

Supplementary Materials

Divergent synthesis of four monomeric ellagitannins toward the total synthesis of an oligomeric ellagitannin, nobotanin K

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1. General Methods

All commercially available reagents were used as received. All moisture and air sensitive reactions were carried out in glassware equipped with rubber septa (or a septum) under the positive pressure of argon or nitrogen. When necessary, the glassware was dried under reduced pressure by heating with a heat-gun and solvents were distilled prior to use. The substrates were azeotropically dried if needed by evaporation of their acetonitrile or toluene solution several times to remove trace water that may be contained to the substrates. The reaction mixture was magnetically stirred. Concentration was performed under reduced pressure.

The reactions were monitored by thin layer chromatography (TLC) and mass spectra (MS). Anhydrous MgSO_4 was used to dry organic layers after extraction, and it was removed by filtration through a cotton pad. The filtrate was concentrated and subjected to further purification protocols if necessary. This sequence was represented as “the general drying procedure” in the following experimental methods.

TLC was performed on Merck pre-coated silica gel 60 F-254 plates or Merck RP-19 F-254 plates. Spots were visualized by exposure to UV light, or by immersion into a solution of 2% anisaldehyde, 5% H_2SO_4 in ethanol or a solution of 10% phosphomolybdic acid in ethanol, followed by heating at ca. 200 °C.

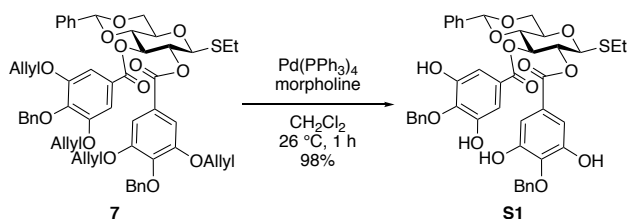
Column chromatography was performed on Merck silica gel 60 (63–200 or 40–63 μm) and Kanto Chemical silica gel 60 N (Spherical, neutral, 40–50 or 63–210 μm), wakogel 50NH₂ (38–63 μm , pH 8.5–11.5), for ordinary phase. The other carrier materials were noted in each case.

The melting points were determined using a Yanagimoto micro-melting point apparatus and uncorrected. Optical rotations were determined using a JASCO DIP-370 polarimeter with a 100 mm cell at 589 nm or a JASCO P-2100 polarimeter with a 100 mm cell at 589 nm. IR spectra were recorded on Shimadzu IRAffinity-1S with an attenuated total reflectance (ATR) sampling unit, and the major absorbance bands are all reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100LC spectrometer for electrospray ionization (ESI) method. The data are reported in units of mass to charge.

Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECX-400 (400 MHz for ^1H and 101 MHz for ^{13}C) or JNM-ECX-500 (500 MHz for ^1H and 126 MHz for ^{13}C) with either TMS or residual proton of deuterated solvent as internal reference in the indicated solvent in each parenthesis. The ^1H NMR spectroscopic data are indicated by a chemical shift (δ), with the multiplicity, the coupling constants, the integration, and the assignments in parentheses in this order. The multiplicities are abbreviated as s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, and br: broad. The ^{13}C NMR spectroscopic data are reported as the chemical shift (δ), with the hydrogen multiplicity obtained from the DEPT spectra and the assignments in parentheses. The multiplicities are abbreviated as s: C, d: CH, t: CH_2 , and q: CH_3 . When the number of the carbon was more than one, the number was added in the parentheses.

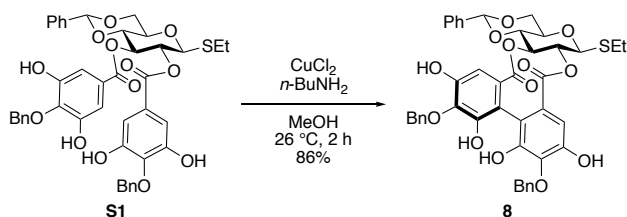
2. Experimental section and spectral data for synthetic compounds

Preparation of oxidative precursor S1



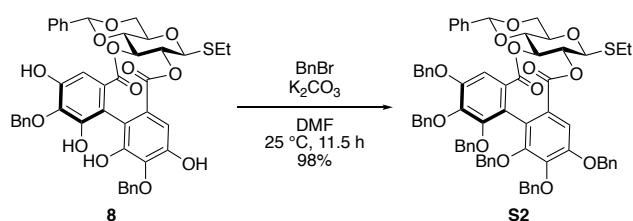
To a solution of **7** (11.3 g, 11.8 mmol) in CH_2Cl_2 (59 mL) were added morpholine (8.2 g, 94 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (137 mg, 118 μmol). The mixture was stirred for 1 h at 26 °C. After the addition of 1 M hydrochloric acid (50 mL), the reaction mixture was extracted with CH_2Cl_2 (40 mL \times 3). The combined organic layer was washed with H_2O . After the general drying procedure, the residue was purified by column chromatography (30 g of SiO_2 , *n*-hexane/ethyl acetate = 4/1 to 2/1) to give **S1** (9.2 g, 12 mmol, 98% yield) as a colorless amorphous solid. Data for **S1**: $[\alpha]_{\text{D}}^{24} +59$ (*c* 0.80, acetone). IR (ATR) 3717–2540, 3032, 2978, 2884, 1717, 1599, 1454, 1352, 1215, 1177, 1053, 914, 746, 696 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 °C) δ 7.46–7.27 (m, 15H, Bn), 7.13 (s, 2H, galloyl), 7.11 (s, 2H, galloyl), 5.85 (br s, 2H, OH), 5.79 (br s, 2H, OH), 5.72 (dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.51 (s, 1H, benzylidene), 5.40 (dd, *J* = 9.7, 9.7 Hz, 1H, H-2), 5.10 (s, 2H, Bn), 5.08 (s, 2H, Bn), 4.78 (d, *J* = 9.7 Hz, 1H, H-1), 4.43 (dd, *J* = 10.3, 5.2 Hz, 1H, H-6), 3.90 (dd, *J* = 9.7, 9.2 Hz, 1H, H-4), 3.84 (dd, *J* = 10.3, 9.7 Hz, 1H, H-6), 3.75 (ddd, *J* = 9.7, 9.7, 5.2 Hz, 1H, H-5), 2.79–2.68 (m, 2H, Et), 1.25 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ^{13}C NMR (126 MHz, CDCl_3 , 24 °C) δ 166.0 (s, galloyl), 165.5 (s, galloyl), 149.1 (s, 2C, galloyl), 149.0 (s, 2C, galloyl), 138.1 (s, galloyl), 138.0 (s, galloyl), 136.8 (s, Ar), 136.7 (s, 2C, Ar), 129.2 (d, Ar), 129.0 (d, 6C, Ar), 128.7 (d, 4C, Ar), 128.4 (d, 2C, Ar), 126.3 (d, 2C, Ar), 125.0 (s, galloyl), 124.8 (s, galloyl), 110.2 (d, 2C, galloyl), 110.1 (d, 2C, galloyl), 101.6 (d, benzylidene), 84.4 (d, C-1), 78.7 (d, C-4), 75.61 (t, Bn), 75.60 (t, Bn), 74.0 (d, C-3), 71.7 (d, C-2), 70.9 (d, C-5), 68.6 (t, C-6), 24.8 (t, Et), 15.0 (q, Et). HRMS (ESI) *m/z* $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{43}\text{H}_{40}\text{O}_{13}\text{SNa}$ 819.2087, found 819.2090.

Preparation of oxidative coupling product 8



To a solution of CuCl_2 (694 mg, 5.18 mmol) in MeOH (35 mL) was added *n*- BuNH_2 (5.5 g, 75 mmol). The mixture was stirred for 10 min at 26 °C. To a solution of **S1** (2.01 g, 2.52 mmol) in MeOH (90 mL) was added the MeOH solution of CuCl_2 /*n*- BuNH_2 . After stirring for 30 min, to the reaction mixture were added further CuCl_2 (221 mg, 1.65 mmol) and *n*- BuNH_2 (1.1 g, 15 mmol). After stirring for 35 min, to the reaction mixture were added further CuCl_2 (167 mg, 1.25 mmol) and *n*- BuNH_2 (1.1 g, 15 mmol). After stirring for 30 min, to the reaction mixture were added further CuCl_2 (248 mg, 1.85 mmol) and *n*- BuNH_2 (0.74 g, 10 mmol). After stirring for 25 min, to the reaction mixture were added Et_2O (50 mL) and 1 M hydrochloric acid (100 mL). The reaction mixture was extracted with Et_2O (100 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (50 g of SiO_2 , *n*-hexane/ethyl acetate = 4/1 to 2/1) to afford **8** (1.72 g, 2.16 mmol, 86% yield) as a brown amorphous solid. Data for **8**: $[\alpha]_{\text{D}}^{25} -67$ (*c* 0.69, acetone). IR (ATR) 3698–2766, 2968, 2874, 1753, 1703, 1607, 1499, 1362, 1221, 1165, 1096, 995, 752, 698 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , 24 °C) δ 7.49 (m, 2H, Bn), 7.42–7.32 (m, 13H, Bn), 6.69 (s, 1H, HHDP), 6.67 (s, 1H, HHDP), 5.76 (br s, 4H, OH), 5.53 (s, 1H, benzylidene), 5.36 (dd, *J* = 9.6, 9.2 Hz, 1H, H-3), 5.092 (s, 2H, Bn), 5.090 (s, 2H, Bn), 5.06 (dd, *J* = 10.1, 9.2 Hz, 1H, H-2), 4.74 (d, *J* = 10.1 Hz, 1H, H-1), 4.41 (dd, *J* = 10.3, 4.8 Hz, 1H, H-6), 3.87 (dd, *J* = 9.6, 9.6 Hz, 1H, H-4), 3.81 (dd, *J* = 10.3, 10.1 Hz, 1H, H-6), 3.60 (ddd, *J* = 10.1, 9.6, 4.8 Hz, 1H, H-5), 2.83–2.67 (m, 2H, Et), 1.30 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ^{13}C NMR (101 MHz, CDCl_3 , 23 °C) δ 168.5 (s, HHDP), 167.6 (s, HHDP), 149.1 (s, HHDP), 149.0 (s, HHDP), 147.4 (s, HHDP), 147.3 (s, HHDP), 136.59 (s, HHDP or Ar), 136.57 (s, HHDP or Ar), 136.5 (s, HHDP or Ar), 135.8 (s, HHDP or Ar), 135.7 (s, HHDP or Ar), 130.1 (s, HHDP), 129.9 (s, HHDP), 129.7 (d, Ar), 129.0 (d, 5C, Ar), 128.8 (d, 5C, Ar), 128.5 (d, 2C, Ar), 126.5 (d, 2C, Ar), 112.7 (s, HHDP), 112.5 (s, HHDP), 107.7 (d, HHDP), 107.3 (d, HHDP), 102.1 (d, benzylidene), 82.8 (d, C-1), 77.6 (d, C-4), 77.4 (d, C-3), 75.7 (t, 2C, Bn), 74.7 (d, C-2), 71.4 (d, C-5), 68.7 (t, C-6), 24.0 (t, Et), 15.2 (q, Et). HRMS (ESI) *m/z* $[\text{M} - \text{H}]^-$ calcd for $\text{C}_{43}\text{H}_{37}\text{O}_{13}\text{S}$ 793.1955, found 793.1951.

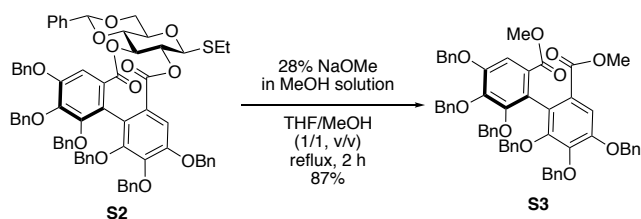
Preparation of benzylated compound S2



To a solution of **8** (734 mg, 923 μ mol) in DMF (10 mL) were added K_2CO_3 (689 mg, 4.99 mmol) and BnBr (0.79 g, 4.6 mmol). The mixture was stirred for 11.5 h at 25 $^{\circ}C$. After addition of ethyl acetate (30 mL) and 1 M hydrochloric acid (30 mL), the reaction mixture was extracted with ethyl acetate (30 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general

drying procedure, the residue was purified by column chromatography (30 g of SiO_2 , *n*-hexane/ethyl acetate = 4/1 to 2/1) to give **S2** (1.05 g, 907 μ mol, 98% yield) as a pale yellow amorphous solid. Data for **S2**: $[\alpha]_D^{24} -91$ (*c* 0.35, $CHCl_3$). IR (ATR) 3065, 3032, 2934, 2872, 1751, 1591, 1454, 1333, 1213, 1171, 1096, 908, 731, 696 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 24 $^{\circ}C$) δ 7.52 (dd, *J* = 7.5, 2.3 Hz, 2H, Ar), 7.49–7.28 (m, 18H, Ar), 7.27–7.20 (m, 6H, Ar), 7.14–7.07 (m, 5H, Ar), 7.00–6.95 (m, 4H, Ar), 6.98 (s, 1H, HHDP), 6.93 (s, 1H, HHDP), 5.60 (s, 1H, benzylidene), 5.45 (dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.21 (d, *J* = 10.9 Hz, 1H, Bn), 5.19 (d, *J* = 10.9 Hz, 1H, Bn), 5.13 (dd, *J* = 10.3, 9.2 Hz, 1H, H-2), 5.12 (d, *J* = 10.9 Hz, 1H, Bn), 5.08 (d, *J* = 10.9 Hz, 1H, Bn), 4.983 (d, *J* = 10.9 Hz, 1H, Bn), 4.978 (d, *J* = 10.9 Hz, 1H, Bn), 4.962 (d, *J* = 10.3 Hz, 1H, Bn), 4.958 (d, *J* = 10.3 Hz, 1H, Bn), 4.81 (d, *J* = 10.9 Hz, 1H, Bn), 4.802 (d, *J* = 10.9 Hz, 1H, Bn), 4.796 (d, *J* = 10.3 Hz, 1H, H-1), 4.66 (d, *J* = 10.3 Hz, 1H, Bn), 4.63 (d, *J* = 10.3 Hz, 1H, Bn), 4.43 (dd, *J* = 10.3, 4.6 Hz, 1H, H-6), 3.92 (dd, *J* = 9.7, 9.7 Hz, 1H, H-4), 3.86 (dd, *J* = 10.3, 9.7 Hz, 1H, H-6), 3.64 (ddd, *J* = 9.7, 9.7, 4.6 Hz, 1H, H-5), 2.87–2.73 (m, 2H, Et), 1.33 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ^{13}C NMR (126 MHz, $CDCl_3$, 23 $^{\circ}C$) δ 168.4 (s, HHDP), 167.6 (s, HHDP), 152.9 (s, 2C, HHDP), 152.8 (s, HHDP), 152.6 (s, HHDP), 144.62 (s, HHDP), 144.59 (s, HHDP), 137.7 (s, 2C, Bn), 137.6 (s, 2C, Bn), 136.9 (s, benzylidene), 136.6 (s, 2C, Bn), 129.6 (d, Ar), 129.0 (s, HHDP), 128.8 (s, HHDP), 128.74 (d, 2C, Ar), 128.69 (d, 2C, Ar), 128.5 (d, 6C, Ar), 128.33 (d, 5C, Ar), 128.27 (d, Ar), 128.11 (d, 4C, Ar), 128.09 (d, 2C, Ar), 127.97 (d, 2C, Ar), 128.0 (d, 2C, Ar), 127.8 (d, 4C, Ar), 127.65 (d, Ar), 127.63 (d, Ar), 126.5 (d, 2C, Ar), 122.3 (s, HHDP), 122.2 (s, HHDP), 107.4 (d, HHDP), 107.0 (d, HHDP), 101.9 (d, benzylidene), 82.9 (d, C-1), 77.6 (d, C-4), 77.1 (d, C-3), 75.7 (t, 2C, Bn), 75.50 (t, Bn), 75.45 (t, Bn), 74.6 (d, C-2), 71.6 (d, C-5), 71.5 (t, Bn), 71.4 (t, Bn), 68.7 (t, C-6), 23.8 (t, Et), 15.2 (q, Et). HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{71}H_{62}O_{13}SNa$ 1177.3809, found 1177.3793.

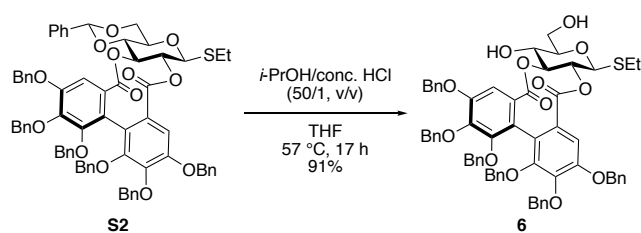
Preparation of known compound S3 for the confirmation of the axial chirality of S2



To a solution of **S2** (1.05 g, 907 μ mol) in MeOH (4.5 mL) and THF (4.5 mL) was added NaOMe (28% in MeOH solution, 739 mg, 207 mg as NaOMe, 3.83 mmol). The mixture was stirred for 2 h at reflux. After cooling to 0 $^{\circ}C$, to the reaction mixture were added ethyl acetate (30 mL) and 1 M hydrochloric acid (30 mL). The reaction mixture was extracted with ethyl acetate (30 mL \times 3). The combined

organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (20 g of SiO_2 , *n*-hexane/ethyl acetate = 6/1 to 1/2) to afford **S3** (714 mg, 787 μ mol, 87% yield) as a pale yellow oil. The 1H and ^{13}C NMR data for **S3** were in agreement with the literature data.¹ The specific optical rotation value of **S3** was $[\alpha]_D^{25} +33.7$ (*c* 0.35, $CHCl_3$), which was in good agreement with the literature data $\{[\alpha]_D^{25} +30.0$ (*c* 5.30, $CHCl_3$)}.¹

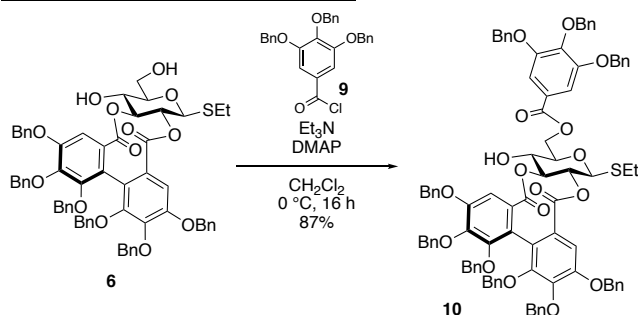
Preparation of common synthetic intermediate 6



procedure, the residue was purified by column chromatography (40 g of SiO_2 , *n*-hexane/ethyl acetate = 2/1 to 1/2) to give

6 (7.25 g, 6.79 mmol, 91% yield) as a pale yellow amorphous solid. Data for **6**: $[\alpha]_D^{24} -49$ (*c* 0.48, CHCl₃). IR (ATR) 3670–3138, 3065, 3030, 2938, 2872, 1751, 1591, 1497, 1371, 1240, 1182, 1096, 750, 696 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, 24 °C) δ 7.52–7.19 (m, 20H, Bn), 7.17–7.07 (m, 6H, Bn), 6.98 (dd, *J* = 7.5, 1.7 Hz, 4H, Bn), 6.97 (s, 1H, HHDP), 6.92 (s, 1H, HHDP), 5.24–5.18 (m, H-3, Bn \times 2), 5.11 (d, *J* = 11.5 Hz, 1H, Bn), 5.10 (d, *J* = 10.9 Hz, 1H, Bn), 5.03 (dd, *J* = 9.7, 9.7 Hz, 1H, H-2), 5.01–4.93 (m, 4H, Bn), 4.83 (d, *J* = 10.9 Hz, 1H, Bn), 4.82 (d, *J* = 10.9 Hz, 1H, Bn), 4.72 (d, *J* = 9.7 Hz, 1H, H-1), 4.68 (d, *J* = 10.9 Hz, 1H, Bn), 4.63 (d, *J* = 10.9 Hz, 1H, Bn), 4.02 (ddd, *J* = 9.7, 9.2, 4.6 Hz, 1H, H-4), 3.99 (ddd, *J* = 12.0, 5.2, 3.4 Hz, 1H, H-6), 3.89 (ddd, *J* = 12.0, 7.5, 4.6 Hz, 1H, H-6), 3.48 (ddd, *J* = 9.7, 4.6, 3.4 Hz, 1H, H-5), 2.85–2.70 (m, 2H, Et), 2.60 (br d, *J* = 4.6 Hz, 1H, 4-OH), 2.06 (br dd, *J* = 7.5, 5.2 Hz, 1H, 6-OH), 1.32 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ¹³C NMR (126 MHz, CDCl₃, 24 °C) δ 168.9 (s, HHDP), 167.6 (s, HHDP), 152.94 (s, HHDP), 152.88 (s, HHDP), 152.8 (s, HHDP), 152.7 (s, HHDP), 144.7 (s, HHDP), 144.5 (s, HHDP), 137.72 (s, Bn), 137.68 (s, Bn), 137.6 (s, 2C, Bn), 136.54 (s, Bn), 136.50 (s, Bn), 129.0 (s, HHDP), 128.7–127.6 (overlapping 30 doublets and 1 singlet: 11 peaks were observed, 31C, Bn and HHDP), 122.3 (s, HHDP), 122.0 (s, HHDP), 107.2 (d, HHDP), 106.9 (d, HHDP), 81.9 (d, C-1), 81.0 (d, C-3), 80.0 (d, C-5), 75.7 (t, 2C, Bn), 75.5 (t, 2C, Bn), 73.9 (d, C-2), 71.4 (t, 2C, Bn), 68.1 (d, C-4), 62.3 (t, C-6), 23.6 (t, Et), 15.3 (q, Et). HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₆₄H₅₈O₁₃SNa 1089.3496, found 1089.3480.

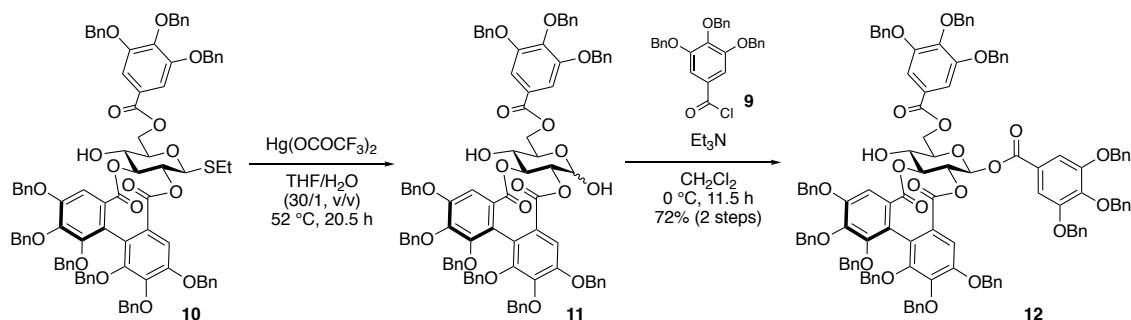
Preparation of mono-gallate **10**



3,4,5-Tri-*O*-benzylgallic acid chloride (**9**) was prepared via the reaction of 3,4,5-tri-*O*-benzylgallic acid with oxalyl chloride and catalytic amount of DMF in toluene according to the literature.² The obtained crude compound was used without further purification. To a solution **6** (2.42 g, 2.27 mmol) in CH₂Cl₂ (15 mL) was added Et₃N (1.17 g, 11.5 mmol). After stirring for 30 min at 0 °C, to the mixture was added a solution of prepared **9** (ca. 3.73 mmol) in CH₂Cl₂ (10 mL) through cannula. Inside of the flask that was the

container of **9** was rinsed with CH₂Cl₂ (10 mL \times 2); the used CH₂Cl₂ was also added to the reaction mixture. The mixture was stirred for 16 h at 0 °C. To the reaction mixture was added saturated aqueous sodium hydrogen carbonate (50 mL), and the aqueous mixture was extracted with CH₂Cl₂ (40 mL \times 3). The combined organic layer was washed with saturated aqueous sodium hydrogen carbonate. After the general drying procedure, the resulting residue was purified by column chromatography (two layered carriers; upper 45 g of SiO₂, lower 5 g of SiO₂·NH₂, *n*-hexane/ethyl acetate = 4/1 to 1/1) to give **10** (2.94 g, 1.97 mmol, 87% yield) as a pale yellow amorphous solid. Data for **10**: $[\alpha]_D^{23} -35$ (*c* 0.45, CHCl₃). IR (ATR) 3734–3129, 2976, 2947, 2882, 1753, 1591, 1454, 1327, 1209, 1111, 1057, 976, 748, 698 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, 24 °C) δ 7.47 (dd, *J* = 8.0, 1.7 Hz, 2H, Bn), 7.45–7.29 (m, 28H, Bn), 7.41 (s, 2H, galloyl), 7.27–7.20 (m, 6H, Bn), 7.13–7.08 (m, 5H, Bn), 7.01–6.95 (m, 4H, Bn), 6.99 (s, 1H, HHDP), 6.94 (s, 1H, HHDP), 5.26 (dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.22 (d, *J* = 11.5 Hz, 1H, Bn), 5.17 (d, *J* = 10.9 Hz, 1H, Bn), 5.14 (s, 2H, Bn), 5.13 (s, 4H, Bn), 5.11 (d, *J* = 11.5 Hz, 1H, Bn), 5.07 (d, *J* = 10.9 Hz, 1H, Bn), 5.05 (dd, *J* = 9.7, 9.7 Hz, 1H, H-2), 4.97 (d, *J* = 10.9 Hz, 3H, Bn), 4.95 (d, *J* = 10.9 Hz, 1H, Bn), 4.87 (dd, *J* = 12.0, 3.4 Hz, 1H, H-6), 4.82 (d, *J* = 10.9 Hz, 1H, Bn), 4.80 (d, *J* = 10.9 Hz, 1H, Bn), 4.72 (d, *J* = 9.7 Hz, 1H, H-1), 4.68 (d, *J* = 10.9 Hz, 1H, Bn), 4.63 (d, *J* = 10.9 Hz, 1H, Bn), 4.51 (dd, *J* = 12.0, 2.3 Hz, 1H, H-6), 3.80 (ddd, *J* = 9.7, 9.2, 4.0 Hz, 1H, H-4), 3.64 (ddd, *J* = 9.7, 3.4, 2.3 Hz, 1H, H-5), 3.24 (br d, *J* = 4.0 Hz, 1H, OH), 2.82 (dq, *J* = 12.6, 7.5 Hz, 1H, Et), 2.72 (dq, *J* = 12.6, 7.5 Hz, 1H, Et), 1.30 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ¹³C NMR (126 MHz, CDCl₃, 24 °C) δ 168.6 (s, HHDP), 167.7 (s, HHDP), 167.2 (s, galloyl), 152.93 (s, HHDP), 152.88 (s, HHDP), 152.78 (s, 2C, galloyl), 152.75 (s, HHDP), 152.7 (s, HHDP), 144.6 (s, HHDP), 144.5 (s, HHDP), 143.2 (s, galloyl), 137.74 (s, Bn), 137.68 (s, Bn), 137.61 (s, Bn), 137.59 (s, Bn), 137.4 (s, Bn), 136.63 (s, 2C, Bn), 136.56 (s, Bn), 136.5 (s, Bn), 129.0 (s, HHDP), 128.9 (s, HHDP), 128.7–127.7 (overlapping 45 doublets: 11 peaks were observed, 45C, Bn), 124.3 (s, galloyl), 122.3 (s, HHDP), 122.1 (s, HHDP), 109.7 (d, 2C, galloyl), 107.1 (d, HHDP), 107.0 (d, HHDP), 82.0 (d, C-1), 80.1 (d, C-3), 79.1 (d, C-5), 75.7 (t, 2C, Bn), 75.5 (t, 2C, Bn), 75.3 (t, Bn), 73.7 (d, C-2), 71.5 (t, 2C, Bn), 71.4 (t, Bn), 71.3 (t, Bn), 67.4 (d, C-4), 63.4 (t, C-6), 23.5 (t, Et), 15.5 (q, Et). HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₉₂H₈₀O₁₇SNa 1511.5014, found 1511.5011.

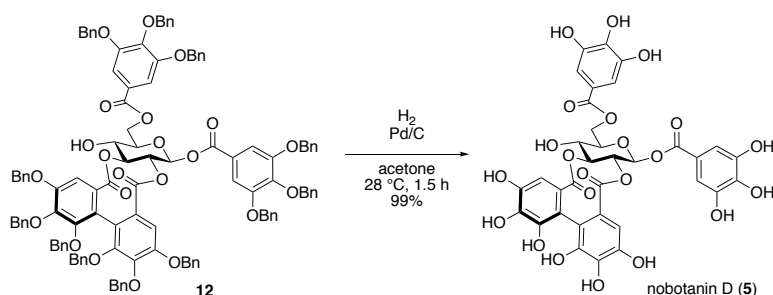
Preparation of β -galloyl ester **12**



A mixture of **10** (1.02 g, 682 μ mol) and $\text{Hg}(\text{OCOCF}_3)_2$ (814 mg, 1.91 mmol) in THF (13.5 mL) and H_2O (0.45 mL) was stirred for 20.5 h at 52 $^\circ\text{C}$. After cooling to 25 $^\circ\text{C}$, to the reaction mixture were added ethyl acetate (20 mL) and saturated aqueous sodium hydrogen carbonate (20 mL). The reaction mixture was extracted with ethyl acetate (25 mL \times 3). The combined organic layer was successively washed with 1 M hydrochloric acid and brine. After the general drying procedure, the resulting crude product was roughly purified by column chromatography (20 g of SiO_2 , *n*-hexane/ethyl acetate = 4/1 to 1/1) to give a crude product, the content of which was mostly **11**. The crude product was used without further purification.

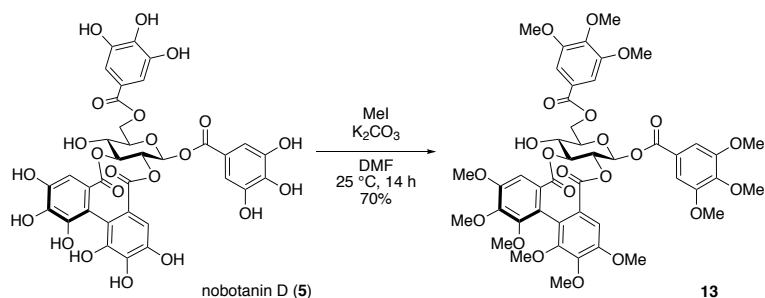
To a solution of the crude **11** in CH_2Cl_2 (5 mL) was added Et_3N (0.37 g, 3.6 mmol). After stirring for 15 min at 0 $^\circ\text{C}$, to the mixture was added a solution of prepared **9** (ca. 0.846 mmol) in CH_2Cl_2 (5 mL) through cannula. Inside of the flask that was the container of **9** was rinsed with CH_2Cl_2 (5 mL); the used CH_2Cl_2 was also added to the reaction mixture. The mixture was stirred for 11.5 h at 0 $^\circ\text{C}$. To the reaction mixture were added CH_2Cl_2 (20 mL) and saturated aqueous sodium hydrogen carbonate (30 mL), and the aqueous mixture was extracted with CH_2Cl_2 (30 mL \times 3). After the general drying procedure, the residue was purified by successive column chromatography (two layered carriers; upper 20 g of SiO_2 , lower 3 g of $\text{SiO}_2\cdot\text{NH}_2$, *n*-hexane/ethyl acetate = 4/1 to 2/1, followed by 20 g of SiO_2 , *n*-hexane/ethyl acetate = 4/1 to 2/1) to afford **12** (909 mg, 0.488 mmol, 72% yield) as a colorless amorphous solid. Data for **12**: $[\alpha]_{\text{D}}^{24} -23$ (*c* 0.37, CHCl_3). IR (ATR) 3624–3217, 3063, 3030, 2945, 2874, 1755, 1589, 1427, 1333, 1177, 1094, 908, 735, 694 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 $^\circ\text{C}$) δ 7.48–7.15 (m, 50H, Bn), 7.43 (s, 2H, galloyl), 7.38 (s, 2H, galloyl), 7.14–7.05 (m, 6H, Bn), 7.02 (s, 1H, HHDP), 7.01–6.93 (m, 4H, Bn), 6.87 (s, 1H, HHDP), 6.16 (d, J = 8.6 Hz, 1H, H-1), 5.43 (dd, J = 9.7, 9.5 Hz, 1H, H-3), 5.34 (dd, J = 9.7, 8.6 Hz, 1H, H-2), 5.18–5.06 (m, 11H, Bn), 5.03–4.95 (m, 9H, Bn), 4.87 (d, J = 10.9 Hz, 1H, Bn), 4.82 (d, J = 10.3 Hz, 1H, Bn), 4.82 (dd, J = 12.6, 1.7 Hz, 1H, H-6), 4.68 (d, J = 10.9 Hz, 1H, Bn), 4.67 (d, J = 10.9 Hz, 1H, Bn), 4.54 (dd, J = 12.6, 1.7 Hz, 1H, H-6), 3.89 (ddd, J = 9.5, 9.5, 5.7 Hz, 1H, H-4), 3.75 (m, 1H, H-5), 3.36 (d, J = 5.7 Hz, 1H, OH). ^{13}C NMR (126 MHz, CDCl_3 , 24 $^\circ\text{C}$) δ 168.7 (s, HHDP), 167.8 (s, HHDP), 167.1 (s, galloyl), 164.4 (s, galloyl), 152.9 (s, 2C, HHDP), 152.8 (s, HHDP), 152.72 (s, 2C, galloyl), 152.70 (s, 2C, galloyl), 152.68 (s, HHDP), 144.7 (s, HHDP), 144.6 (s, HHDP), 143.3 (s, galloyl), 143.1 (s, galloyl), 137.7 (s, Bn), 137.63 (s, Bn), 137.60 (s, Bn), 137.56 (s, Bn), 137.44 (s, Bn), 137.37 (s, Bn), 136.7 (s, 2C, Bn), 136.5 (s, Bn), 136.41 (s, Bn), 136.36 (s, 2C, Bn), 128.9 (s, HHDP), 128.7–127.7 (overlapping 60 doublets and 1 singlet: 16 peaks were observed, 61C, Bn and HHDP), 124.3 (s, galloyl), 123.6 (s, galloyl), 122.3 (s, HHDP), 122.1 (s, HHDP), 109.7 (d, 2C, galloyl), 109.4 (d, 2C, galloyl), 107.2 (d, HHDP), 107.1 (d, HHDP), 91.7 (d, C-1), 78.9 (d, C-3), 75.9 (d, C-5), 75.7 (t, Bn), 75.6 (t, Bn), 75.5 (t, Bn), 75.4 (t, Bn), 75.3 (t, Bn), 75.2 (t, Bn), 74.5 (d, C-2), 71.40 (t, 2C, Bn), 71.37 (t, Bn), 71.3 (t, Bn), 71.1 (t, 2C, Bn), 67.3 (d, C-4), 63.1 (t, C-6). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{118}\text{H}_{98}\text{O}_{22}\text{Na}$ 1889.6447, found 1889.6442.

Preparation of nobotanin D (5)



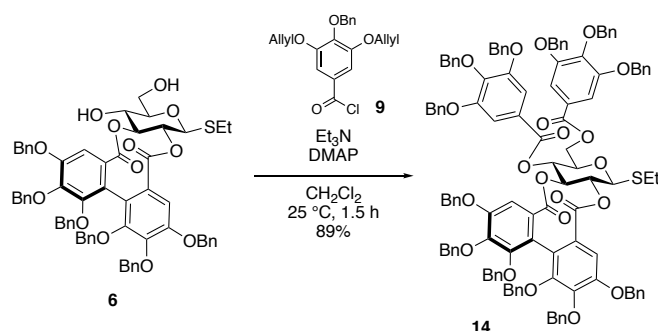
purified by column chromatography (5 g of Sephadex LH-20, MeOH) to afford nobotanin D (**5**) (71.7 mg, 91.2 μ mol, 99% yield) as a pale brown amorphous solid. Data for **5**: $[\alpha]_D^{25} +20$ (c 0.09, MeOH). IR (ATR) 3701–2824, 1717, 1622, 1456, 1350, 1221, 1043, 768 cm^{-1} . ^1H NMR (500 MHz, acetone- d_6 + D_2O , 23 $^\circ\text{C}$) δ 7.13 (s, 2H, galloyl), 7.12 (s, 2H, galloyl), 6.71 (s, 1H, HHDP), 6.42 (s, 1H, HHDP), 6.16 (d, J = 8.6 Hz, 1H, H-1), 5.24 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.06 (dd, J = 9.2, 8.6 Hz, 1H, H-2), 4.61 (dd, J = 12.0, 1.2 Hz, 1H, H-6), 4.46 (dd, J = 12.0, 5.2 Hz, 1H, H-6), 4.08 (m, 1H, H-5), 4.00 (dd, J = 9.7, 9.7 Hz, 1H, H-4). ^{13}C NMR (126 MHz, acetone- d_6 + D_2O , 24 $^\circ\text{C}$) δ 169.6 (s, HHDP), 169.0 (s, HHDP), 167.0 (s, galloyl), 165.4 (s, galloyl), 146.2 (s, 2C, galloyl), 146.0 (s, 2C, galloyl), 145.2 (s, HHDP), 145.1 (s, HHDP), 144.44 (s, HHDP), 144.36 (s, HHDP), 139.9 (s, galloyl), 139.0 (s, galloyl), 136.3 (s, HHDP), 136.2 (s, HHDP), 126.6 (s, HHDP), 126.1 (s, HHDP), 121.0 (s, galloyl), 119.7 (s, galloyl), 114.8 (s, HHDP), 114.5 (s, HHDP), 110.1 (d, 2C, galloyl), 109.8 (d, 2C, galloyl), 107.5 (d, HHDP), 107.1 (d, HHDP), 92.1 (d, C-1), 79.9 (d, C-3), 76.2 (d, C-5), 75.4 (d, C-2), 67.8 (d, C-4), 63.7 (t, C-6). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{34}\text{H}_{26}\text{O}_{22}\text{Na}$ 809.0813, found 809.0816.

Preparation of dodecamethylnobotanin D (13)



successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (15 g of SiO_2 , n -hexane/ethyl acetate = 2/1 to 1/2) to afford **13** (27.5 mg, 28.8 μ mol, 70% yield) as a colorless amorphous solid. Data for **13**: $[\alpha]_D^{24} -32$ (c 0.22, CHCl_3). IR (ATR) 3688–3146, 3019, 2941, 2843, 1755, 1589, 1458, 1335, 1204, 1126, 1001, 758 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 22 $^\circ\text{C}$) δ 7.33 (s, 2H, galloyl), 7.31 (s, 2H, galloyl), 6.83 (s, 1H, HHDP), 6.66 (s, 1H, HHDP), 6.12 (d, J = 8.0 Hz, 1H, H-1), 5.35 (dd, J = 9.7, 9.5 Hz, 1H, H-3), 5.26 (dd, J = 9.5, 8.0 Hz, 1H, H-2), 4.84 (dd, J = 12.6, 4.0 Hz, 1H, H-6), 4.55 (dd, J = 12.6, 2.3 Hz, 1H, H-6), 3.95 (s, 3H, OMe), 3.94 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3.92 (s, 6H, OMe), 3.91 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.87 (m, 1H, H-4), 3.86 (s, 6H, OMe), 3.84 (s, 3H, OMe), 3.81 (ddd, J = 9.7, 4.0, 2.3 Hz, 1H, H-5), 3.67 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.48 (br d, J = 3.4 Hz, 1H, OH). ^{13}C NMR (126 MHz, CDCl_3 , 22 $^\circ\text{C}$) δ 168.6 (s, HHDP), 167.9 (s, HHDP), 167.4 (s, galloyl), 164.3 (s, galloyl), 153.4 (s, HHDP), 153.3 (s, HHDP), 153.2 (s, 2C, galloyl), 153.1 (s, 2C, galloyl), 152.72 (s, HHDP), 152.67 (s, HHDP), 144.34 (s, HHDP), 144.30 (s, HHDP), 143.27 (s, galloyl), 143.0 (s, galloyl), 128.5 (s, HHDP), 128.2 (s, HHDP), 124.1 (s, galloyl), 123.5 (s, galloyl), 121.2 (s, HHDP), 121.1 (s, HHDP), 107.5 (d, 2C, galloyl), 107.4 (d, 2C, galloyl), 105.0 (d, HHDP), 104.8 (d, HHDP), 91.7 (d, C-1), 78.8 (d, C-3), 75.9 (d, C-5), 74.7 (d, C-2), 67.4 (d, C-4), 63.3 (t, C-6), 61.22 (q, OMe), 61.20 (q, OMe), 61.16 (q, 2C, OMe), 61.1 (q, 2C, OMe), 56.5 (q, 2C, OMe), 56.4 (q, 2C, OMe), 56.30 (q, OMe), 56.25 (q, OMe). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{46}\text{H}_{50}\text{O}_{22}\text{Na}$ 977.2691, found 977.2707.

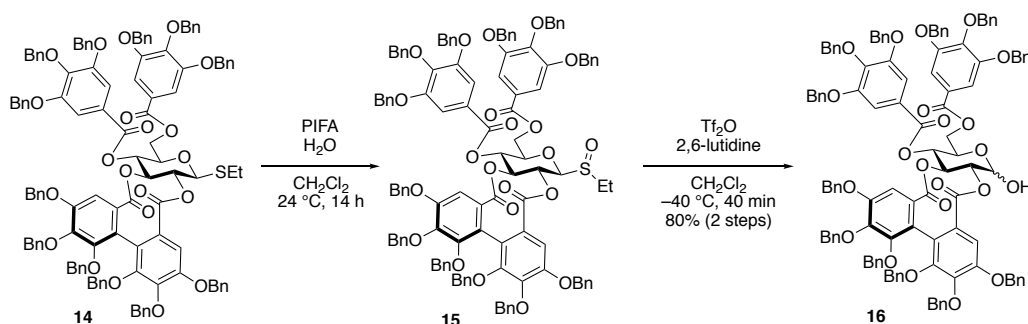
Preparation of digallate 14



To a solution of **6** (51.4 mg, 48.2 μ mol) in CH_2Cl_2 (0.25 mL) were added Et_3N (23.7 mg, 0.234 mmol) and DMAP (13.0 mg, 0.106 mmol). After stirring for 20 min at 0 $^\circ\text{C}$, to the mixture was added a solution of prepared **9** (ca. 0.151 mmol) in CH_2Cl_2 (0.5 mL) through cannula. Inside of the flask that was the container of **9** was rinsed with CH_2Cl_2 (0.5 mL); the used CH_2Cl_2 was also added to the reaction mixture. The mixture was stirred for 1.5 h at 25 $^\circ\text{C}$. To the reaction mixture was added saturated aqueous sodium hydrogen carbonate (20 mL), and the aqueous

mixture was extracted with CH_2Cl_2 (15 mL \times 3). The combined organic layer was washed with H_2O . After the general drying procedure, the resulting residue was purified by column chromatography (two layered carriers; upper 10 g of SiO_2 , lower 5 g of $\text{SiO}_2\cdot\text{NH}_2$, *n*-hexane/ethyl acetate = 4/1 to 2/1) to give **14** (82.0 mg, 42.9 μ mol, 89% yield) as a colorless amorphous solid. Data for **14**: $[\alpha]_D^{25}$ -19 (*c* 0.54, CHCl_3). IR (ATR) 3063, 3032, 2943, 2878, 1753, 1589, 1499, 1429, 1331, 1175, 1098, 735, 694 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 $^\circ\text{C}$) δ 7.47 (dd, J = 8.0, 1.7 Hz, 2H, Bn), 7.44–7.35 (m, 10H, Bn), 7.38 (s, 2H, galloyl), 7.36 (s, 2H, galloyl), 7.34–7.18 (m, 38H, Bn), 7.13–7.03 (m, 6H, Bn), 7.00–6.96 (m, 2H, Bn), 6.95 (s, 1H, HHDP), 6.91 (dd, J = 8.0, 1.7 Hz, 2H, Bn), 6.78 (s, 1H, HHDP), 5.61 (dd, J = 9.7, 9.7 Hz, 1H, H-4), 5.48 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.21 (d, J = 11.5 Hz, 1H, Bn), 5.18 (dd, J = 9.7, 9.2 Hz, 1H, H-2), 5.15–5.06 (m, 10H, Bn), 5.03 (s, 4H, Bn), 4.97 (d, J = 10.9 Hz, 1H, Bn), 4.96 (d, J = 10.9 Hz, 1H, Bn), 4.95 (d, J = 10.9 Hz, 2H, Bn), 4.93 (d, J = 10.9 Hz, 1H, Bn), 4.81 (d, J = 10.9 Hz, 1H, Bn), 4.81 (d, J = 10.9 Hz, 1H, Bn), 4.79 (d, J = 9.7 Hz, 1H, H-1), 4.74 (dd, J = 12.0, 2.9 Hz, 1H, H-6), 4.65 (d, J = 10.9 Hz, 1H, Bn), 4.63 (d, J = 10.9 Hz, 1H, Bn), 4.29 (dd, J = 12.0, 5.2 Hz, 1H, H-6), 4.04 (ddd, J = 9.7, 5.2, 2.9 Hz, 1H, H-5), 2.80 (dq, J = 12.6, 7.5 Hz, 1H, Et), 2.72 (dq, J = 12.6, 7.5 Hz, 1H, Et), 1.28 (dd, J = 7.5, 7.5 Hz, 3H, Et). ^{13}C NMR (126 MHz, CDCl_3 , 24 $^\circ\text{C}$) δ 168.5 (s, HHDP), 167.4 (s, HHDP), 165.8 (s, galloyl), 164.8 (s, galloyl), 153.0 (s, HHDP), 152.84 (s, 2C, galloyl), 152.77 (s, HHDP), 152.7 (s, HHDP), 152.64 (s, 2C, galloyl), 152.61 (s, HHDP), 144.7 (s, HHDP), 144.6 (s, HHDP), 143.4 (s, galloyl), 142.8 (s, galloyl), 137.7 (s, Bn), 137.60 (s, 2C, Bn), 137.57 (s, 2C, Bn), 137.5 (s, Bn), 136.8 (s, 2C, Bn), 136.53 (s, Bn), 136.45 (s, 2C, Bn), 136.4 (s, Bn), 128.9 (s, HHDP), 128.8–127.6 (overlapping 60 doublets and 1 singlet: 17 peaks were observed, 61C, Bn and HHDP), 124.7 (s, galloyl), 123.9 (s, galloyl), 122.2 (s, HHDP), 122.1 (s, HHDP), 109.5 (d, 2C, galloyl), 109.3 (d, 2C, galloyl), 107.5 (d, HHDP), 107.2 (d, HHDP), 82.2 (d, C-1), 78.5 (d, C-3), 76.5 (d, C-5), 75.8 (t, Bn), 75.7 (t, Bn), 75.5 (t, Bn), 75.40 (t, Bn), 75.36 (t, Bn), 75.3 (t, Bn), 74.0 (d, C-2), 71.5 (t, Bn), 71.4 (t, 2C, Bn), 71.3 (t, 2C, Bn), 71.2 (t, Bn), 68.5 (d, C-4), 63.2 (t, C-6), 23.6 (t, Et), 15.3 (q, Et). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{120}\text{H}_{102}\text{O}_{21}\text{SNa}$ 1933.6532, found 1933.6534.

