

New Route to Glycosylated Porphyrins via the Aromatic Nucleophilic Substitution (S_NAr) – Synthesis and Cellular Uptake Studies

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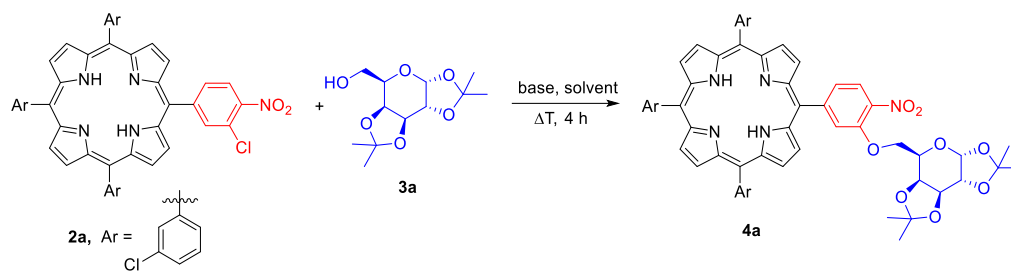
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General experimental methods

Nitration, synthesis of porphyrin-sugar hybrids and deprotection of sugar moieties were carried out using sealed tubes. Chloroform was dried over CaCl_2 and distilled. Triethylamine was stored over KOH. Other solvents were used without further purification. The nitrocompounds **2b-2e** have been synthesized following similar procedure as described for **2a**.¹ The sugar starting materials: **3a**, **3d**, **3e** and **3g** have been purchased from Carbosynth or Sigma Aldrich. Compounds **3b**, **3c** and **3f** were synthesized as described herein. Commercially available chemicals were used as received unless otherwise stated. Reactions were monitored by thin-layer chromatography on aluminium foil plates pre-coated with silica gel (DC Alurolle, Kieselgel 60, F-254; Merck AG) which were observed under visible light and rendered by ultraviolet. Column chromatography was performed with Silica gel (230-400 mesh). ^1H NMR (500 MHz), ^{13}C NMR (125 MHz), ^{19}F NMR (471 MHz) were recorded at 293 K with a Varian NMR System. 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), d (doublet), t (triplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), m (multiplet). Coupling constants J are given in Hz. Mass spectra were measured with a Synapt G2-S HDMS (Waters, ESI-TOF) spectrometer (ESI method and APCI method); m/z intensity values for peaks are given as % of relative intensity. UV/Vis spectra were measured with the LLG-uniSPEC 2 Spectrophotometer.

¹ M. Rosa, M. Malinowski, S. Ostrowski, Modification for Nitration of Halo-Substituted Meso-Tetraarylporphyrins: A Convenient Scale-up in Small Amount of Solvent. *Curr. Org. Synth.*, Manuscript submitted for publication.

Optimisation studies of S_NAr reaction of porphyrin **2a**^a

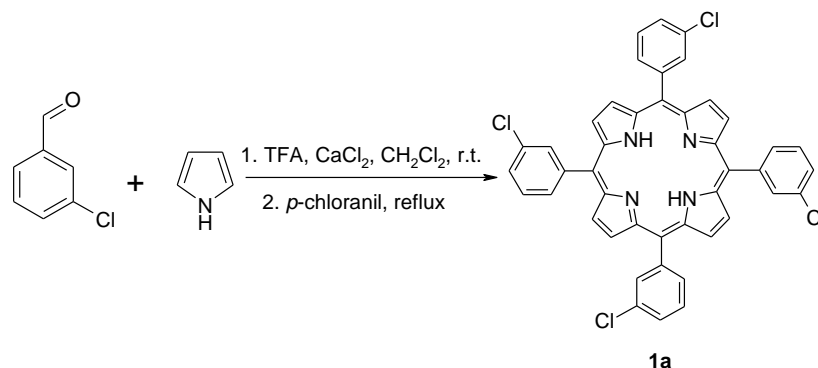


Entry	Solvent	Base (eq)	Temperature [°C]	Yield [%]
1	DMF	NaH (100)	100	0
2	NMP	NaOH (200)	80	0
3	DMF	NaOH (200)	80	17
4	DMF	<i>t</i> -BuOK (200)	80	15
5	DMF	<i>t</i> -BuOK (60)	80	traces
6	NMP	<i>t</i> -BuOK (60)	80	0
7	DMSO	<i>t</i> -BuOK (60)	80	0
8	<i>t</i> -BuOH	<i>t</i> -BuOK (60)	80	0
9	THF	<i>t</i> -BuOK (60)	80	traces
10	Et ₃ N	<i>t</i> -BuOK (60)	80	70
11	Et ₃ N	<i>t</i> -BuOK (60)	65	72
12	Et ₃ N	<i>t</i> -BuOK (60)	50	65
13	Et ₃ N	<i>t</i> -BuOK (20)	65	42
14	Et ₃ N ^b	<i>t</i> -BuOK (20)	65	74
15	Et ₃ N ^{b,c}	<i>t</i> -BuOK (20)	65	76
16	Et ₃ N ^{b,c}	<i>t</i> -BuOK (10)	65	45
17	Et ₃ N ^{b,c}	DBU (20)	65	traces
18	Et ₃ N ^{b,c}	TMG (20)	65	0
19	Et ₃ N ^{b,c}	NaH (20)	65	0
20	Et ₃ N ^{b,c}	Cs ₂ CO ₃ (20)	65	0

^a Typical conditions: porphyrin **2a** (0.013 mmol), carbohydrate **3a** (6eq), solvent (1 mL), 4h. ^b Reaction in 0.35 ml of Et₃N. ^c Reaction with 2 eq of sugar **3a**.

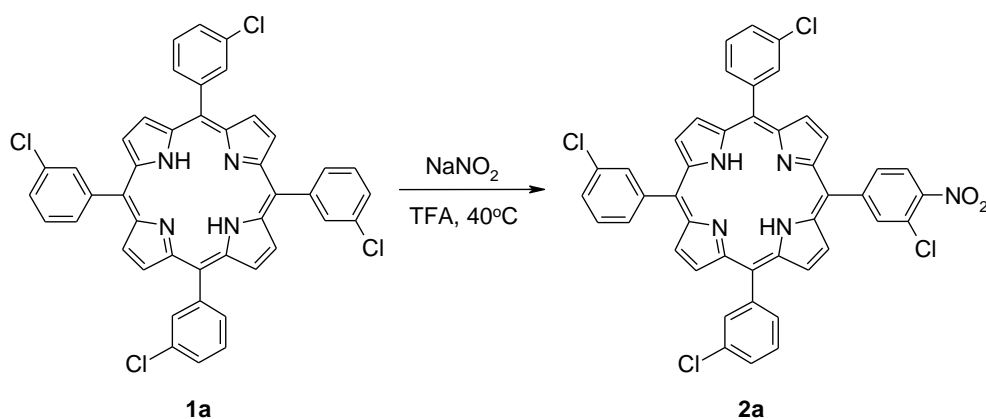
Procedures and characterisation of starting materials

5,10,15,20-tetrakis-(3-chlorophenyl)porphyrin (**1a**)



300 mL of CH₂Cl₂ (distilled over CaCl₂) was added to a three-necked 500 mL round-bottomed flask equipped with a reflux condenser. Flask was shielded from the ambient light. Then 3-chloro-benzaldehyde, 1.53 g (1.8 mL; 16.75 mmol), pyrrole 1.24 g (1.2 mL; 18.43 mmol) and 1.31 g CaCl₂ were added. The mixture was stirred for 5 minutes and 2.0 mL TFA (10.45 mmol) was added. Reaction was stirred for 45 min at room temperature. After that time *p*-chloranil 3.00 g (12.20 mmol) was added and the mixture was refluxed for 10 min. Then TFA was neutralized with an excess of Na₂CO₃ and solvent was evaporated off. Product was purified by column chromatography (eluent: chloroform/*n*-hexane, 3:1) yielding purple solid of porphyrin **1a**: 1.13 g, 36%. Spectroscopic data were in agreement with those of the literature.²

5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrin (**2a**)¹

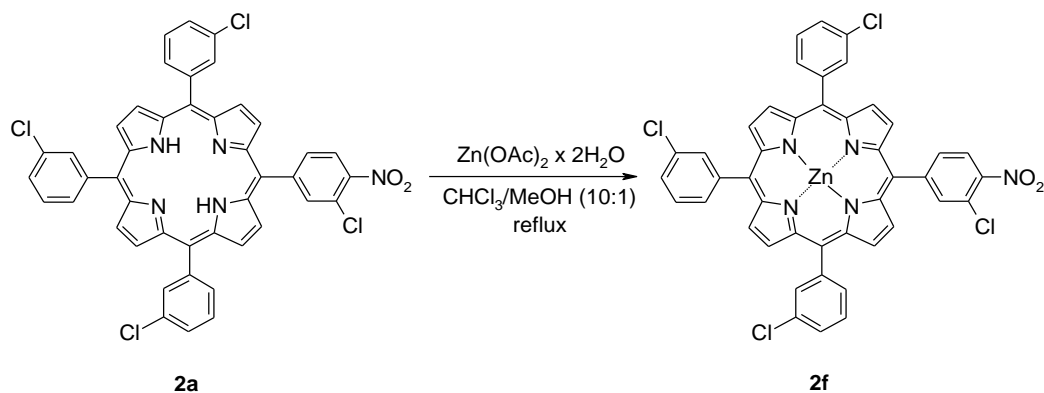


The porphyrin **1a** (200.8 mg, 0.267 mmol) and 147 mg of sodium nitrite (2.13 mmol) were dissolved in 2.4 mL of TFA in a 10 mL sealed tube. The mixture was vigorously stirred (1000 rpm) for 20 min at 40°C. Then reaction was quenched with 2.0 mL of water, diluted with 80 mL of chloroform, transferred to a separatory funnel and washed with 10% aqueous solution of sodium carbonate (50 mL). The organic layer was then subsequently washed 2x75 mL of water and dried over MgSO₄. Then drying agent was filtered off, solvent was evaporated off and a product was separated by column chromatography (eluent: CHCl₃/*n*-hexane, 2:1) yielding

² S. Ostrowski, B. Łopuszyńska, *Synth. Commun.*, **2003**, 33, 4101.

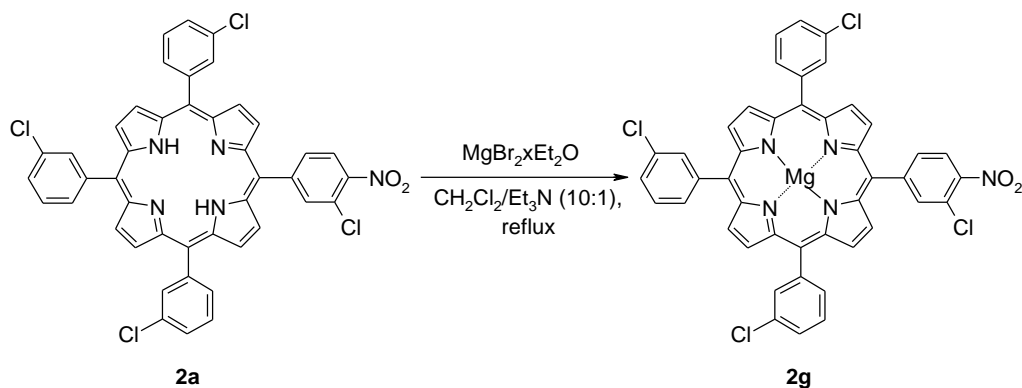
purple solid of porphyrin **2a**: 122.0 mg, 57%. Spectroscopic data were in agreement with those of the literature.²

[5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrinato] zinc(II) (2f)



To a 50 mL round bottomed flask equipped with a reflux condenser 30.0 mg of porphyrin **2a** (0.038 mmol), 150 mg of zinc(II) acetate dihydrate (0.683 mmol), 10 mL of chloroform and 1 mL of methanol were added. The mixture was stirred at reflux for 15 minutes. After cooling to room temperature solvents were evaporated off. Crude product was purified by column chromatography (eluent: chloroform/*n*-hexane, 2:1) yielding purple solid of porphyrin **2f**: 32.0 mg, 99%. Spectroscopic data were in agreement with those of the literature.³

[5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrinato] magnesium(II) (2g)



To a 50 mL round bottomed flask equipped with a reflux condenser 30 mg of porphyrin **2a** (0.038 mmol), 150 mg of magnesium bromide ethyl etherate (0.581 mmol), 10 mL of methylene chloride and 1 mL of triethylamine were added. Mixture was stirred at reflux for 30 minutes. After cooling to r.t. solvents were evaporated off. Crude product was purified by column chromatography (eluent: methylene chloride/methanol/triethylamine, 200:2:1) yielding purple solid of porphyrin **2g**: 26.8 mg, 87%.

¹H NMR (500 MHz, DMSO-*d*₆) δ [ppm] = 8.87-8.77 (m, 8H, H ^{β}); 8.60-8.56 (m, 1H, H-Ar); 8.49 (d, 1H, *J* = 8.1 Hz, H-Ar); 8.41-8.36 (m, 1H, H-Ar); 8.23 (br s, 3H, H-Ar); 8.19-8.13 (m, 3H, H-Ar); 7.93-7.88 (m, 3H, H-Ar); 7.85-7.79 (m, 3H, H-Ar).

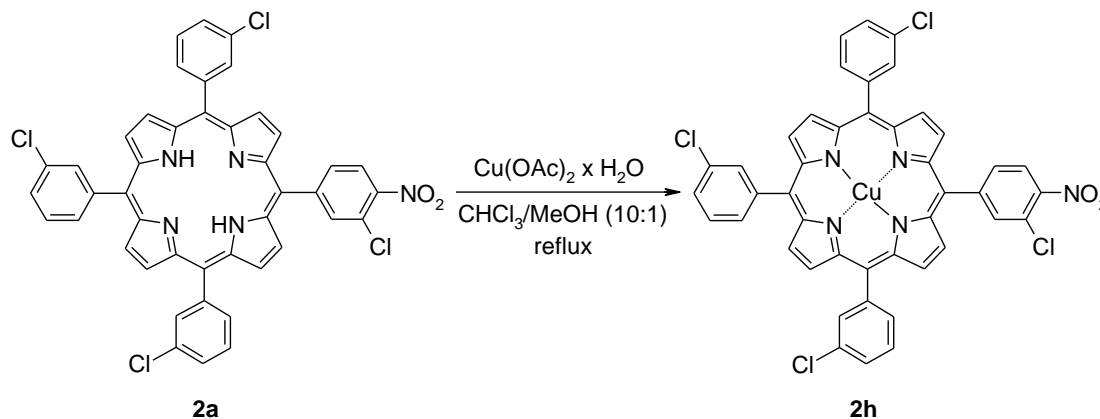
³ S. Ostrowski, S. Grzyb, A. Mikus, *Helv. Chim. Acta*, **2007**, 90, 2000.

MS (ESI) m/z (% rel. int.): 825 (3); 824 (8); 823 (18); 822 (32); 821 (62); 820 (61); 819 (100), 818 (37); 817 (51) (isotope $[M]^+$).

HRMS (ESI): $C_{44}H_{23}N_5O_2Cl_4Mg^+ [M]^+$ (m/z): calc. 817.0456; found 817.0446.

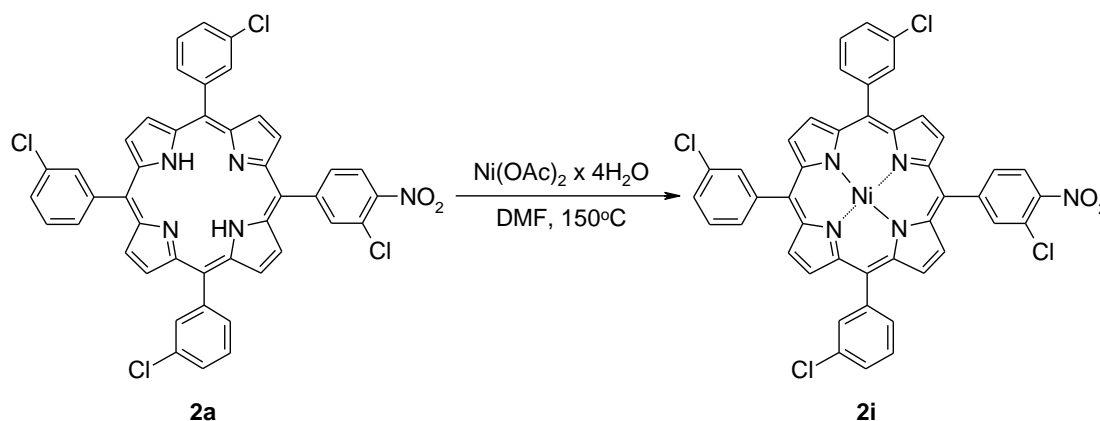
UV-VIS ($CHCl_3$) λ_{max} [nm] (log ϵ): 605.4 (4.05); 564.6 (4.47); 427.2 (5.59, Soret band).

[5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrinato] copper(II) (**2h**)



To a 50 mL round bottomed flask equipped with a reflux condenser 30.0 mg of porphyrin **2a** (0.038 mmol), 150 mg of copper(II) acetate hydrate (0.751 mmol), 10 mL of chloroform and 1 mL of methanol were added. Mixture was stirred at reflux for 15 minutes. After cooling to r.t. solvents were evaporated off. Crude product was purified by column chromatography (eluent: chloroform/*n*-hexane 2:1) yielding pink/purple solid of porphyrin **2h**: 32.0 mg, 99%. Spectroscopic data were in agreement with those of the literature.⁴

[5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrinato] nickel(II) (**2i**)



To a 10 mL sealed tube 30 mg of porphyrin **2a** (0.038 mmol), 150 mg of nickel(II) acetate tetrahydrate (0.603 mmol) and 3 mL of DMF were added. Mixture was stirred at 150°C for 1h. After cooling to r.t. mixture was poured into 30 mL of brine. Formed precipitate was filtered and washed with water 2x20 mL then dried over air for 18 hours. Crude product was purified

⁴ S. Ostrowski, A. Mikus, B. Łopuszyńska, *Tetrahedron*, **2004**, 60, 11951.

by column chromatography (eluent: chloroform/*n*-hexane, 1:1) yielding purple solid of porphyrin **2i**: 11.7 mg, 36%.

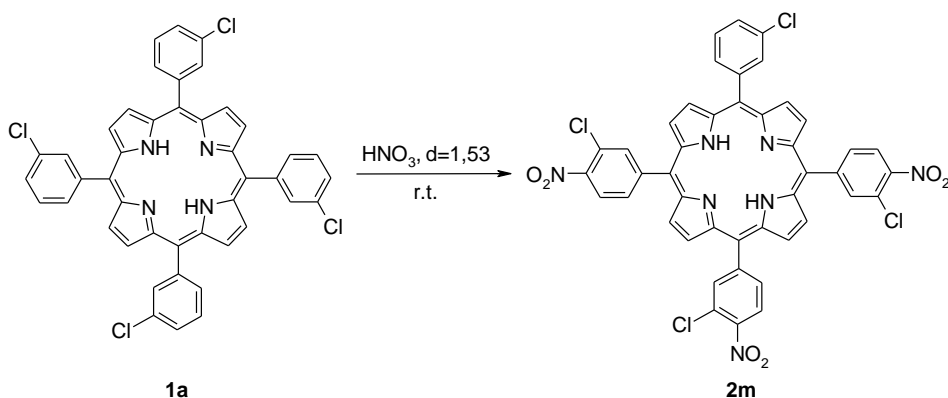
¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.80 (d, 2H, *J* = 5.0 Hz, H^β, AM system), 8.76 (s, 4H, H^β), 8.68 (d, 2H, *J* = 5.0 Hz, H^β, AM system), 8.25-8.21 (m, 2H, H-Ar), 8.08 (dd, 1H, *J* = 8.2 Hz, *J* = 1.6 Hz, H-Ar), 8.02 (m, 3H, H-Ar), 7.91-7.90 (m, 3H, H-Ar), 7.76-7.71 (m, 3H, H-Ar), 7.67-7.61 (m, 3H, H-Ar)

MS (ESI) *m/z* (% rel. int.): 859 (11); 858 (16); 857 (18); 856 (22); 855 (22); 854 (43); 853 (21); 852 (25) [isotope (M+H)⁺].

HRMS (ESI): C₄₄H₂₄N₅O₂Cl₄Ni⁺ [M+H]⁺ (*m/z*): calc.: 852.0038; found: 852.0018

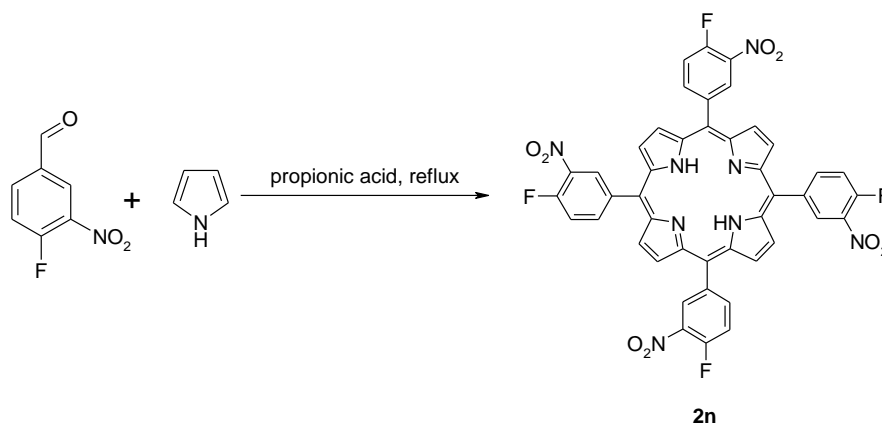
UV-VIS (CHCl₃) λ_{max} [nm] (log ε): 538.6 (0.245), 415.6 (2.755, Soret band)

5,10,15-tris(3-chloro-4-nitrophenyl)porphyrin-20-(3-chlorophenyl)porphyrin (2m)



The porphyrin **1a** 51.0 mg, 0.068 mmol was placed in a 10 mL round bottomed flask. Then 1.0 mL of yellow fuming nitric acid, d=1.53g/mL, (1.53g, 24,282 mmol) was added *via* syringe through a rubber septum. Reaction was stirred for 4 min at room temperature. Then mixture was diluted with 10 mL of chloroform, transferred to a separatory funnel and washed with water (3x10 mL). The organic layer was then dried over MgSO₄/Na₂CO₃. Then drying agent was filtered off, solvent was evaporated off and a product was separated by column chromatography (eluent: CHCl₃) yielding purple solid of porphyrin **2m**: 14.0 mg, 23% and other unpurified polynitroporphyrins. Spectroscopic data were in agreement with those of the literature.⁴

5,10,15,20-tetrakis(4-fluoro-3-nitrophenyl)porphyrin (2n)



In a 50 mL round bottomed flask 11.5 mL of propionic acid, 505 mg of 4-fluoro-3-nitrobenzaldehyde (2.98 mmol) and 208 mg of pyrrole (3.10 mmol) were added. Mixture was heated to reflux and stirred intensively for 1h. After that time, mixture was cooled to room temperature and 50 mL of methanol was added. The mixture was kept at room temperature for 15 min. Then precipitate was filtered off and washed with 150 mL of methanol. Product was purified by column chromatography (eluent: chloroform) yielding purple solid of porphyrin **2n**: 36.4 mg, 6%.

