. The mixture was stirred at room temperature under H_2 for 72 h and then filtered through Celite®. The filter cake was then washed with THF (500 mL) and evaporation of the filtrates afforded **10** as a pale yellow foam (2.24 g, quantitative yield), and as an inseparable mixture of α- and β- anomers (α/β = 1:0.8 from ^{1}H NMR). m.p. 120-122 °C; R_f = 0.67 (RP-TLC, 30:70:0.1 H_2O/MeOH/HCOOH); ***Rt*** = 12.8, 13.3 min (Pursuit 5 C-18, 250 × 4.6 mm, solvent A: H_2O + 0.1% HCOOH, solvent B: MeCN + 0.1% HCOOH; method: gradient 0-100% of B in 20 min; flow: 1 mL/min); IR (neat) ν_{max} 3175, 1701, 1609, 1452, 1343, 1211, 1095, 1040, 766 cm^{-1}; ^{1}H-NMR (300 MHz, acetone-d_6) δ 3.77 (dt, *J* = 4.7, 9.6 Hz, $1H_\beta$), 3.85-4.04 (m, $4H_{\alpha,\beta}$), 4.19-4.28 (m, $2H_\alpha$), 4.33 (dd, *J* = 4.5, 10.0 Hz, $1H_\beta$), 5.13 (dd, *J* = 3.7, 9.7 Hz, $1H_\alpha$), 5.15 (d, *J* = 7.4 Hz, $1H_\beta$), 5.25 (t, *J* = 8.7 Hz, $1H_\beta$), 5.55 (d, *J* = 3.4 Hz, $1H_\alpha$), 5.65 (t, *J* = 10.3 Hz, $1H_\beta$), 5.68 (s, $1H_\beta$), 5.69 (s, $1H_\alpha$), 5.94 (t, *J* = 9.8 Hz, $1H_\alpha$), 7.03 (s, $2H_\beta$), 7.05 (s, $2H_\beta$), 7.06 (s, $2H_\alpha$), 7.07 (s, $2H_\alpha$), 7.30-7.43 (m, $10H_{\alpha,\beta}$); ^{13}C-NMR (75 MHz, acetone-d_6) δ 166.3, 166.3, 166.0, 165.9, 145.9, 145.9, 139.2, 139.0, 139.0, 138.6, 138.5, 129.6, 128.7, 128.7, 127.1, 127.0, 121.2, 121.0, 121.0, 120.6, 110.1, 110.0, 102.2, 102.0, 96.7, 91.7, 80.1, 79.7, 74.6, 73.4, 72.8, 69.9, 69.4, 69.1, 67.2, 63.3; ESIMS *m/z* (%): 1143 (53) $[2M-H]^-$, 684 (100), 571 (99) $[M-H]^-$; HRMS (ESI-TOF) calcd for $C_{27}H_{24}O_{14}Na$ $[M+Na]^+$ 595.1064, found 595.1059.

5-*O*-desgalloylepipunicacortein A (1d).



1d

In a flame-dried 10 mL schlenk flask, compound β-**8** (17,7 mg, 0.031 mmol) was dissolved in dry THF (3.5 ml) under an argon atmosphere and $Pd(OH)_2/C$ (12 mg) was added. The reaction mixture was then repeatedly saturated with H_2 and the reaction progress was monitored by RP-TLC (3:2 H_2O/MeCN, 0.1% HCOOH). Additional amount of $Pd(OH)_2/C$ was added during the reaction in order to consume all of the starting material until a total amount of 51.5 mg was added. After 96 h, the starting material was completely consumed and the reaction mixture was passed through a filter (Acrodisc 13 mm syringe filter, with 0.2 μm nylon membrane). The pellet was washed with THF (3 × 3 mL), then with acetone (3 × 3 mL). The solvents were removed by evaporation to give a residue, which was purified by a simple passage through Sephadex LH-20, eluting with H_2O, to afford **1d** as a yellowish amorphous solid (13,8 mg, 93%). R_f = 0.90 (RP-TLC, 3:2 H_2O/MeCN, 0.1% HCOOH); $[\alpha]^{21}_D$ = –38.9 (c = 0.18, MeOH) [lit.[11] $[\alpha]^{22}_D$ = –37.5 (c = 1, MeOH)]; ^{1}H-NMR (400 MHz, acetone-d_6/D_2O 8:1) δ 3.47-3.76 (m, 4H), 4.66 (t, J = 2.8 Hz, 1H), 4.82 (d, J = 1.8 Hz, 1H), 4.91 (t, J = 2.3 Hz, 1H), 6.40 (s, 1H); ^{13}C-NMR (100 MHz, acetone-d_6/D_2O 8:1) δ 170.8, 166.4, 146.6, 145.6, 143.9, 143.5, 138.2, 134.9, 127.8, 122.5, 118.4, 116.2, 105.2, 81.3, 74.0, 73.7, 72.0, 64.9, 63.7, 61.9 (impurity); ESIMS m/z (%): 481 (100) $[M-H]^-$; HRMS (ESI-TOF) calcd for $C_{20}H_{19}O_{14}$ $[M+H]^+$ 483.0775, found 483.0786.



1d

position	δ_H (mult., *J* in Hz)	δ_C (mult.)	HMQC[a]	HMBC[b]
		glucose		
1	4.86 (d, *1.8*)	64.9	C_1	$C_{1'I}$, $C_{2'I}$, $C_{3'I}$
2	4.91 (t, *2.3*)	81.3	C_2	C_3, $C_{2'I}$, C_I=O
3	4.66 (t, *2.8*)	74.0	C_3	H_2
4	3.47-3.76 (m)	73.7	C_4	
5	3.47-3.76 (m)	72.0	C_5	H_6
6	3.47-3.76 (m)	63.7	C_6	C_5
		aromatics I and II		
$1'_I$		122.5		H_1
$1'_{II}$		127.8		
$2'_I$		118.4		H_1, H_2
$2'_{II}$		116.2		$H_{6'II}$
$3'_I$		143.5 / 143.9		H_1
$3'_{II}$				
$4'_I$		138.2		
$4'_{II}$		134.9		$H_{6'II}$
$5'_I$		146.6		
$5'_{II}$		145.6		$H_{6'II}$
$6'_I$		116.2		
$6'_{II}$	6.40 (s)	105.2	$C_{6'II}$	$C_{2'II}$, $C_{4'II}$, $C_{5'II}$, C_{II}=O
		carbonyls		
C_I=O		166.4		H_2
C_{II}=O		170.8		$H_{6'II}$

[a] Carbons correlate with the protons resonating at the ppm value indicated in the δ_H column.
[b] Indicated carbons and protons correlated with the protons or carbons at the position indicated in the left column.

Additional references

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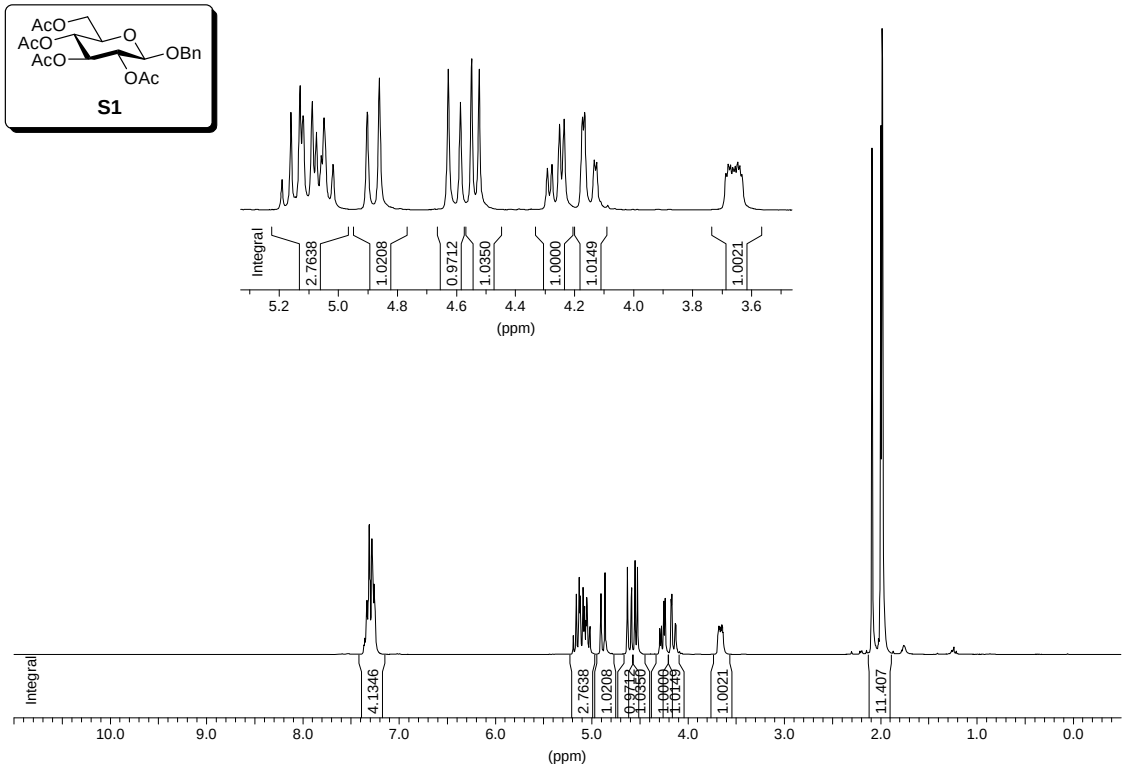
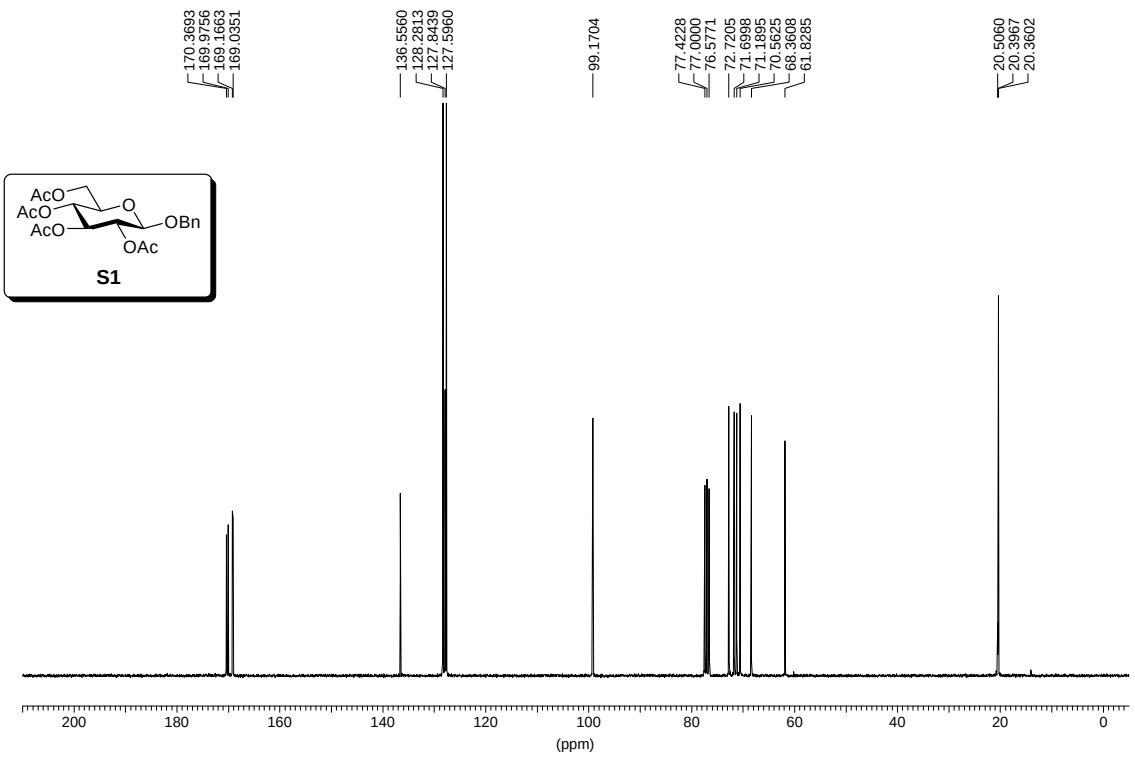
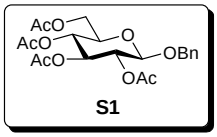
GMA063 / CDCl3 / 300 MHz



GMA063 / CDCl3 / 300 MHz

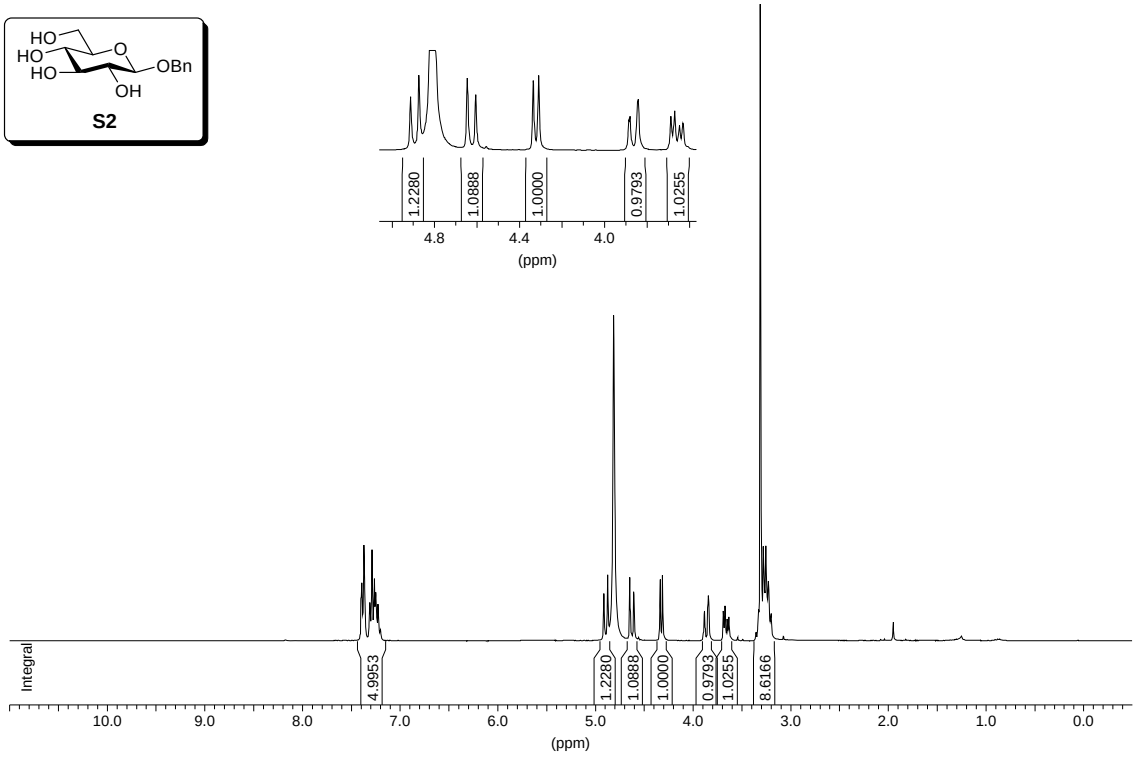




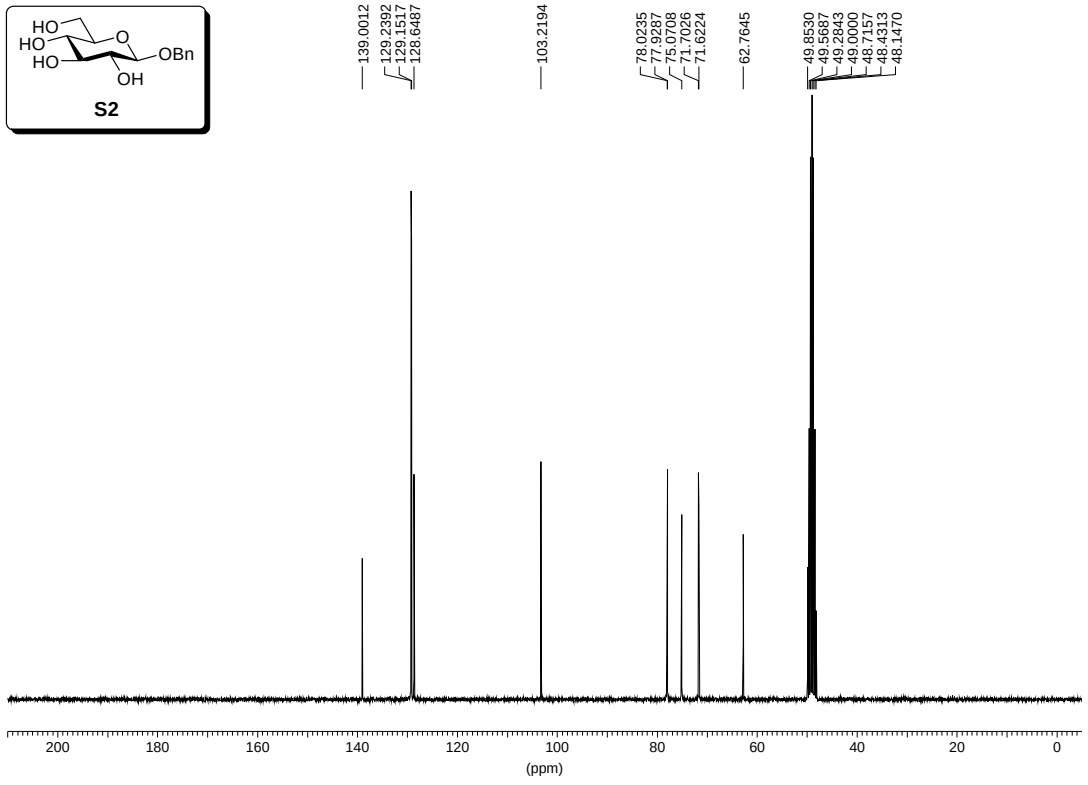
S1

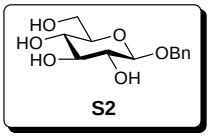
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14468	2209.54	7.3619	4768916	1.6
2	14481	2207.08	7.3538	7968935	2.6
3	14512	2201.23	7.3342	26383532	8.6
4	14552	2193.67	7.3091	63489728	20.8
5	14599	2184.80	7.2795	56355736	18.4
6	14630	2178.94	7.2600	34433216	11.3
7	14640	2177.06	7.2537	27547062	9
8	17919	1557.83	5.1905	9151385	3
9	17968	1548.57	5.1597	29417226	9.6
10	18016	1539.51	5.1295	37549812	12.3
11	18032	1536.49	5.1194	28503142	9.3
12	18082	1527.05	5.0879	32717784	10.7
13	18104	1522.89	5.0741	23549584	7.7
14	18130	1517.98	5.0577	16436442	5.4
15	18145	1515.15	5.0483	27804104	9.1
16	18194	1505.90	5.0175	13731959	4.5
17	18379	1470.96	4.9011	29558994	9.7
18	18444	1458.68	4.8602	39900252	13.1
19	18815	1388.62	4.6267	42576032	13.9
20	18880	1376.35	4.5858	32506356	10.6
21	18940	1365.02	4.5481	45706808	15
22	18981	1357.27	4.5223	42480832	13.9
23	19348	1287.97	4.2914	12611401	4.1
24	19373	1283.25	4.2756	13802807	4.5
25	19413	1275.69	4.2505	25896888	8.5
26	19438	1270.97	4.2347	27412356	9
27	19537	1252.27	4.1724	28011352	9.2
28	19549	1250.01	4.1649	29512212	9.7
29	19601	1240.19	4.1322	15174143	5
30	19614	1237.73	4.1240	14366875	4.7
31	20310	1106.30	3.6861	11025560	3.6
32	20322	1104.03	3.6785	13834620	4.5
33	20334	1101.76	3.6710	13618990	4.5
34	20347	1099.31	3.6628	12809501	4.2
35	20359	1097.04	3.6552	13211534	4.3
36	20373	1094.40	3.6464	14545229	4.8
37	20384	1092.32	3.6395	13340319	4.4
38	20396	1090.06	3.6319	10749750	3.5
39	22854	625.87	2.0853	247066144	80.9
40	22993	599.62	1.9979	258042688	84.5
41	23014	595.66	1.9847	305466048	100
42	23025	593.58	1.9777	290456768	95.1