Preparation of hemiacetal 16



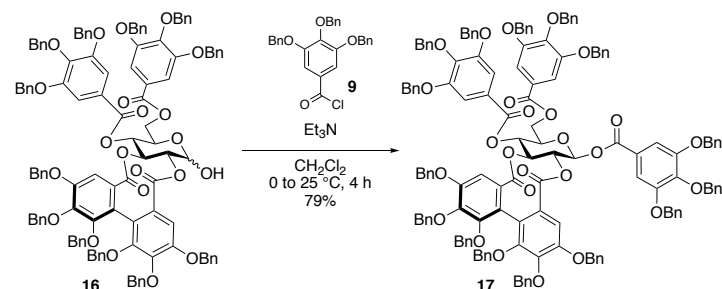
To a solution of **14** (492 mg, 257 μ mol) in CH_2Cl_2 (2.6 mL) were added H_2O (10.0 mg, 555 μ mol) and PIFA (136 mg, 316 μ mol). The mixture was stirred for 14 h at 24 $^\circ\text{C}$. After the addition of saturated aqueous sodium hydrogen carbonate (20 mL), the reaction mixture was extracted with CH_2Cl_2 (15 mL \times 3). After the general drying procedure, the mixture, the main content of which was **15**, was used without further purification.

To a solution of the crude **15** (574 mg) in CH_2Cl_2 (5 mL) was added 2,6-lutidine (59.8 mg, 558 μ mol). After stirring for 30 min at -40 $^\circ\text{C}$, to the mixture was added Tf_2O (172 mg, 610 μ mol). The mixture was additionally stirred for 40 min

at $-40\text{ }^{\circ}\text{C}$. After raising temperature to $0\text{ }^{\circ}\text{C}$, to the reaction mixture was added saturated aqueous sodium hydrogen carbonate (30 mL) and extracted with CH_2Cl_2 (25 mL \times 3). The combined organic layer was washed with H_2O . After the general drying procedure, the resulting residue was purified by column chromatography (20 g of SiO_2 , *n*-hexane/ethyl acetate = 4/1 to 2/1) to give **16** (384 mg, 205 μmol , 80% yield in 2 steps) as a pale yellow amorphous solid.

Partial data for **16**: IR (ATR) 3632–3169, 3063, 3032, 2945, 2876, 1753, 1589, 1427, 1331, 1213, 1175, 1096, 966, 735, 694 cm^{-1} . HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{118}\text{H}_{98}\text{O}_{22}\text{Na}$ 1889.6447, found 1889.6442.

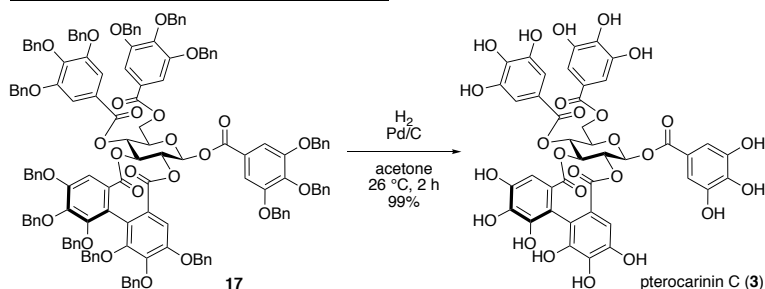
Preparation of β -galloyl ester **17**



To a solution **16** (166 mg, 88.9 μmol) in CH_2Cl_2 (0.5 mL) was added Et_3N (40.7 mg, 402 μmol). After stirring for 10 min at $0\text{ }^{\circ}\text{C}$, to the mixture was added a solution of prepared **9** (ca. 164 μmol) in CH_2Cl_2 (0.5 mL) through cannula. Inside of the flask that was the container of **9** was rinsed with CH_2Cl_2 (0.5 mL \times 2); the used CH_2Cl_2 was also added to the reaction mixture. The mixture was stirred for 4 h at $25\text{ }^{\circ}\text{C}$. To the reaction mixture was added saturated aqueous

sodium hydrogen carbonate (20 mL), and the mixture was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was washed with H_2O . After the general drying procedure, the resulting residue was purified by column chromatography (two layered carriers; upper 15 g of SiO_2 , lower 5 g of $\text{SiO}_2\cdot\text{NH}_2$, *n*-hexane/ethyl acetate = 4/1 to 2/1) to give **17** (161 mg, 70.2 μmol , 79% yield) as a colorless amorphous solid. Data for **17**: $[\alpha]_{\text{D}}^{25} -1.4$ (*c* 0.34, CHCl_3). IR (ATR) 3065, 3030, 2943, 2872, 1732, 1589, 1429, 1339, 1194, 1098, 735, 694 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , $24\text{ }^{\circ}\text{C}$) δ 7.45 (dd, *J* = 8.6, 1.7 Hz, 4H, Bn), 7.41 (s, 2H, galloyl), 7.39 (s, 2H, galloyl), 7.38 (s, 2H, galloyl), 7.38–7.18 (m, 61H, Bn), 7.12–7.03 (m, 6H, Bn), 6.97 (dd, *J* = 7.5, 2.3 Hz, 2H, Bn), 6.91 (dd, *J* = 8.0, 1.7 Hz, 2H, Bn), 6.82 (br s, 1H, HHDP), 6.81 (s, 1H, HHDP), 6.24 (d, *J* = 8.6 Hz, 1H, H-1), 5.68 (dd, *J* = 9.7, 9.2 Hz, 1H, H-4), 5.62 (dd, *J* = 9.2, 8.6 Hz, 1H, H-3), 5.49 (dd, *J* = 8.6, 8.6 Hz, 1H, H-2), 5.21–4.92 (m, 26H, Bn), 4.84 (d, *J* = 10.9 Hz, 1H, Bn), 4.83 (d, *J* = 10.9 Hz, 1H, Bn), 4.73 (dd, *J* = 14.9, 5.2 Hz, 1H, H-6), 4.70 (d, *J* = 10.9 Hz, 1H, Bn), 4.63 (d, *J* = 10.9 Hz, 1H, Bn), 4.33–4.21 (m, 2H, H-5, H-6). ^{13}C NMR (126 MHz, CDCl_3 , $24\text{ }^{\circ}\text{C}$) δ 168.3 (s, HHDP), 167.6 (s, HHDP), 165.7 (s, galloyl), 164.8 (s, galloyl), 164.3 (s, galloyl), 153.0 (s, HHDP), 152.9 (s, 2C, galloyl), 152.80 (s, 2C, galloyl), 152.75 (s, galloyl), 152.7 (s, HHDP), 152.63 (s, 2C, galloyl), 152.61 (s, HHDP), 144.8 (s, 2C, HHDP), 143.5 (s, galloyl), 143.4 (s, galloyl), 142.7 (s, galloyl), 137.7 (s, Bn), 137.63 (s, Bn), 137.58 (s, Bn), 137.5 (s, 2C, Bn), 137.44 (s, Bn), 137.38 (s, Bn), 136.9 (s, 2C, Bn), 136.44 (s, 3C, Bn), 136.41 (s, 2C, Bn), 136.3 (s, Bn), 128.8–127.6 (overlapping 75 doublets and 2 singlets: 18 peaks were observed, 77C, Bn and HHDP), 124.7 (s, galloyl), 123.7 (s, galloyl), 123.4 (s, galloyl), 122.4 (s, HHDP), 122.1 (s, HHDP), 109.6 (d, 2C, galloyl), 109.5 (d, 2C, galloyl), 109.2 (d, 2C, galloyl), 107.5 (d, HHDP), 107.3 (d, HHDP), 91.7 (d, C-1), 77.3 (d, C-3), 75.7 (t, 2C, Bn), 75.4 (t, 3C, Bn), 75.3 (t, 2C, Bn), 74.7 (d, C-2), 73.6 (d, C-5), 71.6 (t, Bn), 71.4 (t, 2C, Bn), 71.3 (t, Bn), 71.2 (t, 4C, Bn), 68.3 (d, C-4), 63.0 (t, C-6). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{146}\text{H}_{120}\text{O}_{26}\text{Na}$ 2311.7966, found 2311.7961.

Preparation of pterocarinin C (**3**)

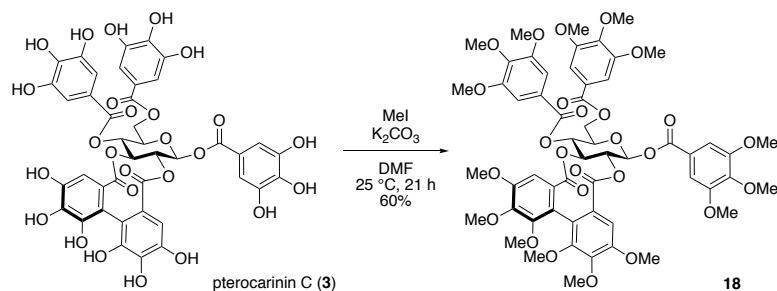


To a solution of **17** (124 mg, 54.0 μmol) in acetone (1.5 mL) was added Pd/C (10 wt% on carbon, 34.8 mg, 3.48 mg as Pd, 32.7 μmol). The mixture was stirred for 2 h at $26\text{ }^{\circ}\text{C}$ under the positive rubber balloon-pressure of hydrogen. The mixture was filtered through a Celite pad to remove excess Pd/C. After the washing of the pad with acetone, acetone was removed by

evaporation. The residue was purified by column chromatography (5 g of Sephadex LH-20, acetone to MeOH) to give pterocarinin C (**3**) (50.4 mg, 53.7 μmol , 99% yield) as a colorless amorphous solid. Data for **3**: $[\alpha]_{\text{D}}^{26} +72$ (*c* 0.07, acetone). $[\alpha]_{\text{D}}^{25} +57$ (*c* 1.0, acetone). IR (ATR) 3696–2446, 2986, 2909, 1715, 1450, 1321, 1207, 1038, 762 cm^{-1} . ^1H NMR (500 MHz, acetone- d_6 , $24\text{ }^{\circ}\text{C}$) δ 7.18 (s, 2H, galloyl), 7.17 (s, 2H, galloyl), 7.14 (s, 2H, galloyl), 6.46 (s, 1H, HHDP), 6.44 (s,

1H, HHDP), 6.36 (d, $J = 8.6$ Hz, 1H, H-1), 5.66–5.58 (m, 2H, H-4, H-3), 5.22 (dd, $J = 9.2, 8.6$ Hz, 1H, H-2), 4.57 (dd, $J = 12.0, 1.7$ Hz, 1H, H-6), 4.53 (ddd, $J = 9.2, 4.0, 1.7$ Hz, 1H, H-5), 4.39 (dd, $J = 12.0, 4.0$ Hz, 1H, H-6). ^{13}C NMR (126 MHz, acetone- d_6 , 24 °C) δ 168.6 (s, HHDP), 168.2 (s, HHDP), 166.0 (s, galloyl), 165.2 (s, galloyl), 164.5 (s, galloyl), 145.8 (s, 2C, galloyl), 145.7 (s, 2C, galloyl), 145.6 (s, 2C, galloyl), 144.63 (s, HHDP), 144.60 (s, HHDP), 144.4 (s, 2C, HHDP), 139.5 (s, galloyl), 139.1 (s, galloyl), 138.6 (s, galloyl), 136.12 (s, HHDP), 136.11 (s, HHDP), 125.8 (s, HHDP), 125.6 (s, HHDP), 120.8 (s, galloyl), 120.1 (s, galloyl), 119.4 (s, galloyl), 114.4 (s, HHDP), 114.2 (s, HHDP), 109.83 (d, 2C, galloyl), 109.78 (d, 2C, galloyl), 109.6 (d, 2C, galloyl), 106.9 (d, HHDP), 106.7 (d, HHDP), 91.6 (d, C-1), 77.0 (d, C-3), 75.0 (d, C-2), 73.7 (d, C-5), 67.4 (d, C-4), 62.3 (t, C-6). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{41}\text{H}_{30}\text{O}_{26}\text{Na}$ 961.0923, found 961.0919.

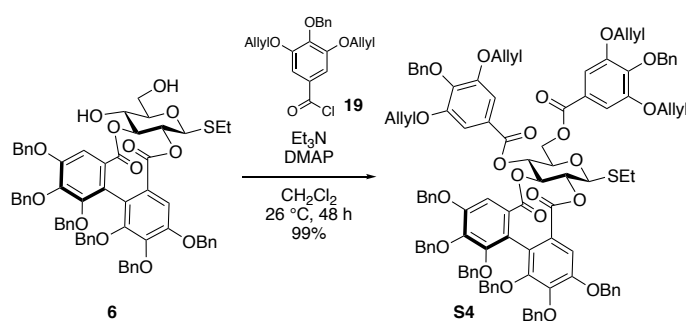
Preparation of pentadecamethylpterocarnin C (18)



To a solution of pterocarnin C (**3**) (42.5 mg, 45.3 μmol) in DMF (1.0 mL) were added K_2CO_3 (205 mg, 1.49 mmol) and MeI (228 mg, 1.61 mmol). The mixture was stirred for 21 h at 25 °C. After cooling 0 °C, to the mixture were added ethyl acetate (20 mL) and 1 M hydrochloric acid (30 mL). The reaction mixture was extracted with ethyl acetate (20

mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by successive column chromatography (20 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 2/1 followed by 15 g of SiO_2 , n -hexane/chloroform = 2/1 to 0/1) to give **18** (31.1 mg, 27.1 μmol , 60% yield) as a colorless amorphous solid. Data for **18**: $[\alpha]_D^{23} +13.2$ (c 1.01, CHCl_3). IR (ATR) 2995, 2940, 2839, 1728, 1589, 1456, 1333, 1209, 1125, 1032, 999, 914, 758, 731 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 °C) δ 7.32 (s, 2H, galloyl), 7.28 (s, 2H, galloyl), 7.24 (s, 2H, galloyl), 6.68 (s, 1H, HHDP), 6.59 (s, 1H, HHDP), 6.23 (d, $J = 8.6$ Hz, 1H, H-1), 5.64–5.56 (m, 2H, H-4, H-3), 5.45 (dd, $J = 9.2, 8.6$ Hz, 1H, H-2), 4.70 (dd, $J = 12.6, 2.9$ Hz, 1H, H-6), 4.38 (dd, $J = 12.6, 6.3$ Hz, 1H, H-6), 4.28 (m, 1H, H-5), 3.94 (s, 6H, OMe), 3.91 (s, 3H, OMe), 3.904 (s, 6H, OMe), 3.899 (s, 3H, OMe), 3.897 (s, 3H, OMe), 3.88 (s, 6H, OMe), 3.864 (s, 3H, OMe), 3.858 (s, 3H, OMe), 3.85 (s, 6H, OMe), 3.69 (s, 3H, OMe), 3.64 (s, 3H, OMe). ^{13}C NMR (126 MHz, CDCl_3 , 24 °C) δ 168.3 (s, HHDP), 167.7 (s, HHDP), 165.8 (s, galloyl), 164.9 (s, galloyl), 164.3 (s, galloyl), 153.4 (s, 2C, HHDP), 153.22 (s, 2C, galloyl), 153.20 (s, 2C, galloyl), 153.0 (s, 2C, galloyl), 152.7 (s, HHDP), 152.6 (s, HHDP), 144.52 (s, HHDP), 144.49 (s, HHDP), 143.4 (s, galloyl), 143.1 (s, galloyl), 142.6 (s, galloyl), 128.2 (s, HHDP), 128.1 (s, HHDP), 124.5 (s, galloyl), 123.6 (s, galloyl), 123.3 (s, galloyl), 121.4 (s, HHDP), 121.0 (s, HHDP), 107.5 (d, 2C, galloyl), 107.21 (d, 2C, galloyl), 107.19 (d, 2C, galloyl), 105.1 (d, HHDP), 105.0 (d, HHDP), 91.7 (d, C-1), 77.3 (d, C-3), 74.8 (d, C-2), 73.6 (d, C-5), 68.5 (d, C-4), 63.2 (t, C-6), 61.21 (q, 2C, OMe), 61.15 (q, OMe), 61.13 (q, OMe), 61.07 (q, 2C, OMe), 61.0 (q, OMe), 56.4 (q, 4C, OMe), 56.34 (q, 2C, OMe), 56.32 (q, OMe), 56.1 (q, OMe). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{56}\text{H}_{60}\text{O}_{26}\text{Na}$ 1171.3271, found 1171.3262.

Preparation of digallate S4

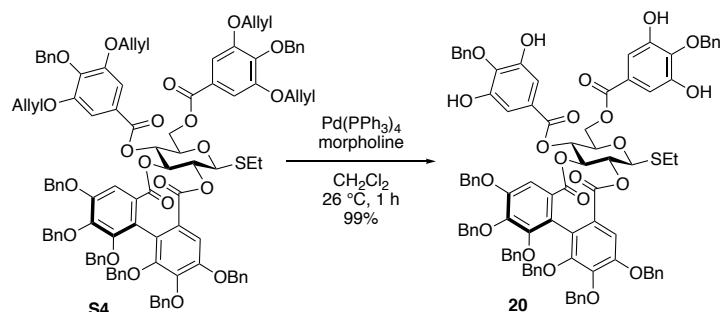


3,5-Di-*O*-allyl-4-*O*-benzylgallic acid chloride (**19**) was prepared via the reaction of 3,5-di-*O*-Allyl-4-*O*-benzylgallic acid with oxalyl chloride and catalytic amount of DMF in toluene according to the literature.³ The obtained crude compound was used without further purification. To a solution **6** (3.38 g, 3.16 mmol) in CH_2Cl_2 (8 mL) were added Et_3N (1.8 g, 18 mmol) and DMAP (481 mg, 3.94 mmol). After stirring for 15 min at 0 °C, to the mixture was further added prepared **19**

(ca. 9.25 mmol) in CH_2Cl_2 (8 mL) through cannula. Inside of the flask that was the container of **19** was rinsed with CH_2Cl_2 (8 mL \times 2); the used CH_2Cl_2 was also added to the reaction mixture. The mixture was stirred for 48 h at 26 °C. To the reaction mixture were added CH_2Cl_2 (20 mL) and saturated aqueous sodium hydrogen carbonate (30 mL) and the mixture

was extracted with CH₂Cl₂ (30 mL × 3). After the general drying procedure, the residue was purified by column chromatography (two layered carriers; upper 25 g of SiO₂, lower 5 g of SiO₂·NH₂, *n*-hexane/ethyl acetate = 4/1 to 2/1) to give **S4** (5.34 g, 3.12 mmol, 99% yield) as a pale yellow amorphous solid. Data for **S4**: [α]_D²² –19 (*c* 0.10, CHCl₃). IR (ATR) 3065, 3032, 2932, 2872, 1724, 1585, 1431, 1329, 1175, 1096, 908, 731, 696 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, 23 °C) δ 7.51–7.19 (m, 30H, Bn), 7.29 (s, 2H, galloyl), 7.26 (s, 2H, galloyl), 7.13–7.03 (m, 6H, Bn), 6.97 (dd, *J* = 7.5, 1.7 Hz, 2H, Bn), 6.94 (s, 1H, HHDP), 6.92 (dd, *J* = 8.0, 1.7 Hz, 2H, HHDP), 6.73 (s, 1H, HHDP), 6.05 (ddt, *J* = 17.2, 10.9, 5.2 Hz, 2H, Allyl), 5.97 (ddt, *J* = 17.2, 10.3, 5.2 Hz, 2H, Allyl), 5.59 (dd, *J* = 9.7, 9.7 Hz, 1H, H-4), 5.46 (dd, *J* = 9.7, 9.7 Hz, 1H, H-3), 5.43 (ddt, *J* = 17.2, 1.7, 1.2 Hz, 2H, Allyl), 5.34 (ddt, *J* = 17.2, 1.7, 1.2 Hz, 2H, Allyl), 5.27 (ddt, *J* = 10.9, 1.7, 1.2 Hz, 2H, Allyl), 5.20 (ddt, *J* = 10.3, 1.7, 1.2 Hz, 2H, Allyl), 5.19 (dd, *J* = 10.3, 9.7 Hz, 1H, H-2), 5.18 (d, *J* = 10.9 Hz, 1H, Bn), 5.14 (d, *J* = 10.9 Hz, 1H, Bn), 5.13 (s, 2H, Bn), 5.11 (d, *J* = 10.9 Hz, 1H, Bn), 5.10 (s, 2H, Bn), 4.99 (d, *J* = 10.9 Hz, 1H, Bn), 4.97 (d, *J* = 10.9 Hz, 1H, Bn), 4.959 (d, *J* = 10.9 Hz, 1H, Bn), 4.956 (d, *J* = 10.9 Hz, 1H, Bn), 4.93 (d, *J* = 10.9 Hz, 1H, Bn), 4.83 (d, *J* = 10.9 Hz, 1H, Bn), 4.81 (d, *J* = 10.9 Hz, 1H, Bn), 4.80 (d, *J* = 10.3 Hz, 1H, H-1), 4.72 (dd, *J* = 12.6, 2.9 Hz, 1H, H-6), 4.64 (d, *J* = 10.9 Hz, 1H, Bn), 4.62 (d, *J* = 10.9 Hz, 1H, Bn), 4.59 (ddd, *J* = 5.2, 1.7, 1.2 Hz, 4H, Allyl), 4.52 (ddd, *J* = 5.2, 1.7, 1.2 Hz, 4H, Allyl), 4.36 (dd, *J* = 12.6, 5.2 Hz, 1H, H-6), 4.05 (ddd, *J* = 9.7, 5.2, 2.9 Hz, 1H, H-5), 2.87–2.70 (m, 2H, Et), 1.31 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ¹³C NMR (126 MHz, CDCl₃, 23 °C) δ 168.4 (s, HHDP), 167.4 (s, HHDP), 165.8 (s, galloyl), 164.8 (s, galloyl), 152.9 (s, HHDP), 152.8 (s, HHDP), 152.69 (s, HHDP), 152.66 (s, galloyl), 152.6 (s, HHDP), 152.5 (s, 2C, galloyl), 144.7 (s, HHDP), 144.6 (s, HHDP), 142.9 (s, galloyl), 142.4 (s, galloyl), 137.7 (s, Bn), 137.61 (s, 2C, Bn), 137.56 (s, 2C, Bn), 137.5 (s, Bn), 136.5 (s, Bn), 136.4 (s, Bn), 133.2 (d, 2C, Allyl), 132.8 (d, 2C, Allyl), 128.9 (s, HHDP), 128.8 (d, 2C, Bn), 128.7 (d, 2C, Bn), 128.61 (s, HHDP), 128.56–127.7 (overlapping 36 doublets: 13 peaks were observed, 36C, Bn), 124.6 (s, galloyl), 123.8 (s, galloyl), 122.2 (s, HHDP), 122.0 (s, HHDP), 118.1 (t, 2C, Allyl), 118.0 (t, 2C, Allyl), 109.12 (d, 2C, galloyl), 109.08 (d, 2C, galloyl), 107.3 (d, HHDP), 107.1 (d, HHDP), 82.1 (d, C-1), 78.4 (d, C-3), 76.7 (d, C-5), 75.73 (t, Bn), 75.68 (t, Bn), 75.44 (t, Bn), 75.38 (t, Bn), 75.14 (t, Bn), 75.07 (t, Bn), 74.0 (d, C-2), 71.4 (t, Bn), 71.2 (t, Bn), 70.1 (t, 4C, Allyl), 68.5 (d, C-4), 63.3 (t, C-6), 23.7 (t, Et), 15.3 (q, Et). HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₁₀₄H₉₄O₂₁SNa 1733.5906, found 1733.5897.

Preparation of oxidative precursor 20

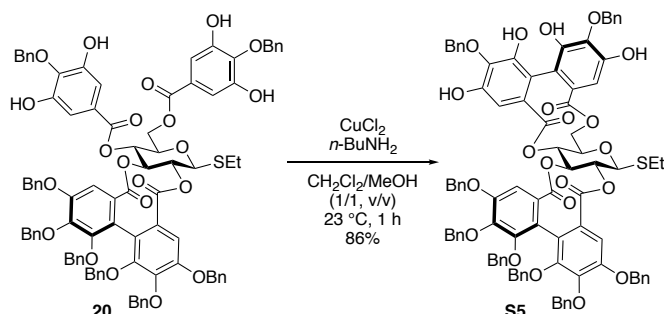


To a solution of **S4** (5.72 g, 3.34 mmol) in CH₂Cl₂ (33 mL) were added Pd(PPh₃)₄ (196 mg, 0.169 mmol) and morpholine (2.40 g, 27.6 mmol). The mixture was stirred for 1 h at 26 °C. After the addition of 1 M hydrochloric acid (30 mL), the reaction mixture was extracted with CH₂Cl₂ (25 mL × 3). After the general drying procedure, the residue was purified by column chromatography (45 g of SiO₂, *n*-hexane/ethyl acetate = 5/1 to 2/1) to afford

20 (5.14 g, 3.31 mmol, 99% yield) as a pale yellow amorphous solid. Data for **20**: [α]_D²² –16 (*c* 0.10, CHCl₃). IR (ATR) 3628–3435, 3065, 3030, 2876, 1753, 1593, 1454, 1337, 1215, 1173, 1053, 746, 696 cm⁻¹. ¹H NMR (500 MHz, CDCl₃, 23 °C) δ 7.45 (dd, *J* = 8.0, 1.7 Hz, 2H, Bn), 7.42–7.35 (m, 3H, Bn), 7.34–7.27 (m, 15H, Bn), 7.26–7.16 (m, 10H, Bn), 7.25 (s, 2H, galloyl), 7.24 (s, 2H, galloyl), 7.13–7.01 (m, 6H, Bn), 6.95 (dd, *J* = 8.0, 1.7 Hz, 2H, Bn), 6.94 (s, 1H, HHDP), 6.91 (dd, *J* = 7.5, 1.7 Hz, 2H, Bn), 6.69 (s, 1H, HHDP), 6.09 (br s, 2H, OH), 6.05 (br s, 2H, OH), 5.58 (dd, *J* = 9.7, 9.7 Hz, 1H, H-4), 5.46 (dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.25 (dd, *J* = 10.3, 9.2 Hz, 1H, H-2), 5.17 (d, *J* = 11.5 Hz, 1H, Bn), 5.104 (d, *J* = 10.9 Hz, 1H, Bn), 5.096 (d, *J* = 11.5 Hz, 1H, Bn), 5.07 (d, *J* = 11.5 Hz, 1H, Bn), 5.05 (d, *J* = 11.5 Hz, 1H, Bn), 5.04 (d, *J* = 11.5 Hz, 1H, Bn), 5.02 (d, *J* = 11.5 Hz, 1H, Bn), 4.96 (d, *J* = 10.9 Hz, 1H, Bn), 4.93 (d, *J* = 10.9 Hz, 2H, Bn), 4.92 (d, *J* = 11.5 Hz, 1H, Bn), 4.88 (d, *J* = 11.5 Hz, 1H, Bn), 4.83 (d, *J* = 10.3 Hz, 1H, H-1), 4.81 (d, *J* = 10.9 Hz, 1H, Bn), 4.79 (d, *J* = 10.9 Hz, 1H, Bn), 4.73 (dd, *J* = 12.6, 4.0 Hz, 1H, H-6), 4.62 (d, *J* = 10.9 Hz, 1H, Bn), 4.61 (d, *J* = 10.9 Hz, 1H, Bn), 4.48 (dd, *J* = 12.6, 2.9 Hz, 1H, H-6), 4.03 (ddd, *J* = 9.7, 4.0, 2.9 Hz, 1H, H-5), 2.91–2.73 (m, 2H, Et), 1.34 (dd, *J* = 7.5, 7.5 Hz, 3H, Et). ¹³C NMR (126 MHz, CDCl₃, 24 °C) δ 168.5 (s, HHDP), 167.5 (s, HHDP), 165.5 (s, galloyl), 165.4 (s, galloyl), 152.9 (s, HHDP), 152.73 (s, HHDP), 152.68 (s, HHDP), 152.5 (s, HHDP), 149.3 (s, 2C, galloyl), 149.2 (s, 2C, galloyl), 144.63 (s, HHDP), 144.61 (s, HHDP), 138.5 (s, galloyl), 138.1 (s, galloyl), 137.7 (s, Bn), 137.60 (s, Bn), 137.57 (s, Bn), 137.5 (s, Bn), 136.8 (s, Bn), 136.7 (s, 1Bn), 136.5 (s, Bn), 136.4 (s, Bn), 129.0–127.5 (overlapping 40 doublets and 2

singlets: 20 peaks were observed, 42C, Bn and HHDP), 124.6 (s, galloyl), 124.1 (s, galloyl), 122.2 (s, HHDP), 122.0 (s, HHDP), 110.1 (d, 2C, galloyl), 110.0 (d, 2C, galloyl), 107.3 (d, HHDP), 107.2 (d, HHDP), 82.2 (d, C-1), 78.4 (d, C-3), 76.7 (d, C-5), 75.7 (t, Bn), 75.62 (t, Bn), 75.57 (t, Bn), 75.43 (t, Bn), 75.41 (t, Bn), 75.38 (t, Bn), 74.1 (d, C-2), 71.4 (t, Bn), 70.8 (t, Bn), 67.9 (d, C-4), 62.9 (t, C-6), 23.7 (t, Et), 15.3 (q, Et). HRMS (ESI) m/z $[M - H]^-$ calcd for $C_{92}H_{77}O_{21}S$ 1549.4678, found 1549.4694.

Preparation of tetraol **S5**

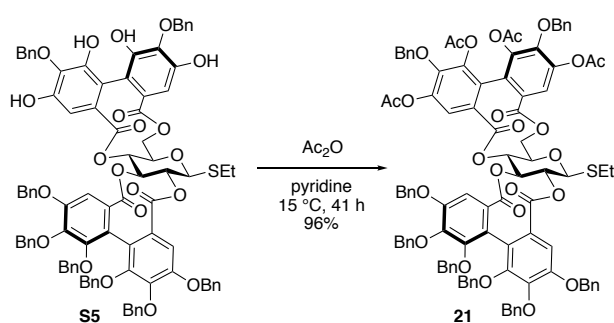


To a solution of **20** (5.05 g, 3.25 mmol) in CH_2Cl_2 (65 mL) and MeOH (65 mL) were added $CuCl_2$ (1.09 g, 8.09 mmol) and $n-BuNH_2$ (4.81 g, 65.8 mmol). The mixture was stirred for 30 min at 23 °C, and further $CuCl_2$ (904 mg, 6.72 mmol) and $n-BuNH_2$ (2.22 g, 41.0 mmol) were added to the mixture. It was stirred for 30 min at the same temperature. To the mixture of 1 M hydrochloric acid (200 mL) and Et_2O (200 mL) was added the reaction mixture.

The reaction mixture was extracted with Et_2O (100 mL ×

3). The combined organic layer was successively washed with 1 M hydrochloric acid, H_2O , and brine. After the general drying procedure, the residue was purified by column chromatography (40 g of SiO_2 , n -hexane/ethyl acetate = 5/1 to 2/1) to afford **S5** (4.34 g, 2.80 mmol, 86% yield) as a brown amorphous solid. Data for **S5**: $[\alpha]_D^{22}$ -43 (c 0.27, acetone). IR (ATR) 3588–3134, 3063, 3030, 2936, 2874, 1751, 1589, 1454, 1364, 1215, 1169, 1092, 968, 737, 696 cm^{-1} . 1H NMR (500 MHz, acetone- d_6 , 24 °C) δ 8.53 (br s, 1H, OH), 8.45 (br s, 1H, OH), 7.87 (br s, 2H, OH), 7.62–7.50 (m, 6H, Bn), 7.50–7.15 (m, 30H, Bn), 7.06 (s, 1H, HHDP), 7.04–6.94 (m, 4H, Bn), 6.87 (s, 1H, HHDP), 6.71 (s, 1H, HHDP), 6.51 (s, 1H, HHDP), 5.39–5.34 (m, 2H, H-6, H-3), 5.28 (d, J = 11.5 Hz, 1H, Bn), 5.25 (d, J = 11.5 Hz, 1H, Bn), 5.23–5.13 (m, 6H, Bn and H-4), 5.09 (dd, J = 10.3, 8.6 Hz, 1H, H-2), 5.05 (d, J = 11.5 Hz, 1H, Bn), 5.02 (dd, J = 10.3 Hz, 1H, H-1), 4.97 (d, J = 10.9 Hz, 2H, Bn), 4.95 (d, J = 10.9 Hz, 1H, Bn), 4.94 (d, J = 10.9 Hz, 1H, Bn), 4.93 (d, J = 10.9 Hz, 1H, Bn), 4.90 (d, J = 10.9 Hz, 1H, Bn), 4.65 (d, J = 10.9 Hz, 1H, Bn), 4.64 (d, J = 10.9 Hz, 1H, Bn), 4.34 (ddd, J = 9.7, 6.9, 1.2 Hz, 1H, H-5), 3.97 (dd, J = 13.2, 1.2 Hz, 1H, H-6), 2.95–2.77 (m, 2H, Et), 1.35 (dd, J = 7.5, 7.5 Hz, 3H, Et). ^{13}C NMR (126 MHz, acetone- d_6 , 24 °C) δ 168.9 (s, HHDP), 168.0 (s, HHDP), 167.8 (s, HHDP), 167.5 (s, HHDP), 153.71 (s, HHDP), 153.67 (s, HHDP), 153.3 (s, HHDP), 153.1 (s, HHDP), 150.6 (s, HHDP), 150.5 (s, HHDP), 150.2 (s, 2C, HHDP), 145.03 (s, HHDP), 144.99 (s, HHDP), 138.71 (s, 2C, Bn), 138.67 (s, 2C, Bn), 138.6 (s, Bn), 138.5 (s, Bn), 137.8 (s, Bn), 137.6 (s, Bn), 137.1 (s, HHDP), 137.0 (s, HHDP), 130.9 (s, HHDP), 130.4 (s, HHDP), 130.3 (s, HHDP), 130.2 (s, HHDP), 129.5–128.4 (overlapping 40 doublets: 15 peaks were observed, 40C, Bn), 122.7 (s, HHDP), 122.2 (s, HHDP), 115.5 (s, HHDP), 115.3 (s, HHDP), 108.4 (d, HHDP), 108.1 (d, HHDP), 108.0 (d, HHDP), 107.4 (d, HHDP), 82.6 (d, C-1), 78.9 (d, C-3), 76.7 (d, C-5), 76.17 (t, Bn), 76.13 (t, Bn), 75.9 (t, 2C, Bn), 75.7 (d, C-2), 74.9 (t, Bn), 74.8 (t, Bn), 72.0 (t, 2C, Bn), 69.5 (d, C-4), 63.8 (t, C-6), 24.2 (t, Et), 15.7 (q, Et). HRMS (ESI) m/z $[M - H]^-$ calcd for $C_{92}H_{75}O_{21}S$ 1547.4522, found 1547.4529.

Preparation of tetraacetate **21**

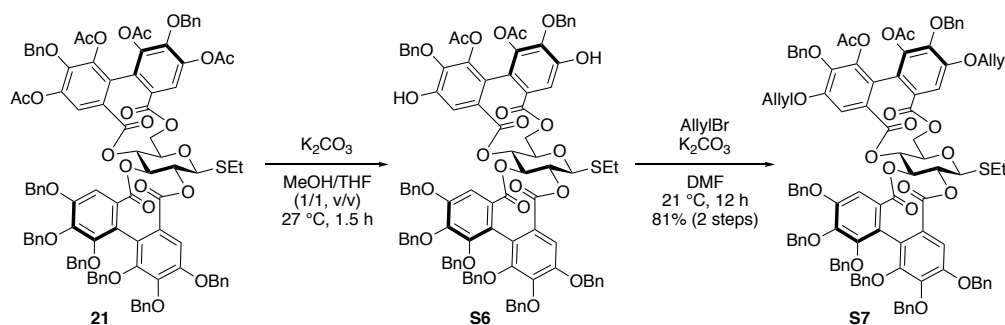


A mixture of **S5** (4.31 g, 2.78 mmol) in pyridine (18 mL) and Ac_2O (9.5 mL) was stirred for 41 h at 15 °C. After cooling to 0 °C, to the reaction mixture were added ethyl acetate (20 mL) and 1 M hydrochloric acid (30 mL). The reaction mixture was extracted with ethyl acetate (30 mL × 3). The combined organic layer was successively washed with 1 M hydrochloric acid and brine. After the general drying procedure, the residue was purified by column chromatography (35 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 2/1) to afford **21** (4.59 g, 2.67

mmol, 96% yield) as a reddish brown amorphous solid. Data for **21**: $[\alpha]_D^{25}$ -36 (c 0.52, $CHCl_3$). IR (ATR) 3065, 3034, 2941, 2876, 1755, 1591, 1454, 1329, 1171, 1049, 905, 725, 696 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 24 °C) δ 7.46 (br d, J = 7.5 Hz, 2H, Bn), 7.42–7.20 (m, 26H, Bn), 7.41 (s, 1H, HHDP), 7.20 (s, 1H, HHDP), 7.16–7.04 (m, 8H, Bn), 6.97 (dd, J

= 6.3, 2.3 Hz, 1H, Bn), 6.92 (s, 1H, HHDP), 6.90 (dd, J = 8.0, 1.7 Hz, 1H, Bn), 6.77 (s, 1H, HHDP), 5.43 (dd, J = 13.2, 6.3 Hz, 1H, H-6), 5.32 (dd, J = 9.7, 8.6 Hz, 1H, H-3), 5.27 (d, J = 12.0 Hz, 1H, Bn), 5.26 (dd, J = 9.7, 9.7 Hz, 1H, H-4), 5.19 (d, J = 11.5 Hz, 1H, Bn), 5.16 (dd, J = 10.3, 8.6 Hz, 1H, H-2), 5.15 (d, J = 10.9 Hz, 1H, Bn), 5.12 (d, J = 10.9 Hz, 1H, Bn), 5.09 (d, J = 11.5 Hz, 1H, Bn), 5.06 (d, J = 12.0 Hz, 1H, Bn), 4.99 (d, J = 10.9 Hz, 1H, Bn), 4.98 (d, J = 10.9 Hz, 1H, Bn), 4.96 (d, J = 10.9 Hz, 1H, Bn), 4.96 (d, J = 10.9 Hz, 1H, Bn), 4.93 (d, J = 10.9 Hz, 1H, Bn), 4.92 (d, J = 10.9 Hz, 1H, Bn), 4.82 (d, J = 10.9 Hz, 1H, Bn), 4.81 (d, J = 10.9 Hz, 1H, Bn), 4.69 (d, J = 10.3 Hz, 1H, H-1), 4.61 (d, J = 11.5 Hz, 1H, Bn), 4.58 (d, J = 10.9 Hz, 1H, Bn), 4.04 (br d, J = 13.2 Hz, 1H, H-6), 3.99 (br dd, J = 9.7, 6.3 Hz, 1H, H-5), 2.89–2.71 (m, 2H, Et), 2.20 (s, 3H, Ac), 2.17 (s, 3H, Ac), 1.99 (s, 3H, Ac), 1.85 (s, 3H, Ac), 1.33 (dd, J = 7.5, 7.5 Hz, 3H, Et). ^{13}C NMR (126 MHz, CDCl_3 , 23 °C) δ 168.6 (s, HHDP), 168.3 (s, Ac), 168.1 (s, Ac), 167.4 (s, Ac), 167.2 (s, Ac), 167.1 (s, HHDP), 165.4 (s, HHDP), 165.2 (s, HHDP), 152.8 (s, 3C, HHDP), 152.2 (s, HHDP), 146.4 (s, HHDP), 146.2 (s, HHDP), 144.5 (s, HHDP), 144.3 (s, HHDP), 144.1 (s, HHDP), 144.0 (s, HHDP), 143.9 (s, HHDP), 143.8 (s, HHDP), 137.8 (s, Bn), 137.61 (s, Bn), 137.58 (s, Bn), 137.5 (s, Bn), 136.8 (s, Bn), 136.74 (s, Bn), 136.65 (s, Bn), 136.5 (s, Bn), 129.1 (s, HHDP), 128.9 (s, HHDP), 128.8 (s, HHDP), 128.8–127.4 (overlapping 40 doublets and 1 singlet: 18 peaks were observed, 41C, Bn and HHDP), 126.0 (s, HHDP), 125.8 (s, HHDP), 122.4 (s, HHDP), 121.4 (s, HHDP), 121.1 (d, HHDP), 120.2 (d, HHDP), 107.7 (d, HHDP), 107.0 (d, HHDP), 82.3 (d, C-1), 77.8 (d, C-3), 76.4 (d, C-5), 75.74 (t, Bn), 75.65 (t, 2C, Bn), 75.6 (t, Bn), 75.5 (t, Bn), 75.3 (t, Bn), 74.1 (d, C-2), 71.3 (t, Bn), 71.1 (t, Bn), 69.3 (d, C-4), 63.5 (t, C-6), 23.3 (t, Et), 20.8 (q, Ac), 20.7 (q, c), 20.4 (q, Ac), 20.3 (q, Ac), 15.1 (q, Et). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{100}\text{H}_{84}\text{O}_{25}\text{SNa}$ 1739.4920, found 1739.4912.

Preparation of allylated compound S7



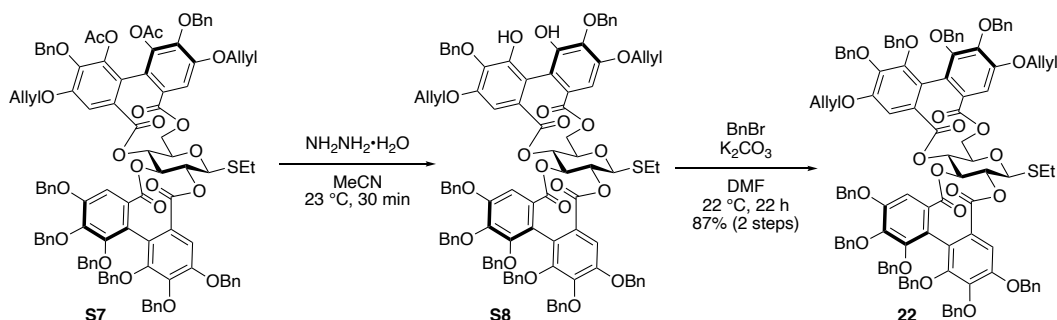
To a solution of **21** (4.52 g, 2.63 mmol) in THF (13 mL) and MeOH (13.5 mL) was added K_2CO_3 (972 mg, 7.03 mmol). The mixture was stirred for 1 h at 27 °C. After stirring for 30 min at 0 °C, to the reaction mixture were added ethyl acetate (30 mL) and 1 M hydrochloric acid (30 mL). The reaction mixture was extracted with ethyl acetate (25 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the mixture, the main content of which was **S6**, was used without further purification.

To a solution of the crude **S6** in DMF (26.5 mL) were added K_2CO_3 (973 mg, 7.04 mmol) and allyl bromide (0.84 g, 6.9 mmol). The mixture was stirred for 12 h at 21 °C. After cooling to 0 °C, to the reaction mixture were added ethyl acetate (30 mL) and 1 M hydrochloric acid (30 mL). The reaction mixture was extracted with ethyl acetate (20 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the resulting residue was purified by column chromatography (35 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 2/1) to afford **S7** (3.65 g, 2.13 mmol, 81% yield in 2 steps) as a pale yellow amorphous solid.