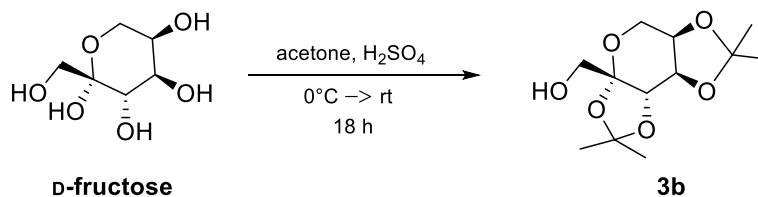
¹H NMR (500 MHz, DMSO-*d*₆) δ [ppm] = 9.02 (br s, 8H, H ^{β}); 8.97-8.92 (m, 4H, H-Ar); 8.68-8.62 (m, 4H, H-Ar); 8.09-8.04 (m, 4H, H-Ar); -3.02 (s, 2H, 2xNH).

MS (ESI) *m/z* (% rel. int.): 870 (2); 869 (11); 868 (41); 867 (100) (isotope [M+H]⁺).

HRMS (APCI): C₄₄H₂₃N₈O₈F₄⁺ [M+H]⁺ (*m/z*): calc. 867.1575; found 867.1567.

UV-VIS (CHCl₃) λ_{max} [nm] (log ϵ): 646.8 (3.24); 590.2 (3.74); 548.8 (4.71); 515.0 (4.24); 422.0 (5.44, Soret band).

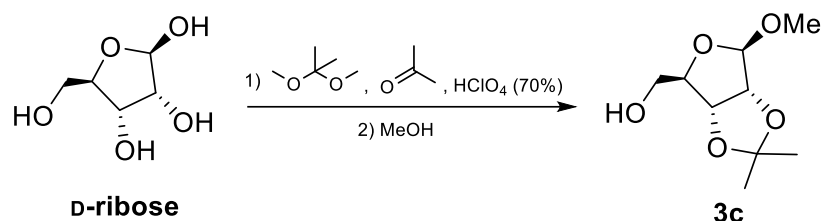
2,3:4,5-di-O-isopropylidene- β -D-fructopyranose (3b)



To a stirred solution of acetone (39 mL) and 95% H₂SO₄ (1.95 mL), D-fructose (2.0 g, 11.1 mmol) was added in portions at 0°C. The resulting mixture was left to warm to the room temperature and stirred overnight. After that time, sulfuric acid was neutralised with 10% NaOH (15 mL). Then the mixture was concentrated and extracted with methylene chloride (2x25 mL). Organic phase was washed with water (2x15 mL), dried over MgSO₄, filtrated and concentrated leading to a crude yellow solid (2.7 g). The pure product **3b** was obtained after recrystallization from a mixture (1:1) of petroleum ether (PE) and diethyl ether (for 2.7 g of crude product, 13.5 mL of PE and 13.5 mL of Et₂O were used). The solvents were heated to boiling then the mixture was left in a fridge for 10 min, resulting in formation of white crystals.

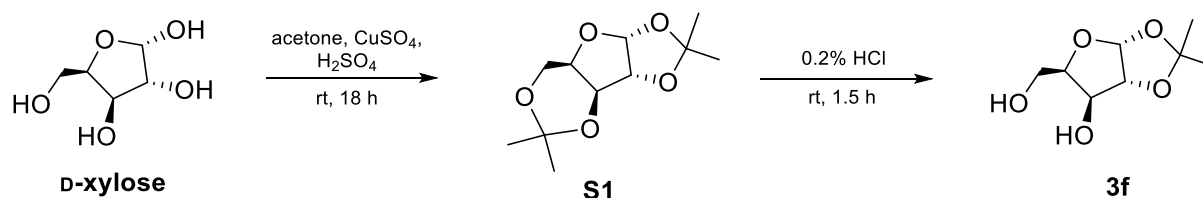
The solids were filtered off, washed with PE furnishing the pure **3b** (1.48 g, 51%). Spectroscopic data were in agreement with those of the literature.⁵

1-O-methyl-2,3-O-isopropylidene-β-D-ribofuranose (3c)



D-Ribose (1.0 g, 6.66 mmol) was suspended in a mixture of acetone (6 mL) and 2,2-dimethoxypropane (2 mL) then stirred for 5 min at room temperature. After that time, the mixture was cooled to 0°C and HClO₄ (70%, 0.32 mL, 3.68 mmol) was added dropwise. The mixture was continued stirring and simultaneously warmed to a room temperature in 35 min. After that time, methanol (1.6 mL) was added and the reaction was continued for 2 hours at room temperature. Then the mixture was neutralised with a saturated solution of Na₂CO₃ (5 mL) and solids were removed by filtration. The filtrate was extracted with EtOAc (3x6 mL). The organic layer was washed with brine (4 mL), dried over MgSO₄, filtered and evaporated off. The crude product was purified by column chromatography (hexane→hexane/ethyl acetate, 75:25) giving pure **3c** as a colorless oil (464 mg, 34%). *R_f* = 0.19 (hexane/ethyl acetate, 75:25). Spectroscopic data were in agreement with those of the literature.⁶

1,2-O-isopropylidene-α-D-xylofuranose (3f)



Step I.

D-Xylose (5.03 g, 33.5 mmol), anhydrous CuSO₄ (9.36 g, 58.64 mmol) were suspended in 150 mL of acetone and stirred for 5 min. Then 1 ml of 95% H₂SO₄ (18.76 mmol) was added. The resulting mixture was stirred for 18 hours at room temperature. After that time solid Na₂CO₃ was added and the mixture was vigorously stirred for 15 min. Then solids were removed by filtration and filtrate was concentrated giving **S1** (6.19 g, 80%) with analytical purity. Spectroscopic data were in agreement with those of the literature.⁷

¹H NMR (CDCl₃, 500 MHz), δ (ppm) = 6.00 (d, *J* = 3.9 Hz, 1H); 4.52 (d, *J* = 3.6 Hz, 1H); 4.30 (d, *J* = 2.4 Hz, 1H); 4.10-4.02 (m, 3H); 1.50 (s, 3H); 1.45 (s, 3H); 1.39 (s, 3H); 1.33 (s, 3H).

⁵ A. Yildirim, *Catal. Lett.*, **2020**, 150, 2566

⁶ J. Lv, C.-Y. Liu, Y.-F. Guo, G.-J. Feng, H. Dong, *Eur. J. Org. Chem.*, **2022**, e202101565

⁷ S. Gupta, S. Bera, D. Mondal, *J. Org. Chem.*, **2020**, 85, 2635

Step II.

6.19 g of sugar **S1** (26.87 mmol) was stirred with 62 mL 0.2% HCl for 90 minutes at room temperature. Then, the mixture was neutralized with solid NaHCO₃ and vigorously stirred for 10 minutes. Afterwards, the mixture was transferred to a separatory funnel and extracted with dichloromethane (3x70 mL). The combined organic phase was dried with MgSO₄. The drying agent was filtered off, and the filtrate was concentrated. The product was purified by column chromatography (hexane→hexane/ethyl acetate, 1:1) giving pure **3f** (1.73 g, 34%) as colorless oil. Spectroscopic data were in agreement with those of the literature.⁸

R_f = 0.16 (hexane/ethyl acetate, 1:1)

¹H NMR (CDCl₃, 500 MHz), δ (ppm) = 5.98 (d, J = 3.7 Hz, 1H); 4.52 (d, J = 3.6 Hz, 1H); 4.33 (t, J = 3.0 Hz, 1H); 4.20 – 4.11 (m, 2H); 4.05 (ddd, J = 12.4, 7.8, 2.2 Hz, 1H); 3.94 (dd, J = 3.7, 1.1 Hz, 1H); 1.49 (s, 3H); 1.32 (s, 3H).

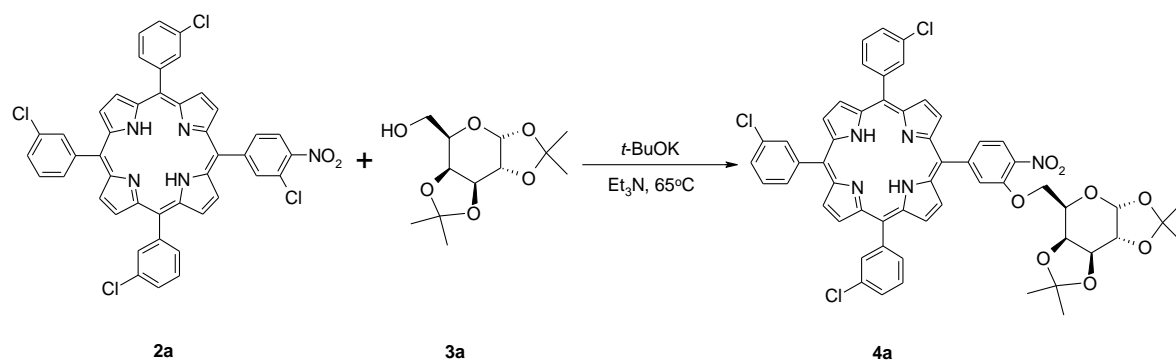
⁸ S. B. Ferreira, A. C. R. Sodero, M. F. C. Cardoso, E. S. Lima, C. R. Kaiser, F. P. Silva, Jr., V. F. Ferreira, J. *Med. Chem.*, **2010**, 53, 2364

Characterization and procedures for the synthesis of porphyrin-sugar hybrids

General procedure for synthesis of porphyrin-sugar hybrids

In a sealed tube (6 mL) porphyrin (0.013 mmol, 1.0 eq), sugar substrate (0.026 mmol, 2.0 eq), 0.35 mL of triethylamine and then 29.5 mg of potassium *tert*-butoxide (0.260 mmol, 20.0 eq) were added. The reaction mixture was stirred for 4 h at 65°C. Then it was cooled to r.t and transferred to a separatory funnel with 20 mL of chloroform. Organic layer was washed with water 3x20 mL and dried with anhydrous MgSO₄. The drying agent was filtered off, then solvent was evaporated on rotary evaporator. Crude product was purified by column chromatography using the indicated eluent.

5-[3-(1,2:3,4-di-O-isopropylidene- α -D-galactopyranosyl-6-oxy)-4-nitrophenyl]-10,15,20-tris(3-chlorophenyl)porphyrin (4a)



Following general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.3 mg of porphyrin **2a** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 99:1 as an eluent giving purple solid of porphyrin **4a** (9.8 mg, 74%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.94-8.84 (m, 8H, H ^{β}); 8.28 (d, J = 7.9 Hz, 1H, H-Ar); 8.24 (s, 3H, H-Ar); 8.12 (d, J = 7.6 Hz, 3H, H-Ar); 8.04 (br s, 1H, H-Ar); 7.91 (d, J = 7.7 Hz, 1H, H-Ar); 7.84-7.79 (m, 3H, H-Ar); 7.75-7.68 (m, 3H, H-Ar); 5.51 (d, J = 4.7 Hz, 1H, H-gal); 4.70 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H, H-gal); 4.50 (d, J = 8.0 Hz, 1H, H-gal); 4.45-4.37 (m, 3H, H-gal); 4.35 (dd, J = 4.8 Hz, J = 2.5 Hz, 1H, H-gal); 1.63 (s, 3H, CH₃), 1.36 (s, 3H, CH₃); 1.34-1.30 (m, 6H, 2x CH₃); -2.85 (s, 2H).

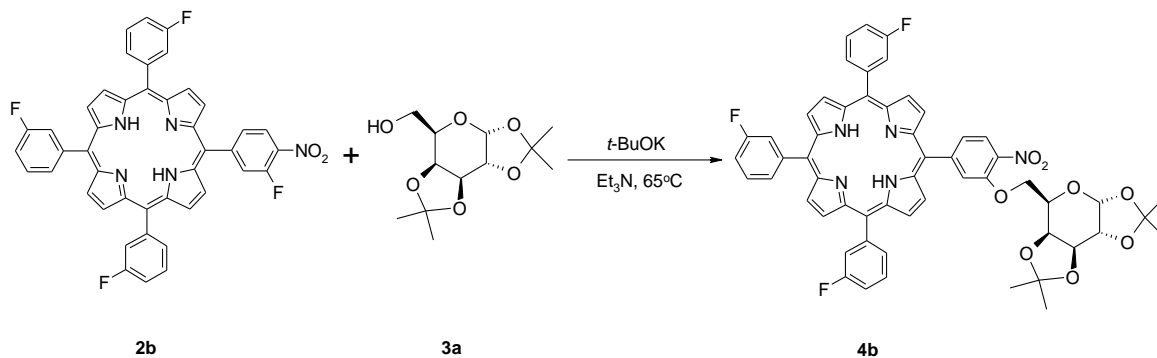
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.8; 148.7; 143.7; 143.6; 139.6; 134.5; 133.2; 132.8; 128.5; 128.4; 128.2; 127.1; 124.2; 121.6; 119.4; 119.3; 119.2; 117.7; 109.7; 109.2; 96.4; 77.4; 71.0; 70.8; 70.7; 68.7; 66.6; 26.3; 26.0, 25.1, 24.5.

MS (ESI) m/z (% rel. int.): 1026 (4); 1025 (13); 1024 (33); 1023 (42); 1022 (100); 1021 (40); 1020 (81) (isotope [M+H]⁺).

HRMS (ESI): C₅₆H₄₅N₅O₈Cl₃⁺ [M+H]⁺ (m/z): calc. 1020.2334; found 1020.2334.

UV-VIS (CHCl₃) λ_{max} [nm] (log ϵ): 644.6 (3.13); 588.4 (3.59); 549.6 (3.67); 515.0 (4.14); 419.2 (5.33, Soret band).

*5-[3-(1,2:3,4-di-O-isopropylidene- α -D-galactopyranosyl-6-oxy)-4-nitrophenyl]-10,15,20-tris(3-fluorophenyl)porphyrin (**4b**)*



Following general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 9.5 mg of porphyrin **2b** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 98:2 as an eluent giving purple solid of porphyrin **4b** (9.5 mg, 75%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.95-8.85 (m, 8H); 8.28 (d, J = 8.1 Hz, 1H, H-Ar); 8.07-8.01 (m, 4H, H-Ar); 8.00-7.95 (m, 3H); 7.92 (d, 1H, J = 8.0 Hz, H-Ar); 7.78-7.71 (m, 3H, H-Ar); 7.57-7.51 (m, 3H); 5.52 (d, 1H, J = 4.9 Hz, H-gal); 4.70 (dd, J = 8.0 Hz, J = 2.5 Hz, 1H, H-gal); 4.51 (d, 1H, J = 8.0 Hz, H-gal), 4.45-4.39 (m, 3H); 4.36 (dd, 1H, J = 4.9 Hz, J = 2.5 Hz, H-gal), 1.64 (s, 3H, CH₃); 1.37 (s, 3H, CH₃); 1.33 (s, 3H, CH₃); 1.32 (s, 3H, CH₃); -2.83 (s, 2H, NH)

¹⁹F NMR (471 MHz, CDCl₃) δ [ppm] = -[115.0 – 114.7] (m, 3F)

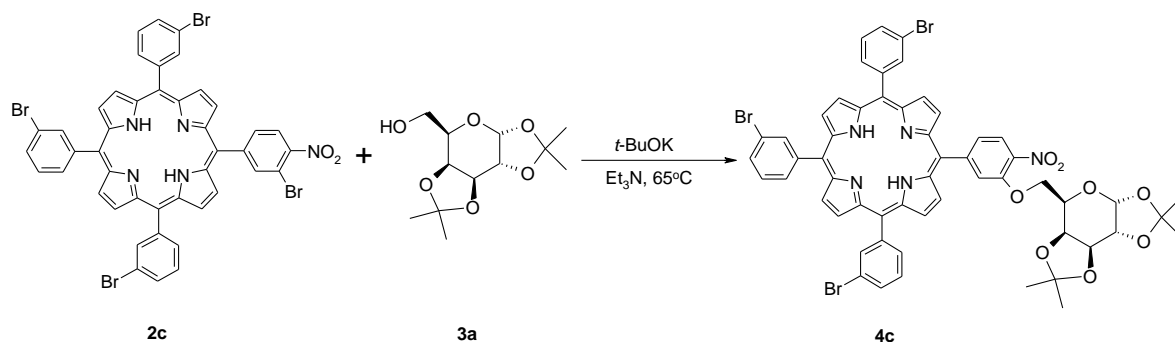
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 161.5 (d, J = 247.4 Hz); 150.8; 148.7; 144.1-143.9 (m); 143.9; 139.6; 137.4; 132.5; 130.7; 128.5-128.2 (m); 127.1; 124.2; 121.8; 121.7; 121.6; 119.5 (d, J = 1.8 Hz); 119.4-119.2 (m); 117.6; 115.3 (d, J = 21.1 Hz); 109.7; 109.2; 96.4; 71.0; 70.8; 70.7; 68.7; 66.6; 26.3; 26.0; 25.1; 24.5.

MS (ESI) m/z (% rel. int.): 976 (1); 975 (4); 974 (16); 973 (57); 972 (100) (isotope [M+H]⁺); 996 (1); 995 (5); 994 (7) (isotope [M+Na]⁺).

HRMS (ESI): C₅₆H₄₅N₅O₈F₃⁺ [M+H]⁺ (m/z): calc. 972.3220; found 972.3232.

UV-VIS (CHCl₃) λ_{max} [nm] (log ϵ): 644.0 (2.59); 588.6 (3.54); 548.8 (3.63); 514.4 (4.22); 419.0 (5.54, Soret band).

5-[3-(1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranosyl-6-oxy)-4-nitrophenyl]-10,15,20-tris(3-bromophenyl)porphyrin (**4c**)



Following general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 12.7 mg of porphyrin **2c** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 99:1 as an eluent giving purple solid of porphyrin **4c** (6.2 mg, 41%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.92-8.84 (m, 8H, H ^{β}); 8.39 (br s, 3H, H-Ar); 8.28 (d, 1H, J = 8.1 Hz, H-Ar); 8.16 (m, 3H, H-Ar); 8.03 (br s, 1H, H-Ar); 7.98-7.94 (m, 3H, H-Ar); 7.93-7.88 (m, 1H, H-Ar); 7.68-7.62 (m, 3H, H-Ar), 5.52-5.48 (m, 1H, H-gal); 4.69 (dd, 1H, J = 8.0 Hz, J = 2.5 Hz, H-gal); 4.49 (d, 1H, J = 8.0 Hz, H-gal); 4.44-4.36 (m, 3H, H-gal); 4.34 (dd, J = 4.8 Hz, J = 2.4 Hz, 1H, H-gal), 1.62 (s, 3H, CH₃); 1.35 (s, 3H, CH₃); 1.32-1.28 (m, 6H, 2xCH₃); -2.88 (s, 2H, NH).

¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.8; 148.7; 143.9; 139.6; 137.3; 133.3; 131.4; 131.4; 128.4; 127.9; 127.1; 124.2; 121.6; 121.4; 119.4; 119.2; 119.2; 117.7; 114.2; 109.7; 109.2; 96.4; 71.0; 70.8; 70.7; 68.7; 66.6; 26.3; 26.0; 25.1; 24.5.

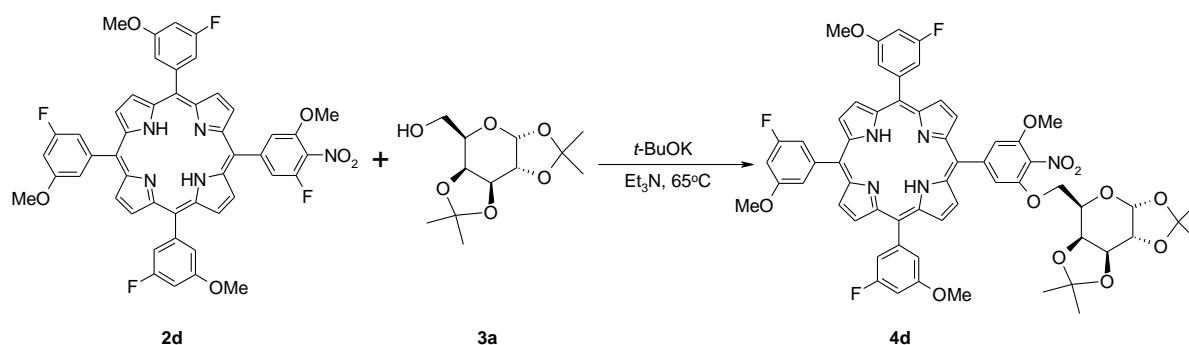
MS (ESI) m/z (% rel. int.): 1160 (7); 1159 (22); 1158 (45); 1157 (52); 1156 (100); 1155 (55); 1154 (94); 1153 (17); 1152 (26) (isotope [M+H]⁺);

1181 (5); 1180 (8); 1179 (13); 1178 (22); 1177 (14); 1176 (20); 1175 (5); 1174 (7) (isotope [M+Na]⁺).

