Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Sonogashira cross-coupling as a key step in the synthesis of new glycoporphyrins

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General experimental methods

All chemical operations were carried out using sealed tubes. Acetonitrile was purified before use by distillation under an argon atmosphere. Triethylamine was dried over KOH. 1,4-dioxane and toluene were dried over molecular sieves (4Å). Other solvents were used without further purification. Commercially available chemicals were used as received unless otherwise stated. Pd-XPhos-G3 and CuI were purchased from Sigma Aldrich. 4-Ethynyl-(2-trimethylsilylethynyl)benzene was obtained following the published procedure.[1] Reactions were monitored by thin-layer chromatography on silica gel plates (60 F254 aluminum sheets) which were observed under visible light and rendered by ultraviolet. The glycals derivatives were spotted by spraying with vanillin (15%) + sulfuric acid (2,5%) in EtOH followed by heating or by spraying with 5% ethanolic phosphomolybdic acid followed by heating. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) were recorded at 293 K unless otherwise stated. Chemical shifts are given in ppm (δ) and are referenced to the internal solvent signal or to TMS used as an internal standard. Multiplicities are declared as follows: s (singlet), br s (broad singlet), br d (broad d), br t (broad t), d (doublet), t (triplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), td (triplet of doublets), tdd (triplet of doublet of doublets), m (multiplet). Coupling constants *J* are given in Hz. Infrared spectrum (IR) was recorded on a FT-IR (Nicolet Avatar 370 DTGS) with a diamond crystal and a GladiATR tool, and the data are reported in reciprocal centimeters (cm^{-1}) in the range 4000−600 cm^{-1}. Optical rotations were measured on a polarimeter at 589 nm. [α] is expressed in deg·cm^3· g^{-1}·dm^{-1}, and c is expressed in g/100 cm^3. High Resolution Mass Spectra (Electrospray Ionization, ESI) were obtained on a LTQ Orbitrap Velos spectrometer in a positive ionization mode. UV/Vis spectra were measured with the LLG-*uniSPEC* 2 Spectrophotometer.

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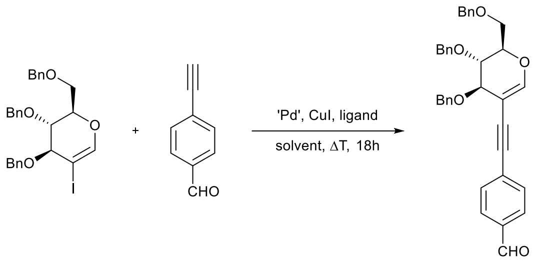
[1] J. Rotzler, S. Drayss, O. Hampe, D. Häussinger, M. Mayor; *Chem. Eur. J.* **2013**,19, 2089 – 2101

Optimisation studies of Sonogashira reaction on aldehyde **2**[a]

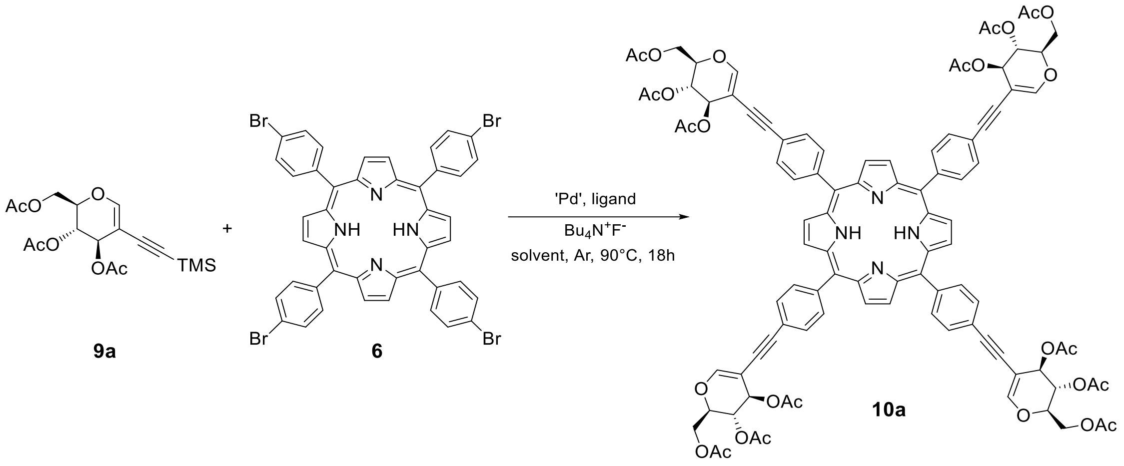


1 **2** **3**

entry	T [°C]	solvent (ratio)	catalyst (eq)	ligand (eq)	cocatalyst (eq)	yield[b] [%]
1	80	DMF	$\mathrm{Pd(OAc)_2}$ (0.05)	----	----	0[c,d]
2	"	DMF	$\mathrm{Pd(PPh_3)_2Cl_2}$ (0.10)	----	CuI (0.20)	0[d,e]
3	"	*t*-BuOH	"	----	"	7[d,e]
4	"	1,4-dioxane	"	----	"	28[d,e]
5	"	toluene	"	----	"	29[d,e]
6	"	$\mathrm{NEt_3}$	"	----	"	21[d]
7	"	1,4-dioxane/$\mathrm{NEt_3}$ (1:1)	"	----	"	25[f]
8	"	toluene/$\mathrm{NEt_3}$ (1:1)	"	----	"	44[f]
9	70	toluene/$\mathrm{NEt_3}$ (1:1)	"	----	"	43[f]
10	90	toluene/$\mathrm{NEt_3}$ (1:1)	"	----	"	39[f]
11	80	toluene/$\mathrm{NEt_3}$ (1:1)	"	----	"	40[g]
12	"	"	"	----	"	51
13	70	"	"	----	"	43
14	90	"	"	----	"	33
15	80	"	$\mathrm{Pd(PPh_3)_4}$ (0.10)	----	"	59
16	80	"	"	----	----	35
17	"	"	$\mathrm{Pd(PPh_3)_2Cl_2}$ (0.10)	$\mathrm{PPh_3}$ (0.20)	CuI (0.20)	49
18	"	"	"	$\mathrm{PPh_3}$ (0.10)	"	44
19	"	"	$\mathrm{Pd(OAc)_2}$ (0.10)	$\mathrm{PPh_3}$ (0.40)	"	35
20	"	"	"	$\mathrm{PPh_3}$ (0.20)	"	25
21	"	"	$\mathrm{PdCl_2}$ (0.175)	"	"	46
22	"	"	$\mathrm{PdCl_2}$ (0.10)	"	"	53
23	"	"	"	XPhos (0.20)	"	63
24	"	"	"	RuPhos (0.20)	"	43
25	"	"	"	XantPhos (0.20)	"	10
26	"	"	"	XantPhos (0.10)	"	20
27	"	"	"	XPhos (0.20)	"	60[h]
28	"	"	"	"	CuI (0.10)	70
29	**"**	**"**	**Pd-XPhos-G3 (0.10)**	**XPhos (0.10)**	**CuI (0.20)**	**86**[i]
30	60	"	"	"	"	85
31	"	"	"	"	CuI (0.10)	85
32	"	"	Pd-XPhos-G3 (0.05)	XPhos (0.05)	CuI (0.05)	75
33	40	"	Pd-XPhos-G3 (0.10)	XPhos (0.10)	CuI (0.10)	77
34	60	"	PEPPSI™-IPr (0.10)	----	"	24

[a] General conditions: perbenzylated 2-iodo-D-glucal (0.110 mmol, 1.0 eq), 4-ethynylbenzalehyde (0.130 mmol, 1.2 eq), Pd catalyst (0.1 eq), CuI cocatalyst (0.2 eq), toluene (0.5 mL), triethylamine (0.5 mL), 80°C, 18h, argon atmosphere. [b] Determined from crude mixture by the ^{1}H NMR experiment with the internal standard (DMF). [c] 1.5 eq of $\mathrm{Cs_2CO_3}$ was used. [d] Reaction in 0.5 mL of solvent. [e] 2.0 eq of triethylamine was used. [f] Reaction in 1,4-dioxane/toluene (0.25 mL) and triethylamine (0.25 mL). [g] Reaction in toluene (0.125 mL) and triethylamine (0.125 mL). [h] Reaction under air atmosphere. [i] Corresponds to 85% of isolated product.

Optimisation studies of sila-Sonogashira reaction on alkyne **9a**[a]

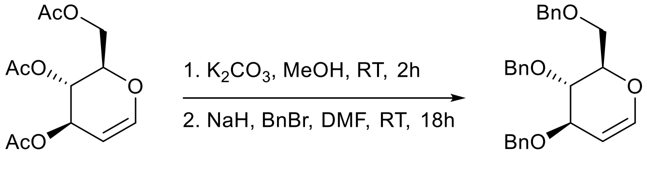


Entry	Catalyst (eq)	Ligand (eq)	solvent	yield[b] [%]
1	Pd-XPhos-G3 (0.20)	XPhos (0.20)	toluene/NEt_3 (1:1)	0[c]
2	"	"	"	56
3	Pd-XPhos-G3 (0.15)	XPhos (0.15)	"	66
4	Pd-XPhos-G3 (0.20)	XPhos (0.20)	1,4-Dioxane/NEt_3 (1:1)	75
5	"	"	1,4-Dioxane (+ NEt_3, 8.0 eq)	42
6	"	"	NEt_3	13
7	"	"	1,4-Dioxane /NEt_3 (4:1)	43
8	"	"	1,4-Dioxane /NEt_3 (1:4)	55
9	"	"	*t*-BuOH/NEt_3 (1:1)	54
10	"	"	DMF/NEt_3 (1:1)	48
11	**Pd-XPhos-G3 (0.15)**	**XPhos (0.15)**	**1,4-Dioxane/NEt_3 (1:1)**	**85**
12	Pd-XPhos-G3 (0.20)	XPhos (0.20)	"	71[d]
13	"	----	"	60
14	"	XPhos (0.40)	"	48
15	$PdCl_2$ (0.20)	XPhos (0.20)	"	45
16	$Pd(PPh_3)_2Cl_2$ (0.20)	"	"	40
17	$Pd(OAc)_2$ (0.20)	"	"	54
18	Pd-RuPhos-G3 (0.15)	RuPhos (0.15)	"	56
19	Pd-XantPhos-G3 (0.15)	XantPhos (0.15)	"	42
20	Pd-XPhos-G3 (0.15)	PPh_3 (0.15)	"	39
21	Pd-XPhos-G3 (0.20)	XPhos (0.20)	"	8[e]

[a] General conditions: porphyrin **6** (0.024 mmol, 1.0 eq), glycal **8a** (0.190 mmol, 8.0 eq), $Bu_4N^+F^-$ (0.194 mmol, 8.2 eq), Pd-XPhos-G3 (0.005 mmol, 0.2 eq), XPhos (0.005 mmol, 0.2 eq), 1,4-dioxane (2.5 mL), triethylamine (2.5 mL), 18 h, 90°C, argon atmosphere. [b] Yield of isolated product. [c] The reaction was performed on peracetylated 2-ethynyl-D-glucal as a glycal substrate. [d] Reaction time was 1.5 h. [e] KF was used instead of $Bu_4N^+F^-$.

Procedures and characterisation of new products

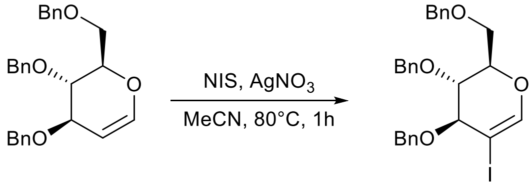
*3,4,6-tri-O-benzyl-D-glucal (**S2**)*



S1 **S2**

Peracetylated glycal **S1** (10.00 g, 36.7 mmol, 1.0 eq) was dissolved in methanol (220 mL), then K_2CO_3 was added (0.51 g, 3.67 mmol, 0.1 eq). The resulting mixture was stirred at room temperature for 2 hours. After that time the mixture was concentrated and the residue was used directly for the next step. The residue was dissolved in DMF (226 mL), cooled in an ice bath, then NaH (60 w% in mineral oil, 9.02 g, 225.5 mmol, 6.1 eq) was added in small portions. Then, benzyl bromide was added (25.6 mL, 214.9 mmol, 5.9 eq) and the mixture was stirred at room temperature overnight. The solvent was evaporated off and the residue was purified by flash chromatography (hexane/ethyl acetate, 19:1) yielding glycal **S2** as a white solid (11.63 g, 76%, $\boldsymbol{R_f}$ = 0.19 (hexane/ethyl acetate, 19:1). The characterization data were in agreement with those of the literature.[2]

*3,4,6-tri-O-benzyl-2-iodo-D-glucal (**1**)*



S2 **1**

To a flame dried flask (Schlenk technique), equipped with a condenser, freshly distilled MeCN (90 mL) was added, under argon. Then, it was charged with glycal **S2** (4.50 g, 10.8 mmol, 1.0 eq) and heated to 60°C. Next, NIS (2.89 g, 12.9 mmol, 1.2 eq) and $AgNO_3$ (0.39 g, 2.27 mmol, 0.2 eq) were added, under argon. The mixture was stirred at 80°C for 1h, shielded from light. Then, ethyl acetate was added, diluted mixture was filtrated through a short pad of Celite®, and washed with ethyl acetate. The filtrate was then concentrated, residual solid was purified by flash chromatography (hexane/ethyl acetate, 9:1) yielding pinkish powder of glycal **1** (3.80 g, 65%, $\boldsymbol{R_f}$ = 0.21 (hexane/ethyl acetate, 9:1)). The characterization data were in agreement with those of the literature.[3]

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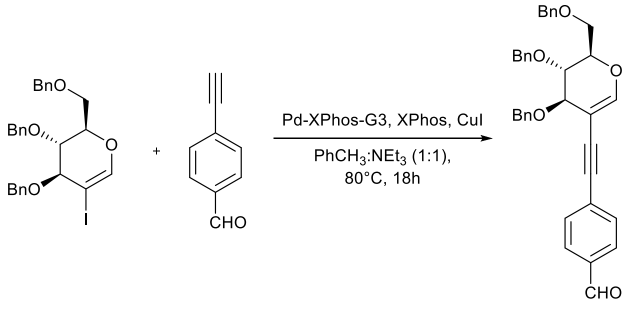
[2] S. J. Moons, R. A. Mensink, J. P. J. Bruekers, M. L. A. Vercammen, L. M. Jansen, T. J. Boltje; *J. Org. Chem.* **2019**, 84, 7, 4486-4500

[3] S. Jana, J. D. Rainier; *Org. Lett.* **2013**, 15, 17, 4426-4429

*3,4,6-tri-O-benzyl-2-(2-(4-formylphenyl)ethynyl)-D-glucal (**3**)*



1 **2** **3**

Glycal **1** (59.9 mg, 0.11 mmol, 1.0 eq) and aldehyde **2** (18.3 mg, 0.13 mmol, 1.2 eq) were placed inside a reaction vessel. Next, catalytic system consisting of Pd-XPhos-G3 (9.2 mg, 0.011 mmol, 0.1 eq), XPhos (5.2 mg, 0.011 mmol, 0.1 eq), CuI (4.0 mg, 0.022 mmol, 0.2 eq) were added. The vessel was equipped with a stir bar and flushed with argon. Solids were dissolved in a mixture of toluene (0.5 mL) and triethylamine (0.5 mL), added through a rubber septum under argon. Mixture was stirred at 80°C, for 18 h. Ethyl acetate was then added to the crude mixture and the mixture was filtrated through Celite®, and washed several times with ethyl acetate. Then filtrate was concentrated and the residual solid was purified by flash chromatography (hexane/ethyl acetate, 85:15), yielding white powder of desired aldehyde **3** (52.0 mg, 86%).

R_f = 0.26 (hexane/ethyl acetate, 85:15); $[\alpha]_D^{20}$= +9.2 (3.00, $CHCl_3$); **m.p.** 108-109°C

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 9.99 (s, 1H, -CHO); 7.82 – 7.79 (m, 2H, H-2'$_{Ar}$); 7.50 – 7.47 (m, 2H, H-3'$_{Ar}$); 7.39 – 7.26 (m, 15H, H-benzyl); 7.01 (br s, 1H, H-1$_{glycal}$); 4.87 (d, J = 11.5 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.75 (d, J = 11.6 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.74 (d, J = 11.5 Hz, 1H, -O-CH$_A\underline{H_B}$Ph); 4.64 (d, J = 11.5 Hz, 1H, -O-CH$_A\underline{H_B}$Ph); 4.56 (s, 2H, -O-C$\underline{H_2}$Ph); 4.37 – 4.32 (m, 1H, H-5$_{glycal}$); 4.25 (dt, J = 5.0, 0.9 Hz, 1H, H-3$_{glycal}$); 3.94 (dd, J = 6.1, 5.0 Hz, 1H, H-4$_{glycal}$); 3.84 (dd, J = 10.8, 5.9, 1H, -C$\underline{H_A}$H$_B$OBn); 3.76 (dd, J = 10.8, 3.7 Hz, 1H, -CH$_A\underline{H_B}$OBn).

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 191.5; 151.9; 137.9; 137.8; 135.0; 131.6; 130.3; 129.7; 128.65; 128.58; 128.1; 128.04; 128.03; 127.96; 127.91; 127.89; 98.0; 91.4; 88.9; 77.2; 74.9; 73.6; 73.2; 72.7; 72.4; 68.2.

HRMS (TOF ES+): $C_{36}H_{32}O_5Na$ $[M+Na]^+$ (*m/z*): calc. 567.2147; found 567.2158.

*The general procedure for **3** with the yield determined with the internal standard* (^{1}H NMR)

Following the procedure described for **3**, the mixture was stirred at elevated temperature for 18 h. Ethyl acetate was then added to the crude mixture and the mixture was filtrated through a Celite® pad, and washed several times with ethyl acetate. Then filtrate was concentrated. The residue was dissolved in small amount of $CDCl_3$ and equimolar amount of DMF (the internal standard; 0.11 mmol, 8.5 µl) was added to the solution. The sample is to be mixed thoroughly. Then ^{1}H NMR experiment was performed. Signals of interest in ^{1}H NMR spectra:

δ = 8.02 ppm – internal standard signal – integration should be normalized to 1.00

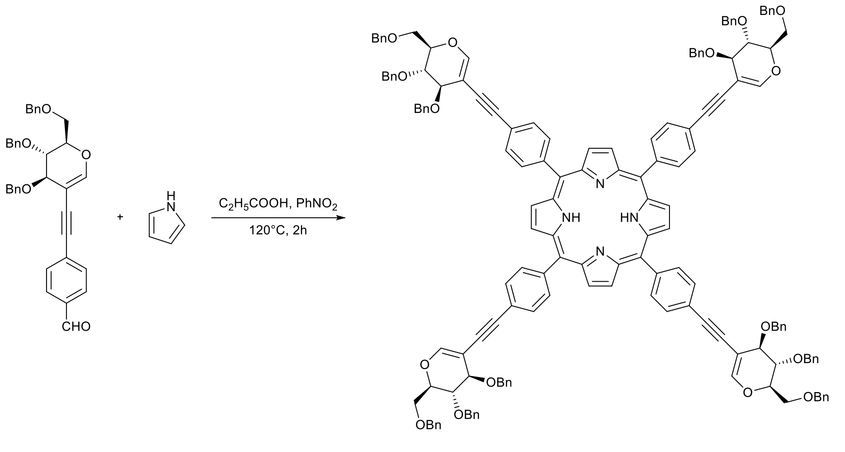
There are two signals useful for NMR yield determination, both giving equally good approximation of the yield:

δ = 9.99 ppm – proton from the CHO group

δ = 7.01 ppm – H-1 (pseudoanomeric signal)

*5,10,15,20-tetrakis(4-(2-(3,4,6-tri-O-benzyl-D-glucal-2-yl)ethynyl)phenyl)porphyrin (**5**)*

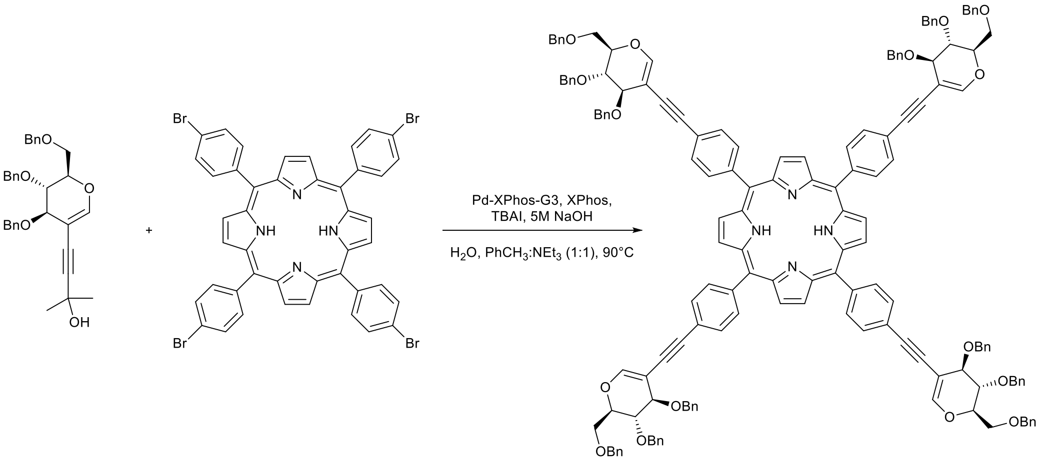
Procedure 1 - *Adler-Longo strategy*



3 **5**

Aldehyde **3** (99.9 mg, 0.184 mmol, 1.0 eq) was dissolved in propionic acid (0.37 mL) and nitrobenzene (0.60 mL) in a round bottom flask equipped with a condenser and a stir bar. The mixture was then heated to 120°C and pyrrole (0.015 mL, 0.216 mmol, 1.17 eq) was added. The resulting mixture was refluxed for 75 minutes and shielded from light. After that time, flask was cooled to room temperature and placed inside an ice bath. Then, 3 mL of cold methanol were added. Suspension was filtered on a sintered disc filter funnel and thoroughly washed with methanol. Resulting solid was purified by flash chromatography (DCM/$CHCl_3$, 1:1) yielding mixture of product and pyrrole impurities. The mixture was recrystallized (ethyl acetate/hexane, 5:3, v/v, 1 mL of ethyl acetate for 100 mg of aldehyde **3** used in the reaction, solvents added at room temperature, then left at -20°C for 1 hour), yielding violet powder of desired porphyrin **5** (11.0 mg, 10%). This procedure proved difficult to reproduce.

Procedure 2 – *Sonogashira approach with β-alkyne elimination*



7c **6** **5**

Porphyrin **6** (9.2 mg, 0.01 mmol, 1.0 eq), glycal **7c** (40.3 mg, 0.08 mmol, 8.0 eq), Pd-XPhos-G3 (1.7 mg, 0.002 mmol, 0.2 eq), XPhos (1.3 mg, 0.002 mmol, 0.2 eq) and TBAI (0.4 mg, 0.001 mmol, 0.1 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Next, solids were dissolved in mixture of toluene (1.5 mL), triethylamine (1.5 mL), then distilled water (0.35 mL) and 5M aqueous solution of NaOH (0.05 mL, 0.24 mmol, 24.0 eq) were added through a rubber septum under argon. The vessel was sealed and vigorously stirred at 90°C for 18 h, shielded from light. Upon completion, 2.5 mL of DCM and 2.5 mL of 10% $NaHCO_3$ aqueous solution were added and stirred further for 30 minutes. Then, crude mixture was transferred to a separatory funnel and extracted 3 times with 10 mL of DCM. Combined organic layers were washed 2 times with 10 mL of distilled water and dried over anhydrous $MgSO_4$. The mixture was filtered off. Solvents were evaporated and the residue was purified by flash chromatography (DCM/$CHCl_3$/NEt_3, 50:50:1) yielding a mixture of product **5** and sugar impurities. Sugar impurities were removed as follows: residual solid (as violet film on flask's sides) was washed with methanol and left suspended in methanol overnight. Decanting methanol and drying gave desired product **5** as violet powder with analytical purity (17.7 mg, 76%). **m.p.** > 300°C

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.89 (s, 8H, H^{β} - pyrrole); 8.17 (d, J = 7.8 Hz, 8H, $H_{A,A'}$ - aryl); 7.79 (d, J = 7.7 Hz, 8H, $H_{B,B'}$ - aryl); 7.52 (d, J = 7.5 Hz, 8H, H-benzyl); 7.42 – 7.28 (m, 52H, H-benzyl); 7.11 (s, 4H, H-1_{glycal}); 5.07 (d, J = 11.5 Hz, 4H, -O-C$\underline{H_A}$$H_B$Ph); 4.88 (d, J = 11.5 Hz, 4H, -O-C$H_A$$\underline{H_B}$Ph); 4.83 (d, J = 11.6 Hz, 4H, -O-C$\underline{H_A}$$H_B$Ph); 4.70 (d, J = 11.6 Hz, 4H, -O-C$H_A$$\underline{H_B}$Ph); 4.62 (s, 8H, -O-C$\underline{H_2}$Ph); 4.42 – 4.35 (m, 8H, H-3_{glycal} and H-5_{glycal}); 4.02 (dd, J = 6.6, 5.1 Hz, 4H, H-4_{glycal}); 3.91 (dd, J = 10.7, 5.7 Hz, 4H, -C$\underline{H_A}$$H_B$OBn); 3.82 (dd, J = 10.7, 3.5 Hz, 4H, -C$H_A$$\underline{H_B}$OBn); -2.76 (s, 2H, NH).

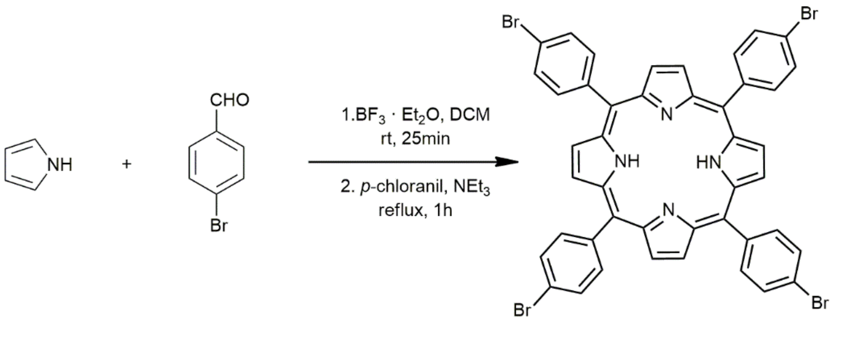
^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 151.1; 141.6; 138.4; 138.03; 137.97; 134.7; 129.7; 128.7; 128.6; 128.6; 128.2; 128.1; 128.0; 127.9; 127.9; 123.6; 119.9; 98.5; 89.3; 87.9; 77.3; 75.4; 73.7; 73.4; 73.1; 72.6; 68.4.

UV-Vis ($CHCl_3$): λ_{max} [nm] (log ε): 648.8 (3.27); 592.8 (3.32); 556.2 (3.65); 519.6 (3.81); 424.0 (4.89, Soret band).

MS (ESI) m/z (% rel. int.): 2373 (2); 2372 (17); 2371 (50); 2370 (100); 2369 (99); 2368 (39) (isotope $[M+H]^+$).

HRMS (ESI): $C_{160}H_{135}N_4O_{16}^+$ $[M+H]^+$ (m/z): calc. 2367.9868; found 2367.9801.