GMA067 / MeOD / 300



GMA067 / MeOD / 300 MHz

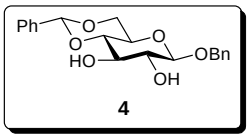




S2

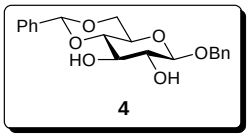
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14363	2218.67	7.3923	38106116	9.1
2	14401	2211.49	7.3684	63011128	15
3	14494	2193.93	7.3099	25161592	6
4	14530	2187.13	7.2873	60051608	14.3
5	14570	2179.57	7.2621	40990200	9.8
6	14594	2175.04	7.2470	31894022	7.6
7	14616	2170.89	7.2332	12589014	3
8	14631	2168.05	7.2237	24227474	5.8
9	14669	2160.88	7.1998	7386398	1.8
10	18304	1474.42	4.9126	31067736	7.4
11	18367	1462.52	4.8730	43626836	10.4
12	18466	1443.83	4.8107	214520176	51.1
13	18729	1394.16	4.6452	41749272	9.9
14	18791	1382.45	4.6062	32157416	7.7
15	19222	1301.06	4.3350	40432636	9.6
16	19262	1293.51	4.3098	43198888	10.3
17	19945	1164.52	3.8801	19570540	4.7
18	20007	1152.82	3.8411	29636416	7.1
19	20251	1106.74	3.6875	19691888	4.7
20	20279	1101.45	3.6699	22921396	5.5
21	20314	1094.84	3.6479	14490172	3.5
22	20341	1089.74	3.6309	15680128	3.7
23	20822	998.91	3.3282	20571660	4.9
24	20851	993.43	3.3100	419792736	100
25	20902	983.80	3.2779	62382736	14.9
26	20921	980.21	3.2660	34176980	8.1
27	20942	976.25	3.2527	62520720	14.9
28	20982	968.69	3.2276	39390240	9.4
29	21029	959.82	3.1980	17880858	4.3

GMB125 / CDCl3 / 300



4

GMB125 / DMSO / 300 MHz



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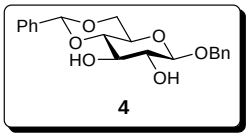
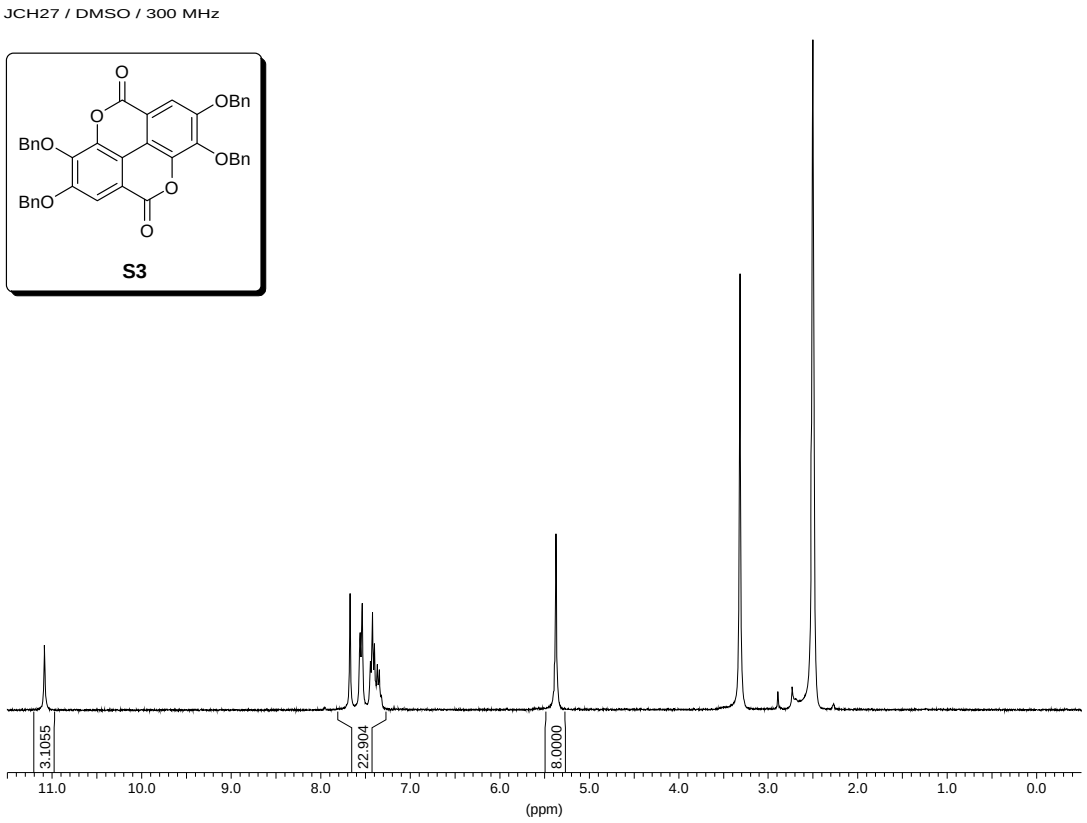


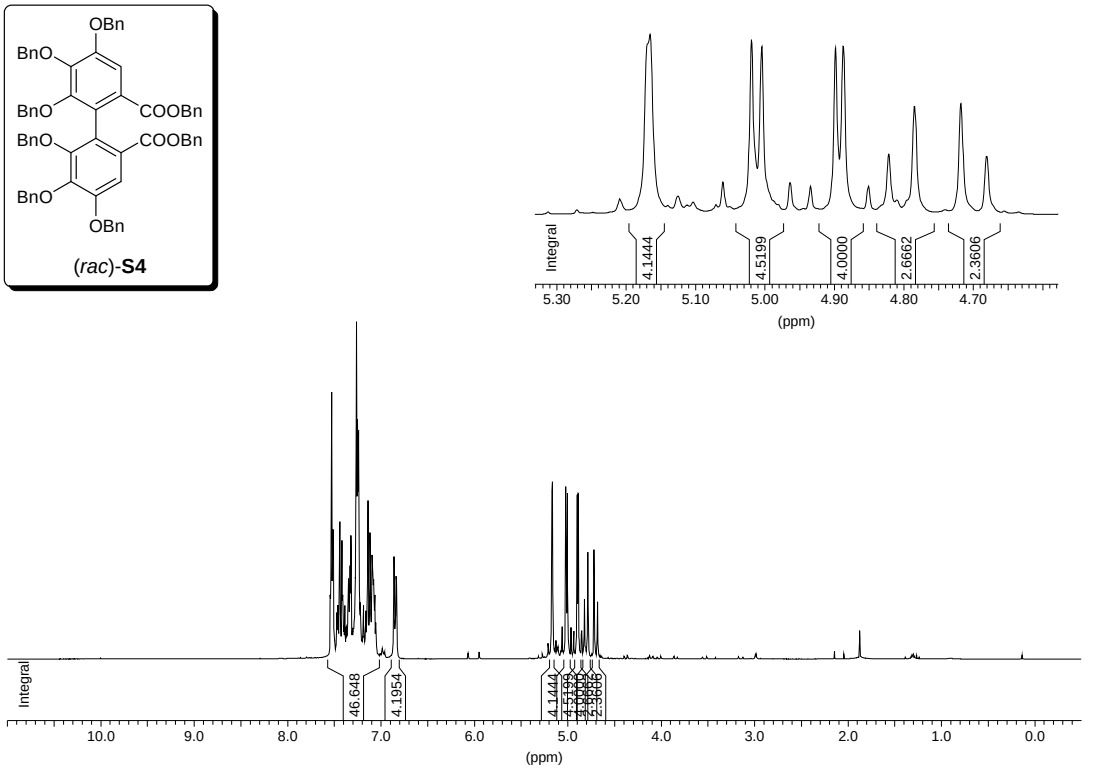
4

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14229	2254.29	7.5111	34859900	12.3
2	14250	2250.33	7.4978	51140448	18.1
3	14269	2246.74	7.4859	59948408	21.2
4	14278	2245.04	7.4802	56061232	19.8
5	14439	2214.64	7.3789	163808144	57.9
6	14454	2211.80	7.3695	283006784	100
7	14473	2208.22	7.3575	117001816	41.3
8	14498	2203.49	7.3418	39590348	14
9	14527	2198.02	7.3236	18306668	6.5
10	14628	2178.94	7.2600	65987448	23.3
11	17362	1662.64	5.5397	96083008	34
12	18283	1488.71	4.9602	44582544	15.8
13	18344	1477.19	4.9218	56866800	20.1
14	18764	1397.88	4.6576	60003928	21.2
15	18825	1386.36	4.6192	47185488	16.7
16	18989	1355.39	4.5160	53352192	18.9
17	19030	1347.64	4.4902	56379056	19.9
18	19178	1319.69	4.3971	24171752	8.5
19	19204	1314.78	4.3807	25882256	9.1
20	19234	1309.12	4.3618	28049474	9.9
21	19259	1304.40	4.3461	27628748	9.8
22	20053	1154.45	3.8465	27062120	9.6
23	20071	1151.05	3.8352	23843600	8.4
24	20107	1144.25	3.8125	57576880	20.3
25	20119	1141.99	3.8050	61136296	21.6
26	20166	1133.11	3.7754	47946340	16.9
27	20437	1081.94	3.6049	24597516	8.7
28	20465	1076.65	3.5873	35820688	12.7
29	20486	1072.68	3.5741	55670080	19.7
30	20507	1068.72	3.5608	44824372	15.8
31	20535	1063.43	3.5432	34741168	12.3
32	20553	1060.03	3.5319	25621594	9.1
33	20609	1049.45	3.4967	18950896	6.7
34	20635	1044.54	3.4803	19691664	7
35	20661	1039.63	3.4639	27549516	9.7
36	20686	1034.91	3.4482	22642720	8
37	20710	1030.38	3.4331	10507769	3.7
38	20736	1025.47	3.4168	8904985	3.1

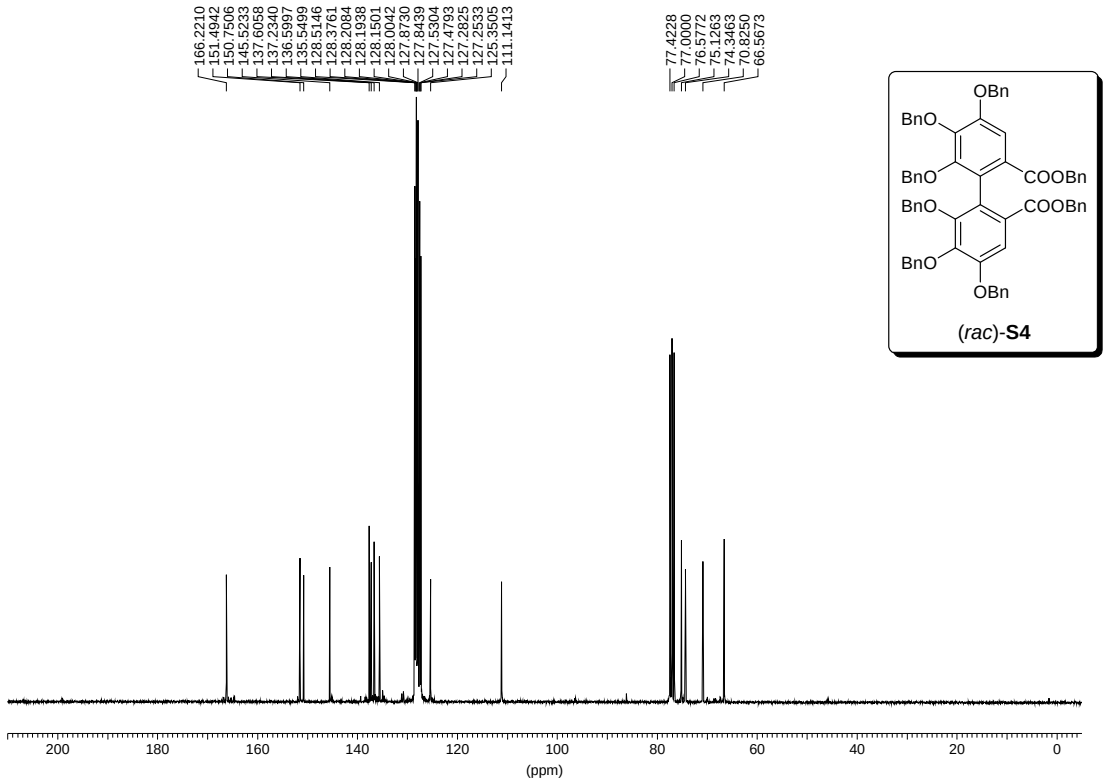


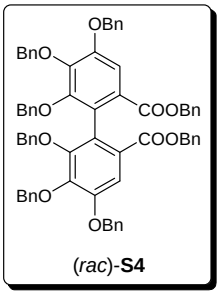
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	8509	3326.19	11.0825	43019680	9.8
2	13935	2301.51	7.6684	76651520	17.5
3	14111	2268.27	7.5576	51288280	11.7
4	14148	2261.28	7.5344	70428056	16.1
5	14295	2233.52	7.4419	32598838	7.4
6	14331	2226.73	7.4192	64577160	14.7
7	14370	2219.36	7.3947	43933892	10
8	14415	2210.86	7.3664	30383728	6.9
9	14452	2203.88	7.3431	27069672	6.2
10	17587	1611.84	5.3705	115910464	26.4
11	20857	994.31	3.3129	285819968	65.1
12	22149	750.32	2.5000	438790048	100