Data for **S7**: $[\alpha]_{\text{D}}^{24}$ –49 (c 0.26, CHCl_3). IR (ATR) 3065, 3032, 2934, 2874, 1753, 1591, 1454, 1325, 1240, 1171, 1094, 908, 731, 696 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 °C) δ 7.49–7.20 (m, 24H, Bn), 7.17–7.02 (m, 11H, Bn), 7.06 (s, 1H, HHDP), 7.00–6.90 (m, 5H, Bn), 6.92 (s, 1H, HHDP), 6.90 (s, 1H, HHDP), 6.71 (s, 1H, HHDP), 6.11 (dddd, J = 17.2, 10.9, 5.2, 5.2 Hz, 1H, Allyl), 6.04 (dddd, J = 17.2, 10.9, 5.2, 5.2 Hz, 1H, Allyl), 5.49 (dddd, J = 17.2, 1.7, 1.7, 1.7 Hz, 1H, Allyl), 5.44 (dd, J = 13.2, 6.3 Hz, 1H, H-6), 5.43 (dddd, J = 17.2, 1.7, 1.7, 1.7 Hz, 1H, Allyl), 5.35 (dddd, J = 10.9, 1.7, 1.2, 1.2 Hz, 1H, Allyl), 5.31 (dd, J = 9.7, 8.6 Hz, 1H, H-3), 5.31–5.25 (m, 5H, H-4, Allyl, and Bn), 5.20 (d, J = 11.5 Hz, 1H, Bn), 5.16 (dd, J = 10.3, 8.6 Hz, 1H, H-2), 5.11 (d, J = 10.9 Hz, 1H, Bn), 5.07 (d, J = 10.9 Hz, 1H, Bn), 5.04 (d, J = 10.9 Hz, 1H, Bn), 5.01 (d, J = 12.6 Hz, 1H, Bn), 4.97 (d, J = 10.9 Hz, 2H, Bn), 4.94 (d, J = 10.3 Hz, 1H, Bn), 4.93 (d, J = 10.9 Hz, 1H, Bn), 4.85 (d, J = 11.5 Hz, 1H, Bn), 4.81 (d, J = 10.9 Hz, 1H, Bn), 4.71 (m, 1H, Allyl), 4.70 (d, J = 10.3 Hz, 1H, H-1), 4.66–4.55 (m, 5H, Allyl and Bn), 4.04 (br d, J = 13.2 Hz, 1H, H-6), 3.99 (br dd, J = 9.2, 6.3 Hz, 1H, H-5), 2.89–2.75 (m, 2H,

Et), 1.96 (s, 3H, Ac), 1.82 (s, 3H, Ac), 1.35 (dd, $J = 7.5, 7.5$ Hz, 3H, Et). ^{13}C NMR (126 MHz, CDCl_3 , 24 °C) δ 168.7 (s, HHDP), 168.0 (s, Ac), 167.8 (s, Ac), 167.1 (s, HHDP), 166.4 (s, HHDP), 166.1 (s, HHDP), 152.8 (s, HHDP), 152.8 (s, 2C, HHDP), 152.3 (s, HHDP), 152.2 (s, HHDP), 152.1 (s, HHDP), 144.5 (s, HHDP), 144.4 (s, HHDP), 143.7 (s, HHDP), 143.6 (s, HHDP), 143.0 (s, HHDP), 142.9 (s, HHDP), 137.8 (s, Bn), 137.7 (s, Bn), 137.64 (s, Bn), 137.58 (s, 2C, Bn), 137.5 (s, Bn), 137.0 (s, Bn), 136.5 (s, Bn), 132.5 (d, Allyl), 132.4 (d, Allyl), 129.0 (s, HHDP), 128.9 (s, HHDP), 128.7–127.5 (overlapping 40 doublets and 2 singlets: 16 peaks were observed, 42 C, Bn and HHDP), 122.3 (s, HHDP), 121.5 (s, HHDP), 121.1 (s, 2C, HHDP), 118.54 (t, Allyl), 118.50 (t, Allyl), 110.8 (d, HHDP), 109.8 (d, HHDP), 107.9 (d, HHDP), 107.1 (d, HHDP), 82.4 (d, C-1), 77.9 (d, C-3), 76.7 (d, C-5), 75.71 (t, Bn), 75.67 (t, Bn), 75.44 (t, Bn), 75.42 (t, Bn), 74.8 (t, Bn), 74.7 (t, Bn), 74.3 (d, C-2), 71.4 (t, Bn), 71.2 (t, Bn), 70.3 (t, Allyl), 70.1 (t, Allyl), 69.1 (d, C-4), 63.3 (t, C-6), 23.5 (t, Et), 20.6 (q, Ac), 20.5 (q, Ac), 15.1 (q, Et). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{102}\text{H}_{88}\text{O}_{23}\text{SNa}$ 1735.5335, found 1735.5348.

Preparation of benzylated compound 22

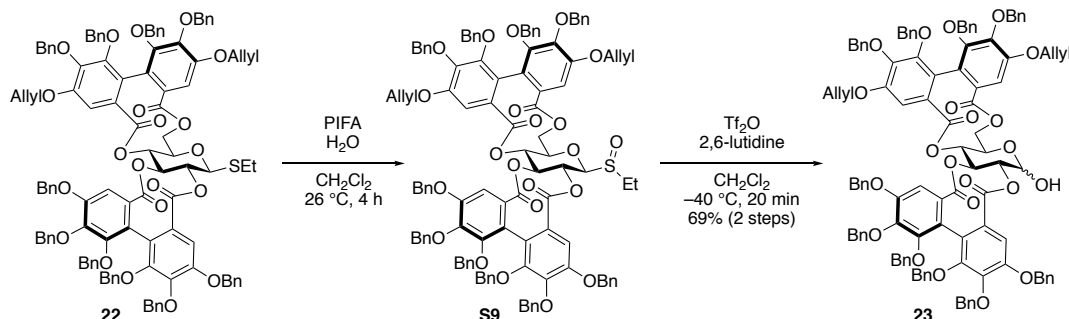


To a solution of **S7** (3.62 g, 2.11 mmol) in MeCN (21 mL) was added $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ (0.27 g, 6.2 mmol). The mixture was stirred for 30 min at 23 °C. After the addition of ethyl acetate (25 mL) and 1 M hydrochloric acid (25 mL) to the reaction mixture, it was extracted with ethyl acetate (20 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the afforded product **S8** was used without further purification.

To a solution of the crude **S8** in DMF (10.5 mL) and THF (10.5 mL) were added K_2CO_3 (1.51 g, 10.9 mmol) and BnBr (1.87 g, 10.9 mmol). The mixture was stirred for 22 h at 22 °C. After the addition of ethyl acetate (30 mL) and 1 M hydrochloric acid (30 mL), the reaction mixture was extracted with ethyl acetate (30 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (35 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 3/1) to afford **22** (3.34 g, 1.84 mmol, 88% yield) as a pale yellow amorphous solid. Data for **22**: $[\alpha]_{\text{D}}^{24} -51$ (c 0.31, CHCl_3). IR (ATR) 3063, 3030, 2936, 2874, 1749, 1591, 1454, 1331, 1238, 1173, 1094, 908, 731, 694 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 °C) δ 7.47 (dd, $J = 8.0, 1.7$ Hz, 2H, Bn), 7.44–7.17 (m, 26H, Bn), 7.15–7.00 (m, 17H, Bn), 6.99–6.91 (m, 3H, Bn), 6.93 (s, 1H, HHDP), 6.92 (s, 1H, HHDP), 6.89 (dd, $J = 8.0, 1.7$ Hz, 2H, Bn), 6.83 (s, 1H, HHDP), 6.77 (s, 1H, HHDP), 6.11 (dddd, $J = 17.2, 10.3, 5.2, 5.2$ Hz, 1H, Allyl), 6.05 (dddd, $J = 17.2, 10.3, 5.2, 5.2$ Hz, 1H, Allyl), 5.48 (dddd, $J = 17.2, 1.7, 1.7, 1.7$ Hz, 1H, Allyl), 5.42 (dddd, $J = 17.2, 1.7, 1.7, 1.7$ Hz, 1H, Allyl), 5.38 (dd, $J = 13.2, 6.3$ Hz, 1H, H-6), 5.35 (dd, $J = 9.7, 8.6$ Hz, 1H, H-3), 5.34 (dddd, $J = 10.3, 1.7, 1.7, 1.7$ Hz, 1H, Allyl), 5.264 (dddd, $J = 10.3, 1.7, 1.7, 1.7$ Hz, 1H, Allyl), 5.256 (dd, $J = 9.7, 9.7$ Hz, 1H, H-4), 5.21 (d, $J = 11.5$ Hz, 1H, Bn), 5.18 (dd, $J = 10.3, 8.6$ Hz, 1H, H-2), 5.17 (d, $J = 10.3$ Hz, 1H, Bn), 5.11 (d, $J = 10.9$ Hz, 1H, Bn), 5.011 (d, $J = 10.9$ Hz, 1H, Bn), 5.008 (d, $J = 10.3$ Hz, 1H, Bn), 5.00 (d, $J = 10.9$ Hz, 1H, Bn), 4.99 (d, $J = 11.5$ Hz, 1H, Bn), 4.964 (d, $J = 10.9$ Hz, 1H, Bn), 4.959 (d, $J = 10.9$ Hz, 1H, Bn), 4.94 (d, $J = 10.3$ Hz, 1H, Bn), 4.93 (d, $J = 10.3$ Hz, 1H, Bn), 4.92 (d, $J = 11.5$ Hz, 1H, Bn), 4.91 (d, $J = 10.3$ Hz, 1H, Bn), 4.87 (d, $J = 10.9$ Hz, 1H, Bn), 4.81 (d, $J = 10.9$ Hz, 1H, Bn), 4.80 (d, $J = 10.9$ Hz, 1H, Bn), 4.79 (d, $J = 10.3$ Hz, 1H, Bn), 4.78 (d, $J = 11.5$ Hz, 1H, Bn), 4.71 (d, $J = 10.3$ Hz, 1H, H-1), 4.69–4.57 (m, 5H, Allyl, Bn), 4.55 (dddd, $J = 12.6, 5.2, 1.7, 1.7$ Hz, 1H, Allyl), 4.06 (dd, $J = 13.2, 1.2$ Hz, 1H, H-6), 4.01 (ddd, $J = 9.7, 6.3, 1.2$ Hz, 1H, H-5), 2.90–2.76 (m, 2H, Et), 1.35 (dd, $J = 7.5, 7.5$ Hz, 3H, Et). ^{13}C NMR (126 MHz, CDCl_3 , 24 °C) δ 168.6 (s, HHDP), 167.5 (s, HHDP), 167.2 (s, HHDP), 167.1 (s, HHDP), 152.9 (s, HHDP), 152.74 (s, 2C, HHDP), 152.71 (s, 2C, HHDP), 152.5 (s, HHDP), 152.34 (s, HHDP), 152.32 (s, HHDP), 144.6 (s, 2C, HHDP), 144.5 (s, HHDP), 144.4 (s, HHDP), 137.80 (s, Bn), 137.76 (s, Bn), 137.72 (s, Bn), 137.68 (s, Bn), 137.63 (s, Bn), 137.58 (s, Bn), 137.56 (s, 2C, Bn), 136.5 (s, Bn), 136.2 (s, Bn), 132.9 (d, Allyl), 132.8 (d, Allyl), 129.0 (s, HHDP), 128.8–127.5 (overlapping 50 doublets and 3 singlets: 22 peaks were observed, 53C, Bn and HHDP), 123.7 (s, HHDP), 123.5 (s, HHDP),

122.3 (s, HHDP), 121.7 (s, HHDP), 118.12 (t, Allyl), 118.07 (t, Allyl), 108.1 (d, HHDP), 107.44 (d, HHDP), 107.37 (d, HHDP), 107.1 (d, HHDP), 82.4 (d, C-1), 78.2 (d, C-3), 76.7 (d, C-5), 75.7 (t, Bn), 75.61 (t, Bn), 75.58 (t, Bn), 75.5 (t, Bn), 75.4 (t, 2C, Bn), 75.2 (t, Bn), 74.9 (t, Bn), 74.3 (d, C-2), 71.4 (t, Bn), 70.8 (t, Bn), 70.2 (t, Allyl), 70.1 (t, Allyl), 69.3 (d, C-4), 63.4 (t, C-6), 23.5 (t, Et), 15.1 (q, Et). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{112}H_{96}O_{21}SNa$ 1831.6063, found 1831.6061.

Preparation of hemiacetal **23**

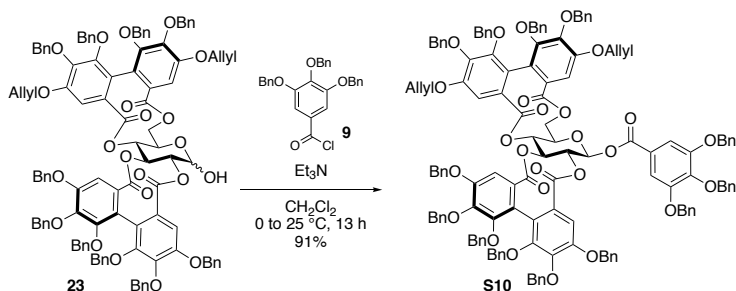


To a solution of **22** (2.82 g, 1.56 mmol) in CH_2Cl_2 (31 mL) were added H_2O (56.0 mg, 3.11 mmol) and PIFA (738 mg, 1.72 mmol). The mixture was stirred for 3.5 h at 26 °C, and further PIFA (52.2 mg, 0.121 mmol) was added to the mixture. It was stirred for 30 min at the same temperature. After the addition of saturated aqueous sodium hydrogen carbonate (50 mL), the reaction mixture was extracted with ethyl acetate (40 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the mixture, the main content of which was **S9**, was used without further purification.

To a solution of the crude **S9** in CH_2Cl_2 (31 mL) was added 2,6-lutidine (0.87 g, 8.2 mmol). The mixture was stirred for 15 min at -40 °C, and Tf_2O (0.86, 3.1 mmol) was added to the mixture. It was stirred for 20 min at -40 °C. After warming to 0 °C, to the reaction mixture were added H_2O (50 mL) and 1 M hydrochloric acid (40 mL). The reaction mixture was extracted with CH_2Cl_2 (40 mL \times 3). The combined organic layer was washed with 1 M hydrochloric acid. After the general drying procedure, the residue was purified by column chromatography (40 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 1/1) to afford **23** (1.91 g, 1.08 mmol, 69% yield in 2 steps) as a yellow amorphous solid.

Partial data for **23**: IR (ATR) 3626–3188, 3065, 3030, 2876, 1751, 1591, 1454, 1329, 1207, 1094, 968, 746, 696 cm^{-1} . HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{110}H_{92}O_{22}Na$ 1787.5978, found 1787.5988.

Preparation of β -galloyl ester **S10**

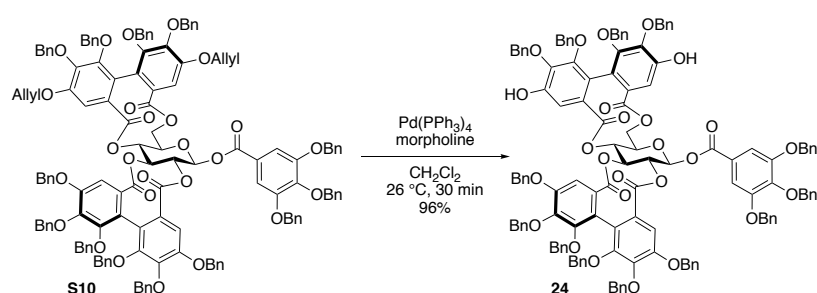


To a solution **23** (4.02 g, 2.28 mmol) in CH_2Cl_2 (15 mL) was added Et_3N (1.17 g, 11.5 mmol). After stirring for 45 min at 0 °C, to the mixture was added a solution of prepared **9** (ca. 4.54 mmol) in CH_2Cl_2 (15 mL) through cannula. Inside of the flask that was the container of **9** was rinsed with CH_2Cl_2 (15 mL \times 2); the used CH_2Cl_2 was also added to the reaction mixture. The mixture was

stirred for 30 min at 0 °C and further 12.5 h at 25.0 °C. After the addition of CH_2Cl_2 (50 mL) and saturated aqueous sodium hydrogen carbonate (50 mL), the mixture was extracted with CH_2Cl_2 (30 mL \times 3). The combined organic layer was washed with saturated aqueous sodium hydrogen carbonate. After the general drying procedure, the resulting residue was purified by column chromatography (40 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 2/1) to give **S10** (4.54 g, 2.08 mmol, 91% yield) as a pale yellow amorphous solid. Data for **S10**: $[\alpha]_D^{25}$ -38 (c 0.20, $CHCl_3$). IR (ATR) 3065, 3032, 2940, 2874, 1748, 1589, 1429, 1333, 1236, 1173, 1094, 907, 727, 694 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 24 °C) δ 7.42 (s, 2H, galloyl), 7.45–7.34 (m, 12H, Bn), 7.34–7.18 (m, 28H, Bn), 7.17–7.03 (m, 16H, Bn), 7.00 (dd, J = 6.9, 2.3 Hz, 2H, Bn), 6.97–6.87 (m, 7H, Bn), 6.91 (s, 2H, HHDP), 6.84 (s, 1H, HHDP), 6.82 (s, 1H, HHDP), 6.16 (d, J = 8.6 Hz, 1H, H-1), 6.10 (dddd, J = 17.8, 10.9, 5.2, 5.2 Hz, 1H, Allyl), 5.99 (m, 1H, Allyl), 5.52 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.47 (dd, J = 9.7, 8.6 Hz, 1H, H-2), 5.46 (m, 1H, Allyl), 5.37 (m, 1H, Allyl), 5.36 (br dd, J = 13.2, 7.5 Hz, 1H, H-6), 5.34 (dd, J = 9.7, 9.2 Hz, 1H, H-4), 5.21 (m, 1H, Allyl), 5.16–5.06 (m, 7H, Bn), 5.06 (m, 1H, Allyl), 5.06–4.87 (m, 13H, Bn), 4.834 (d, J = 10.9 Hz, 1H, Bn), 4.829 (d,

$J = 10.9$ Hz, 1H, Bn), 4.80 (d, $J = 10.9$ Hz, 1H, Bn), 4.78 (d, $J = 10.9$ Hz, 1H, Bn), 4.66 (d, $J = 10.9$ Hz, 2H, Bn), 4.70–4.57 (m, 2H, Allyl), 4.57–4.47 (m, 2H, Allyl), 4.15 (m, 1H, H-5), 4.01 (br d, $J = 13.2$ Hz, 1H, H-6). ^{13}C NMR (126 MHz, CDCl_3 , 23 °C) δ 168.5 (s, HHDP), 167.4 (s, HHDP), 167.3 (s, HHDP), 167.1 (s, HHDP), 164.3 (s, HHDP), 152.8 (s, 2C, HHDP), 152.74 (s, 2C, galloyl), 152.70 (s, 2C, HHDP), 152.68 (s, HHDP), 152.5 (s, HHDP), 152.4 (s, HHDP), 152.3 (s, HHDP), 144.63 (s, 2C, HHDP), 144.56 (s, HHDP), 144.5 (s, HHDP), 143.5 (s, galloyl), 137.8 (s, Bn), 137.71 (s, 2C, Bn), 137.66 (s, Bn), 137.62 (s, Bn), 137.57 (s, Bn), 137.5 (s, 2C, Bn), 137.4 (s, Bn), 136.43 (s, Bn), 136.40 (s, 2C, Bn), 136.2 (s, Bn), 132.83 (d, Allyl), 132.76 (d, Allyl), 128.8–127.6 (overlapping 65 doublets and 4 singlets: 18 peaks were observed, 69C, Bn and HHDP), 123.7 (s, HHDP), 123.6 (s, galloyl), 123.3 (s, galloyl), 122.4 (s, HHDP), 121.7 (s, HHDP), 118.1 (t, Allyl), 118.0 (t, Allyl), 109.5 (d, 2C, galloyl), 108.1 (d, HHDP), 107.4 (d, HHDP), 107.3 (d, HHDP), 107.1 (d, HHDP), 91.7 (d, C-1), 76.7 (d, C-3), 75.7 (t, Bn), 75.64 (t, Bn), 75.57 (t, Bn), 75.5 (t, Bn), 75.4 (t, Bn), 75.3 (t, Bn), 75.24 (t, Bn), 75.22 (t, Bn), 75.1 (d, C-2), 74.9 (t, Bn), 73.1 (d, C-5), 71.3 (t, Bn), 71.2 (t, 2C, Bn), 70.8 (t, Bn), 70.1 (t, Allyl), 70.0 (t, Allyl), 69.0 (d, C-4), 62.9 (t, C-6). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{138}\text{H}_{114}\text{O}_{26}\text{Na}$ 2209.7496, found 2209.7477.

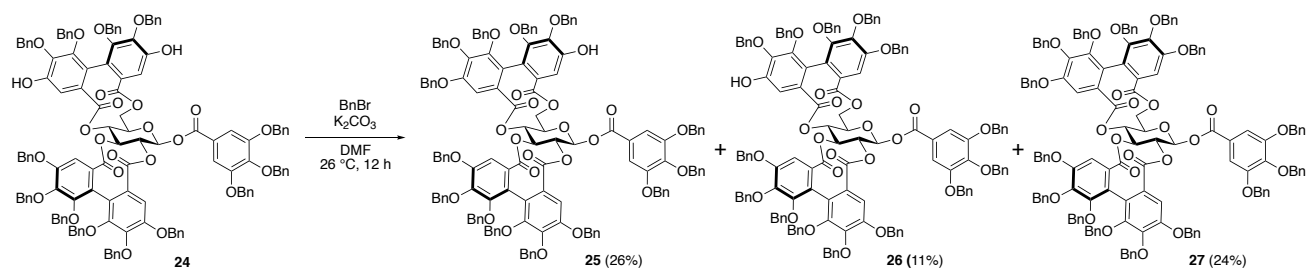
Preparation of diol **24**



To a solution of **S10** (1.53 g, 698 μmol) in CH_2Cl_2 (14 mL) were added morpholine (0.25 g, 2.9 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (11.7 mg, 10.1 μmol). The mixture was stirred for 30 min at 26 °C. After cooling to 0 °C, the reaction mixture was added saturated aqueous ammonium chloride (50 mL). The reaction mixture was extracted with CH_2Cl_2 (40 mL \times 3). The combined organic layer

was washed with H_2O . After the general drying procedure, the residue was purified by column chromatography (30 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 1/1) to afford **24** (1.42 g, 671 μmol , 96% yield) as a pale yellow amorphous solid. Data for **24**: $[\alpha]_{\text{D}}^{25} -53$ (c 0.24, CHCl_3). IR (ATR) 3605–3298, 3063, 3030, 2951, 2876, 1748, 1589, 1429, 1337, 1169, 1061, 968, 746, 694 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 24 °C) δ 7.41 (s, 2H, galloyl), 7.48–7.17 (m, 45H, Bn), 7.17–7.02 (m, 15H, Bn), 6.99–6.86 (m, 5H, Bn), 6.95 (s, 2H, HHDP), 6.92 (s, 1H, HHDP), 6.84 (s, 1H, HHDP), 6.15 (d, $J = 8.6$ Hz, 1H, H-1), 5.73 (s, 1H, OH), 5.62 (br s, 1H, OH), 5.53 (dd, $J = 9.7, 9.2$ Hz, 1H, H-3), 5.45 (dd, $J = 9.2, 8.6$ Hz, 1H, H-2), 5.41 (dd, $J = 13.2, 6.3$ Hz, 1H, H-6), 5.33 (dd, $J = 9.7, 9.7$ Hz, 1H, H-4), 5.23 (d, $J = 11.5$ Hz, 1H, Bn), 5.21 (d, $J = 12.0$ Hz, 1H, Bn), 5.15–5.06 (m, 7H, Bn), 5.03–4.88 (m, 8H, Bn), 4.85–4.75 (m, 5H, Bn), 4.72 (d, $J = 11.5$ Hz, 1H, Bn), 4.70 (d, $J = 11.5$ Hz, 1H, Bn), 4.64 (d, $J = 10.9$ Hz, 1H, Bn), 4.60 (d, $J = 10.9$ Hz, 1H, Bn), 4.11 (m, 1H, H-5), 4.01 (br d, $J = 13.2$ Hz, 1H, H-6). ^{13}C NMR (126 MHz, CDCl_3 , 24 °C) δ 168.3 (s, HHDP), 167.4 (s, HHDP), 167.3 (s, HHDP), 167.2 (s, HHDP), 164.3 (s, HHDP), 152.8 (s, HHDP), 152.74 (s, 2C, galloyl), 152.70 (s, 2C, HHDP), 152.4 (s, HHDP), 151.0 (s, HHDP), 150.8 (s, HHDP), 149.74 (s, HHDP), 149.71 (s, HHDP), 144.7 (s, HHDP), 144.4 (s, HHDP), 143.4 (s, galloyl), 141.70 (s, HHDP), 141.66 (s, HHDP), 137.76 (s, Bn), 137.68 (s, Bn), 137.66 (s, Bn), 137.6 (s, Bn), 137.5 (s, Bn), 137.4 (s, Bn), 137.3 (s, Bn), 136.8 (s, Bn), 136.7 (s, Bn), 136.49 (s, Bn), 136.46 (s, 2C, Bn), 136.2 (s, Bn), 129.3 (s, HHDP), 129.2 (s, HHDP), 129.0–127.5 (overlapping 65 doublets and 2 singlets: 25 peaks were observed, 67C, Bn and HHDP), 123.4 (s, galloyl), 122.50 (s, HHDP), 122.48 (s, HHDP), 122.4 (s, HHDP), 121.7 (s, HHDP), 110.0 (d, HHDP), 109.51 (d, 2C, galloyl), 109.50 (d, HHDP), 107.3 (d, HHDP), 107.2 (d, HHDP), 91.7 (d, C-1), 76.5 (d, C-3), 76.1 (t, 2C, Bn), 75.6 (t, 2C, Bn), 75.5 (t, Bn), 75.34 (t, Bn), 75.26 (t, 2C, Bn), 75.1 (d, C-2), 74.9 (t, Bn), 73.1 (d, C-5), 71.3 (t, Bn), 71.2 (t, 2C, Bn), 70.7 (t, Bn), 69.1 (d, C-4), 62.9 (t, C-6). HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{132}\text{H}_{106}\text{O}_{26}\text{Na}$ 2129.6870, found 2129.6889.

Preparation of mono-benzylated compounds **25** and **26**, and di-benzylated compound **27**



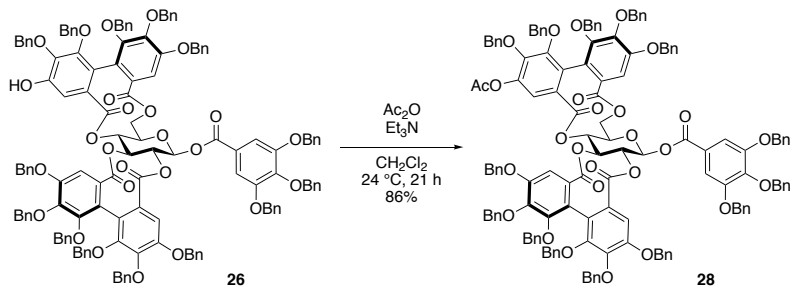
To a solution of **24** (301 mg, 143 μmol) in DMF (2.8 mL) were added K_2CO_3 (20.9 mg, 151 μmol) and BnBr (24.3 mg, 142 μmol). The mixture was stirred for 12 h at 26 $^\circ\text{C}$. After the addition of Et_2O (5 mL) and saturated aqueous ammonium chloride (10 mL), the reaction mixture was extracted with Et_2O (15 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (25 g of SiO_2 , *n*-hexane/toluene/ethyl acetate = 15/8/2 to 5/8/2) to remove **27** (80.0 mg, 35.0 μmol , 24% yield) as a colorless amorphous solid and **24** (89.0 mg, 42.2 μmol , 30% yield) as a pale yellow amorphous solid. Compounds **25** and **26** were obtained as their mixture. Therefore, the mixture was further purified by repeating column chromatography (50 g of SiO_2 , *n*-hexane/toluene/ethyl acetate = 5/4/1 to 5/8/2) three times to afford **25** (82.9 mg, 37.7 μmol , 26% yield) and **26** (35.6 mg, 16.2 μmol , 11% yield), each as a colorless amorphous solid. Data for **25**: $[\alpha]_{\text{D}}^{21} -43$ (*c* 0.19, CHCl_3). IR (ATR) 3578–3144, 3065, 3032, 2926, 2874, 1753, 1589, 1454, 1337, 1094, 750, 696 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 22 $^\circ\text{C}$) δ 7.49–7.14 (m, 42H, Bn), 7.43 (s, 2H, galloyl), 7.14–7.00 (m, 20H, Bn), 6.99–6.89 (m, 8H, Bn), 6.96 (s, 1H, HHDP), 6.96 (s, 1H, HHDP), 6.82 (s, 1H, HHDP), 6.80 (s, 1H, HHDP), 6.12 (d, *J* = 8.0 Hz, 1H, H-1), 5.73 (s, 1H, OH), 5.49 (dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.44 (dd, *J* = 9.2, 8.0 Hz, 1H, H-2), 5.41 (dd, *J* = 13.8, 6.3 Hz, 1H, H-6), 5.35 (dd, *J* = 9.7, 9.7 Hz, 1H, H-4), 5.20–4.88 (m, 20H, Bn), 4.83 (d, *J* = 12.0 Hz, 2H, Bn), 4.81 (d, *J* = 10.9 Hz, 1H, Bn), 4.79 (d, *J* = 10.9 Hz, 1H, Bn), 4.75 (d, *J* = 11.5 Hz, 1H, Bn), 4.66 (d, *J* = 11.5 Hz, 2H, Bn), 4.64 (d, *J* = 10.9 Hz, 1H, Bn), 4.22 (dd, *J* = 9.7, 6.3 Hz, 1H, H-5), 4.03 (d, *J* = 13.8 Hz, 1H, H-6). ^{13}C NMR (126 MHz, CDCl_3 , 22 $^\circ\text{C}$) δ 168.5 (s, HHDP), 167.33 (s, HHDP), 167.28 (s, HHDP), 167.26 (s, HHDP), 164.3 (s, galloyl), 152.9 (s, 2C, HHDP), 152.8 (s, 3C, galloyl), 152.7 (s, HHDP), 152.6 (s, HHDP), 152.4 (s, HHDP), 150.7 (s, HHDP), 149.7 (s, HHDP), 144.8 (s, HHDP), 144.7 (s, HHDP), 144.5 (s, HHDP), 143.4 (s, galloyl), 141.7 (s, HHDP), 137.8 (s, Bn), 137.71 (s, Bn), 137.65 (s, Bn), 137.6 (s, Bn), 137.5 (s, 2C, Bn), 137.4 (s, Bn), 137.2 (s, Bn), 136.7 (s, Bn), 136.5 (s, 2C, Bn), 136.40 (s, Bn), 136.38 (s, Bn), 136.2 (s, Bn), 129.1 (s, HHDP), 128.9–127.7 (overlapping 70 doublets and 3 singlets: 21 peaks were observed, 73C, Bn and HHDP), 123.5 (s, HHDP), 123.3 (s, galloyl), 122.6 (s, HHDP), 122.4 (s, HHDP), 121.8 (s, HHDP), 110.0 (d, HHDP), 109.5 (d, 2C, galloyl), 107.6 (d, HHDP), 107.3 (d, 2C, HHDP), 91.7 (d, C-1), 76.8 (d, C-3), 76.0 (t, Bn), 75.71 (t, Bn), 75.67 (t, Bn), 75.6 (t, Bn), 75.4 (t, 2C, Bn), 75.3 (t, 2C, Bn), 75.1 (d, C-2), 74.9 (t, Bn), 73.1 (d, C-5), 71.5 (t, Bn), 71.3 (t, Bn), 71.2 (t, 2C, Bn), 70.7 (t, Bn), 69.1 (d, C-4), 62.8 (t, C-6). HRMS (ESI) *m/z* $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{139}\text{H}_{112}\text{O}_{26}\text{Na}$ 2219.7340, found 2219.7340.

Data for **26**: $[\alpha]_{\text{D}}^{23} -37$ (*c* 0.09, CHCl_3). IR (ATR) 3590–3146, 3063, 3032, 2940, 2880, 1755, 1591, 1454, 1335, 1177, 1094, 970, 746, 696 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 21 $^\circ\text{C}$) δ 7.47 (dd, *J* = 8.6, 1.7 Hz, 2H, Bn), 7.44–7.13 (m, 48H, Bn), 7.41 (s, 2H, galloyl), 7.13–7.03 (m, 14H, Bn), 7.02 (s, 1H, HHDP), 6.96–6.87 (m, 6H, Bn), 6.93 (s, 2H, HHDP), 6.85 (s, 1H, HHDP), 6.16 (d, *J* = 8.6 Hz, 1H, H-1), 5.60 (br s, 1H, OH), 5.54 (br dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.47 (dd, *J* = 9.2, 8.6 Hz, 1H, H-2), 5.41 (dd, *J* = 13.2, 6.3 Hz, 1H, H-6), 5.34 (dd, *J* = 9.7, 9.7 Hz, 1H, H-4), 5.22 (d, *J* = 11.5 Hz, 1H, Bn), 5.17 (d, *J* = 11.5 Hz, 1H, Bn), 5.14–5.05 (m, 9H, Bn), 5.03–4.90 (m, 9H, Bn), 4.84 (d, *J* = 10.9 Hz, 1H, Bn), 4.83 (d, *J* = 10.9 Hz, 1H, Bn), 4.80 (d, *J* = 10.9 Hz, 1H, Bn), 4.79 (d, *J* = 10.9 Hz, 1H, Bn), 4.76 (d, *J* = 10.9 Hz, 1H, Bn), 4.64 (d, *J* = 10.9 Hz, 1H, Bn), 4.62 (d, *J* = 12.6 Hz, 1H, Bn), 4.60 (d, *J* = 10.3 Hz, 1H, Bn), 4.11 (m, 1H, H-5), 4.02 (d, *J* = 13.2 Hz, 1H, H-6). ^{13}C NMR (126 MHz, CDCl_3 , 21 $^\circ\text{C}$) δ 168.2 (s, HHDP), 167.45 (s, HHDP), 167.37 (s, HHDP), 167.1 (s, HHDP), 164.3 (s, galloyl), 152.9 (s, HHDP), 152.8 (s, 2C, HHDP), 152.73 (s, 2C, galloyl), 152.70 (s, HHDP), 152.40 (s, HHDP), 152.36 (s, HHDP), 150.9 (s, HHDP), 149.6 (s, HHDP), 144.8 (s, HHDP), 144.7 (s, HHDP), 144.4 (s, HHDP), 143.4 (s, galloyl), 141.7 (s, HHDP), 137.8 (s, Bn), 137.73 (s, Bn), 137.67 (s, Bn), 137.61 (s, Bn), 137.58 (s, Bn), 137.5 (s, Bn), 137.40 (s, Bn), 137.38 (s, Bn), 136.9 (s, Bn), 136.49 (s, Bn), 136.45 (s, Bn), 136.4 (s, 2C, Bn), 136.1 (s, Bn), 129.1 (s, HHDP), 128.8–127.6 (overlapping 70 doublets and 3 singlets: 22 peaks were observed, 73C, Bn and HHDP), 123.7 (s, HHDP), 123.3 (s, galloyl), 122.6 (s, HHDP), 122.5 (s, HHDP), 121.6 (s, HHDP), 109.5 (d, 2C, galloyl), 109.4 (d, HHDP), 108.3 (d, HHDP), 107.4 (d, HHDP), 107.1 (d,

HHDP), 91.7 (d, C-1), 76.4 (d, C-3), 76.0 (t, Bn), 75.68 (t, Bn), 75.65 (t, Bn), 75.6 (t, Bn), 75.5 (t, Bn), 75.32 (t, Bn), 75.25 (t, 2C, Bn), 75.2 (t, Bn), 75.1 (d, C-2), 75.0 (t, Bn), 73.1 (d, C-5), 71.3 (t, Bn), 71.2 (t, 2C, Bn), 70.8 (t, Bn), 69.0 (d, C-4), 63.0 (t, C-6). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{139}H_{112}O_{26}Na$ 2219.7340, found 2219.7341.

Data for **27**: $[\alpha]_D^{22} -36$ (c 0.21, $CHCl_3$). IR (ATR) 3063, 3030, 2941, 2876, 1753, 1589, 1454, 1335, 1173, 1063, 908, 735, 696 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 22 °C) δ 7.49–7.37 (m, 20H, Bn), 7.43 (s, 2H, galloyl), 7.36–7.18 (m, 30H, Bn), 7.16–6.99 (m, 20H, Bn), 7.00 (s, 1H, HHDP), 6.97–6.88 (m, 5H, Bn), 6.95 (s, 1H, HHDP), 6.81 (s, 1H, HHDP), 6.80 (s, 1H, HHDP), 6.12 (d, J = 8.0 Hz, 1H, H-1), 5.48 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.45 (dd, J = 9.2, 8.0 Hz, 1H, H-2), 5.41 (dd, J = 13.2, 6.3 Hz, 1H, H-6), 5.35 (dd, J = 9.7, 9.7 Hz, 1H, H-4), 5.22 (d, J = 11.5 Hz, 1H, Bn), 5.18 (d, J = 11.5 Hz, 1H, Bn), 5.16–5.07 (m, 10H, Bn), 5.06–4.95 (m, 8H, Bn), 4.93 (d, J = 10.9 Hz, 1H, Bn), 4.913 (d, J = 10.9 Hz, 1H, Bn), 4.908 (d, J = 10.9 Hz, 1H, Bn), 4.87 (d, J = 10.9 Hz, 1H, Bn), 4.83 (d, J = 10.9 Hz, 1H, Bn), 4.814 (d, J = 10.9 Hz, 1H, Bn), 4.806 (d, J = 10.3 Hz, 1H, Bn), 4.78 (d, J = 10.9 Hz, 1H, Bn), 4.66 (d, J = 10.9 Hz, 2H, Bn), 4.23 (dd, J = 9.7, 6.3 Hz, 1H, H-5), 4.05 (d, J = 13.2 Hz, 1H, H-6). ^{13}C NMR (126 MHz, $CDCl_3$, 24 °C) δ 168.5 (s, HHDP), 167.4 (s, HHDP), 167.3 (s, HHDP), 167.1 (s, HHDP), 164.3 (s, galloyl), 152.9 (s, 3C, HHDP), 152.8 (s, HHDP), 152.8 (s, 2C, galloyl), 152.7 (s, HHDP), 152.5 (s, HHDP), 152.4 (s, 2C, HHDP), 144.83 (s, HHDP), 144.82 (s, HHDP), 144.7 (s, HHDP), 144.5 (s, HHDP), 143.5 (s, galloyl), 137.8 (s, Bn), 137.73 (s, Bn), 137.70 (s, Bn), 137.64 (s, Bn), 137.58 (s, Bn), 137.54 (s, 2C, Bn), 137.47 (s, Bn), 137.4 (s, Bn), 136.49 (s, Bn), 136.45 (s, 4C, Bn), 136.2 (s, Bn), 128.7–127.7 (overlapping 75 doublets and 4 singlets: 19 peaks were observed, 79C, Bn and HHDP), 123.9 (s, HHDP), 123.8 (s, HHDP), 123.3 (s, galloyl), 122.5 (s, HHDP), 121.8 (s, HHDP), 109.6 (d, 2C, galloyl), 108.3 (d, HHDP), 107.6 (d, HHDP), 107.34 (d, HHDP), 107.27 (d, HHDP), 91.8 (d, C-1), 76.8 (d, C-3), 75.7 (t, Bn), 75.6 (t, 2C, Bn), 75.38 (t, Bn), 75.35 (t, Bn), 75.3 (t, 2C, Bn), 75.1 (t, Bn), 74.9 (d, C-2), 73.2 (d, C-5), 71.5 (t, Bn), 71.4 (t, Bn), 71.30 (t, Bn), 71.26 (t, 3C, Bn), 70.8 (t, Bn), 69.1 (d, C-4), 62.9 (t, C-6). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{146}H_{118}O_{26}Na$ 2309.7809, found 2309.7819.

Preparation of acetate **28** for the structure confirmation of **26**

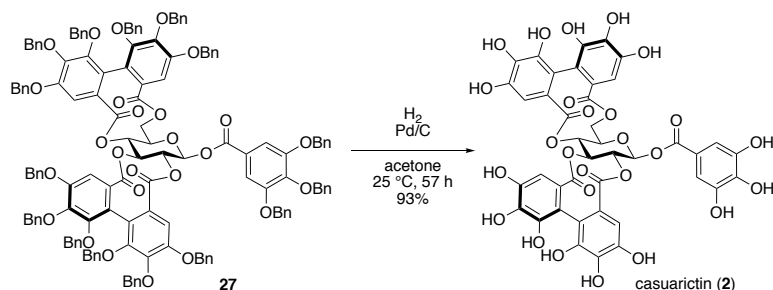


To a solution of **26** (35.8 mg, 16.3 μ mol) in CH_2Cl_2 (1.0 mL) were added Et_3N (29.2 mg, 289 μ mol) and Ac_2O (4.2 mg, 74 μ mol). The mixture was stirred for 21 h at 24 °C. After the addition of CH_2Cl_2 (10 mL) and saturated aqueous ammonium chloride (15 mL), the reaction mixture was extracted with CH_2Cl_2 (15 mL \times 3). After the general drying procedure, the residue was purified by

column chromatography (15 g of SiO_2 , n -hexane/ethyl acetate = 4/1 to 2/1) to afford **28** (31.5 mg, 14.1 μ mol, 86% yield) as a colorless amorphous solid. Data for **28**: $[\alpha]_D^{22} -34$ (c 0.32, $CHCl_3$). IR (ATR) 3063, 3032, 2945, 2880, 1755, 1591, 1429, 1337, 1186, 1067, 748, 696 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 22 °C) δ 7.48 (br dd, J = 8.6, 1.7 Hz, 2H, Bn), 7.43 (s, 2H, galloyl), 7.42–7.03 (m, 60H, Bn), 7.11 (s, 1H, HHDP), 7.04 (s, 1H, HHDP), 7.00 (dd, J = 7.5, 1.7 Hz, 2H, Bn), 6.94 (dd, J = 7.5, 2.3 Hz, 2H, Bn), 6.90 (dd, J = 7.5, 1.7 Hz, 2H, Bn), 6.87 (dd, J = 8.0, 1.7 Hz, 2H, Bn), 6.82 (s, 1H, HHDP), 6.81 (s, 1H, HHDP), 6.13 (d, J = 8.0 Hz, 1H, H-1), 5.47 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.46 (dd, J = 9.2, 8.0 Hz, 1H, H-2), 5.44 (dd, J = 13.2, 6.3 Hz, 1H, H-6), 5.36 (dd, J = 9.7, 9.7 Hz, 1H, H-4), 5.24 (d, J = 10.3 Hz, 1H, Bn), 5.22 (d, J = 10.3 Hz, 1H, Bn), 5.16–4.93 (m, 17H, Bn), 4.89 (d, J = 10.9 Hz, 1H, Bn), 4.87 (d, J = 10.9 Hz, 1H, Bn), 4.83 (d, J = 10.9 Hz, 1H, Bn), 4.81 (d, J = 10.9 Hz, 1H, Bn), 4.79 (d, J = 10.9 Hz, 1H, Bn), 4.78 (d, J = 10.9 Hz, 1H, Bn), 4.65 (d, J = 10.9 Hz, 1H, Bn), 4.64 (d, J = 10.9 Hz, 1H, Bn), 4.60 (d, J = 10.9 Hz, 1H, Bn), 4.20 (dd, J = 9.7, 6.3 Hz, 1H, H-5), 4.05 (d, J = 13.2 Hz, 1H, H-6), 2.18 (s, 3H, Ac). ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C) δ 168.9 (s, Ac), 168.3 (s, HHDP), 167.4 (s, HHDP), 167.2 (s, HHDP), 166.6 (s, HHDP), 164.3 (s, galloyl), 153.1 (s, HHDP), 152.82 (s, HHDP), 152.77 (s, HHDP), 152.7 (s, 3C, galloyl and HHDP), 152.5 (s, HHDP), 152.3 (s, HHDP), 152.1 (s, HHDP), 147.5 (s, HHDP), 145.0 (s, HHDP), 144.7 (s, HHDP), 144.4 (s, HHDP), 144.3 (s, HHDP), 143.4 (s, galloyl), 137.8 (s, Bn), 137.59 (s, Bn), 137.55 (s, Bn), 137.5 (s, Bn), 137.41 (s, Bn), 137.36 (s, Bn), 137.30 (s, Bn), 137.28 (s, Bn), 137.26 (s, Bn), 136.42 (s, 3C, Bn), 136.37 (s, Bn), 136.1 (s, Bn), 129.2 (s, HHDP), 128.8–127.6 (overlapping 70C doublets and 4 singlets: 21 peaks were observed, 74C, Bn and HHDP), 123.4 (s, HHDP), 123.3 (s, galloyl), 122.6 (s, HHDP), 121.6 (s, HHDP), 117.0 (d, HHDP), 109.5 (d, 2C, galloyl),

108.4 (d, HHDP), 107.3 (d, HHDP), 107.2 (d, HHDP), 91.8 (d, C-1), 76.5 (d, C-3), 75.73 (t, Bn), 75.67 (t, Bn), 75.6 (t, Bn), 75.5 (t, Bn), 75.3 (t, 2C, Bn), 75.23 (t, Bn), 75.18 (t, Bn), 75.1 (d, C-2), 75.0 (t, Bn), 73.1 (d, C-5), 71.4 (t, Bn), 71.3 (t, Bn), 71.2 (t, 2C, Bn), 70.8 (t, Bn), 69.1 (d, C-4), 63.0 (t, C-6), 20.7 (q, Ac). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{141}H_{114}O_{27}Na$ 2261.7445, found 2261.7442.