HRMS (ESI): C₅₆H₄₅N₅O₈Br₃⁺ [M+H]⁺ (m/z): calc. 1152.0818; found 1152.0801.

UV-VIS (CHCl₃) λ_{max} [nm] (log ϵ): 645.0 (3.24); 589.8 (3.68); 550.6 (3.79); 515.4 (4.27); 419.8 (5.46, Soret band).

*5-[3-(1,2:3,4-di-O-isopropylidene- α -D-galactopyranosyl-6-oxy)-5-methoxy-4-nitrophenyl]-10,15,20-tris(3-fluoro-5-methoxyphenyl)porphyrin (**4d**)*



Following general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 11.1 mg of porphyrin **2d** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 98:2 as an eluent giving purple solid of porphyrin **4d** (8.9 mg, 63%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.97-8.88 (m, 8H, H^B); 7.61-7.54 (m, 7H, H-Ar); 7.52 (s, 1H, H-Ar); 7.13-7.07 (m, 3H, H-Ar); 5.47 (d, 1H, J = 4.9 Hz, H-gal); 4.64 (dd, 1H, J = 8.0 Hz, J = 2.3 Hz, H-gal); 4.42-4.30 (m, 4H, H-gal); 4.29-4.24 (m, 1H, H-gal); 4.02-3.98 (m, 12H, 4xO-CH₃); 1.56 (s, 3H, CH₃); 1.33 (s, 3H, CH₃); 1.32-1.29 (m, 6H, 2xCH₃); -2.89 (s, 2H, NH).

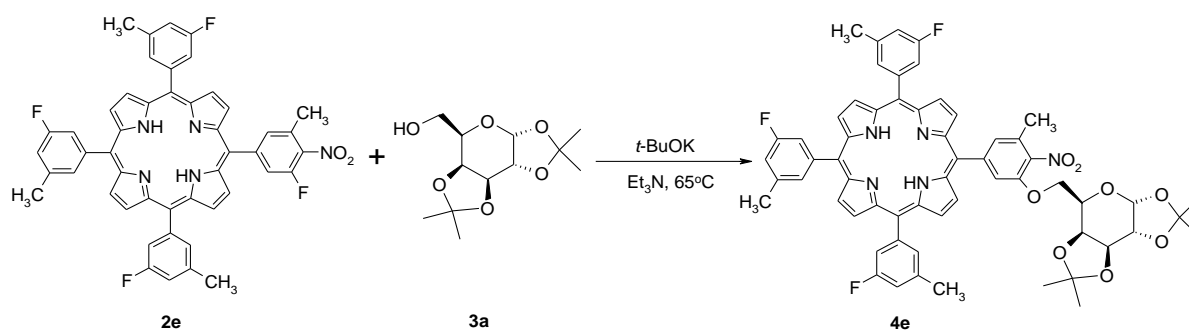
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 162.0 (d, J = 246.1 Hz); 159.3-159.1 (m); 149.8 (J = 96.7 Hz); 145.6; 144.5-144.2 (m); 132.5-130.0 (m), 132.1; 119.4 (d, J = 2.3 Hz); 119.4-119.2 (m); 118.2; 117.3-116.9 (m); 114.8 (d, J = 22.3 Hz); 112.6 (d, J = 125.1 Hz); 109.6; 109.1; 101.9-101.4 (m); 96.3; 70.8; 70.7; 70.6; 48.5; 68.4; 66.3; 57.0; 56.0; 26.3; 26.00; 25.1; 24.4.

MS (ESI) m/z (% rel. int.): 1095 (2); 1094 (15); 1093 (59); 1092 (100); (isotope [M+H]⁺).

HRMS (ESI): C₆₀H₅₃N₅O₁₂F₃⁺ [M+H]⁺ (m/z): calc. 1092.3643; found 1092.3661.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 642.4 (3.69); 588.2 (4.14); 546.8 (4.08); 513.4 (4.66); 419.0 (5.95, Soret band).

*5-[3-(1,2:3,4-di-O-isopropylidene- α -D-galactopyranosyl-6-oxy)-5-methyl-4-nitrophenyl]-10,15,20-tris(3-fluoro-5-methylphenyl)porphyrin (**4e**)*



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.2 mg of porphyrin **2e** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH, 99:1 as an eluent giving purple solid of porphyrin **4e** (9.2 mg, 69%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.92-8.85 (m, 8H, H ^{β}); 7.85-7.79 (m, 4H, H-Ar); 7.78-7.70 (m, 4H, H-Ar); 7.37-7.32 (m, 3H, H-Ar); 5.47 (d, 1H, J = 4.9 Hz, H-gal); 4.68-4.63 (m, 1H, H-gal); 4.43-4.30 (m, 4H, H-gal); 4.29-4.24 (m, 1H, H-gal); 2.69-2.64 (m, 9H, CH₃); 2.61 (s, 3H, CH₃); 1.58-1.55 (m, 3H, CH₃); 1.33 (s, 3H, CH₃); 1.32-1.28 (m, 6H, CH₃); -2.88 (s, 2H, NH).

¹⁹F NMR (471 MHz, CDCl₃) δ [ppm] = -[121.2 – 120.9] (m, 3F).

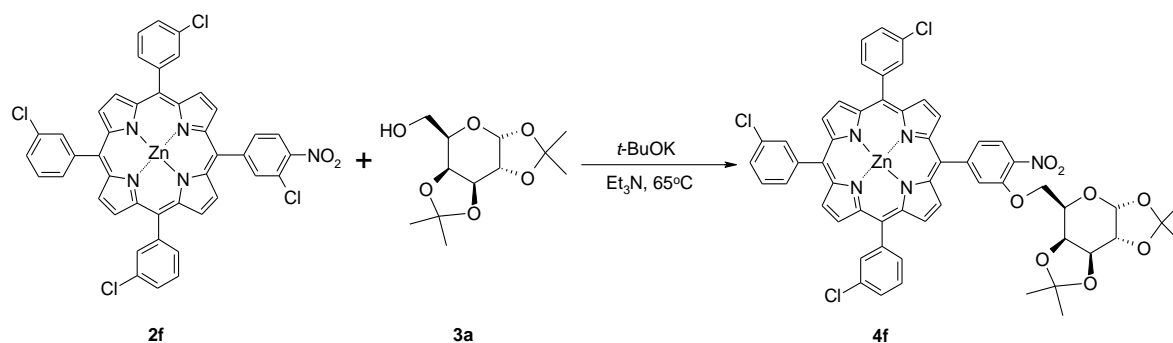
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 161.5; (d, J = 246.7 Hz); 148.6; 145.1; 143.8-143.5 (m); 142.0; 138.7-138.5 (m) 131.7; 129.7-129.4 (m); 119.6-119.5 (m); 119.5-119.3 (m); 119.0 (d, J = 21.1 Hz); 118.3; 118.0; 116.0-115.6 (m); 109.6; 109.1; 96.4; 70.9; 70.8; 70.7; 68.4; 66.4; 26.3; 26.0; 25.1; 24.4; 21.7; 17.6.

MS (ESI) m/z (% rel. int.): 1031 (1); 1030 (12); 1029 (55); 1028 (100) (isotope [M+H]⁺).

HRMS (ESI): C₆₀H₅₃N₅O₈F₃⁺ [M+H]⁺ (m/z): calc. 1028.3846; found 1028.3862.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 644.2 (3.24); 589.4 (3.61); 548.4 (3.66); 514.4 (4.16); 417.4 (5.30, Soret band).

[5-[3-(1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranosyl-6-oxy)-4-nitrophenyl]-10,15,20-tris(3-chlorophenyl)porphyrinato] zinc(II) (**4f**)



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 11.2 mg of porphyrin **2f** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH, 98:2 as an eluent giving purple solid of porphyrin **4f** (10.4 mg, 74%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 9.00-8.92 (m, 8H, H ^{β}); 8.28 (m, 1H, H-Ar); 8.22 (s, 3H, H-Ar); 8.14-8.08 (m, 3H, H-Ar); 8.03-7.98 (m, 1H, H-Ar); 7.95-7.89 (m, 1H, H-Ar); 7.82-7.77 (m, 3H, H-Ar); 7.73-7.66 (m, 3H, H-Ar); 5.41-5.36 (m, 1H, H-gal); 4.65 (dd, 1H, J = 8.0

Hz, $J = 2.1$ Hz, H-gal); 4.49-4.44 (m, 1H, H-gal); 4.39-4.30 (m, 3H, H-gal); 4.30-4.26 (m, 1H, H-gal); 1.37 (s, 3H, CH₃); 1.32-1.25 (m, 9H, 3xCH₃).

¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.7; 150.7; 150.6; 150.4; 150.4; 150.3; 150.3; 150.2; 149.6; 149.5; 149.5; 144.4; 144.3; 139.4; 134.4; 134.4; 133.1; 133.0; 132.7; 132.6; 132.5; 132.4; 131.9; 131.8; 128.2; 128.0; 128.0; 127.0; 124.0; 121.5; 121.4; 120.3; 120.2; 120.2; 118.6; 109.6; 109.1; 96.3; 70.9; 70.8; 70.7; 68.7; 68.6; 68.6; 66.5; 26.2; 26.0; 25.0; 24.5.

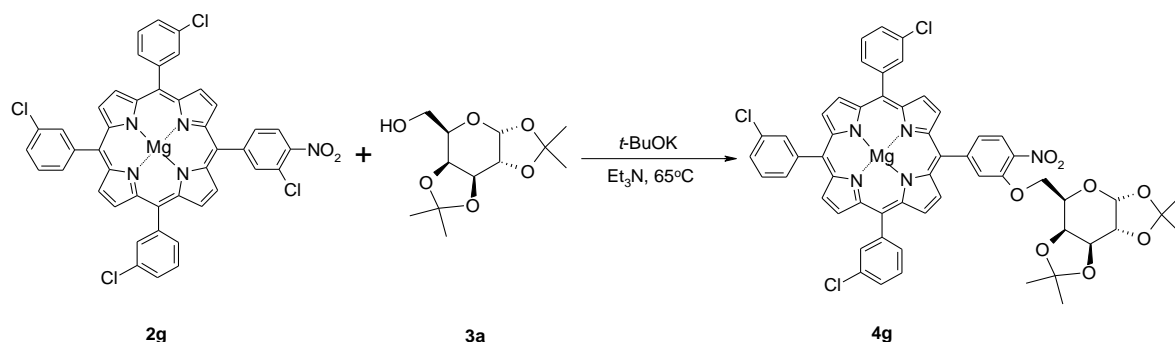
MS (ESI) m/z (% rel. int.): 1112 (20); 1111 (28); 1110 (44); 1109 (50); 1108 (88); 1107 (62); 1106 (100); 1105 (35); 1104 (50) (isotope [M+Na]⁺);

1090 (10); 1089 (14); 1088 (29); 1087 (45); 1086 (59); 1085 (68); 1084 (62); 1083 (71); 1082 (38); 1081 (35), (isotope [M]⁺ and [M+H]⁺).

HRMS (ESI): C₅₆H₄₂N₅O₈Cl₃Zn⁺ [M+H]⁺ (m/z): calc. 1081.1390; found 1081.1418.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 595.8 (3.78); 555.8 (4.40); 425.0 (5.54, Soret band).

[5-[3-(1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranosyl-6-oxy-)-4-nitrophenyl]-10,15,20-tris(3-chlorophenyl)porphyrinato] magnesium (II) (**4g**)



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.7 mg porphyrin **2g** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CH₂Cl₂/MeOH/Et₃N, 100:2:1, as an eluent giving purple solid of porphyrin **4g** (5.3 mg, 39%).

¹H NMR (500 MHz, DMSO-*d*₆) δ [ppm] = 8.91-8.89 (m, 1H, H^β); 8.87 (d, 1H, $J = 4.5$ Hz, H^β); 8.81-8.76 (m, 6H, H^β); 8.29 (d, 1H, $J = 8.2$ Hz, H-Ar); 8.25-8.12 (m, 7H, H-Ar); 7.94-7.88 (m, 4H, H-Ar); 7.85-7.79 (m, 3H, H-Ar); 5.47-5.43 (m, 1H, H-gal); 4.66-4.61 (m, 1H, H-gal); 4.55-4.49 (m, 1H, H-gal); 4.42-4.34 (m, 3H, H-gal); 4.25-4.19 (m, 1H, H-gal); 1.48-1.44 (m, 3H, CH₃); 1.28 (s, 3H, CH₃); 1.24-1.21 (m, 3H, CH₃); 1.19 (s, 3H, CH₃).

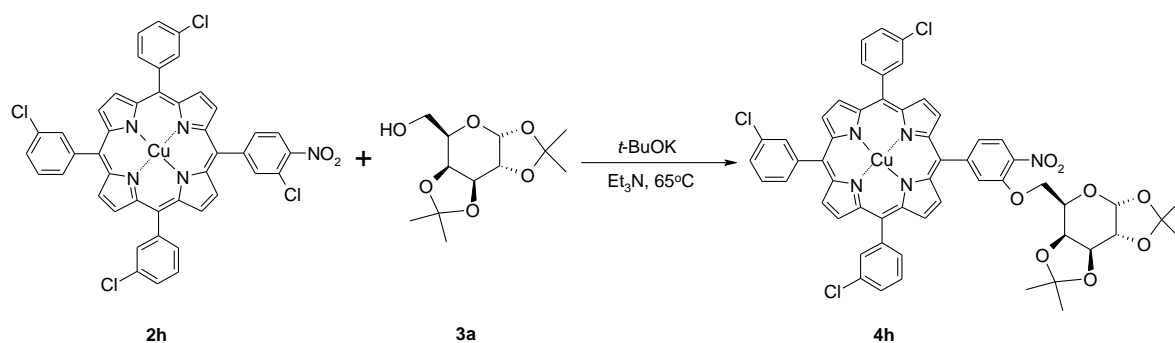
¹³C NMR (125 MHz, DMSO-*d*₆) δ [ppm] = 149.5; 149.5; 149.1; 149.0; 149.0; 148.8; 148.6; 145.0; 139.0; 133.6; 132.9; 132.0; 132.0; 131.9; 131.8; 131.5; 128.3; 127.6; 127.2; 123.2; 120.1; 120.0; 120.0; 119.2; 108.6; 108.1; 95.6; 70.3; 69.9; 69.8; 68.8; 68.8; 66.4; 66.3; 25.8; 25.8; 24.9; 24.2.

MS (ESI) m/z (% rel. int.): 1071 (6); 1070 (13); 1069 (26); 1068 (46); 1067 (59); 1066 (100); 1065 (50); 1064 (69) (isotope $[M+Na]^+$).

HRMS (ESI): $C_{56}H_{42}N_5O_8Cl_3MgNa^+$ $[M+Na]^+$ (m/z): calc. 1064.1847; found 1064.1851.

UV-VIS ($CHCl_3$) λ_{max} [nm] (log ϵ): 604.0 (3.76); 564.6 (4.16); 427.2 (5.51, Soret band).

[5-[3-(1,2:3,4-di-*O*-isopropylidene- α -*D*-galactopyranosyl-6-oxy)-4-nitrophenyl]-10,15,20-tris(3-chlorophenyl)porphyrinato] copper(II) (**4h**)



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 11.2 mg porphyrin **2h** (0.013 mmol), 6.8 mg of sugar **3a** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using $CHCl_3/\text{MeOH}$, 99:1 as an eluent giving purple solid of porphyrin **4h** (3.8 mg, 27%).

^1H NMR and ^{13}C NMR spectra were not measured due to paramagnetic properties of compound **4h**.

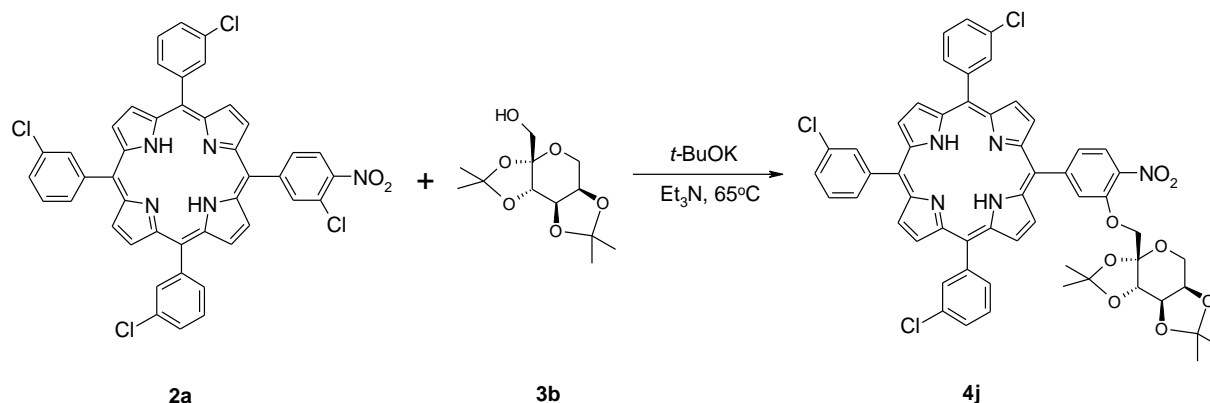
MS (ESI) m/z (% rel. int.): 1111 (5); 1110 (7); 1109 (20); 1108 (32); 1107 (65); 1106 (54); 1105 (100); 1104 (42); 1103(66) (isotope $[M+Na]^+$);

2195 (3); 2194 (5); 2193 (8); 2192 (12); 2191 (19); 2190 (24); 2189 (29); 2188 (32); 2187 (29); 2186 (20); 2185 (20); 2184 (7); 2183 (5) (isotope $[2M+Na]^+$).

HRMS (ESI): $C_{56}H_{42}N_5O_8Cl_3CuNa^+$ $[M+Na]^+$ (m/z): calc. 1103.1293; found 1103.1321.

UV-VIS ($CHCl_3$) λ_{max} [nm] (log ϵ): 539.2 (4.53); 416.4 (5.78, Soret band).

5-[3-(2,3:4,5-di-*O*-isopropylidene- β -*D*-fructopyranosyl-1-oxy)-4-nitrophenyl]-10,15,20-tris(3-chlorophenyl)porphyrin (**4j**)



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.3 mg of porphyrin **2a** (0.013 mmol), 6.8 mg of sugar **3b** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The reaction was stirred for 18 h. The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 99:1 as an eluent giving purple solid of porphyrin **4j** (8.5 mg, 64%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.91-8.84 (m, 8H, H ^{β}); 8.26-8.21 (m, 4H, H-Ar); 8.14-8.09 (m, 3H, H-Ar); 8.06 (d, 1H, J = 5.2 Hz, H-Ar); 7.94 (d, 1H, J = 8.1 Hz, H-Ar); 7.84-7.79 (m, 3H, H-Ar); 7.75-7.68 (m, 3H, H-Ar); 4.86 (br s, 1H, H-gal); 4.72 (dd, 1H, J = 8.0 Hz, J = 2.8 Hz, H-gal); 4.52-4.46 (m, 1H, H-gal); 4.33-4.26 (m, 1H, H-gal); 4.25-4.12 (m, 1H, H-gal); 3.99-3.94 (m, 1H, H-gal); 3.67 (d, 1H, J = 13.1 Hz) 1.61 (s, 3H, CH₃); 1.58 (s, 3H, CH₃); 1.34-1.28 (m, 6H, 2x CH₃); -2.86 (s, 2H, NH)

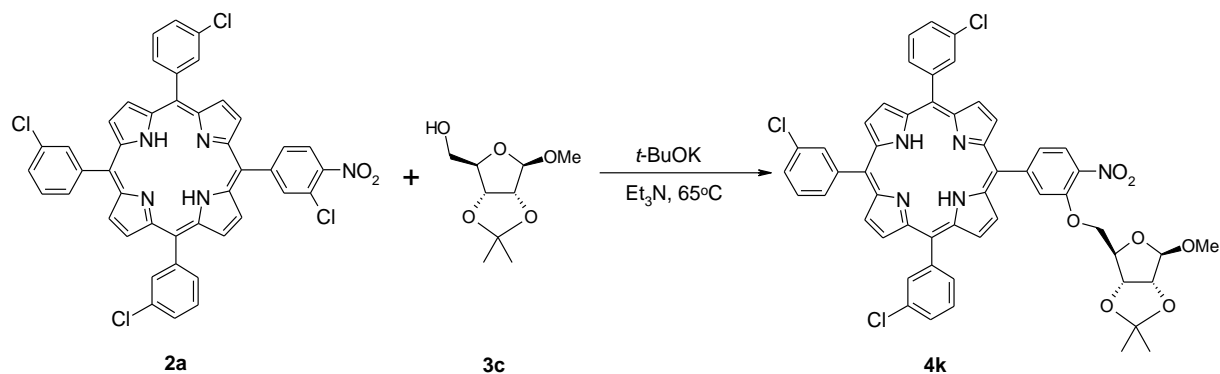
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.3; 150.3; 150.2; 148.5; 143.7; 143.6; 143.6; 139.6; 134.5; 133.2; 132.9; 128.5; 128.4; 128.1; 124.0; 121.7; 121.6; 119.5; 119.3; 119.2; 117.6; 109.7; 109.2; 109.2; 101.5; 71.0; 70.2; 70.1; 70.0; 61.6; 26.9; 26.0; 25.5; 24.0.

MS (ESI) m/z (% rel. int.): 970 (6); 969 (12); 968 (33); 967 (45); 966 (100); 965 (46); 964 (77) (isotope [M+H]⁺).

HRMS (ESI): C₅₃H₄₁N₅O₇Cl₃⁺ [M+H]⁺ (m/z): calc. 964.2072; found 964.2082.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 644.8 (3.40); 589.2 (3.75); 549.4 (3.81); 514.8 (4.26); 418.4 (5.39, Soret band).