ANA185 / CDCl3 / 300 MHz



ANA185 / CDCl3 / 300 MHz



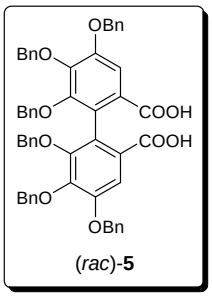


(*rac*)-**S4**

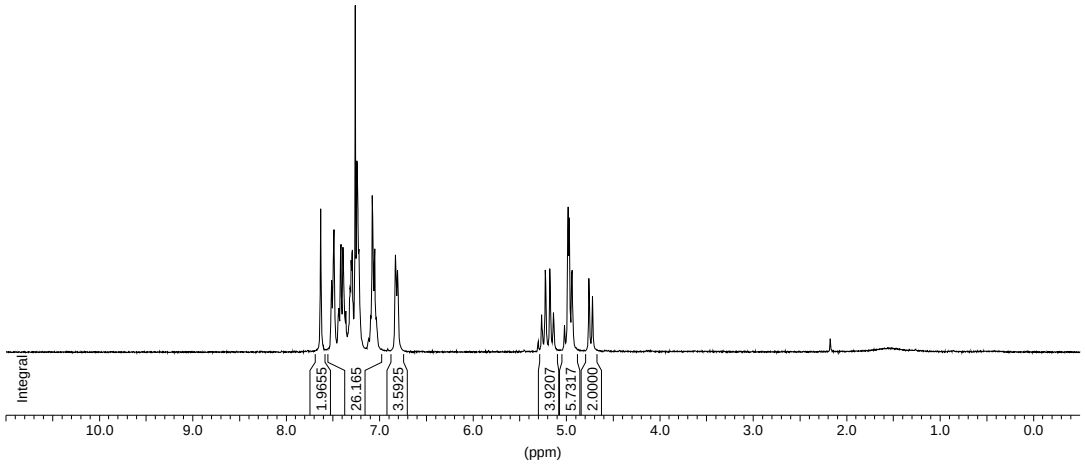
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14066	2263.16	7.5406	74240944	19.0
2	14076	2261.28	7.5343	98188648	25.1
3	14090	2258.63	7.5255	309102048	79.1
4	14110	2254.86	7.5129	149926880	38.3
5	14116	2253.72	7.5092	140046640	35.8
6	14181	2241.45	7.4683	53588164	13.7
7	14192	2239.37	7.4613	62212364	15.9
8	14202	2237.48	7.4550	39498172	10.1
9	14214	2235.22	7.4475	44608840	11.4
10	14226	2232.95	7.4399	159291216	40.7
11	14234	2231.44	7.4349	69431704	17.8
12	14257	2227.09	7.4204	64190240	16.4
13	14267	2225.21	7.4141	137148720	35.1
14	14278	2223.13	7.4072	103714752	26.5
15	14286	2221.62	7.4022	57730756	14.8
16	14297	2219.54	7.3953	38586032	9.9
17	14312	2216.71	7.3858	61706392	15.8
18	14337	2211.99	7.3701	37306080	9.5
19	14368	2206.13	7.3506	72637984	18.6
20	14378	2204.24	7.3443	93070320	23.8
21	14394	2201.22	7.3342	77599432	19.8
22	14403	2199.52	7.3286	108326504	27.7
23	14418	2196.69	7.3191	143221360	36.6
24	14445	2191.59	7.3021	33637156	8.6
25	14454	2189.89	7.2965	34885104	8.9
26	14467	2187.44	7.2883	40002064	10.2
27	14479	2185.17	7.2807	64714672	16.6
28	14491	2182.90	7.2732	101867360	26.1
29	14505	2180.26	7.2644	288327616	73.7
30	14512	2178.94	7.2600	390962624	100.0
31	14528	2175.92	7.2499	277876576	71.1
32	14545	2172.71	7.2392	265143136	67.8
33	14557	2170.44	7.2317	89089720	22.8
34	14567	2168.55	7.2254	66682540	17.1
35	14578	2166.48	7.2185	64924608	16.6
36	14628	2157.03	7.1870	61984132	15.9
37	14671	2148.91	7.1599	55769232	14.3
38	14686	2146.08	7.1505	45158652	11.6
39	14694	2144.57	7.1455	81596544	20.9
40	14705	2142.49	7.1385	183459120	46.9
41	14729	2137.96	7.1234	48546536	12.4
42	14745	2134.94	7.1134	146185424	37.4
43	14759	2132.29	7.1046	49079952	12.6
44	14774	2129.46	7.0951	120205168	30.7

45	14784	2127.57	7.0888	107020864	27.4
46	14796	2125.31	7.0813	87283792	22.3
47	14804	2123.80	7.0763	91831080	23.5
48	14824	2120.02	7.0637	74148928	19.0
49	14841	2116.81	7.0530	41987072	10.7
50	15142	2059.97	6.8636	103652456	26.5
51	15149	2058.64	6.8592	118441432	30.3
52	15182	2052.41	6.8384	95922216	24.5
53	15192	2050.52	6.8321	89830912	23.0
54	17841	1550.27	5.1653	205441856	52.5
55	18008	1518.73	5.0602	37230856	9.5
56	18073	1506.46	5.0193	199523952	51.0
57	18097	1501.92	5.0042	191754416	49.0
58	18162	1489.65	4.9633	36478576	9.3
59	18208	1480.96	4.9344	32147332	8.2
60	18266	1470.01	4.8979	190231408	48.7
61	18283	1466.80	4.8872	192267072	49.2
62	18341	1455.85	4.8507	32432708	8.3
63	18388	1446.97	4.8211	68965728	17.6
64	18447	1435.83	4.7840	123624064	31.6
65	18553	1415.81	4.7173	126700864	32.4
66	18612	1404.67	4.6802	66313172	17.0

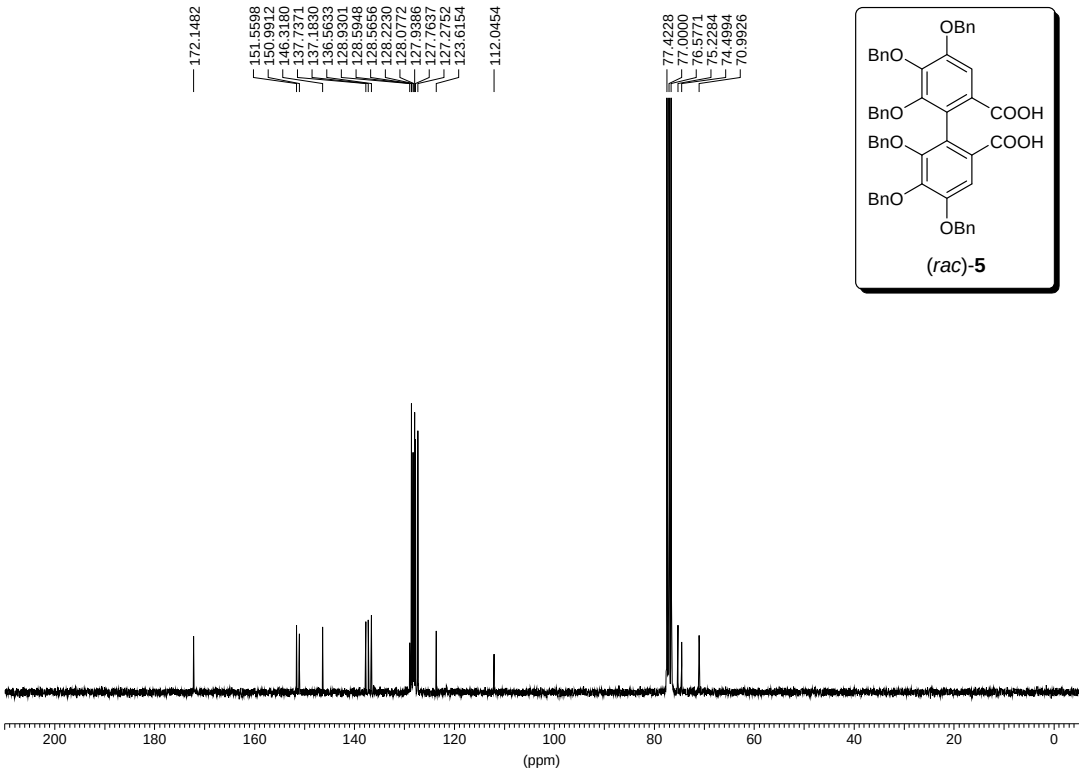
JCH29 / CDCl3 / 300 MHz



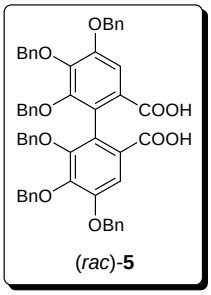
(*rac*)-**5**



JCH29 / CDCl3 / 300 MHz



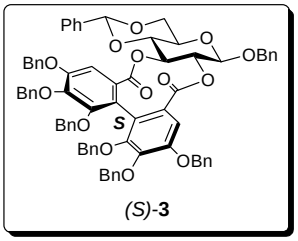
(*rac*)-**5**



(*rac*)-**5**

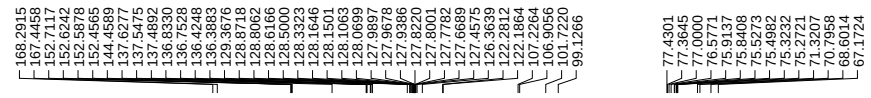
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14038	2290.17	7.6306	117646112	41.4
2	14228	2254.29	7.5111	59321120	20.9
3	14265	2247.31	7.4878	100815024	35.5
4	14348	2231.63	7.4356	36605848	12.9
5	14383	2225.02	7.4135	88658608	31.2
6	14423	2217.47	7.3884	86276632	30.4
7	14469	2208.78	7.3594	34015876	12
8	14540	2195.37	7.3147	53068304	18.7
9	14561	2191.41	7.3015	75658336	26.6
10	14578	2188.20	7.2908	84127848	29.6
11	14627	2178.94	7.2600	283923584	100
12	14659	2172.90	7.2399	156860256	55.2
13	14687	2167.61	7.2222	86382048	30.4
14	14894	2128.52	7.0920	29863222	10.5
15	14922	2123.23	7.0744	128736432	45.3
16	14959	2116.25	7.0511	85163376	30
17	14987	2110.96	7.0335	28492296	10
18	15313	2049.40	6.8284	80116200	28.2
19	15345	2043.35	6.8082	67557744	23.8
20	17803	1579.17	5.2616	31098376	11
21	17862	1568.03	5.2245	67578936	23.8
22	17941	1553.11	5.1748	68859000	24.3
23	18001	1541.78	5.1370	32691064	11.5
24	18190	1506.08	5.0181	22532362	7.9
25	18248	1495.13	4.9816	119380528	42
26	18273	1490.41	4.9659	110373880	38.9
27	18316	1482.29	4.9388	67492992	23.8
28	18604	1427.90	4.7576	60640240	21.4
29	18663	1416.76	4.7205	46590820	16.4

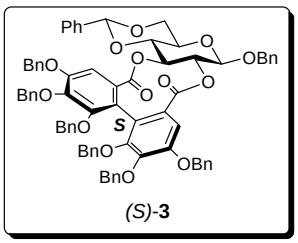
GMB131-S / CDCl3 / 300 MHz



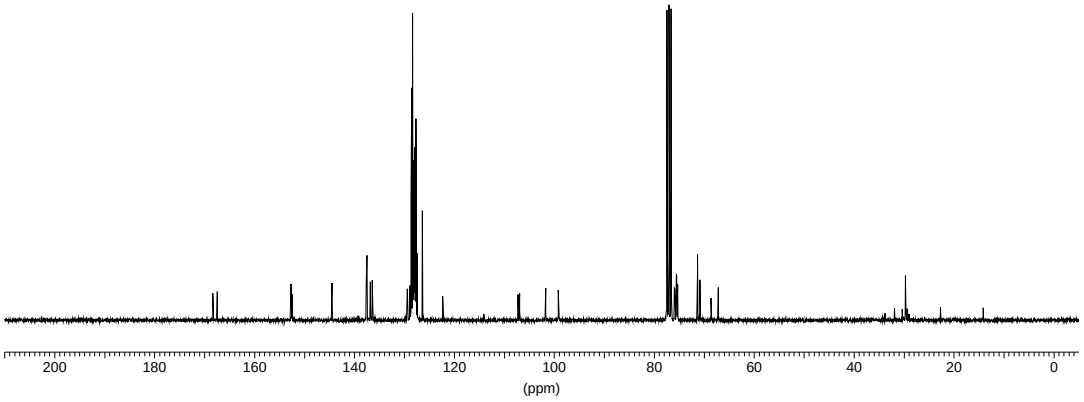
(S)-**3**

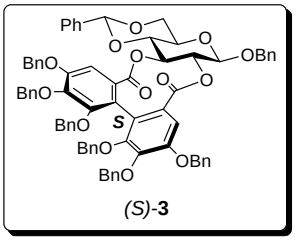
GMB131-S / CDCl3 / 300 MHz





(S)-**3**



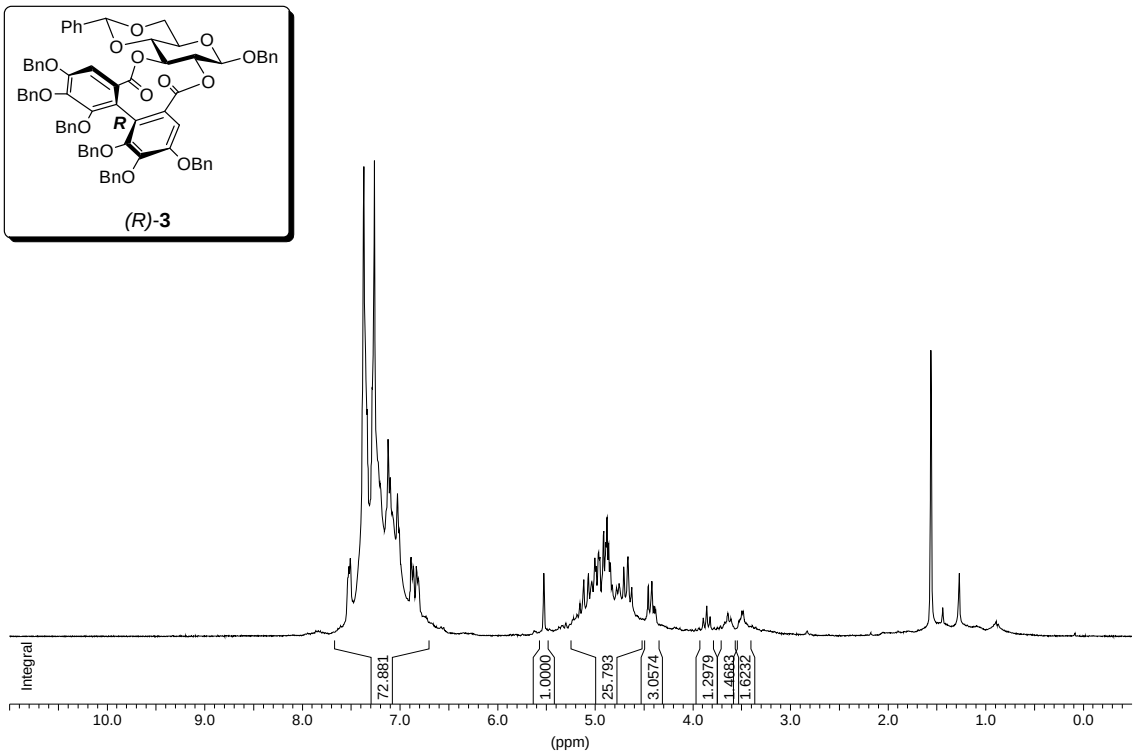


(S)-**3**

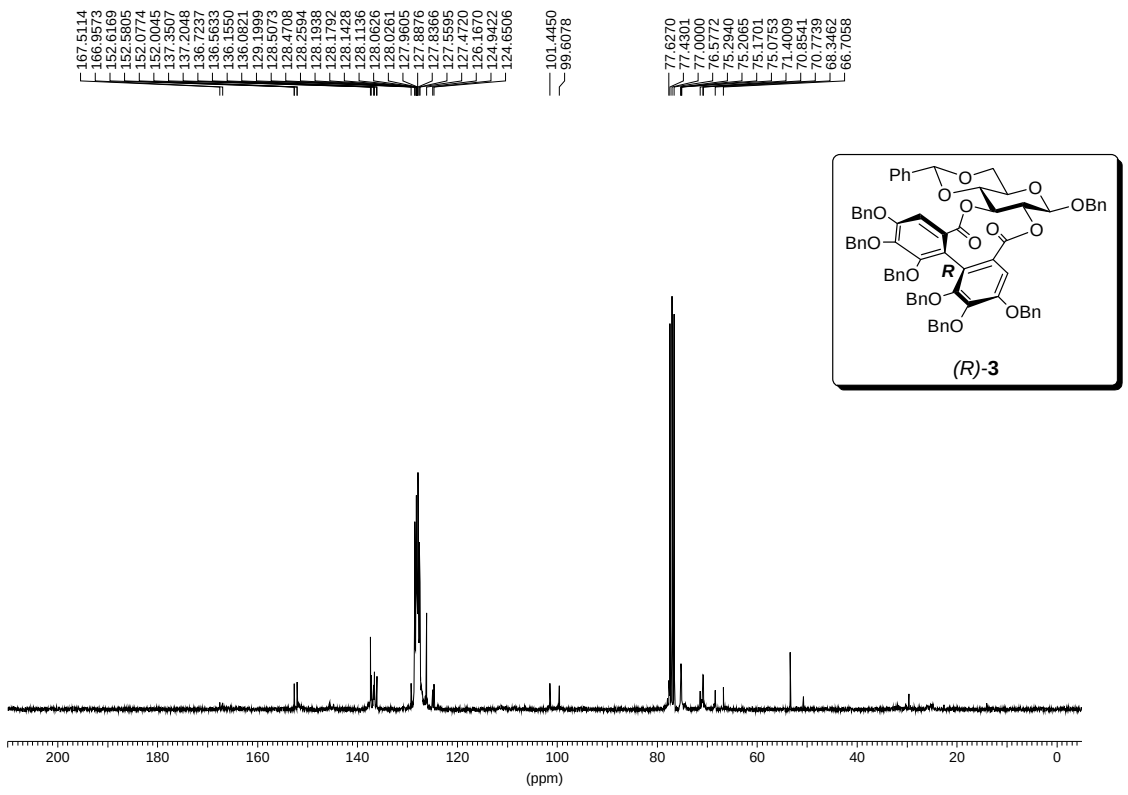
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14134	2262.79	7.5394	52354200	18.7
2	14154	2259.01	7.5268	62685480	22.4
3	14234	2243.91	7.4765	103361472	36.9
4	14280	2235.22	7.4475	104934864	37.5
5	14295	2232.39	7.4381	113167784	40.4
6	14326	2226.53	7.4186	280116800	100
7	14356	2220.87	7.3997	216054240	77.1
8	14402	2212.18	7.3707	108271800	38.7
9	14432	2206.52	7.3519	98369600	35.1
10	14465	2200.28	7.3311	121193984	43.3
11	14472	2198.96	7.3267	122169192	43.6
12	14578	2178.94	7.2600	175214704	62.6
13	14629	2169.31	7.2279	61896860	22.1
14	14756	2145.33	7.1480	94525136	33.7
15	14768	2143.06	7.1404	106295760	37.9
16	14792	2138.53	7.1253	140329632	50.1
17	14804	2136.26	7.1178	117850432	42.1
18	14821	2133.05	7.1071	79921728	28.5
19	14964	2106.05	7.0171	61989336	22.1
20	15006	2098.12	6.9907	156839936	56
21	15029	2093.77	6.9762	55444020	19.8
22	15267	2048.83	6.8265	82397848	29.4
23	17182	1687.19	5.6215	72403248	25.8
24	17445	1637.52	5.4560	17436352	6.2
25	17495	1628.08	5.4246	35760000	12.8
26	17547	1618.26	5.3919	21565892	7.7
27	17820	1566.70	5.2201	35458572	12.7
28	17831	1564.63	5.2132	32282522	11.5
29	17877	1555.94	5.1842	79765984	28.5
30	17912	1549.33	5.1622	27237700	9.7
31	17923	1547.25	5.1553	27199882	9.7
32	17970	1538.38	5.1257	58713972	21
33	18011	1530.63	5.0999	87834040	31.4
34	18069	1519.68	5.0634	38510768	13.7
35	18144	1505.52	5.0162	92520488	33
36	18168	1500.99	5.0011	52514796	18.7
37	18201	1494.75	4.9804	140992272	50.3
38	18224	1490.41	4.9659	62020884	22.1
39	18256	1484.37	4.9457	48362728	17.3
40	18327	1470.96	4.9011	48716844	17.4
41	18370	1462.84	4.8740	39402320	14.1
42	18423	1452.83	4.8407	87704344	31.3
43	18481	1441.88	4.8042	61364380	21.9
44	18536	1431.49	4.7696	47148564	16.8
45	18603	1418.84	4.7274	35710600	12.7