*5,10,15,20-tetrakis(4-bromophenyl)porphyrin (**6**)*



6

4-Bromobenzaldehyde (2.09 g, 11.27 mmol, 1.0 eq) and pyrrole (0.81 ml, 11.67 mmol, 1.04 eq) were dissolved in dichloromethane (750 ml), then $BF_3 \cdot Et_2O$ (0.14 ml, 1.17 mmol, 0.1 eq) was added. The resulting mixture was stirred in darkness at room temperature for 25 minutes. After that, *p*-chloranil (2.09 g, 8.50 mmol, 0.75 eq) and NEt_3 (0.39 ml, 2.80 mmol, 0.25 eq) were added. This mixture was then stirred in reflux for an hour. Next, crude mixture was concentrated to dryness and purified by flash chromatography (hexane/$CHCl_3$, 1:2) yielding violet crystalline powder of porphyrin **6** (1.36 g, 52%, R_f = 0.80 (hexane/$CHCl_3$, 1:2). The characterization data were in agreement with those of the literature[4].

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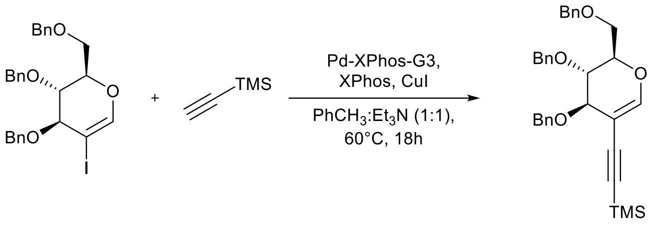
[4] Z. Dou, L. Xu, Y. Zhi, Y. Zhang, H. Xia, Y. Mu, X. Liu, *Chem. Eur. J.*, **2016**, 29, 9919 - 9922

*3,4,6-tri-O-benzyl-2-(2-trimethylsilylethynyl)-D-glucal (**7a**)*

Procedure 1 – *Pd-XPhos-G3 as a catalyst*



1 **7a**

Glycal **1** (671 mg, 1.24 mmol, 1.0 eq) and catalytic system consisting of Pd-XPhos-G3 (53.0 mg, 0.006 mmol, 0.05 eq), XPhos (29.6 mg, 0.006 mmol, 0.05 eq) and CuI (11.2 mg, 0.006 mmol, 0.05 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Toluene (2.8 mL), triethylamine (2.8 mL) and ethynyltrimethylsilane (0.21 mL, 1.49 mmol, 1.2 eq) were added subsequently through rubber septum, under argon. The vessel was sealed and the resulting mixture was stirred at 60°C for 18 h. After completion, DCM was added to the mixture. Afterwards, the diluted mixture was filtrated through short pad of Celite® and washed several times with DCM. Filtrate was concentrated, residue was purified by flash chromatography (hexane/ethyl acetate, 17:1) yielding yellowish oil of glycal **7a** (358 mg, 56%).

Procedure 2 – *Pd(PPh$_3$)$_4$ as a catalyst*

Glycal **1** (552 mg, 1.02 mmol , 1.0 eq) and catalytic system consisting of Pd(PPh$_3$)$_4$ (119 mg, 0.103 mmol, 0.1 eq) and CuI (37.7 mg, 0.209 mmol, 0.2 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Toluene (2.3 mL), triethylamine (2.3 mL) and ethynyltrimethylsilane (0.17 mL, 1.22 mmol, 1.2 eq) were subsequently added through a rubber septum, under argon. The vessel was sealed and the resulting mixture was stirred for 18h, at 80°C. Then, DCM was added to the mixture. Afterwards, the diluted mixture was filtrated through a short pad of Celite® and washed several times with DCM. Filtrate was concentrated, residue was purified by flash chromatography (hexane/ethyl acetate, 17:1), yielding yellowish oil of glycal **7a** (398 mg, 76%).

$\boldsymbol{R_f}$ = 0.24 (hexane/ethyl acetate, 17:1); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$= +24.1 (1.00, CHCl$_3$);

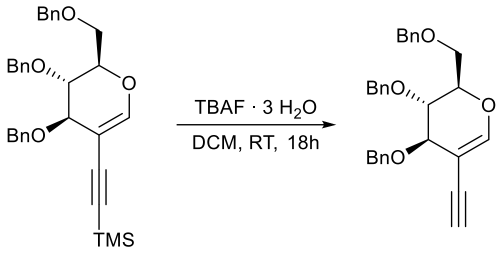
IR (film): 3062, 3030, 2955, 2865, 2143, 1620, 1496, 1453, 1364, 1248, 1179, 1087, 1069, 1027, 838, 732, 696 cm^{-1}.

^{1}H NMR (500 MHz, CDCl$_3$) δ [ppm] = 7.38 – 7.28 (m, 13H, H-benzyl); 7.25 – 7.22 (m, 2H, H-benzyl); 6.88 (br s, 1H, H-1); 4.89 (d, *J* = 11.3 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.72 (d, *J* = 11.5 Hz, 1H, O-C$\underline{H_A}$H$_B$Ph); 4.69 (d, *J* = 11.4 Hz, 1H, -O-CH$_A$$\underline{H_B}$Ph); 4.58 (d, *J* = 11.5 Hz, 1H, -O-CH$_A$$\underline{H_B}$Ph); 4.53 (s, 2H, -O-CH$_2$Ph); 4.22 (td, *J* = 6.2, 3.6 Hz, 1H, H-5); 4.18 (dt, *J* = 5.3, 1.0 Hz, 1H, H-3); 3.85 (dd, *J* = 6.8, 5.3 Hz, 1H, H-4); 3.78 (dd, *J* = 10.9, 5.7 Hz, 1H, -C$\underline{H_A}$H$_B$OBn); 3.72 (dd, *J* = 10.7, 3.6 Hz, 1H, -CH$_A$$\underline{H_B}$OBn); 0.19 (s, 9H, -C$\underline{H_3}$).

^{13}C NMR (125 MHz, CDCl$_3$) δ [ppm] = 151.7; 138.3; 138.00; 137.95; 128.6; 128.54; 128.47; 128.1; 128.01; 127.99; 127.9; 127.82; 127.84; 102.3; 98.5; 94.1; 77.1; 75.3; 73.6; 73.3; 73.0; 72.5; 68.3; 0.2.

HRMS (ESI): $C_{32}H_{37}O_4Si$ $[M+H^+]^+$ (*m/z*): calc. 513.2456; found 513.2465.

*3,4,6-tri-O-benzyl-2-ethynyl-D-glucal (**7b**)*



7a **7b**

Glycal **7a** (398 mg, 0.776 mmol, 1.0 eq) was dissolved in DCM (6 mL), then TBAF · 3 H_2O (245 mg, 0.776 mmol, 1.0 eq) was added. The resulting mixture was stirred at room temperature overnight. Then solvent was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate, 9:1) yielding glycal **7b** (182 mg, 53%) as yellowish oil.

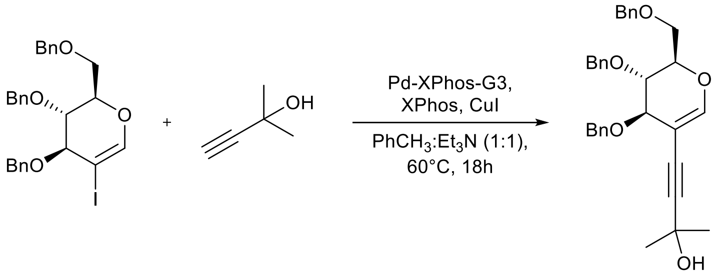
R$_f$ = 0.34 (hexane/ethyl acetate, 9:1); $[\alpha]_D^{20}$ = +21.0 (0.50, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.37 – 7.27 (m, 13H, H-benzyl); 7.26 – 7.23 (m, 2H, H-benzyl); 6.90 (br s, 1H, H-1); 4.86 (d, *J* = 11.3 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.72 (d, *J* = 11.6 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.66 (d, *J* = 11.3 Hz, 1H, -O-CH$_A\underline{H_B}$Ph); 4.59 (d, *J* = 11.6 Hz, 1H, -O-CH$_A\underline{H_B}$Ph); 4.53 (s, 2H, -O-C$\underline{H_2}$Ph); 4.27 (tdd, *J* = 6.0, 3.6, 1.0 Hz, 1H, H-5); 4.16 (dt, *J* = 5.1, 1.0 Hz, 1H, H-3); 3.86 (dd, *J* = 6.4, 5.0 Hz, 1H, H-4); 3.79 (dd, *J* = 10.8, 5.9 Hz, 1H, -C$\underline{H_A}$H$_B$OBn); 3.71 (dd, *J* = 10.8, 3.6 Hz, 1H, -CH$_A\underline{H_B}$OBn); 2.88 (s, 1H, -C≡CH).

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 151.9; 138.2; 138.0; 137.9; 128.6; 128.54; 128.49; 128.1; 128.03; 128.00; 127.88; 127.86; 97.2; 81.0; 77.2; 77.1; 74.9; 73.6; 73.2; 72.8; 72.5; 68.3.

HRMS (ESI+): $C_{29}H_{29}O_4$ $[M+H]^+$ m/z calc. 441.1971; found 441.1973.

*3,4,6-tri-O-benzyl-2-(2-(2-hydroxyprop-2-yl)ethynyl)-D-glucal (**7c**)*



1 **7c**

Glycal **1** (548 mg, 1.01 mmol, 1.0 eq), Pd-XPhos-G3 (85.6 mg, 0.101 mmol, 0.1 eq), XPhos (48.1 mg, 0.104 mmol, 0.1 eq) and CuI (18.2 mg, 0.101 mmol, 0.1 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Then, toluene (4.6 mL), triethylamine (4.6 mL) and 2-methylbut-3-yn-2-ol (118 µL, 1.21 mmol, 1.2 eq) were added consecutively through a rubber septum, under argon. Mixture was sealed and stirred at 60°C, for 18 h. Then ethyl acetate was added, crude mixture was filtrated through short pad of Celite® and washed with ethyl acetate. Filtrate was concentrated and the residue was purified by flash chromatography (hexane/ethyl acetate, 75:25) yielding yellowish oil of glycal **7c** (371 mg, 73%).

R$_f$ = 0.32 (hexane/ethyl acetate, 75:25); $[\alpha]_D^{20}$ = +5.2 (1.00, $CHCl_3$);

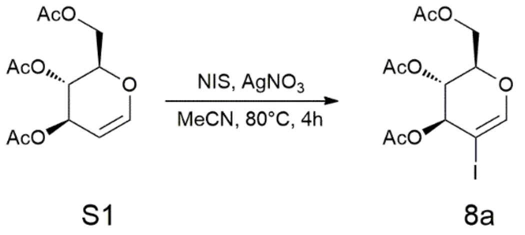
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.39 – 7.27 (m, 13H, H-benzyl); 7.26 – 7.22 (m, 2H, H-benzyl); 6.80 (br s, 1H, H-1); 4.82 (d, *J* = 11.5 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.72 (d, *J* = 11.5 Hz, 1H, -O-C$\underline{H_A}$H$_B$Ph); 4.68 (d, *J* = 11.6 Hz, 1H, -

O-CH$_{A}\underline{H}_{B}$Ph); 4.60 (d, *J* = 11.6 Hz, 1H, -O-CH$_{A}\underline{H}_{B}$Ph); 4.54 (s, 2H, -O-C$\underline{H}_{2}$Ph); 4.26 – 4.21 (m, 1H, H-5); 4.14 – 4.12 (m, 1H, H-3); 3.86 (dd, *J* = 6.7, 5.2 Hz, 1H, H-4); 3.79 (dd, *J* = 10.7, 5.8 Hz, 1H, -C$\underline{H}_{A}$H$_{B}$OBn); 3.72 (dd, *J* = 10.8, 3.6 Hz, 1H, -CH$_{A}\underline{H}_{B}$OBn); 1.51 (s, 6H, -C$\underline{H}_{3}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 150.5; 138.3; 137.9; 137.8; 128.5; 128.45; 128.43; 127.93; 127.87; 127.77; 127.76; 97.6; 93.6; 78.8; 76.9; 75.3; 73.5; 73.1; 72.8; 72.2; 68.2; 65.6; 31.54; 31.48.

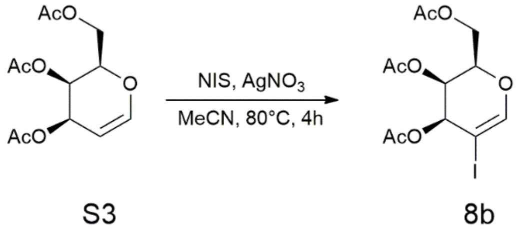
HRMS (ESI): $C_{32}H_{34}O_5Na$ $[M+Na]^+$ (*m/z*): calc. 521.2299; found 521.2300.

*3,4,6-tri-O-acetyl-2-iodo-D-glucal (**8a**)*



To a flame dried flask (Schlenk technique), equipped with a condenser, freshly distilled MeCN (50 mL) was added, under argon. Then, it was charged with glycal **S1** (5.00 g, 18.35 mmol, 1.0 eq) and heated to 80°C. Next, NIS (4.95 g, 22.0 mmol, 1.2 eq) and $AgNO_3$ (0.62 g, 3.65 mmol. 0.2 eq) were added, under argon. The mixture was stirred in darkness at 80°C for 4h. Crude mixture was concentrated to dryness and purified by flash chromatography (cyclohexane/ethyl acetate, 8:2) yielding yellowish solid of glycal **8a** (3.36 g, 46%, ***R$_f$*** = 0.32 (cyclohexane/ethyl acetate, 8:2)). The characterization data were in agreement with those of the literature.[5]

*3,4,6-tri-O-acetyl-2-iodo-D-galactal (**8b**)*



To a flame dried flask (Schlenk technique), equipped with a condenser, freshly distilled MeCN (15 mL) was added, under argon. Then, it was charged with glycal **S3** (1.50 g, 5.50 mmol, 1.0 eq) and heated to 80°C. Next, NIS (1.49 g, 6.61 mmol, 1.2 eq) and $AgNO_3$ (0.187 g, 1.10 mmol, 0.2 eq) were added, under argon. The mixture was stirred in darkness at 80°C for 3h. Crude mixture was concentrated to dryness and purified by flash chromatography (hexane/ethyl acetate, 7:3) yielding yellowish solid of glycal **8b** (1.28 g, 58%, ***R$_f$*** = 0.32 (hexane/ethyl acetate, 7:3)). The characterization data were in agreement with those of the literature.[5]

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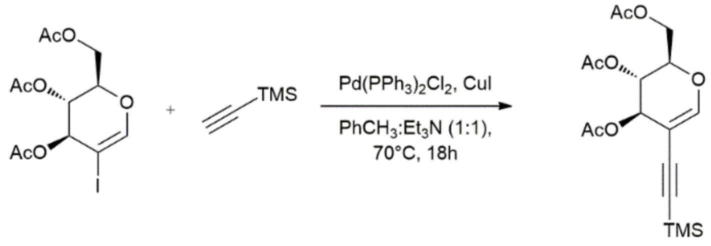
[5] S. Dharuman, Y.D. Vankar, *Org. Lett.* **2014**, 16, 4, 1172 – 1175

*3,4,6-tri-O-acetyl-2-(2-trimethylsilylethynyl)-*D*-glucal (**9a**)*



8a

9a

To a sealed tube, glycal **8a** (600 mg, 1.507 mmol, 1.0 eq), $Pd(PPh_3)_2Cl_2$ (52.9 mg, 0.075 mmol, 0.05 eq), CuI (28.8 mg, 0.151 mmol, 0.1 eq), toluene (8.5 mL) and triethylamine (8.5 mL) were added. The vessel was equipped with a stir bar and flushed with argon. Ethynyltrimethylsilane (0.26 ml, 1.82 mmol, 1.2 eq) was added subsequently through a rubber septum, under argon. Vessel was tightly sealed and the mixture was stirred at 70°C for 18h. After that, crude mixture was transferred to a flask. The mixture was concentrated to dryness. Residual solid was purified by flash chromatography (hexane/ethyl acetate, 7:3) yielding yellowish oil of glycal **9a** (546mg, 98%).

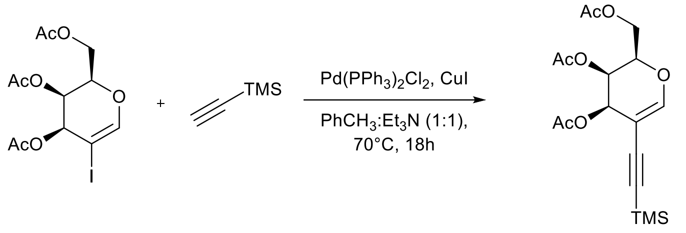
R$_f$ = 0.40 (hexane/ethyl acetate, 7:3); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ = +28.5 (1.00, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 6.88 (d, *J* = 1.1 Hz, 1H, H-1$_{glycal}$); 5.55 – 5.53 (m, 1H, H-3$_{glycal}$); 5.18 (dd, *J* = 7.4, 5.7 Hz, 1H, H-4$_{glycal}$); 4.39 (dd, , *J* = 12.2, 5.9 Hz, 1H, H-6$_{glycal}$); 4.32 – 4.27 (m, 1H, H-5$_{glycal}$); 4.18 (dd, *J* = 12.2, 3.2 Hz, 1H, H-6'$_{glycal}$); 2.09 (s, 3H, $C\underline{H_3}COO$-); 2.08 (s, 3H, $C\underline{H_3}COO$-); 2.07 (s, 3H, $C\underline{H_3}COO$-); 0.15 (s, 9H, $(C\underline{H_3})_3Si$-C≡C-(C-2$_{glycal}$)).

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 170.6 ($\underline{C}OO$-); 170.1 ($\underline{C}OO$-); 169.5 ($\underline{C}OO$-); 151.2 (C-1$_{glycal}$); 99.0 (C-2$_{glycal}$); 97.4 (-$\underline{C}$≡C-(C-2$_{glycal}$)); 95.6 (-C≡$\underline{C}$-(C-2$_{glycal}$)); 74.5 (C-5$_{glycal}$); 67.3 (C-3$_{glycal}$); 66.5 (C-4$_{glycal}$); 61.2 (C-6$_{glycal}$); 20.90 ($\underline{C}H_3COO$-); 20.85 ($\underline{C}H_3COO$-); 20.80 ($\underline{C}H_3COO$-); 0.00 (($\underline{C}H_3)_3Si$-C≡C-(C-2$_{glycal}$)).

HRMS (ESI): $C_{76}H_{63}N_4O_{16}$ $[M+H]^+$ m/z calc. 369.1364; found 369.1364.

*3,4,6-tri-O-acetyl-2-(2-trimethylsilylethynyl)-*D*-galactal (**9b**)*

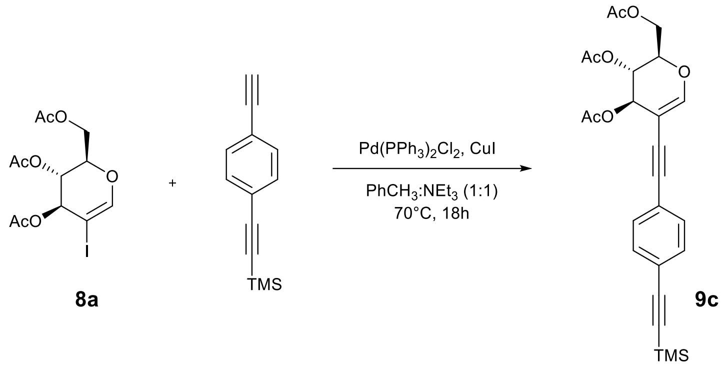


8b

9b

To a sealed tube, glycal **8b** (527 mg, 1.32 mmol, 1.0 eq), $Pd(PPh_3)_2Cl_2$ (46.5 mg, 0.066 mmol, 0.05 eq) and CuI (25.6 mg, 0.134 mmol, 0.1 eq) were added. The vessel was equipped with a stir bar and flushed with argon. Toluene (7.4 mL), triethylamine (7.4 mL) and ethynyltrimethylsilane (0.22 mL, 1.59 mmol, 1.2 eq) were added subsequently through a rubber septum, under argon. Vessel was tightly sealed and the mixture was stirred at 70°C for 21h. Then, ethyl acetate was added to the crude mixture, diluted mixture was filtrated through short pad of Celite®, washed with ethyl acetate and concentrated. Residual solid was purified by flash chromatography (hexane/ethyl acetate, 7:3) yielding yellowish oil of glycal **9b** (423 mg, 86%, ***R$_f$*** = 0.32 (hexane/ethyl acetate, 7:3). The characterization data were in agreement with those of the literature.[6]

*3,4,6-tri-O-acetyl-2-(2-(4-(2-trimethylsilylethynyl)phenyl)ethynyl)-D-glucal (**9c**)*



To a sealed tube, glycal **8a** (126.5 mg, 0.318 mmol, 1.0 eq), $Pd(PPh_3)_2Cl_2$ (22.3 mg, 0.032 mmol, 0.1 eq), CuI (12.2 mg, 0.064 mmol, 0.2 eq), 4-ethynyl-(2-trimethylsilylethynyl)benzene (75.6 mg, 0.381 mmol, 1.2 eq). The vessel was equipped with a stir bar and flushed with argon. Toluene (1.8 mL) and triethylamine (1.8 mL) were added subsequently through a rubber septum, under argon. Vessel was tightly sealed and the mixture was stirred at 70°C for 18h. After that, crude mixture was transferred to a flask. The mixture was concentrated to dryness. Residual solid was purified by flash chromatography (hexane/ethyl acetate, 7:3) yielding yellowish oil of glycal **9c** (127.2 mg, 88%).

R$_f$ = 0.15 (hexane/ethyl acetate, 8:2); $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{20}}$ = +31.8 (0.50, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 7.39 – 7.35 (m, 2H, $H_{AA'}$ – aryl); 7.29 – 7.26 (m, 2H, $H_{BB'}$ – aryl); 6.94 (d, *J* = 1.0 Hz, 1H, H-1); 5.60 (dt, *J* = 5.4, 0.9 Hz, 1H, H-3); 5.23 (dd, *J* = 6.9, 5.4 Hz, 1H, H-4); 4.43 (dd, *J* = 12.1, 6.1 Hz, 1H, H-6); 4.39 – 4.34 (m, 1H, H-5); 4.22 (dd, *J* = 12.1, 3.2 Hz, 1H, H-6'); 2.10 (s, 3H, $C\underline{H_3}COO$-); 2.10 (s, 3H, $C\underline{H_3}COO$-); 2.09 (s, 3H, $C\underline{H_3}COO$-); 0.24 (s, 9H, -$Si(C\underline{H_3})_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 170.6; 170.2; 169.5; 151.0; 132.0; 131.0; 123.3; 122.8; 104.7; 97.2; 96.3; 90.0; 85.7; 74.6; 67.3; 66.5; 61.2; 21.0; 20.9; 20.8; 0.0.

HRMS (ESI): $C_{25}H_{29}O_7Si$ $[M+H]^+$ m/z calc. 469.1632; found 469.1676.

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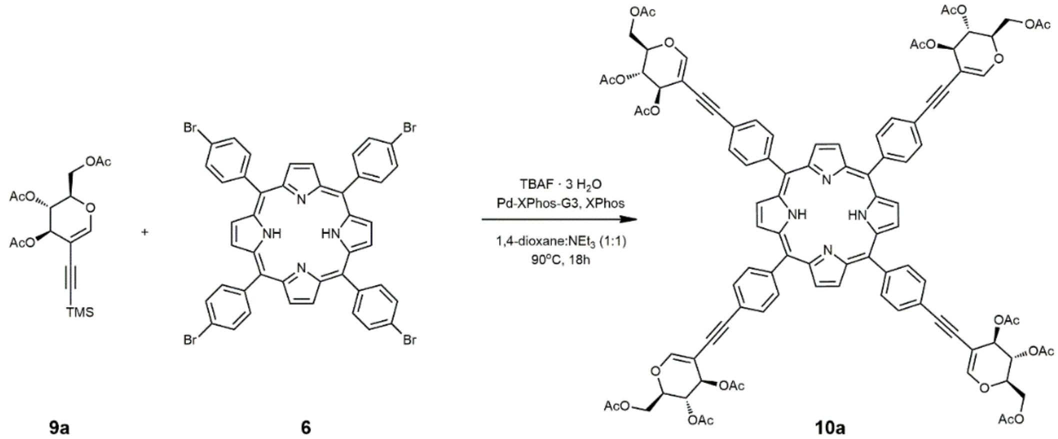
[6] D. C. Koester, D. B. Werz; *Beilstein J. Org. Chem.* **2012**, 8, 675-682

*5,10,15,20-tetrakis(4-(2-(3,4,6-tri-O-acetyl-D-glucal-2-yl)ethynyl)phenyl)porphyrin (**10a**)*



9a **6** **10a**

Porphyrin **6** (22.0 mg, 0.024 mmol, 1.0 eq), glycal **9a** (69.8 mg, 0.189 mmol, 8.0 eq), Pd-Xhos-G3 (3.0 mg, 0.004 mmol, 0.15 eq), XPhos (1.7 mg, 0.004 mmol, 0.15 eq) and TBAF · 3 H_2O (61.2 mg, 0.194 mmol, 8.2 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Then 1,4-dioxane (2.5 ml) and NEt_3 (2.5 ml) were added through a rubber septum, under argon. Resulting mixture was stirred in darkness at 90°C for 18h. Then, the mixture was concentrated to dryness and residue was purified by flash chromatography (DCM/EA/NEt_3, 80:20:1) yielding violet solid of porphyrin **10a** (35.9 mg, 85%) Analytical sample was obtained after recrystallization (cyclohexane:$CHCl_3$ 5:1 v/v; 0.2 mL of chloroform for 7 mg of porphyrin **10a**, chloroform added at room temperature, heated to boiling, cyclohexane added at room temperature and resulting mixture left at - 20°C for 3 h).

R_f = 0.45 (hexane/ethyl acetate, 25:75); **m.p.** > 300°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.85 (s, 8H, H^{β}–pyrrole); 8.16 (d, *J* = 8.4 Hz, 4H, $H_{A,A'}$-aryl); 7.78 (d, *J* = 8.4 Hz, 4H, $H_{B,B'}$-aryl); 7.11 (d, *J* = 1.2 Hz, 4H, H-1_{glycal}); 5.77 (br d, *J* = 5.4 Hz, 4H, H-3_{glycal}); 5.34 (dd, *J* = 6.9, 5.4 Hz, 4H, H-4_{glycal}); 4.51 (dd, *J* = 12.0, 6.0 Hz, 4H, H-6_{glycal}); 4.49–4.42 (m, 4H, H-5_{glycal}); 4.30 (dd, *J* = 12.0, 3.1 Hz, 4H, H-$6'_{glycal}$); 2.26 (s, 12H, $C\underline{H_3}COO$-(C-3_{glycal})); 2.16 (s, 12H, $C\underline{H_3}COO$-(C-4_{glycal})); 2.16 (s, 12H, $C\underline{H_3}COO$-(C-6_{glycal})); -2.81 (s, 2H, NH).