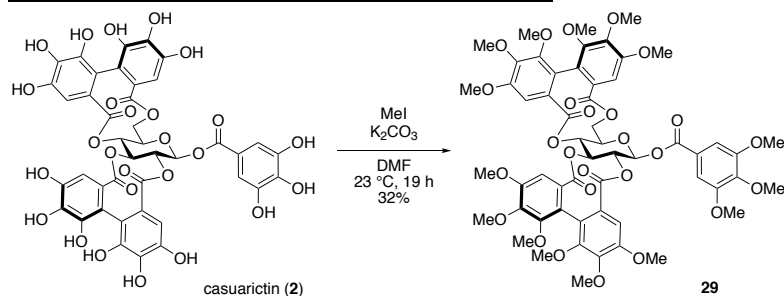
Preparation of casuarictin (2)



To a solution of **27** (32.3 mg, 14.1 μ mol) in acetone (1.0 mL) was added Pd/C (10 wt% on carbon, 4.4 mg, 0.44 mg as Pd, 4.1 μ mol). The mixture was stirred for 36 h at 25 °C under the positive rubber balloon-pressure of hydrogen, and further Pd/C (10 wt% on carbon, 16.6 mg, 1.66 mg as Pd, 15.6 μ mol) was added to the mixture. It was stirred for additional 21 h at

25 °C under the positive rubber balloon-pressure of hydrogen. The mixture was filtered through a Celite pad to remove excess Pd/C. After washing of the pad with acetone, acetone was removed by evaporation. The residue was purified by column chromatography (5 g of Sephadex LH-20, acetone to MeOH) to afford casuarictin (**2**) (12.3 mg, 13.1 μ mol, 93% yield) as a pale brown amorphous solid. The 1H NMR spectrum and specific optical rotation for **2** were in agreement with the literature data.⁴ Data for **2**: $[\alpha]_D^{23} +26$ (c 0.12, MeOH). IR (ATR) 3703–2396, 1732, 1614, 1447, 1317, 1184, 1043, 758 cm^{-1} . 1H NMR (500 MHz, acetone- d_6 , 21 °C) δ 7.17 (s, 2H, galloyl), 6.67 (s, 1H, HHDP), 6.53 (s, 1H, HHDP), 6.45 (s, 1H, HHDP), 6.36 (s, 1H, HHDP), 6.22 (d, J = 8.6 Hz, 1H, H-1), 5.45 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.38 (dd, J = 13.2, 6.9 Hz, 1H, H-6), 5.19 (dd, J = 9.2, 8.6 Hz, 1H, H-2), 5.18 (dd, J = 10.3, 9.7 Hz, 1H, H-4), 4.51 (br dd, J = 10.3, 6.9 Hz, 1H, H-5), 3.88 (br d, J = 13.2 Hz, 1H, H-6). ^{13}C NMR (126 MHz, acetone- d_6 , 22 °C) δ 169.2 (s, HHDP), 168.6 (s, HHDP), 168.0 (s, HHDP), 167.8 (s, HHDP), 165.0 (s, galloyl), 146.3 (s, 2C, galloyl), 145.2 (s, 2C, HHDP), 145.10 (s, HHDP), 145.07 (s, HHDP), 144.70 (s, HHDP), 144.66 (s, 2C, HHDP), 144.6 (s, HHDP), 139.9 (s, galloyl), 136.7 (s, HHDP), 136.6 (s, 2C, HHDP), 136.2 (s, HHDP), 126.5 (s, HHDP), 126.1 (s, HHDP), 125.9 (s, 2C, HHDP), 119.9 (s, galloyl), 116.1 (s, HHDP), 115.9 (s, HHDP), 115.0 (s, HHDP), 114.2 (s, HHDP), 110.3 (d, 2C, galloyl), 108.3 (d, HHDP), 107.6 (d, HHDP), 107.3 (d, HHDP), 107.2 (d, HHDP), 92.2 (d, C-1), 77.2 (d, C-3), 75.9 (d, C-2), 73.5 (d, C-5), 69.1 (d, C-4), 63.0 (t, C-6). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{41}H_{28}O_{26}Na$ 959.0767, found 959.0765.

Preparation of pentadecamethylcasuarictin (29)

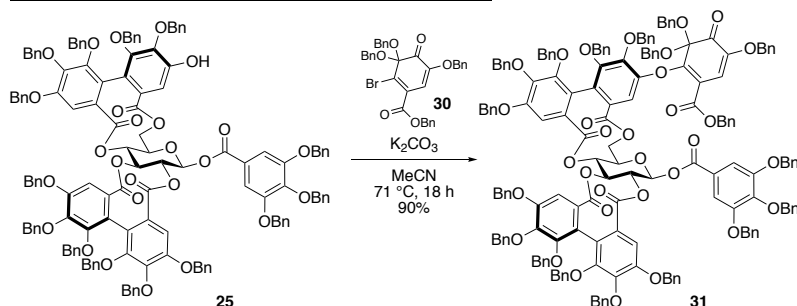


To a solution of casuarictin (**2**) (15.6 mg, 16.7 μ mol) in DMF (1.0 mL) were added K_2CO_3 (77.3 mg, 559 μ mol) and MeI (79.8 mg, 562 μ mol). After stirring for 14 h at 23 °C, to the mixture were further added K_2CO_3 (131 mg, 945 μ mol) and MeI (79.8 mg, 562 μ mol). The mixture was additionally stirred for 5 h at 23 °C. After the addition of Et_2O (5 mL) and

saturated aqueous ammonium chloride (5 mL), the reaction mixture was extracted with Et_2O (10 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (10 g of SiO_2 , n -hexane/ethyl acetate = 2/1 to 1/2) to afford **29** (6.2 mg, 5.4 μ mol, 32% yield) as a colorless amorphous solid. Data for **29**: $[\alpha]_D^{21} -8.5$ (c 0.05, $CHCl_3$). IR (ATR) 2941, 2868, 1755, 1591, 1464, 1337, 1204, 1103, 1065, 754 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 22 °C) δ 7.35 (s, 2H, galloyl), 6.80 (s, 1H, HHDP), 6.75 (s, 1H, HHDP), 6.65 (s, 1H, HHDP), 6.63 (s, 1H, HHDP), 6.10 (d, J = 8.6 Hz, 1H, H-1), 5.41 (dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.35 (dd, J = 9.2, 8.6 Hz, 1H, H-2), 5.33 (dd, J = 13.2, 6.3 Hz, 1H, H-6), 5.24 (dd, J = 9.7, 9.7 Hz, 1H, H-4), 4.18 (dd, J = 9.7, 6.3 Hz, 1H, H-5), 4.01 (d, J = 13.2 Hz, 1H, H-6), 3.97 (s, 3H, OMe), 3.96 (s, 3H, OMe), 3.94 (s, 3H, OMe), 3.920 (s, 3H, OMe), 3.915 (s, 3H, OMe), 3.91 (s, 3H, OMe), 3.89 (s, 9H, OMe), 3.86 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.66 (s, 3H, OMe). ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C) δ 168.5 (s, HHDP), 167.43 (s, HHDP), 167.39 (s, HHDP), 166.9 (s, HHDP), 164.3 (s, galloyl), 153.4 (s, HHDP), 153.34 (s, 2C, HHDP), 153.31

(s, HHDP), 153.2 (s, 2C, galloyl), 152.7 (s, HHDP), 152.51 (s, HHDP), 152.45 (s, HHDP), 152.38 (s, HHDP), 144.7 (s, HHDP), 144.5 (s, HHDP), 144.4 (s, 2C, HHDP), 143.4 (s, galloyl), 128.3 (s, 2C, HHDP), 128.2 (s, HHDP), 128.0 (s, HHDP), 123.2 (s, galloyl), 122.8 (s, HHDP), 122.5 (s, HHDP), 121.4 (s, HHDP), 120.9 (s, HHDP), 107.5 (d, 2C, galloyl), 105.9 (d, HHDP), 105.6 (d, HHDP), 105.4 (d, HHDP), 104.9 (d, HHDP), 91.8 (d, C-1), 76.9 (d, C-3), 75.2 (d, C-2), 73.0 (d, C-5), 69.0 (d, C-4), 62.9 (t, C-6), 61.23 (q, 2C, OMe), 61.20 (q, OMe), 61.16 (q, OMe), 61.13 (q, 2C, OMe), 61.10 (q, OMe), 61.0 (q, OMe), 60.8 (q, OMe), 56.4 (q, 2C, OMe), 56.3 (q, 2C, OMe), 56.2 (q, OMe), 56.0 (q, OMe). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{56}H_{58}O_{26}Na$ 1169.3114, found 1169.3127.

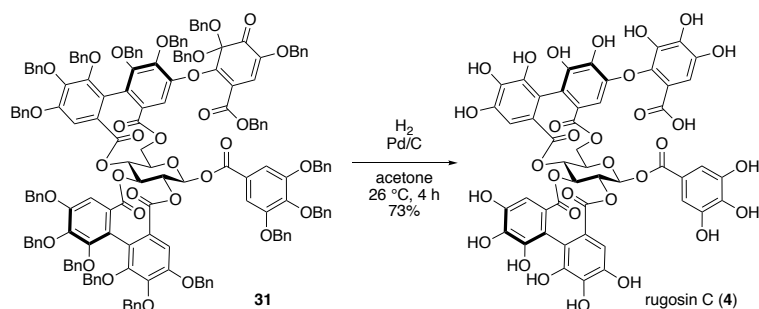
Preparation of orthoquinone derivative **31**



A mixture of **25** (53.2 mg, 24.2 μ mol), orthoquinonemonoketal (*o*-qK) **30** (205 mg, 328 μ mol), and K_2CO_3 (24.7 mg, 179 μ mol) in MeCN (2.4 mL) was stirred for 18 h at 70 °C under dark. After cooling to 0 °C, to the reaction mixture were added ethyl acetate (5 mL) and saturated aqueous ammonium chloride (10 mL). The reaction mixture was extracted with ethyl acetate (15 mL \times 3). The

combined organic layer was successively washed with H_2O and brine. After the general drying procedure, the residue was purified by column chromatography (10 g of SiO_2 , *n*-hexane/ethyl acetate = 5/1 to 2/1) to afford **31** (59.6 mg, 21.7 μ mol, 90% yield) as a yellow oil. Data for **31**: $[\alpha]_D^{22}$ –39 (*c* 0.10, $CHCl_3$). IR (ATR) 3065, 3032, 2953, 2874, 1751, 1589, 1454, 1335, 1063, 746, 696 cm^{-1} . 1H NMR (500 MHz, $CDCl_3$, 21 °C) δ 7.50–7.16 (m, 40H, Bn), 7.41 (s, 2H, galloyl), 7.16–6.91 (m, 47H, Bn), 7.12 (s, 1H, HHDP), 6.95 (s, 1H, HHDP), 6.88–6.83 (m, 3H, Bn), 6.86 (s, 1H, HHDP), 6.80 (s, 1H, HHDP), 6.48 (br s, 1H, *o*-qK), 6.12 (br d, J = 8.0 Hz, 1H, H-1), 5.51 (br dd, J = 9.7, 9.2 Hz, 1H, H-3), 5.42–5.35 (m, 2H, H-2 and H-6), 5.30 (dd, J = 9.7, 9.7 Hz, 1H, H-4), 5.18–4.55 (m, 36H, Bn), 4.20 (m, 1H, H-5), 3.87 (d, J = 13.2 Hz, 1H, H-6). ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C) δ 188.4 (s, *o*-qK), 168.5 (s, HHDP), 167.4 (s, HHDP), 167.0 (s, HHDP), 166.7 (s, HHDP), 164.3 (s, galloyl), 163.5 (s, *o*-qK), 153.8 (s, *o*-qK), 153.0 (s, HHDP), 152.9 (s, HHDP or *o*-qK), 152.8 (s, HHDP or *o*-qK), 152.73 (s, 2C, galloyl), 152.68 (s, HHDP or *o*-qK), 152.65 (s, HHDP or *o*-qK), 152.58 (s, HHDP or *o*-qK), 152.5 (s, HHDP or *o*-qK), 152.3 (s, HHDP or *o*-qK), 151.7 (s, HHDP or *o*-qK), 147.9 (s, *o*-qK), 144.8 (s, HHDP), 144.7 (s, HHDP), 144.5 (s, HHDP), 144.4 (s, HHDP), 143.4 (s, galloyl), 137.7 (s, Bn), 137.59 (s, 2C, Bn), 137.55 (s, Bn), 137.50 (s, 3C, Bn), 137.4 (s, Bn), 137.3 (s, Bn), 137.1 (s, Bn), 136.9 (s, Bn), 136.40 (s, 3C, Bn), 136.35 (s, Bn), 136.1 (s, Bn), 135.3 (s, Bn), 135.2 (s, Bn), 128.9–127.5 (overlapping 90 doublets and 4 singlets: 22 peaks were observed, 94C, Bn and HHDP), 125.2 (s, HHDP), 123.3 (s, galloyl or HHDP), 123.2 (s, galloyl or HHDP), 122.5 (s, HHDP), 121.7 (s, HHDP), 111.2 (d, *o*-qK), 110.7 (d, HHDP), 109.5 (d, 2C, galloyl), 107.5 (d, HHDP), 107.3 (d, 2C, HHDP), 95.8 (s, acetal), 91.7 (d, C-1), 77.1 (d, C-3), 75.7 (t, Bn), 75.6 (t, 2C, Bn), 75.4 (t, 2C, Bn), 75.24 (t, 2C, Bn), 75.19 (t, 2C, Bn), 75.1 (t, Bn), 75.0 (d, C-2), 72.9 (d, C-5), 71.5 (t, Bn), 71.3 (t, Bn), 71.2 (t, 3C, Bn), 70.8 (t, Bn), 70.6 (t, Bn), 68.8 (d, C-4), 67.7 (t, Bn), 62.6 (t, C-6). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{174}H_{140}O_{32}Na$ 2763.9225, found 2763.9242.

Preparation of rugosin C (**4**)

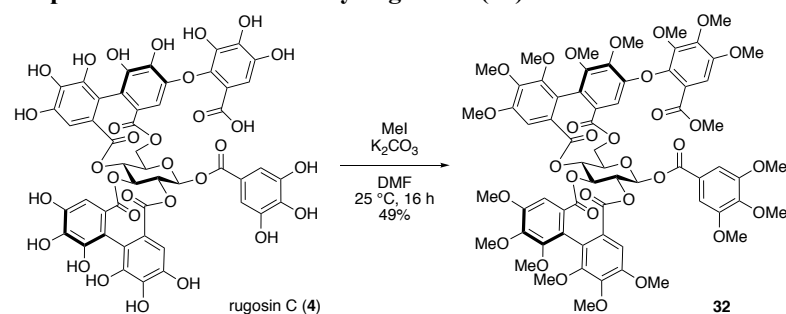


To a solution of **31** (59.6 mg, 21.7 μ mol) in acetone (2 mL) was added Pd/C (10 wt% on carbon, 11.7 mg, 1.17 mg as Pd, 11.0 μ mol). The mixture was stirred for 4 h at 26 °C under the positive rubber balloon-pressure of hydrogen. The mixture was filtered through a Celite pad to remove excess Pd/C. After washing of the pad with acetone, acetone was removed by evaporation. The residue was purified by

column chromatography (5 g of Sephadex LH-20, MeOH) to afford rugosin C (**4**) (17.6 mg, 15.9 μ mol, 73% yield) as colorless amorphous solid. The 1H NMR spectrum and specific optical rotation value of **4** were in agreement with the

literature data.⁵ Data for **4**: $[\alpha]_D^{22} +80$ (*c* 0.15, acetone). IR (ATR) 3696–2851, 2974, 2851, 1732, 1614, 1454, 1317, 1186, 1038, 756, 696 cm^{-1} . ^1H NMR (500 MHz, acetone- d_6 , 22 °C) δ 7.15 (s, 2H, galloyl), 7.14 (br s, 1H, HHDP or valoneoyl), 6.54 (s, 1H, HHDP or valoneoyl), 6.45 (s, 1H, HHDP or valoneoyl), 6.40 (s, 1H, HHDP or valoneoyl), 6.38 (s, 1H, HHDP or valoneoyl), 6.19 (d, *J* = 8.6 Hz, 1H, H-1), 5.44 (dd, *J* = 9.7, 9.2 Hz, 1H, H-3), 5.28 (dd, *J* = 13.2, 6.3 Hz, 1H, H-6), 5.14 (dd, *J* = 9.2, 8.6 Hz, 1H, H-2), 5.07 (dd, *J* = 9.7, 9.7 Hz, 1H, H-4), 4.46 (dd, *J* = 9.7, 6.3 Hz, 1H, H-5), 3.79 (d, *J* = 13.2 Hz, 1H, H-6). ^{13}C NMR (126 MHz, acetone- d_6 + D_2O , 22 °C) δ 169.5 (s, HHDP), 168.8 (s, HHDP), 168.14 (s, valoneoyl), 168.08 (s, valoneoyl), 167.8 (s, valoneoyl), 165.2 (s, galloyl), 147.0 (s, valoneoyl), 146.12 (s, valoneoyl), 146.07 (s, 2C, galloyl), 145.2 (s, HHDP or valoneoyl), 145.1 (s, HHDP or valoneoyl), 145.0 (s, HHDP or valoneoyl), 144.6 (s, HHDP or valoneoyl), 144.44 (s, HHDP or valoneoyl), 144.40 (s, HHDP or valoneoyl), 143.0 (s, HHDP or valoneoyl), 140.0 (s, galloyl), 139.9 (s, valoneoyl), 139.6 (s, valoneoyl), 137.3 (s, valoneoyl), 137.1 (s, valoneoyl), 136.7 (s, valoneoyl), 136.5 (s, HHDP), 136.2 (s, HHDP), 125.9 (s, HHDP or valoneoyl), 125.6 (s, HHDP or valoneoyl), 125.5 (s, HHDP or valoneoyl), 125.0 (s, HHDP or valoneoyl), 119.2 (s, galloyl), 117.6 (s, valoneoyl), 115.94 (s, valoneoyl), 115.91 (s, valoneoyl), 114.9 (s, HHDP), 114.4 (s, HHDP), 110.1 (d, 2C, galloyl), 109.6 (d, valoneoyl), 107.3 (d, valoneoyl), 107.1 (d, 2C, HHDP), 105.9 (d, valoneoyl), 91.9 (d, C-1), 77.2 (d, C-3), 75.8 (d, C-2), 73.1 (d, C-5), 69.0 (d, C-4), 63.0 (t, C-6). HRMS (ESI) *m/z* $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{48}\text{H}_{32}\text{O}_{31}\text{Na}$ 1127.0825, found 1127.0823.

Preparation of octadecamethylrugosin C (**32**)



To a solution of synthesized rugosin C (**4**) (16.7 mg, 15.1 μmol) in DMF (0.50 mL) were added K_2CO_3 (79.3 mg, 574 μmol) and MeI (159 mg, 1.12 mmol). The mixture was stirred for 16 h at 25 °C. To the reaction mixture were added Et_2O (10 mL) and 1 M hydrochloric acid (10 mL). The mixture was extracted with Et_2O (15 mL \times 3). The combined organic layer was successively washed with H_2O and brine. After

the general drying procedure, the residue was purified by column chromatography (10 g of SiO_2 , *n*-hexane/ethyl acetate = 2/1 to 1/2) to afford **32** (10.0 mg, 7.37 μmol , 49% yield) as a colorless amorphous solid. The ^1H NMR spectrum of **32** was in good agreement with the literature data.⁶ Data for **32**: $[\alpha]_D^{17} +16$ (*c* 0.05, acetone). IR (ATR) 3005, 2941, 2849, 1749, 1593, 1458, 1339, 1204, 1167, 756 cm^{-1} . ^1H NMR (500 MHz, acetone- d_6 , 22 °C) δ 7.32 (s, 2H, galloyl), 7.25 (s, 1H, valoneoyl), 6.83 (s, 2H, HHDP and valoneoyl), 6.69 (s, 1H, HHDP), 6.50 (s, 1H, valoneoyl), 6.26 (d, *J* = 8.6 Hz, 1H, H-1), 5.54 (dd, *J* = 10.3, 9.2 Hz, 1H, H-3), 5.22 (dd, *J* = 9.2, 8.6 Hz, 1H, H-2), 5.16 (dd, *J* = 13.8, 6.3 Hz, 1H, H-6), 5.07 (dd, *J* = 10.3, 9.7 Hz, 1H, H-4), 4.42 (dd, *J* = 9.7, 6.3 Hz, 1H, H-5), 4.06 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.889 (s, 3H, OMe), 3.886 (s, 3H, OMe), 3.87 (s, 6H, OMe), 3.864 (s, 3H, OMe), 3.856 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.821 (d, *J* = 6.3 Hz, 1H, H-6), 3.815 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.763 (s, 3H, OMe), 3.760 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.70 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.60 (s, 3H, OMe). ^{13}C NMR (126 MHz, acetone- d_6 , 22 °C) δ 168.6 (s, HHDP), 168.2 (s, HHDP), 167.6 (s, valoneoyl), 167.5 (s, valoneoyl), 165.7 (s, valoneoyl), 164.5 (s, galloyl), 154.3 (s, 2C, galloyl), 154.19 (s, HHDP or valoneoyl), 154.17 (s, HHDP or valoneoyl), 154.15 (s, HHDP or valoneoyl), 153.7 (s, HHDP or valoneoyl), 153.6 (s, HHDP or valoneoyl), 153.6 (s, HHDP or valoneoyl), 153.5 (s, HHDP or valoneoyl), 153.4 (s, HHDP or valoneoyl), 151.5 (s, valoneoyl), 148.1 (s, valoneoyl), 147.8 (s, HHDP or valoneoyl), 145.3 (s, HHDP or valoneoyl), 145.0 (s, valoneoyl), 144.94 (s, HHDP or valoneoyl), 144.91 (s, HHDP), 144.4 (s, galloyl), 142.7 (s, valoneoyl), 129.7 (s, HHDP or valoneoyl), 129.6 (s, HHDP or valoneoyl), 129.24 (s, HHDP or valoneoyl), 129.22 (s, HHDP or valoneoyl), 124.4 (s, galloyl), 124.2 (s, valoneoyl), 123.6 (s, HHDP or valoneoyl), 121.9 (s, HHDP or valoneoyl), 121.5 (s, HHDP), 120.5 (s, valoneoyl), 109.4 (d, HHDP or valoneoyl), 109.3 (d, HHDP or valoneoyl), 108.2 (d, 2C, galloyl), 106.5 (d, HHDP or valoneoyl), 106.1 (d, HHDP or valoneoyl), 106.0 (d, HHDP or valoneoyl), 92.3 (d, C-1), 76.9 (d, C-3), 76.2 (d, C-2), 73.2 (d, C-5), 70.0 (d, C-4), 63.7 (t, C-6), 61.6 (q, OMe), 61.3 (q, OMe), 61.23 (q, OMe), 61.14 (q, OMe), 61.11 (q, OMe), 61.07 (q, 2C, OMe), 61.05 (q, OMe), 60.95 (q, OMe), 60.88 (q, OMe), 60.8 (q, OMe), 56.6 (q, 2C, OMe), 56.5

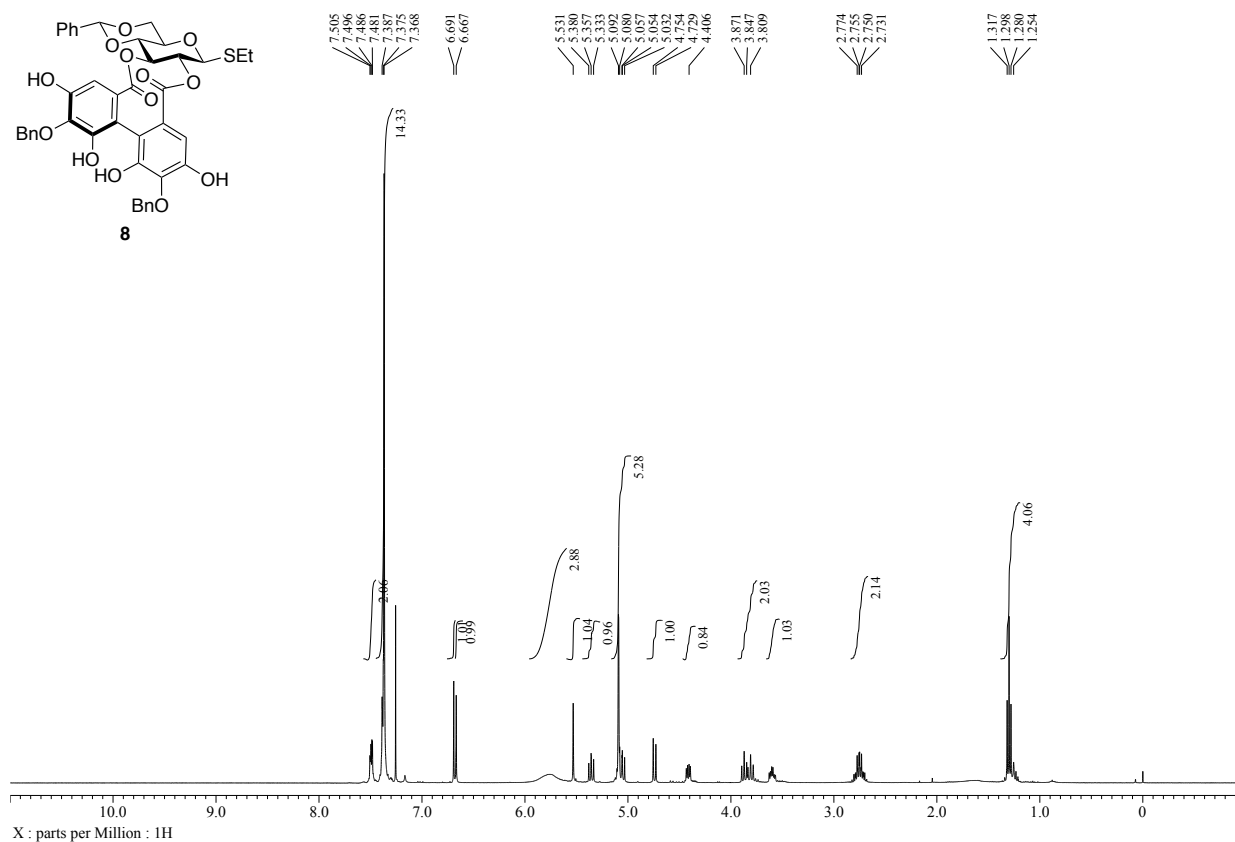
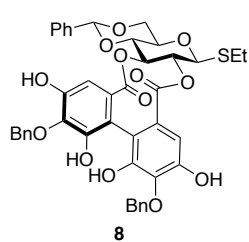
(q, OMe), 56.41 (q, OMe), 56.39 (q, OMe), 56.1 (q, OMe), 52.5 (q, OMe). HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{66}H_{68}O_{31}Na$ 1379.3642, found 1379.3649.

3. References

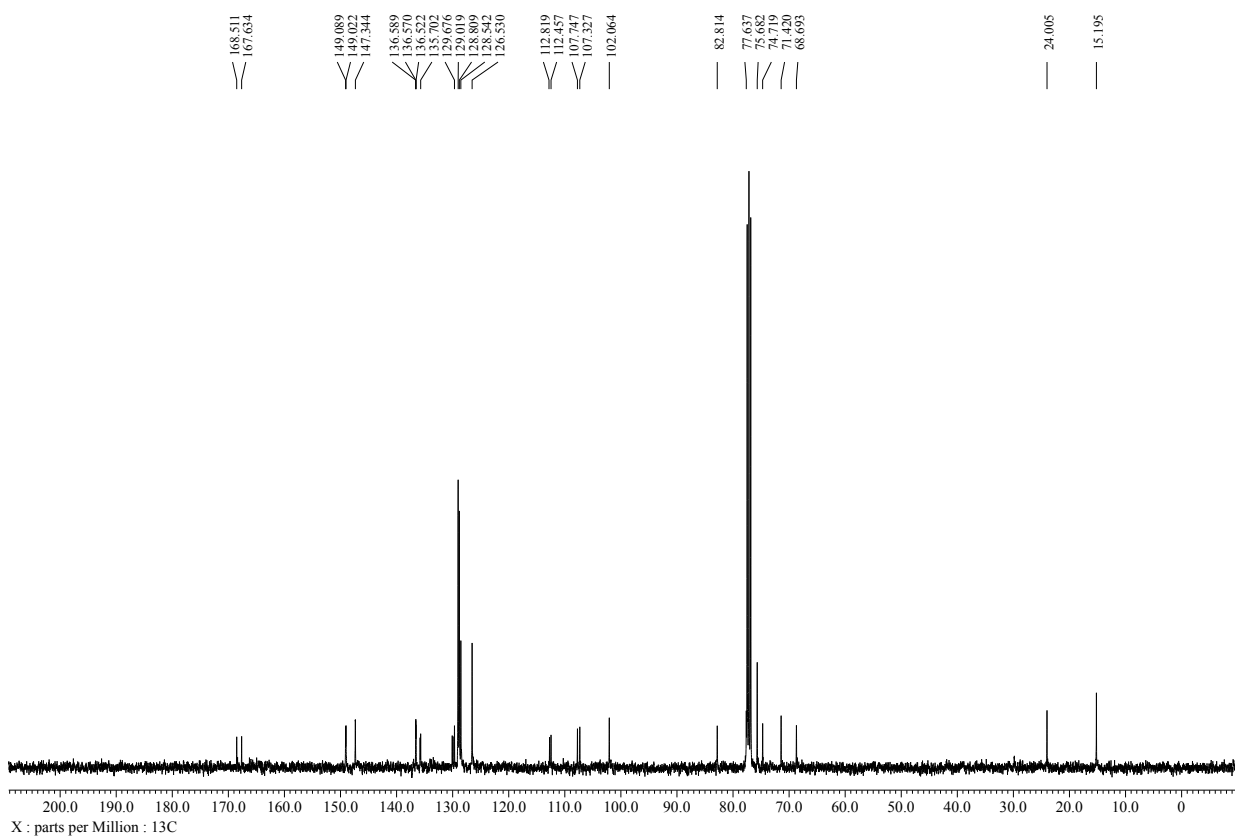
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- 6) Yoshida, T.; Ohwashi, W.; Haba, K.; Ohbayashi, H.; Ishihara, K.; Okano, Y.; Shingu, T.; Okuda, T. Tannins and related polyphenols of melastomataceous plants. II. Nobotanins B, C and E, hydrolyzable tannin dimer and trimers from Tibouchina semidecandra COGN. *Chem. Pharm. Bull.* **1991**, *39*, 2264–2270.

Compound 8

^1H NMR (400 MHz, CDCl_3)

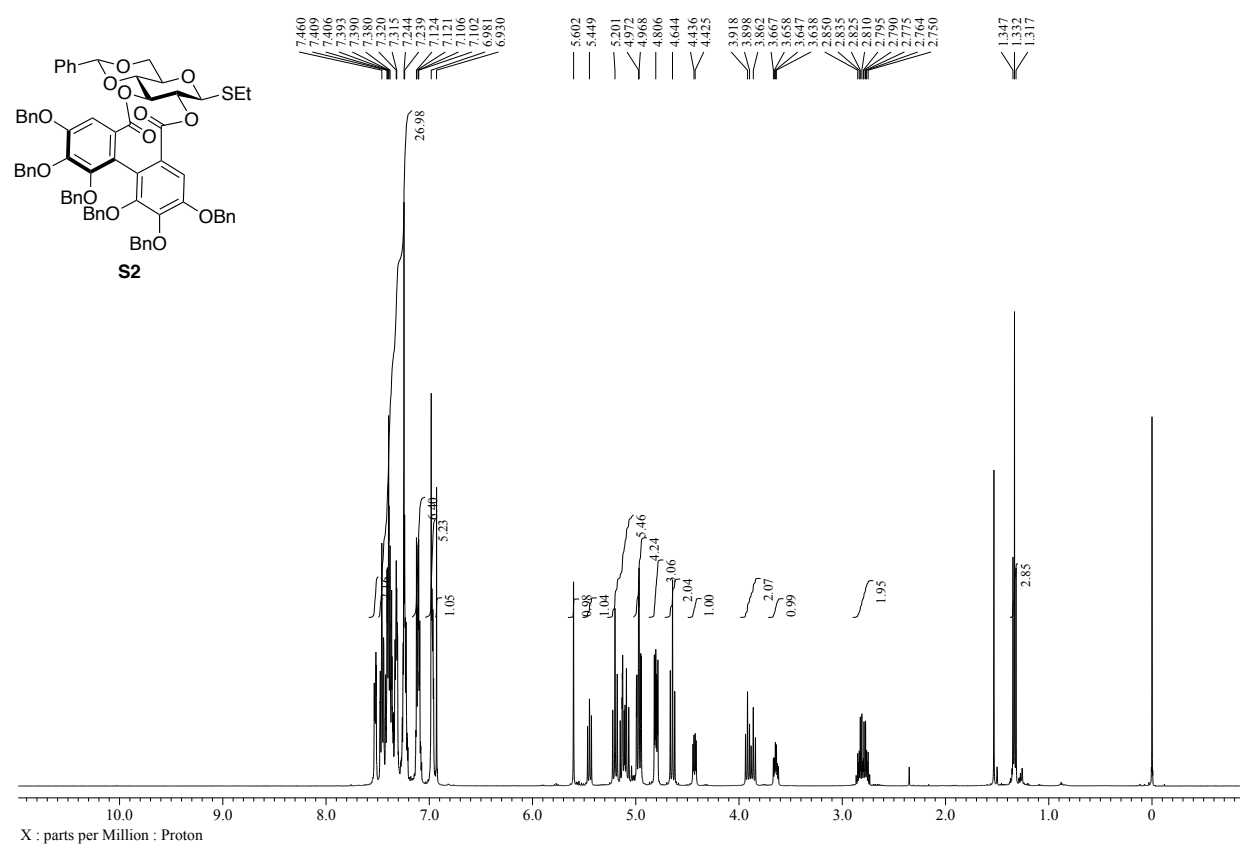


^{13}C NMR (101 MHz, CDCl_3)

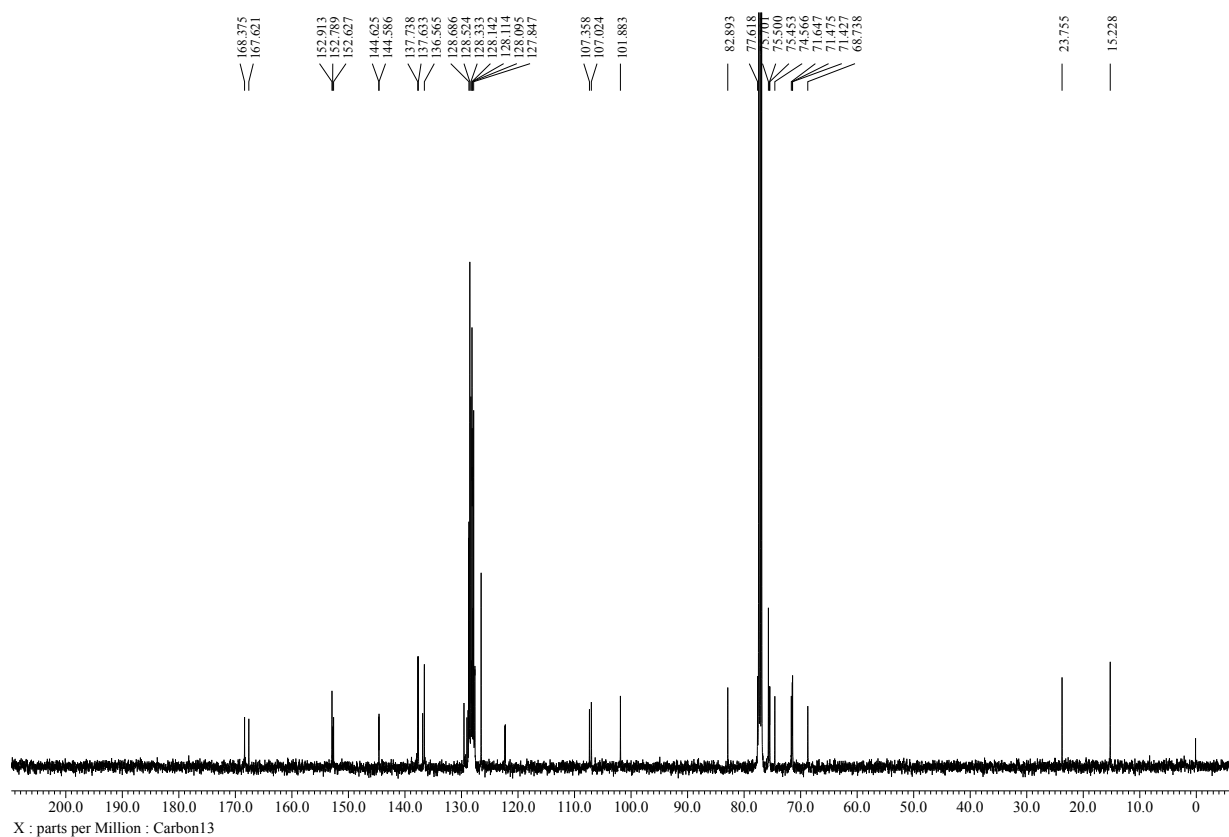


Compound S2

^1H NMR (500 MHz, CDCl_3)

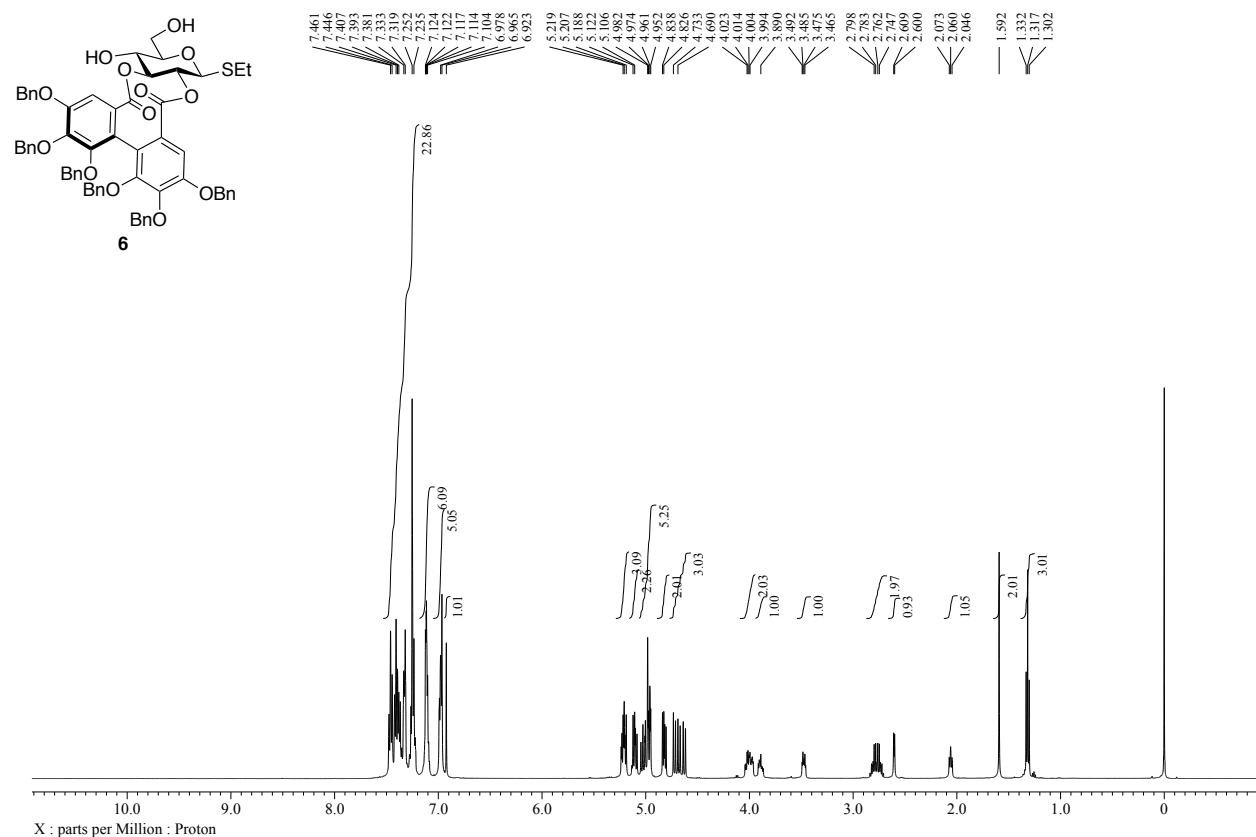


^{13}C NMR (126 MHz, CDCl_3)

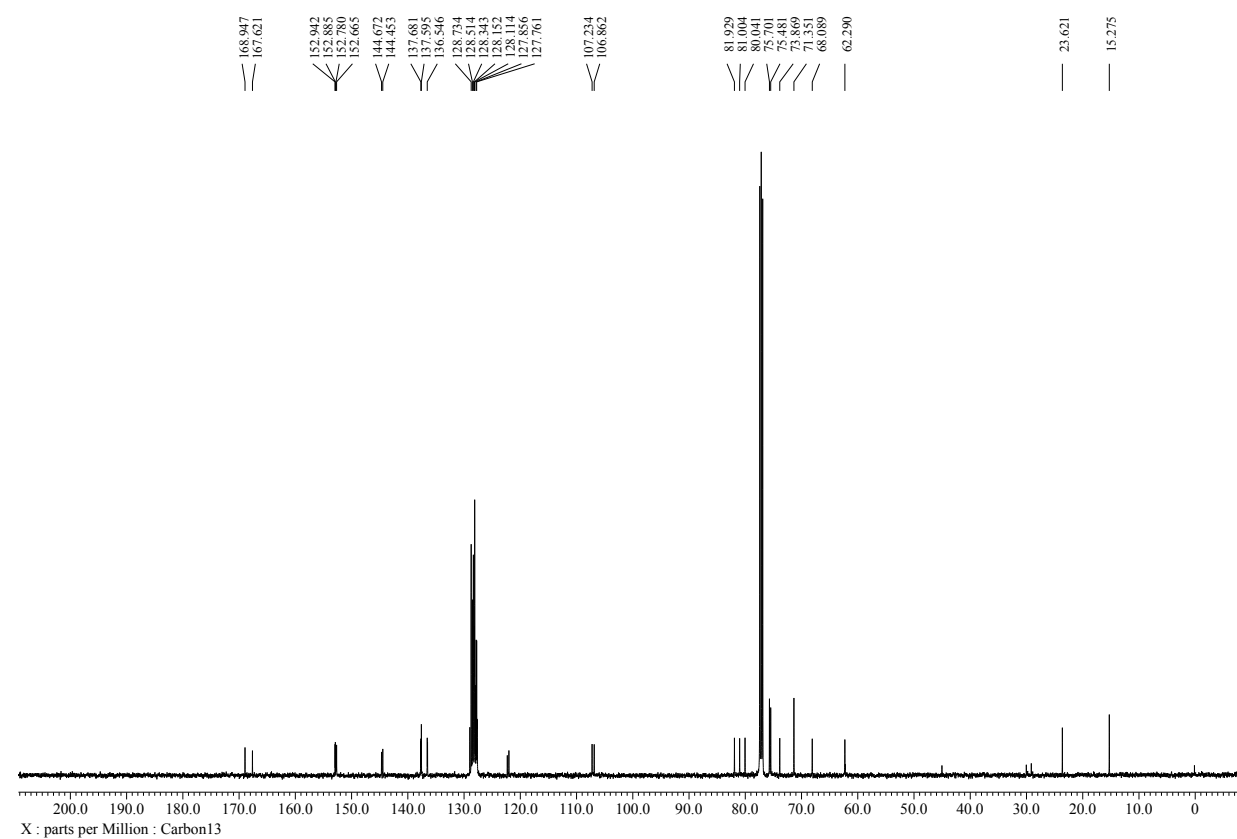


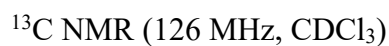
Compound 6

^1H NMR (500 MHz, CDCl_3)