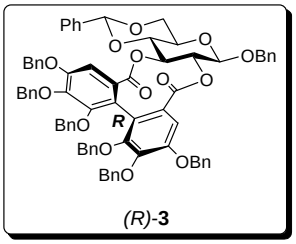
46	18659	1408.26	4.6922	44105364	15.7
47	18695	1401.46	4.6695	46624756	16.6
48	18716	1397.50	4.6563	38295176	13.7
49	18752	1390.70	4.6337	35156252	12.6
50	18995	1344.81	4.4808	18971996	6.8
51	19020	1340.09	4.4650	20313032	7.3
52	19051	1334.23	4.4455	21507422	7.7
53	19075	1329.70	4.4304	18305368	6.5
54	19780	1196.57	3.9868	19033954	6.8
55	19830	1187.12	3.9554	39071540	13.9
56	19868	1179.95	3.9315	37741980	13.5
57	19922	1169.75	3.8975	17384740	6.2
58	20333	1092.13	3.6389	11385500	4.1
59	20359	1087.22	3.6225	13418364	4.8
60	20384	1082.50	3.6068	19708284	7
61	20409	1077.78	3.5910	23022608	8.2
62	20459	1068.34	3.5596	7174242	2.6

GMB131-R / CDCl3 / 300



GMB131-R (polar fraction) / CDCl3 / 300 MHz



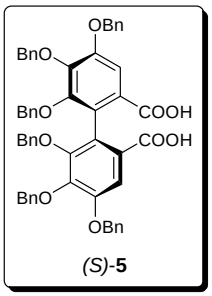


(R)-**3**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14214	2257.32	7.5211	40319000	14.7
2	14235	2253.35	7.5079	45034292	16.4
3	14457	2211.43	7.3682	271772256	98.8
4	14511	2201.23	7.3342	131016752	47.6
5	14629	2178.94	7.2600	275091680	100
6	14723	2161.19	7.2009	88568128	32.2
7	14854	2136.45	7.1184	113902568	41.4
8	14889	2129.84	7.0964	91647344	33.3
9	14921	2123.80	7.0763	71332032	25.9
10	15003	2108.32	7.0247	82403976	30
11	15035	2102.27	7.0045	61338028	22.3
12	15225	2066.39	6.8850	45626320	16.6
13	15262	2059.40	6.8617	40267788	14.6
14	15310	2050.34	6.8315	40234964	14.6
15	15341	2044.49	6.8120	33394644	12.1
16	17388	1657.92	5.5240	36275520	13.2
17	17974	1547.25	5.1553	18939584	6.9
18	18035	1535.73	5.1169	32609496	11.9
19	18111	1521.38	5.0691	36072872	13.1
20	18171	1510.05	5.0313	31518856	11.5
21	18217	1501.36	5.0024	45323944	16.5
22	18241	1496.83	4.9873	40511016	14.7
23	18278	1489.84	4.9640	48704600	17.7
24	18299	1485.88	4.9508	45810688	16.7
25	18361	1474.17	4.9118	60816328	22.1
26	18395	1467.75	4.8904	54401752	19.8
27	18416	1463.78	4.8772	68908104	25
28	18444	1458.50	4.8595	53671816	19.5
29	18468	1453.96	4.8444	42464204	15.4
30	18501	1447.73	4.8237	29793048	10.8
31	18570	1434.70	4.7803	28062812	10.2
32	18613	1426.58	4.7532	30374894	11
33	18690	1412.04	4.7048	40170120	14.6
34	18754	1399.95	4.6645	46026980	16.7
35	18817	1388.06	4.6248	28257998	10.3
36	19088	1336.88	4.4543	29296804	10.6
37	19145	1326.11	4.4185	31830200	11.6
38	19183	1318.94	4.3946	17262356	6.3
39	19207	1314.41	4.3795	15273186	5.6
40	19986	1167.29	3.8893	10602212	3.9
41	20039	1157.29	3.8559	17428548	6.3
42	20093	1147.09	3.8220	11344535	4.1
43	20334	1101.58	3.6703	8192102	3
44	20382	1092.51	3.6401	13378126	4.9
45	20433	1082.88	3.6080	10062365	3.7

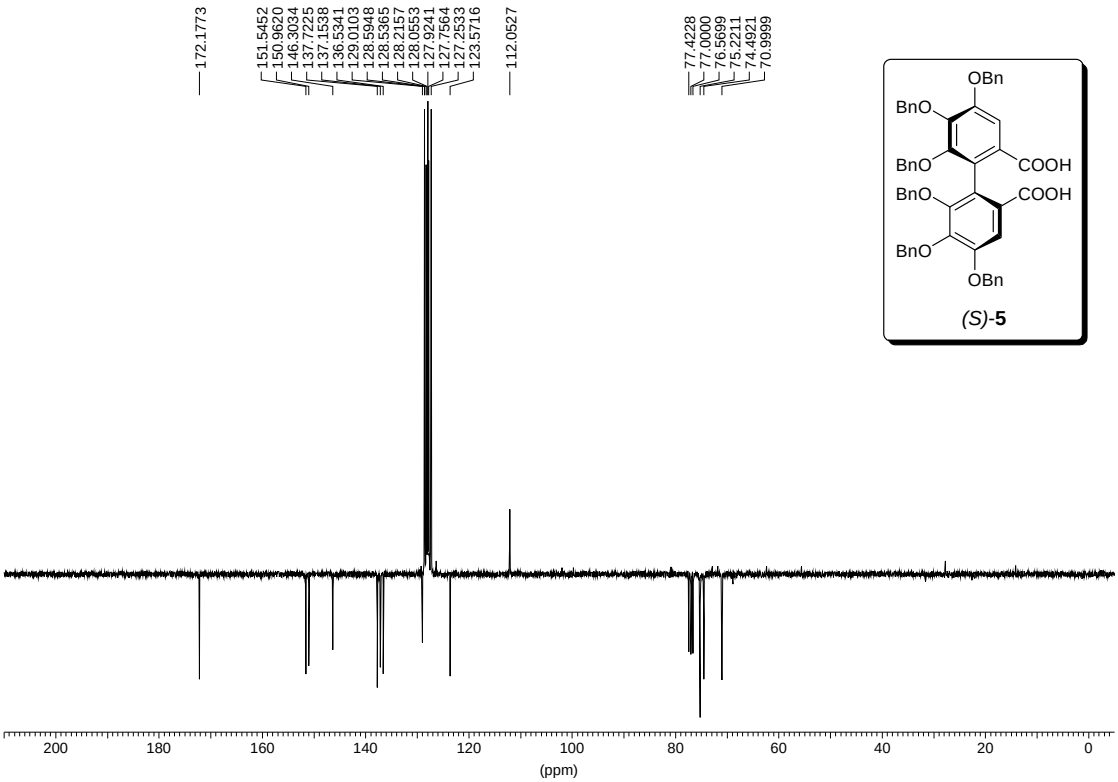
46	20562	1058.52	3.5269	8954205	3.3
47	20585	1054.18	3.5124	10131955	3.7
48	20611	1049.27	3.4960	14833769	5.4
49	20633	1045.11	3.4822	14197631	5.2
50	20656	1040.77	3.4677	8472395	3.1
51	20678	1036.61	3.4539	7260473	2.6
52	20684	1035.48	3.4501	7479225	2.7

JCH52-S / CDCl3 / 300 MHz

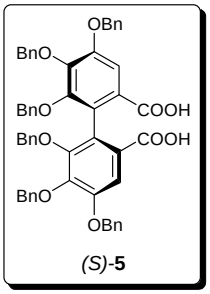


(S)-**5**

JCH52-S / CDCl3 / 300 MHz

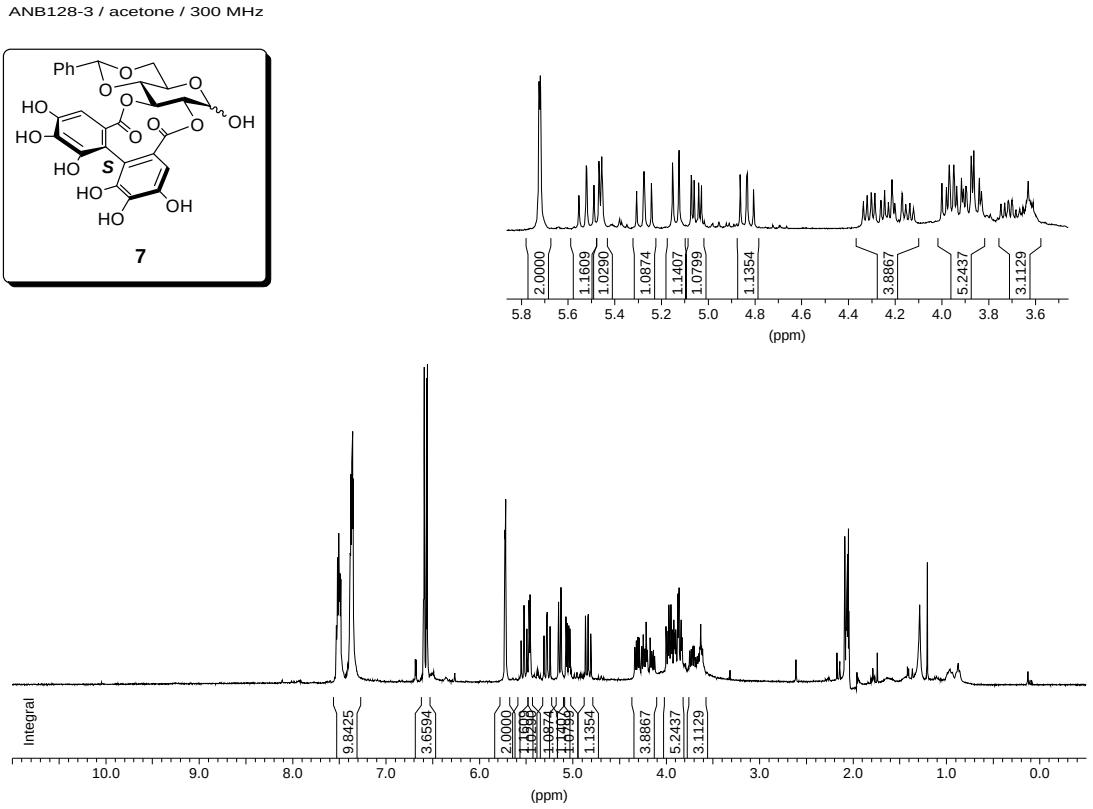


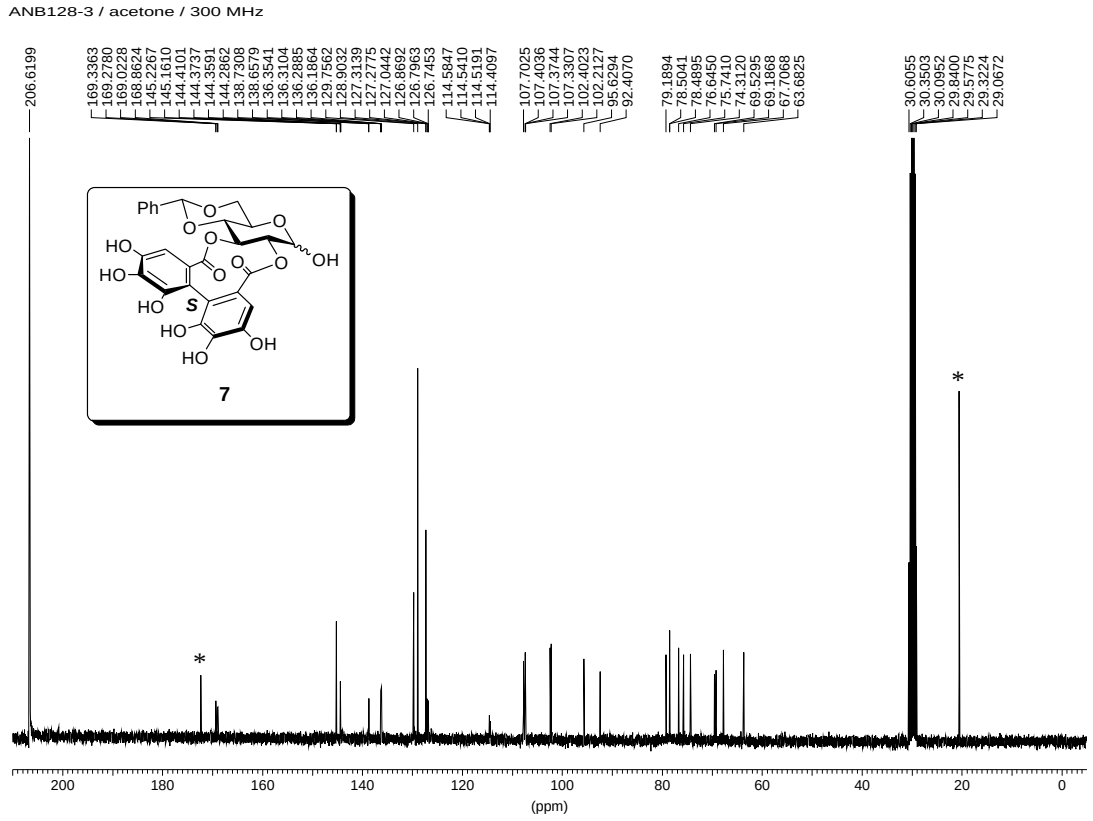
(S)-**5**



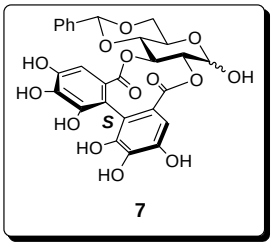
(S)-**5**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14038	2290.36	7.6312	136568176	39.60
2	14230	2254.11	7.5104	65140568	18.90
3	14266	2247.31	7.4878	105681416	30.60
4	14341	2233.14	7.4406	31950858	9.30
5	14351	2231.25	7.4343	38759524	11.20
6	14385	2224.83	7.4129	98236912	28.50
7	14425	2217.28	7.3877	93602072	27.1
8	14436	2215.20	7.3808	70916736	20.5
9	14472	2208.40	7.3582	38191840	11.1
10	14529	2197.64	7.3223	42830384	12.4
11	14540	2195.56	7.3154	55996564	16.2
12	14560	2191.79	7.3028	79173624	22.9
13	14579	2188.20	7.2908	90081072	26.1
14	14628	2178.94	7.2600	345128352	100
15	14659	2173.09	7.2405	167180576	48.4
16	14670	2171.01	7.2336	143870384	41.7
17	14688	2167.61	7.2222	82367728	23.9
18	14928	2122.29	7.0712	135985712	39.4
19	14966	2115.11	7.0473	85815464	24.9
20	15317	2048.83	6.8265	82071592	23.8
21	15349	2042.79	6.8063	64826784	18.8
22	15358	2041.09	6.8007	62392136	18.1
23	17804	1579.17	5.2616	32292788	9.4
24	17864	1567.84	5.2239	71605552	20.7
25	17944	1552.73	5.1735	74043920	21.5
26	18005	1541.21	5.1351	34463228	10
27	18190	1506.27	5.0187	26130204	7.6
28	18249	1495.13	4.9816	150063568	43.5
29	18276	1490.03	4.9646	109909720	31.8
30	18311	1483.42	4.9426	70227976	20.3
31	18333	1479.27	4.9288	32493766	9.4
32	18603	1428.28	4.7589	65127940	18.9
33	18663	1416.95	4.7211	50194152	14.5