5-[4-nitro-3-(1-*O*-methyl-2,3-*O*-isopropylidene- β -D-ribofuranosyl-5-oxy)phenyl]-10,15,20-tris(3-chlorophenyl)porphyrin (**4k**)



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.3 mg of porphyrin **2a** (0.013 mmol), 5.3 mg of sugar **3c** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The reaction mixture was stirred for 18 h. The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 99:1 as an eluent giving purple solid of porphyrin **4k** (6.5 mg, 52%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.91 (d, 2H, H ^{β}); 8.88 (s, 4H, H ^{β}); 8.84 (d, 2H, H ^{β}); 8.27-8.21 (m, 4H, H-Ar); 8.14-8.09 (m, 3H, H-Ar); 7.97-7.90 (m, 2H, H-Ar); 7.84-7.79 (m, 3H, H-Ar); 7.75-7.68 (m, 3H, H-Ar); 4.97-4.94 (m, 2H, H-ryb); 4.71-4.66 (m, 1H, H-ryb); 4.63 (d, 1H, J = 6.1 Hz, H-ryb); 4.34-4.27 (m, 1H, H-ryb); 4.25-4.18 (m, 1H, H-ryb); 3.16 (s, 3H, O-CH₃); 1.51 (s, 3H, CH₃); 1.36 (s, 3H, CH₃); -2.86 (s, 2H, 2xNH).

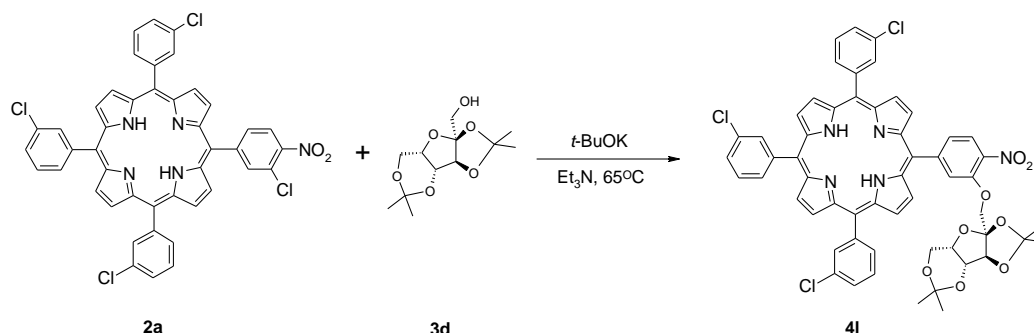
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.1; 148.6; 143.6; 143.6; 140.0; 134.5; 133.2; 132.8; 128.5; 128.5; 128.2; 127.2; 124.1; 121.3; 119.5; 119.3; 117.4; 112.8; 110.0; 85.2; 84.2; 82.0; 70.4; 55.2; 26.6; 25.1.

MS (ESI) m/z (% rel. int.): 970 (6); 969 (12); 968 (33); 967 (45); 966 (100); 965 (46); 964 (77) (isotope [M+H]⁺).

HRMS (ESI): C₅₃H₄₁N₅O₇Cl₃⁺ [M+H]⁺ (m/z): calc. 964.2072; found 964.2082.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 644.8 (3.40); 589.2 (3.75); 549.4 (3.81); 514.8 (4.26); 418.4 (5.39, Soret band).

*5-[4-nitro-3-(2,3:4,6-di-O-isopropylidene- α -L-sorbofuranosyl-1-oxy)phenyl]-10,15,20-tris(3-chlorophenyl)porphyrin (**4l**)*



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.3 mg of porphyrin **2a** (0.013 mmol), 6.8 mg of sugar **3d** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The reaction mixture was stirred for 18 h. The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH 99:1 as an eluent giving purple solid of porphyrin **4l** (9.3 mg, 70%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.94–8.86 (m, 8H, H ^{β}); 8.28–8.23 (m, 4H, H-Ar); 8.16–8.10 (m, 4H, H-Ar); 7.93 (d, 1H, J = 8.1 Hz, H-Ar); 7.85–7.79 (m, 3H, H-Ar); 7.76–7.68 (m, 3H, H-Ar); 4.89 (s, 1H, H-sorb); 4.71–4.63 (m, 1H, H-sorb); 4.51–4.45 (m, 1H, H-sorb); 4.44 (s, 1H, H-sorb); 4.17 (s, 1H, H-sorb); 3.99 (m, 1H, H-sorb); 3.87 (d, 1H, J = 13.7 Hz, H-sorb); 1.63 (s, 3H, CH₃); 1.58 (s, 3H, CH₃); 1.39 (s, 3H, CH₃); 1.25 (s, 3H, CH₃); -2.83 (s, 2H, NH).

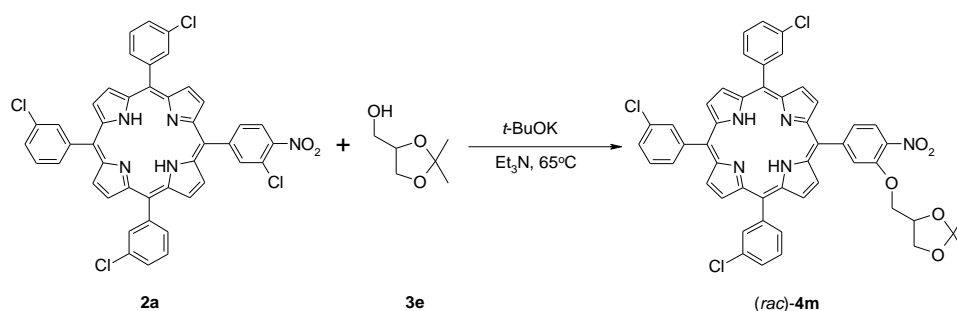
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.3; 150.2; 148.6; 143.7; 143.6; 139.5; 134.5; 134.5; 133.2; 132.8; 128.5; 128.4; 128.1; 127.3; 127.3; 124.0; 121.5; 121.4; 119.4; 119.3; 119.2; 117.6; 113.6; 112.9; 97.5; 84.2; 73.2; 72.8; 68.7; 60.4; 29.1; 28.0; 26.6; 18.6.

MS (ESI) m/z (% rel. int.): 1031 (1); 1030 (12); 1029 (55); 1028 (100) (isotope [M+H]⁺).

HRMS (ESI): C₆₀H₅₃N₅O₈F₃⁺ [M+H]⁺ (m/z): calc. 1028.3846; found 1028.3862.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 645.0 (3.60); 588.6 (3.91); 549.2 (4.19); 515.4 (4.45); 416.8 (5.35, Soret band).

*5-[4-nitro-3-(1,2-isopropylidene-glycerol-3-oxy)-phenyl]-10,15,20-tris(3-chlorophenyl)porphyrin ((rac)-**4m**)*



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 10.3 mg of porphyrin **2a** (0.013 mmol), 3.4 mg of alcohol **3e** (0.026 mmol), 0.35 mL of triethylamine and 29.5 mg of potassium *tert*-butoxide (0.263 mmol). The reaction mixture was stirred for 18 h. The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃ as an eluent giving purple solid of porphyrin (*rac*)-**4m** (7.2 mg, 62%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.93-8.82 (m, 8H, H ^{β}); 8.26 (d, 1H, 8.1 Hz, H-Ar); 8.23 (br s, 3H, H-Ar); 8.11 (m, 3H, H-Ar); 7.99 (br s, 1H, H-Ar); 7.93 (d, 1H, J = 7.7 Hz, H-Ar); 7.84-7.78 (m, 3H, H-Ar); 7.75-7.68 (m, 3H, H-Ar); 4.59-4.53 (m, 1H, H-gly); 4.36-4.29 (m, 1H, H-gly); 4.28-4.20 (m, 2H, H-gly); 4.11 (dd, 1H, J = 8.5 Hz J = 5.9 Hz, H-gly); 1.37 (s, 6H, CH₃); -2.87 (s, 2H, NH).

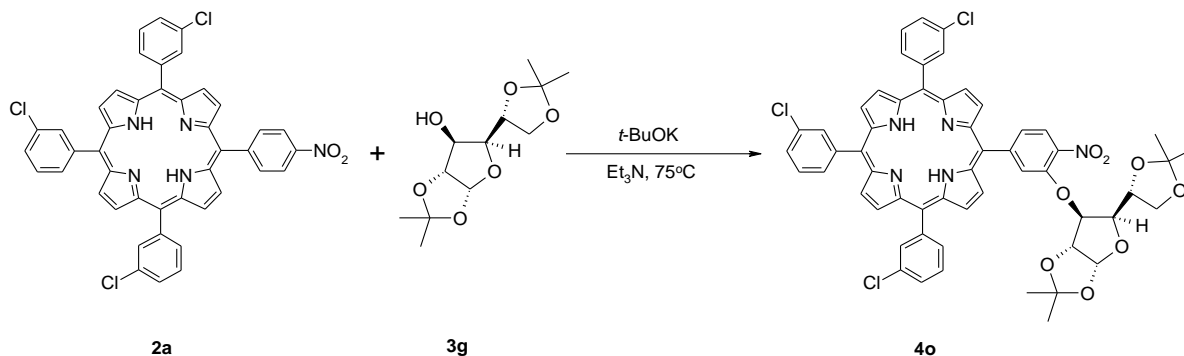
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.4; 148.6; 143.6; 143.6; 139.7; 134.5; 133.2; 132.8; 128.5; 128.5; 128.2; 127.2; 124.1; 121.4; 119.5; 119.3; 117.5; 110.0; 73.8; 70.0; 66.8; 26.8; 25.5.

MS (ESI) m/z (% rel. int.): 898 (4); 897 (11); 896 (31); 895 (41); 894 (100); 893 (41); 892 (89) (isotope [M+H]⁺).

HRMS (ESI): C₅₀H₃₇N₅O₅Cl₃⁺ [M+H]⁺ (m/z): calc. 892.1860; found 892.1852.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 644.8 (3.41); 589.0 (3.74); 549.4 (3.81); 514.8 (4.26); 419.2 (5.45, Soret band).

*5-[3-(1,2:5,6-Di-*O*-isopropylidene- α -D-glucofuranosyl-3-oxy)-4-nitrophenyl]10,15,20-tris(3-chlorophenyl)porphyrin (**4o**)*



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 20.6 mg of porphyrin **2a** (0.026 mmol), 13.6 mg of sugar **3g** (0.052 mmol), 0.7 mL of triethylamine and 73.0 mg of potassium *tert*-butoxide (0.65 mmol). The reaction mixture was stirred for 48 h at 75°C. The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH, 99:1 as an eluent giving purple solid of porphyrin **4o** (15.4 mg, 58%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.95-8.84 (m, 8H, H ^{β}); 8.29-8.21 (m, 4H, H-Ar); 8.17 (br s, 1H, H-Ar); 8.12 (m, 3H, H-Ar); 7.99 (d, 1H, J = 8.2 Hz, H-Ar); 7.85-7.80 (m, 3H, H-Ar); 7.76-7.69 (m, 3H, H-Ar); 6.10 (br s, 1H, H-glu); 5.01 (br s, 1H, H-glu); 4.93-4.88 (m, 1H, H-

glu); 4.69-4.63 (m, 1H, H-glu); 4.27-4.20 (m, 2H, H-glu); 4.12-4.07 (m, 1H, H-glu); 1.38-1.34 (m, 3H, CH₃); 1.31-1.25 (m, 3H, CH₃); 1.24-1.18 (m, 6H, 2xCH₃); -2.85 (s, 2H, NH).

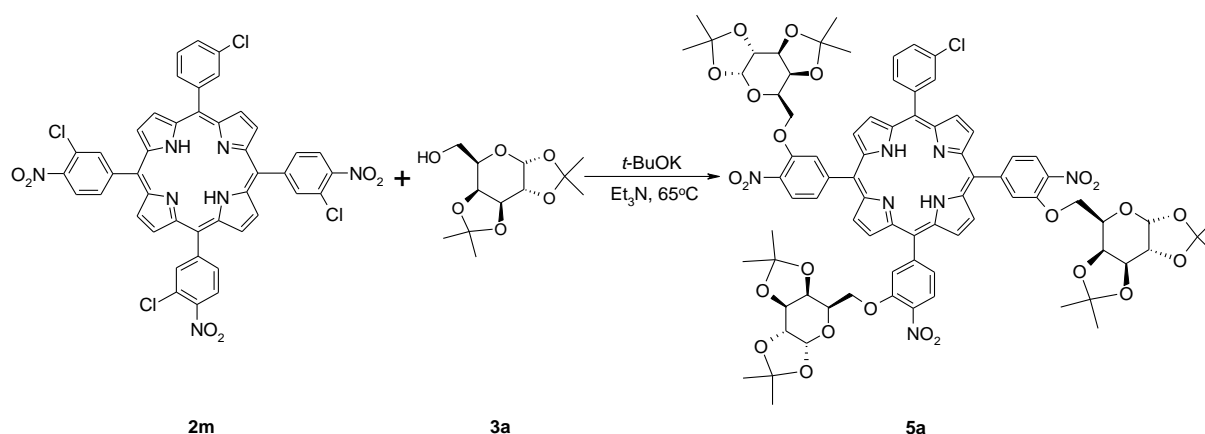
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 149.2; 149.2; 148.6; 143.6; 143.6; 140.4; 140.3; 134.5; 133.2; 132.8; 132.8; 128.5; 128.5; 128.2; 128.2; 128.0; 127.9; 124.2; 122.7; 122.6; 122.5; 119.6; 119.3; 119.3; 117.3; 114.2; 114.1; 112.5; 112.5; 109.7; 109.6; 105.2; 82.9; 82.8; 82.8; 82.6; 80.9; 72.2; 67.7; 27.0; 26.7; 26.3; 25.2.

MS (ESI) m/z (% rel. int.): 1027 (3); 1026 (7); 1025 (20); 1024 (36); 1023 (54); 1022 (100); 1021 (51); 1020 (87) (isotope [M+H]⁺).

HRMS (ESI): C₅₆H₄₅N₅O₈Cl₃⁺ [M+H]⁺ (m/z): calc. 1020.2334; found 1020.2349.

UV-VIS (CHCl₃) λ_{\max} [nm] (log ϵ): 645.4 (3.43); 589.4 (3.78); 550.4 (3.84); 514.8 (4.27); 420.0 (5.52, Soret band).

5,10,15-tris[3-(1,2:3,4-di-O-isopropylidene- α -D-galactopyranosyl-6-oxy)-4-nitrophenyl]-20-(3-chlorophenyl)porphyrin (5a)



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 11.5 mg of porphyrin **2m** (0.013 mmol), 20.4 mg of sugar **3a** (0.078 mmol), 0.35 mL of triethylamine and 35.0 mg of potassium *tert*-butoxide (0.312 mmol). The work-up performed as in general procedure. Final product was isolated by column chromatography using CHCl₃/MeOH, 96:4 as an eluent giving purple solid of porphyrin **5a** (6.3 mg, 31%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.94-8.83 (m, 8H, H-Ar); 8.32-8.26 (m, 3H, H-Ar); 8.22 (s, 1H, H-Ar); 8.11 (m, 1H, H-Ar); 8.01 (s, 3H, H-Ar); 7.94-7.86 (m, 3H, H-Ar); 7.83 (m, 1H, H-Ar); 7.73 (m, 1H, H-Ar); 5.51-5.46 (m, 3H, H-gal), 4.68 (m, 3H, H-gal); 4.49 (m, 3H, H-gal); 4.38 (s, 9H, H-gal); 4.35-4.31 (m 3H, H-gal); 1.61 (s, 9H, CH₃); 1.34 (s, 9H, CH₃); 1.30 (s, 18H, CH₃); -2.89 (s, 2H, NH).

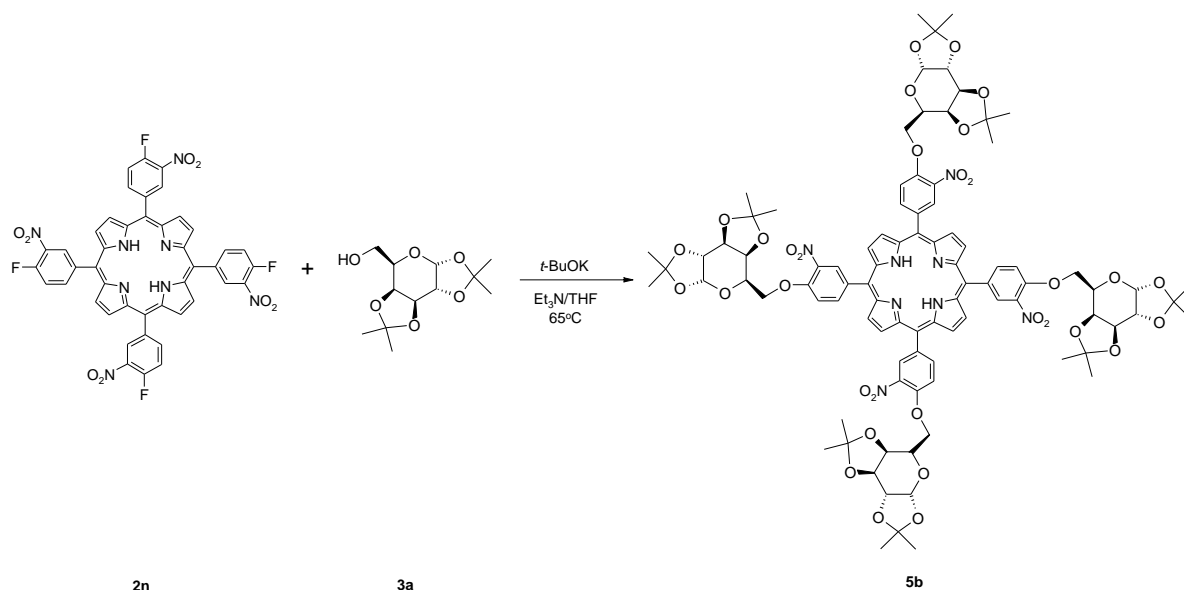
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.8; 150.8; 148.4; 148.3; 139.7; 134.5; 134.4; 133.3; 132.8; 132.8; 128.6; 128.2; 127.1; 124.2; 121.5; 121.6; 121.4; 119.9; 118.3; 118.3; 118.2; 118.1; 114.1; 109.7; 109.2; 96.4; 70.9; 70.8; 70.7; 68.7; 66.6; 26.3; 26.0; 25.1; 24.5.

MS (APCI) m/z (% rel. int.): 1563 (2); 1562 (11); 1561 (34); 1560 (72); 1559 (87); 1558 (100) (isotope $[M+H]^+$).

HRMS (APCI): $C_{80}H_{81}N_7O_{24}Cl^+ [M+H]^+$ (m/z): calc. 1558.5021; found 1558.5009.

UV-VIS ($CHCl_3$) λ_{max} [nm] (log ϵ): 644.6 (3.40); 590.6 (3.82); 550.8 (3.91); 515.8 (4.33); 422.6 (5.57, Soret band).

*5,10,15,20-tetrakis[4-(1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranosyl-6-oxy)-3-nitrophenyl]porphyrin (5b)*



Following the general procedure for the synthesis of porphyrin-sugar hybrids. Starting from 11.3 mg of porphyrin **2n** (0.013 mmol), 27.1 mg of sugar **3a** (0.104 mmol), 0.25 mL of triethylamine, 0.1 mL of tetrahydrofuran and 37.9 mg of potassium *tert*-butoxide (0.338 mmol). The work-up performed as in general procedure. Final product was isolated after two purifications by column chromatography the first one used $CHCl_3/MeOH$, 96:4 as an eluent. The analytical sample was obtained after second column chromatography (eluent: ethyl acetate/*n*-hexane 2:3) giving purple solid of porphyrin **5b** (15.3 mg, 64%).

1H NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.92-8.85 (m, 8H, H^B); 8.72 (s, 4H, H-Ar); 8.41-8.32 (m, 4H, H-Ar); 7.61-7.53 (m, 4H, H-Ar); 5.67 (d, 4H, $J = 4.9$ Hz, H-gal); 4.80 (dd, 4H, $J = 7.8$ Hz, $J = 2.5$ Hz, H-gal); 4.66-4.55 (m, 12H, H-gal); 4.50-4.42 (m, 8H, H-gal); 1.69 (s, 12H, CH_3); 1.57 (s, 12H, CH_3); 1.47 (s, 12H, CH_3); 1.43 (s, 12H, CH_3); -2.87 (s, 2H, NH).

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] = 152.3; 139.5; 139.4; 138.6; 134.6; 130.6; 117.8; 113.8; 113.7; 109.8; 109.3; 96.6; 71.0; 71.0; 70.8; 68.7; 66.5; 26.3; 26.2; 25.2; 24.6.

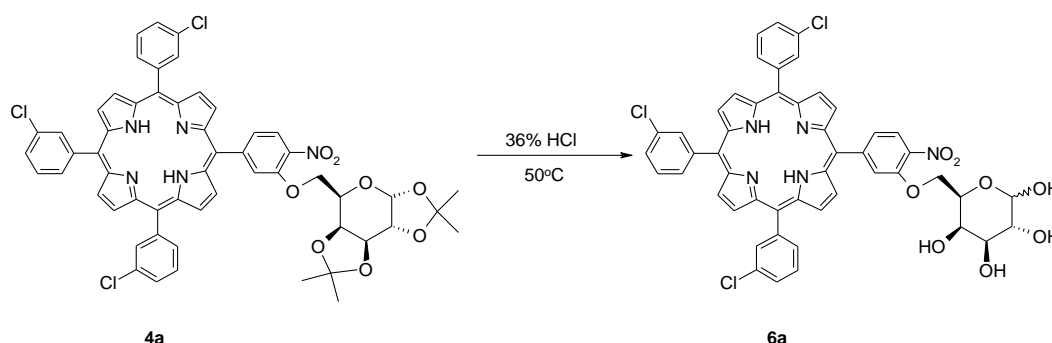
MS (APCI) m/z (% rel. int.): 1832 (2); 1831 (7); 1830 (21); 1829 (51); 1828 (100); 1827 (93); (isotope $[M+H]^+$).