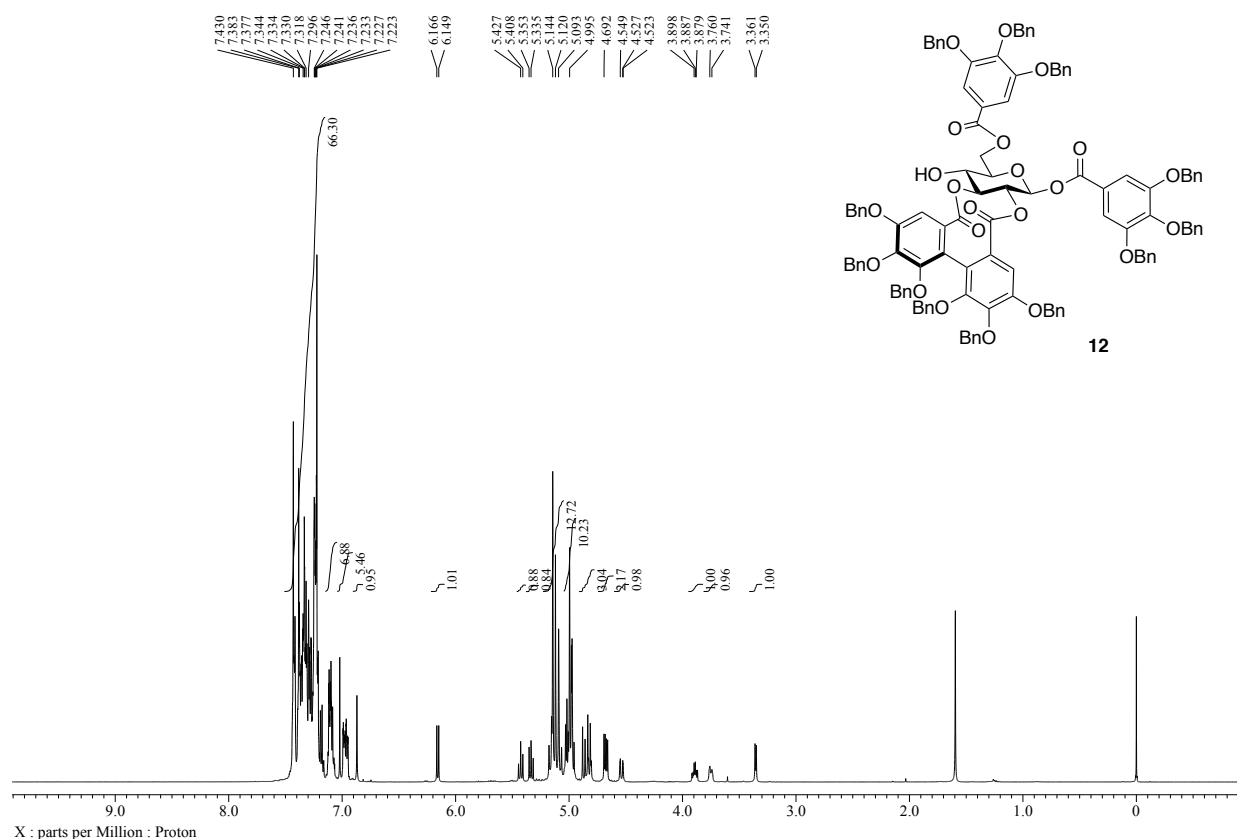
^{13}C NMR (126 MHz, CDCl_3)



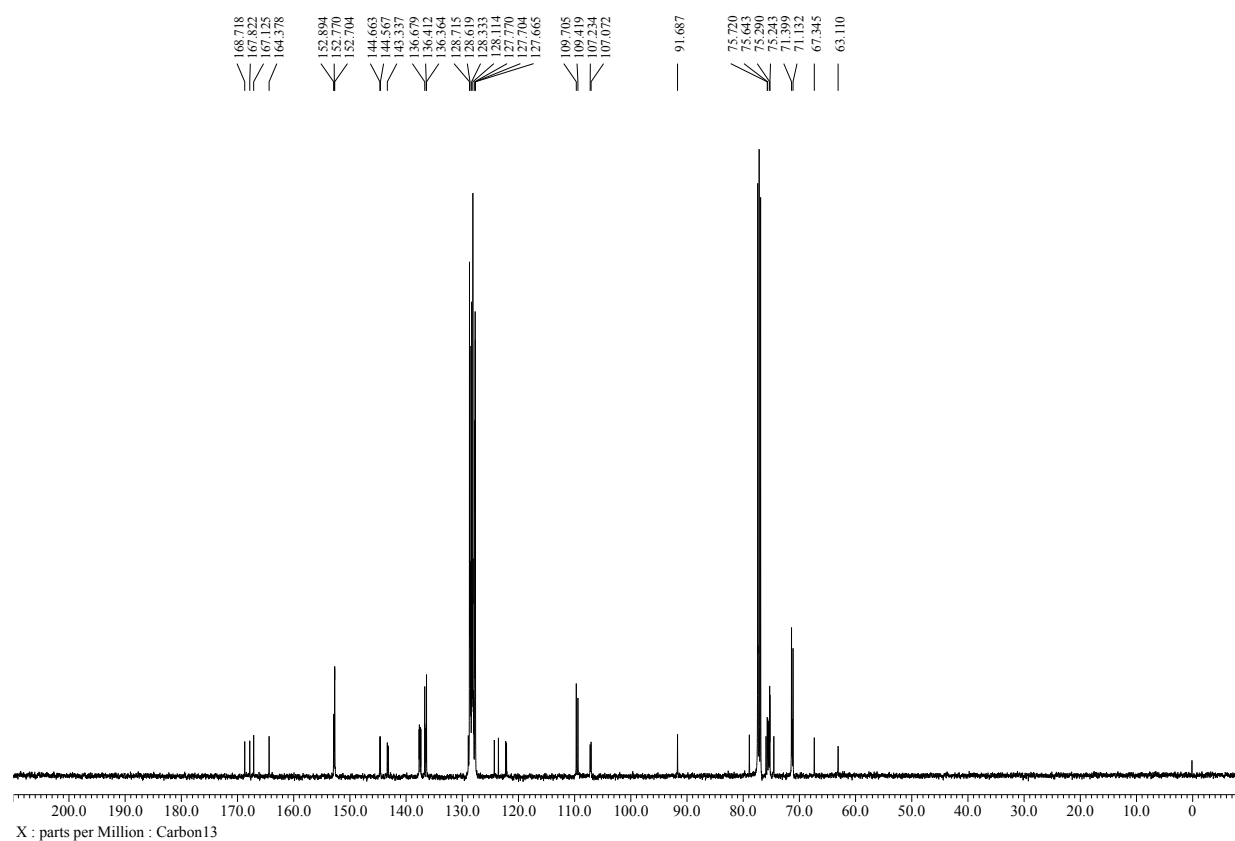
¹H NMR (500 MHz, CDCl₃)

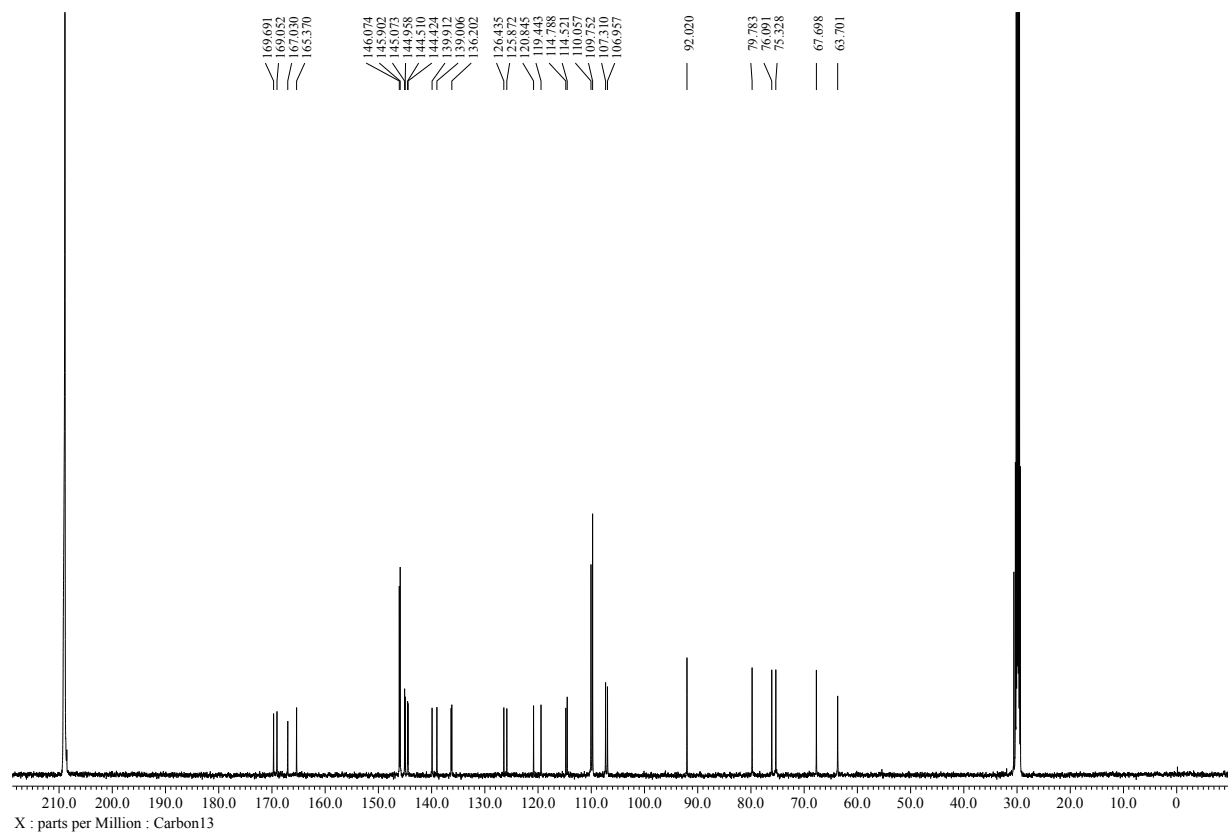
Compound 12

^1H NMR (500 MHz, CDCl_3)



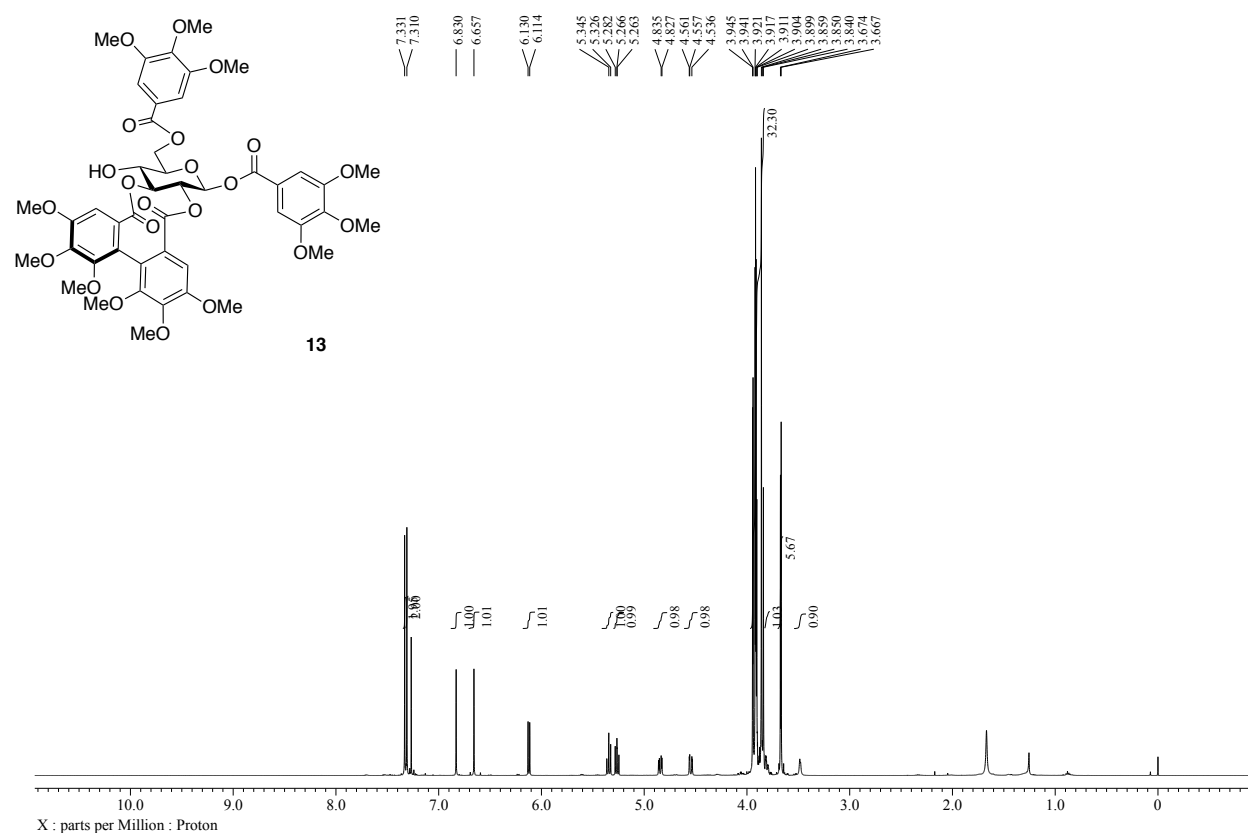
^{13}C NMR (126 MHz, CDCl_3)



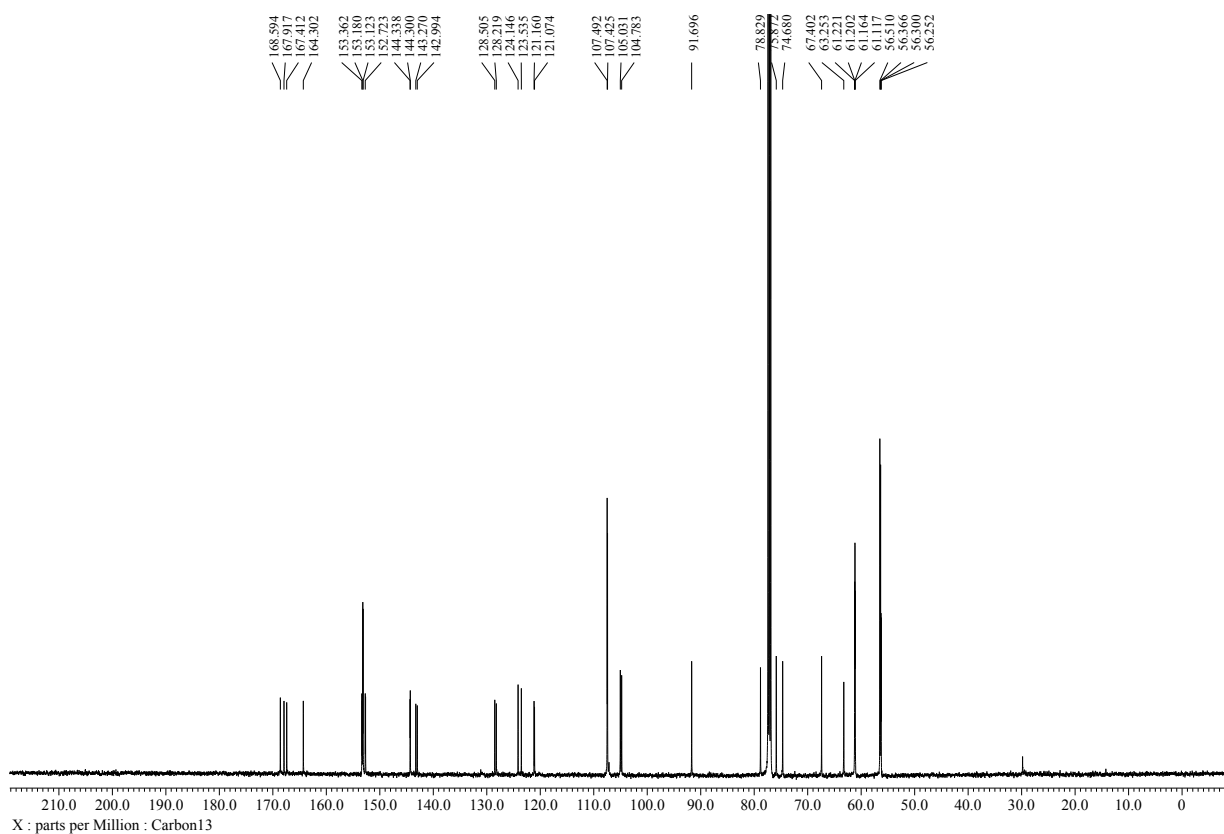
¹H NMR (500 MHz, acetone-*d*₆ + D₂O)

Compound 13

^1H NMR (500 MHz, CDCl_3)

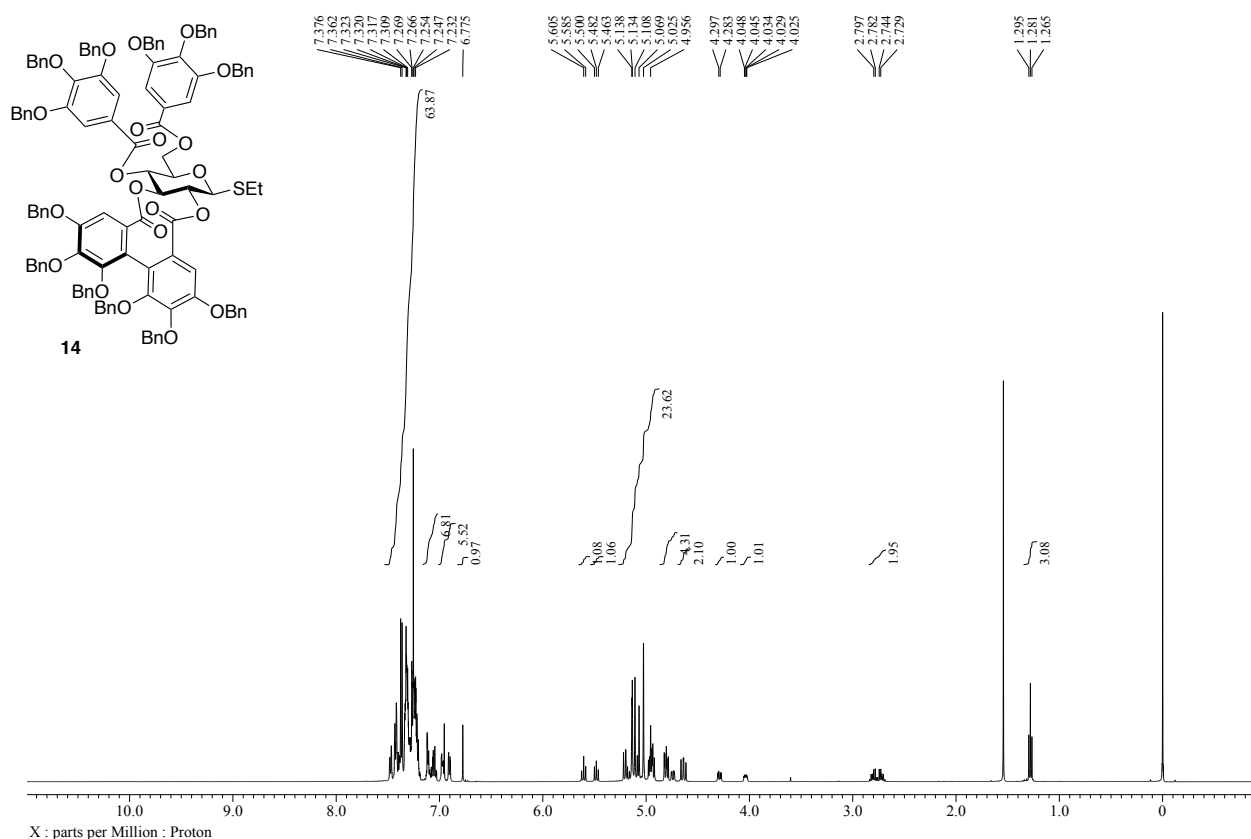


^{13}C NMR (126 MHz, CDCl_3)

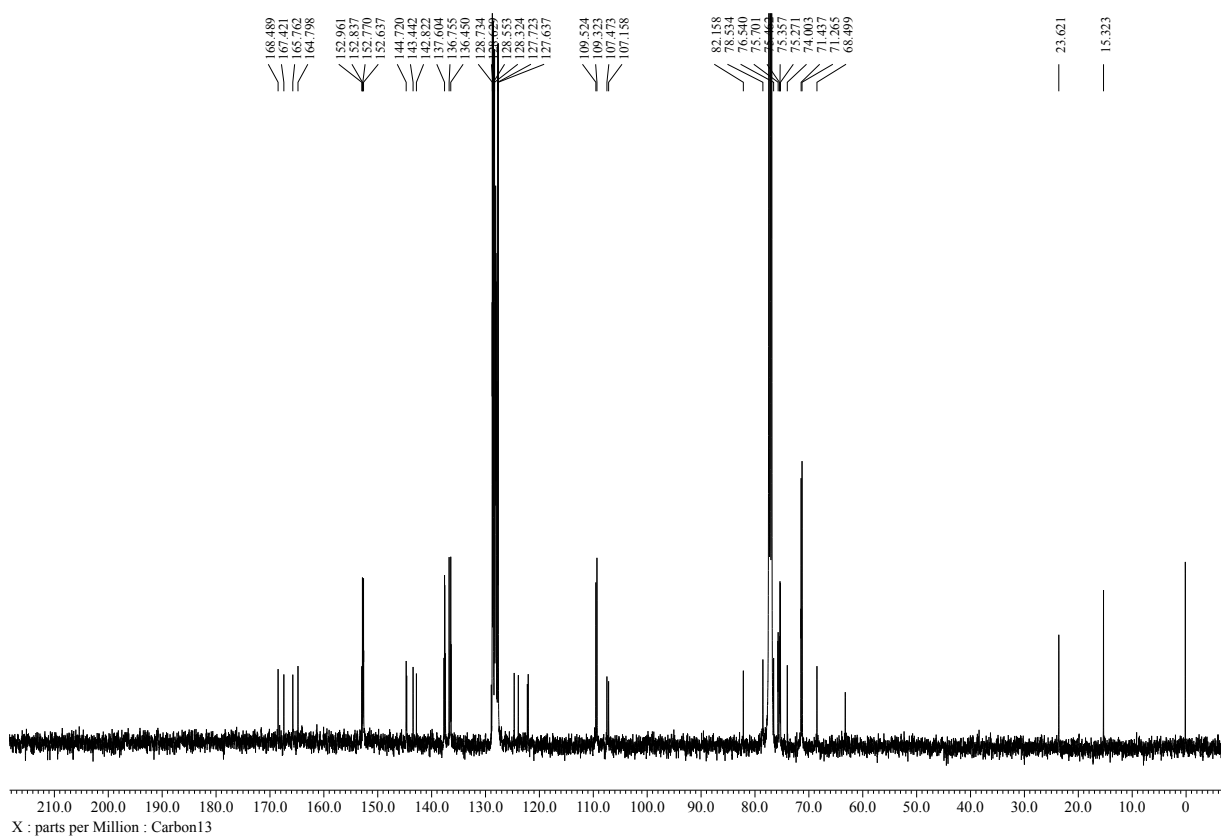


Compound 14

^1H NMR (500 MHz, CDCl_3)

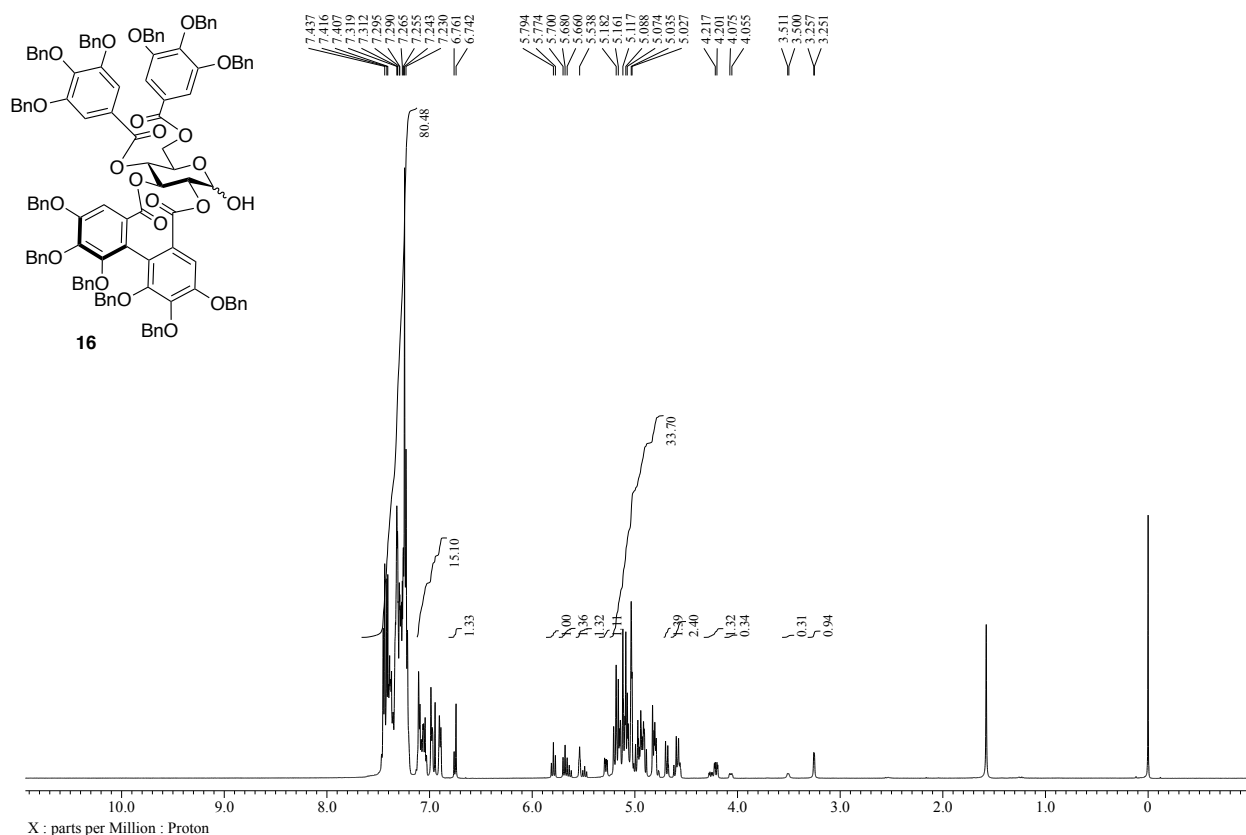


^{13}C NMR (126 MHz, CDCl_3)

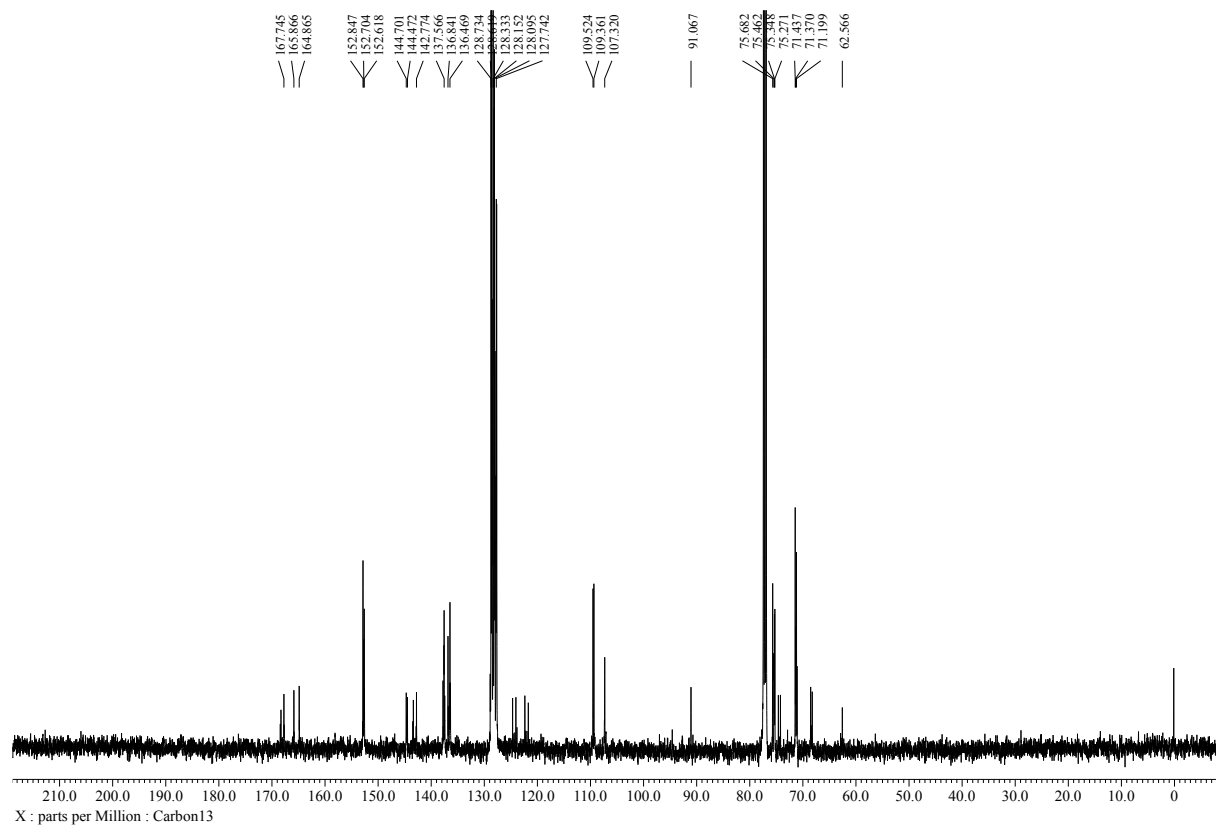


Compound 16

^1H NMR (500 MHz, CDCl_3)

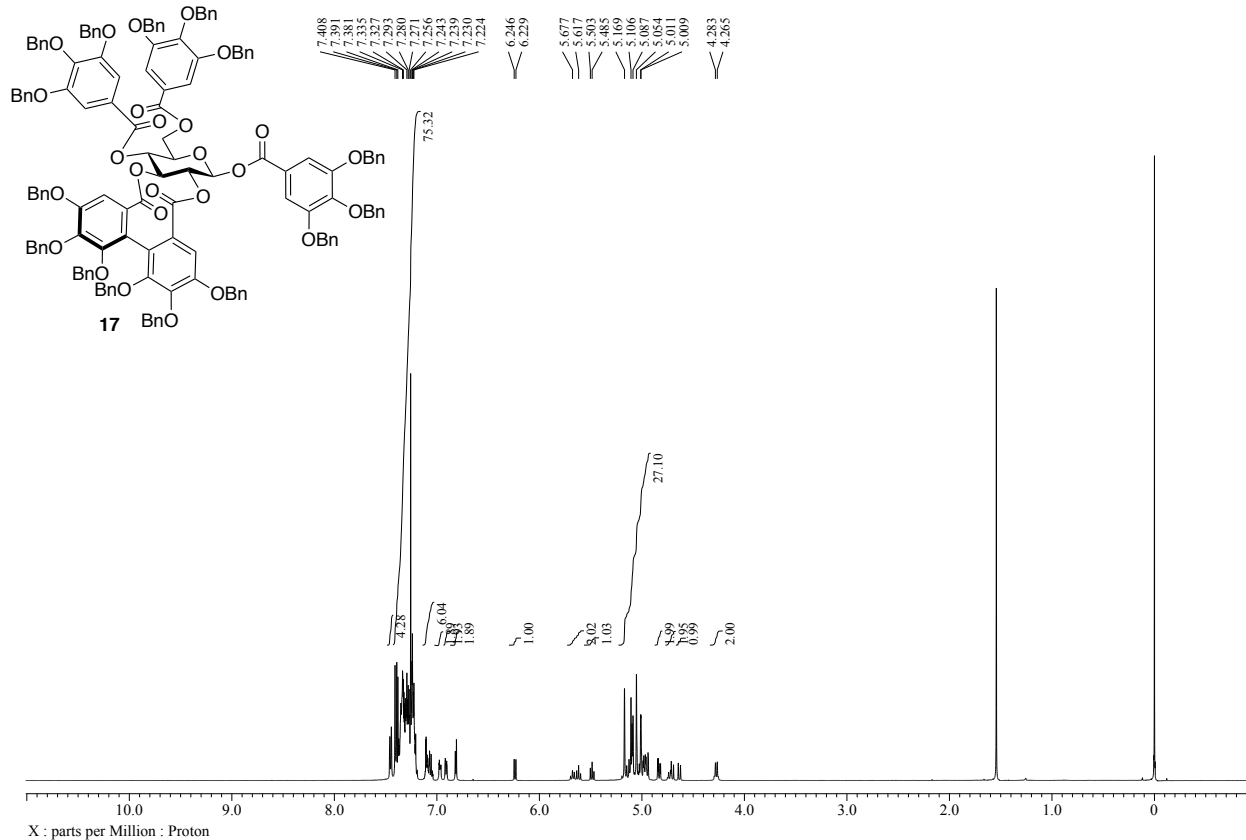


^{13}C NMR (126 MHz, CDCl_3)

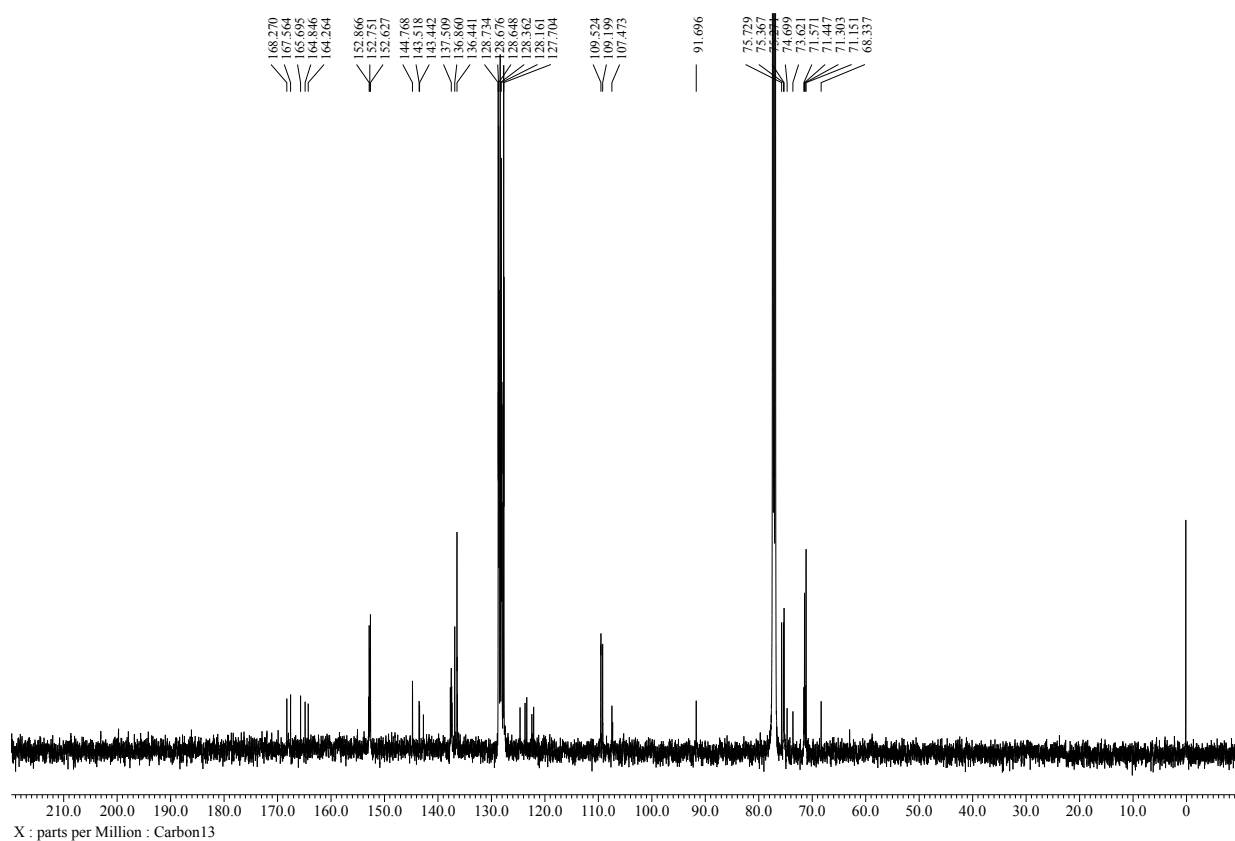


Compound 17

^1H NMR (500 MHz, CDCl_3)

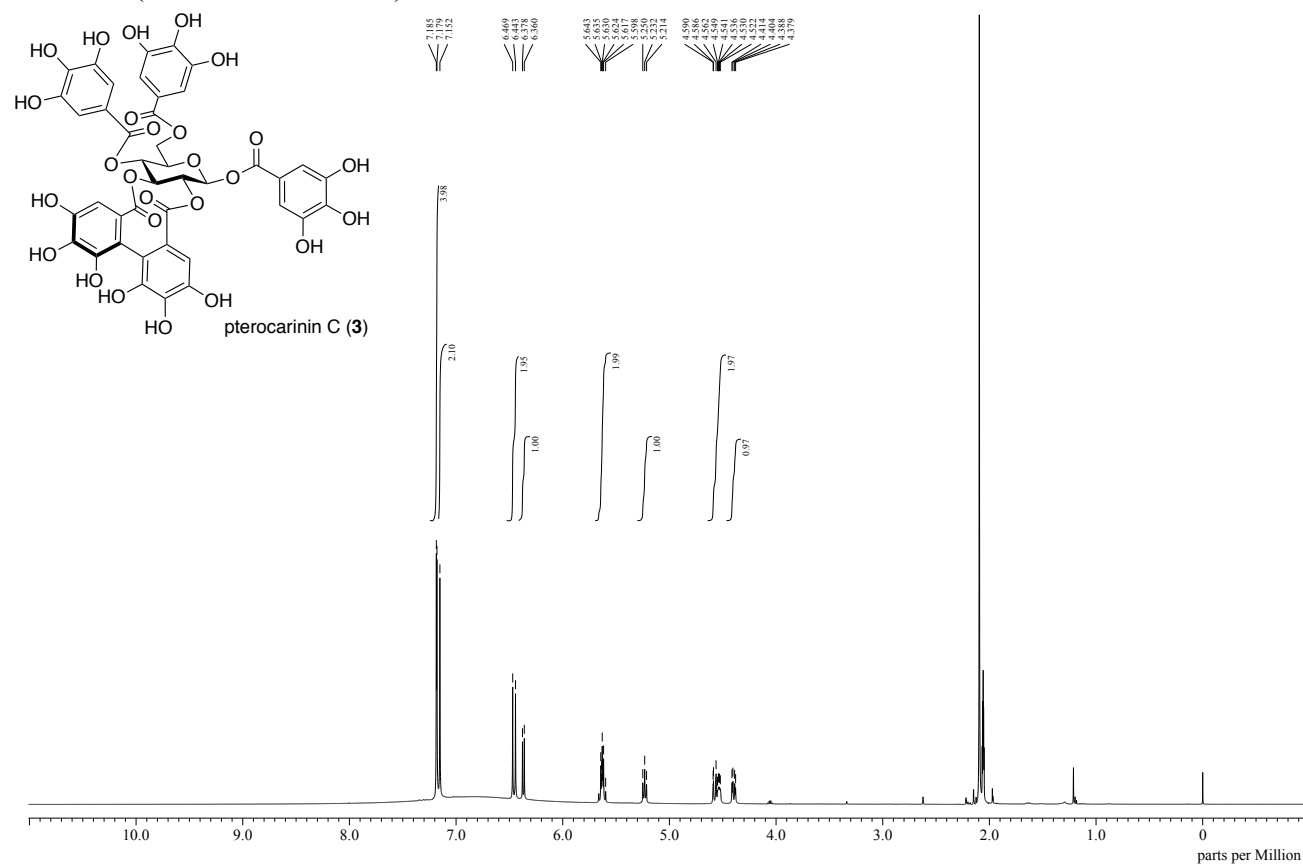


^{13}C NMR (126 MHz, CDCl_3)

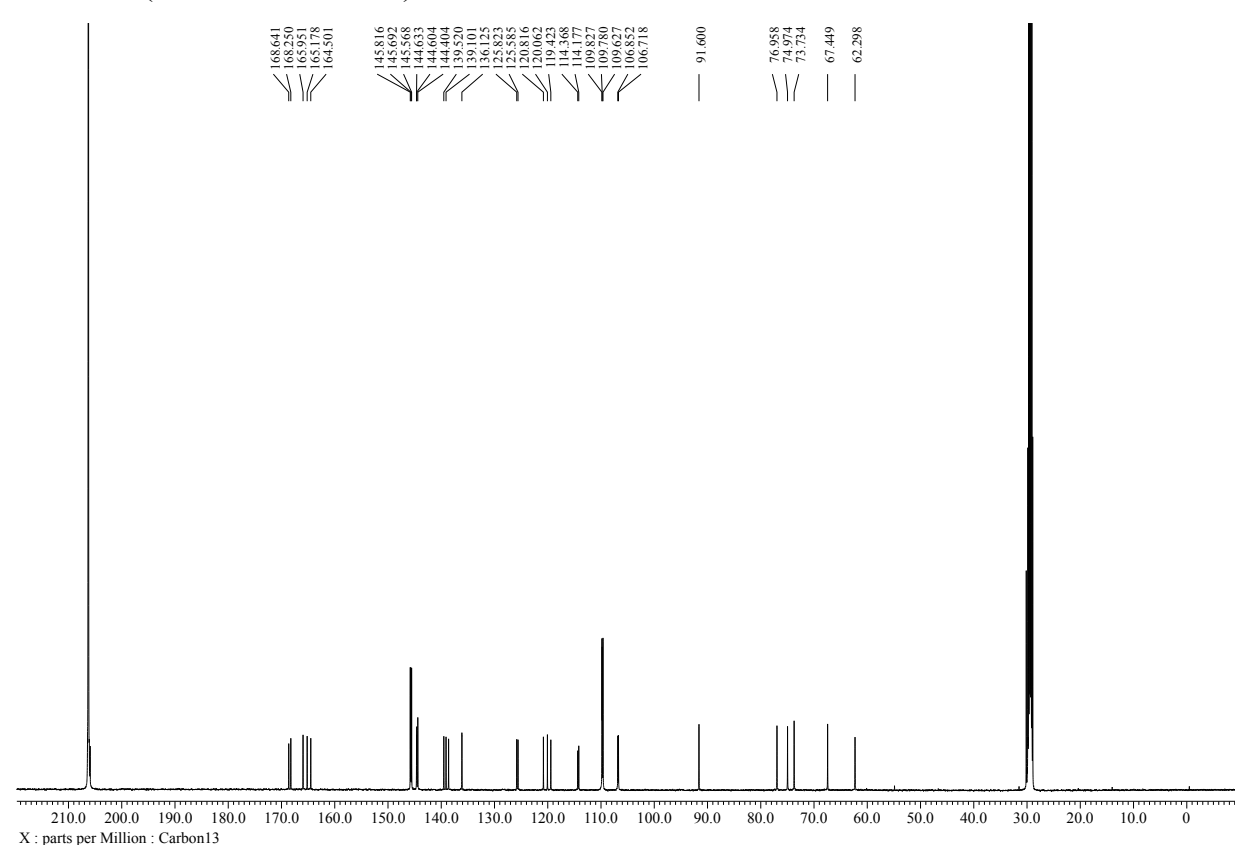


Pterocarinin C (3)

¹H NMR (500 MHz, acetone-d₆)

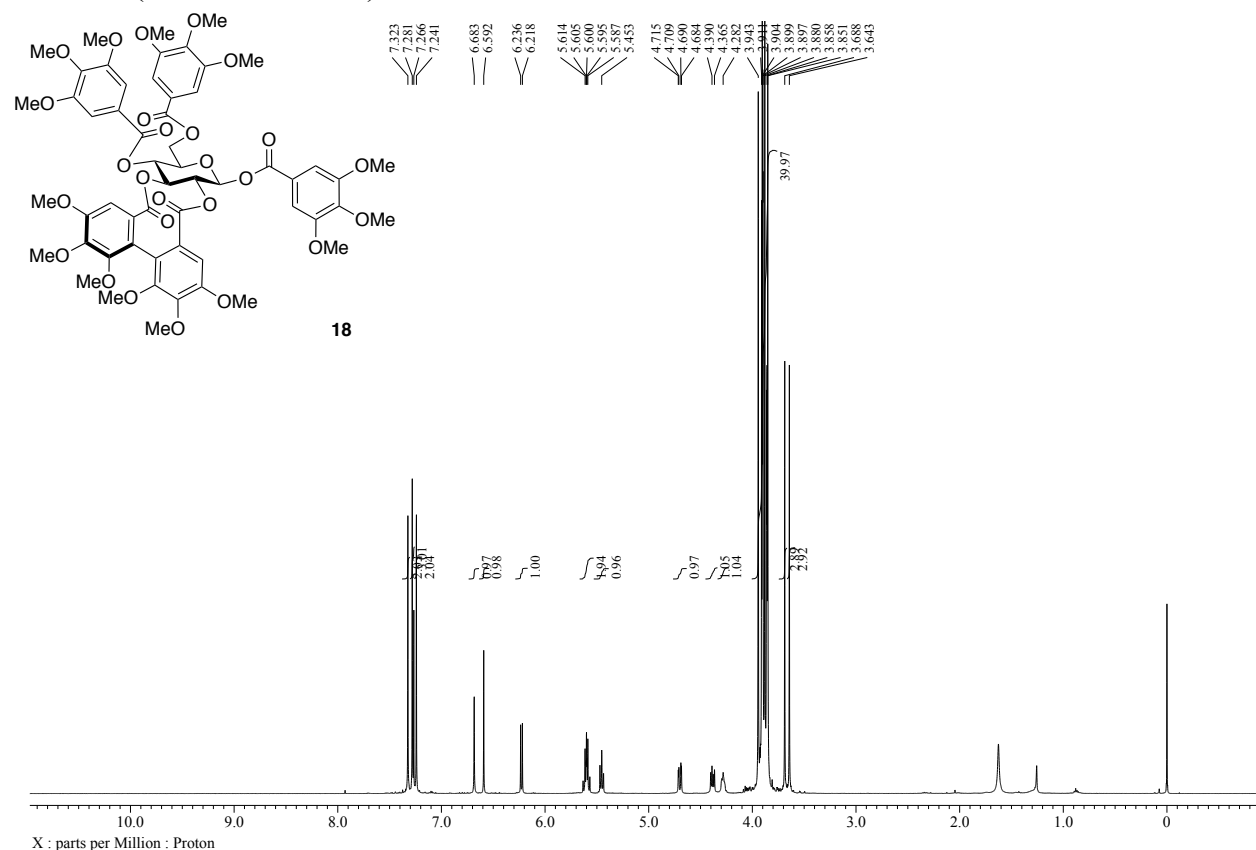


¹³C NMR (126 MHz, acetone-d₆)