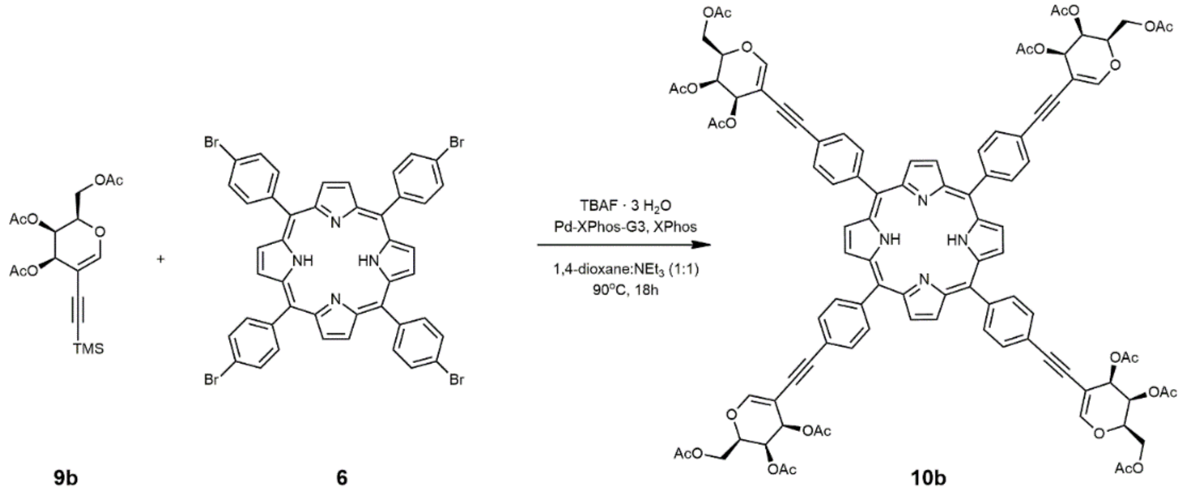
^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 170.7 ($\underline{C}OO$-(C-6_{glycal})); 170.4 ($\underline{C}OO$-(C-3_{glycal})); 169.6 ($\underline{C}OO$-(C-4_{glycal})); 151.1 (C-1_{glycal}); 142.0 (C-4_{Ar}); 134.7 (C-2_{Ar}); 129.7 (C-3_{Ar}); 122.9 (C-1_{Ar} or C_{meso}); 119.8 (C-1_{Ar} or C_{meso}); 97.4 (C-2_{glycal}); 90.2 ($\underline{C}\equiv C$-(C-2_{glycal})); 85.0 ($C\equiv\underline{C}$-(C-2)); 74.7 (C-5_{glycal}); 67.5 (C-3_{glycal}); 66.7 (C-4_{glycal}); 61.3 (C-6_{glycal}); 21.2 ($\underline{C}H_3COO$-); 21.0 ($\underline{C}H_3COO$-); 20.9 ($\underline{C}H_3COO$-).

UV – Vis ($CHCl_3$); λ_{max} [nm] (log ε): 648.8 (3.53); 592.6 (3.60); 555.4 (3.95); 518.0 (4.11); 425.2 (5.51, Soret band).

MS (ES+) m/z (% rel. int.): 921.27 (6); 920.77 (7); 920.27 (16); 919.77 (31); 919.26 (65); 918.77 (100); 918.26 (82) (isotope $[M+2Na]^{2+}$).

HRMS (ESI): $C_{100}H_{86}N_4O_{28}Na_2$ $[M+2Na]^{2+}$ m/z calc. 918.2607; found 918.2606.

*5,10,15,20-tetrakis(4-(2-(3,4,6-tri-O-acetyl-D-galactal-2-yl)ethynyl)phenyl)porphyrin (**10b**)*



9b **6** **10b**

Porphyrin **6** (22.0 mg, 0.024 mmol, 1.0 eq), glycal **9b** (69.8 mg, 0.189 mmol, 8.0 eq), Pd-Xhos-G3 (3.0 mg, 0.004 mmol, 0.15 eq), XPhos (1.7 mg, 0.004 mmol, 0.15 eq) and TBAF · 3 H_2O (61.2 mg, 0.194 mmol, 8.2 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Then 1,4-dioxane (2.5 ml) and NEt_3 (2.5 ml) were added through a rubber septum, under argon. Resulting mixture was stirred in darkness at 90°C for 18h. Then, the mixture was concentrated to dryness and residue was purified by flash chromatography (DCM:EA:NEt_3, 80:20:1) yielding violet solid of porphyrin **10b** (33.4 mg, 79%).

***R*$_f$** = 0.45 (hexane/ethyl acetate, 25:75); **m.p.** > 300°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.84 (s,8H, H^{β} - pyrrole); 8.17 – 8.13 (m, 8H, $H_{A,A'}$-aryl); 7.79 – 7.76 (m, 8H, $H_{B,B'}$-aryl); 7.11 (d, J = 1.5 Hz, 4H, H-1_{glycal}), 5.93 – 5.88 (m, 4H, H-3_{glycal}), 5.59 (dd, *J* = 4.4, 1.9 Hz, 4H, H-4_{glycal}); 4.49 (dd, *J* = 7.3, 5.7 Hz, 4H, H-5_{glycal}); 4.37 (dd, *J* = 11.7, 7.2 Hz, 4H, H-6_{glycal}); 4.31 (dd, *J* = 11.7, 5.5 Hz, 4H, H-$6'_{glycal}$); 2.24 (s, 12H, $C\underline{H}_3COO$-(C_{glycal})); 2.22 (s, 12H, $C\underline{H}_3COO$-(C_{glycal})); 2.15 (s, 12H, $C\underline{H}_3COO$-(C_{glycal})); -2.81 (s, 2H, NH).

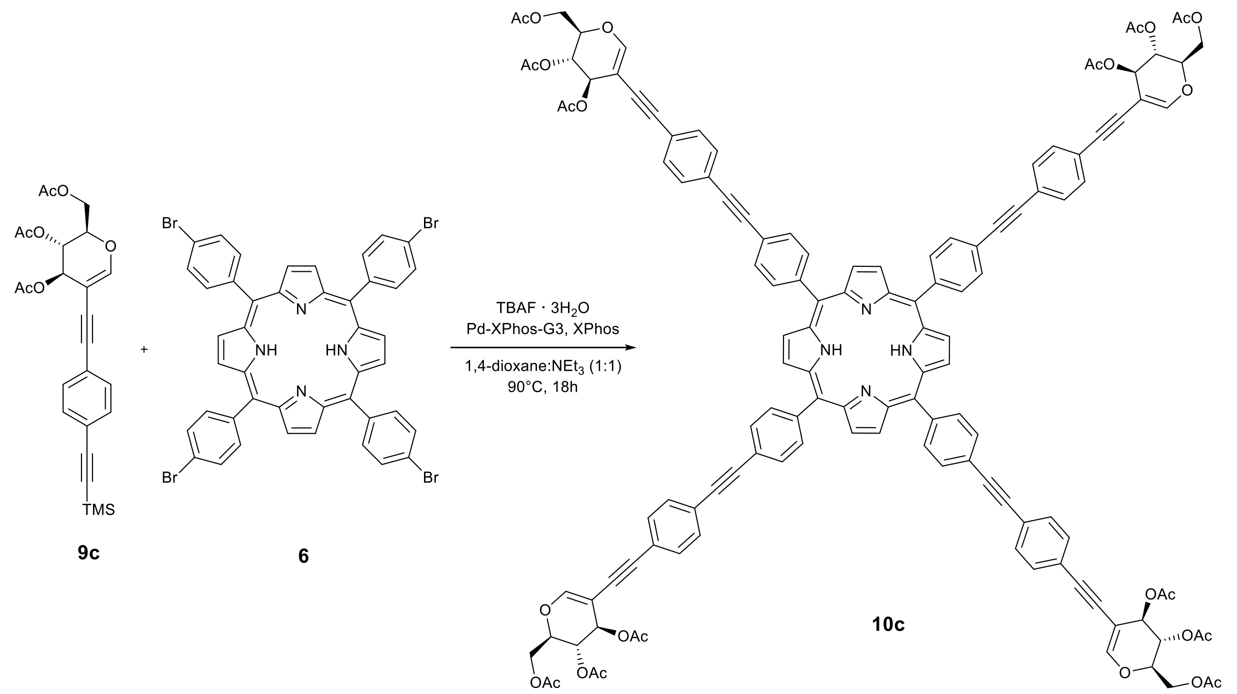
^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 170.6 ($\underline{C}OO$-(C_{glycal})); 170.5 ($\underline{C}OO$-(C_{glycal})); 170.3 ($\underline{C}OO$-(C_{glycal})); 151.1 (C-1_{glycal}); 141.9 (C-4_{Ar}); 134.7 (C-2_{Ar}); 129.7 (C-3_{Ar}); 123.0 (C-1_{Ar} or C_{meso}); 119.8 (C-1_{Ar} or C_{meso}); 97.3 (C-2_{glycal}); 90.4 ($\underline{C}\equiv C$-(C-2_{glycal})); 85.0 ($C\equiv\underline{C}$-(C-2)); 73.9 (C-5_{glycal}); 64.6 (C-3_{glycal}); 63.4 (C-4_{glycal}); 61.9 (C-6_{glycal}); 20.98 ($\underline{C}H_3$-COO-); 20.91 ($\underline{C}H_3COO$-); 20.86 ($\underline{C}H_3COO$-).

UV – Vis ($CHCl_3$); λ_{max} [nm] (log ε): 648.4 (3.60); 592.4 (3.69); 555.6 (4.03); 518.8 (4.18); 435.4 (5.55, Soret band).

MS (ESI) *m/z* (% rel. int.): 1796.6 (2); 1795.6 (8); 1794.6 (23); 1793.6 (62); 1792.6 (100); 1791.6 (93) (isotope $[M+H]^+$).

HRMS (ESI): $C_{100}H_{87}N_4O_{28}$ $[M+H]^+$ m/z calc. 1791.5501; found 1791.5510.

*5,10,15,20-tetrakis(4-(2-(4-(2-(3,4,6-tri-O-acetyl-D-glucal-2-yl)ethynyl)phenyl)ethynyl)phenyl)porphyrin (**10c**)*



9c **6** **10c**

Porphyrin **6** (15.1 mg, 0.016 mmol, 1.0 eq), glycal (60.0 mg, 0.128 mmol, 8.0 eq), Pd-Xhos-G3 (2.7 mg, 0.003 mmol, 0.2 eq), XPhos (1.5 mg, 0.003 mmol, 0.2 eq) and TBAF · 3 H_2O (41.4 mg, 0.131 mmol, 8.2 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Then, 1,4-dioxane (1.7 mL) and NEt_3 (1.7 mL) were added through a rubber septum, under argon. Resulting mixture was stirred in darkness at 90°C for 18h. Then, the mixture was concentrated to dryness and the residue was purified by flash chromatography (hexane/DCM 1:1, to pure DCM, to DCM/ethyl acetate/triethylamine 90:10:1, to DCM/ethyl acetate/triethylamine 80:20:1) yielding violet powder of porphyrin (23.0 mg, 65%).

R_f = 0.60 (hexane/ethyl acetate, 25:75) ; **m.p.** > 300°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.88 (s, 8H, H^{β} – pyrrole); 8.24 – 8.19 (m, 8H, $H_{AA'}$ – aryl$_1$); 7.96 – 7.91 (m, 8H, $H_{BB'}$ – aryl$_1$); 7.63 – 7.59 (m, 8H, $H_{AA'}$ – aryl$_2$); 7.46 – 7.41 (m, 8H, $H_{BB'}$ – aryl$_2$); 7.00 (d, *J* = 1.1 Hz, 4H, H-1$_{glycal}$); 5.66 (dt, *J* = 5.4, 1.0 Hz, 4H, H-3$_{glycal}$); 5.28 (dd, *J* = 6.9, 5.4 Hz, 4H, H-4$_{glycal}$); 4.47 (dd, *J* = 12.1, 6.1 Hz, 4H, H-6$_{glycal}$); 4.43 – 4.37 (m, 4H, H-5$_{glycal}$); 4.25 (dd, *J* = 12.1, 3.2 Hz, 4H, H-6'$_{glycal}$); 2.17 (s, 12H, $C\underline{H_3}COO$-); 2.13 (s, 24H, $C\underline{H_3}COO$-); -2.77 (s, 2H, NH).

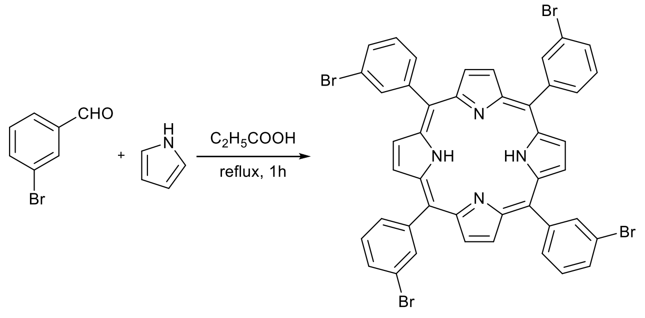
^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 170.6; 170.3; 169.6; 151.1; 142.4; 134.8; 131.8; 131.3; 130.2; 123.4; 123.0; 122.9; 119.8; 97.3; 91.2; 90.5; 90.2; 85.8; 74.6; 67.3; 66.6; 61.2; 21.0; 20.91; 20.86.

MS (ESI) m/z (% rel. int.): 2195.7 (10); 2194.7 (40); 2193.7 (69); 2192.7 (100); 2191.7 (45) (isotope $[M+H]^+$).

HRMS (ESI): $C_{132}H_{103}N_4O_{28}$ $[M+H]^+$ m/z calc. 2191.6753; found 2191.6705.

UV – Vis ($CHCl_3$); λ_{max} [nm] (log *ε*): 648.4 (3.55); 591.4 (3.58); 554.8 (3.90); 518.8 (4.03); 425.8 (5.39, Soret band).

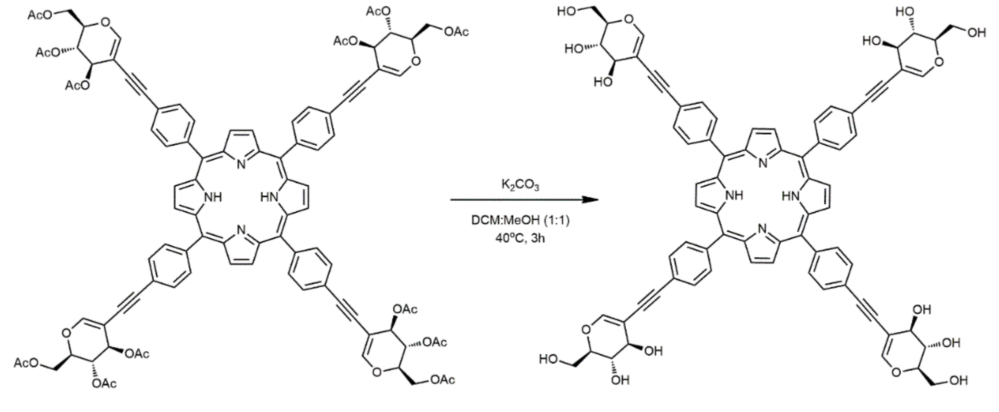
*5,10,15,20-tetrakis(3-bromophenyl)porphyrin (**11**)*



11

Propionic acid (42 mL) was added to a round bottom flask equipped with a condenser and a stir bar. Next, 3-bromobenzaldehyde (0.94 mL, 8.11 mmol, 1.0 eq) and pyrrole (0.56 mL, 8.11 mmol, 1.0 eq) were added consecutively. The mixture was refluxed for 1 h and shielded from light. After that time, the flask was cooled to room temperature and placed in an ice bath. Then, while stirring, cold methanol (35 mL) was added. The resulting mixture was stirred for additional 30 minutes. The crude mixture was then filtrated on a Büchner funnel, and afterwards, precipitated solid was thoroughly rinsed with methanol. Air drying of obtained solid yielded desired porphyrin **11** as a violet powder (480 mg, 25%). The characterization data were in agreement with those of the literature.[7]

*5,10,15,20-tetrakis(4-(2-(D-glucal-2-yl)ethynyl)phenyl)porphyrin (**12a**)*



10a **12a**

Porphyrin **10a** (32.4 mg, 0.018 mmol, 1.0 eq), potassium carbonate (14.9 mg, 0.108 mmol, 6.0 eq), methanol (0.5 mL) and dichloromethane (0.5 mL) were added to a reaction vessel. Resulting mixture was stirred in darkness at 40°C for 3 hours. Next, crude mixture was transferred into a flask and concentrated to dryness. The solid was purified by flash chromatography (DCM/MeOH, 7:3, to pure MeOH) yielding violet solid of porphyrin **12a** (19.9 mg, 86%).

R_f = 0.68 (dichloromethane/methanol, 7:3); **m.p.** > 300°C

^{1}H NMR (500 MHz, DMSO-d_6) δ [ppm]: 8.88 (s, 8H, H^{β}–pyrrole); 8.20 (d, *J* = 8.1 Hz, 8H, $H_{A,A'}$-aryl); 7.84 (d, *J* = 8.1 Hz, 8H, $H_{B,B'}$-aryl); 7.07 (br s, 4H, H-1_{glycal}); 5.57–5.50 (m, 4H, OH); 5.46 (br s, 4H, OH); 4.87–4.82 (m, 4H, OH); 4.12–4.07 (m, 4H, H-3_{glycal}); 3.91 (ddd, *J* = 8.0, 5.5, 2.7 Hz, 4H, H-5_{glycal}); 3.78–3.69 (m, 8H, H-6_{glycal}); 3.67–3.61 (m, 4H, H-4_{glycal}); -2.92 (s, 2H, NH).

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[7] L. Duan, Y.-L. Wang, X.-S. Fan, J.-Y. Wang; *Chem. Lett.* **2008**, 37, 1, 112-113

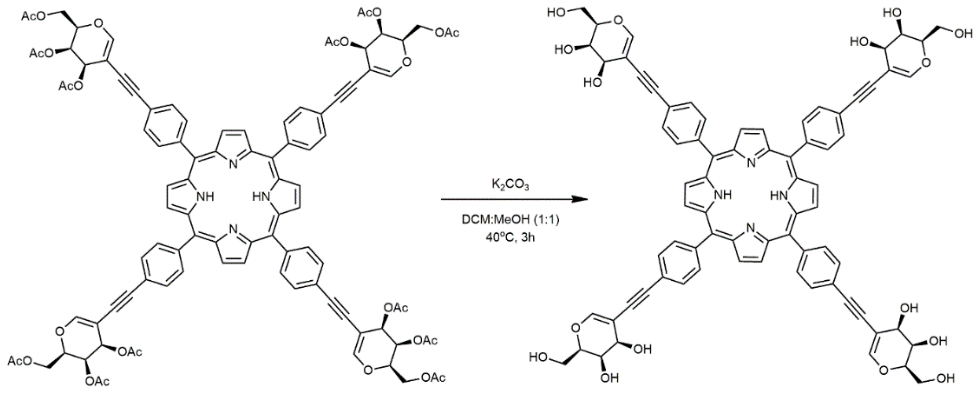
^{13}C NMR (125 MHz; DMSO-d$_6$) δ [ppm]: 150.2 (C-1$_{\text{glycal}}$); 140.3 (C-4$_{\text{Ar}}$); 134.5 (C-2$_{\text{Ar}}$); 129.5 (C-3$_{\text{Ar}}$); 123.6 (C$_{meso}$ or C-1$_{\text{Ar}}$); 119.6 (C$_{meso}$ or C-1$_{\text{Ar}}$); 100.6 (C-2$_{\text{glycal}}$); 89.4 (C≡$\underline{\text{C}}$-(C-2)); 88.1 ($\underline{\text{C}}$≡C-(C-2)); 80.6 (C-5$_{\text{glycal}}$); 68.7 (C-3$_{\text{glycal}}$); 68.0 (C-4$_{\text{glycal}}$); 60.0 (C-6$_{\text{glycal}}$).

UV-Vis (DMSO); λ$_{\text{max}}$ [nm] (log ε): 649.2 (3.87); 594.8 (3.82); 556.2 (4.18); 519.4 (4.23); 426.2 (5.56, Soret band).

MS (ESI) *m/z* (% rel. int.): 1294.4 (1); 1293.4 (9); 1292.4 (18); 1291.4 (18); 1290.4 (12); 1289.4 (38); 1288.4 (86); 1287.4 (100) (isotope [M+H]$^+$).

HRMS (ESI): $C_{76}H_{63}N_4O_{16}$ [M+H]$^+$ m/z calc. 1287.4234; found 1287.4235.

*5,10,15,20-tetrakis(4-(2-(D-galactal-2-yl)ethynyl)phenyl)porphyrin (**12b**)*



10b **12b**

Porphyrin **10b** (18.0 mg, 0.01 mmol, 1.0 eq), potassium carbonate (8.3 mg, 0.06 mmol, 6.0 eq), methanol (0.5 mL) and dichloromethane (0.5 mL) were added to a reaction vessel. Resulting mixture was stirred in darkness at 40°C for 3 hours. Next, crude mixture was transferred into a flask and concentrated to dryness. The solid was purified by flash chromatography (DCM/MeOH, 7:3, to pure MeOH) yielding violet solid of porphyrin **12b** (9.4 mg, 73%).

R$_f$ = 0.65 (dichloromethane/methanol, 7:3); **m.p.** > 300°C

^{1}H NMR (500 MHz, DMSO-d$_6$) δ [ppm]: 8.87 (s, 8H, H$^{\beta}$ - pyrrole); 8.19 (d, *J* = 7.7 Hz, 8H, H$_{A,A'}$-aryl); 7.83 (d, *J* = 7.9 Hz 8H, H$_{B,B'}$-aryl); 7.02 (br s, 4H, H-1$_{\text{glycal}}$); 4.40 (d, *J* = 3.4Hz, 4H, H-3$_{\text{glycal}}$); 4.02 (br t, *J* = 6.4Hz, 4H, C-5$_{\text{glycal}}$); 3.92 (d, *J* = 4.7Hz , 4H, C-4$_{\text{glycal}}$) 3.72 – 3.66 (m, 8H, H-6$_{\text{glycal}}$); -2.92 (s, 2H, NH).

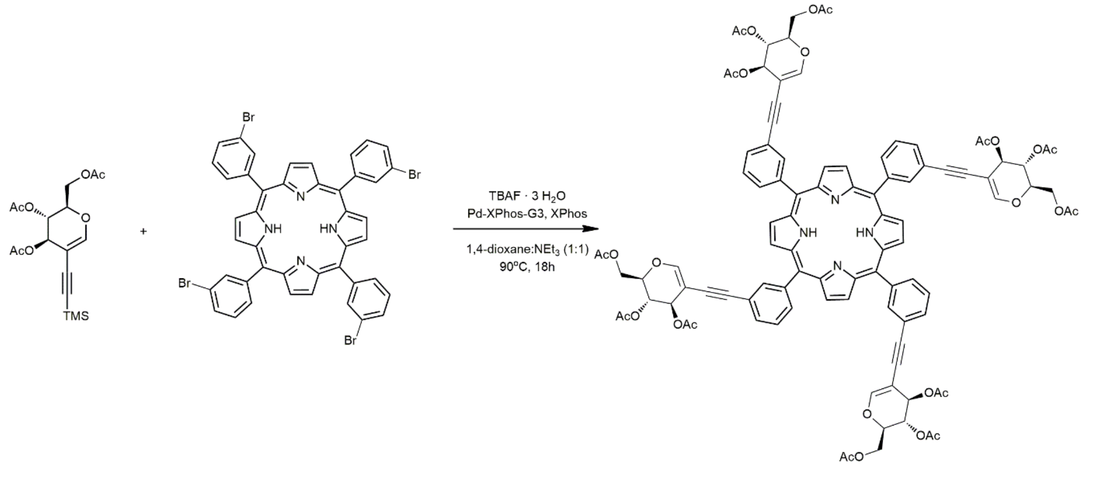
^{13}C NMR (125 MHz; DMSO-d$_6$) δ [ppm]: 150.5 (C-1$_{\text{glycal}}$); 140.3 (C-4$_{\text{Ar}}$); 134.5 (C-2$_{\text{Ar}}$); 129.5 (C-3$_{\text{Ar}}$); 123.7 (C$_{meso}$ or C-1$_{\text{Ar}}$); 119.6 (C$_{meso}$ or C-1$_{\text{Ar}}$); 100.3 (C-2$_{\text{glycal}}$); 89.7 ($\underline{\text{C}}$≡C-(C-2$_{\text{glycal}}$)); 88.4 (C≡$\underline{\text{C}}$-(C-2$_{\text{glycal}}$)); 78.9 (C-5$_{\text{glycal}}$); 64.7 (C-3$_{\text{glycal}}$); 64.1 (C-4$_{\text{glycal}}$); 60.0 (C-6$_{\text{glycal}}$).

UV – Vis (DMSO); λ$_{\text{max}}$ [nm] (log ε): 648.8 (3.66); 593.2 (3.63); 555.8 (3.98); 519.2 (4.09); 425.6 (5.37, Soret band).

MS (ESI) *m/z* (% rel. int.): 1291.4 (1); 1290.4 (12); 1289.4 (38); 1288.4 (86); 1287.4 (100) (isotope [M+H]$^+$).

HRMS (ESI): $C_{76}H_{63}N_4O_{16}$ [M+H]$^+$ m/z calc. 1287.4234; found 1287.4227.

*5,10,15,20-tetrakis(3-(2-(3,4,6-tri-O-acetyl-D-glucal-2-yl)ethynyl)phenyl)porphyrin (**13a**)*



9a **11** **13a**

Porphyrin **11** (17.3 mg, 0.019 mmol, 1.0 eq), glycal **9a** (55.0 mg, 0.149 mmol, 8.0 eq), Pd-Xhos-G3 (2.4 mg, 0.003 mmol, 0.2 eq), XPhos (1.3 mg, 0.003 mmol, 0.2 eq) and TBAF · 3 H_2O (48.3 mg, 0.153 mmol, 8.2 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Then 1,4-dioxane (2.0 mL) and NEt_3 (2.0 mL) were added through a rubber septum, under argon. Resulting mixture was stirred in darkness at 90°C for 18h. Then, the mixture was concentrated to dryness and residue was purified by flash chromatography (DCM:EA:NEt_3, 80:20:1) yielding violet solid of porphyrin **13a** (20.0 mg, 60%). Analytical sample was obtained after recrystallization (cyclohexane/$CHCl_3$, 5:1 v/v; 0.2 mL of chloroform for 10 mg of porphyrin **13a**, solvents added at room temperature, then left at - 20°C for 3 h).

R_f = 0.62 (hexane/ethyl acetate, 3:7); **m.p.** > 300°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.85 (s, 8H, H$^{\beta}$-pyrrole); 8.24 (br s, 4H, H-2$_{Ar}$); 8.16 – 8.10 (m, 4H, H-6$_{Ar}$); 7.83 – 7.78 (m, 4H, H-4$_{Ar}$); 7.73 – 7.66 (m, 4H, H-5$_{Ar}$); 6.99 (br s, 4H, H-1$_{glycal}$); 5.67 – 5.64 (m, 4H, H-3$_{glycal}$); 5.26 (br t, *J* = 6.0 Hz, 4H, H-4$_{glycal}$); 4.43 (dd, *J* = 12.0, 6.1 Hz, 4H, H-6$_{glycal}$); 4.39 – 4.35 (m, 4H, H-5$_{glycal}$); 4.22 (dd, *J* = 12.0, 2.8 Hz, 4H, H-6'$_{glycal}$); 2.11 – 2.07 (m, 36H, $C\underline{H}_3COO$-); -2.85 (s, 2H, NH).