HRMS (APCI): $C_{92}H_{99}N_8O_{32}^+ [M+H]^+$ (m/z): calc. 1827.6365; found 1827.6353.

UV-VIS (CHCl_3) λ_{max} [nm] ($\log \epsilon$): 649.0 (3.45); 591.6 (3.72); 554.2 (3.88); 517.6 (4.23); 424.2 (5.54, Soret band).

Characterization and procedures for deprotected sugar hybrids

5-[3-(*D*-galactopyranosyl-6-oxy-)-4-nitro-phenyl]-10,15,20-tris-(3-chlorophenyl)porphyrin (**6a**)



In a 10 mL sealed tube 49.0 mg of porphyrin **4a** (0.052 mmol) and 3.0 mL of 36% HCl_{aq} were added. The reaction mixture was stirred vigorously at 50°C for 20 min. Mixture was cooled to r.t. and transferred to a separatory funnel with 30 mL of CHCl₃ and 30 mL of saturated aqueous solution of sodium carbonate. Organic phase was separated and water phase was extracted 2x10 mL of CHCl₃. Combined organic phases were washed with 10 mL of saturated solution of sodium carbonate and then with 10 mL of water. Solvent was evaporated off. Crude product was purified by column chromatography (eluent: CHCl₃/MeOH, 94:6) yielding purple solid of porphyrin **6a** (31.6 mg, 70%) as a mixture of two inseparable isomers (A:B, ratio 2.8:1).

¹H NMR (500 MHz, DMSO-*d*₆) δ [ppm] = 9.02-8.94 (m, 2H, H ^{β} , isom A+B); 8.86 (br s, 6H, H ^{β} , isom A+B); 8.32-8.26 (m, 3H, H-Ar, isom A+B); 8.24 (br s, 1H, H-Ar, isom A+B); 8.21-8.16 (m, 3H, H-Ar, isom A+B); 7.96-7.90 (m, 4H, H-Ar, isom A+B); 7.87-7.81 (m, 3H, H-Ar, isom A+B); 6.57 (d, 0.63H, *J* = 6,8 Hz, H-gal-isom A); 6.29 (d, 0.63H, *J* = 4.7 Hz, H-gal-isom A); 6.20 (m, 0.24H, H-gal-isom B); 6.11 (d, 0.24H, *J* = 6.3 Hz, H-gal-isom B); 5.20 (d, 0.24H, *J* = 4.6Hz, H-gal-isom B); 5.14 (d, 0.24H, *J* = 6.6 Hz, H-gal-isom B); 5.11-5.07 (m, 0.24H, H-gal-isom B); 5.05 (d, 0.24H, *J* = 6.7 Hz, H-gal-isom B); 4.91 (t, 0.63H, *J* = 4.2 Hz, H-gal-isom A); 4.85-4.79 (m, 0.48H, H-gal-isom B); 4.76 (d, 0.24H, *J* = 4.2 Hz, H-gal-isom B); 4.69 (d, 0.63H, *J* = 4.6 Hz H-gal-isom A); 4.66 (d, 0.63H, *J* = 5.6Hz, H-gal-isom A); 4.53 (d, 0.63H, *J* = 4.3 Hz, H-gal-isom A); 4.52-4.47 (m, 0.63H, H-gal-isom A); 4.44-4.35 (m, 1.50H, H-gal-isom A + H-gal-isom B); 4.34-4.25 (m, 2.52H, H-gal-isom A); 3.98-3.91 (m, 0.72H, H-gal-isom B); 3.90-3.85 (0.63H, H-gal-isom A); 3.83-3.79 (m, 0.63H, H-gal-isom A); 3.77-3.73 (m, 0.63H, H-gal-isom A); 3.68-3.58 (m, 0.96H, H-gal-isom B); 3.50-3.43 (m, 0.63H, H-gal-isom A); 3.23-3.16 (m, 0.72H, H-gal-isom B); -3.02 (s, 2H, NH isom A+B).

¹³C NMR (125 MHz, DMSO-*d*₆) δ [ppm] = 150.4; 147.8; 147.7; 143.5; 134.1; 133.3; 132.5; 129.3; 128.9; 124.0; 119.3; 119.1; 92.2; 73.5; 72.7; 72.2; 69.4; 68.9.

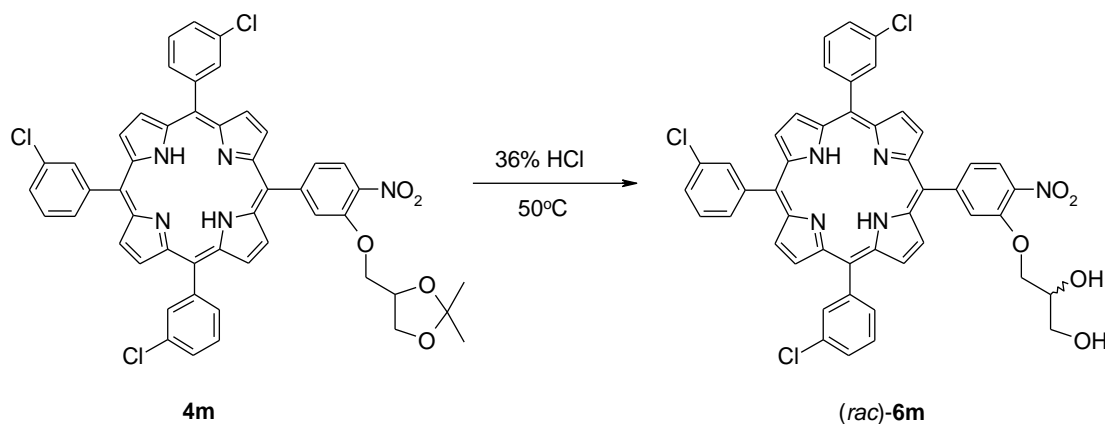
MS (ESI) *m/z* (% rel. int.): 967 (16); 966 (30); 965 (44); 964 (83); 963 (50); 962 (67) (isotope [M+Na]⁺);

946 (11); 945 (19); 944 (48); 943 (52); 942 (100); 941 (54); 940 (92) (isotope [M+H]⁺).

HRMS (ESI): C₅₀H₃₇N₅O₈Cl₃⁺ [M+H]⁺ (*m/z*): calc. 940.1708; found 940.1688.

UV-VIS (CHCl₃) λ_{max} [nm] (log ϵ): 642.6 (3.45); 590.2 (3.97); 550.2 (3.97); 515.6 (4.47); 420.0 (5.74, Soret band).

5-[3-(glycerol-1-oxy)-4-nitrophenyl]-10,15,20-tris-(3-chlorophenyl)porphyrin ((rac)-6m)



In a 6 mL sealed tube 16.1 mg of porphyrin (*rac*)-**4m** (0.018 mmol) and 1.0 mL of 36% HCl_{aq} were added. The reaction mixture was stirred vigorously at 50°C for 30 min. Mixture was cooled to r.t. and transferred to a separatory funnel with 20 mL of CHCl₃ and 20 mL of saturated aqueous solution of sodium carbonate. Organic phase was separated and water phase was extracted 2x10 mL of CHCl₃. Combined organic phases were washed with 10 mL of saturated solution of sodium carbonate and then with 10 mL of water. Solvent was evaporated off. Crude product was purified by column chromatography (eluent: CHCl₃/MeOH, 95:5) yielding purple solid of porphyrin (*rac*)-**6m** (13.5 mg, 88%).

¹H NMR (500 MHz, CDCl₃) δ [ppm] = 8.93-8.86 (m, 6H, H ^{β}); 8.84 (d, 2H, J = 4.6 Hz); 8.32 (d, 1H, J = 8.1 Hz, H-Ar); 8.23 (br s, 3H, H-Ar); 8.13-8.09 (m, 3H, H-Ar); 7.98 (br s, 1H, H-Ar); 7.95 (d, 1H, 8.3 Hz, H-Ar); 7.83-7.79 (m, 3H, H-Ar); 7.74-7.67 (m, 3H, H-Ar); 4.42-4.36 (m, 1H, H-gly); 4.35-4.30 (m, 1H, H-gly); 4.19 (s, 1H, H-gly); 3.92-3.81 (m, 2H, H-gly); 3.08 (br s, 1H, OH); 2.24 (br s, 1H, OH); -2.86 (br s, 2H, NH).

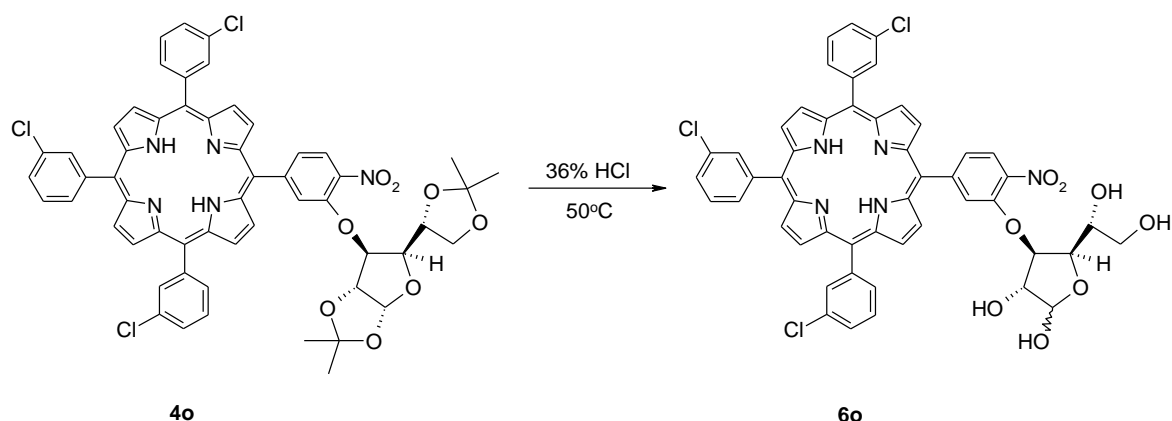
¹³C NMR (125 MHz, CDCl₃) δ [ppm] = 150.7; 149.3; 143.6; 143.6; 139.2; 134.5; 133.2; 132.8; 128.5; 128.5; 128.2; 127.4; 124.5; 121.4; 119.6; 119.3; 117.2; 72.0; 71.9; 69.8; 63.4.

MS (APCI) m/z (% rel. int.): 858 (3); 857 (11); 856 (28); 855 (34); 854 (100); 853 (42); 852 (83) (isotope [M+H]⁺).

HRMS (APCI): C₄₇H₃₃N₅O₅Cl₃⁺ [M+H]⁺ (m/z): calc. 852.1547; found 852.1556.

UV-VIS (CHCl₃) λ_{max} [nm] (log ϵ): 644.6 (3.50); 589.2 (3.83); 550.6 (3.92); 515.2 (4.35); 419.6 (5.54, Soret band).

5-[3-(D-glucofuranosyl-3-oxy)-4-nitrophenyl]-10,15,20-tris-(3-chlorophenyl)porphyrin (6o)



In a 6 mL sealed tube 12.2 mg of porphyrin **4o** (0.012 mmol) and 1 mL of 36% HCl_{aq} were added. The reaction mixture was stirred vigorously at 50°C for 30 min. Then it was cooled to r.t. and transferred to a separatory funnel with 20 mL of CHCl₃ and 20 mL of saturated aqueous solution of sodium carbonate. Organic phase was separated and water phase was extracted 2x10 mL of CHCl₃. Combined organic phases were washed with 10 mL of saturated solution of sodium carbonate and then with 10 mL of water. Solvent was evaporated off. Crude product was purified by column chromatography (eluent: CHCl₃/MeOH, 95:5) yielding purple solid of porphyrin **6o** (6.9 mg, 61%) as a mixture of two inseparable isomers (A:B, ratio 1:1.2)..

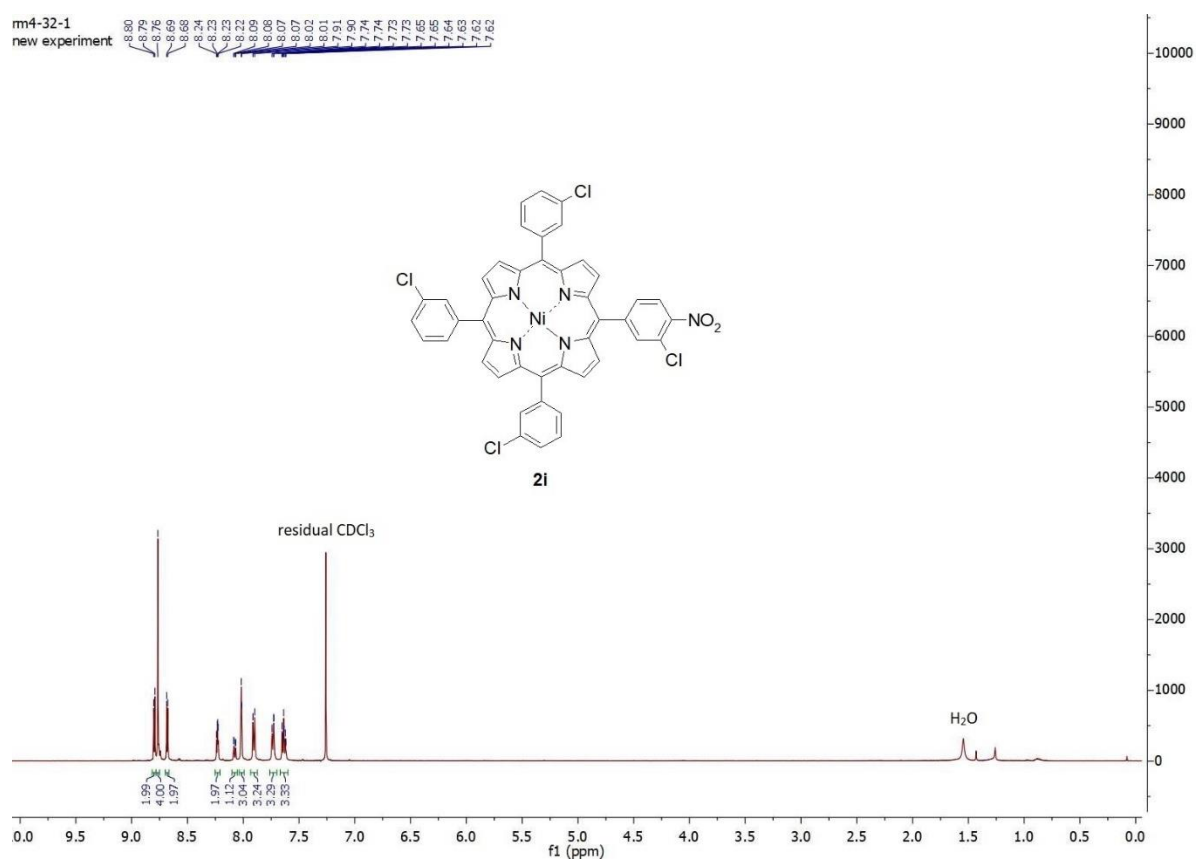
¹H NMR (500 MHz, Acetone-d₆) δ [ppm] = 9.53-9.35 (m, 2H, H^β); 9.37 (br s, 6H, H^β); 9.06-9.01 (m, 1H, H-Ar); 8.78-8.81 (m, 3H, H-Ar); 8.69-8.62 (m, 3H, H-Ar); 8.62-8.58 (m, 1H, H-Ar); 8.38-8.24 (m, 7H, H-Ar); 6.31 (s, 0.45H, H-glu isom A); 5.99 (s, 0.45H, H-glu isom A); 5.59 (s, 0.55H-glu isom B); 5.36 (m, 0.55H, H-glu isom B); 5.30-5.15 (m, 1.65H, H-glu isom B); 4.99-4.94 (m, 0.45H, H-glu isom A); 4.75-4.69 (m, 0.45H, H-glu isom A); 4.38-4.29 (m, 1H, H-glu isom A + isom B); 4.28-4.18 (m, 1.65H, H-glu isom B); 4.17-4.02 (m, 2.55H, H-glu isom A + isom B); 3.98-3.94 (m, 0.45H, H-glu isom A); 3.76-3.71 (m, 0.45H, H-glu isom A); -2.40 (s, 2H, 2xNH).

MS (APCI) *m/z* (% rel. int.): 944 (23); 943 (35); 942 (100); 941 (32); 940 (78) (isotope [M+H]⁺).

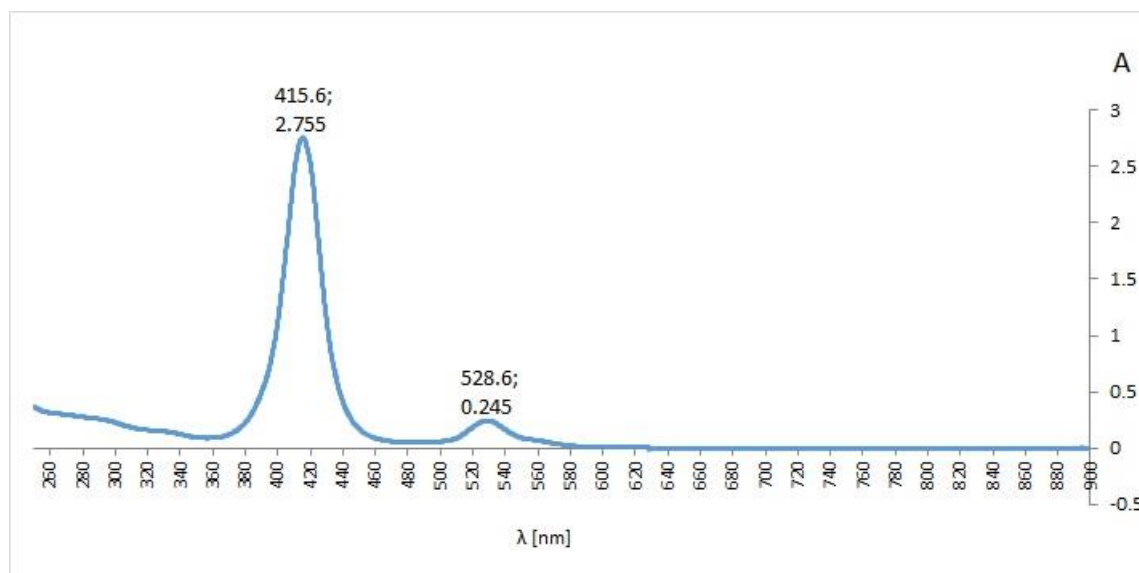
HRMS (APCI): C₅₀H₃₇N₅O₈Cl₃⁺ [M+H]⁺ (*m/z*): calc. 940.1708; found 940.1717.

UV-VIS (CHCl₃) λ_{max} [nm] (log ε): 644.4 (3.40); 589.6 (3.78); 550.0 (3.84); 515.2 (4.30); 419.8 (5.55, Soret band).