* Traces of acetic acid in acetone-d_6



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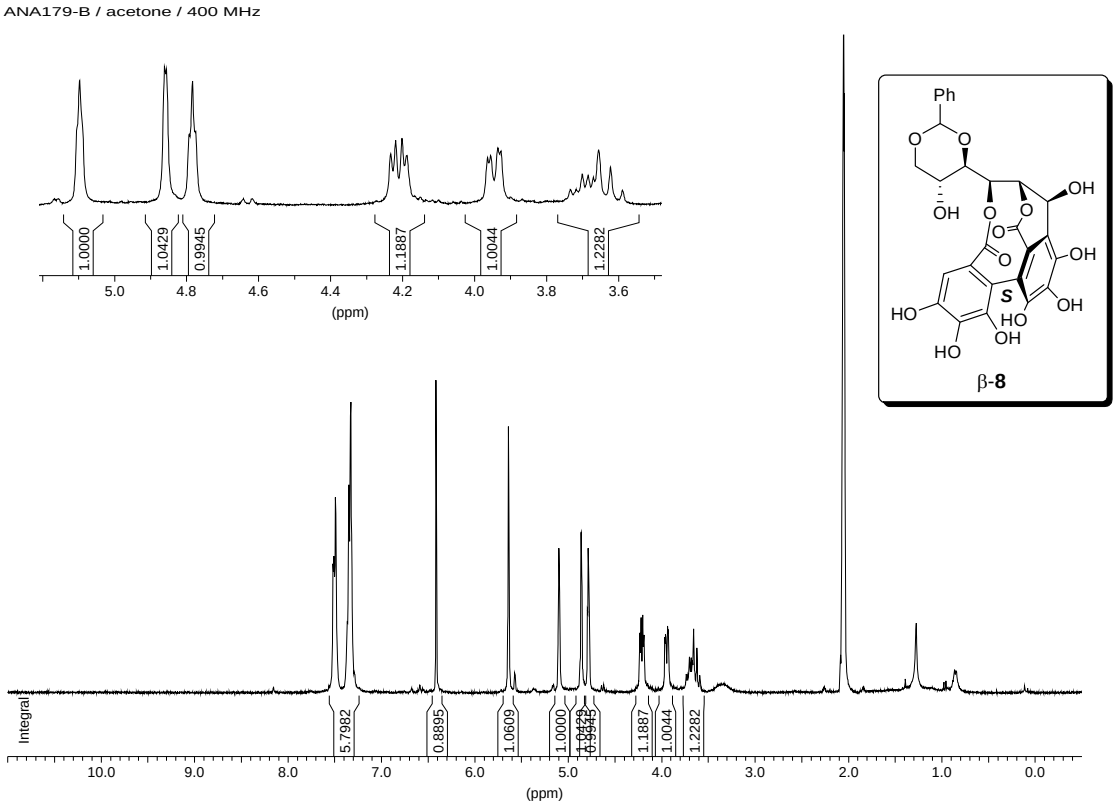
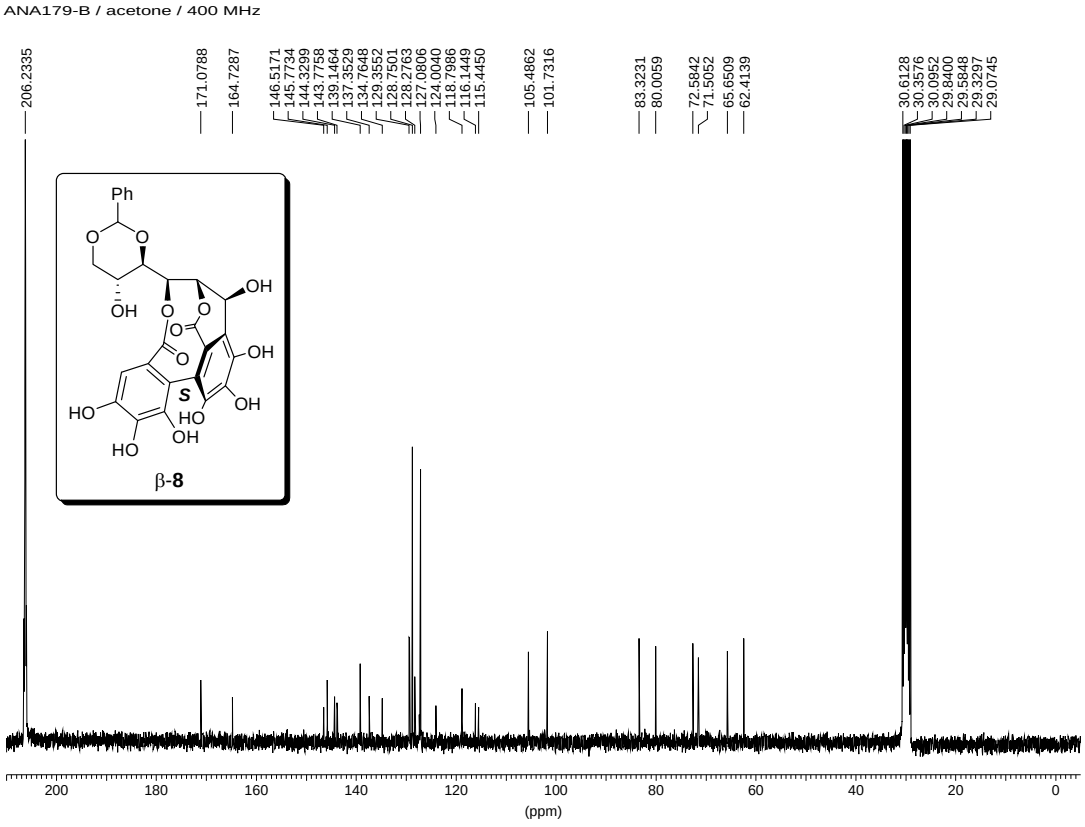
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	7526	2260.12	7.5305	83540024	19.3
2	7549	2255.78	7.5160	174586320	40.3
3	7568	2252.19	7.5040	206544160	47.7
4	7577	2250.49	7.4984	169035968	39
5	7590	2248.03	7.4902	149004816	34.4
6	7601	2245.96	7.4833	140621104	32.4
7	7745	2218.76	7.3927	64975944	15
8	7754	2217.06	7.3870	92581696	21.4
9	7765	2214.98	7.3801	187511984	43.3
10	7774	2213.28	7.3744	286476928	66.1
11	7791	2210.07	7.3637	301896864	69.6
12	7798	2208.75	7.3593	337196800	77.8
13	7801	2208.19	7.3574	339064768	78.2
14	7809	2206.68	7.3524	274379840	63.3
15	7820	2204.60	7.3455	85839488	19.8
16	9013	1979.30	6.5948	391964832	90.4
17	9024	1977.23	6.5879	429482784	99.1
18	9063	1969.86	6.5634	414873344	95.7
19	9075	1967.60	6.5558	433454944	100
20	10398	1717.75	5.7234	238724000	55.1
21	10407	1716.05	5.7177	251462272	58
22	10669	1666.57	5.5528	58110480	13.4
23	10720	1656.94	5.5208	106006800	24.5
24	10771	1647.31	5.4887	74111752	17.1
25	10806	1640.70	5.4666	112370280	25.9
26	10825	1637.11	5.4547	121519016	28
27	11062	1592.36	5.3056	64956432	15
28	11111	1583.10	5.2747	95896608	22.1
29	11114	1582.54	5.2728	95387600	22
30	11163	1573.28	5.2420	77726944	17.9
31	11307	1546.09	5.1514	110389072	25.5
32	11350	1537.97	5.1243	131730632	30.4
33	11434	1522.11	5.0715	90394880	20.9
34	11453	1518.52	5.0595	82931408	19.1
35	11483	1512.85	5.0407	78949968	18.2
36	11502	1509.27	5.0287	75197984	17.3
37	11766	1459.41	4.8626	91120160	21
38	11809	1451.29	4.8355	87556800	20.2
39	11815	1450.16	4.8318	96364184	22.2
40	11858	1442.04	4.8047	68997144	15.9
41	12603	1301.35	4.3359	47022532	10.8
42	12629	1296.44	4.3196	57374968	13.2
43	12657	1291.15	4.3020	61819312	14.3
44	12683	1286.24	4.2856	62158920	14.3
45	12723	1278.68	4.2604	49697956	11.5

46	12748	1273.96	4.2447	65708400	15.2
47	12774	1269.05	4.2283	46595772	10.7
48	12799	1264.33	4.2126	82899472	19.1
49	12819	1260.55	4.2000	46670560	10.8
50	12868	1251.30	4.1692	62023180	14.3
51	12893	1246.58	4.1535	44708632	10.3
52	12919	1241.67	4.1371	46337532	10.7
53	12945	1236.76	4.1207	38405772	8.9
54	13138	1200.31	3.9993	75575752	17.4
55	13169	1194.46	3.9798	68966728	15.9
56	13189	1190.68	3.9672	105766432	24.4
57	13218	1185.20	3.9490	106096160	24.5
58	13239	1181.24	3.9358	74312200	17.1
59	13270	1175.38	3.9163	85552160	19.7
60	13284	1172.74	3.9074	69478928	16
61	13303	1169.15	3.8955	74052568	17.1
62	13338	1162.54	3.8735	121343976	28
63	13355	1159.33	3.8628	133959624	30.9
64	13392	1152.35	3.8395	89071200	20.5
65	13406	1149.70	3.8307	69360600	16
66	13539	1124.59	3.7470	45988976	10.6
67	13565	1119.68	3.7306	48270704	11.1
68	13592	1114.58	3.7136	52431392	12.1
69	13614	1110.42	3.6998	53117776	12.3
70	13641	1105.32	3.6828	38039640	8.8
71	13667	1100.41	3.6665	39170560	9
72	13689	1096.26	3.6526	42276380	9.8
73	13693	1095.50	3.6501	37213844	8.6
74	13702	1093.80	3.6444	36595984	8.4
75	13724	1089.65	3.6306	84005200	19.4
76	13736	1087.38	3.6230	54743232	12.6
77	13746	1085.49	3.6167	51439084	11.9
78	13759	1083.04	3.6086	52940884	12.2
79	16198	622.44	2.0739	73114152	16.9
80	16213	619.61	2.0645	119483664	27.6
81	16225	617.34	2.0569	178613616	41.2
82	16236	615.27	2.0500	217127584	50.1
83	16248	613.00	2.0424	140082720	32.3
84	16260	610.73	2.0349	64653696	14.9


ANA179-B / acetone / 400 MHz
1.0000
1.0429
0.9945
1.1887
1.0044
1.2282
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
(ppm)
Ph
OH
OH
OH
OH
HO
HO
HO
OH
S
β-8
Integral
5.7982
0.8895
1.0609
1.0000
1.0429
0.9945
1.1887
1.0044
1.2282
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


ANA179-B / acetone / 400 MHz
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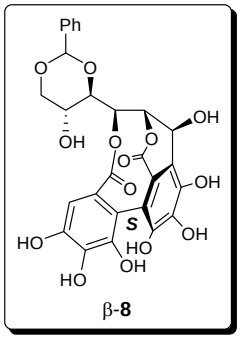
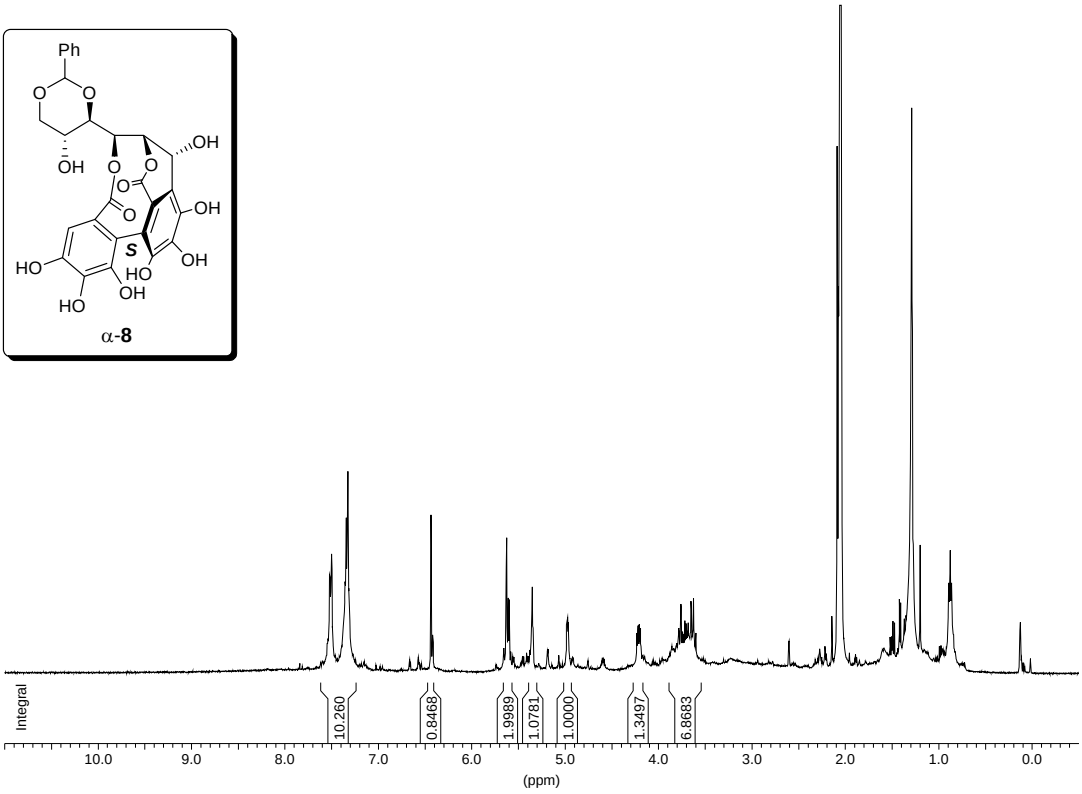
171.0788
164.7287
146.5171
145.7734
144.3299
143.7758
139.1464
137.3529
134.7648
129.3552
128.7501
128.2763
127.0806
124.0040
118.7986
116.1449
115.4450
105.4862
101.7316
83.3231
80.0059
72.5842
71.5052
65.6509
62.4139
30.6128
30.3576
30.0952
29.8400
29.5848
29.3297
29.0745
Ph
OH
OH
OH
OH
HO
HO
HO
OH
S
β-8
200
180
160
140
120
100
80
60
40
20
0
(ppm)



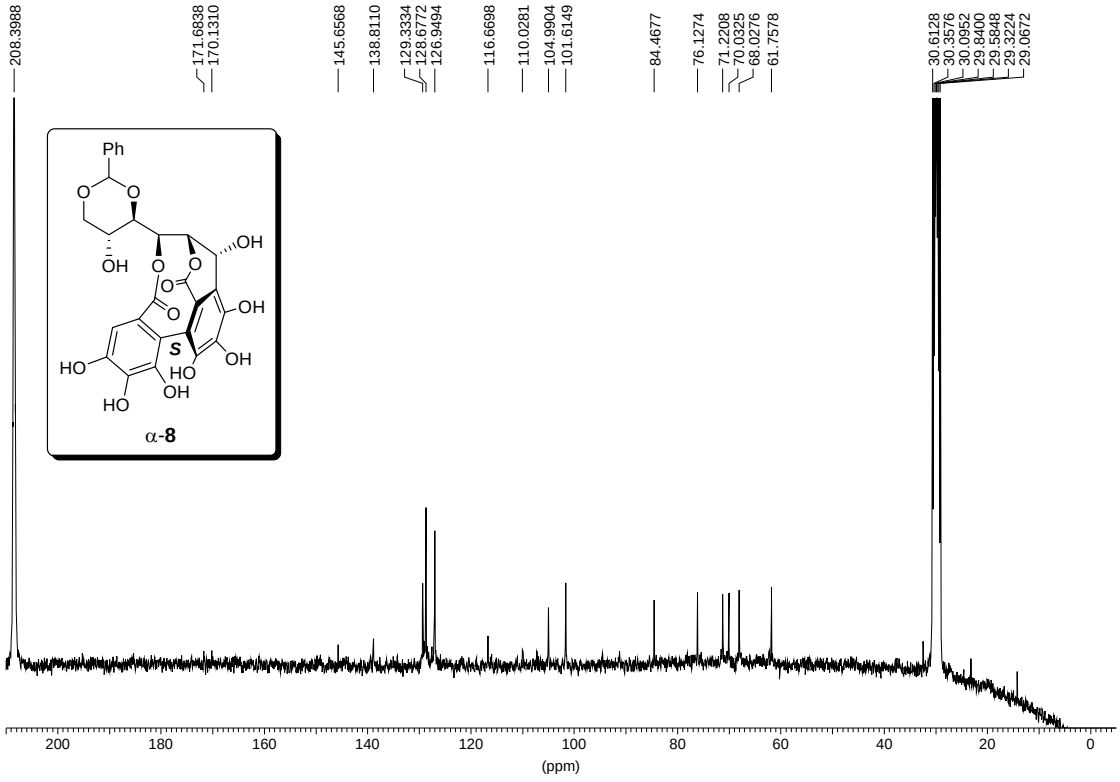
β-**8**

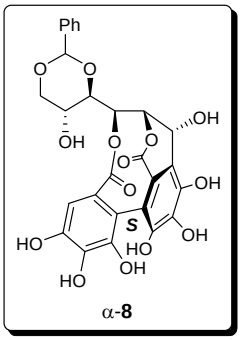
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	9842	2255.59	7.5154	83780016	14.7
2	9855	2253.13	7.5072	88762080	15.5
3	9884	2247.65	7.4889	126962656	22.2
4	9891	2246.33	7.4845	116567704	20.4
5	10085	2209.70	7.3625	46358536	8.1
6	10111	2204.79	7.3461	135128160	23.7
7	10142	2198.93	7.3266	189180032	33.1
8	10149	2197.61	7.3222	181031024	31.7
9	11594	1924.73	6.4130	203252112	35.6
10	12825	1692.26	5.6384	173118112	30.3
11	13686	1529.66	5.0967	93945376	16.5
12	14061	1458.84	4.8607	104625480	18.3
13	14070	1457.14	4.8550	102711144	18
14	14170	1438.26	4.7921	53510536	9.4
15	14184	1435.62	4.7833	93811312	16.4
16	14198	1432.97	4.7745	55814192	9.8
17	15060	1270.19	4.2321	38857048	6.8
18	15081	1266.22	4.2189	48893200	8.6
19	15110	1260.74	4.2007	50507156	8.8
20	15131	1256.78	4.1874	37358292	6.5
21	15487	1189.55	3.9634	35888828	6.3
22	15501	1186.90	3.9546	37642384	6.6
23	15533	1180.86	3.9345	43406800	7.6
24	15547	1178.22	3.9257	40813856	7.1
25	15853	1120.43	3.7332	12089353	2.1
26	15877	1115.90	3.7180	11817798	2.1
27	15906	1110.42	3.6998	23249874	4.1
28	15931	1105.70	3.6841	22490648	3.9
29	15955	1101.17	3.6690	21114428	3.7
30	15978	1096.82	3.6545	41492704	7.3
31	16030	1087.00	3.6218	29009736	5.1
32	16082	1077.18	3.5891	11316653	2
33	18505	619.61	2.0645	229480384	40.2
34	18517	617.34	2.0569	418512128	73.3
35	18528	615.27	2.0500	571044416	100
36	18540	613.00	2.0424	421937472	73.9
37	18551	610.92	2.0355	238229760	41.7