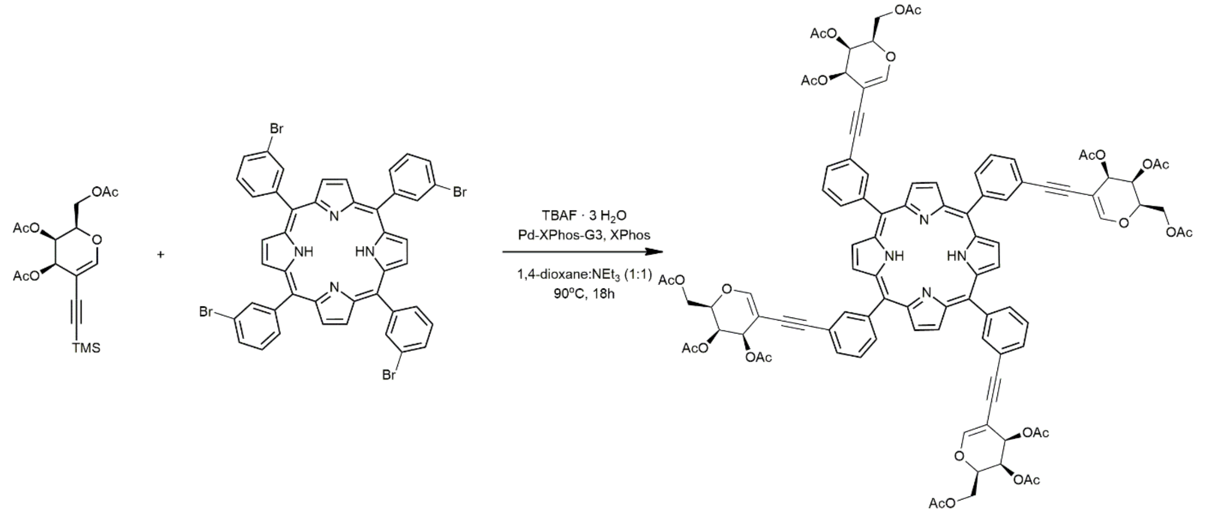
^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 170.6 ($\underline{C}OO$-(C$_{glycal}$)); 170.3 ($\underline{C}OO$-(C$_{glycal}$)); 169.6 ($\underline{C}OO$-(C$_{glycal}$)); 151.1 (C-1$_{glycal}$); 142.3 (C-3$_{Ar}$); 136.9 (C-2$_{Ar}$); 134.4 (C-6$_{Ar}$); 130.9 (C-4$_{Ar}$); 127.0 (C-5$_{Ar}$); 121.9 (C-1$_{Ar}$ or C$_{meso}$); 119.4 (C-1$_{Ar}$ or C$_{meso}$); 97.2 (C-2$_{glycal}$); 90.3 ($\underline{C}\equiv C$-(C-2$_{glycal}$)); 84.1 ($C\equiv\underline{C}$-(C-2)); 74.6 (C-5$_{glycal}$); 67.4 (C-3$_{glycal}$); 66.6 (C-4$_{glycal}$); 61.2 (C-6$_{glycal}$); 21.0 ($\underline{C}H_3COO$-); 20.9 ($\underline{C}H_3COO$-); 20.8 ($\underline{C}H_3COO$-).

UV – Vis ($CHCl_3$); λ_{max} [nm] (log ε): 646.0 (4.01); 590.0 (4.25); 550.0 (4.41); 516.0 (4.75); 419.0 (5.83, Soret band).

MS (ESI) *m/z* (% rel. int.): 1794.3 (4); 1793.6 (20); 1792.6 (94); 1791.6 (100) (isotope $[M+H]^+$).

HRMS (ESI): $C_{100}H_{87}N_4O_{28}$ $[M+H]^+$ m/z calc. 1791.5501; found 1791.5533.

*5,10,15,20-tetrakis(3-(2-(3,4,6-tri-O-acetyl-D-galactal-2-yl)ethynyl)phenyl)porphyrin (**13b**)*



9b **11** **13b**

Porphyrin **11** (21.7 mg, 0.023 mmol, 1.0 eq), glycal **9b** (68.5 mg, 0.185 mmol, 8.0 eq), Pd-XPhos-G3 (4.4 mg, 0.005 mmol, 0.2 eq), XPhos (2.3 mg, 0.005 mmol, 0.2 eq) and TBAF · 3 H_2O (60.3 mg, 0.19 mmol, 8.2 eq) were added to a reaction vessel. The vessel was equipped with a stir bar and flushed with argon. Then 1,4-dioxane (2.2 mL) and NEt_3 (2.2 mL) were added through a rubber septum, under argon. Resulting mixture was stirred at 90°C for 18h, shielded from light. Then, the mixture was concentrated and the residue was purified by flash chromatography (dichloromethane/ethyl acetate/NEt_3, 80:20:1) yielding violet powder of porphyrin **13** (32.7 mg, 78%). Analytical sample was obtained after recrystallization (cyclohexane/$CHCl_3$, 5:1 v/v; 0.4 mL of chloroform for 16 mg of porphyrin **13b**, solvents added at room temperature, then left at -20°C for 1 h).

R_f = 0.62 (hexane/ethyl acetate, 25:75); **m.p.** > 300°C

^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 8.84 (s, 8H, H^β-pyrrole); 8.23 (br s, 4H, H-2_{Ar}); 8.13 (br s, 4H, H-6_{Ar}); 7.83 – 7.78 (m, 4H, H-4_{Ar}); 7.74 – 7.67 (m, 4H, H-5_{Ar}); 6.99 (d, *J* = 1.2 Hz, 4H, H-1_{glycal}); 5.81 – 5.77 (m, 4H, H-3_{glycal}); 5.52 – 5.48 (m, 4H, H-4_{glycal}); 4.44 – 4.38 (m, 4H, H-5_{glycal}); 4.29 (dd, *J* = 11.8, 7.2 Hz, 4H, H-6_{glycal}); 4.24 (dd, *J* = 11.9, 5.7 Hz, 4H, H-$6'_{glycal}$); 2.14 (s, 12H, $C\underline{H}_3COO$-(C-3_{glycal})); 2.09 (s, 12H, $C\underline{H}_3COO$-(C-4_{glycal})); 2.06 – 2.03 (m, 12H, $C\underline{H}_3COO$-(C-6_{glycal})); -2.86 (s, 2H, NH).

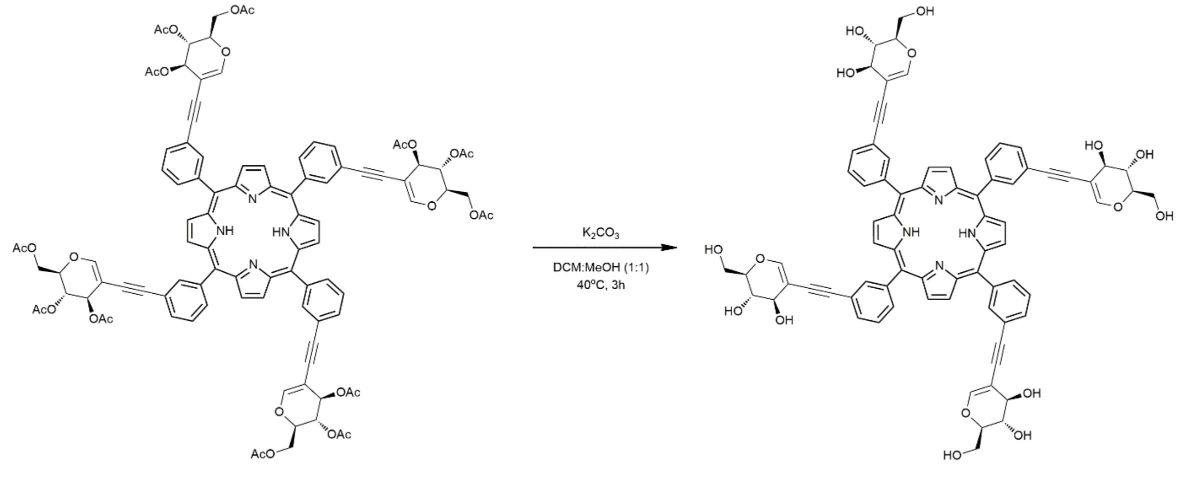
^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: 170.6 ($\underline{C}OO$-(C_{glycal})); 170.3 ($\underline{C}OO$-(C_{glycal})); 170.2 ($\underline{C}OO$-(C_{glycal})); 151.1 (C-1_{glycal}); 142.3 (C-3_{Ar}); 137.0 (C-2_{Ar}); 134.3 (C-6_{Ar}); 130.8 (C-4_{Ar}); 127.0 (C-5_{Ar}); 122.0 (C-1_{Ar} or C_{meso}); 119.4 (C-1_{Ar} or C_{meso}); 97.1 (C-2_{glycal}); 90.5 ($\underline{C}$≡C-(C-2_{glycal})); 84.0 (C≡$\underline{C}$-(C-2_{glycal})); 73.8 (C-5_{glycal}); 64.5 (C-3_{glycal}); 63.2 (C-4_{glycal}); 61.8 (C-6_{glycal}); 20.85 ($\underline{C}H_3COO$-); 20.84 ($\underline{C}H_3COO$-); 20.79 ($\underline{C}H_3COO$-).

UV – Vis ($CHCl_3$); λ_{max} [nm] (log ε): 645.6 (3.93); 590.0 (4.18); 550.2 (4.31); 516.0 (4.72); 420.8 (5.93, Soret band).

MS (ESI) *m/z* (% rel. int.): 1795.6 (5); 1794.6 (23); 1793.6 (58); 1792.6 (100); 1791.6 (81) (isotope $[M+H]^+$).

HRMS (ESI): $C_{100}H_{87}N_4O_{28}$ $[M+H]^+$ m/z calc. 1791.5501; found 1791.5503.

*5,10,15,20-tetrakis(3-(2-(D-glucal-2-yl)ethynyl)phenyl)porphyrin (**14a**)*



13a **14a**

Porphyrin **13a** (15.9 mg, 0.009 mmol, 1.0 eq), potassium carbonate (7.5 mg, 0.054 mmol, 6.0 eq), methanol (0.5 mL) and dichloromethane (0.5 mL) were added to a reaction vessel. Resulting mixture was stirred in darkness at 40°C for 3 hours. Next, crude mixture was transferred into a flask and concentrated to dryness. The solid was purified by flash chromatography (DCM/MeOH, 7:3, to pure MeOH) yielding violet solid of porphyrin **14a** (6.9 mg, 60%).

R_f = 0.67 (dichloromethane/methanol, 7:3); **m.p.** > 300°C

^{1}H NMR (500 MHz, DMSO-d$_6$) δ [ppm]: 8.87 (s, 8H, H$^\beta$-pyrrole); 8.25 – 8.20 (m, 4H, H-2$_{Ar}$); 8.20 – 8.15 (m, 4H, H-6$_{Ar}$); 7.90 – 7.85 (m, 4H, H-4$_{Ar}$); 7.84 – 7.79 (m, 4H, H-5$_{Ar}$); 6.96 (br s, 4H, H-1$_{glycal}$); 5.51 (br s, 8H, OH); 4.86 (br s, 4H, OH); 3.97 (d, *J* = 6.1 Hz, 4H, H-3$_{glycal}$); 3.82 – 3.77 (m, 4H, H-5$_{glycal}$); 3.70 – 3.60 (m, 8H, H-6$_{glycal}$); 3.53 (dd, *J* = 7.8, 6.5 Hz, 4H, H-4$_{glycal}$); -2.96 (s, 2H, NH).

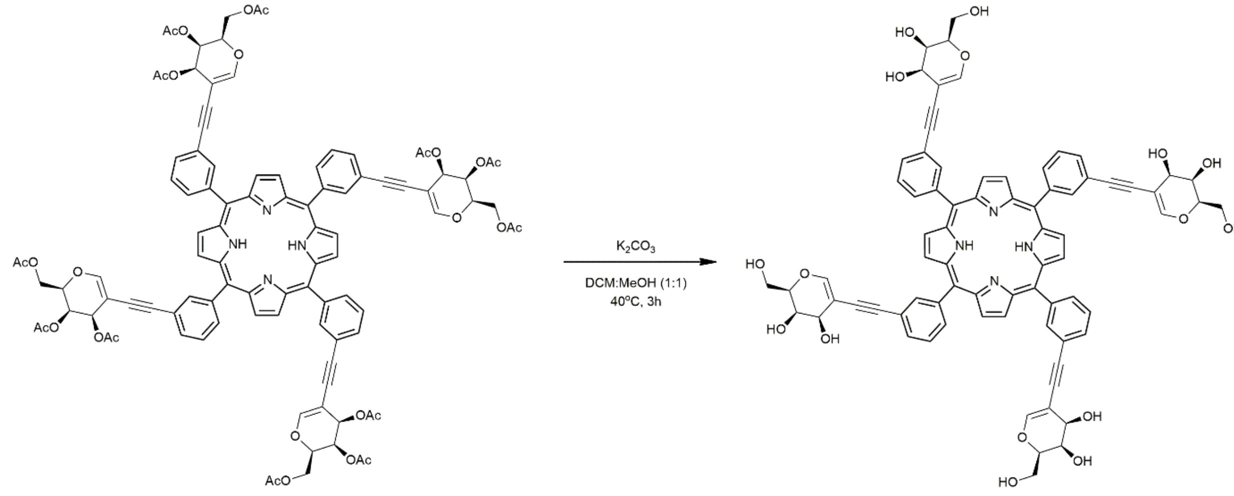
^{13}C NMR (125 MHz; DMSO-d$_6$) δ [ppm]: 150.2 (C-1$_{glycal}$); 141.4 (C-3$_{Ar}$); 136.4 (C-2$_{Ar}$); 133.5 (C-6$_{Ar}$); 130.4 (C-4$_{Ar}$); 127.4 (C-5$_{Ar}$); 122.5 (C-1$_{Ar}$ or C$_{meso}$); 119.2 (C-1$_{Ar}$ or C$_{meso}$); 100.5 (C-2$_{glycal}$); 88.5 ($\underline{C}$≡C-(C-2$_{glycal}$)); 88.1 (C≡$\underline{C}$-(C-2$_{glycal}$)); 80.5 (C-5$_{glycal}$); 68.6 (C-3$_{glycal}$); 67.9 (C-4$_{glycal}$); 59.9 (C-6$_{glycal}$).

UV – Vis (DMSO); λ$_{max}$ [nm] (log ε): 645.6 (3.52); 590.0 (3.64); 550.4 (3.81); 515.8 (4.20); 422.6 (5.47, Soret band).

MS (ESI) *m/z* (% rel. int.): 1294.4 (1); 1293.4 (4); 1291.4 (8); 1290.4 (14); 1289.4 (39); 1288.4 (84); 1287.4 (100) (isotope [M+H]$^+$).

HRMS (ESI): $C_{76}H_{63}N_4O_{16}$ [M+H]$^+$ m/z calc. 1287.4234; found 1287.4230.

*5,10,15,20-tetrakis(3-(2-(D-galactal-2-yl)ethynyl)phenyl)porphyrin (**14b**)*



13b **14b**

Porphyrin **13b** (32.7 mg, 0.018 mmol, 1.0 eq), potassium carbonate (14.9 mg, 0.108 mmol, 6.0 eq), methanol (0.5 mL) and dichloromethane (0.5 mL) were added to a reaction vessel. Resulting mixture was stirred in darkness at 40°C for 3 hours. Next, crude mixture was transferred into a flask and concentrated to dryness. The solid was purified by flash chromatography (DCM/MeOH, 7:3, into pure MeOH) yielding violet solid of porphyrin **14b** (13.2 mg, 57%).

R$_f$ = 0.68 (dichloromethane/methanol, 7:3); **m.p.** > 300°C

^{1}H NMR (500 MHz, DMSO-d$_6$) δ [ppm]: 8.87 (s, 8H, H$^{\beta}$-pyrrole); 8.23 - 8.19 (m, 4H, H-2$_{Ar}$); 8.19 – 8.14 (m, 4H, H-6$_{Ar}$); 7.89 – 7.84 (m, 4H, H-4$_{Ar}$); 7.84 – 7.79 (m, 4H, H-5$_{Ar}$); 6.92 (br s, 4H, H-1$_{glycal}$); 5.06 (br s, 4H, OH); 4.89 (br s, 4H, OH); 4.84 (br s, 4H, OH); 4.29 (br s, 4H, H-3$_{glycal}$); 3.96 – 3.89 (m, 4H, H-5$_{glycal}$); 3.84 – 3.78 (m, 4H, H-4$_{glycal}$); 3.66 – 3.55 (m, 8H, H-6$_{glycal}$); -2.96 (s, 2H, NH).

^{13}C NMR (125 MHz; DMSO-d$_6$) δ [ppm] = 150.5 (C-1$_{glycal}$); 141.4 (C-3$_{Ar}$); 136.4 (C-2$_{Ar}$); 133.4 (C-6$_{Ar}$); 130.4 (C-4$_{Ar}$); 127.4 (C-5$_{Ar}$); 122.6 (C-1$_{Ar}$ or C$_{meso}$); 119.3 (C-1$_{Ar}$ or C$_{meso}$); 100.1 (C-2$_{glycal}$); 88.8 ($\underline{C}$≡C-(C-2$_{glycal}$)); 88.4 (C≡$\underline{C}$-(C-2$_{glycal}$)); 78.8 (C-5$_{glycal}$); 64.6 (C-3$_{glycal}$); 64.0 (C-4$_{glycal}$); 60.0 (C-6$_{glycal}$).

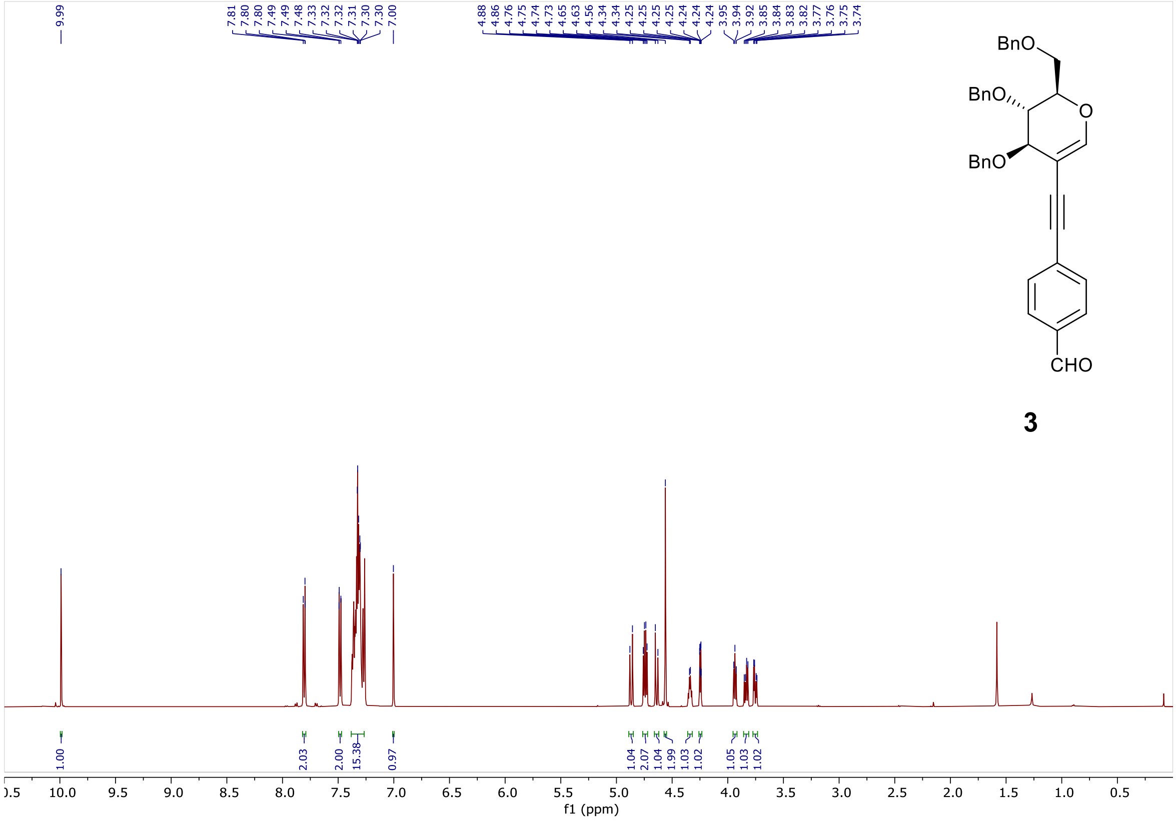
UV – Vis (DMSO); λ$_{max}$ [nm] (log ε): 645.8 (3.26); 596.0 (3.52); 554.4 (3.76); 516.0 (3.95); 423.8 (5.51, Soret band).

MS (ESI) *m/z* (% rel. int.): 1290.4 (6); 1289.4 (38); 1288.4 (84); 1287.4 (100) (isotope [M+H]$^+$).

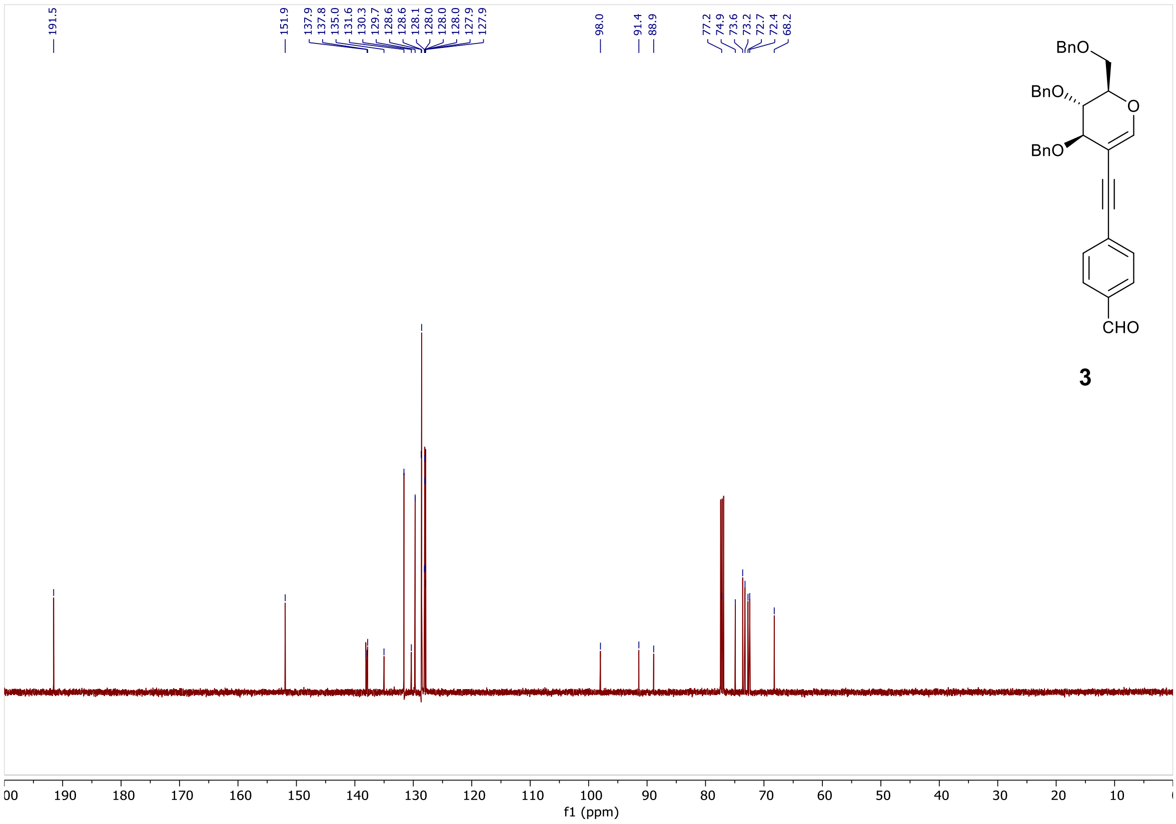
HRMS (ESI): $C_{76}H_{63}N_4O_{16}$ [M+H]$^+$ m/z calc. 1287.4234; found 1287.4227.