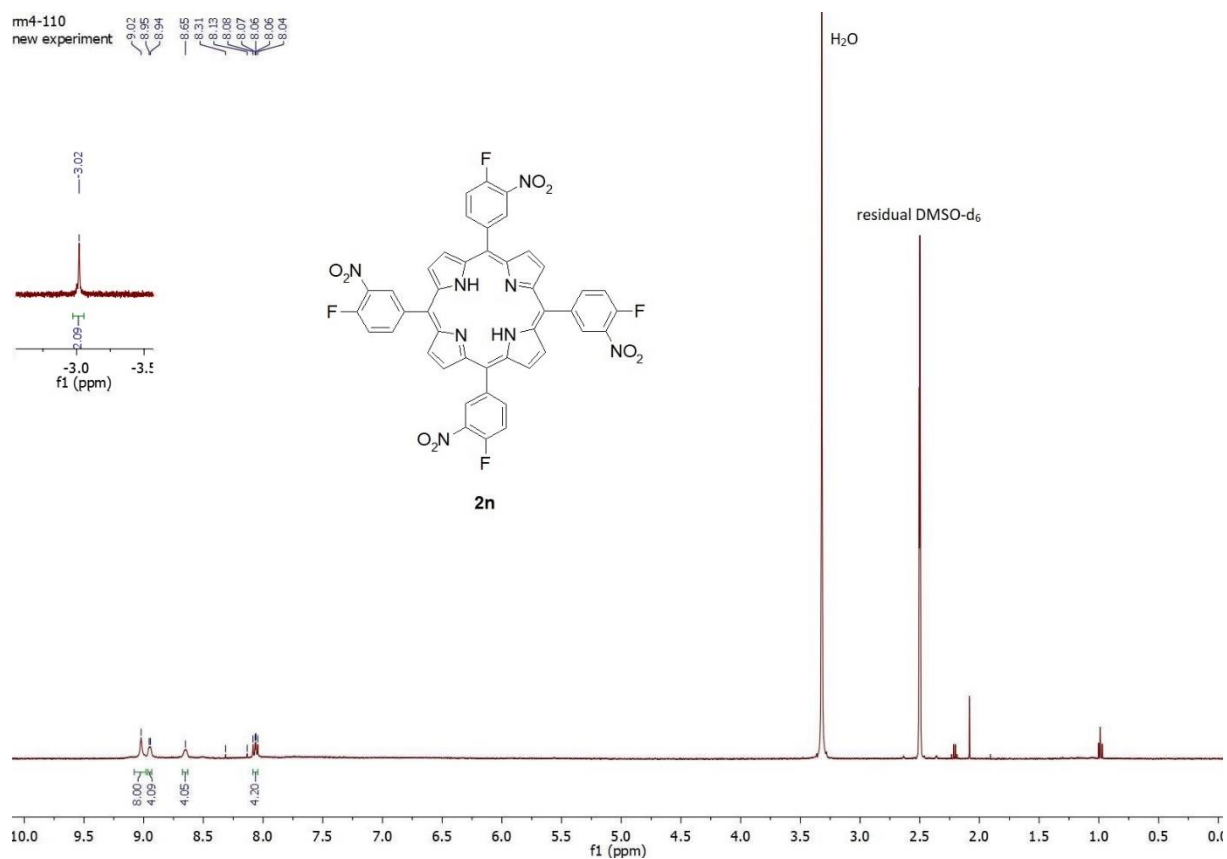
¹H NMR spectrum of **2i**



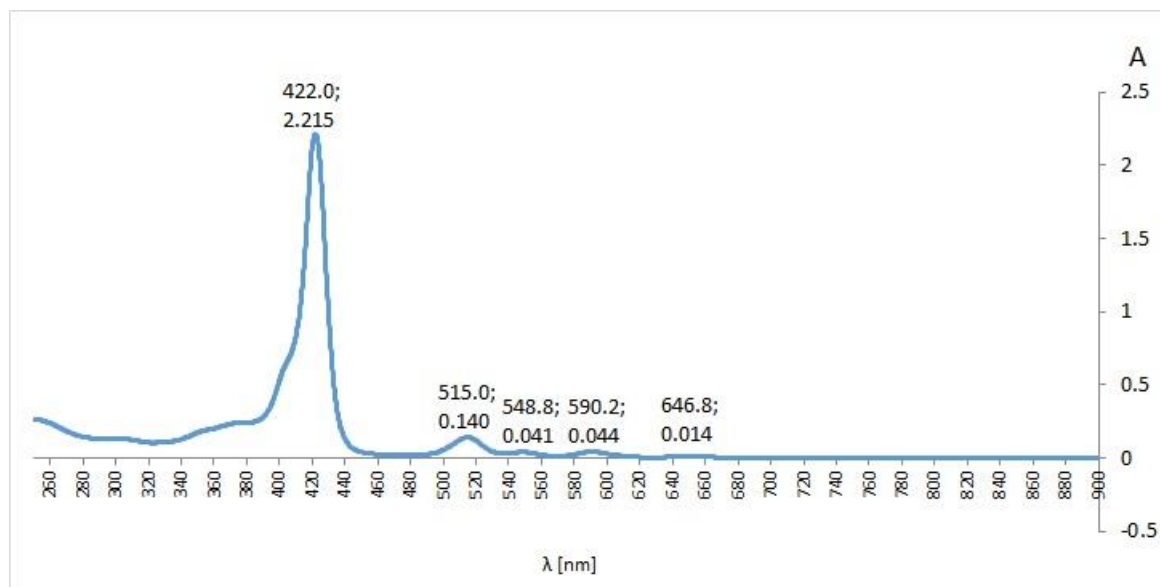
UV-VIS spectrum of **2i**



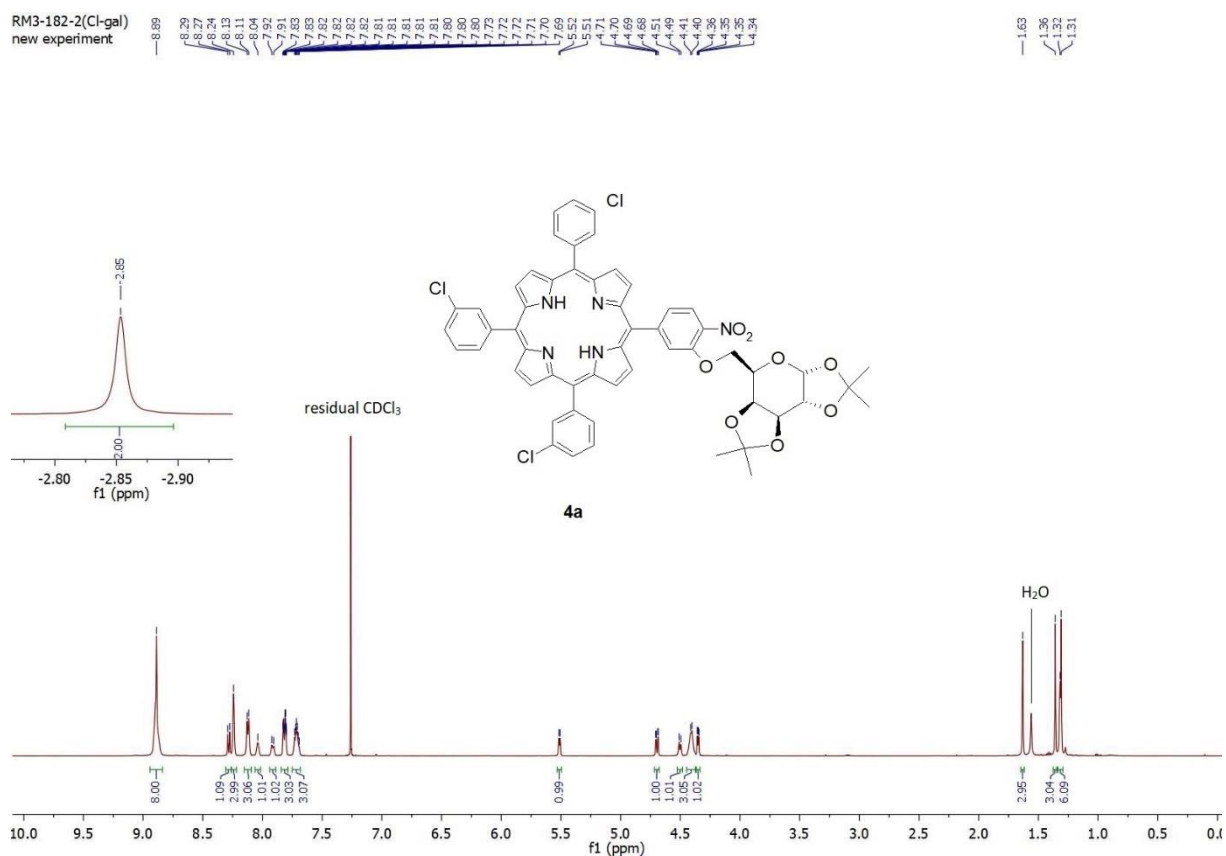
^1H NMR of **2n**



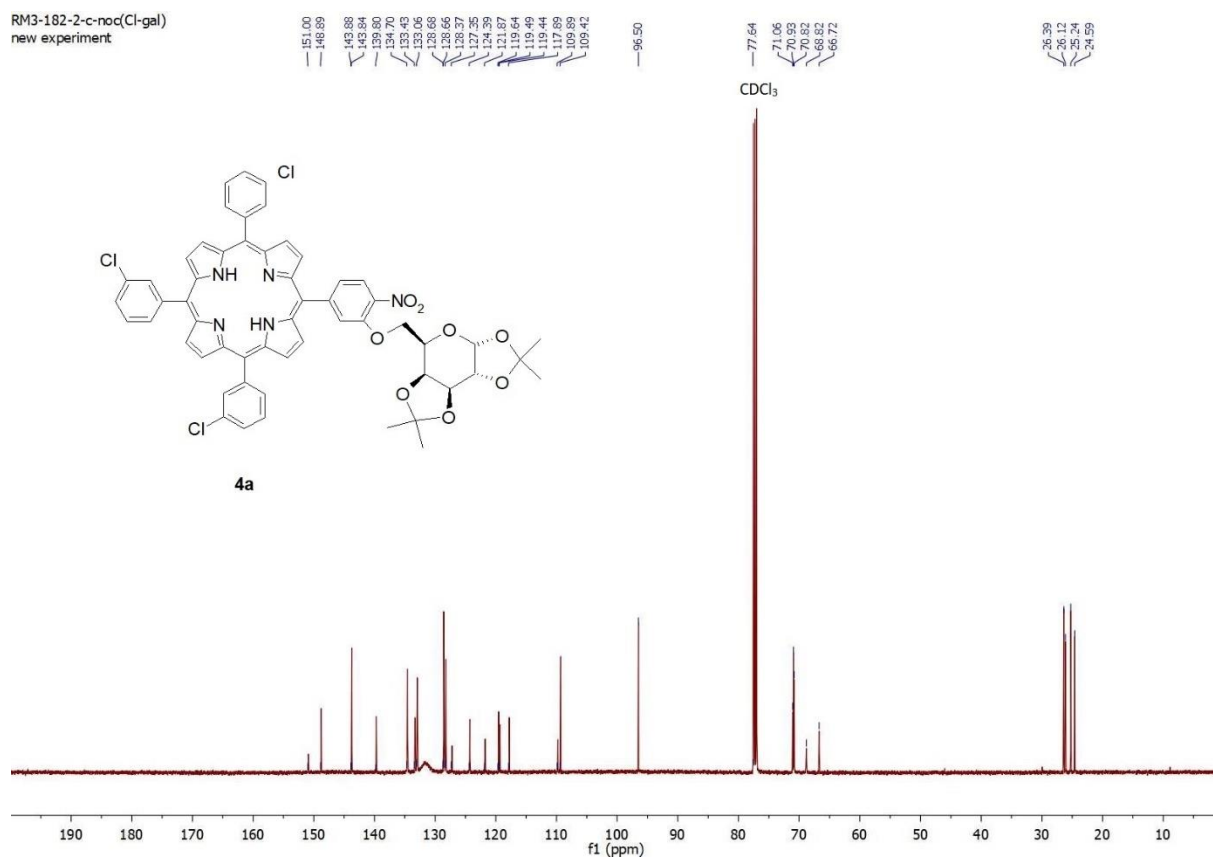
UV-VIS spectrum of **2n**



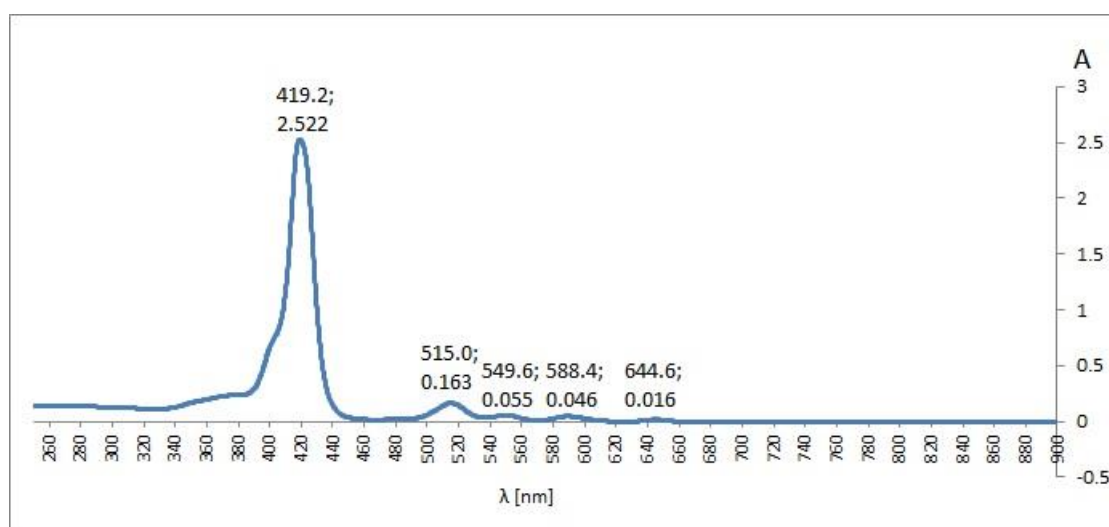
¹H NMR of 4a



¹³C NMR of 4a



UV-VIS spectrum of **4a**



Chemical structure of compound **4b** is shown, which is a complex molecule featuring a central porphyrin-like core with various substituents, including a fluorinated phenyl group, a nitro group, and a complex sugar derivative. The structure is labeled **4b**.

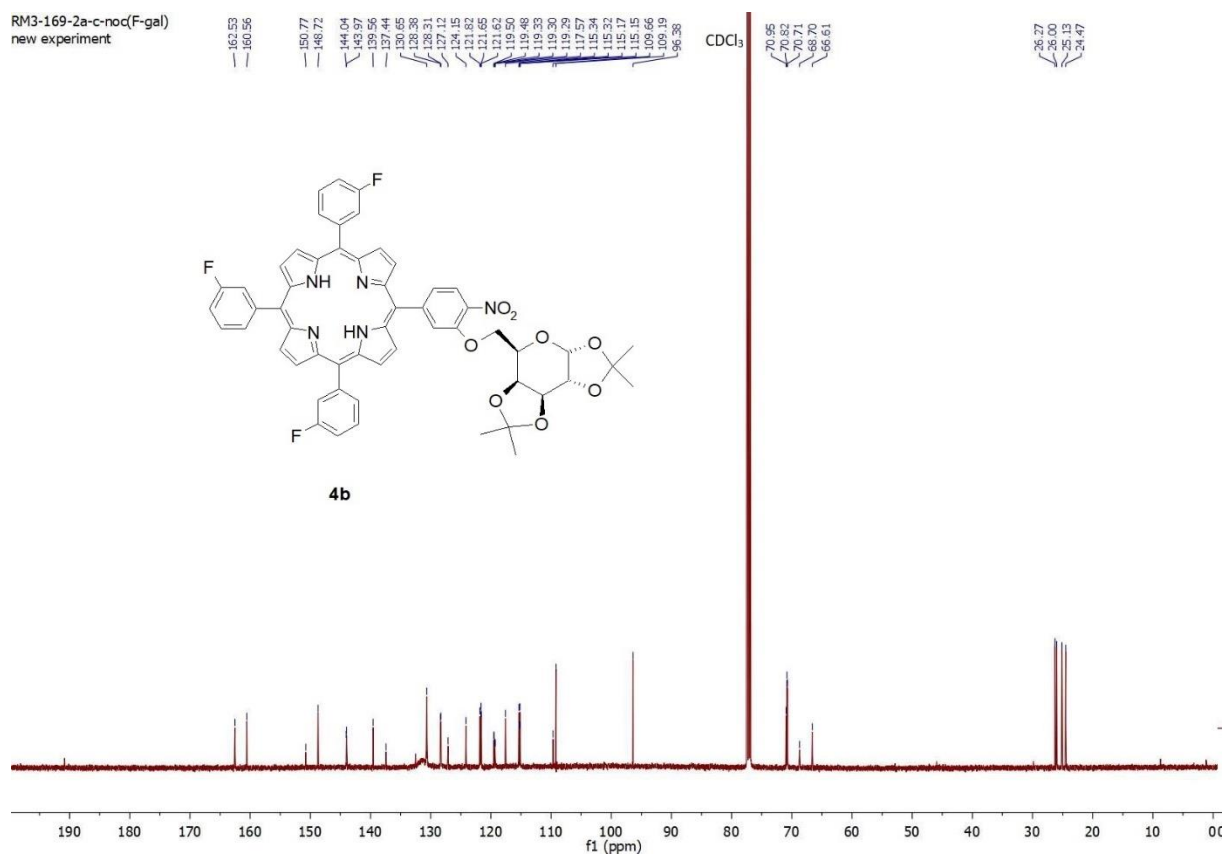
¹H NMR spectrum (CDCl₃) of compound **4b**. The spectrum shows peaks corresponding to the structure, with integrations provided for several regions. The x-axis is labeled f1 (ppm) and ranges from 0.0 to 10.0. The y-axis is labeled residual CDCl₃. The chemical structure of **4b** is shown above the spectrum.

Chemical structure of compound **4b** is shown, which is a complex molecule featuring a central porphyrin-like core substituted with various groups, including a fluorinated phenyl ring, a nitro group, and a complex sugar derivative. The structure is labeled **4b**.

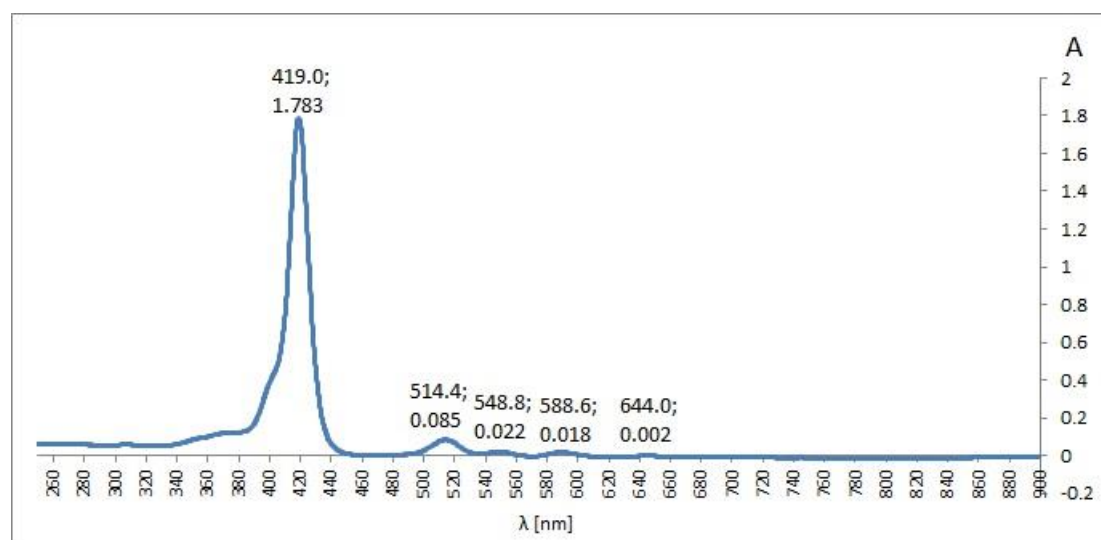
The ^{13}C NMR spectrum displays a single sharp peak at $\delta = 114.84$ ppm, corresponding to the chemical shift of the compound. The x-axis is labeled δ (ppm) and ranges from 0 to 210. The peak is integrated with a value of 3.00.