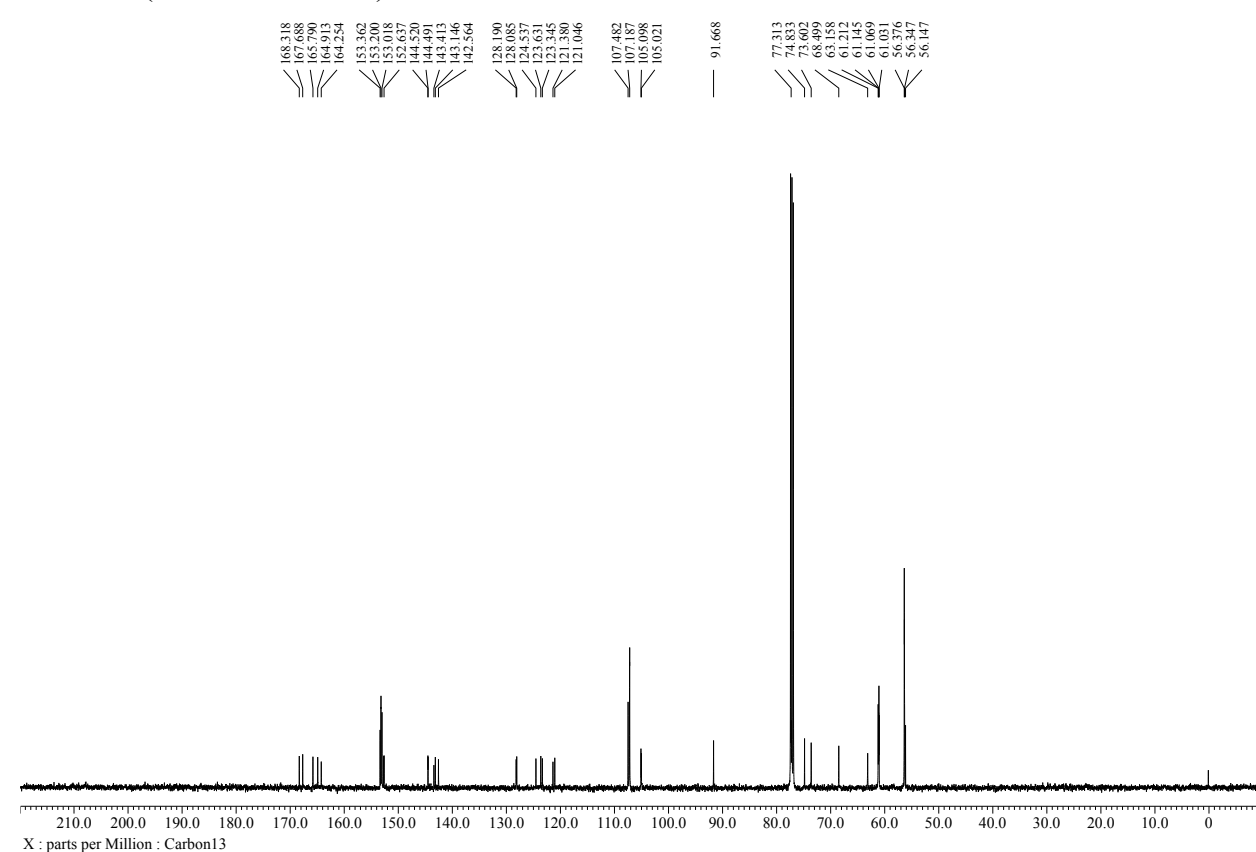


Compound 18

^1H NMR (500 MHz, CDCl_3)

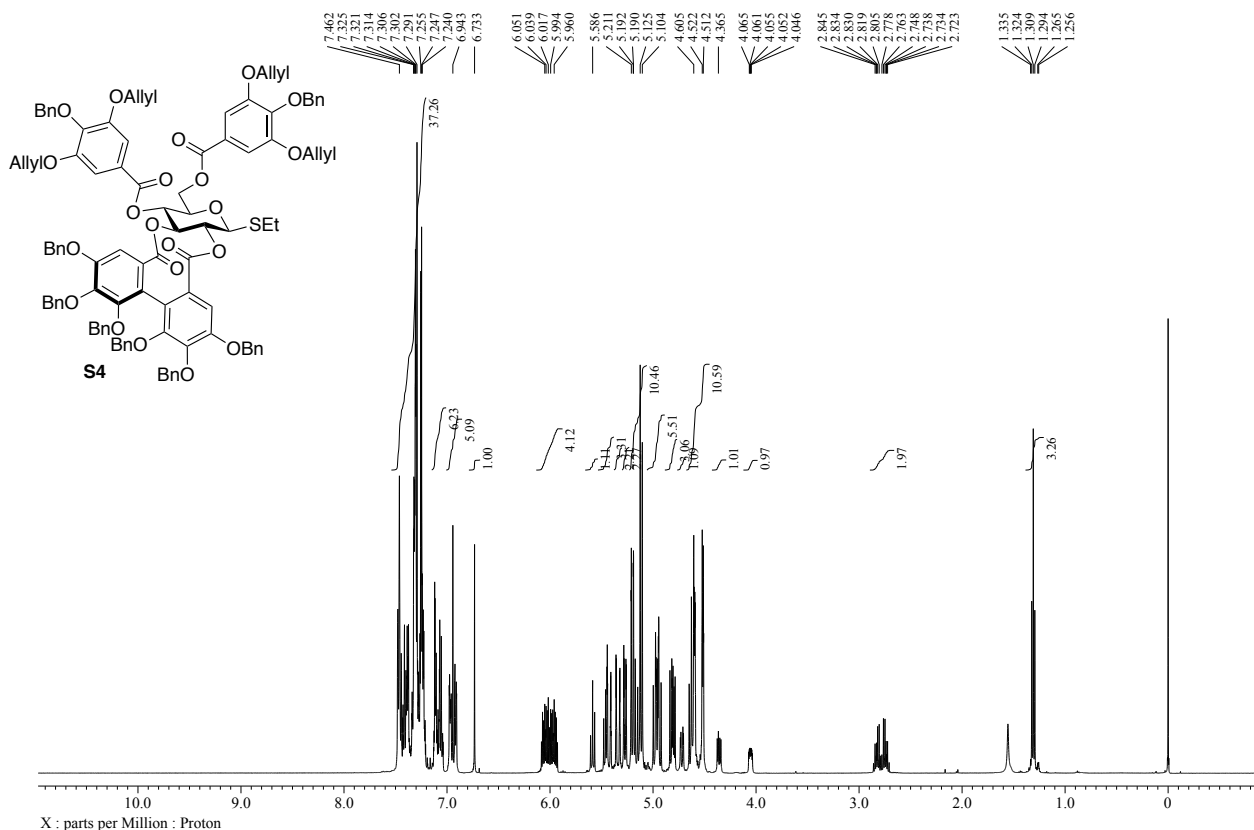


^{13}C NMR (126 MHz, CDCl_3)

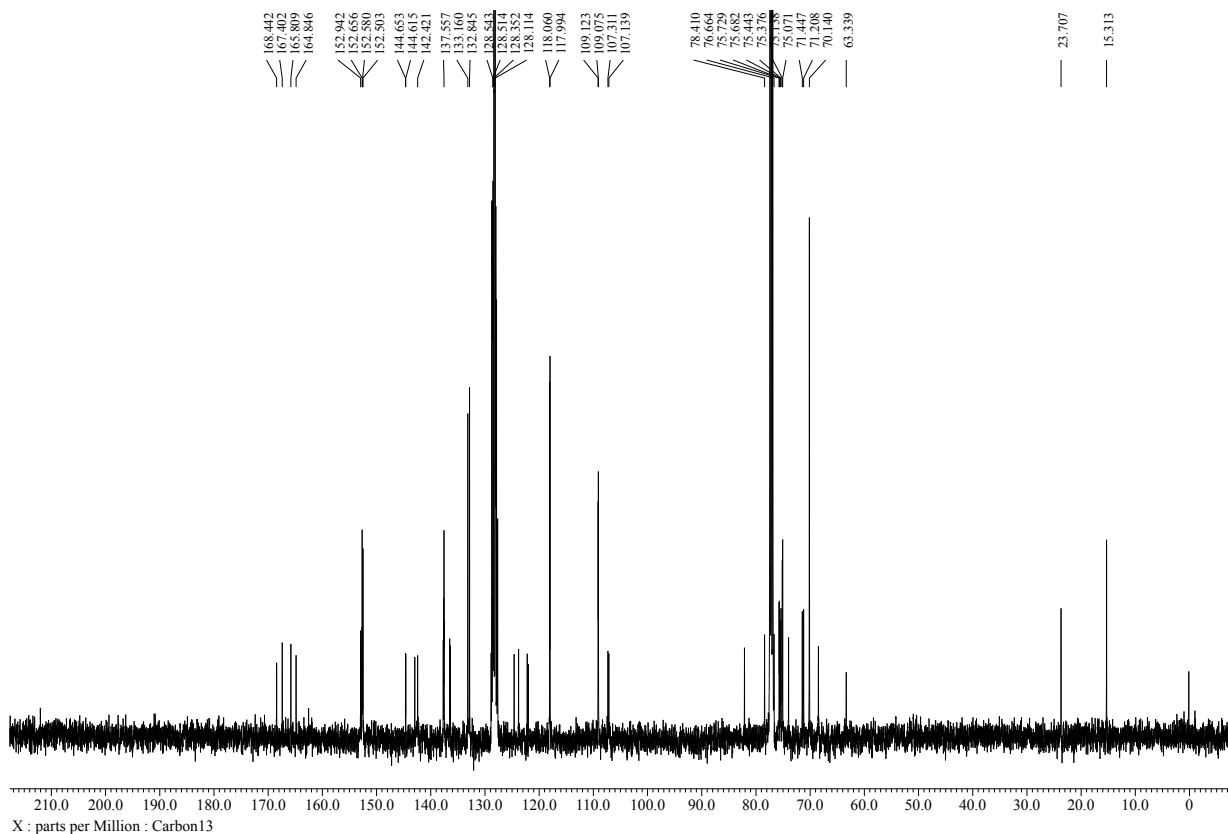


Compound S4

^1H NMR (500 MHz, CDCl_3)

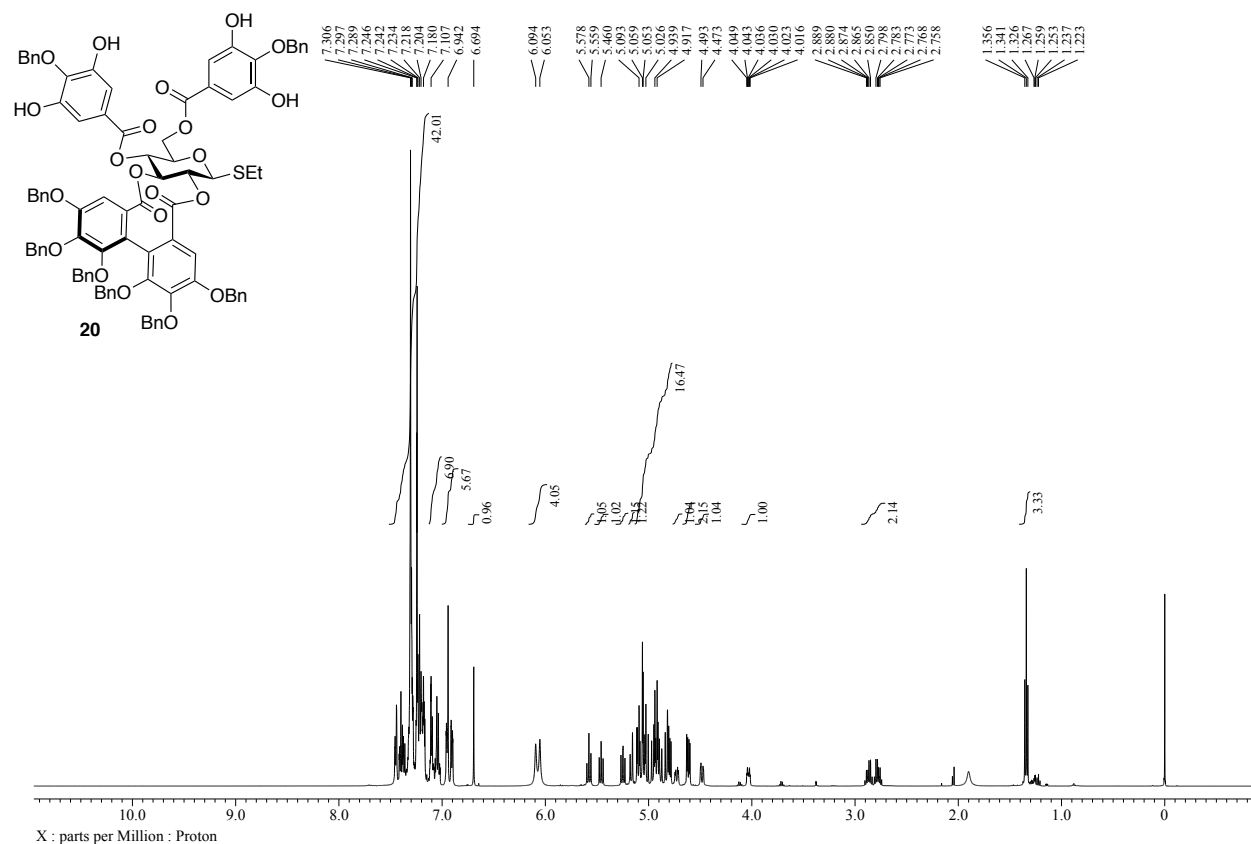


^{13}C NMR (126 MHz, CDCl_3)

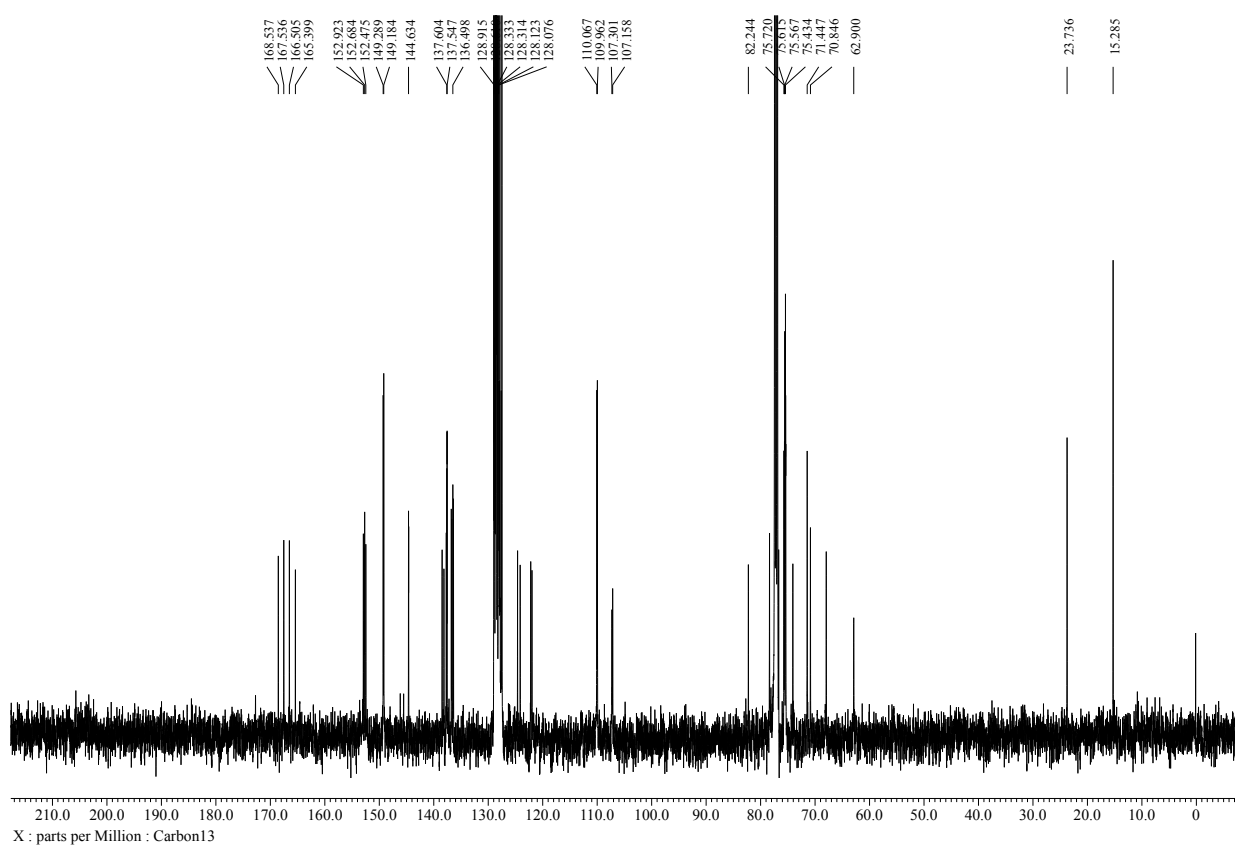


Compound 20

^1H NMR (500 MHz, CDCl_3)

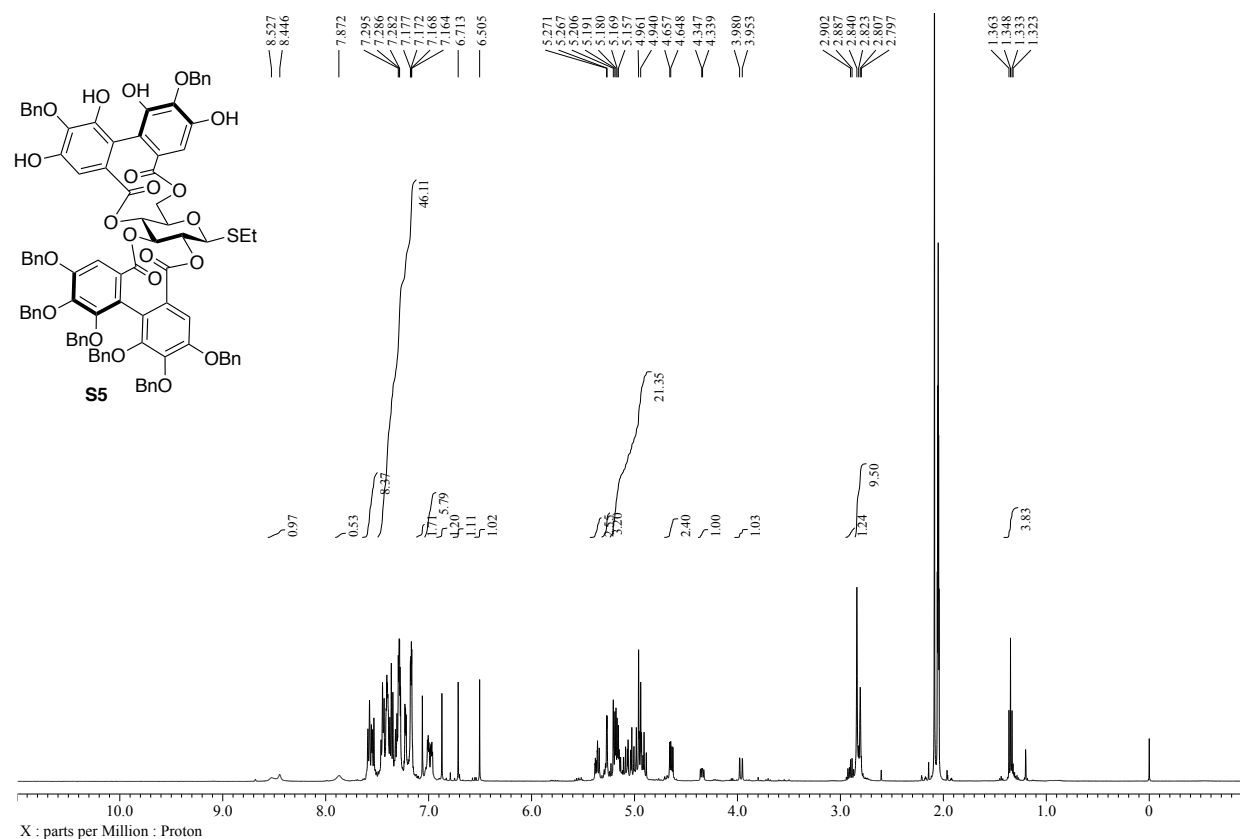


^{13}C NMR (126 MHz, CDCl_3)

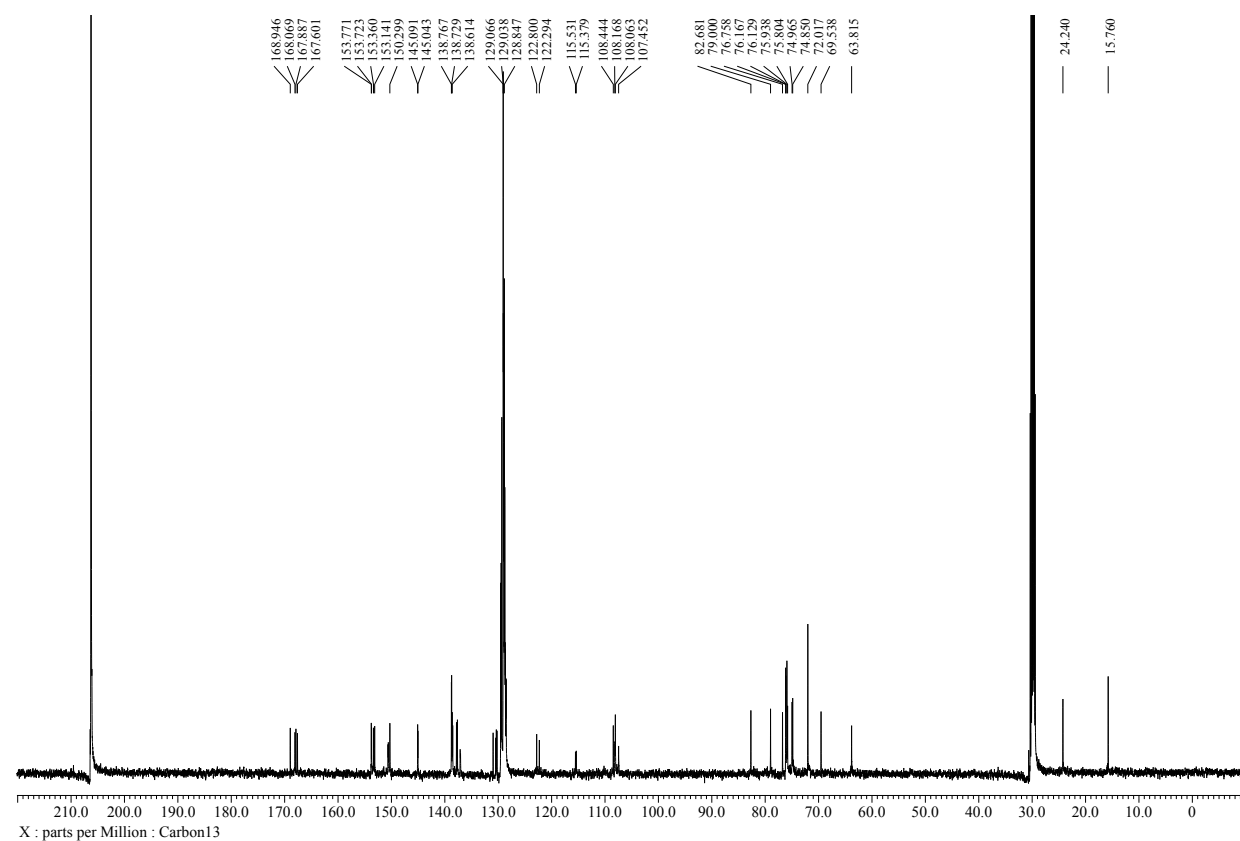


Compound S5

¹H NMR (500 MHz, acetone-*d*₆)

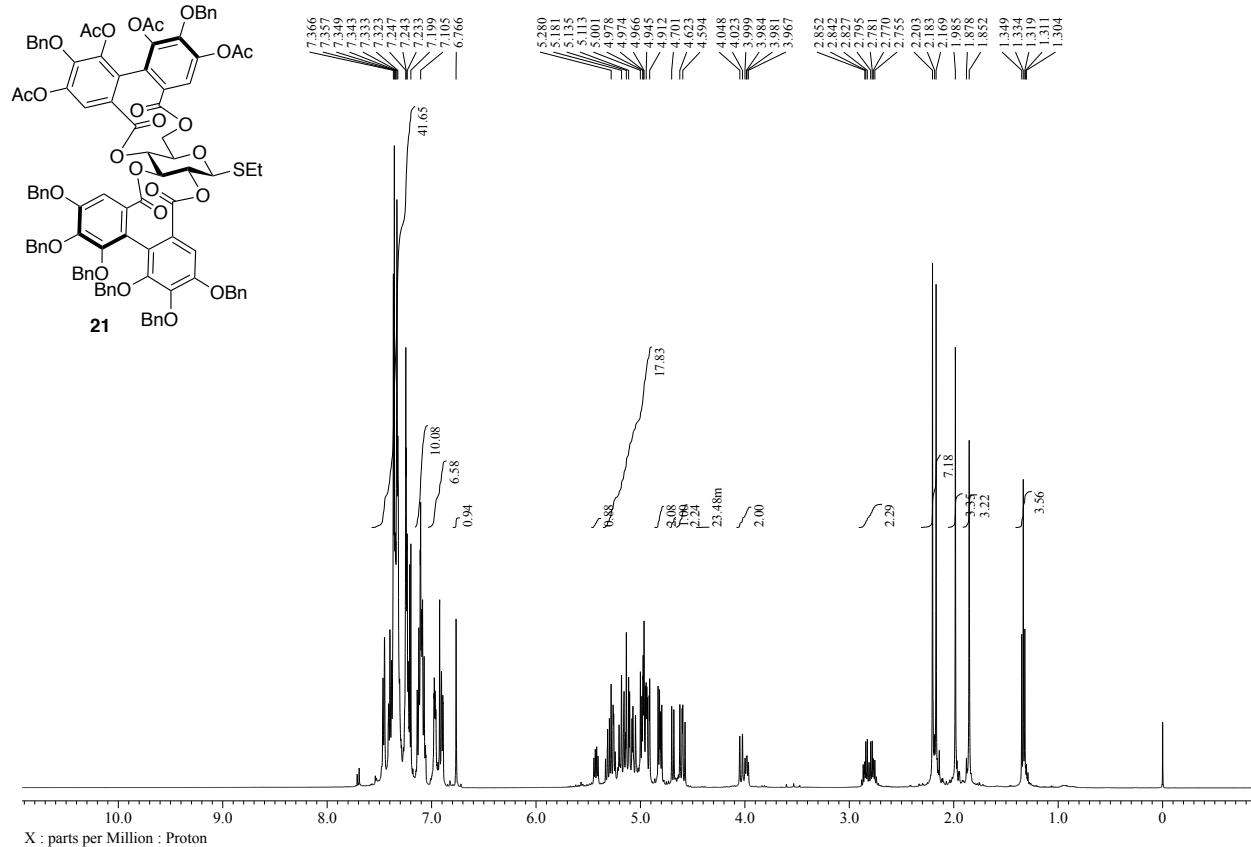


¹³C NMR (126 MHz, acetone-*d*₆)

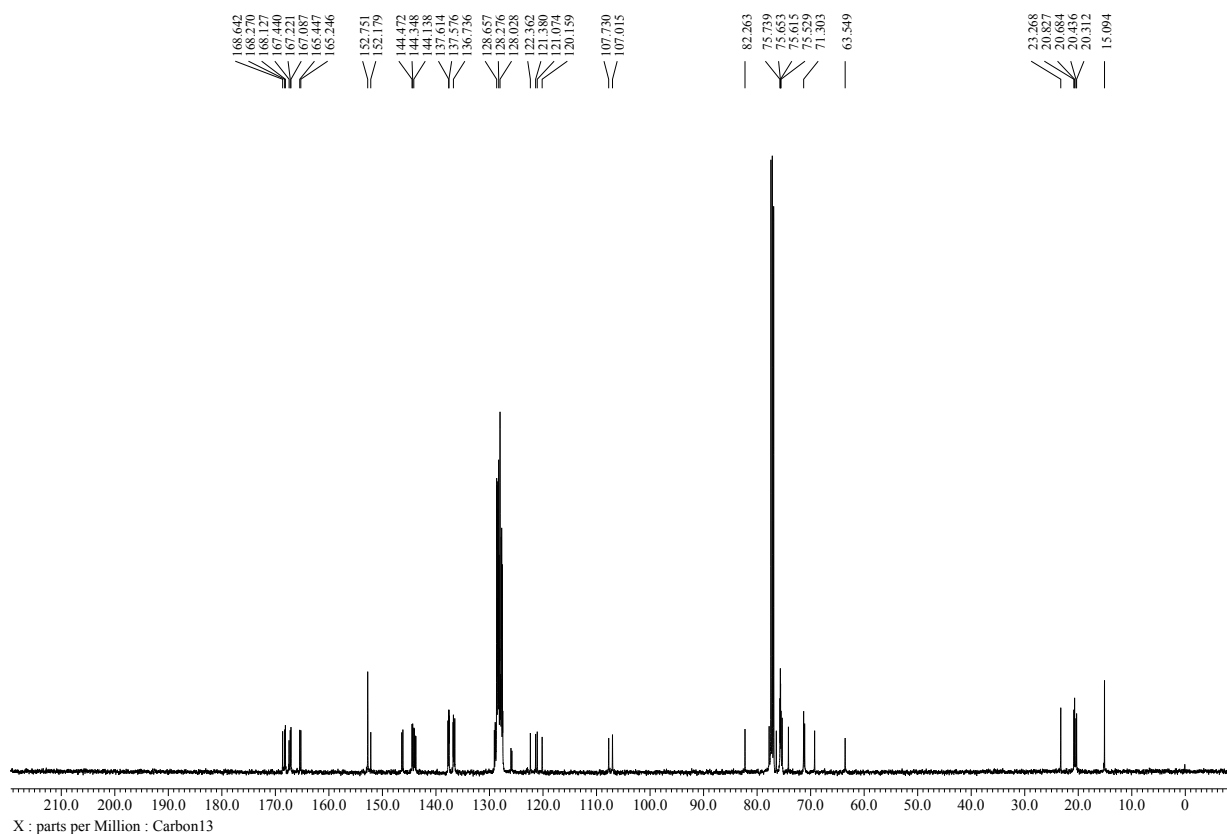


Compound 21

^1H NMR (500 MHz, CDCl_3)

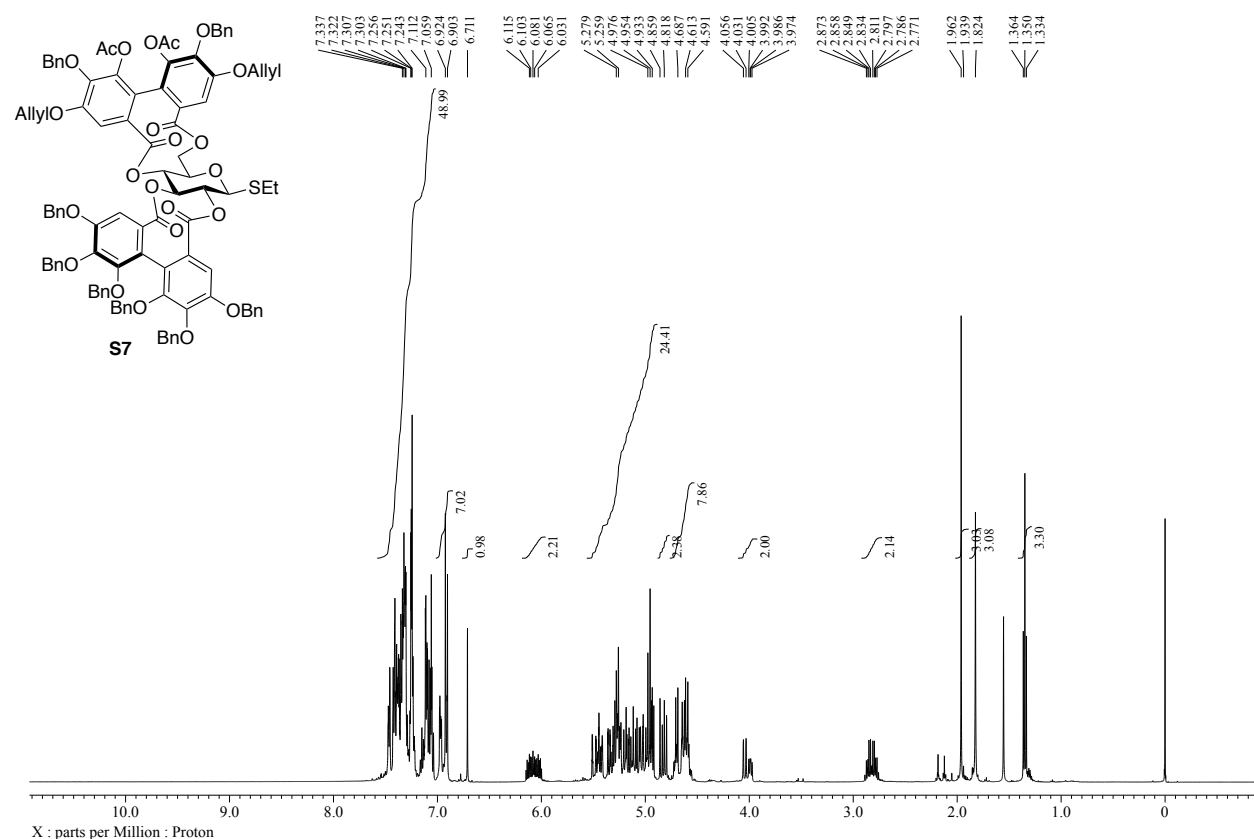


^{13}C NMR (126 MHz, CDCl_3)

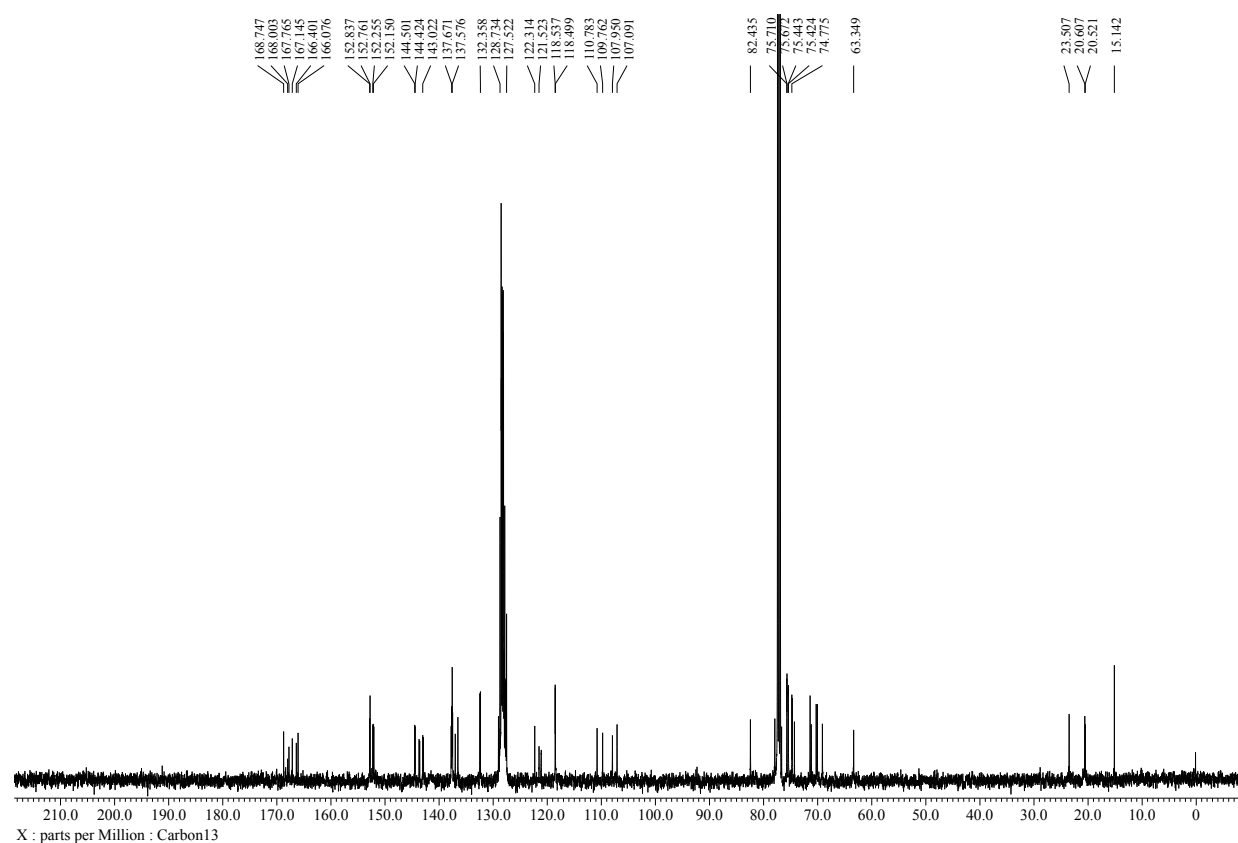


Compound S7

^1H NMR (500 MHz, CDCl_3)

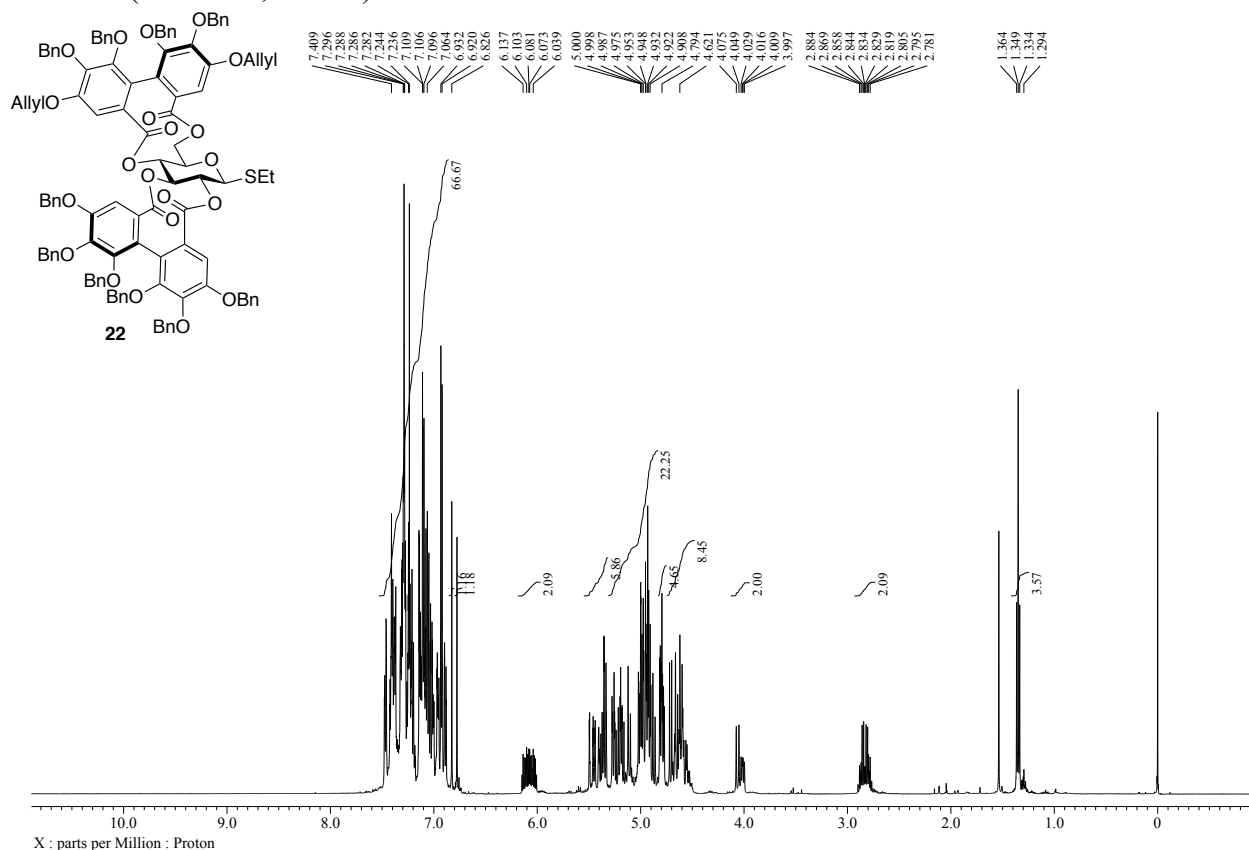


^{13}C NMR (126 MHz, CDCl_3)

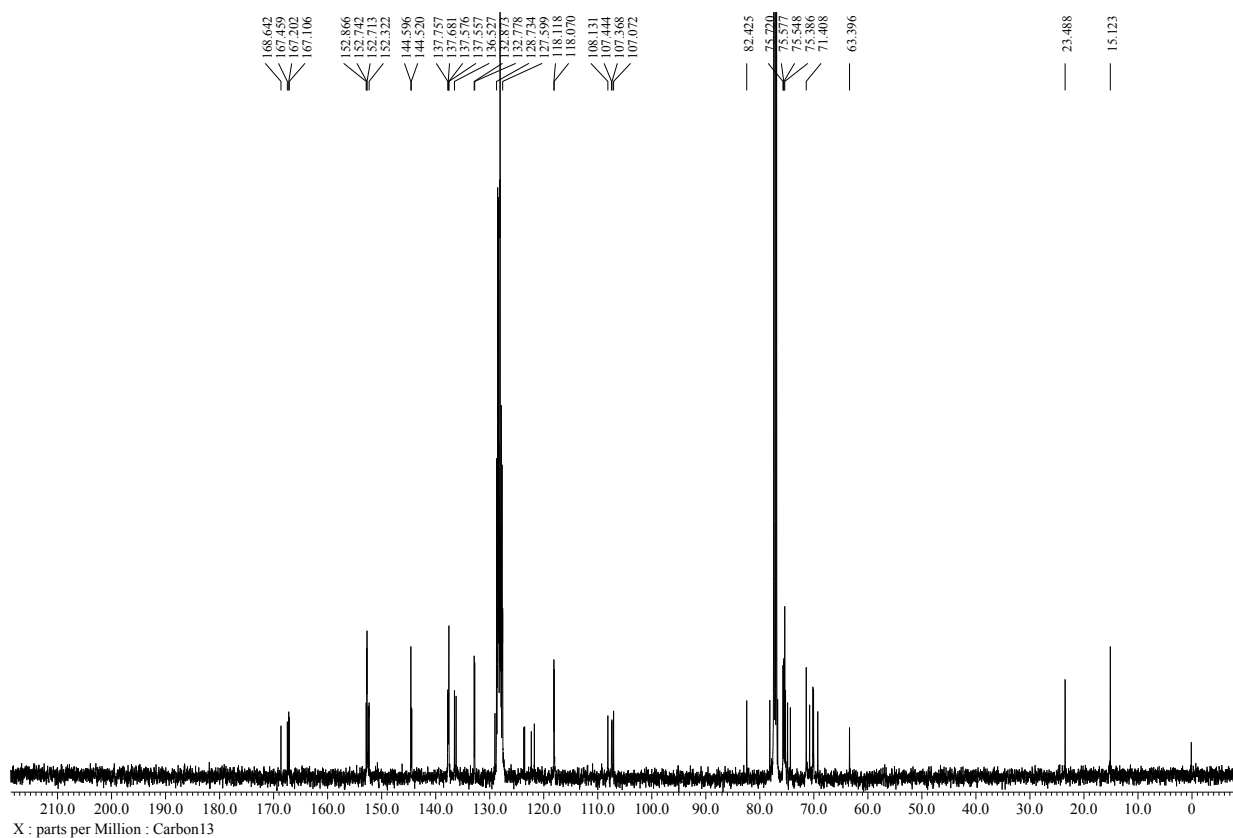


Compound 22

^1H NMR (500 MHz, CDCl_3)