ANA184-C / acetone / 300 MHz



ANB129-D / acetone / 300 MHz

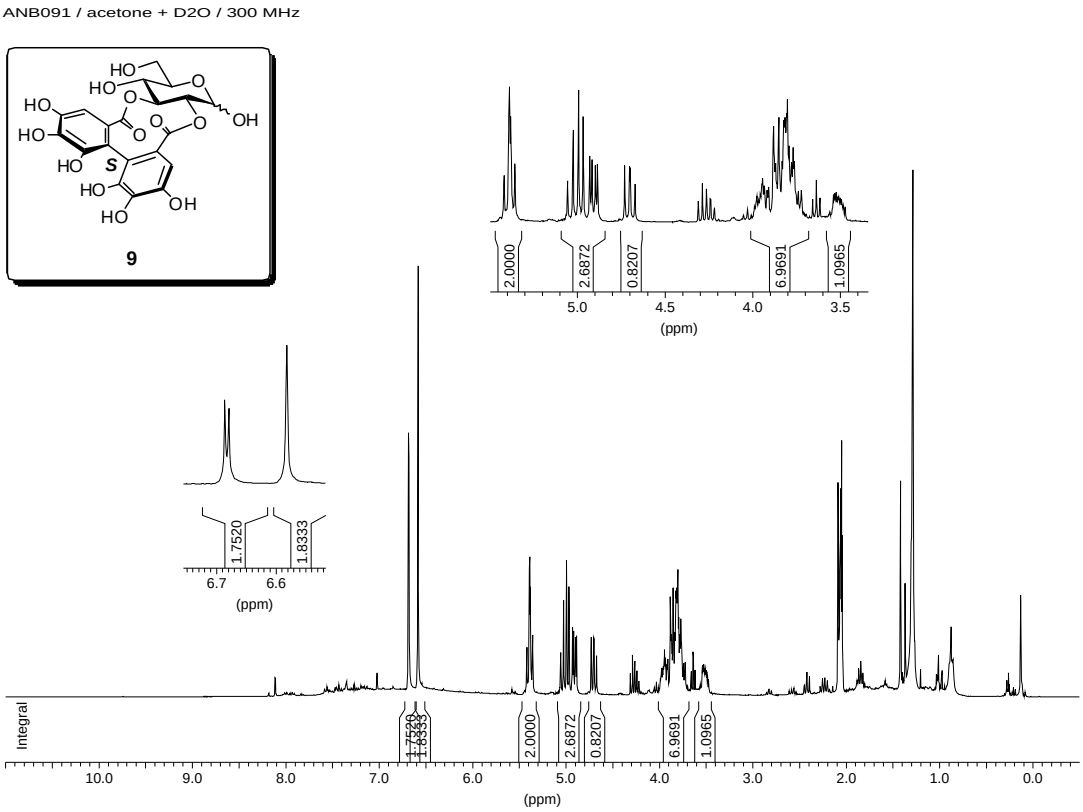




α-**8**

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	17111	3016.90	7.5398	3596144	0.9
2	17143	3009.07	7.5202	12237014	2.9
3	17153	3006.63	7.5141	11713036	2.8
4	17176	3001.00	7.5001	15038347	3.6
5	17182	2999.53	7.4964	12964499	3.1
6	17195	2996.36	7.4885	5326320	1.3
7	17412	2943.29	7.3558	11310963	2.7
8	17420	2941.34	7.3510	11084601	2.7
9	17434	2937.91	7.3424	19861324	4.8
10	17463	2930.82	7.3247	26064110	6.3
11	17480	2926.66	7.3143	10438850	2.5
12	17487	2924.95	7.3100	9489064	2.3
13	18920	2574.54	6.4343	20277984	4.9
14	20241	2251.51	5.6270	17216606	4.1
15	20271	2244.18	5.6086	9134295	2.2
16	20290	2239.53	5.5970	8909749	2.1
17	20681	2143.92	5.3581	6376718	1.5
18	20692	2141.23	5.3513	10607604	2.5
19	20702	2138.78	5.3452	5839642	1.4
20	21295	1993.78	4.9828	5547512	1.3
21	21306	1991.09	4.9761	6388929	1.5
22	21313	1989.37	4.9718	6552925	1.6
23	21324	1986.68	4.9651	5855504	1.4
24	22527	1692.51	4.2299	4471856	1.1
25	22547	1687.62	4.2177	5451362	1.3
26	22569	1682.24	4.2042	5585897	1.3
27	22588	1677.60	4.1926	5120827	1.2
28	23221	1522.81	3.8058	3077296	0.7
29	23257	1514.00	3.7838	5100854	1.2
30	23294	1504.96	3.7612	8316235	2
31	23304	1502.51	3.7551	7995297	1.9
32	23326	1497.13	3.7416	4639209	1.1
33	23345	1492.48	3.7300	4230922	1
34	23365	1487.59	3.7178	6085204	1.5
35	23385	1482.70	3.7056	5734215	1.4
36	23403	1478.30	3.6946	4745713	1.1
37	23422	1473.66	3.6829	5832350	1.4
38	23476	1460.45	3.6499	8703358	2.1
39	23518	1450.18	3.6243	9085879	2.2
40	23557	1440.64	3.6004	4438933	1.1
41	26075	824.91	2.0616	155258672	37.2
42	26084	822.71	2.0561	234060080	56.1

43	26094	820.27	2.0500	416900224	100
44	26102	818.31	2.0451	226217600	54.3
45	26111	816.11	2.0396	106353888	25.5


ANB091 / acetone + D2O / 300 MHz
9
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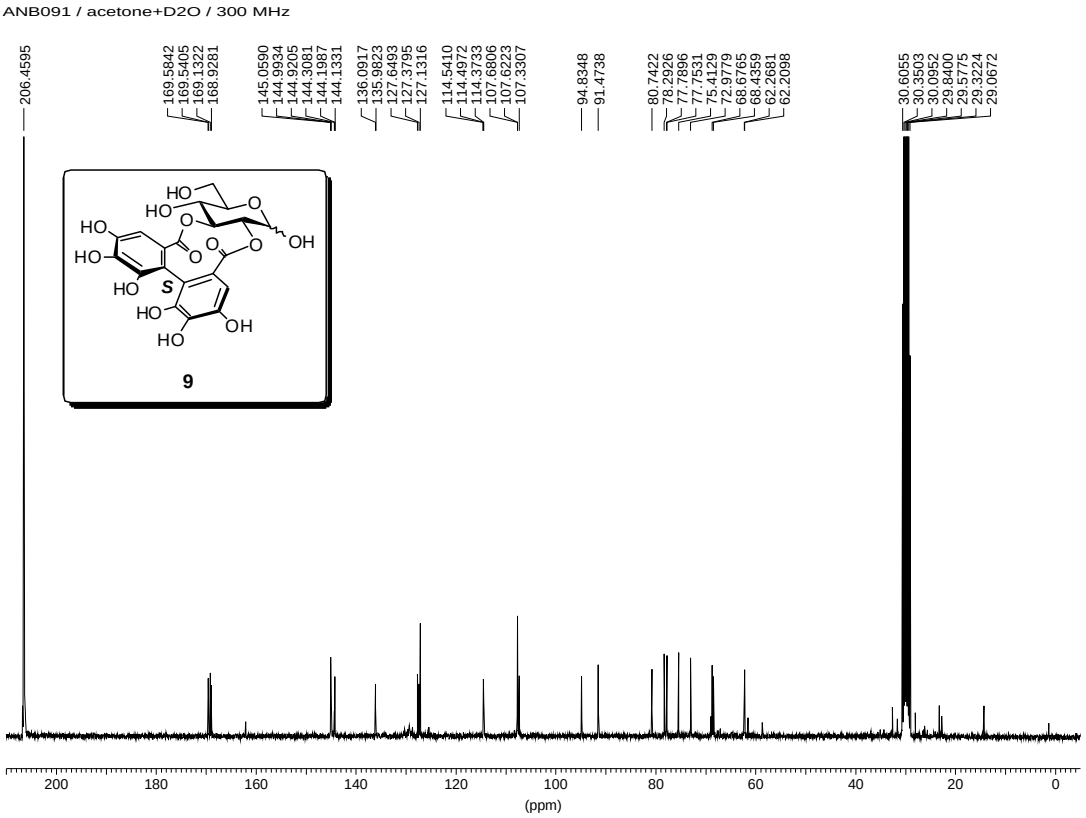
2.6872
0.8207
6.9691
1.0965
5.0
4.5
4.0
3.5
(ppm)
1.7520
1.8333
6.7
6.6
(ppm)
Integral
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


ANB091 / acetone+D2O / 300 MHz
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169.5405
169.1322
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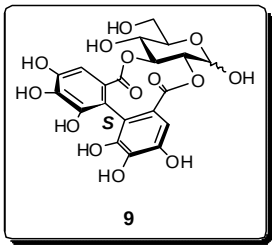
144.9934
144.9205
144.3081
144.1987
144.1331
136.0917
135.9823
127.6493
127.3795
127.1316
114.5410
114.4972
114.3733
107.6806
107.6223
107.3307
94.8348
91.4738
80.7422
78.2926
77.7896
77.7531
75.4129
72.9779
68.6765
68.4359
62.2681
62.2098
30.6055
30.3503
30.0952
29.8400
29.5775
29.3224
29.0672
9
200
180
160
140
120
100
80
60
40
20
0
(ppm)

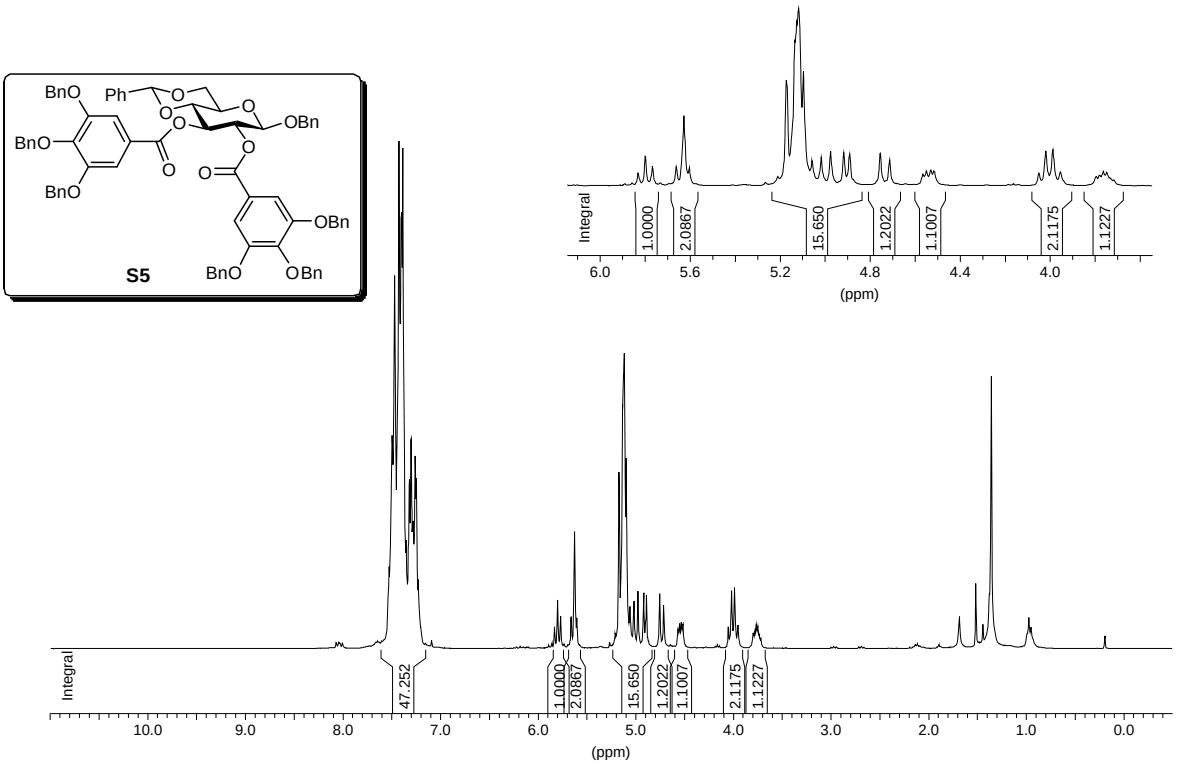


9

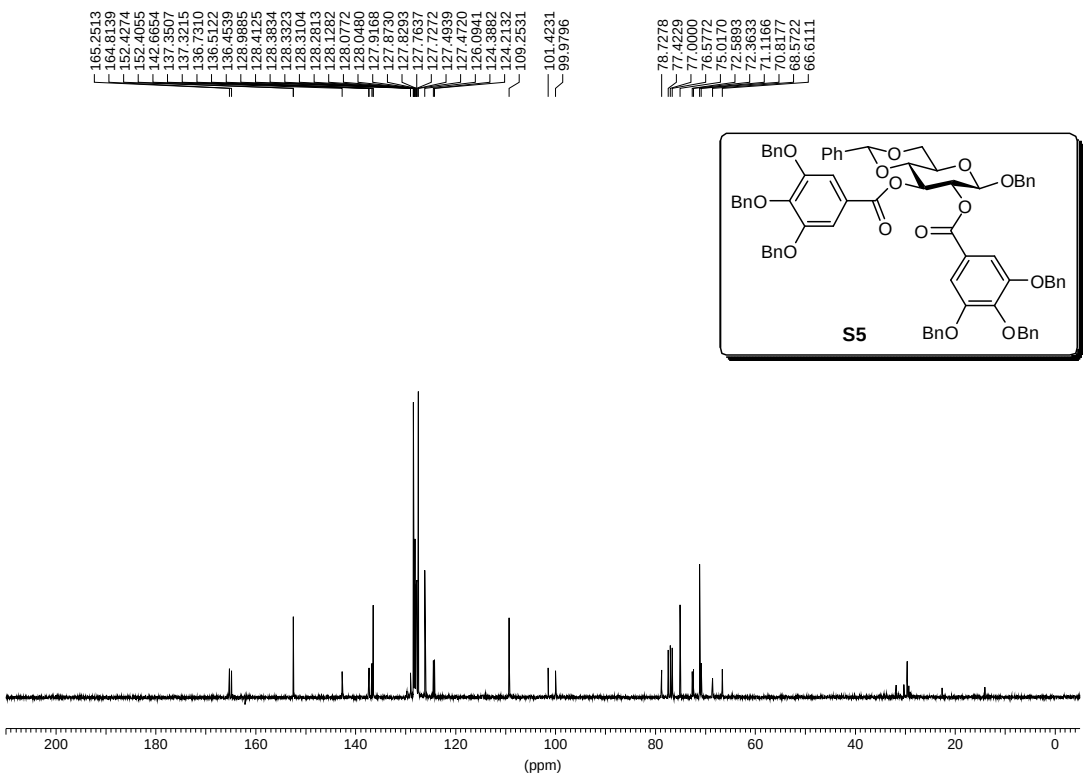
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	15550	2006.69	6.6861	279459936	61.2
2	15561	2004.61	6.6791	252330240	55.3
3	15716	1975.34	6.5816	456465440	100
4	17565	1626.16	5.4182	51362940	11.3
5	17613	1617.10	5.3880	147604976	32.3
6	17626	1614.64	5.3798	115376216	25.3
7	17664	1607.47	5.3559	64191152	14.1
8	18141	1517.39	5.0558	45616348	10
9	18192	1507.75	5.0237	100948552	22.1
10	18241	1498.50	4.9928	144097792	31.6
11	18284	1490.38	4.9658	115671168	25.3
12	18343	1479.24	4.9287	72438264	15.9
13	18362	1475.65	4.9167	68811464	15.1
14	18394	1469.61	4.8966	62368660	13.7
15	18413	1466.02	4.8846	63635248	13.9
16	18659	1419.56	4.7298	62225960	13.6
17	18702	1411.44	4.7028	61699752	13.5
18	18710	1409.93	4.6977	59720888	13.1
19	18753	1401.81	4.6707	42138240	9.2
20	19858	1193.14	3.9754	29158396	6.4
21	19874	1190.11	3.9653	25065348	5.5
22	19887	1187.66	3.9572	30927706	6.8
23	19910	1183.32	3.9427	48879336	10.7
24	19925	1180.48	3.9332	40120480	8.8
25	19950	1175.76	3.9175	35408164	7.8
26	19963	1173.31	3.9093	38805584	8.5
27	20008	1164.81	3.8810	105108928	23
28	20026	1161.41	3.8697	64711076	14.2
29	20057	1155.56	3.8502	114569416	25.1
30	20085	1150.27	3.8326	66980280	14.7
31	20101	1147.25	3.8225	111336448	24.4
32	20114	1144.79	3.8143	114539872	25.1
33	20127	1142.34	3.8061	119413872	26.2
34	20135	1140.83	3.8011	134122096	29.4
35	20149	1138.18	3.7923	83508336	18.3
36	20171	1134.03	3.7785	65394692	14.3
37	20186	1131.19	3.7690	81843072	17.9
38	20198	1128.93	3.7615	67006344	14.7
39	20233	1122.32	3.7394	34472640	7.6
40	20260	1117.22	3.7225	35517668	7.8
41	20550	1062.45	3.5400	30443886	6.7
42	20563	1060.00	3.5318	32279918	7.1
43	20576	1057.54	3.5236	33061712	7.2
44	20599	1053.20	3.5091	28330512	6.2
45	20613	1050.56	3.5003	27167082	6

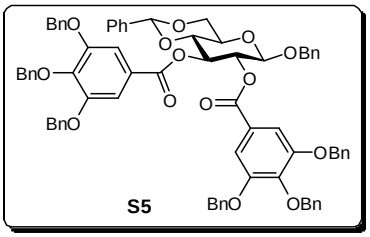
46	20627	1047.91	3.4915	25284098	5.5
47	20640	1045.46	3.4834	19067768	4.2
48	20659	1041.87	3.4714	17118906	3.8
49	22895	619.61	2.0645	160898816	35.2
50	22907	617.34	2.0569	220025312	48.2
51	22918	615.27	2.0500	271195904	59.4
52	22930	613.00	2.0424	187959200	41.2
53	22942	610.73	2.0349	93564776	20.5