NMR and UV/Vis spectra of new compounds

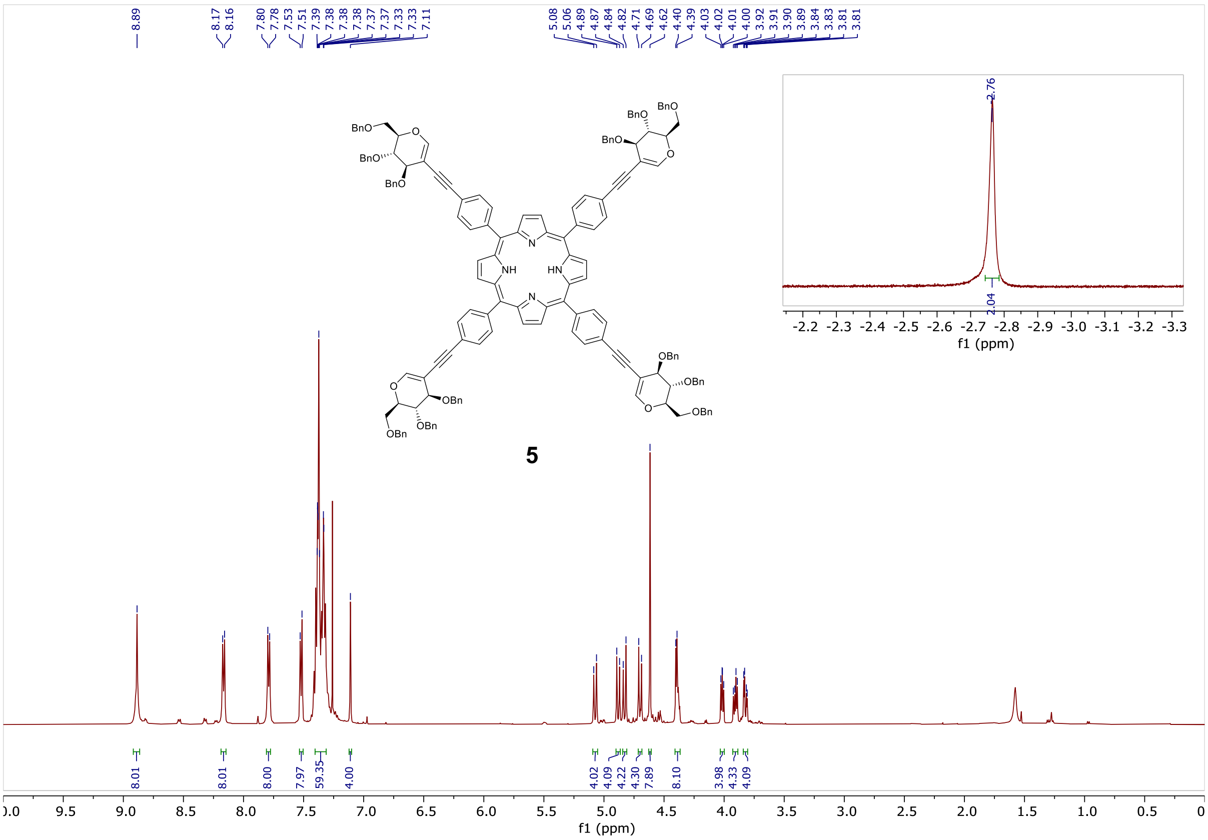
^{1}H NMR of **3**



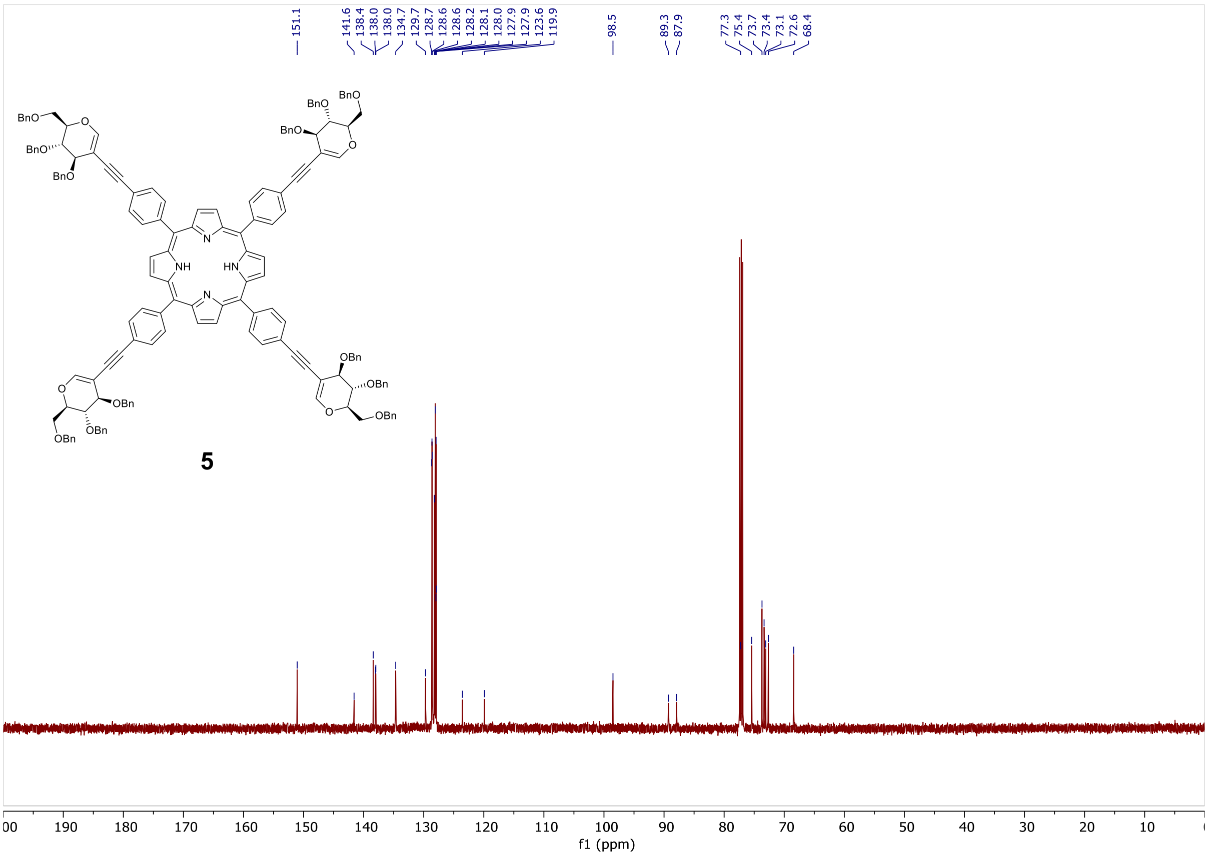
^{13}C NMR of **3**



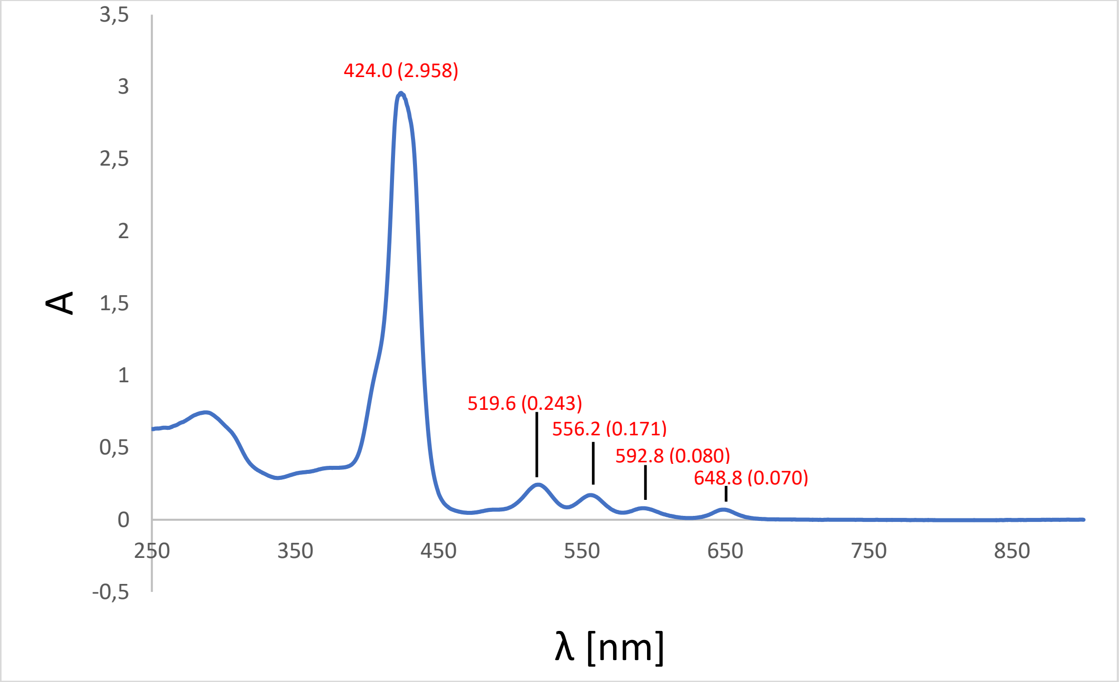
^{1}H NMR of **5**



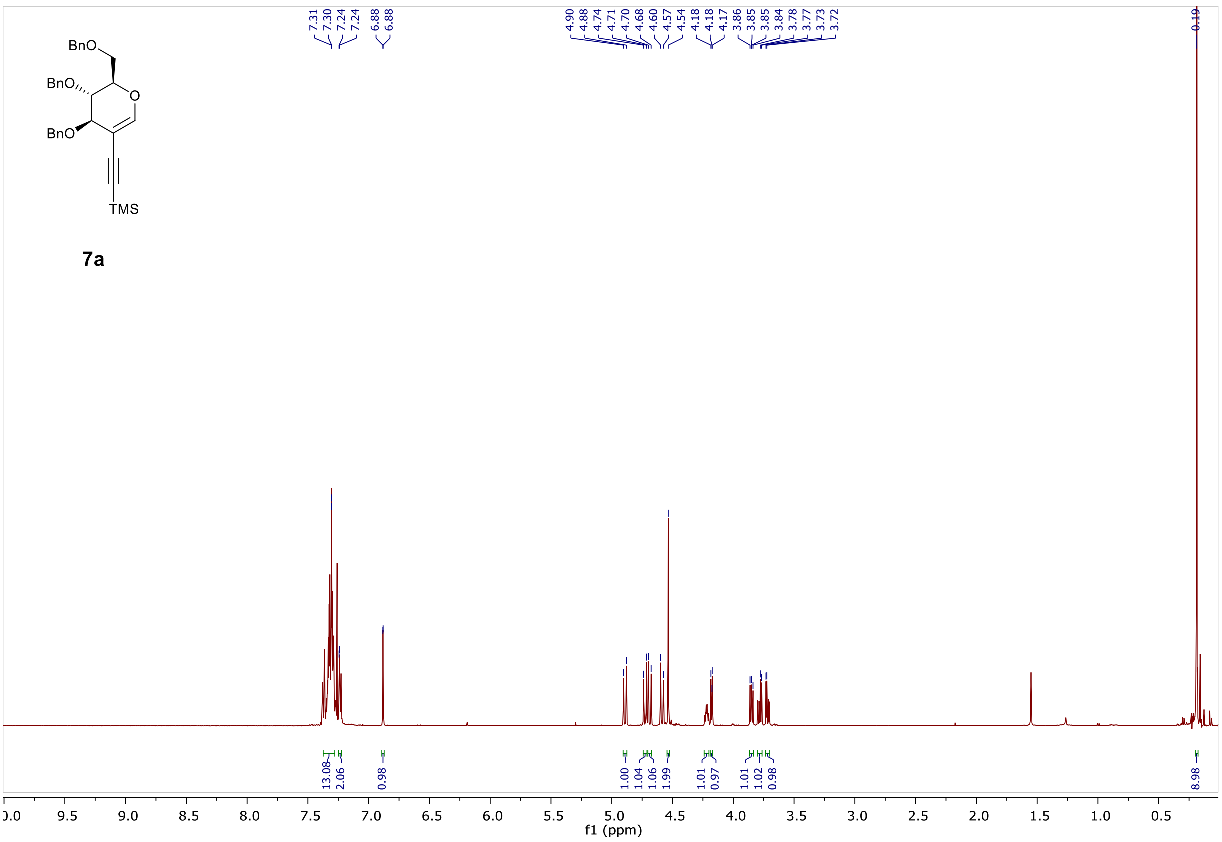
^{13}C NMR of **5**



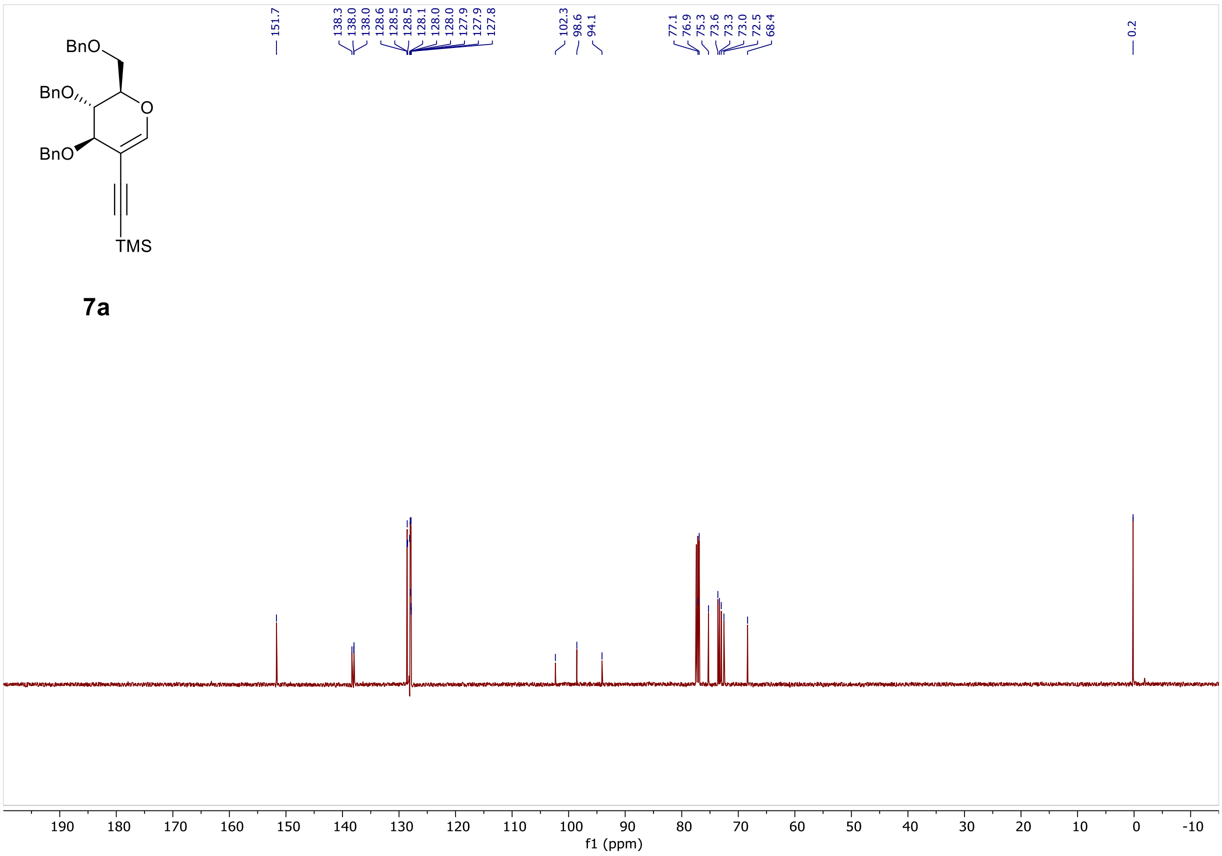
UV-Vis spectrum of **5**



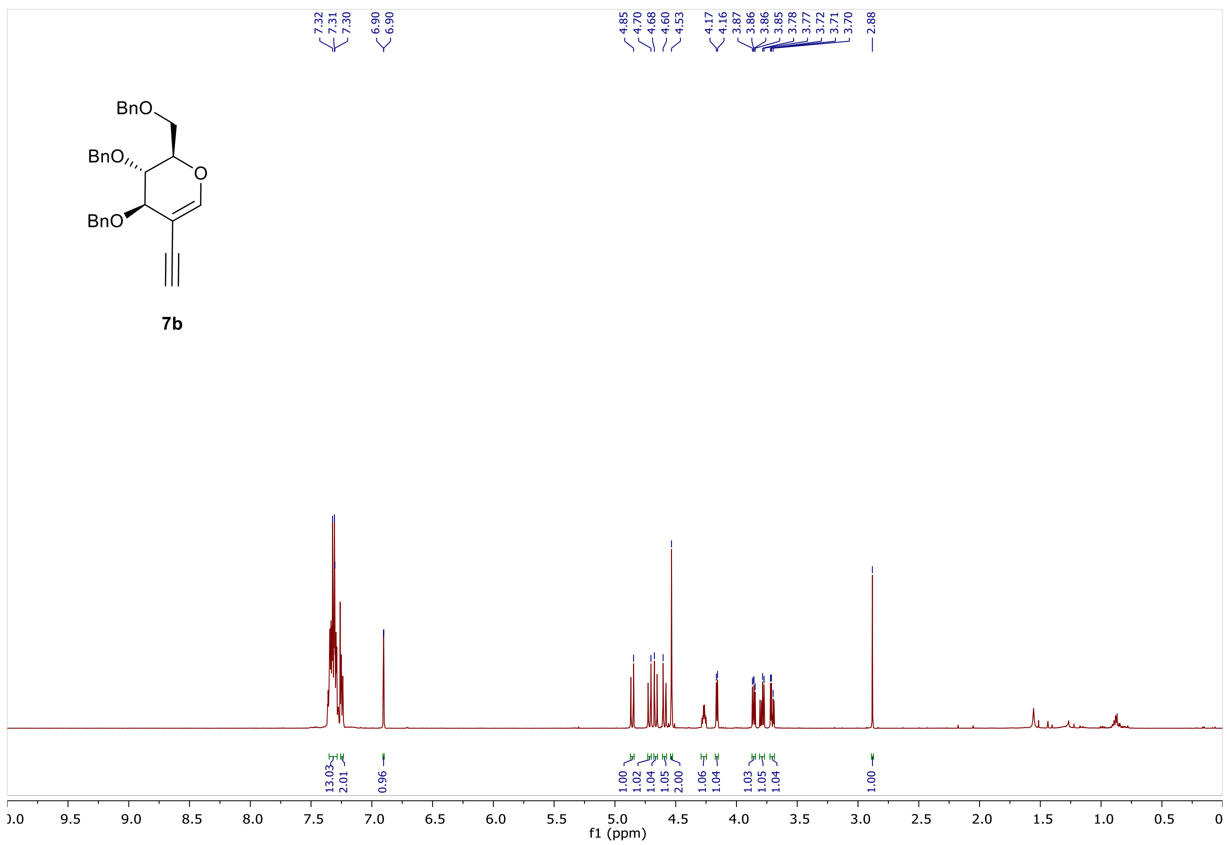
^{1}H NMR of **7a**



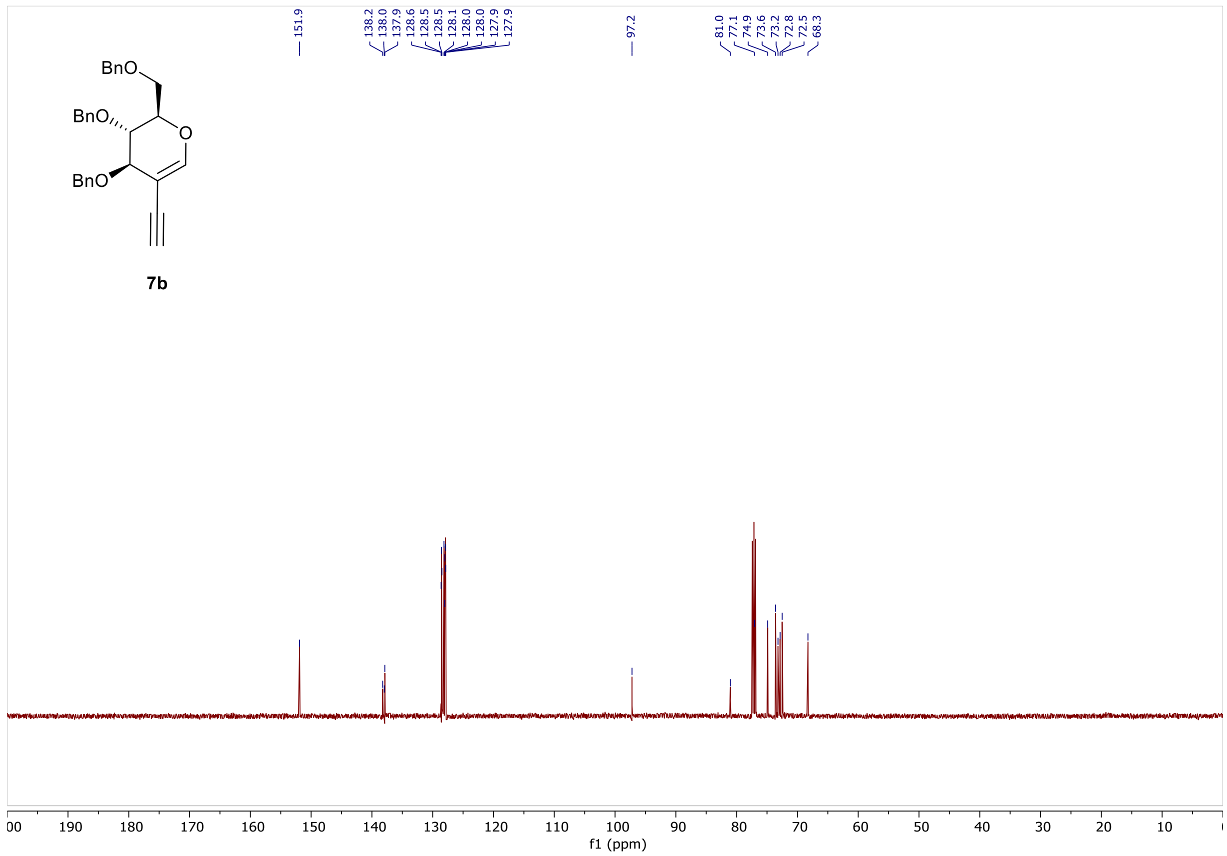
^{13}C NMR of **7a**



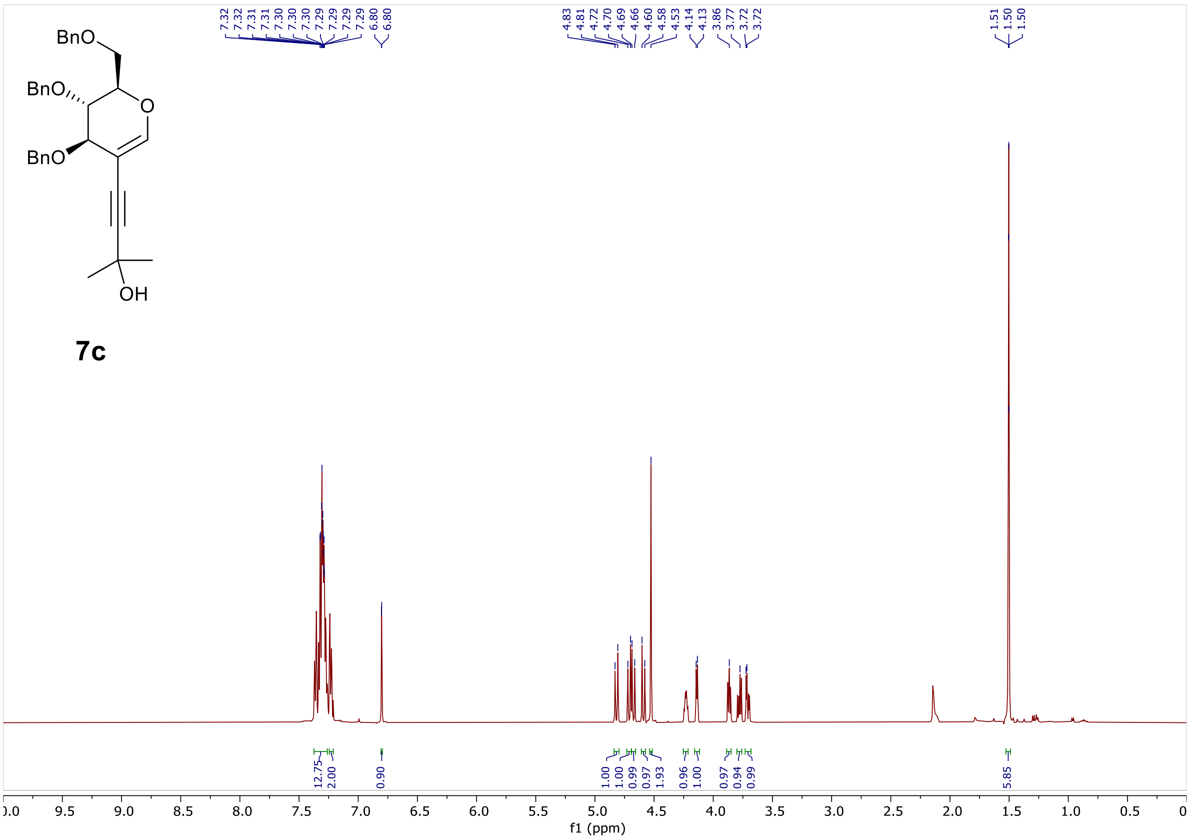
^{1}H NMR of **7b**



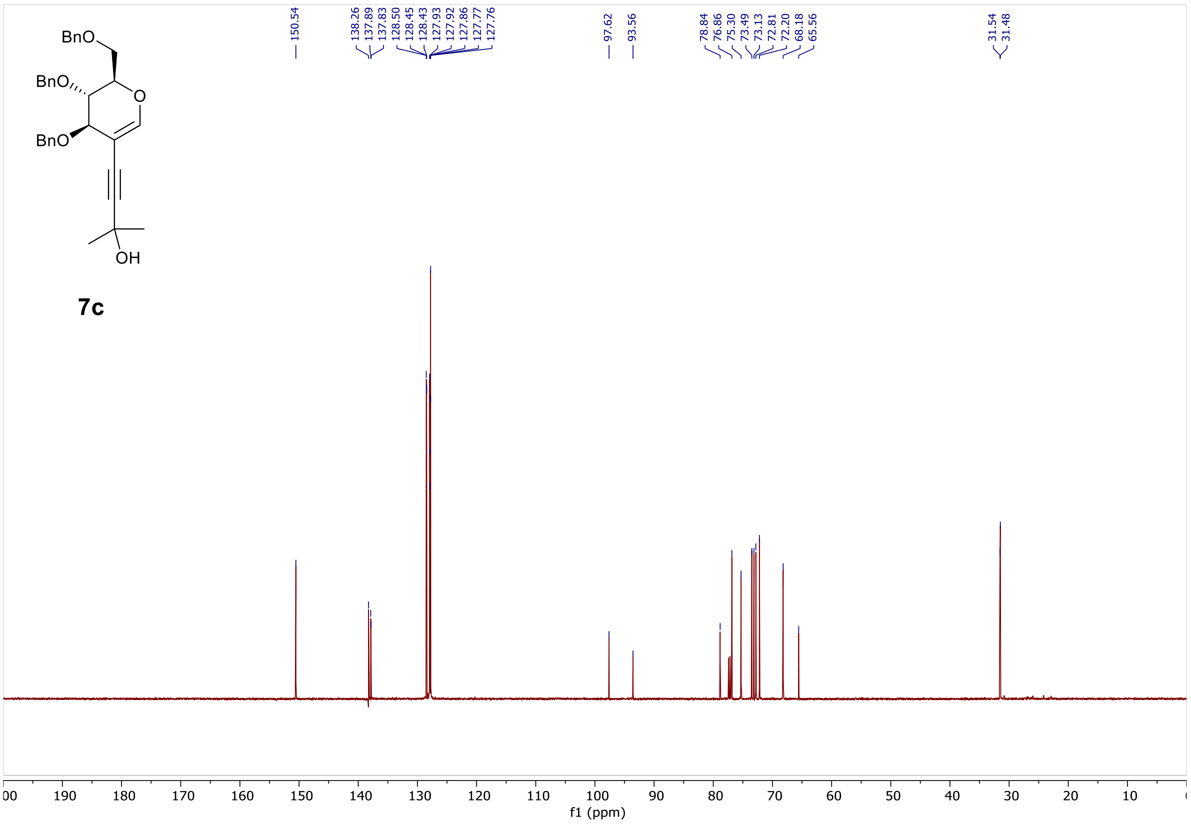
^{13}C NMR of **7b**



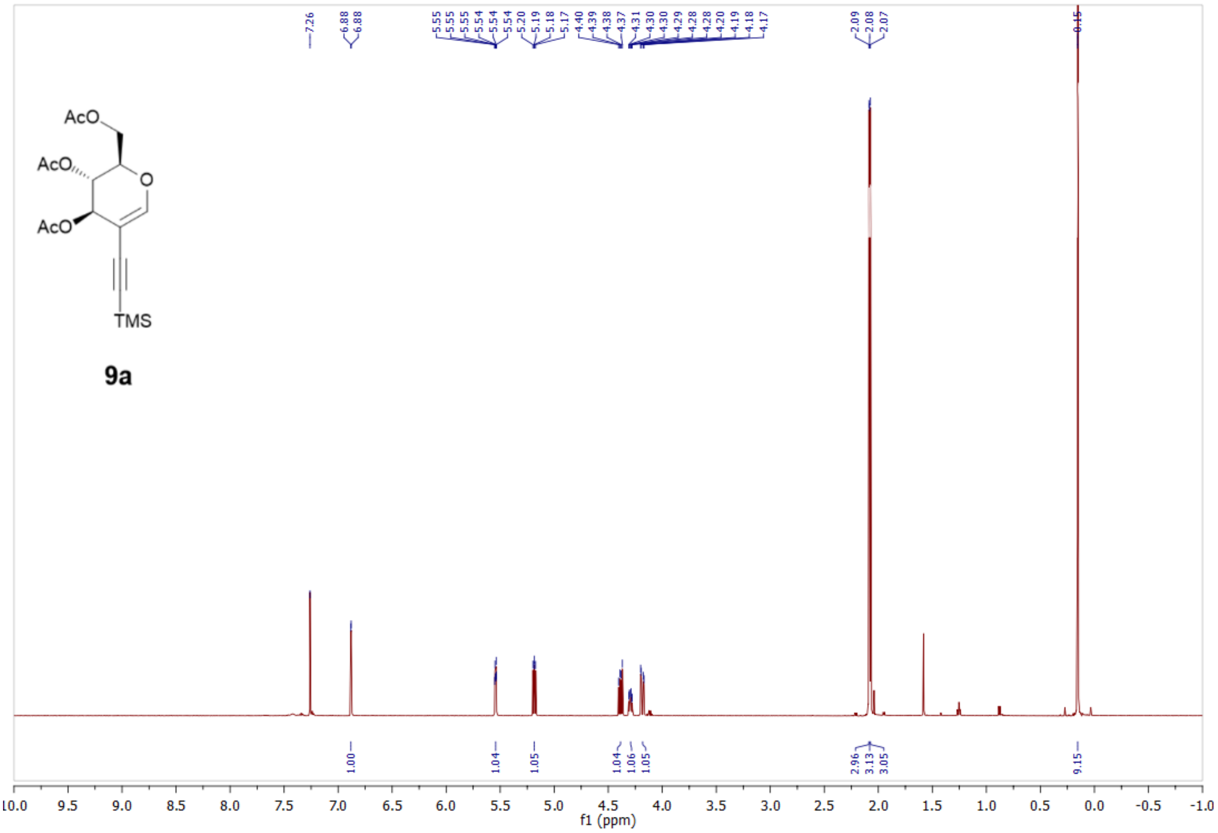
^{1}H NMR of **7c**



^{13}C NMR of **7c**



^{1}H NMR of **9a**



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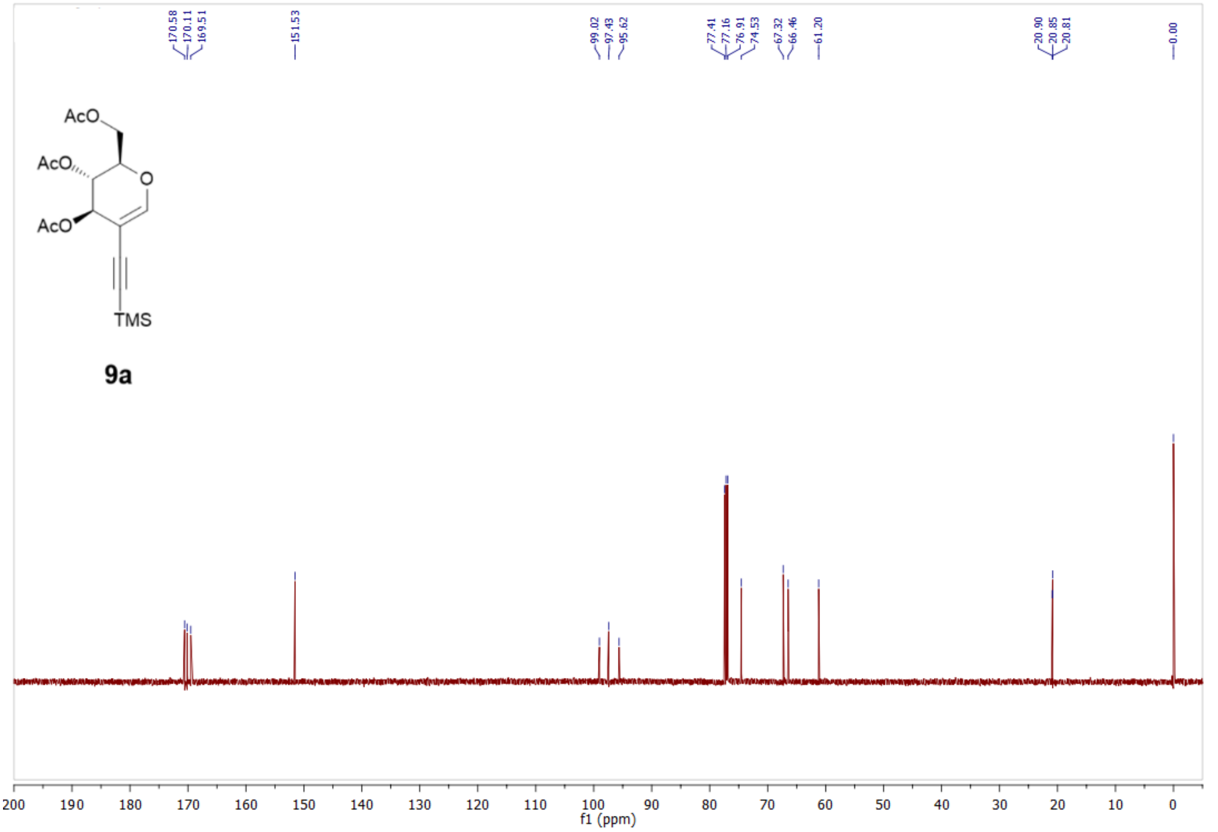