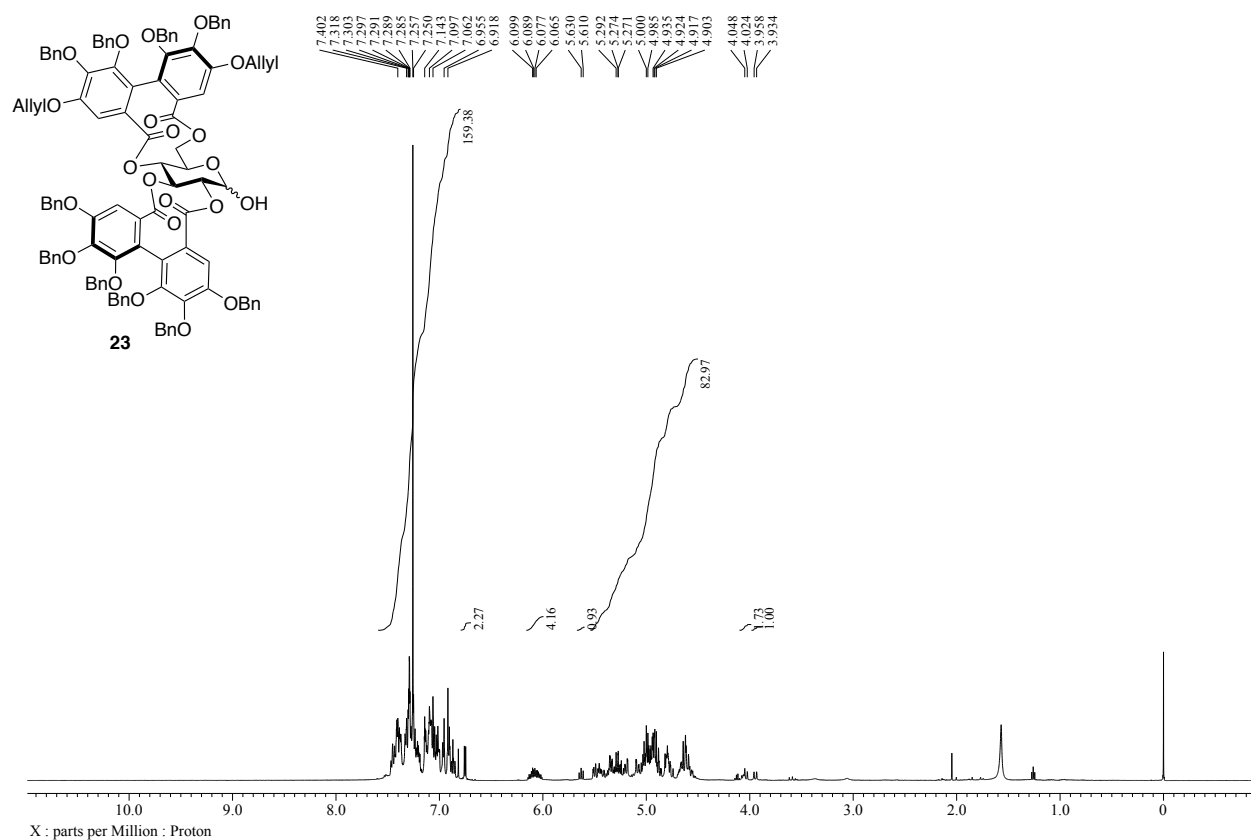


^{13}C NMR (126 MHz, CDCl_3)

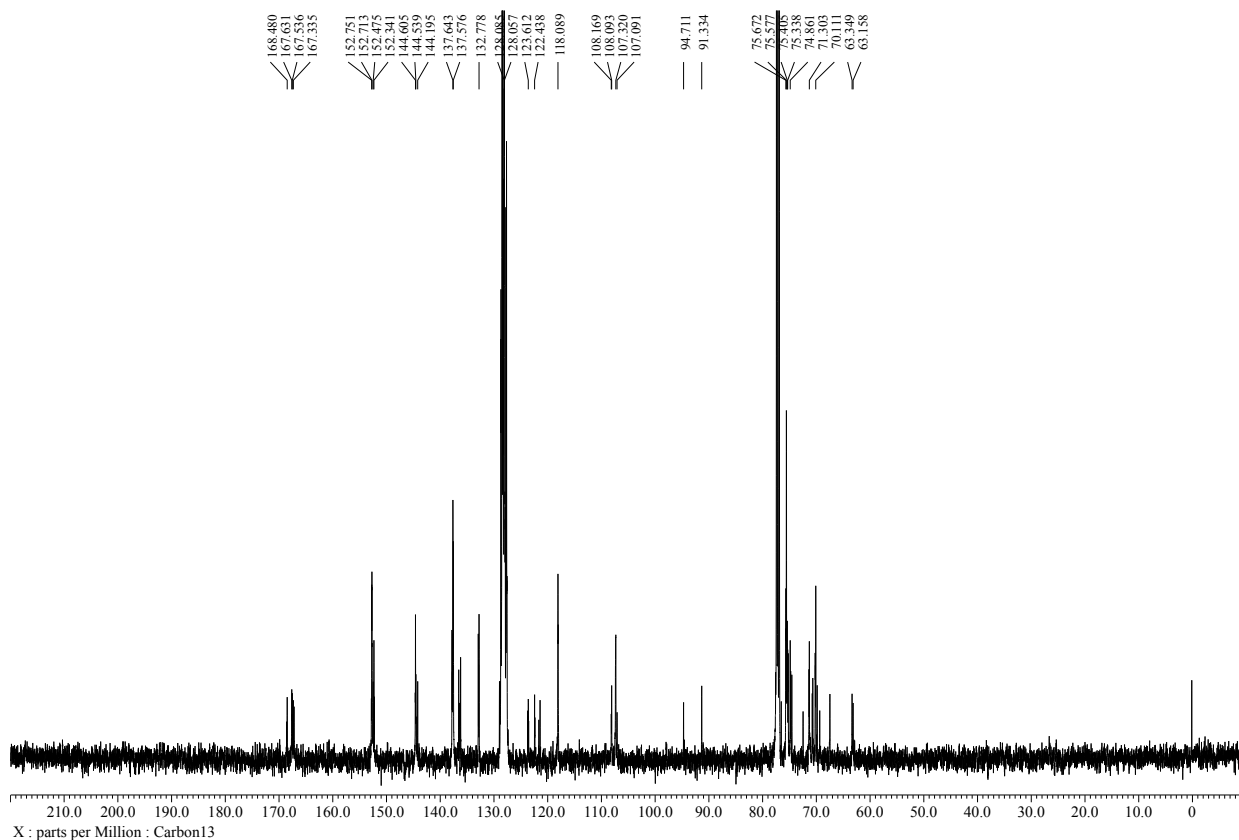


Compound 23

^1H NMR (500 MHz, CDCl_3)

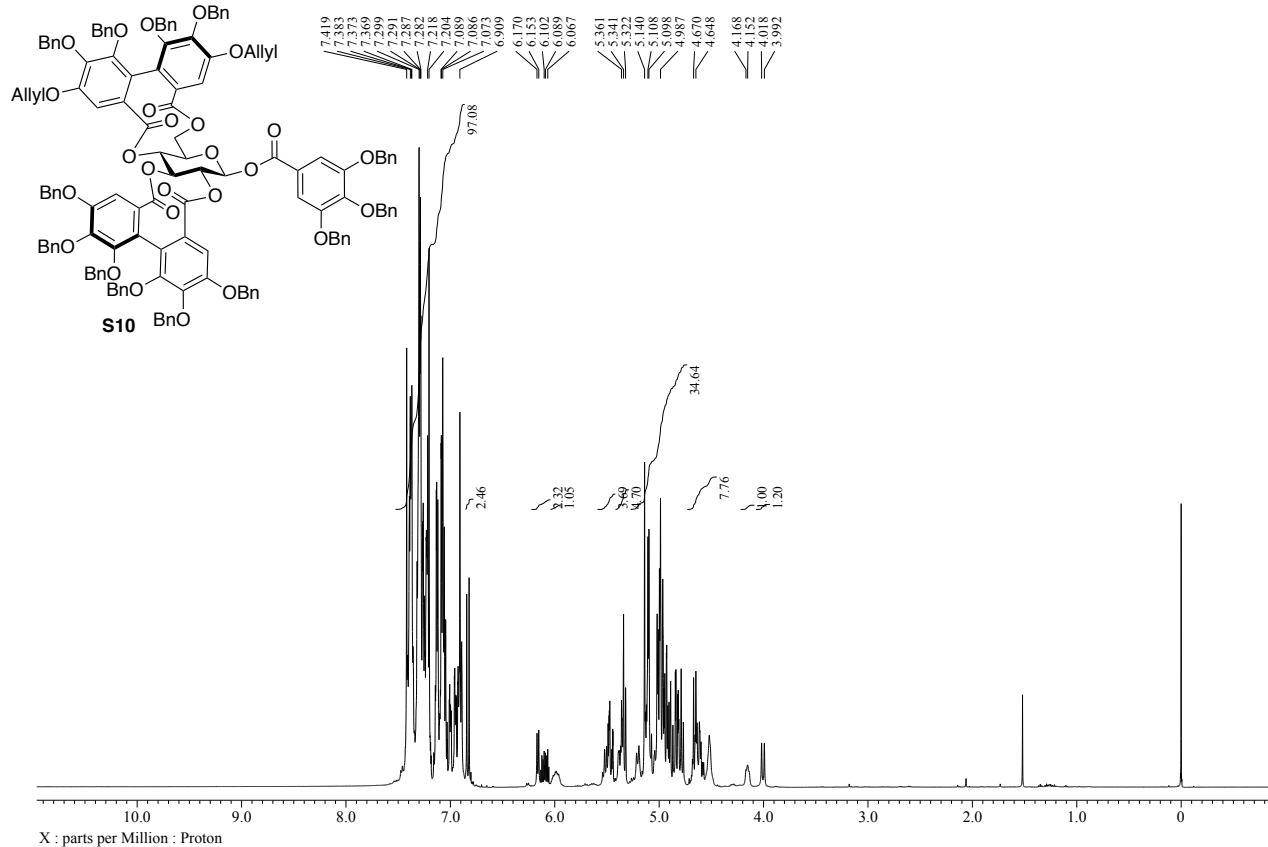


^{13}C NMR (126 MHz, CDCl_3)

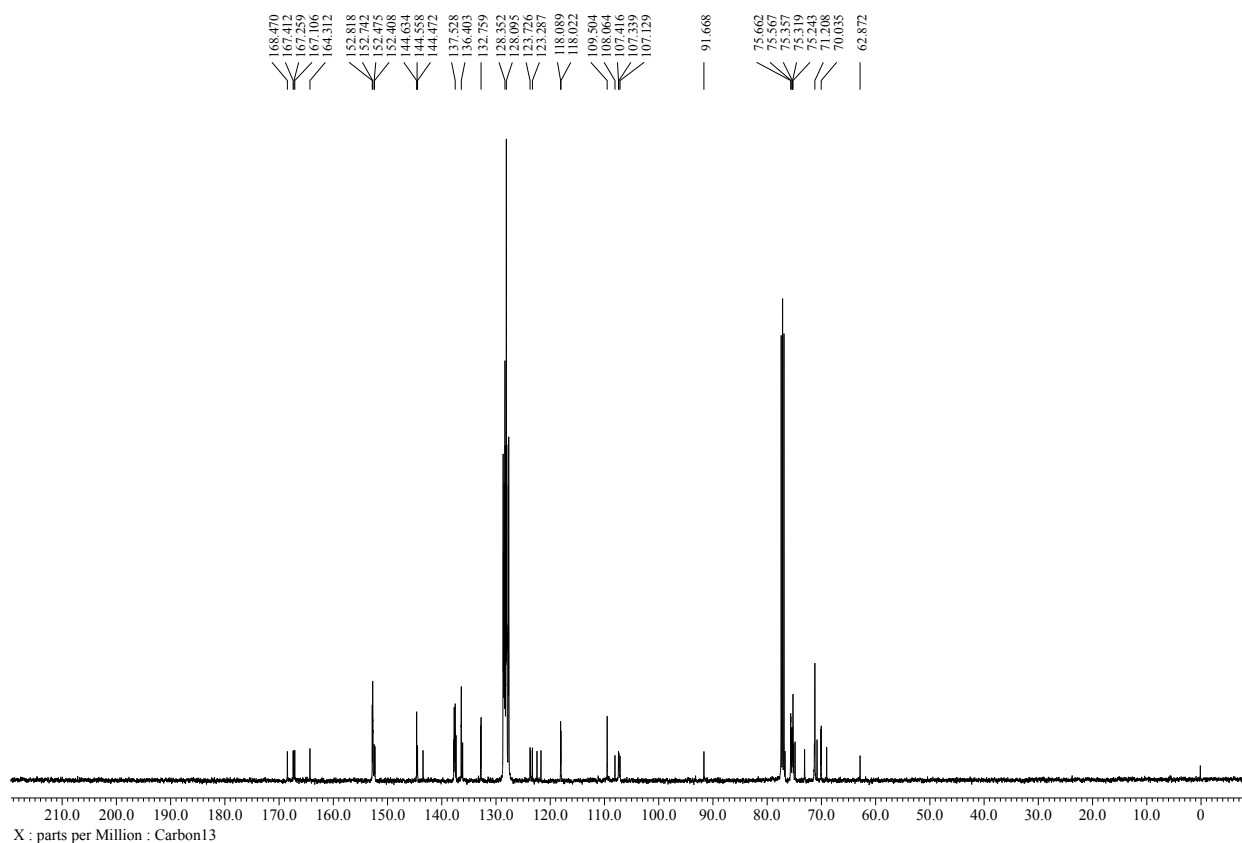


Compound S10

^1H NMR (500 MHz, CDCl_3)

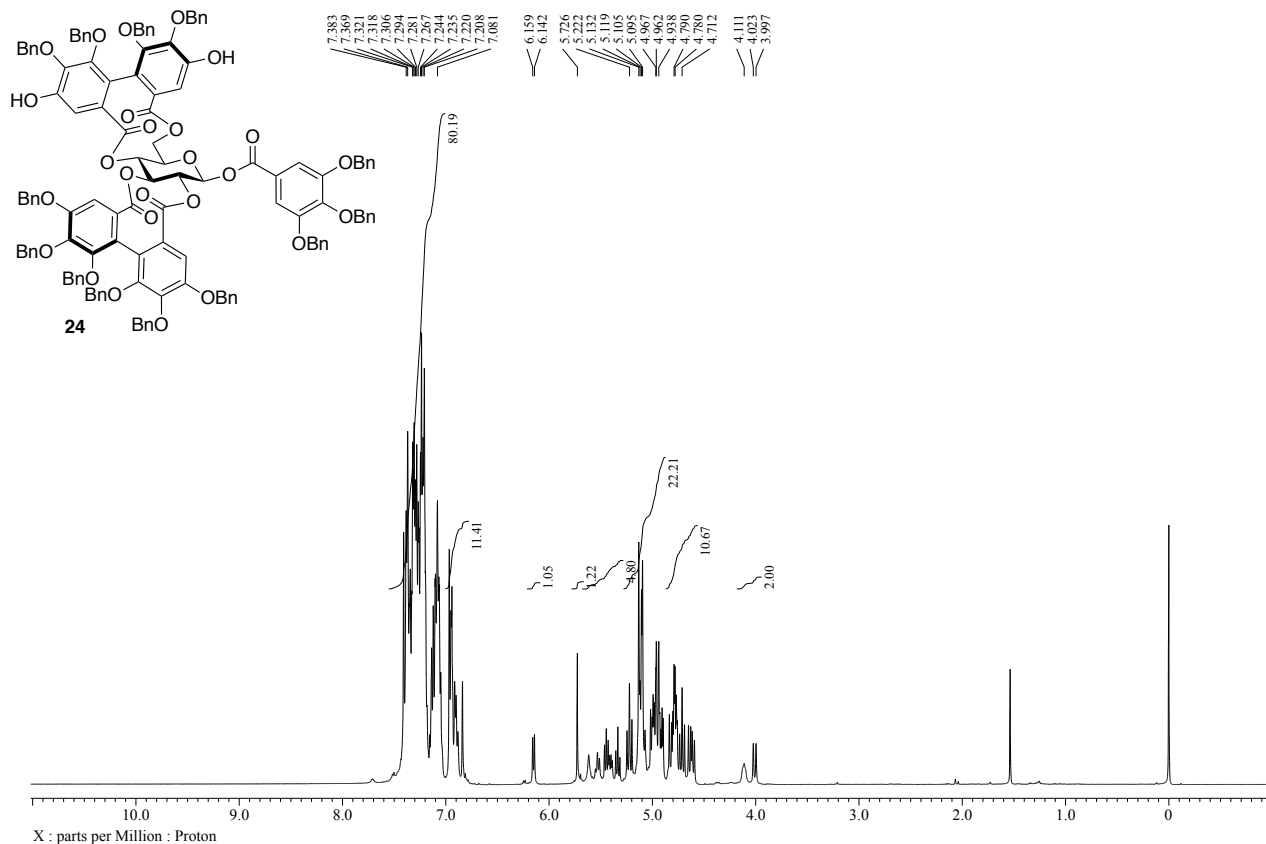


^{13}C NMR (126 MHz, CDCl_3)

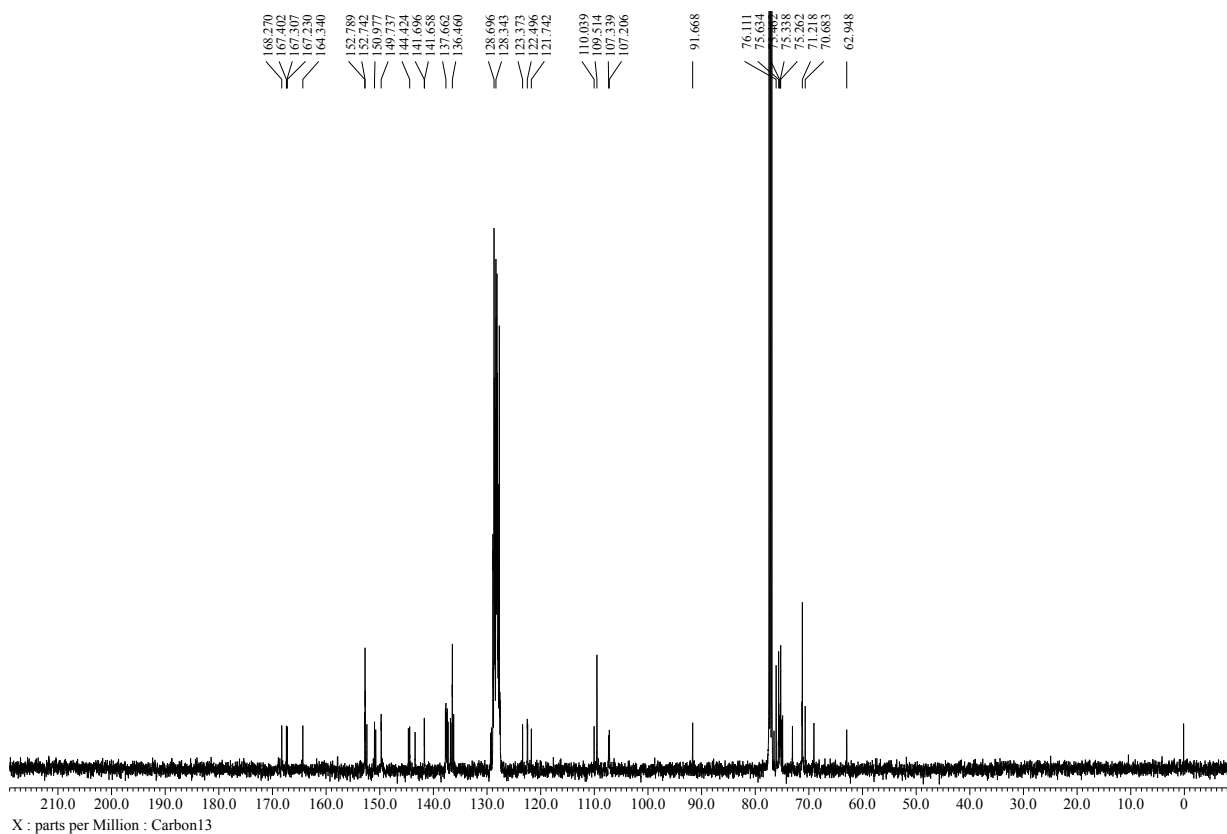


Compound 24

^1H NMR (500 MHz, CDCl_3)

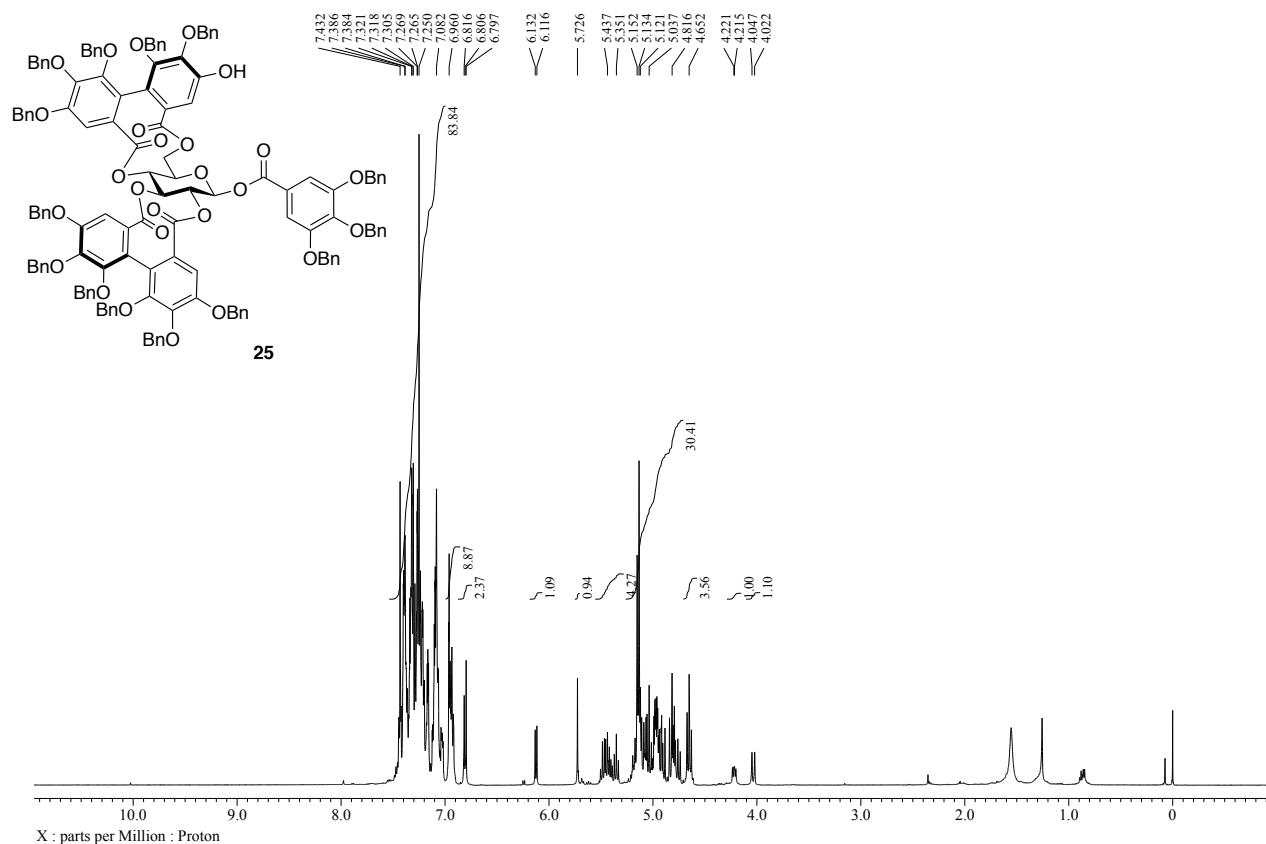


^{13}C NMR (126 MHz, CDCl_3)

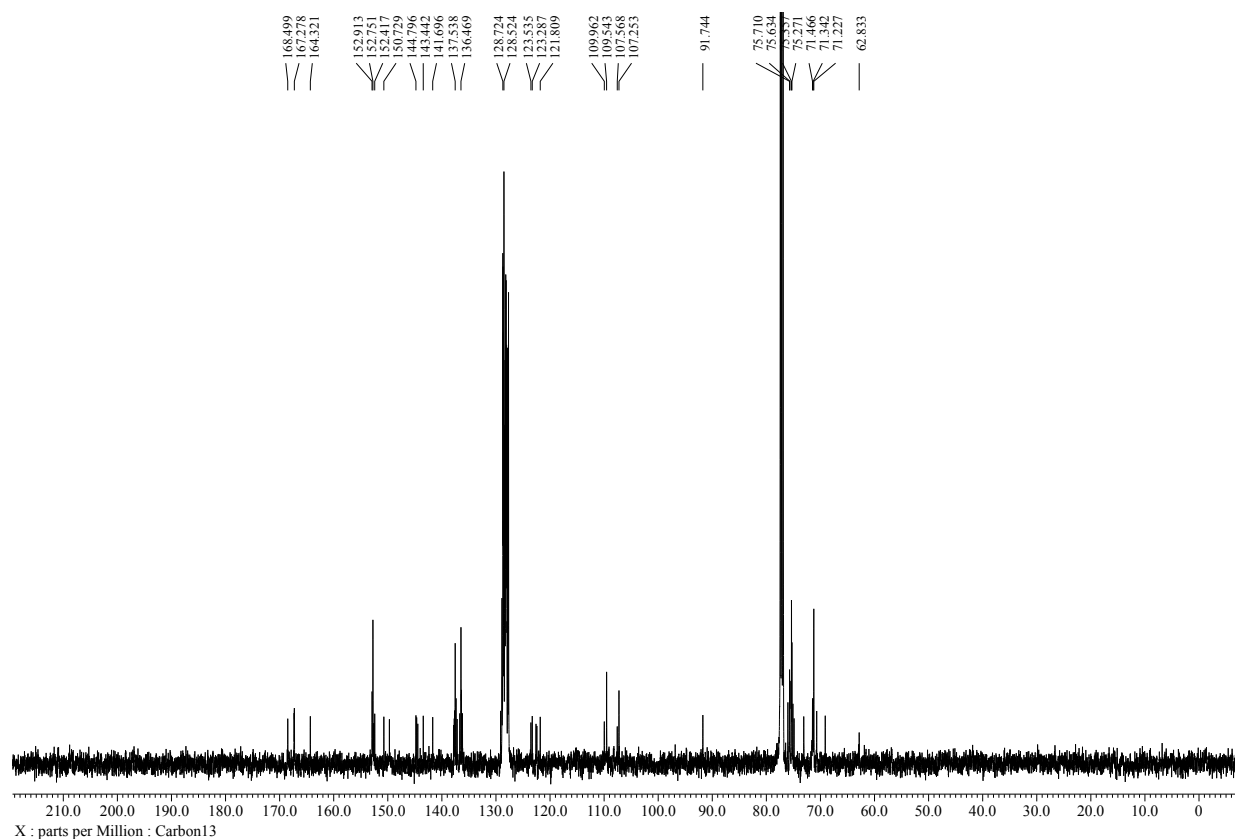


Compound 25

^1H NMR (500 MHz, CDCl_3)

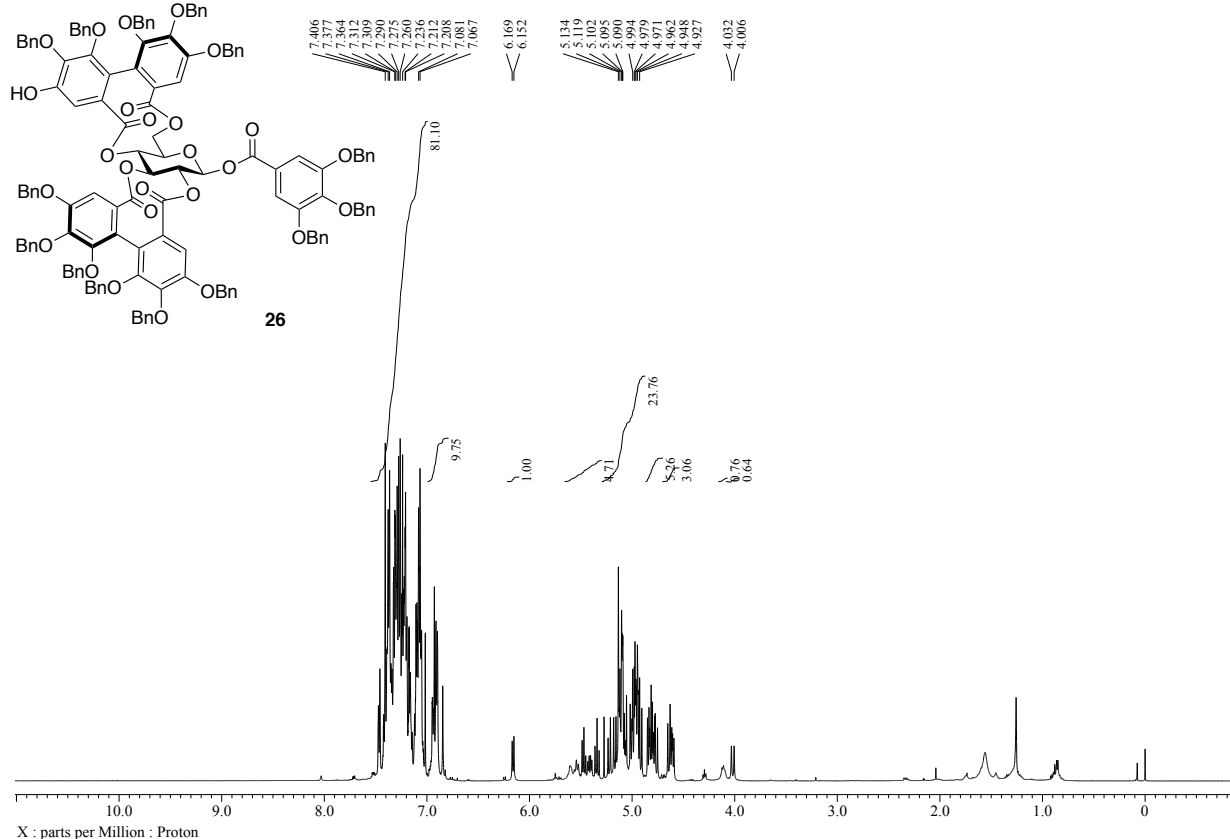


^{13}C NMR (126 MHz, CDCl_3)

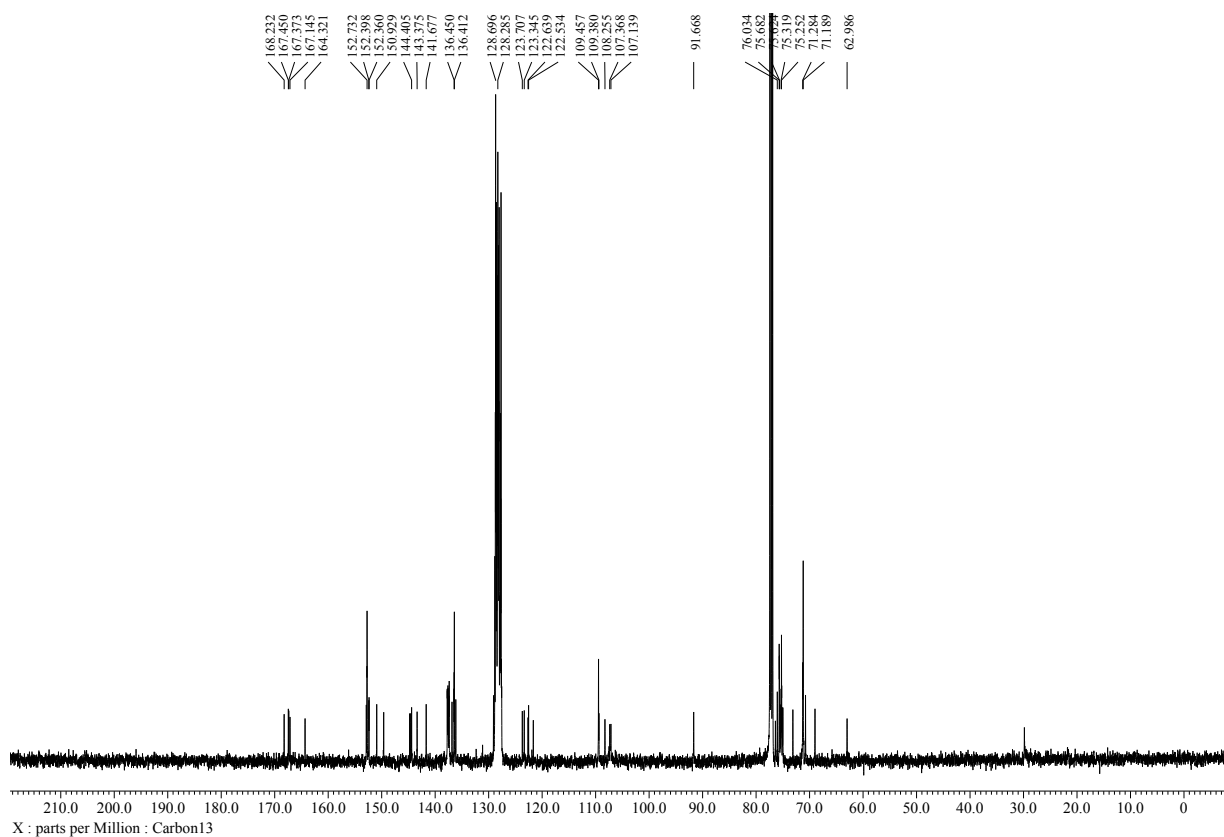


Compound 26

^1H NMR (500 MHz, CDCl_3)

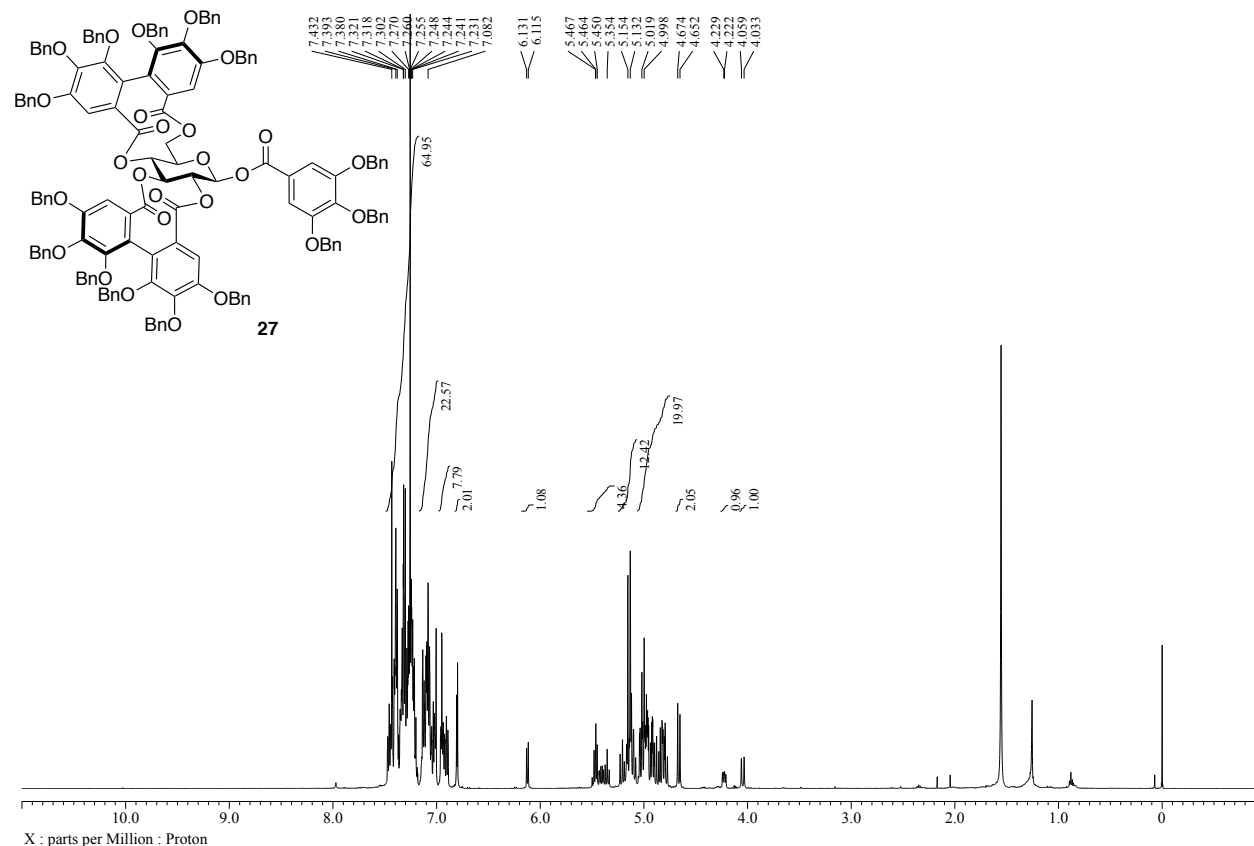


^{13}C NMR (126 MHz, CDCl_3)

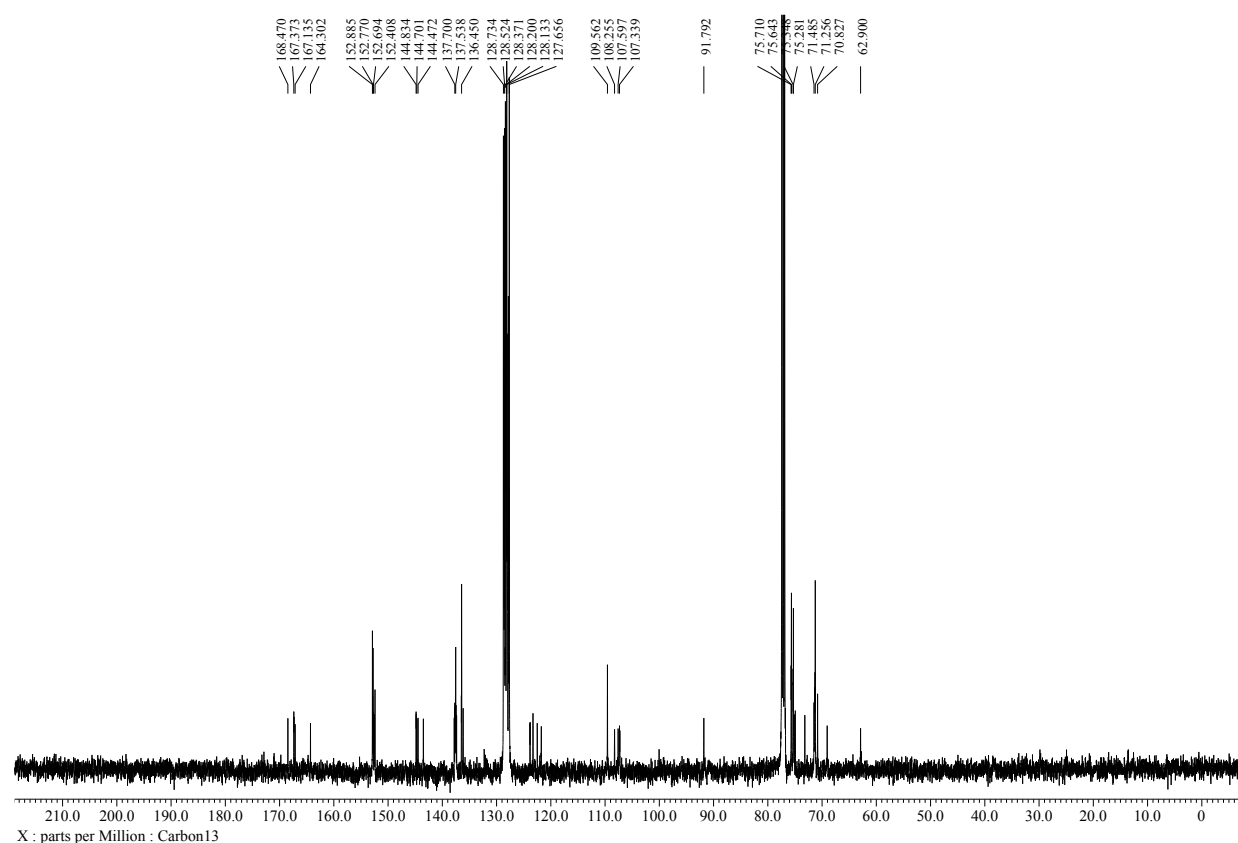


Compound 27

^1H NMR (500 MHz, CDCl_3)

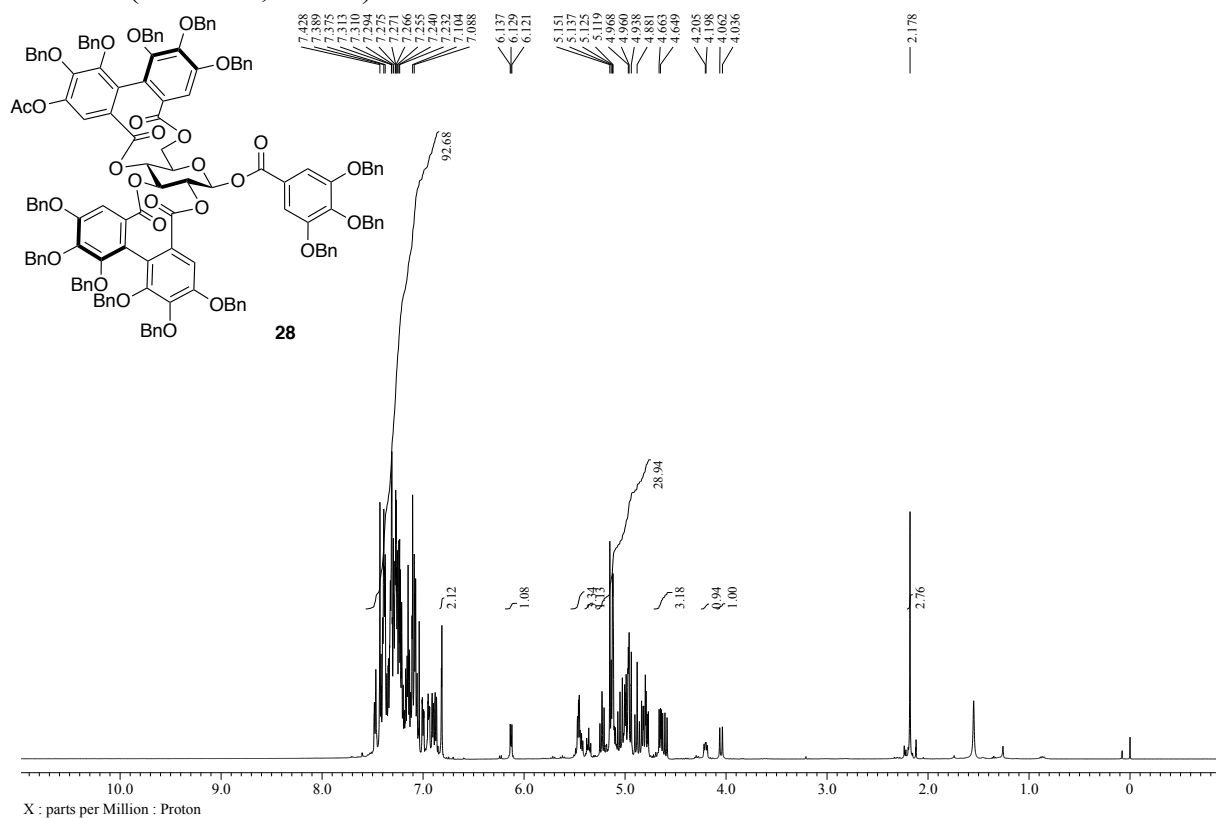


^{13}C NMR (126 MHz, CDCl_3)