¹³C of **4b**

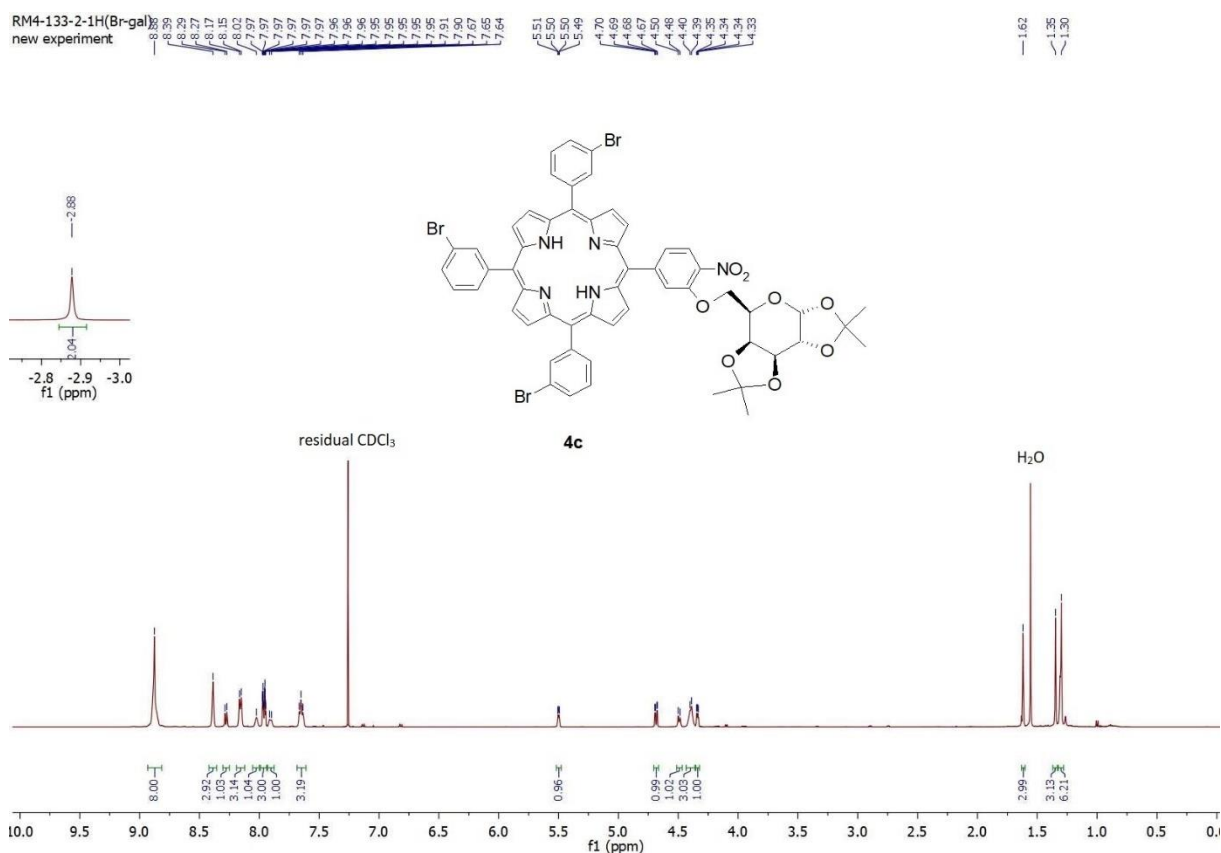
RM3-169-2a-c-noc(F-gal)
new experiment



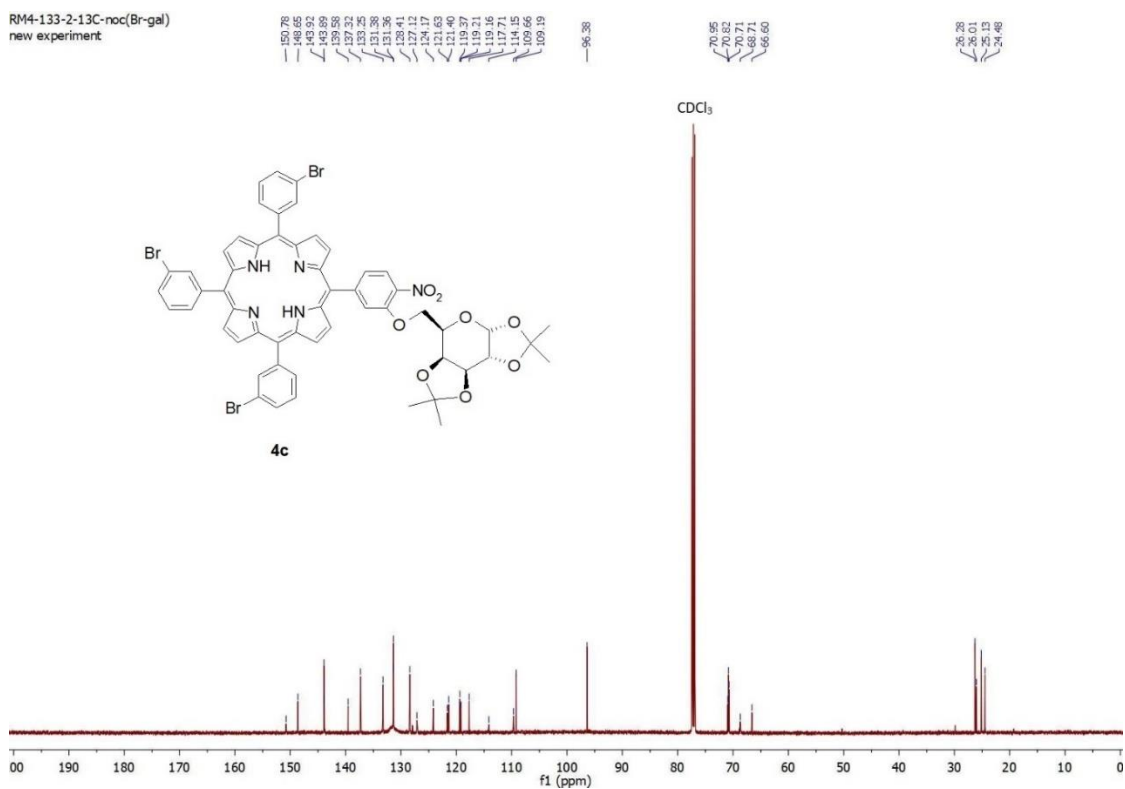
UV-VIS spectrum of **4b**



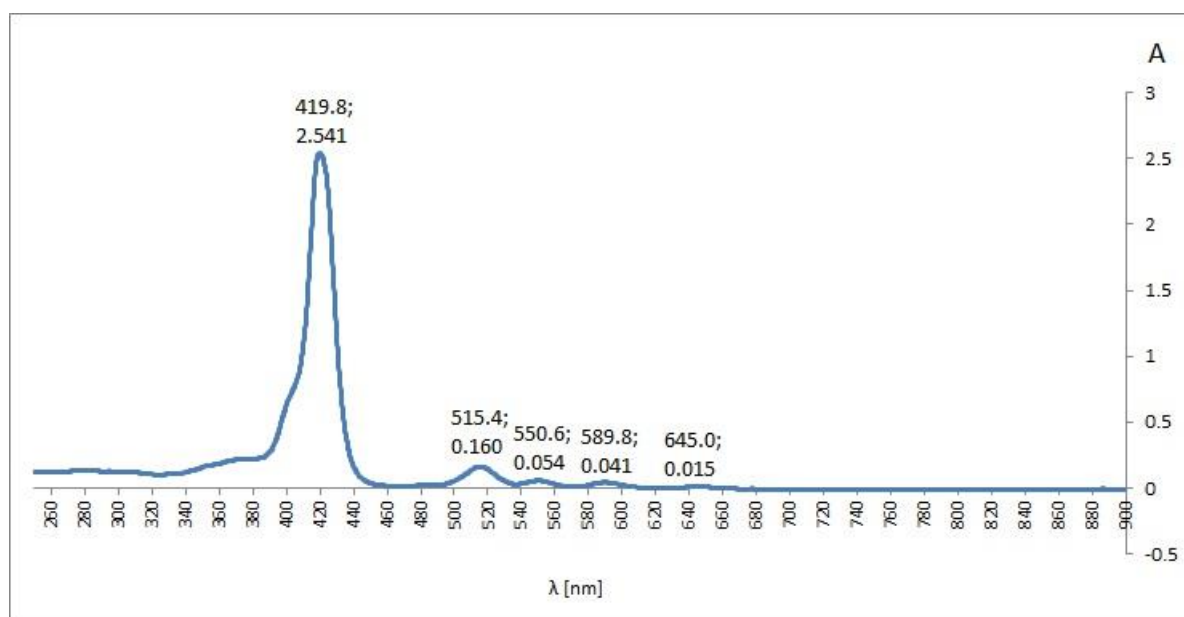
¹H NMR of 4c



¹³C NMR of 4c



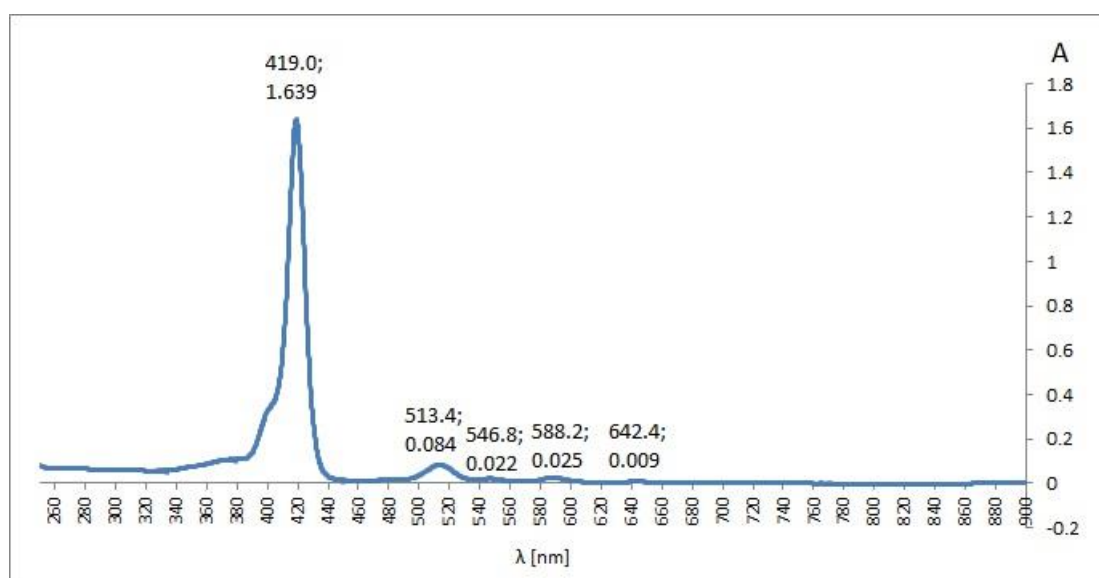
UV-VIS spectrum of **4c**



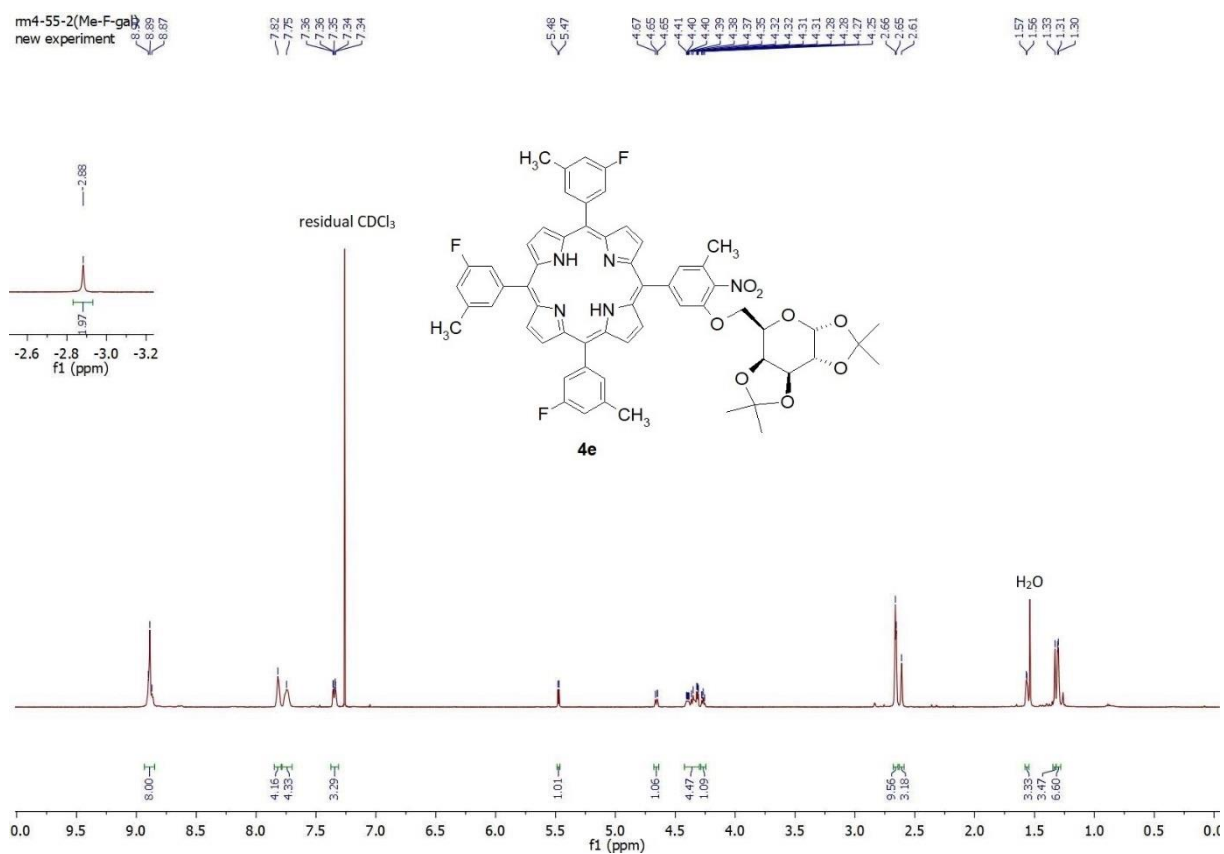
rm4-23-2(1)(OMe-F)
new experiment



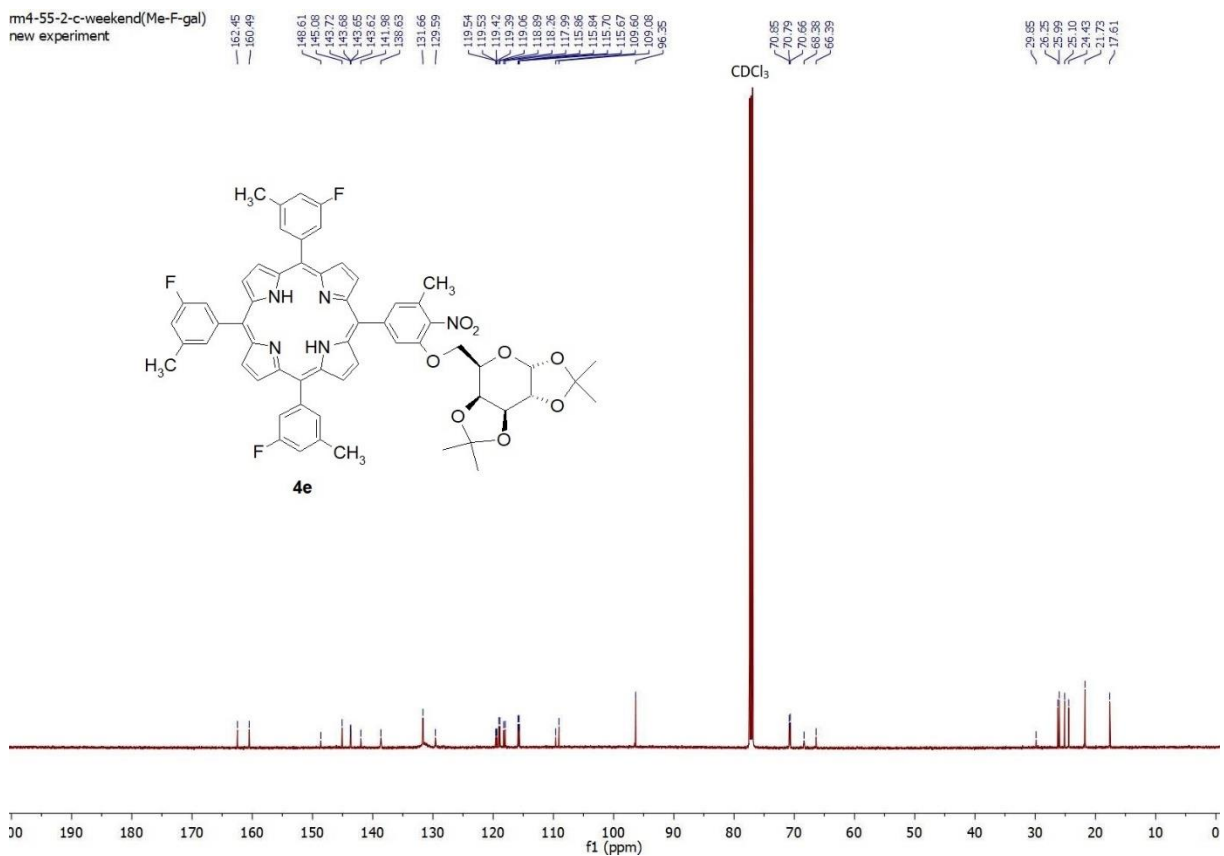
UV-VIS spectrum of **4d**



¹H NMR of 4e

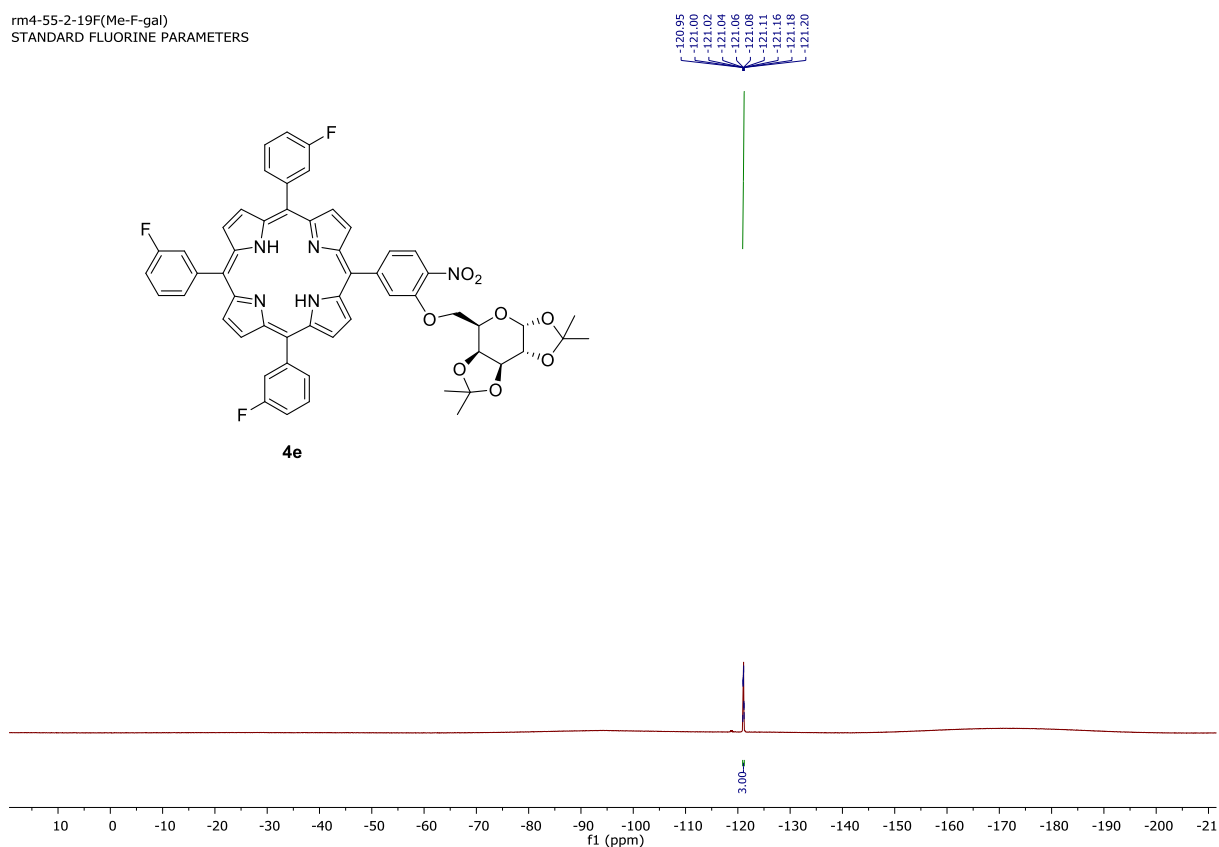


¹³C NMR of 4e

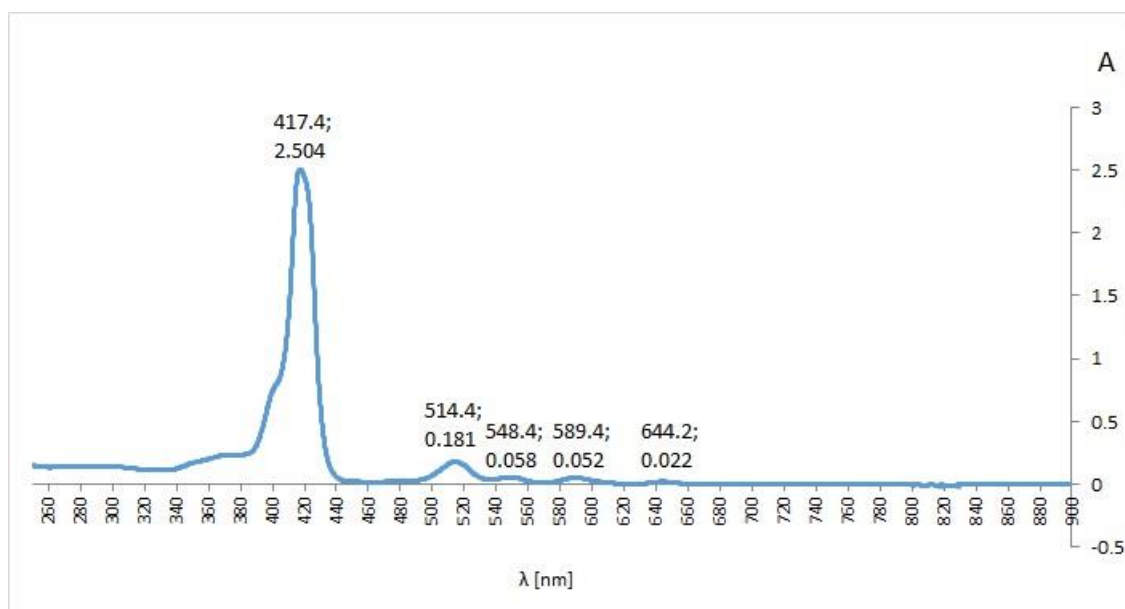


^{19}F NMR of **4e**

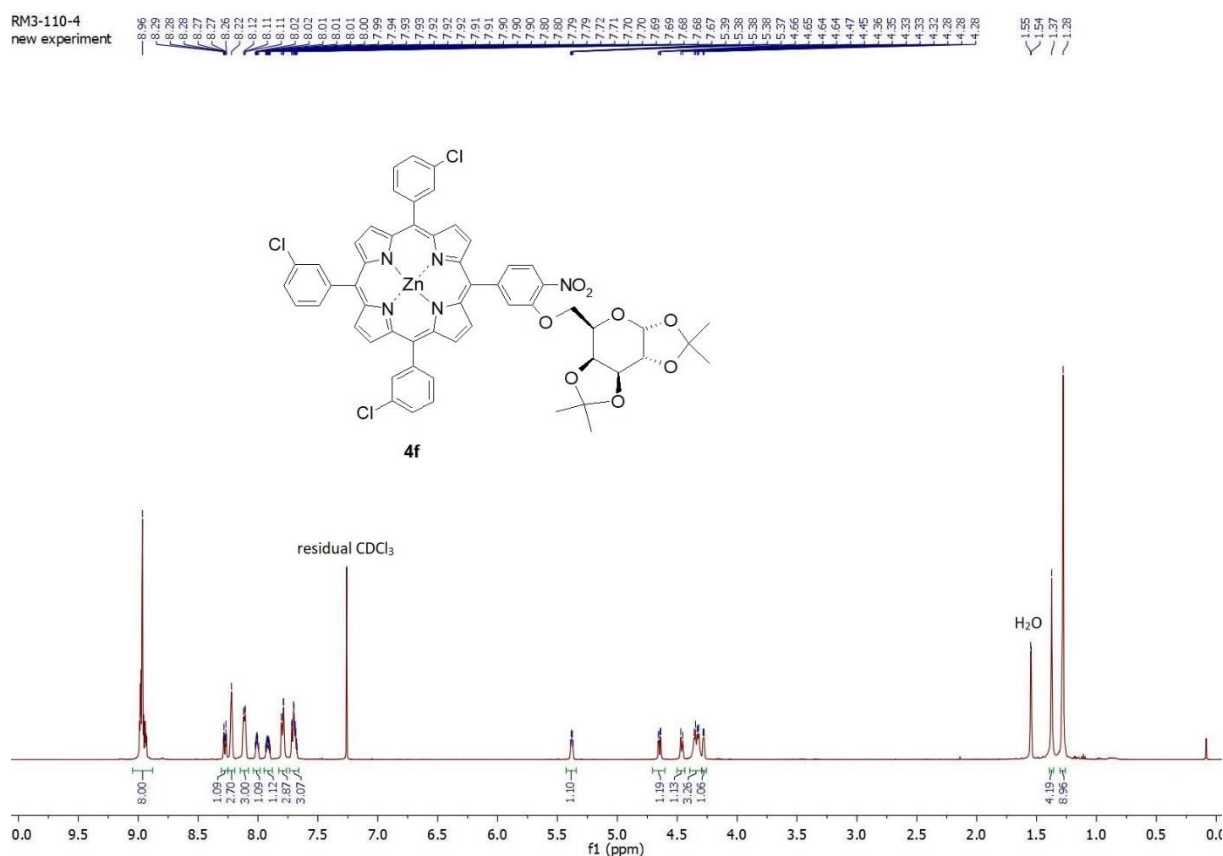
rm4-55-2-19F(Me-F-gal)
STANDARD FLUORINE PARAMETERS