GMB144 / CDCl3 / 300



GMB144 / CDCl3 / 300 MHz

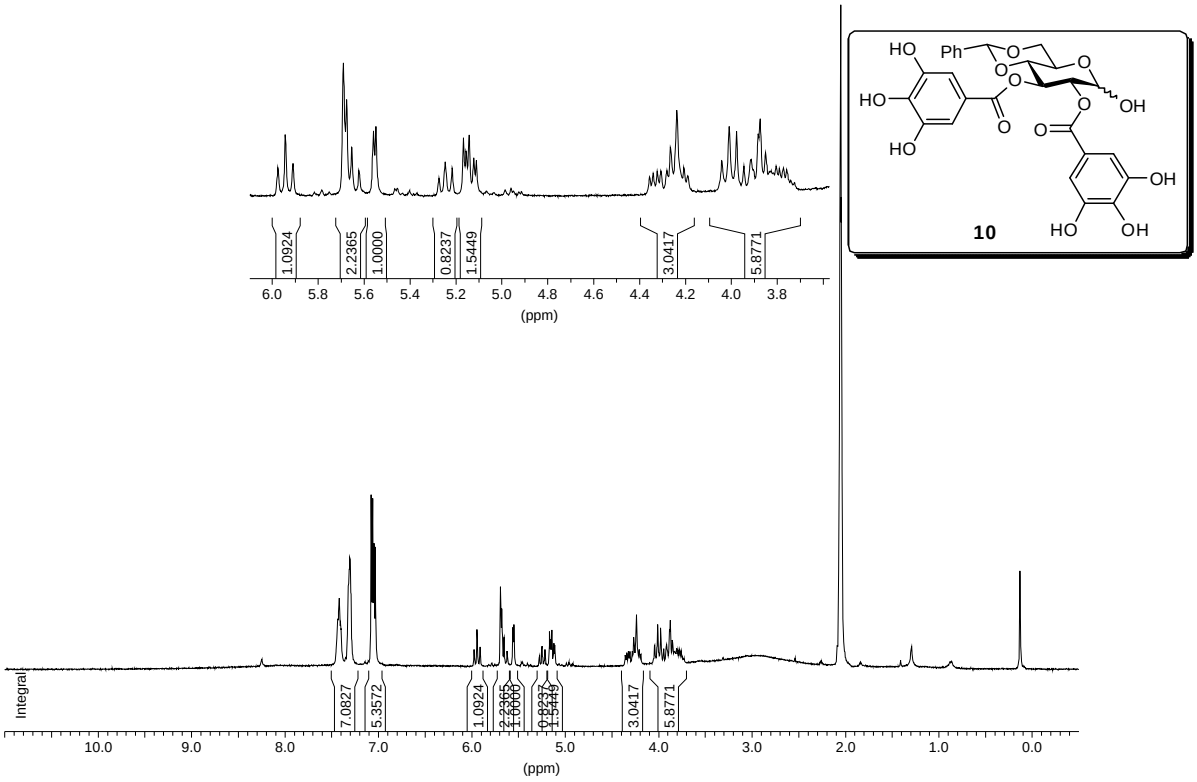




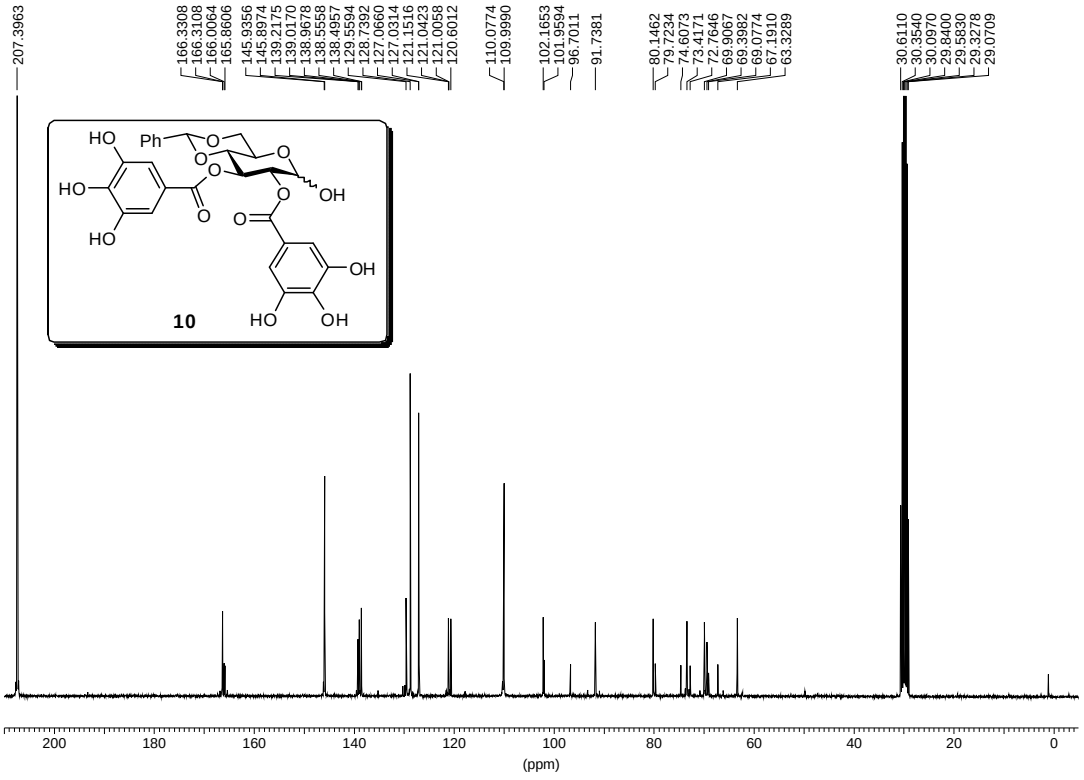
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14196	2257.88	7.5230	42454440	16.1
2	14242	2249.19	7.4941	110366176	42
3	14283	2241.45	7.4683	193308320	73.5
4	14352	2228.42	7.4249	263008544	100
5	14389	2221.43	7.4016	223014784	84.8
6	14398	2219.73	7.3959	226077600	86
7	14417	2216.15	7.3840	259510960	98.7
8	14470	2206.14	7.3506	55955028	21.3
9	14516	2197.45	7.3217	84530808	32.1
10	14524	2195.94	7.3166	87592592	33.3
11	14550	2191.03	7.3003	108766704	41.4
12	14577	2185.93	7.2833	66204112	25.2
13	14614	2178.94	7.2600	99778440	37.9
14	14637	2174.60	7.2455	88339120	33.6
15	14664	2169.50	7.2285	35663072	13.6
16	16885	1750.07	5.8311	10977319	4.2
17	16936	1740.44	5.7990	25021608	9.5
18	16986	1731.00	5.7675	16547744	6.3
19	17156	1698.90	5.6605	16360507	6.2
20	17210	1688.70	5.6266	60449664	23
21	17247	1681.71	5.6033	15621739	5.9
22	17933	1552.16	5.1716	91330560	34.7
23	17992	1541.02	5.1345	126527512	48.1
24	18006	1538.38	5.1257	142182000	54.1
25	18019	1535.92	5.1175	153158048	58.2
26	18053	1529.50	5.0961	98660464	37.5
27	18114	1517.98	5.0577	21566890	8.2
28	18179	1505.71	5.0168	24413642	9.3
29	18244	1493.43	4.9759	29523640	11.2
30	18339	1475.49	4.9162	28662902	10.9
31	18380	1467.75	4.8904	27505564	10.5
32	18596	1426.96	4.7545	28240784	10.7
33	18662	1414.49	4.7129	22291340	8.5
34	18897	1370.11	4.5651	9591045	3.6
35	18922	1365.39	4.5493	12809747	4.9
36	18952	1359.73	4.5305	13542051	5.1
37	18976	1355.20	4.5154	12550285	4.8
38	19716	1215.45	4.0497	10840222	4.1
39	19765	1206.20	4.0189	29799832	11.3
40	19815	1196.75	3.9875	31237356	11.9
41	19868	1186.74	3.9541	11884184	4.5
42	20120	1139.16	3.7955	7828567	3
43	20145	1134.43	3.7798	9042015	3.4
44	20171	1129.52	3.7635	12317544	4.7
45	20196	1124.80	3.7477	11454320	4.4

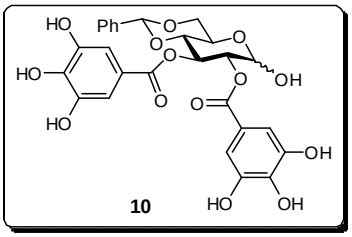
46	20220	1120.27	3.7326	6729738	2.6
47	20246	1115.36	3.7163	4811151	1.8

GMB120 / acetone / 300 MHz



GMB159 / acetone / 300 MHz

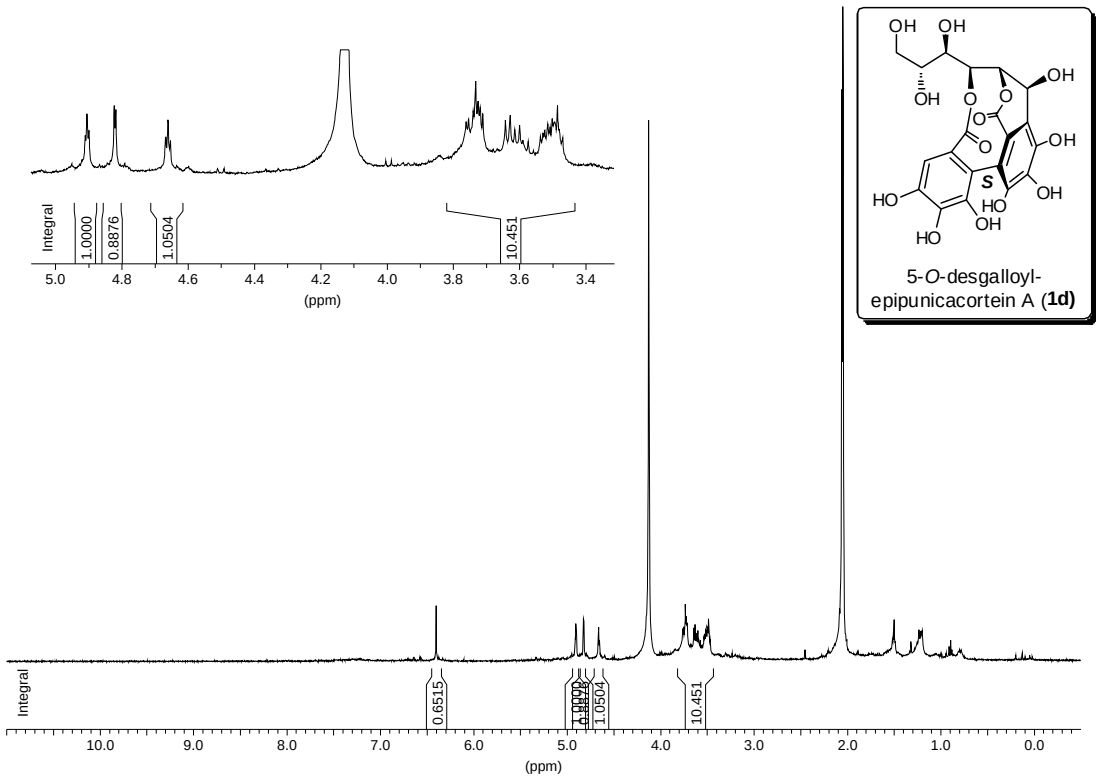




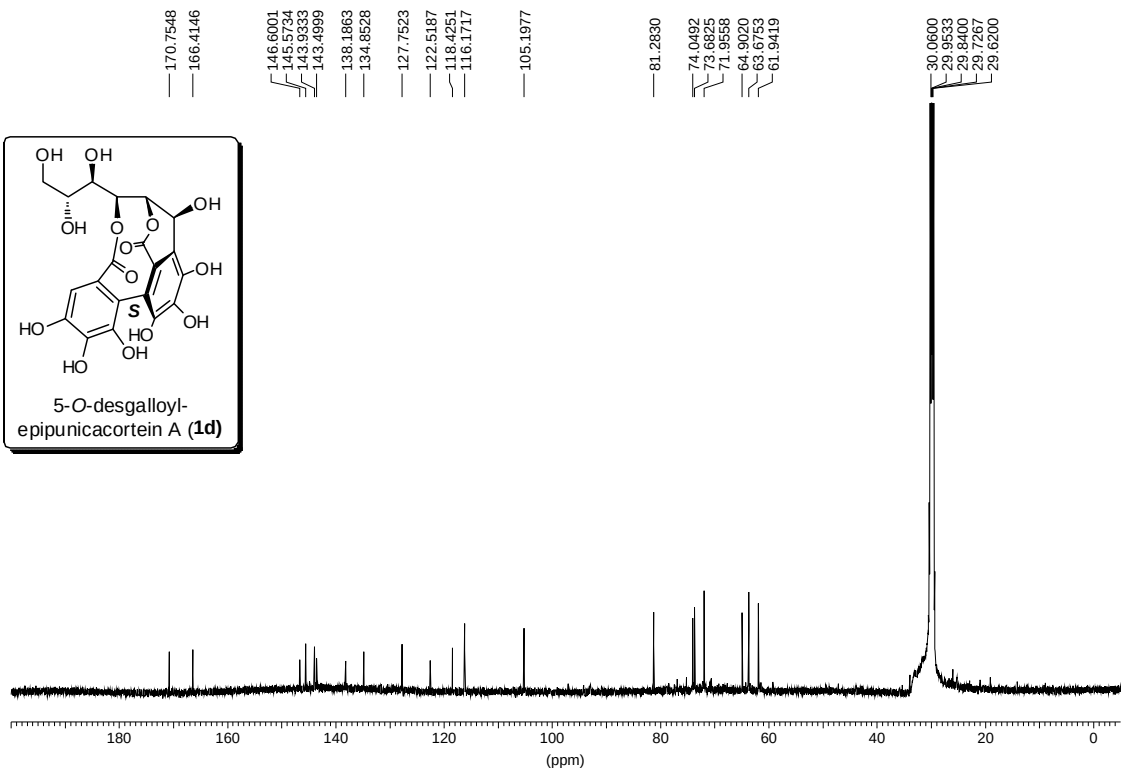
Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	14367	2230.28	7.4310	34591396	8.1
2	14392	2225.56	7.4153	46082540	10.8
3	14409	2222.35	7.4046	29700110	7
4	14566	2192.70	7.3058	72412656	17
5	14579	2190.25	7.2977	70965160	16.6
6	14933	2123.39	7.0749	112341512	26.3
7	14955	2119.24	7.0611	110126664	25.8
8	14978	2114.90	7.0466	81373816	19.1
9	15000	2110.74	7.0328	79006096	18.5
10	16681	1793.29	5.9750	13284201	3.1
11	16733	1783.47	5.9423	25903164	6.1
12	16785	1773.65	5.9096	14731844	3.4
13	17134	1707.74	5.6900	53543860	12.5
14	17156	1703.59	5.6762	39368088	9.2
15	17192	1696.79	5.6535	21115976	4.9
16	17243	1687.16	5.6214	12105188	2.8
17	17342	1668.46	5.5591	27361888	6.4
18	17360	1665.06	5.5478	29088176	6.8
19	17796	1582.73	5.2735	9220433	2.2
20	17838	1574.79	5.2470	15353432	3.6
21	17888	1565.35	5.2156	13107604	3.1
22	17966	1550.62	5.1665	24644996	5.8
23	17984	1547.22	5.1552	19636934	4.6
24	18005	1543.26	5.1420	25715988	6
25	18037	1537.21	5.1218	16988188	4
26	18055	1533.82	5.1105	16044423	3.8
27	19255	1307.20	4.3554	9620726	2.3
28	19279	1302.67	4.3403	11008547	2.6
29	19308	1297.19	4.3221	11793546	2.8
30	19332	1292.66	4.3070	11961737	2.8
31	19374	1284.73	4.2806	12106155	2.8
32	19399	1280.01	4.2648	21000618	4.9
33	19444	1271.51	4.2365	35422904	8.3
34	19492	1262.44	4.2063	13213062	3.1
35	19519	1257.34	4.1893	10089915	2.4
36	19754	1212.97	4.0415	15968237	3.7
37	19806	1203.15	4.0087	29124480	6.8
38	19857	1193.51	3.9767	27137640	6.4
39	19907	1184.07	3.9452	13841486	3.2
40	19958	1174.44	3.9131	16432122	3.8
41	20006	1165.38	3.8829	26186284	6.1
42	20020	1162.73	3.8741	32073952	7.5
43	20058	1155.56	3.8502	19079620	4.5
44	20130	1141.96	3.8049	13909239	3.3
45	20154	1137.43	3.7898	12834925	3
46	20180	1132.52	3.7734	13141479	3.1

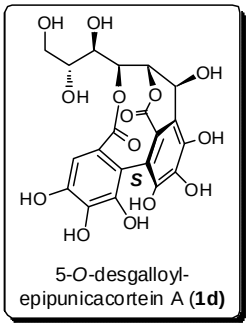
47	20205	1127.80	3.7577	12482035	2.9
48	20231	1122.89	3.7413	8353512	2
49	20256	1118.16	3.7256	7468301	1.7
50	22897	619.42	2.0638	172413488	40.4
51	22908	617.34	2.0569	314327296	73.6
52	22919	615.27	2.0500	427137984	100
53	22930	613.19	2.0431	325623936	76.2
54	22941	611.11	2.0362	188743248	44.2