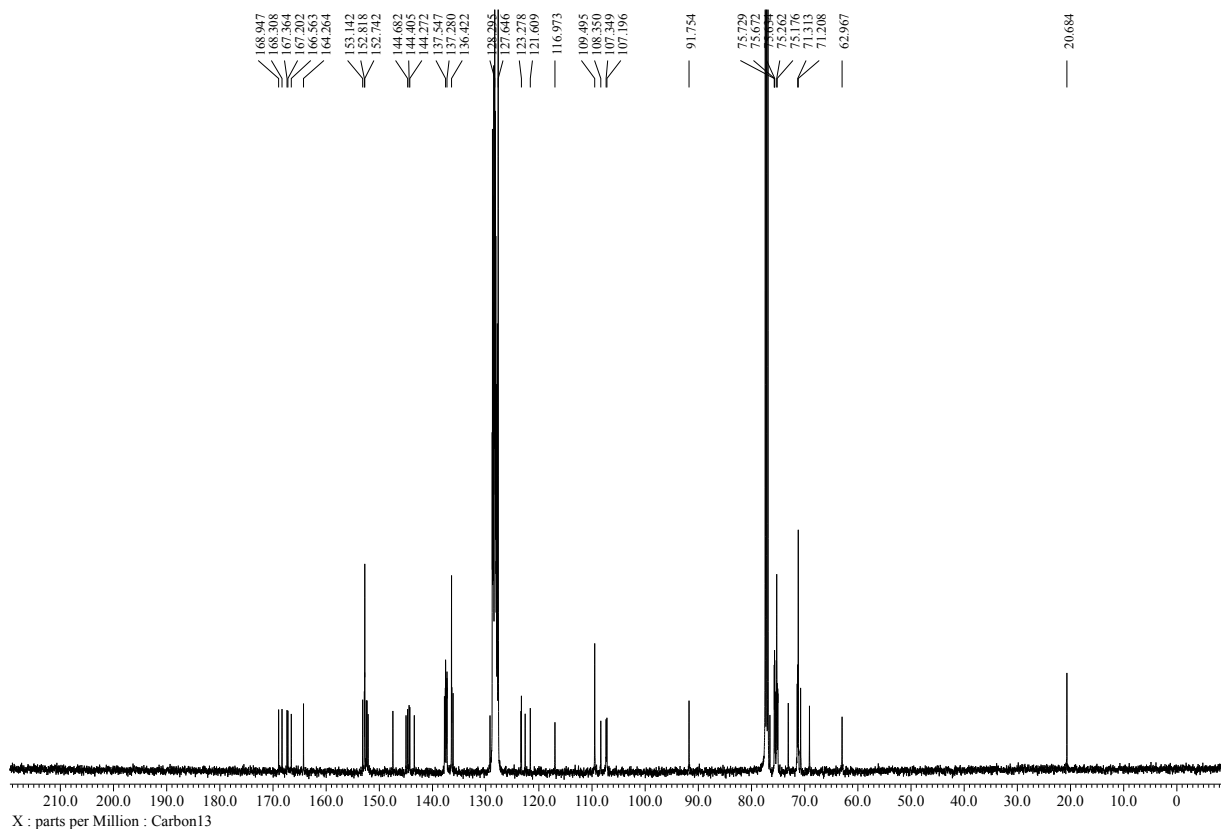


Compound 28

^1H NMR (500 MHz, CDCl_3)

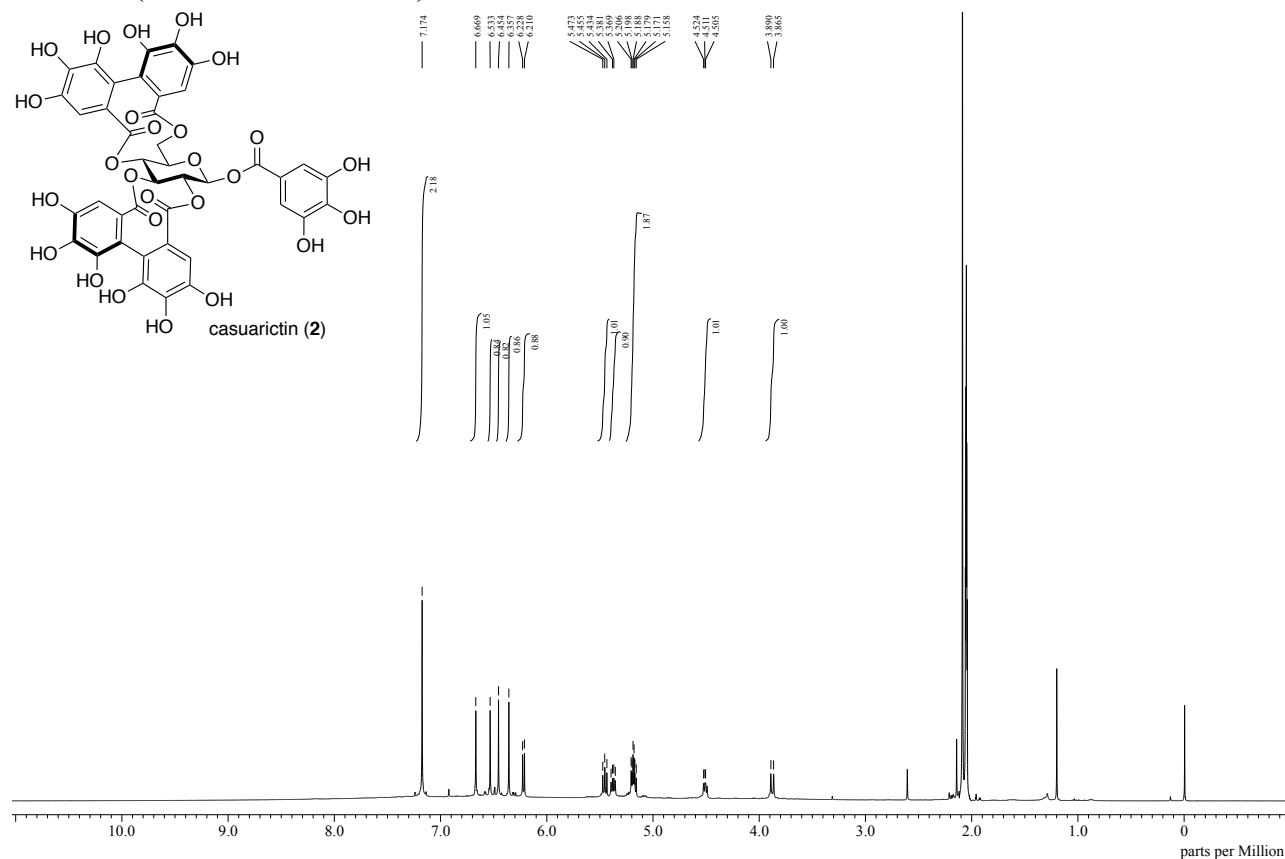


^{13}C NMR (126 MHz, CDCl_3)

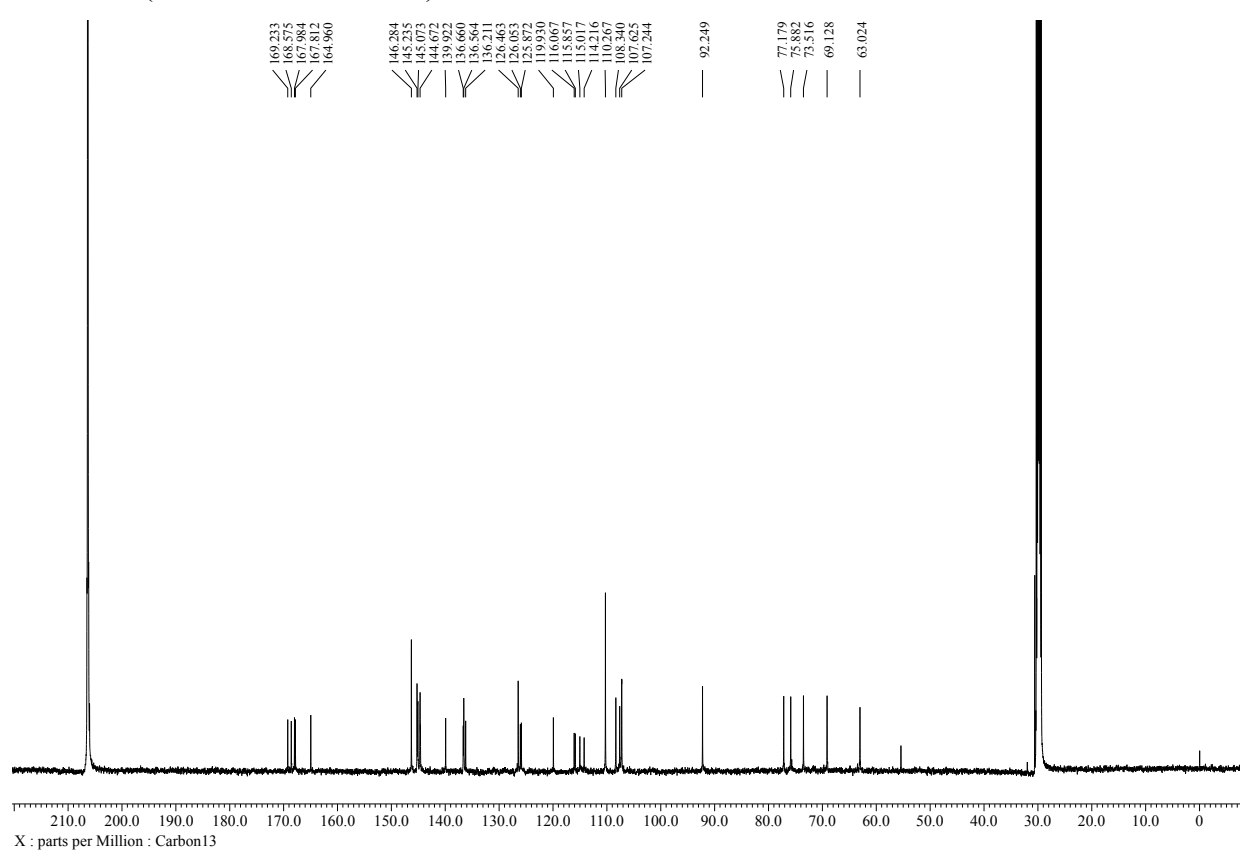


Casuarictin (2)

^1H NMR (500 MHz, acetone- d_6)

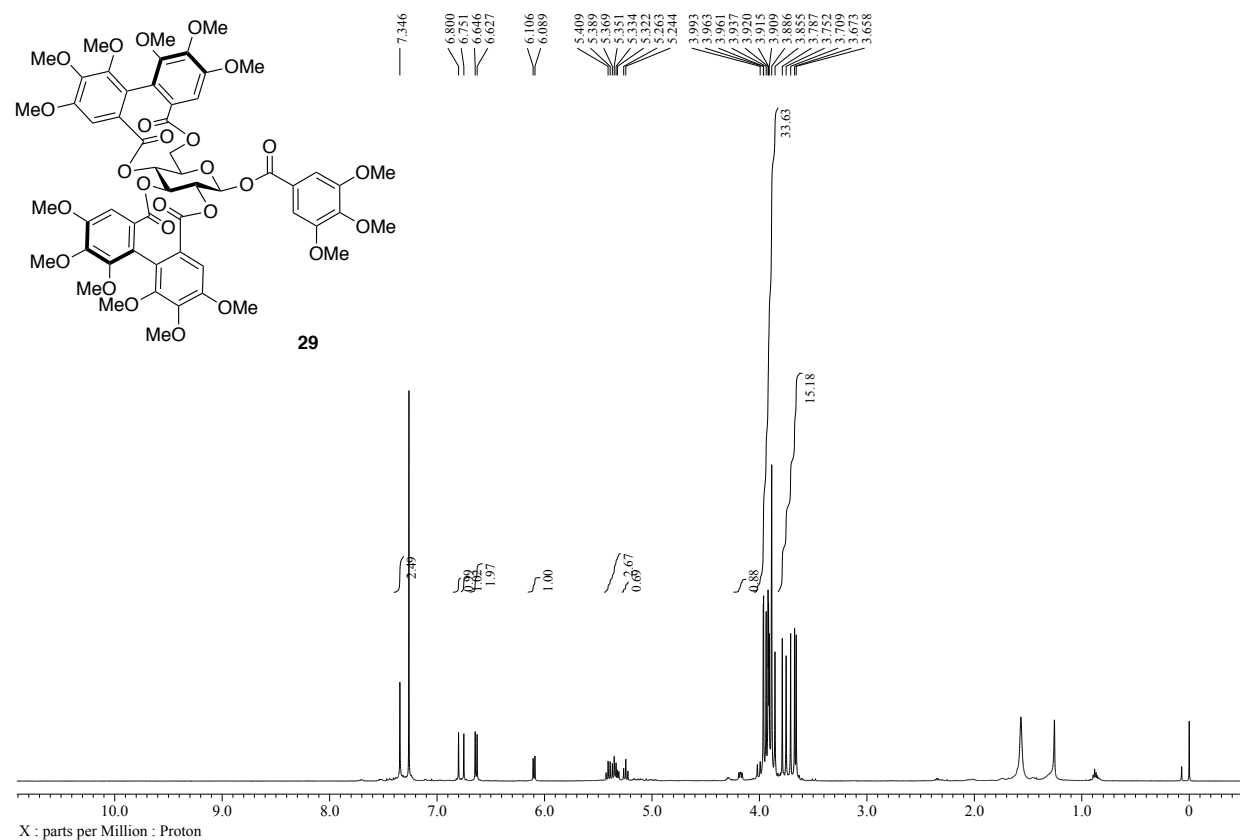


^{13}C NMR (126 MHz, acetone- d_6)

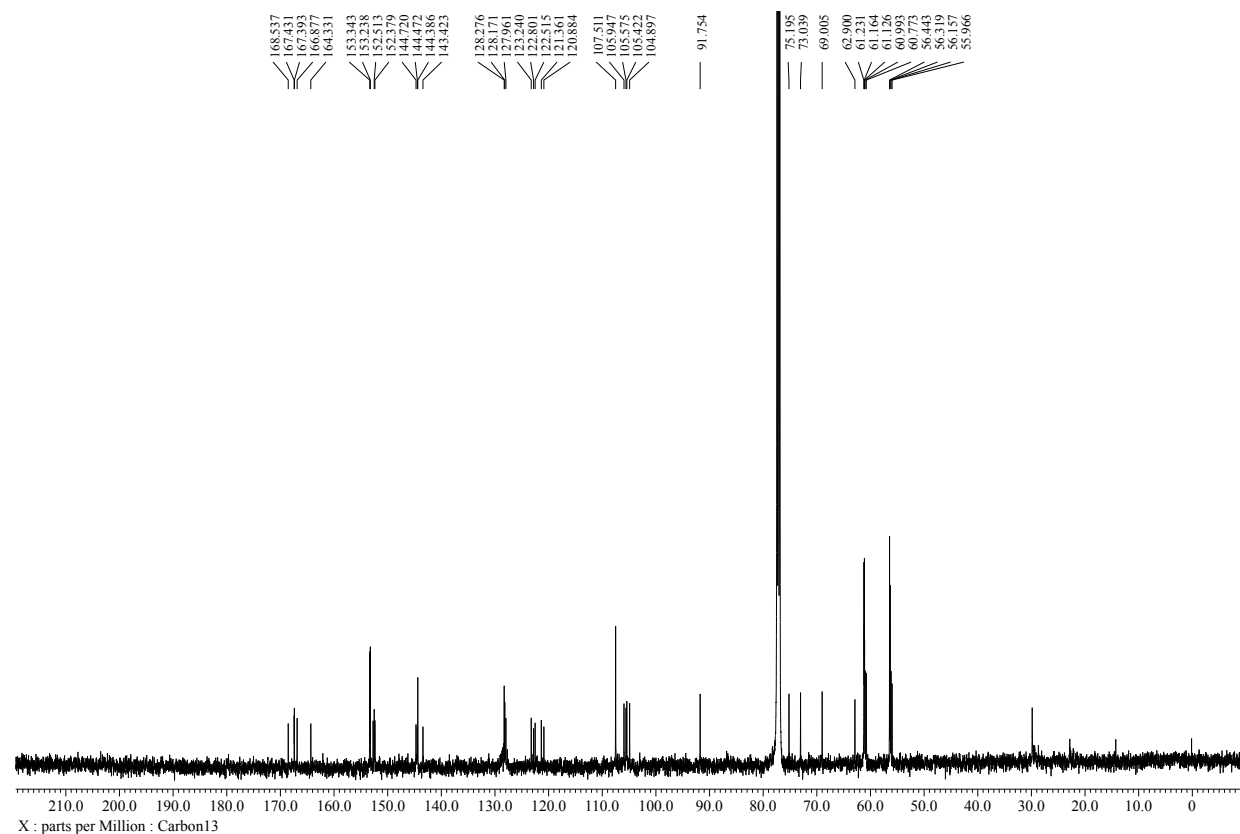


Compound 29

^1H NMR (500 MHz, CDCl_3)

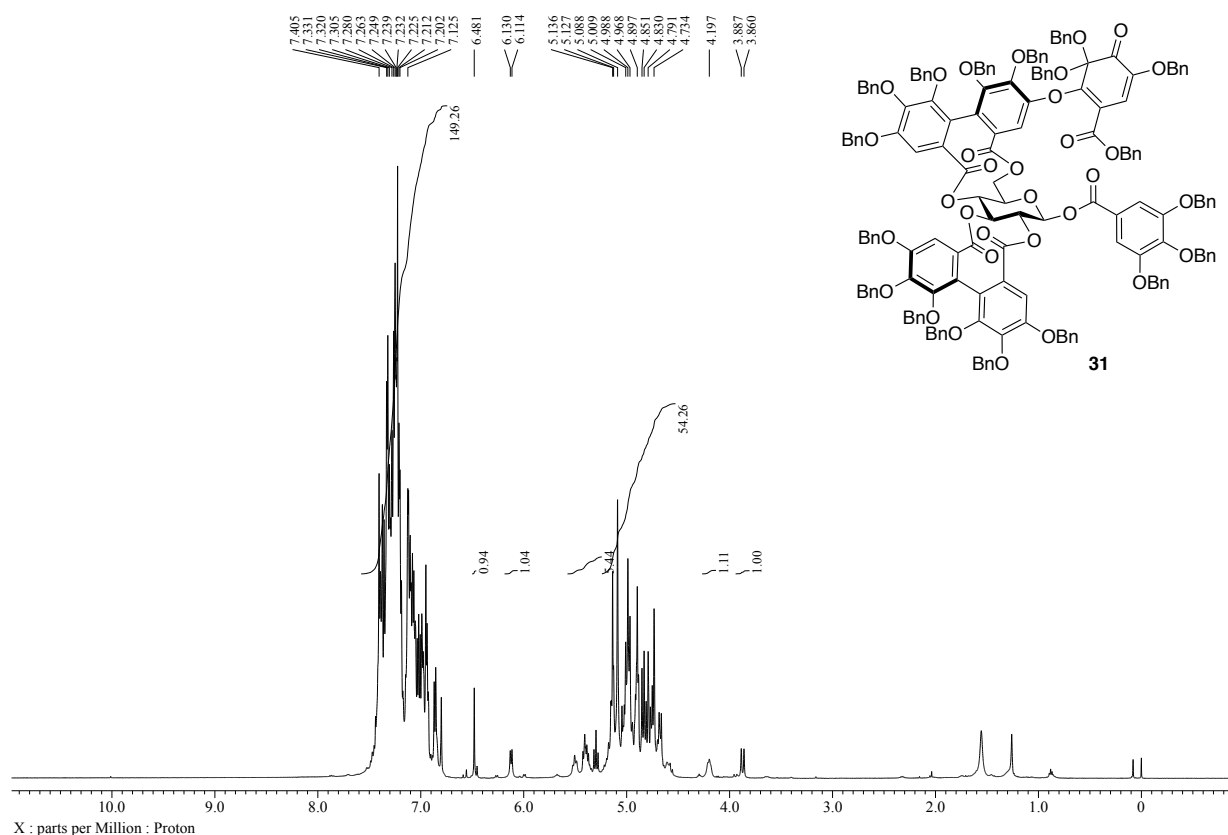


^{13}C NMR (126 MHz, CDCl_3)

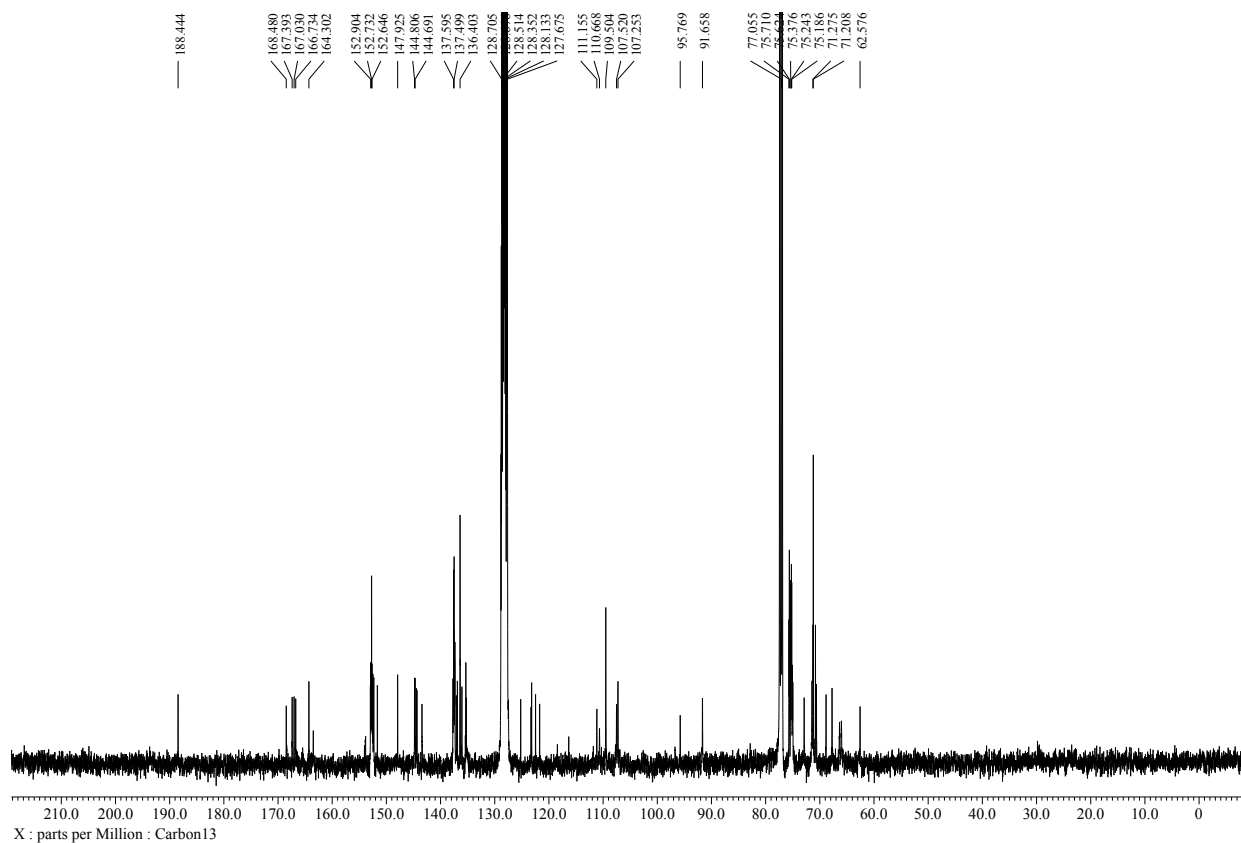


Compound 31

^1H NMR (500 MHz, CDCl_3)

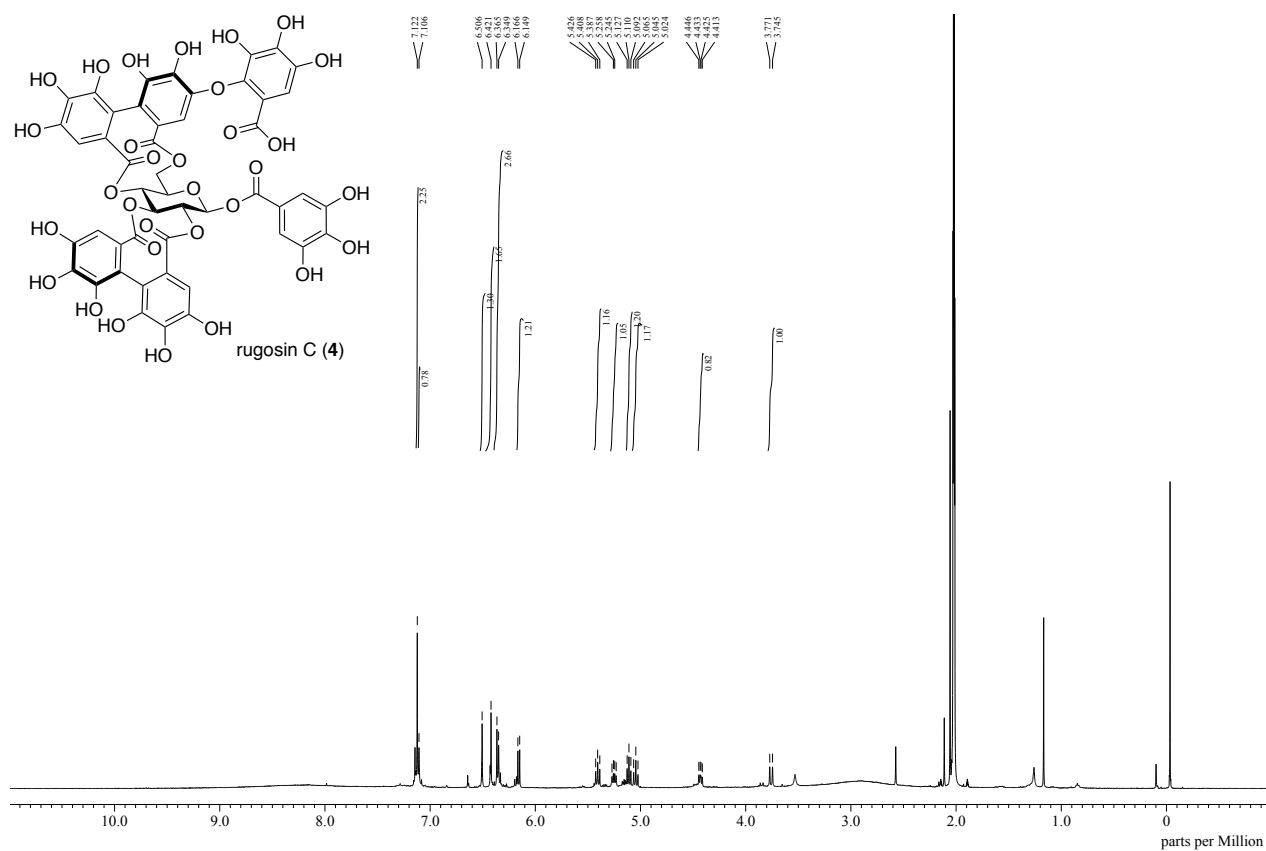


^{13}C NMR (126 MHz, CDCl_3)

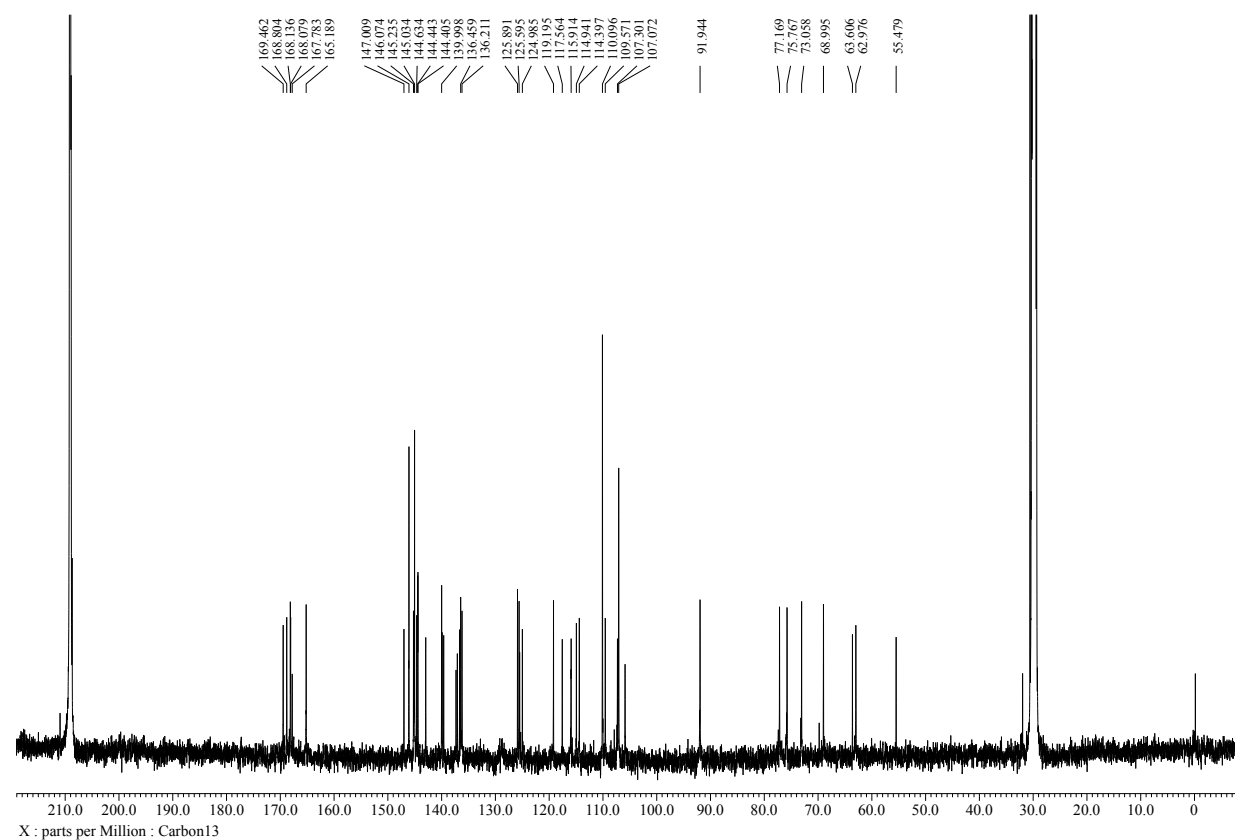


Rugosin C (4)

^1H NMR (500 MHz, acetone- d_6)

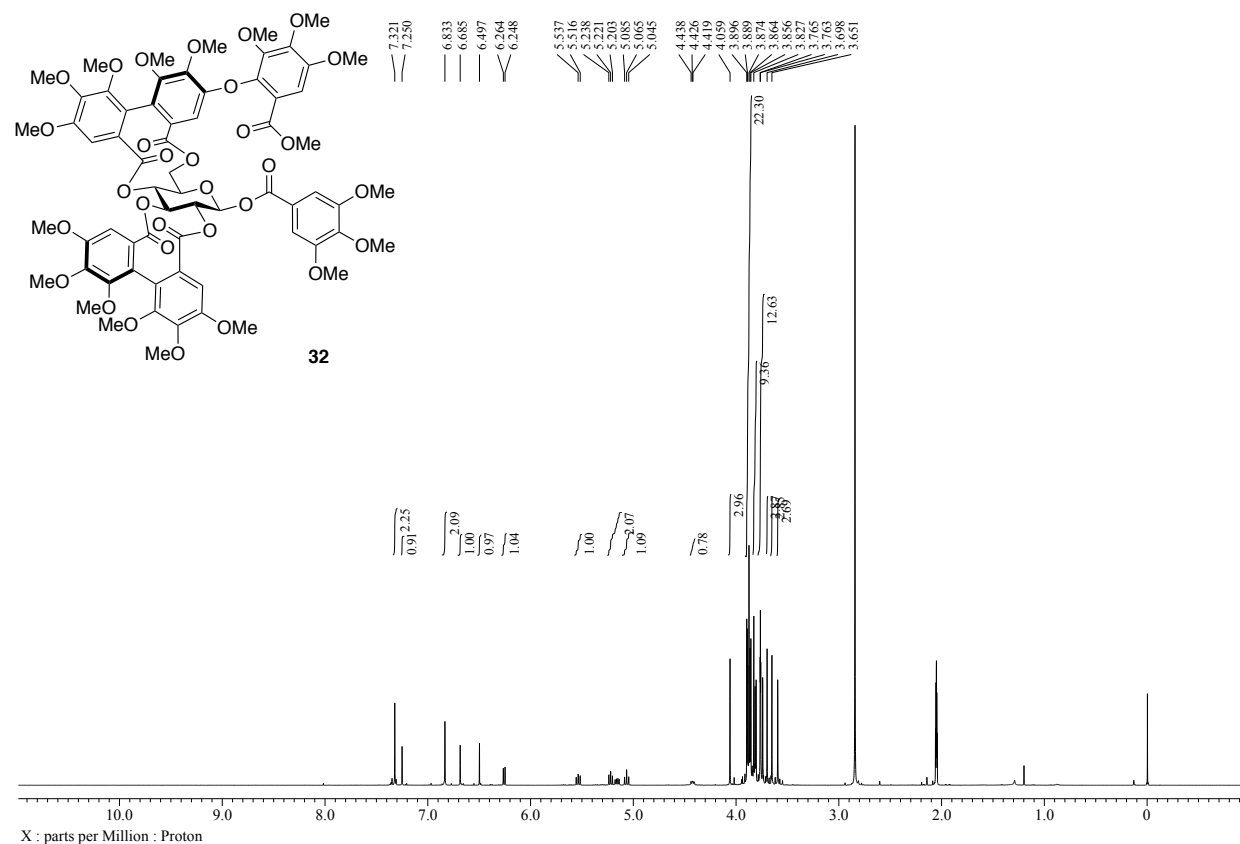


^{13}C NMR (126 MHz, acetone- d_6)

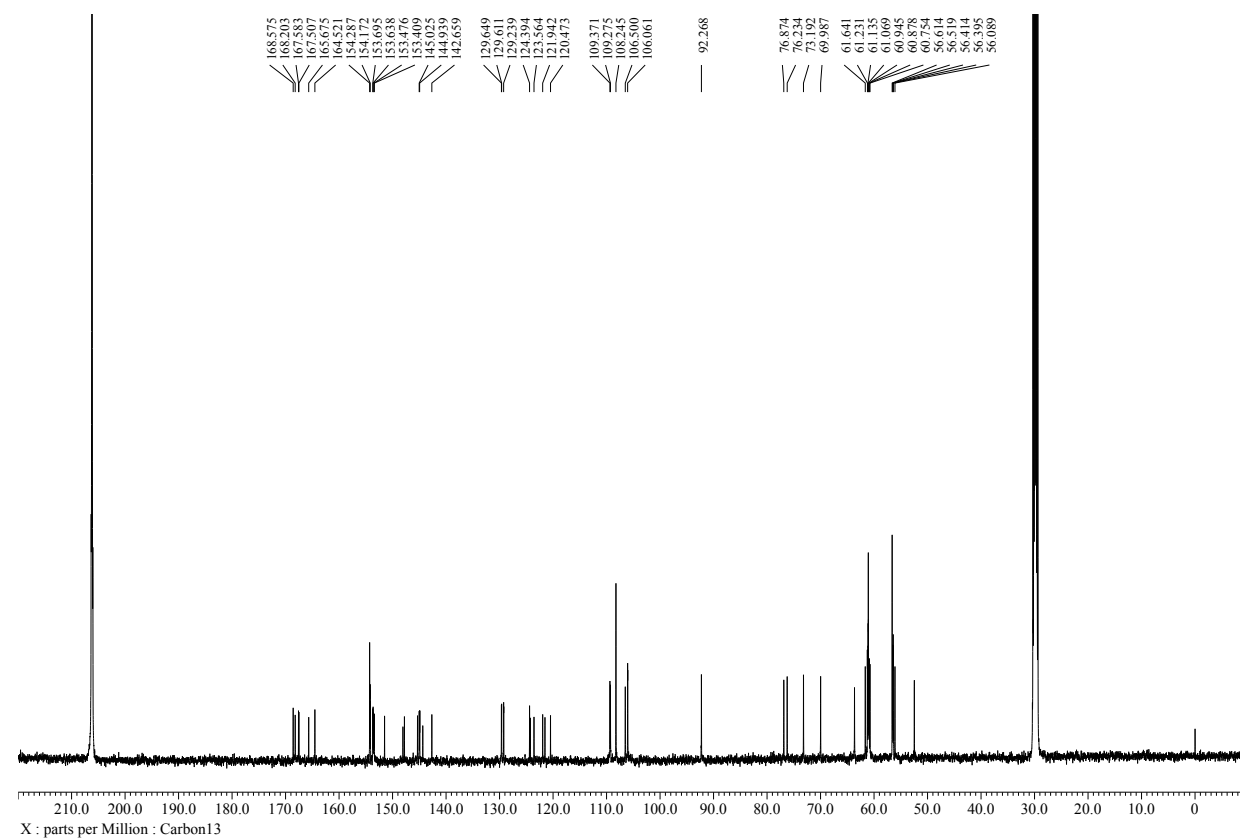


Compound 32

^1H NMR (500 MHz, acetone- d_6)

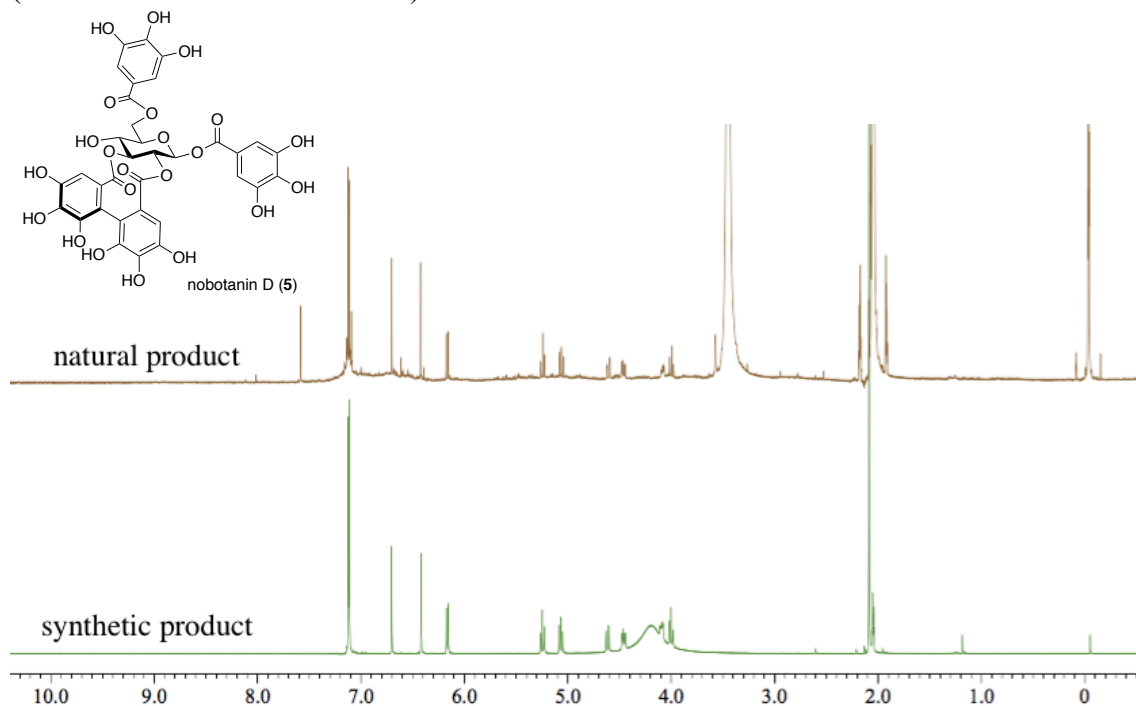


^{13}C NMR (126 MHz, acetone- d_6)



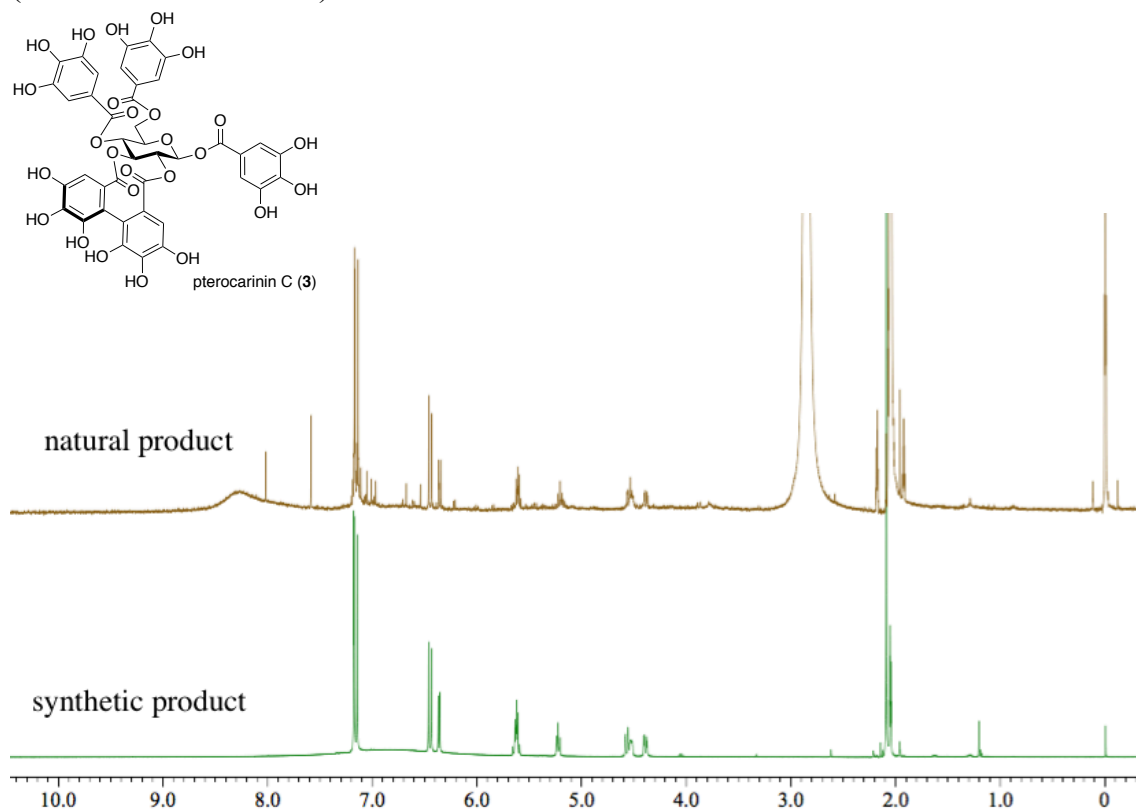
5. ^1H NMR spectra of the synthetic and natural nobotanin D (5)

(500 MHz in acetone- d_6 + D_2O)

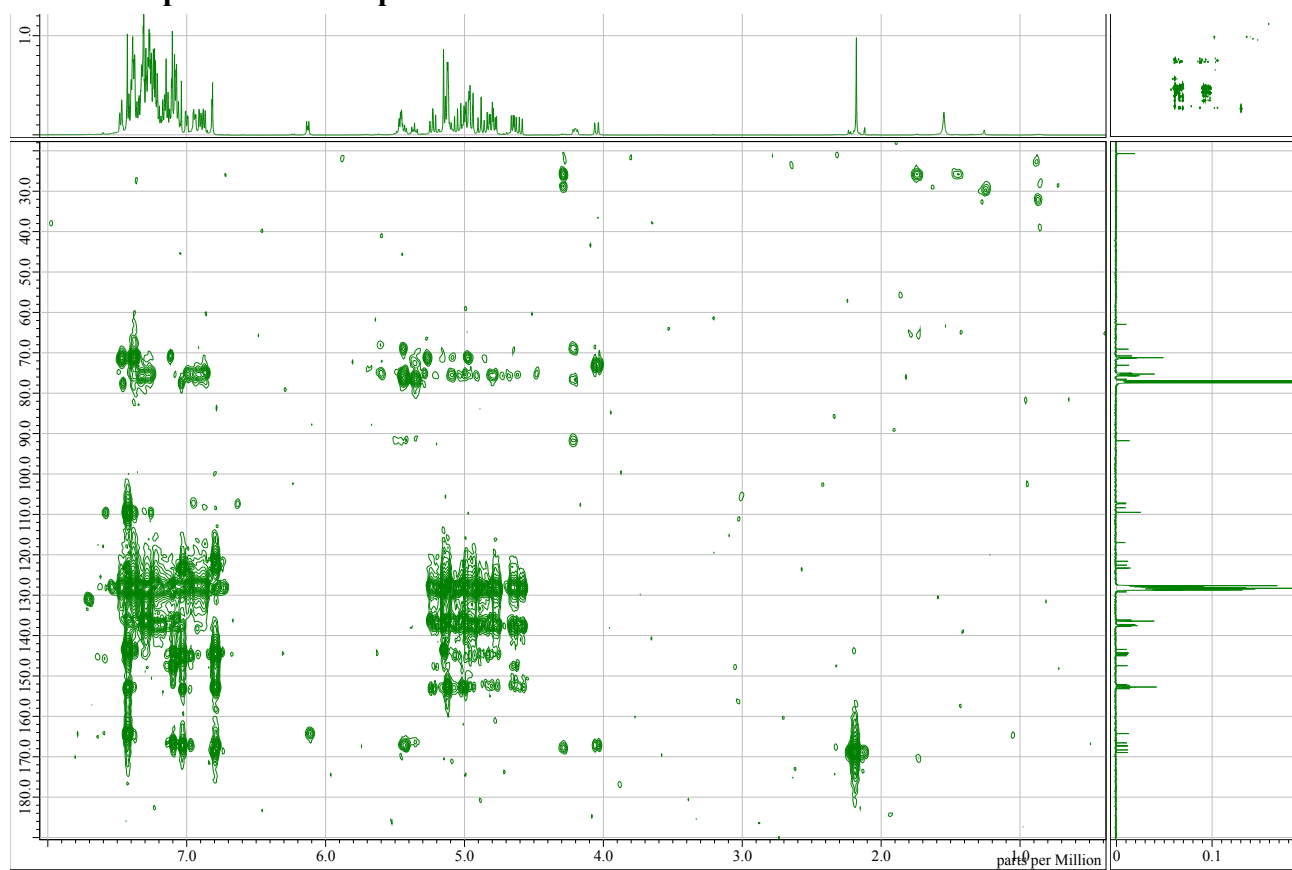


6. ^1H NMR spectra of the synthetic and natural pterocarnin C (3)

(500 MHz in acetone- d_6)



7. HMBC spectrum of compound 28



expanded spectrum