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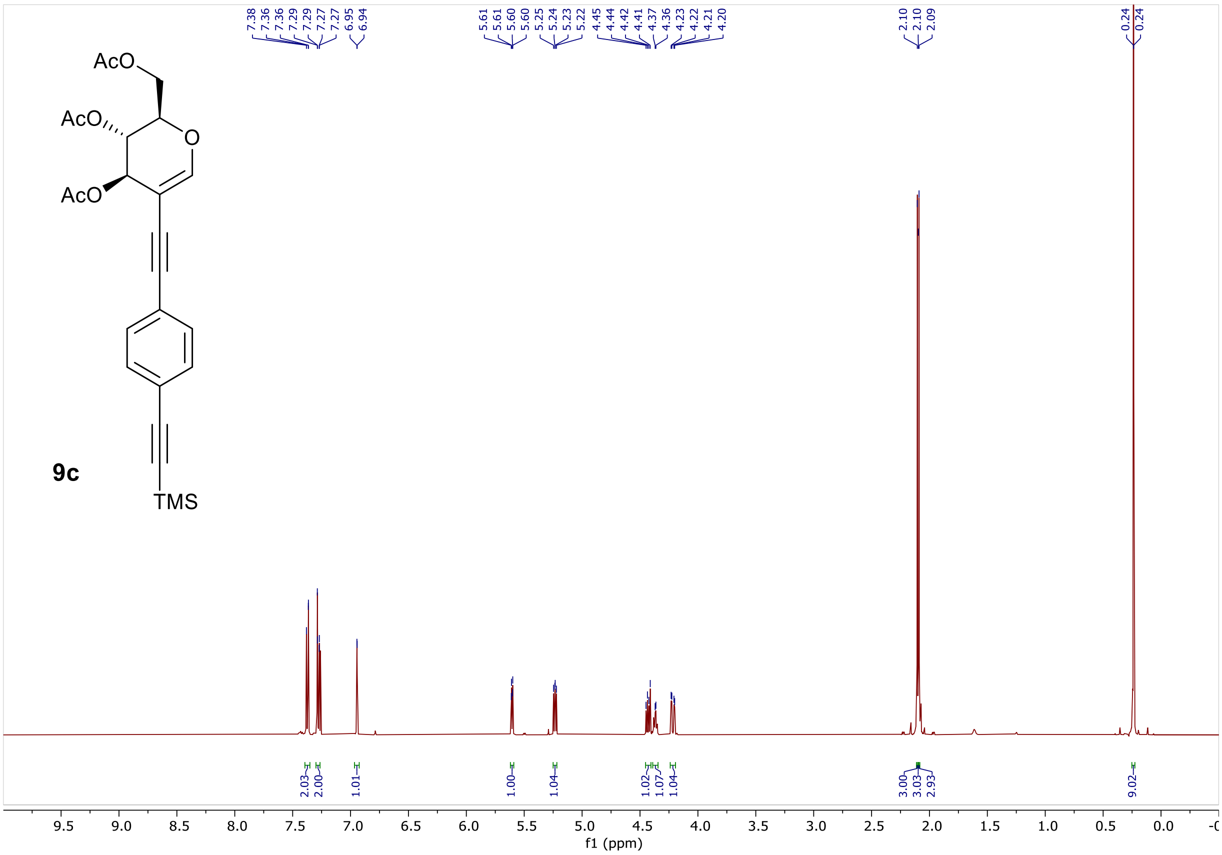
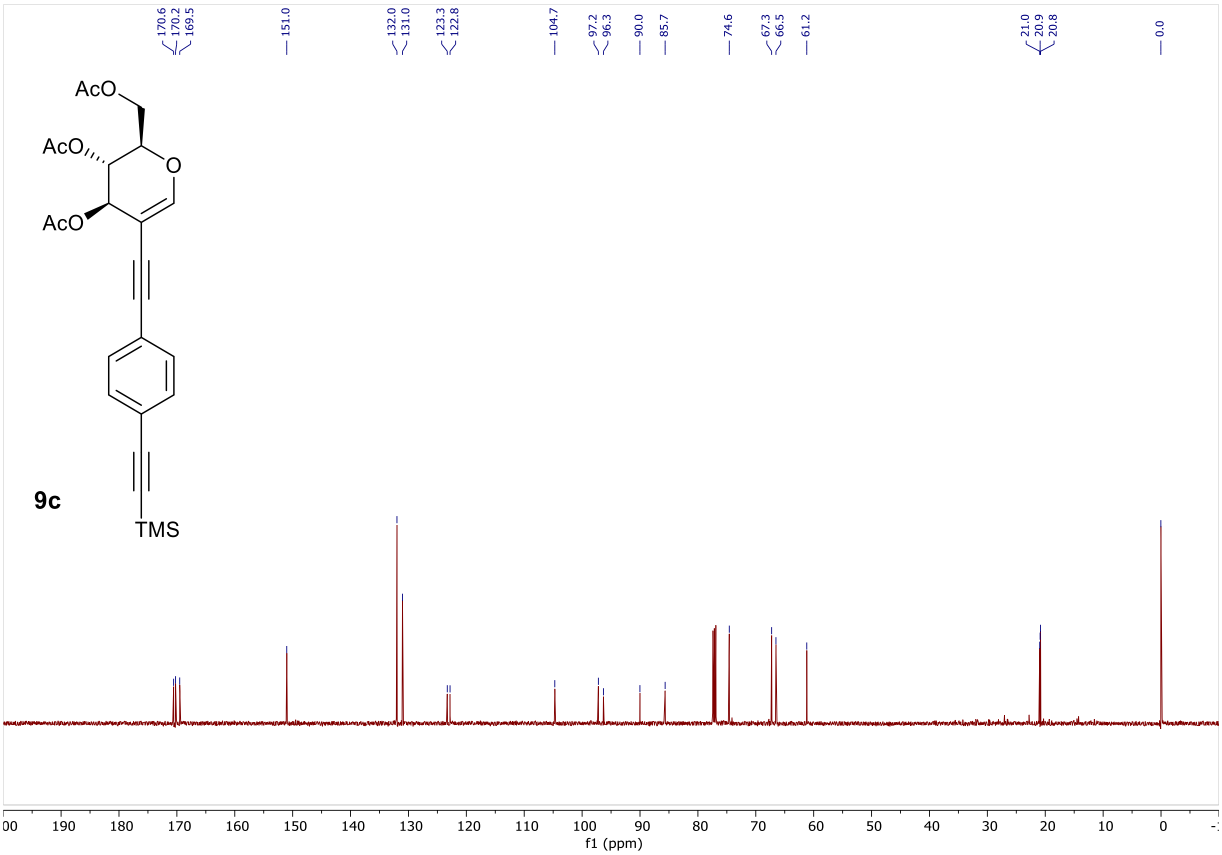
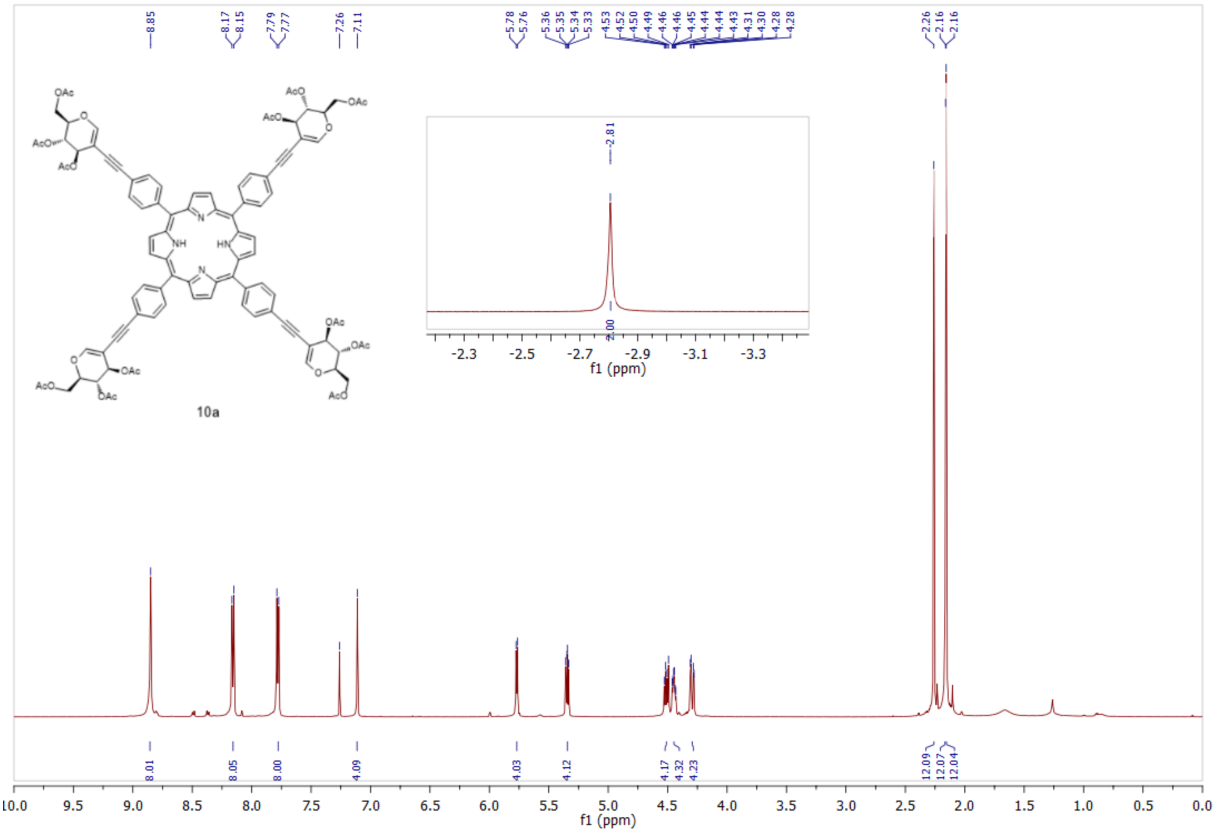