ANB132 / acetone + D2O / 400 MHz



ANB132 / acetone + D2O / 700 MHz

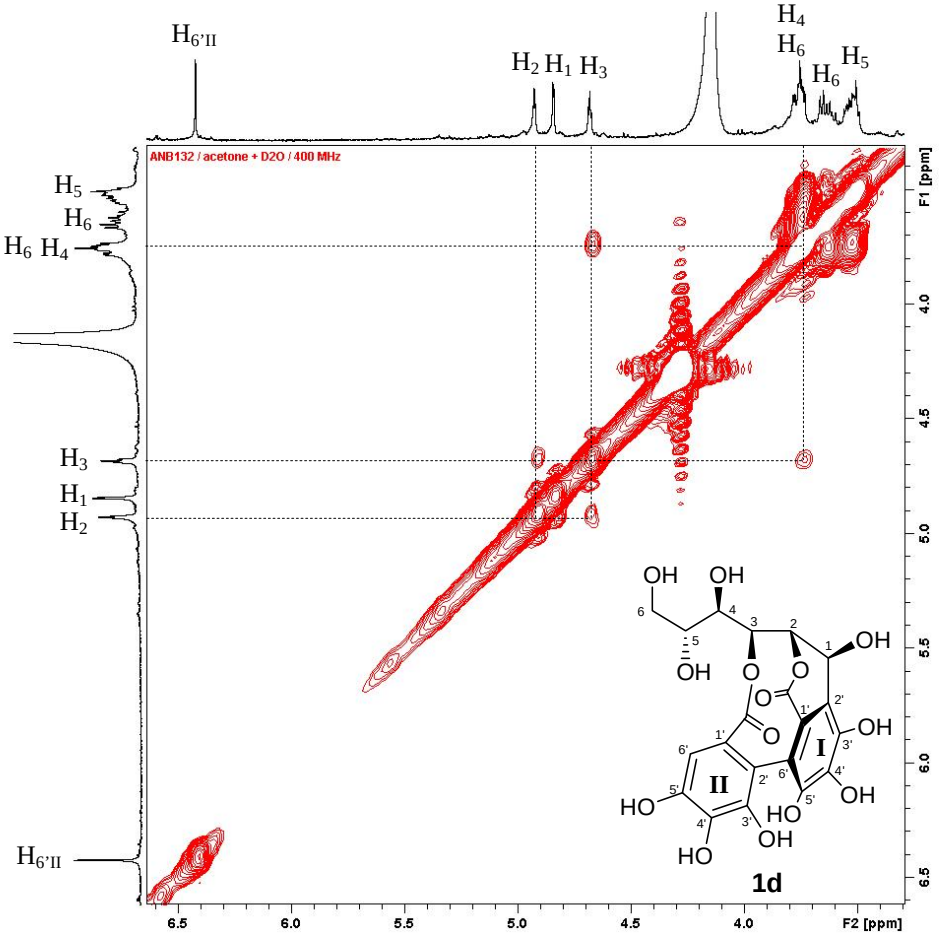




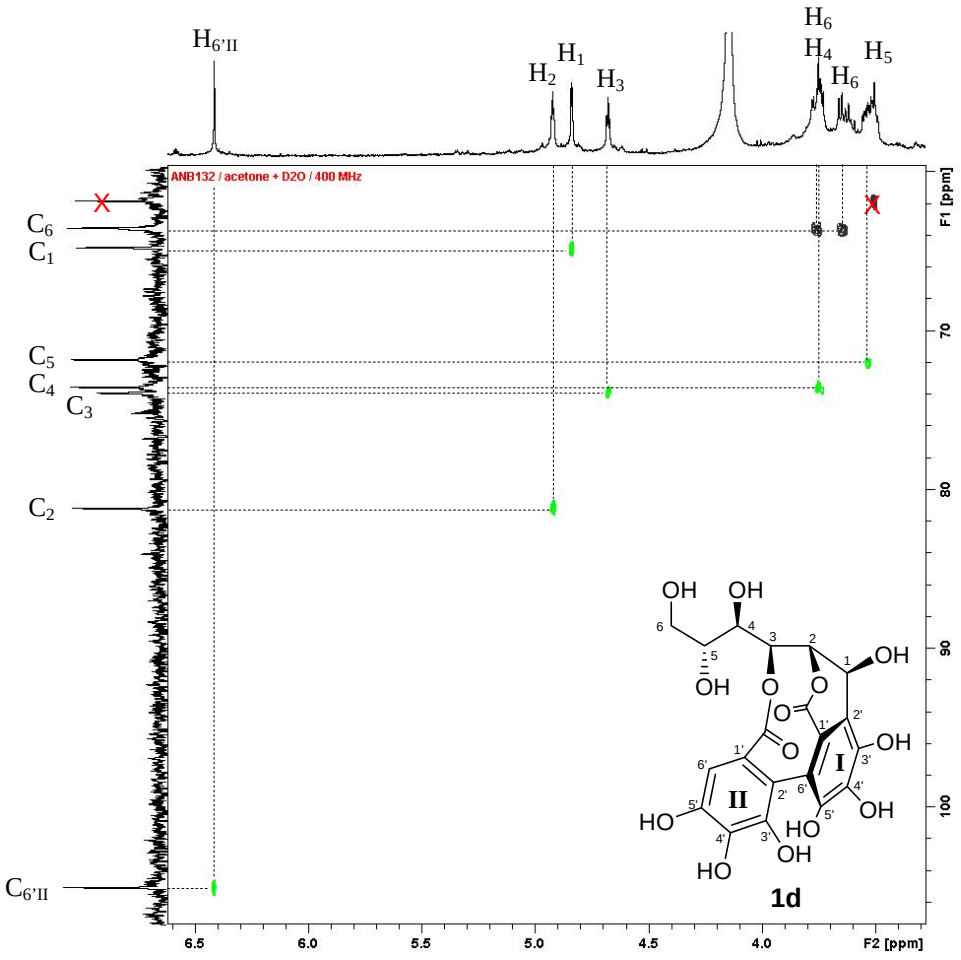
5-*O*-desgalloyl-epipunicacortein A (**1d**)

Peak Nr.	Data Point	Frequency	PPM	Intensity	%Int.
1	16002	2560.63	6.3995	22883876	7
2	18360	1964.93	4.9107	10237276	3.1
3	18369	1962.65	4.9050	15560459	4.7
4	18378	1960.38	4.8994	11419893	3.5
5	18499	1929.81	4.8230	17527060	5.3
6	18506	1928.04	4.8185	16507023	5
7	18745	1867.67	4.6676	9755505	3
8	18756	1864.89	4.6607	14021730	4.3
9	18767	1862.11	4.6538	8864376	2.7
10	19601	1651.42	4.1272	222677824	67.8
11	20180	1505.14	3.7616	13581372	4.1
12	20193	1501.86	3.7534	14200167	4.3
13	20214	1496.55	3.7402	16280302	5
14	20226	1493.52	3.7326	23618884	7.2
15	20239	1490.24	3.7244	18645908	5.7
16	20248	1487.96	3.7187	17111658	5.2
17	20260	1484.93	3.7111	15595108	4.7
18	20369	1457.40	3.6423	13916445	4.2
19	20391	1451.84	3.6284	15279323	4.6
20	20414	1446.03	3.6139	11579298	3.5
21	20437	1440.22	3.5994	12751497	3.9
22	20452	1436.43	3.5899	9024115	2.7
23	20478	1429.86	3.5735	8695014	2.6
24	20535	1415.46	3.5375	10052471	3.1
25	20548	1412.18	3.5293	10712378	3.3
26	20557	1409.90	3.5236	11441523	3.5
27	20571	1406.37	3.5148	13021095	4
28	20582	1403.59	3.5078	12278170	3.7
29	20592	1401.06	3.5015	14380900	4.4
30	20604	1398.03	3.4939	13495195	4.1
31	20618	1394.49	3.4851	17598772	5.4
32	20642	1388.43	3.4699	9592655	2.9
33	22874	824.56	2.0607	145909104	44.4
34	22882	822.54	2.0557	235314080	71.6
35	22891	820.27	2.0500	328625248	100
36	22900	817.99	2.0443	237550464	72.3
37	22909	815.72	2.0386	130078344	39.6

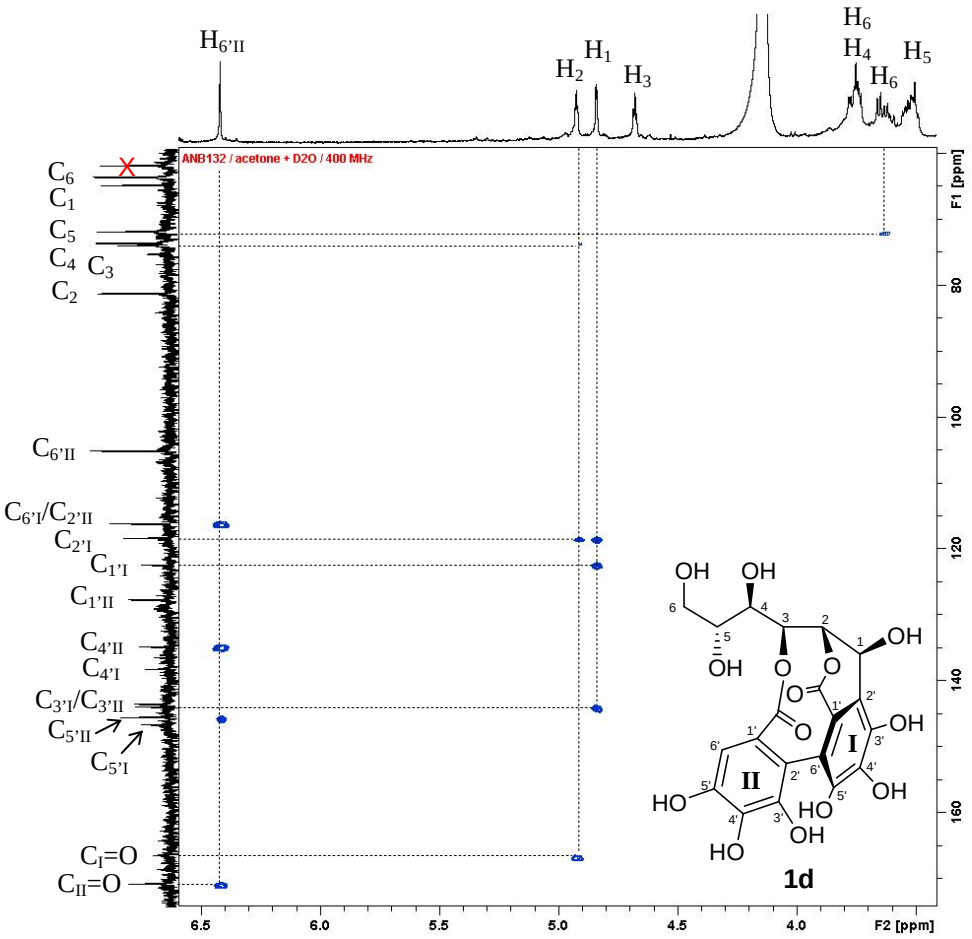
COSY ^{1}H-^{1}H of compound 1d



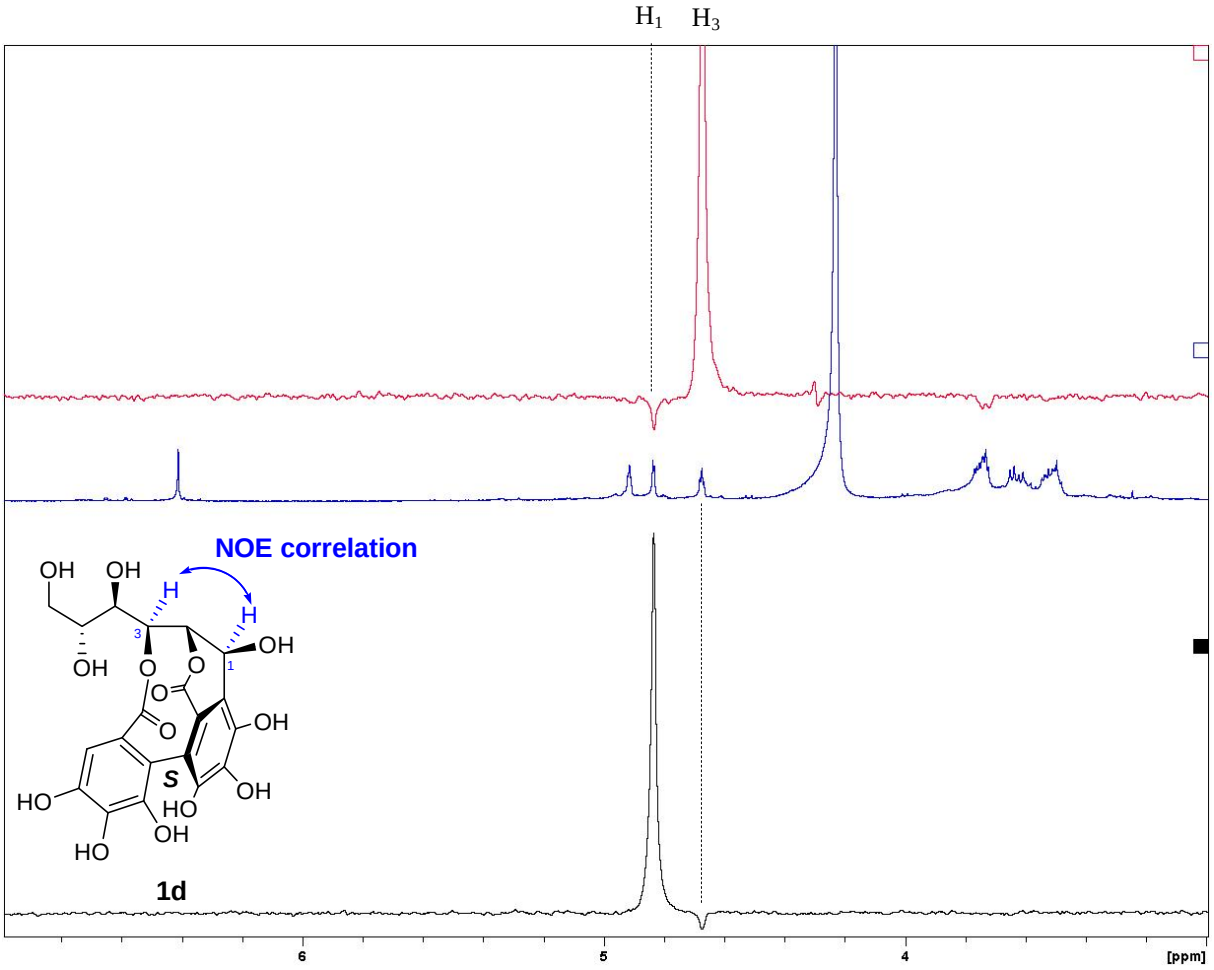
HSQC ^{1}H-^{13}C of compound 1d



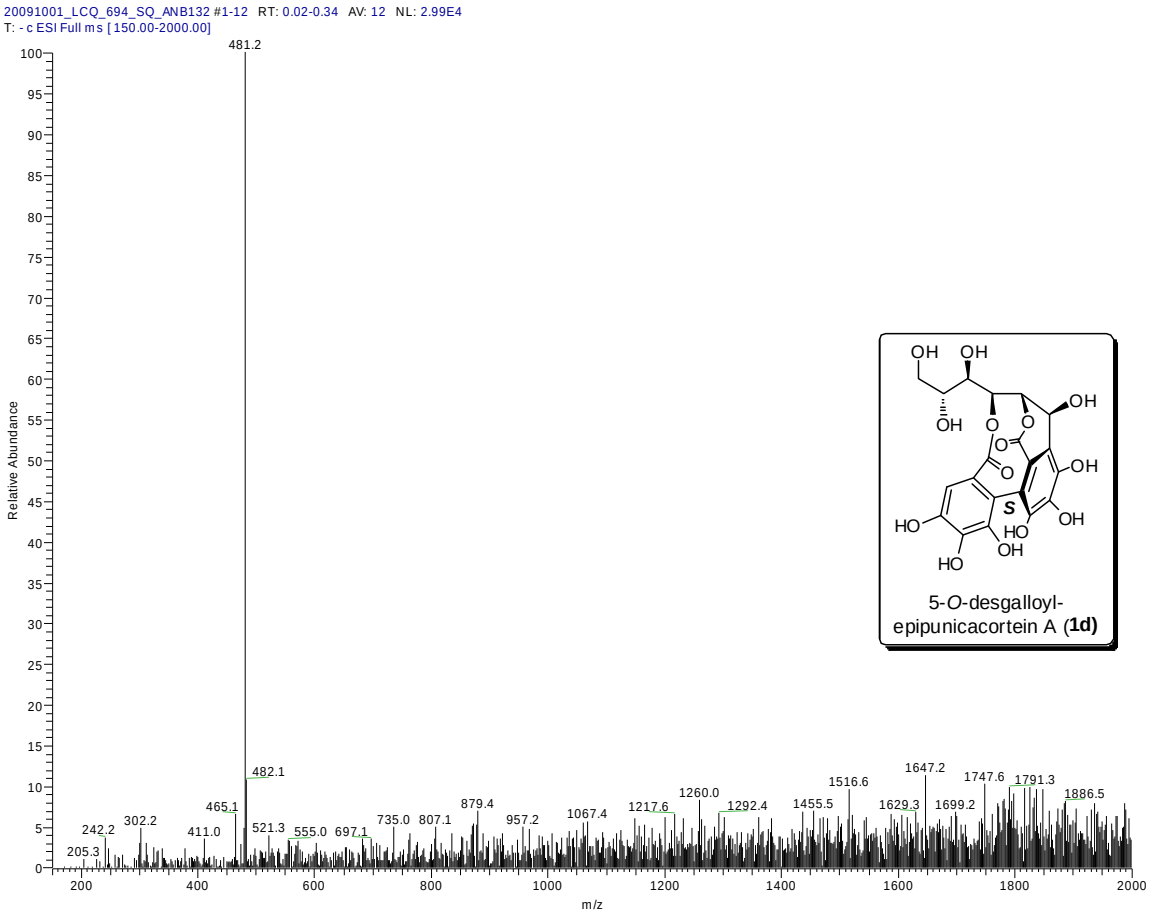
HMBC ^{1}H-^{13}C of compound 1d



Selective ROESY of compound 1d



ESIMS of compound 1d



HRMS (ESI-TOF) of compound 1d