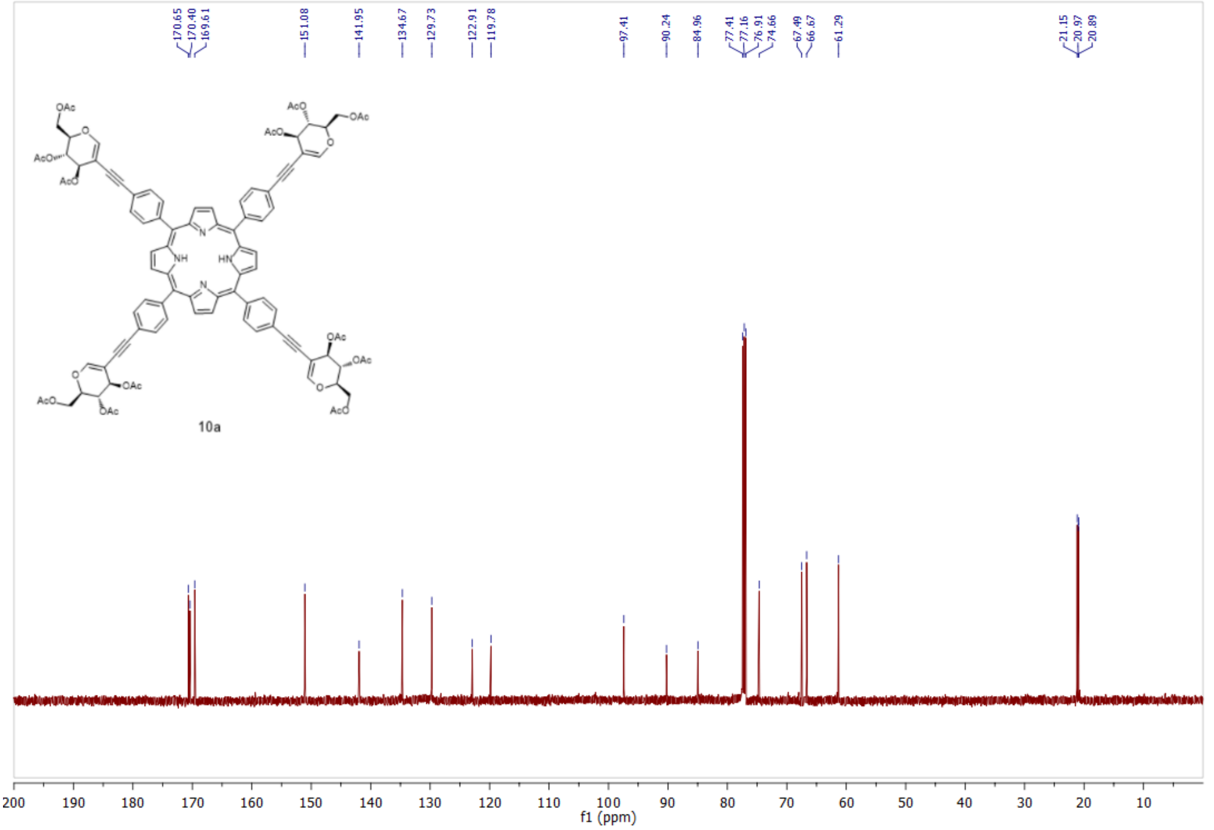
^{13}C NMR of **9c**



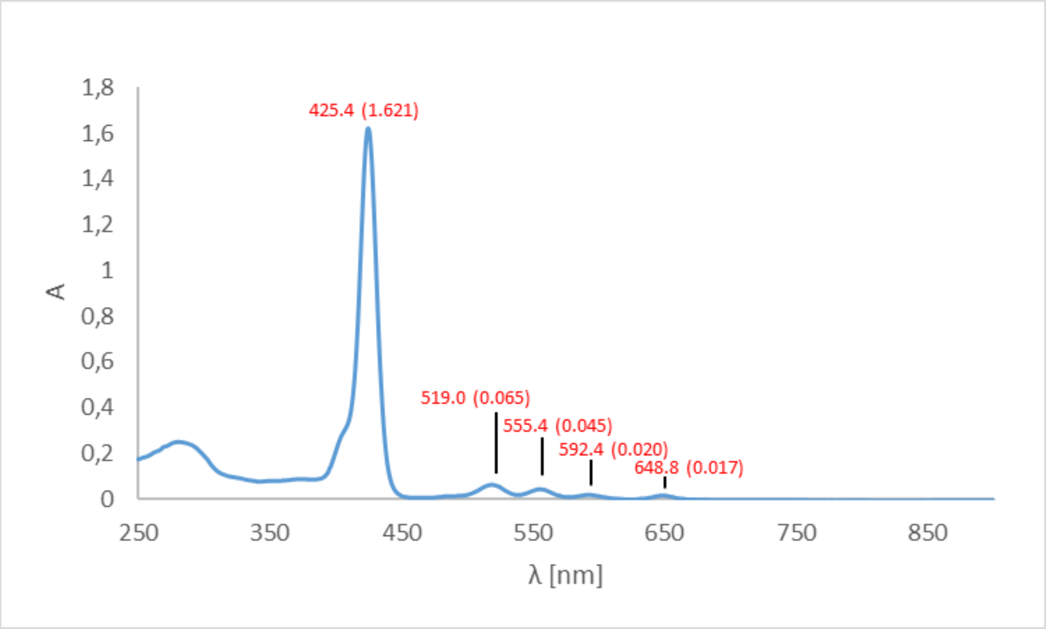
^{1}H NMR of **10a**



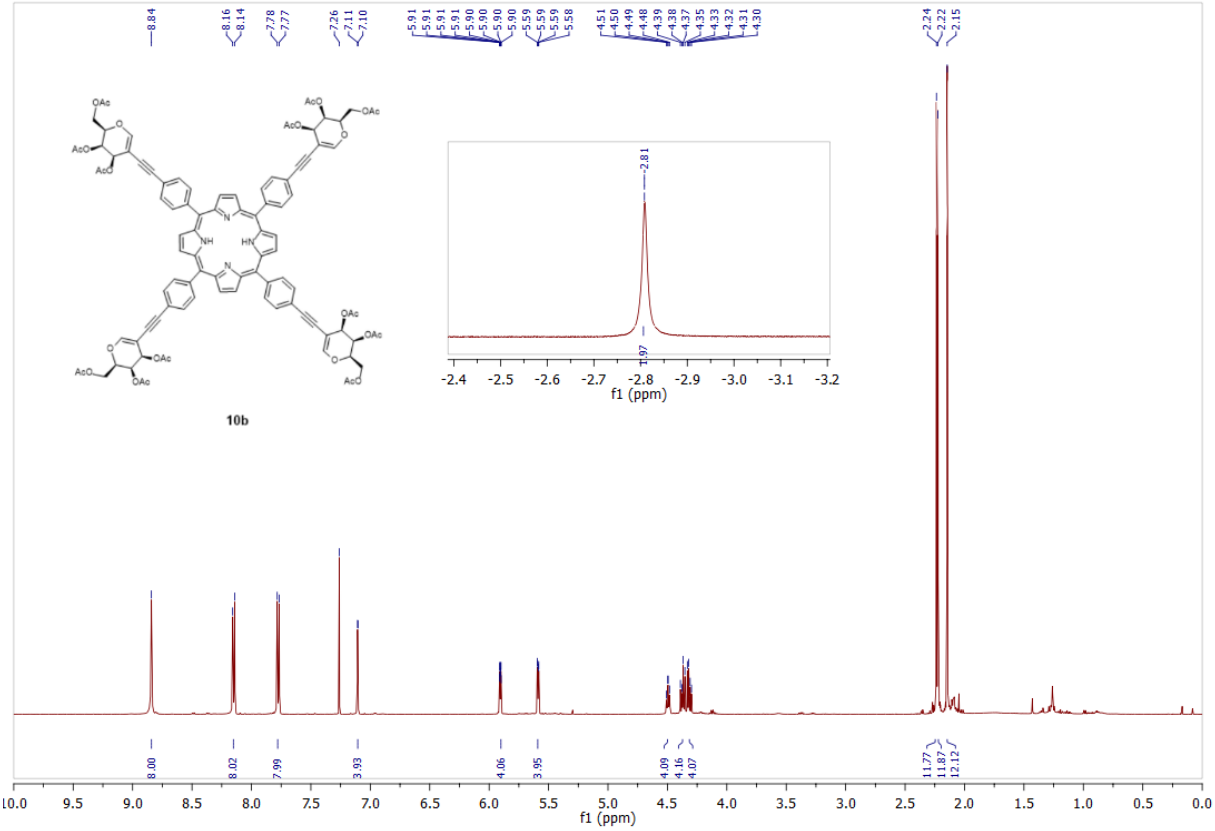
^{13}C NMR of **10a**



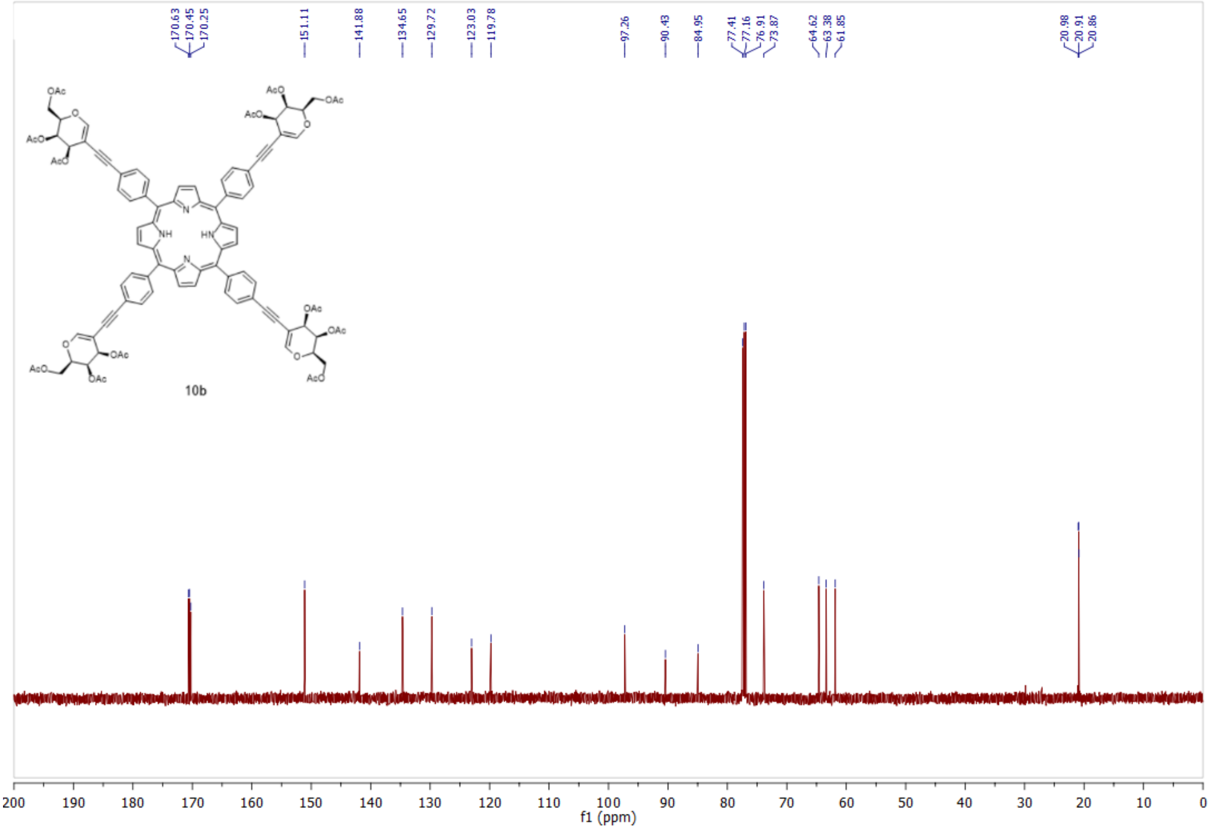
UV-Vis spectrum of **10a**



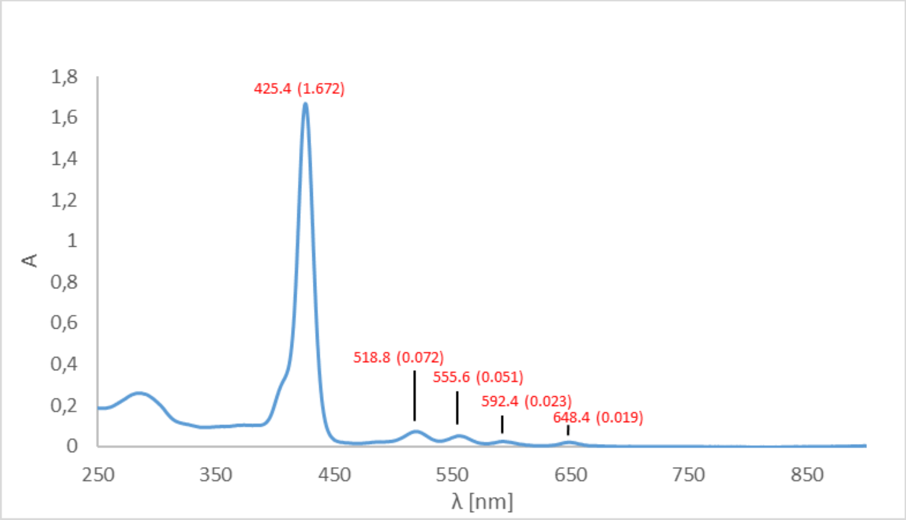
^{1}H NMR of **10b**



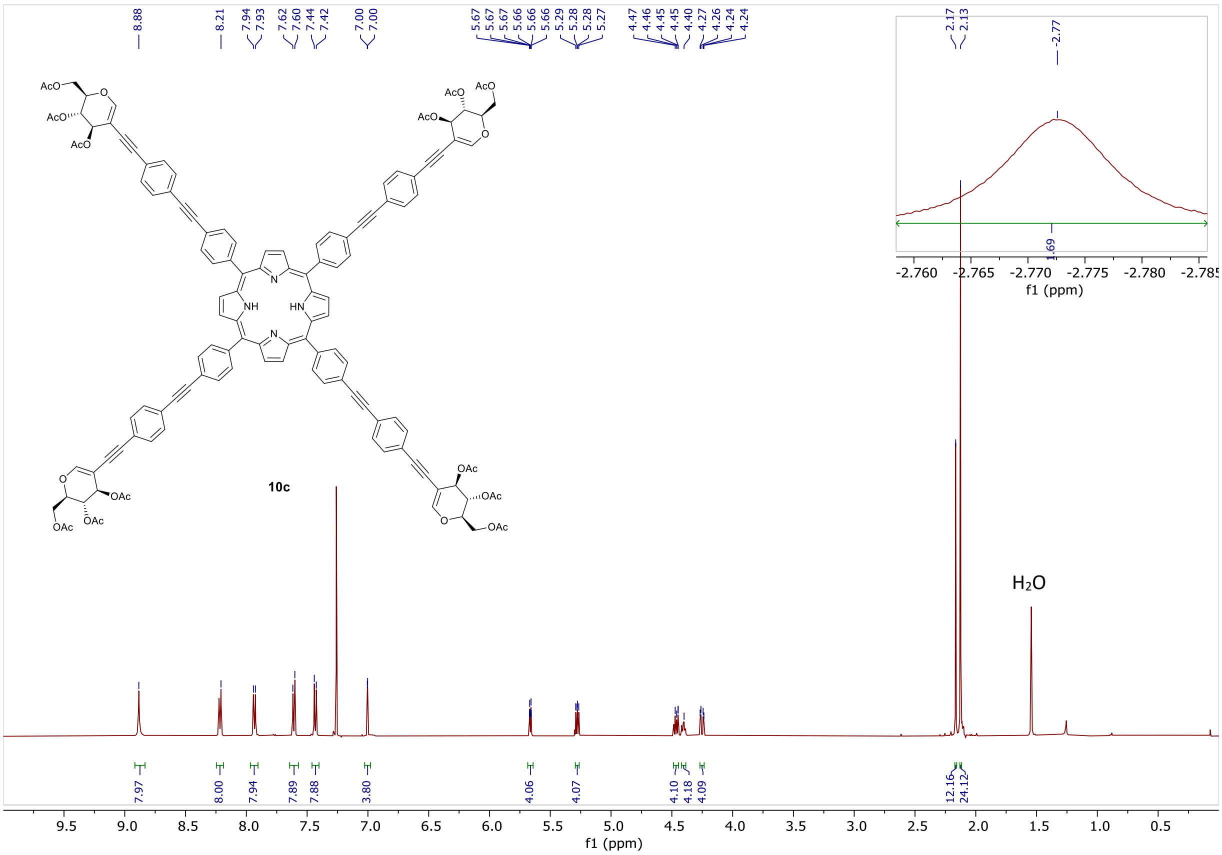
^{13}C NMR of **10b**



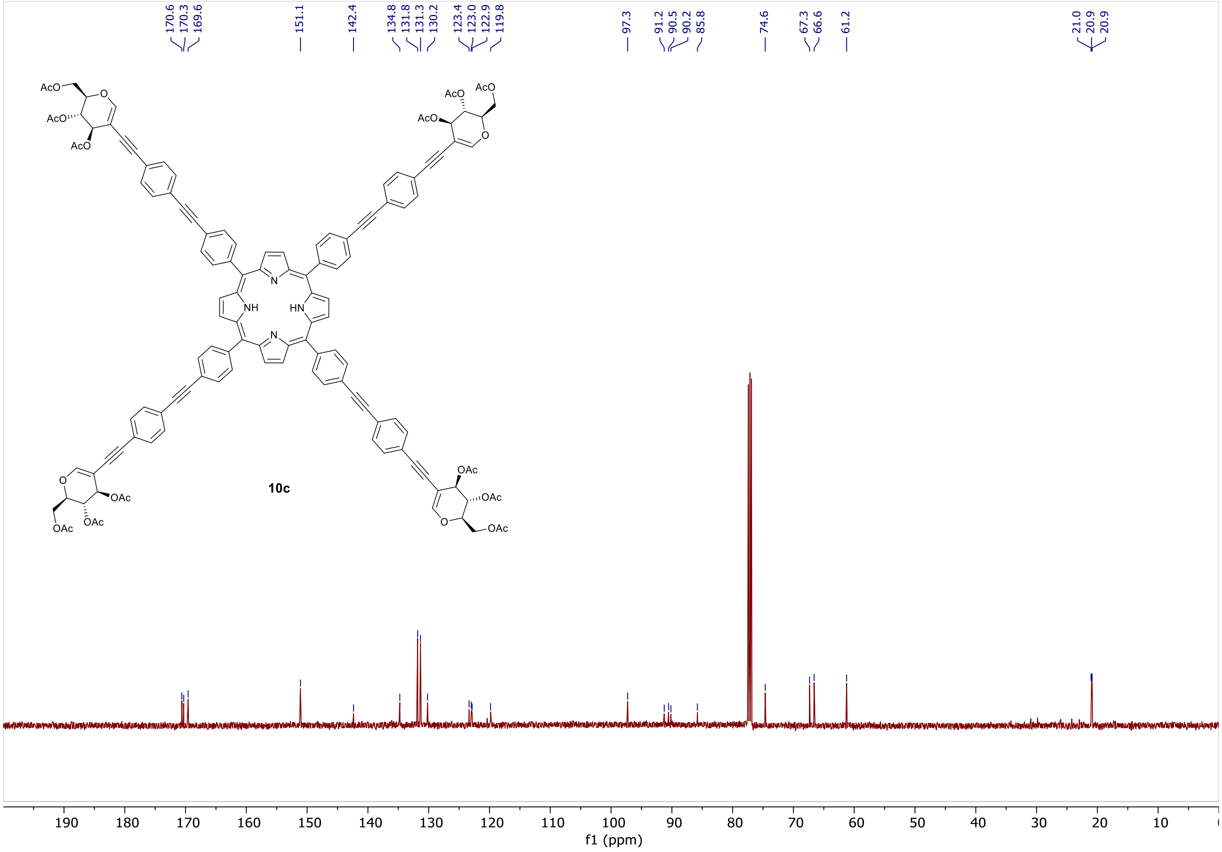
UV-Vis spectrum of **10b**



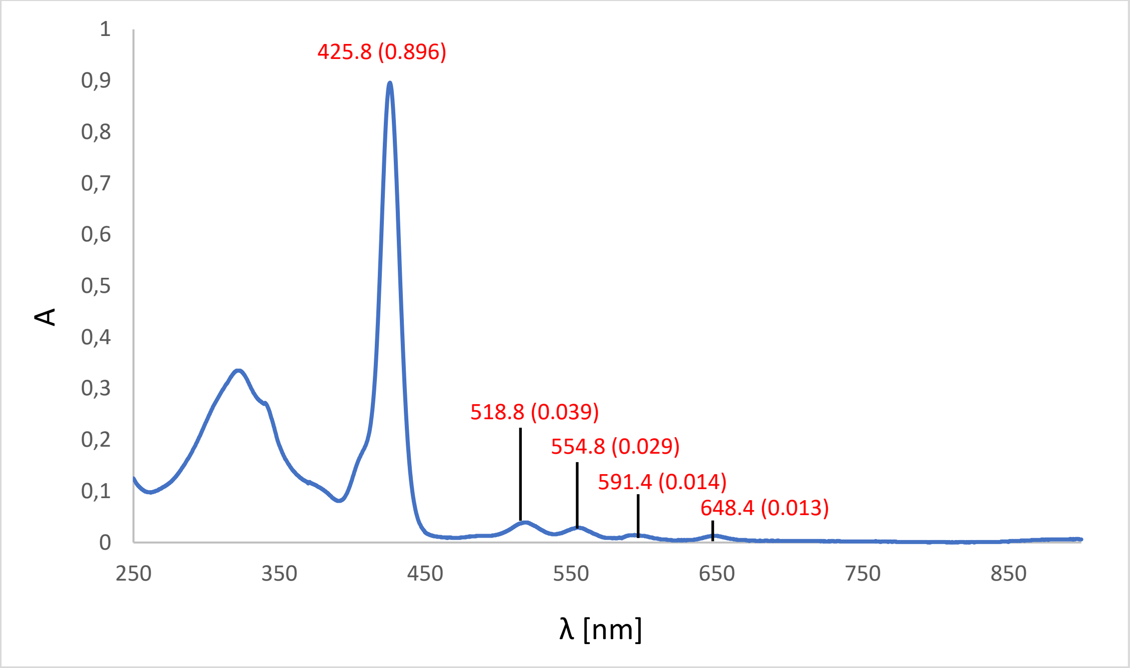
^{1}H NMR of **10c**



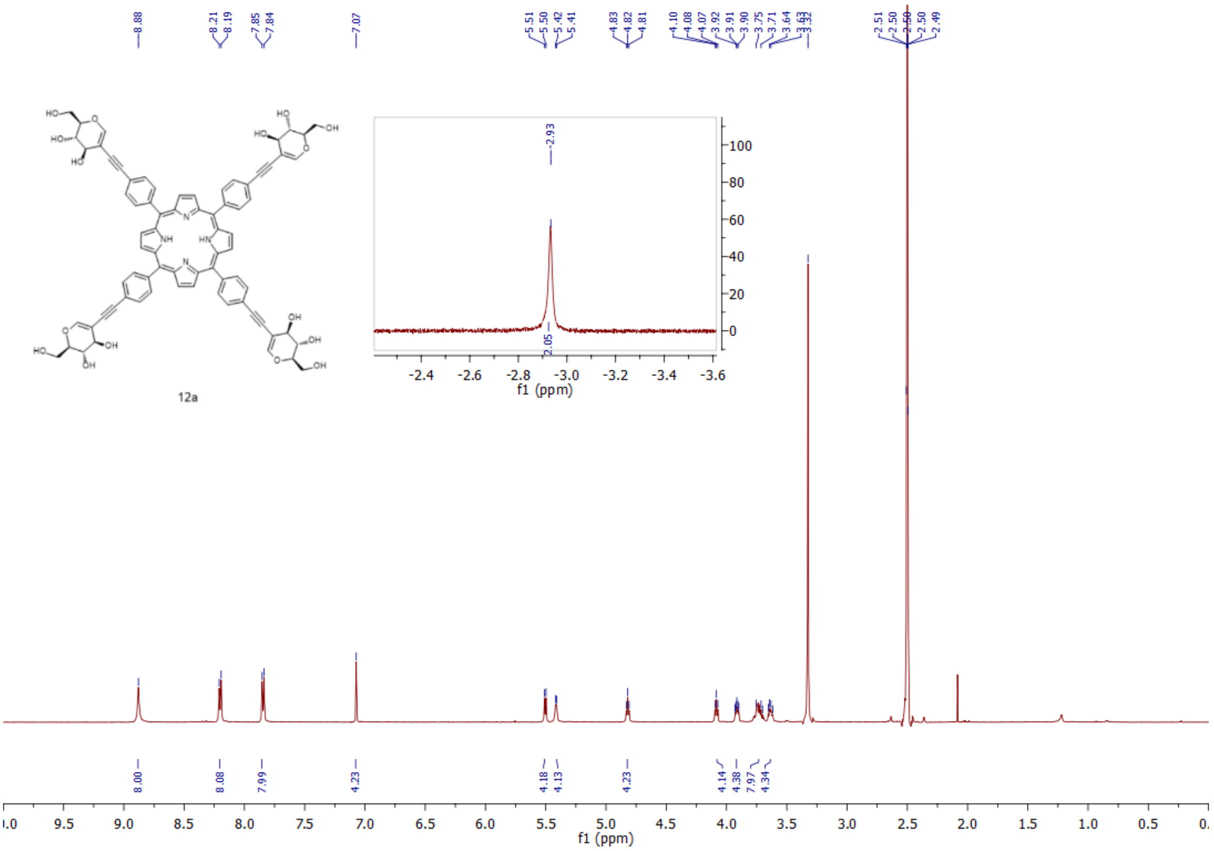
^{13}C NMR of **10c**



UV-Vis spectrum of **10c**



^{1}H NMR of **12a**



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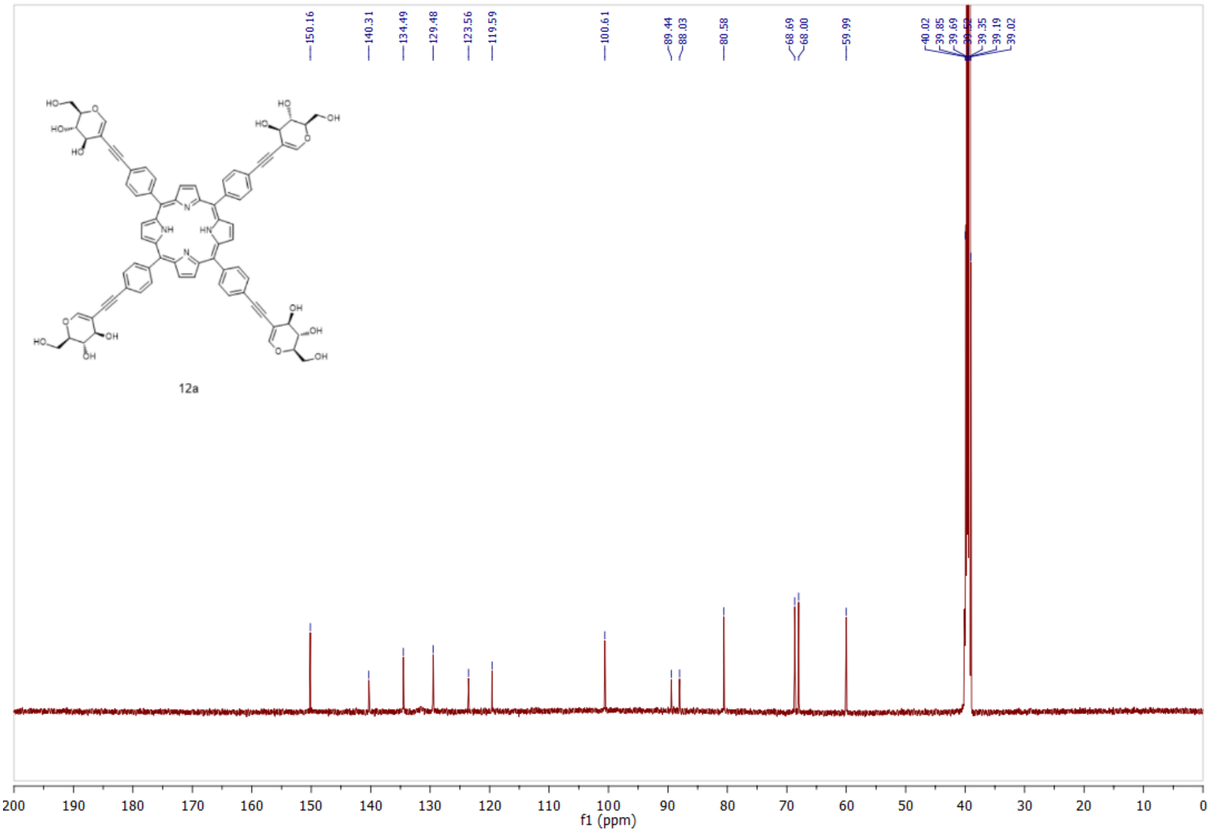
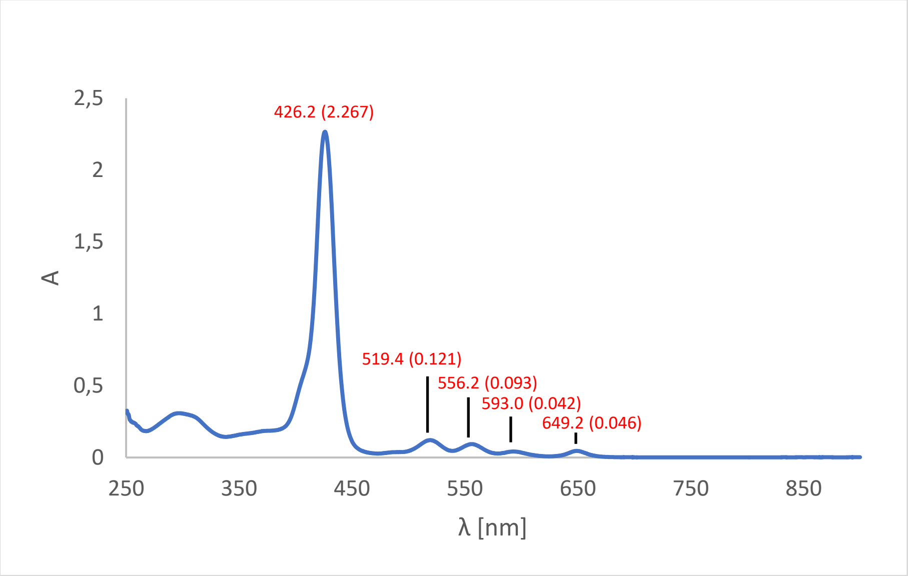
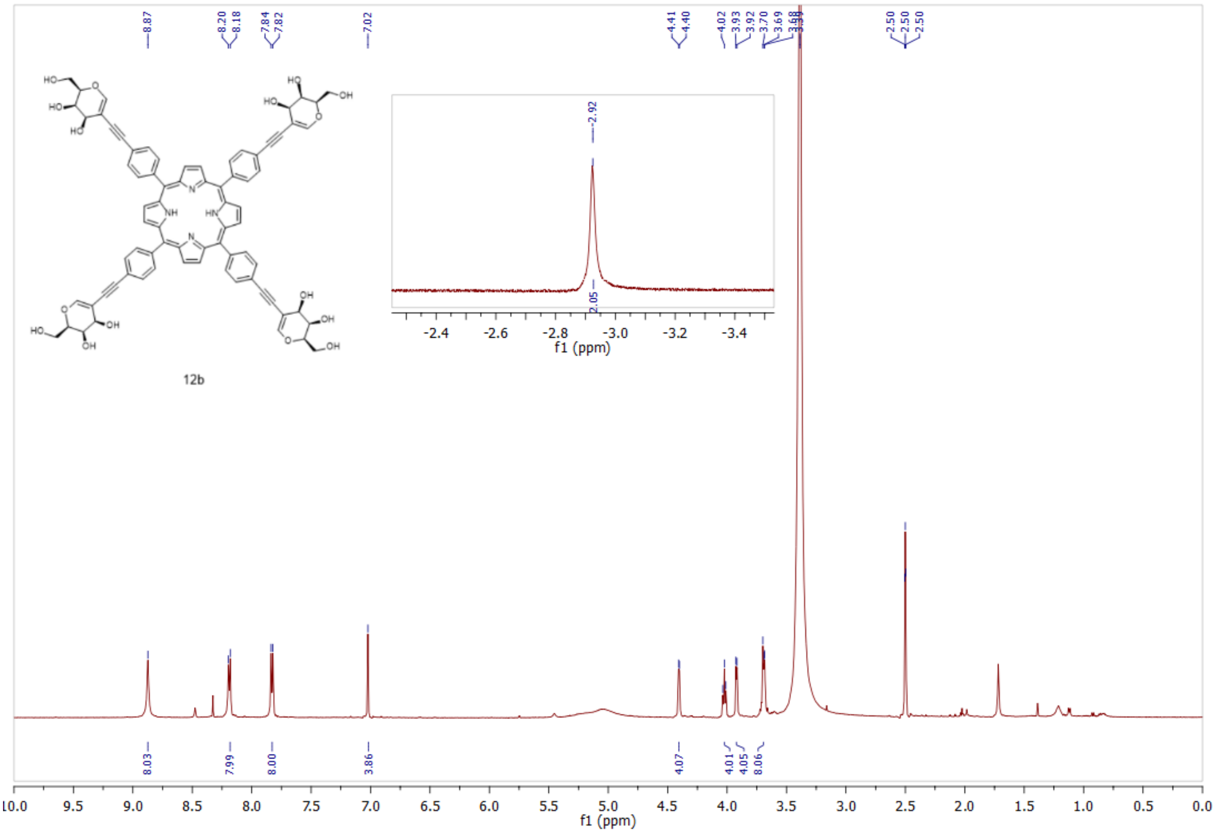


UV-Vis of **12a**


426.2 (2.267)
519.4 (0.121)
556.2 (0.093)
593.0 (0.042)
649.2 (0.046)
A
2,5
2
1,5
1
0,5
0
250
350
450
550
650
750
850
λ [nm]

^{1}H NMR of **12b**



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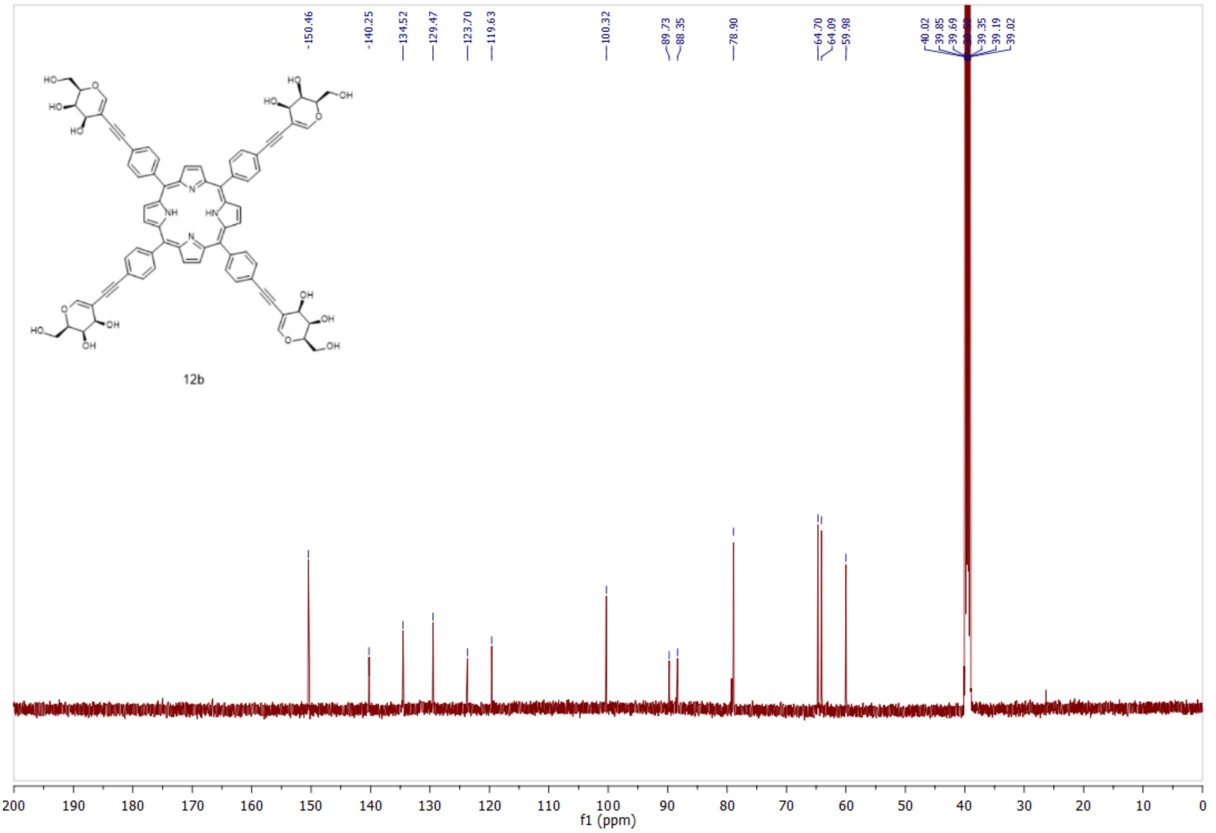
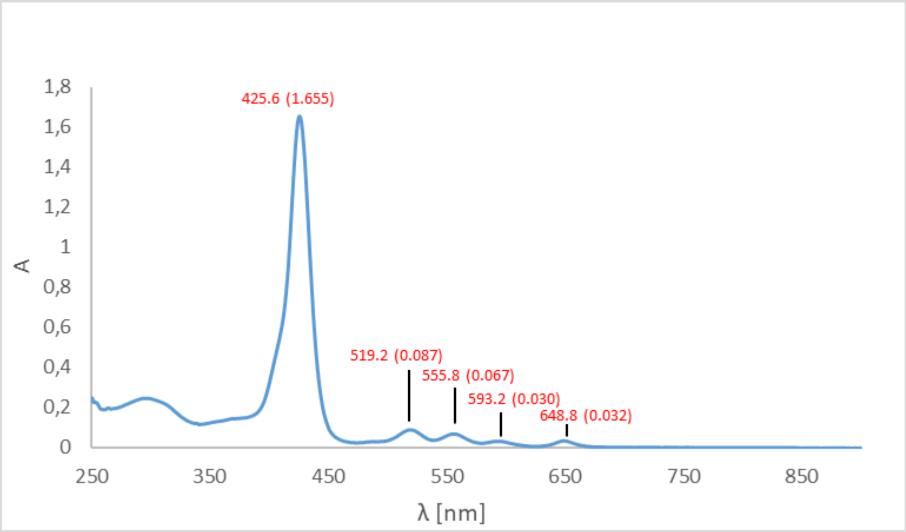


UV-Vis spectrum of **12b**



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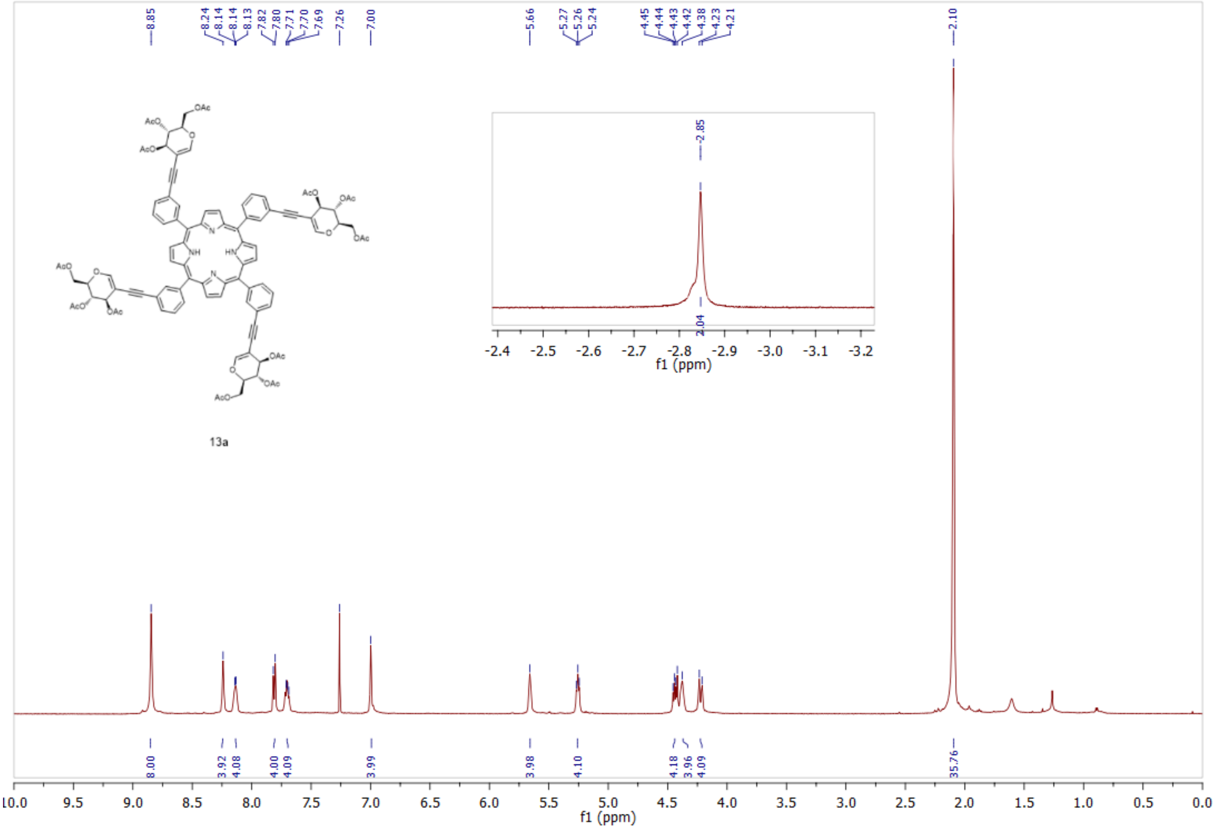
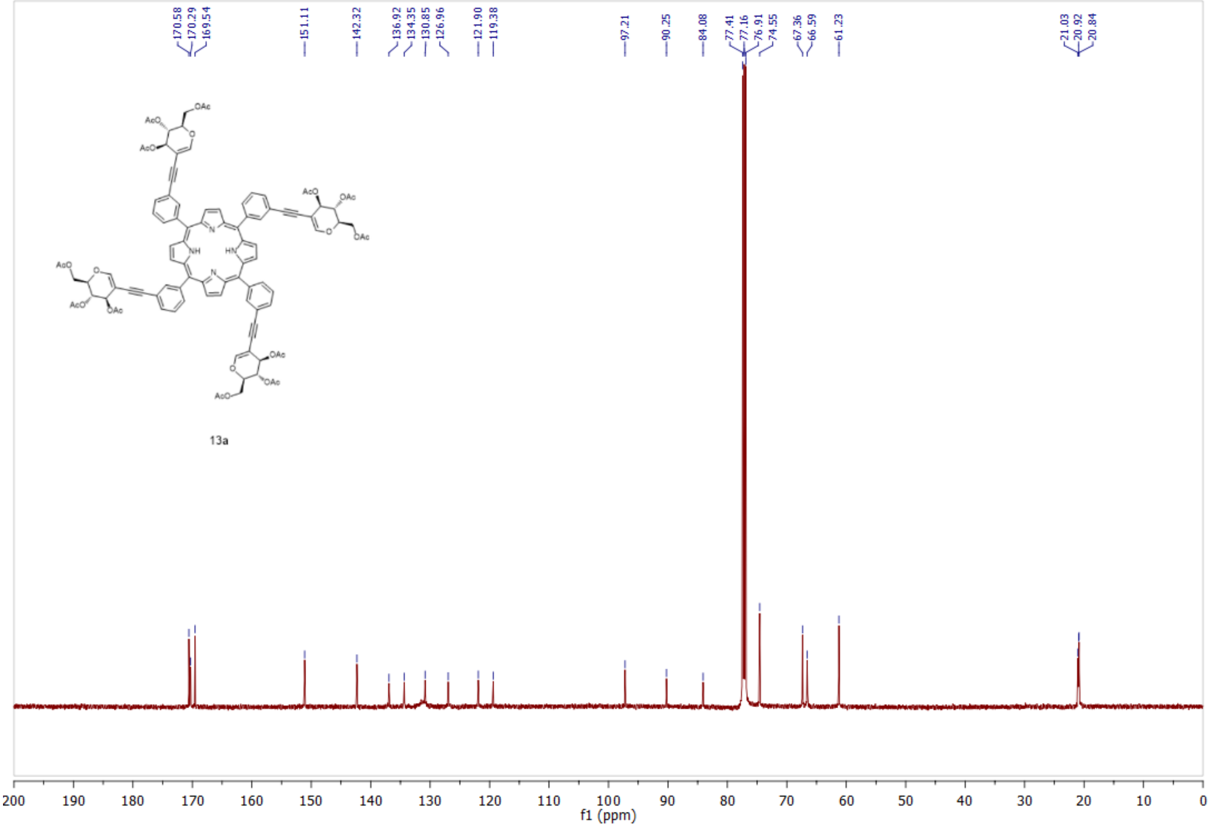
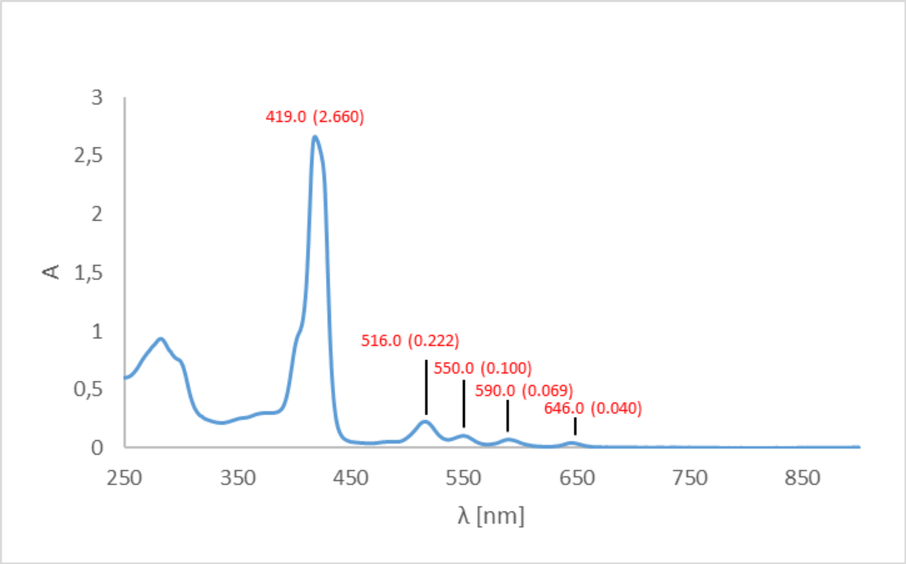


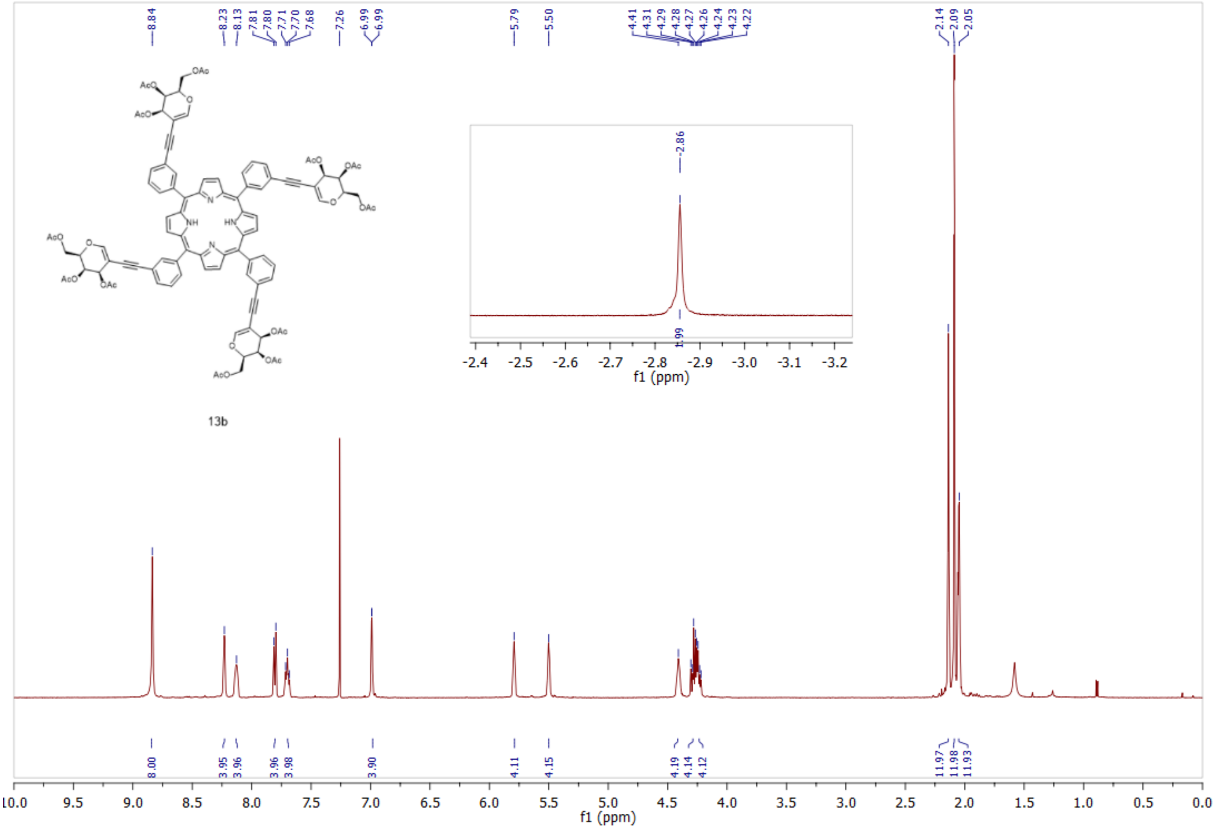
^{13}C NMR of **13a**



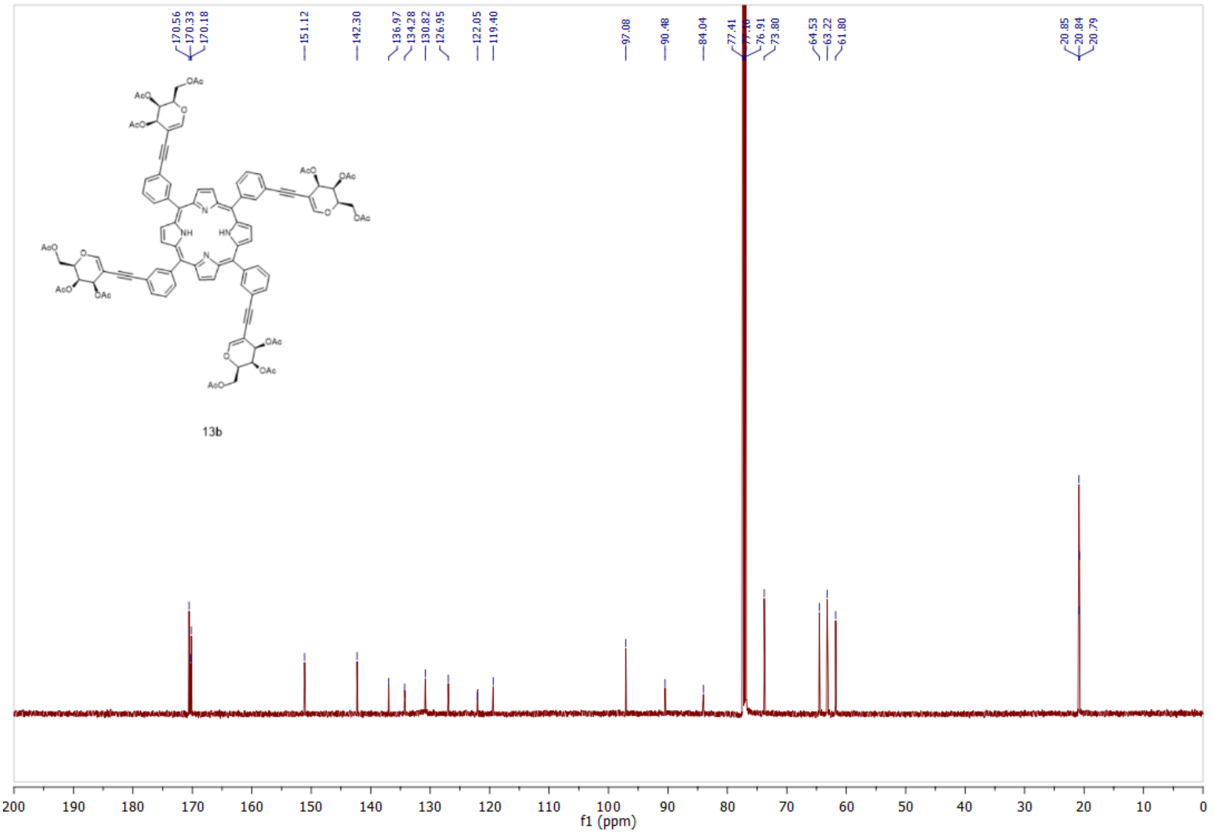
UV-Vis spectrum of **13a**



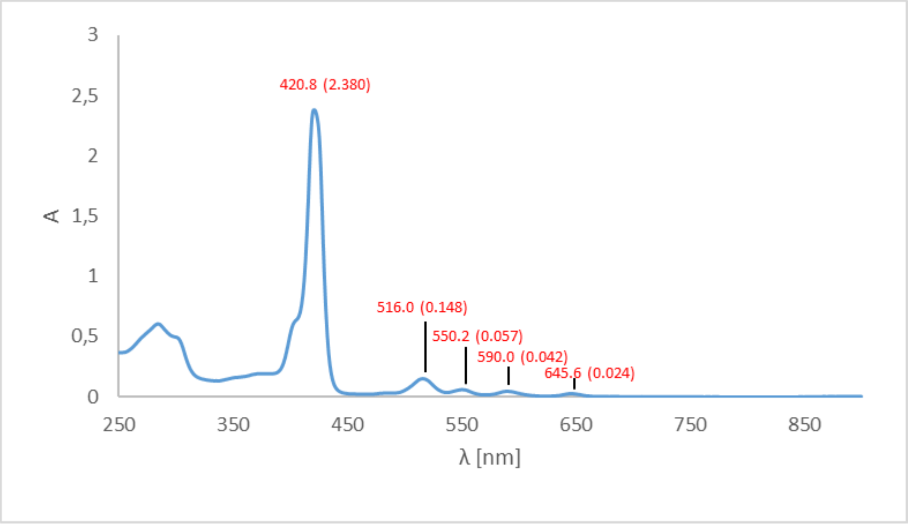
^{1}H NMR of **13b**



^{13}C NMR of **13b**



UV-Vis spectrum of **13b**



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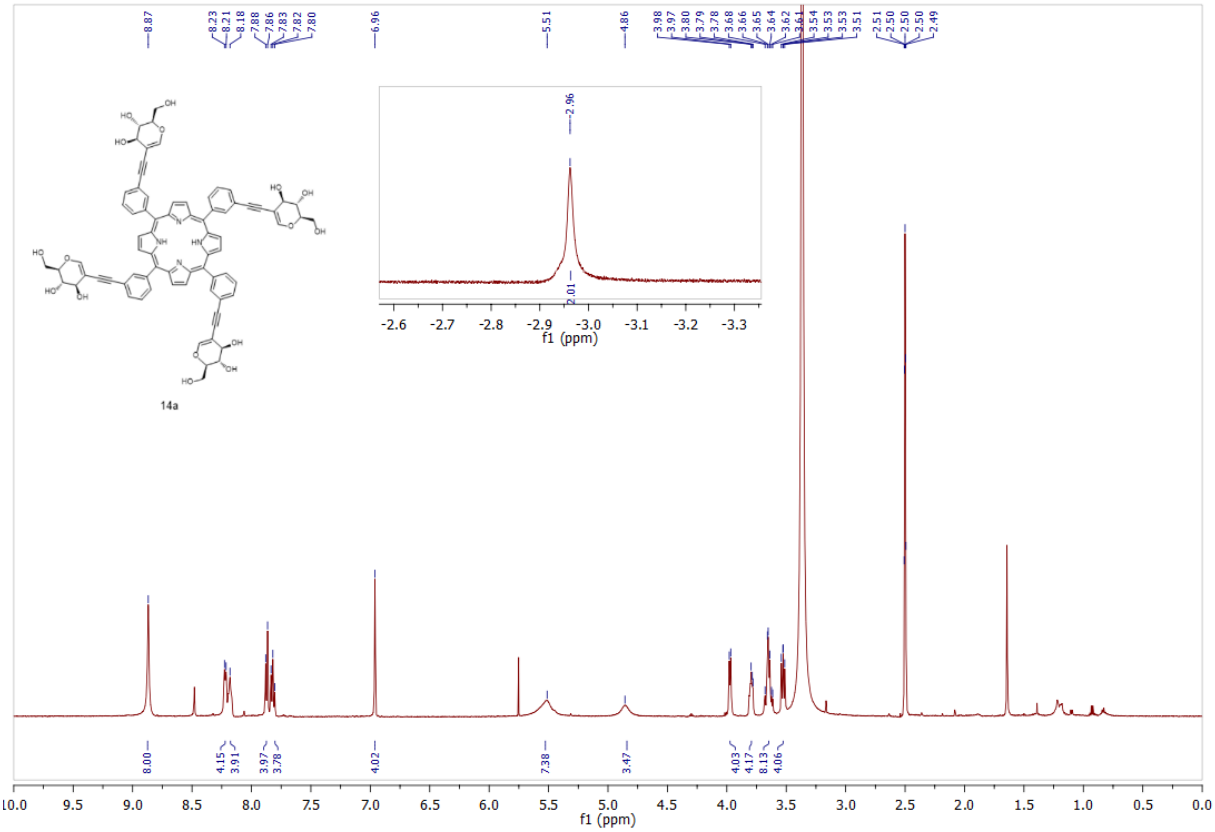

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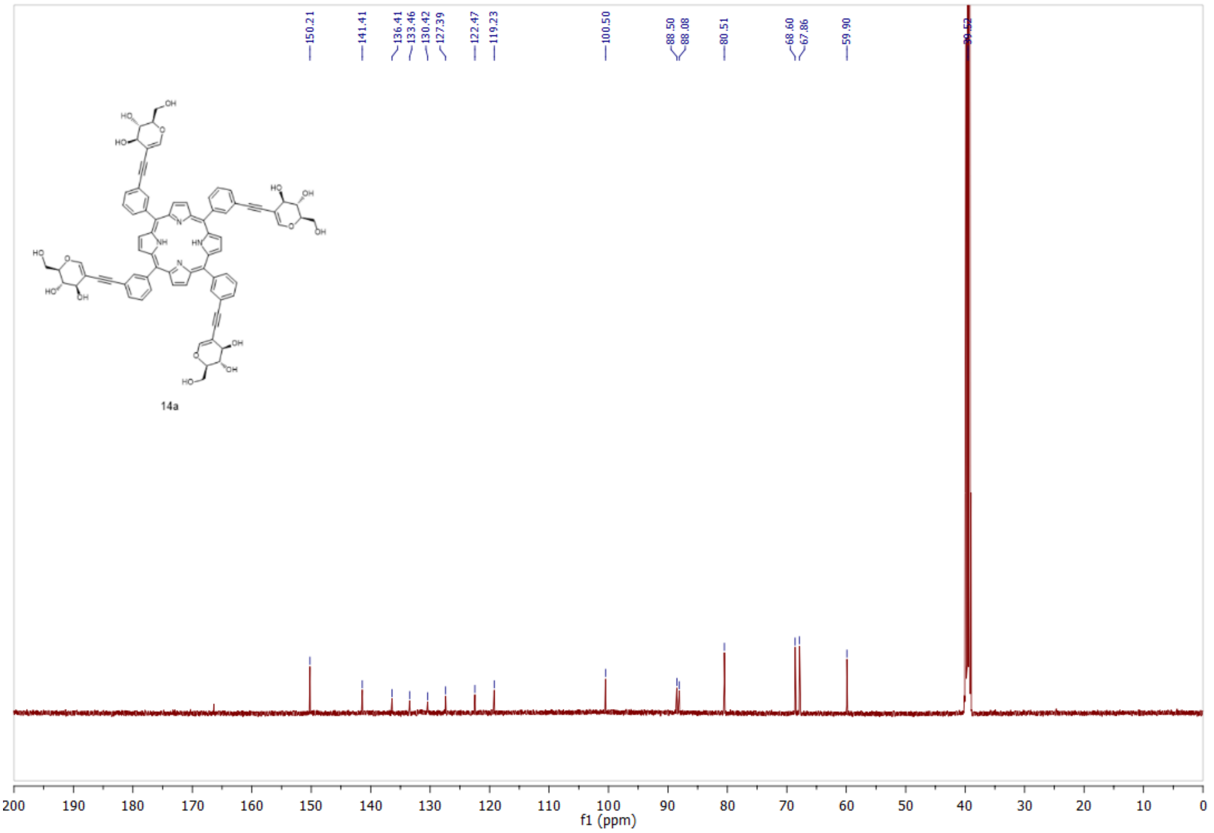
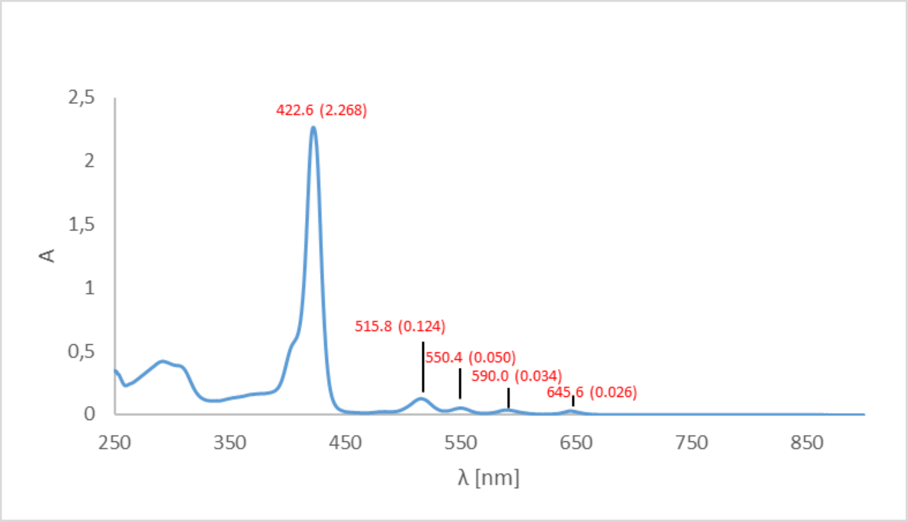
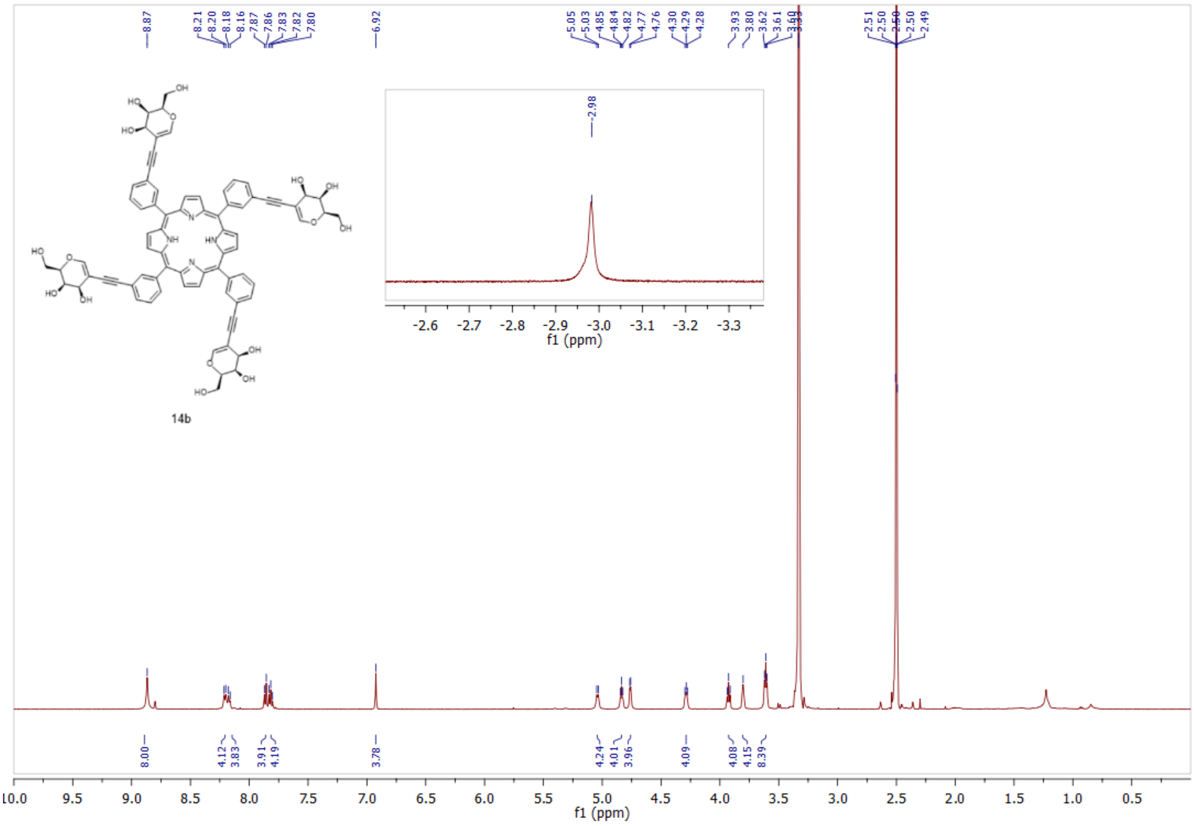


UV-Vis spectrum of **14a**



^{1}H NMR of **14b**



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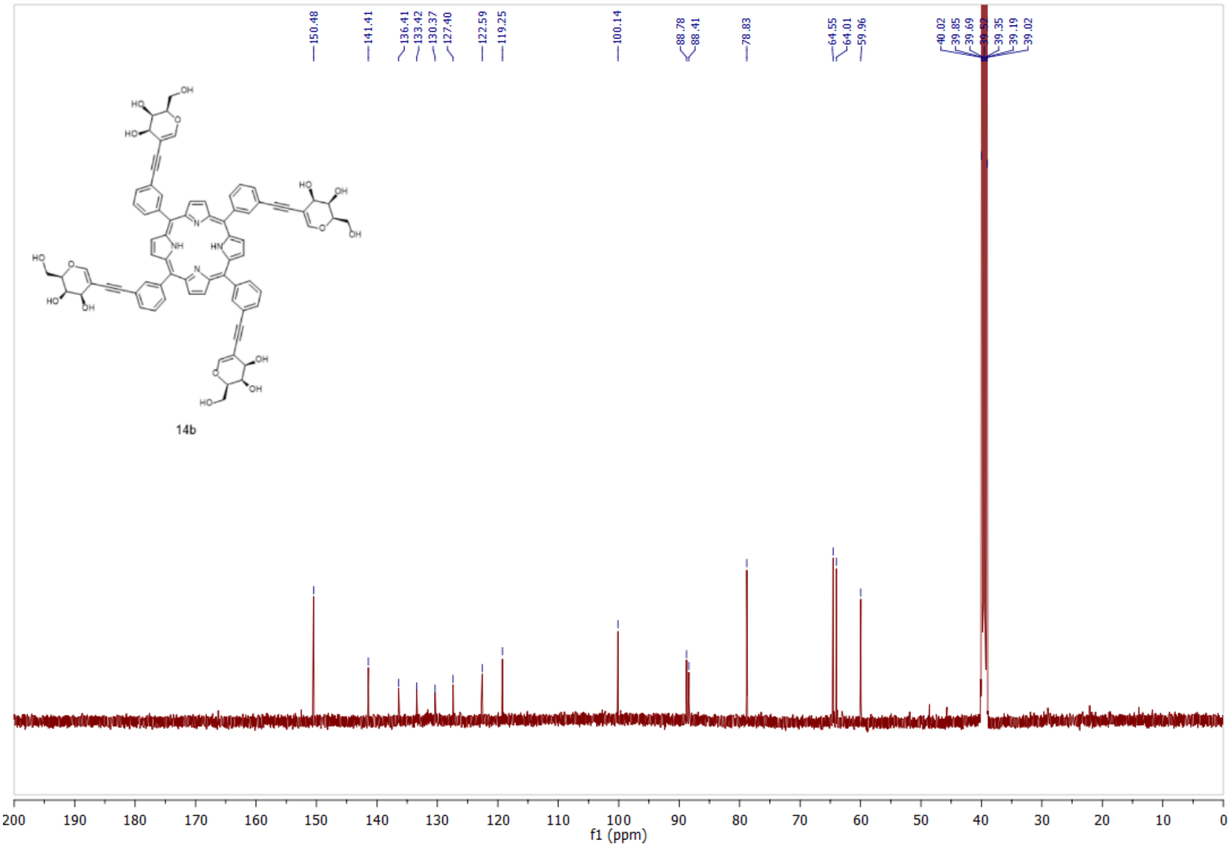

UV-Vis spectrum of **14b**