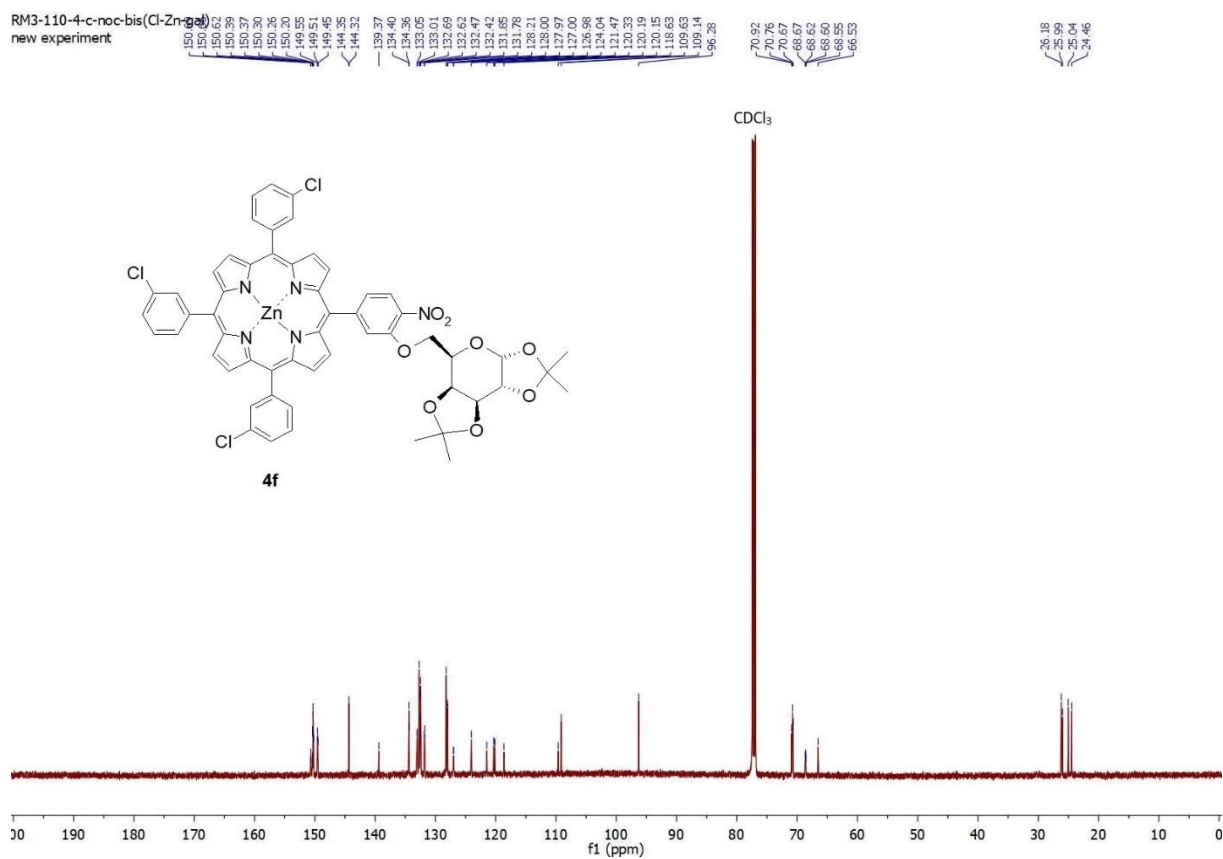
UV-VIS spectrum of **4e**



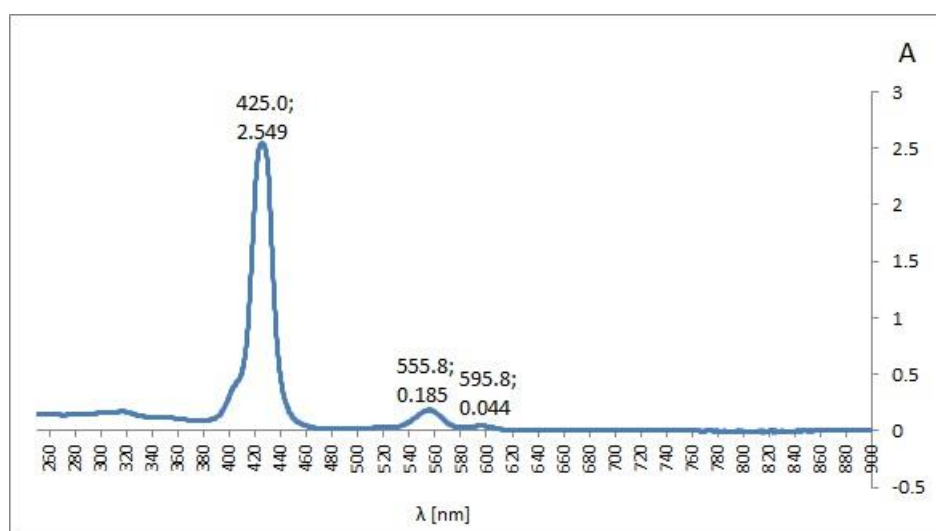
¹H NMR of **4f**



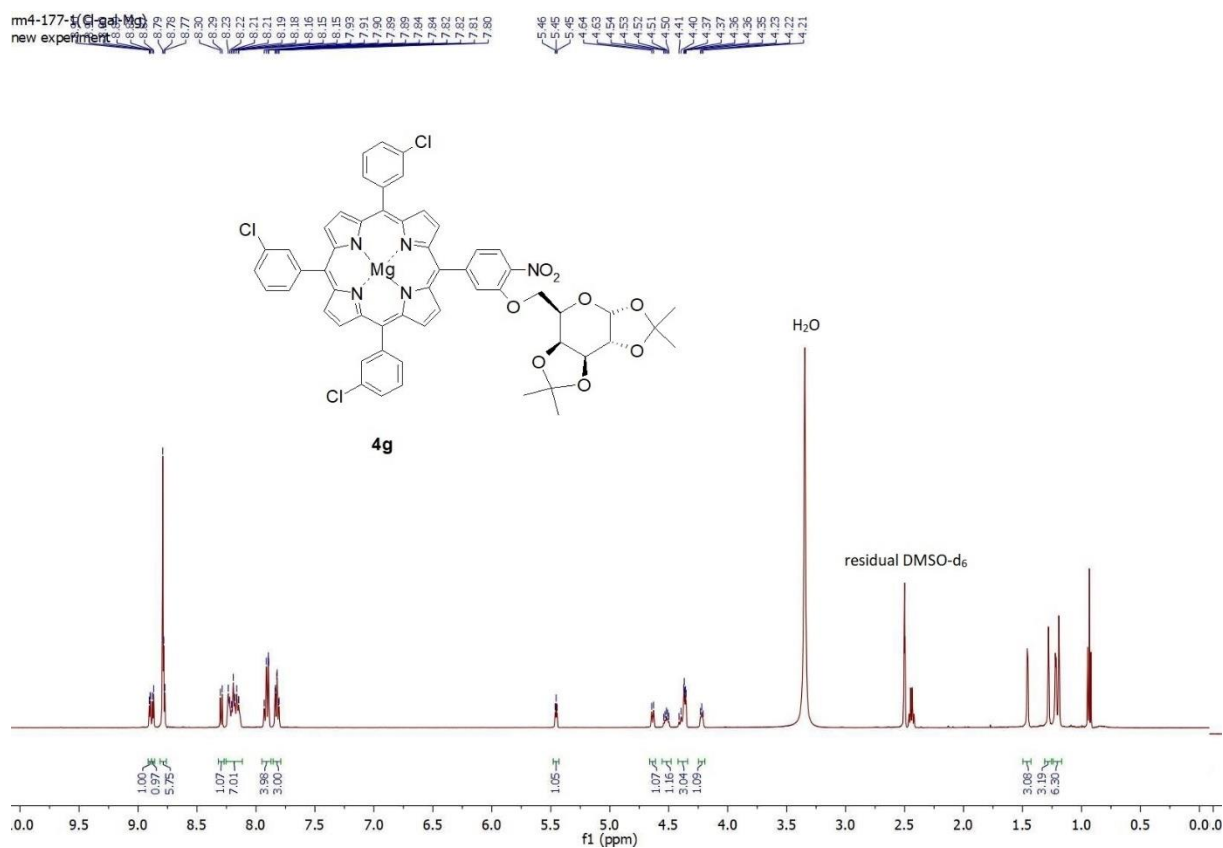
¹³C NMR of **4f**



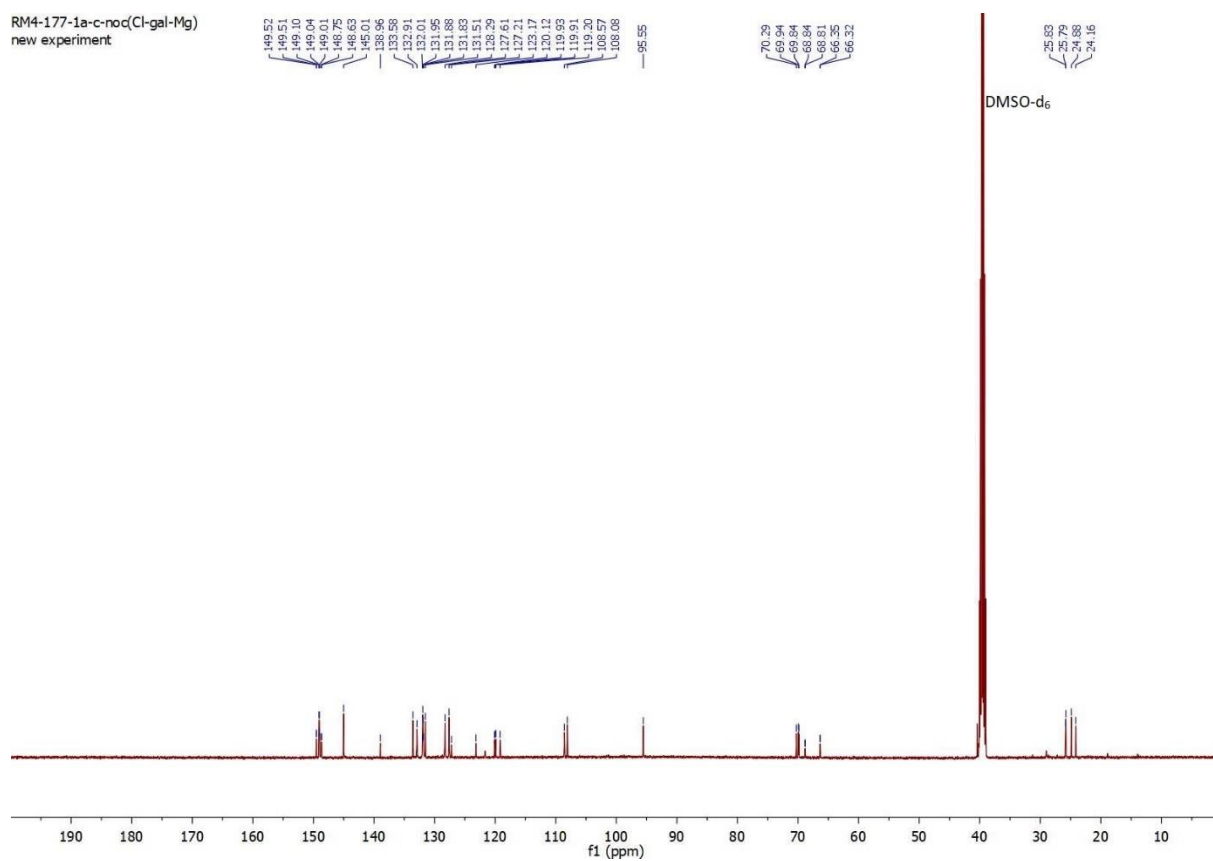
UV-VIS spectrum of **4f**



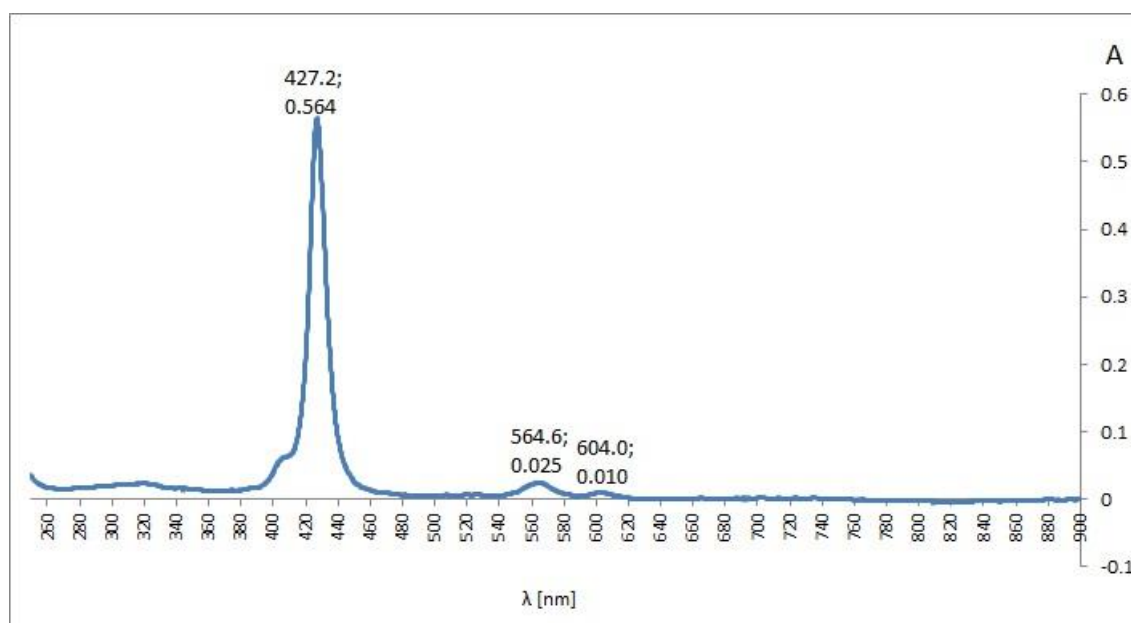
¹H NMR of **4g**



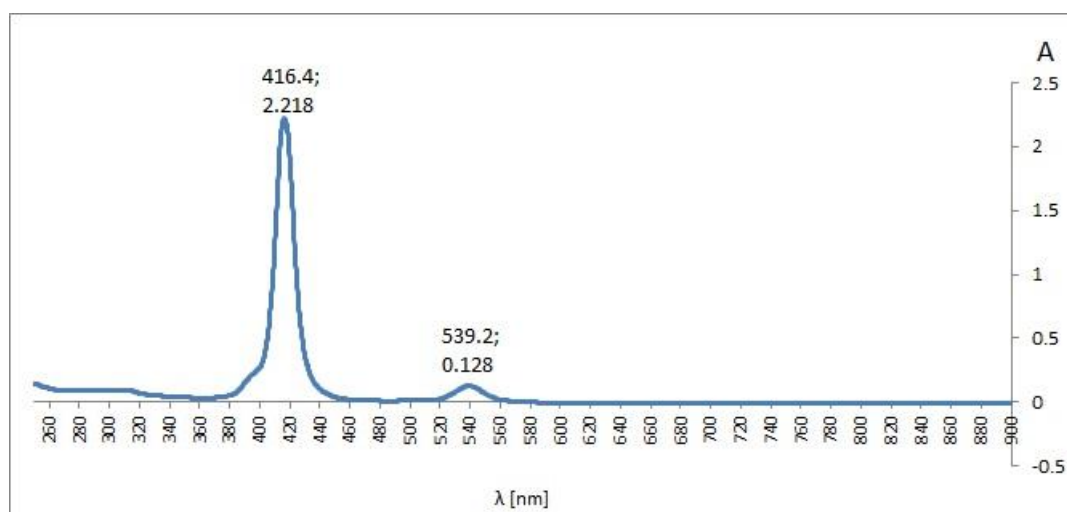
¹³C NMR of **4g**



UV-VIS spectrum of **4g**



UV-VIS spectrum of **4h**



RM4-30-2-H
new experiment

residual CDCl₃

4j

H₂O

Chemical structure of 4j is shown, featuring a phthalocyanine core substituted with two 4-chlorophenyl groups, one 4-nitrophenyl group, and one 4-(4,4,4-trimethyl-1,3-dioxol-2-yloxy)phenyl group.

Integration values are provided for several peak regions: 7.81, 4.00, 3.05, 1.02, 1.01, 3.00, 3.07, 0.98, 1.00, 1.02, 1.02, 1.00, 1.00, 0.99, 3.05, 3.12, and 6.22.

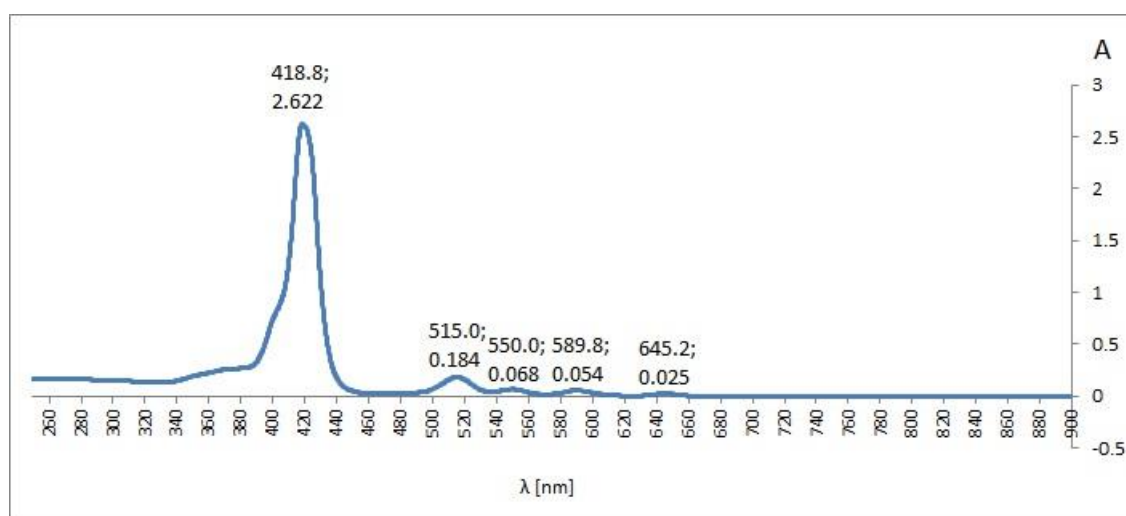
RM4-30-2-c-2h(Cl-fru)
new experiment

Chemical structure of **4j** is shown above the spectrum. The structure is a complex molecule featuring a central macrocyclic core with multiple nitrogen atoms. It is substituted with a 4-chlorophenyl group, a 4-nitrophenyl group, and a 4-chlorophenyl group. The macrocycle is also substituted with a 4-chlorophenyl group and a 4-nitrophenyl group. The molecule is labeled **4j**.

1H NMR spectrum (CDCl₃) of compound **4j**. The x-axis represents the chemical shift in ppm, ranging from 0 to 20. The spectrum shows a sharp singlet at 7.10 ppm (CDCl₃), a multiplet between 6.5 and 7.5 ppm, and several peaks in the 2.5-3.5 ppm region. The following table lists the chemical shifts (ppm) for the peaks observed in the spectrum:

Chemical Shift (ppm)
7.10
7.06
7.05
6.16
3.53
3.57
3.48
2.41
2.40
150.28
150.26
150.23
146.46
143.65
143.64
143.61
139.63
134.46
133.21
133.18
132.86
132.85
132.74
128.74
128.44
123.98
121.71
121.62
119.46
119.39
119.23
117.59
109.74
109.19
101.55
101.54

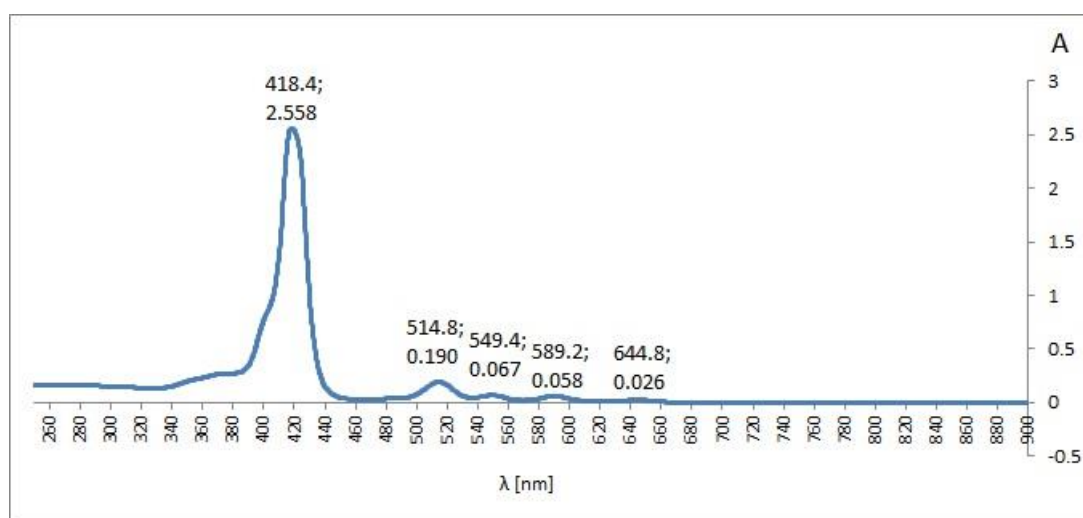
UV-VIS spectrum of **4j**



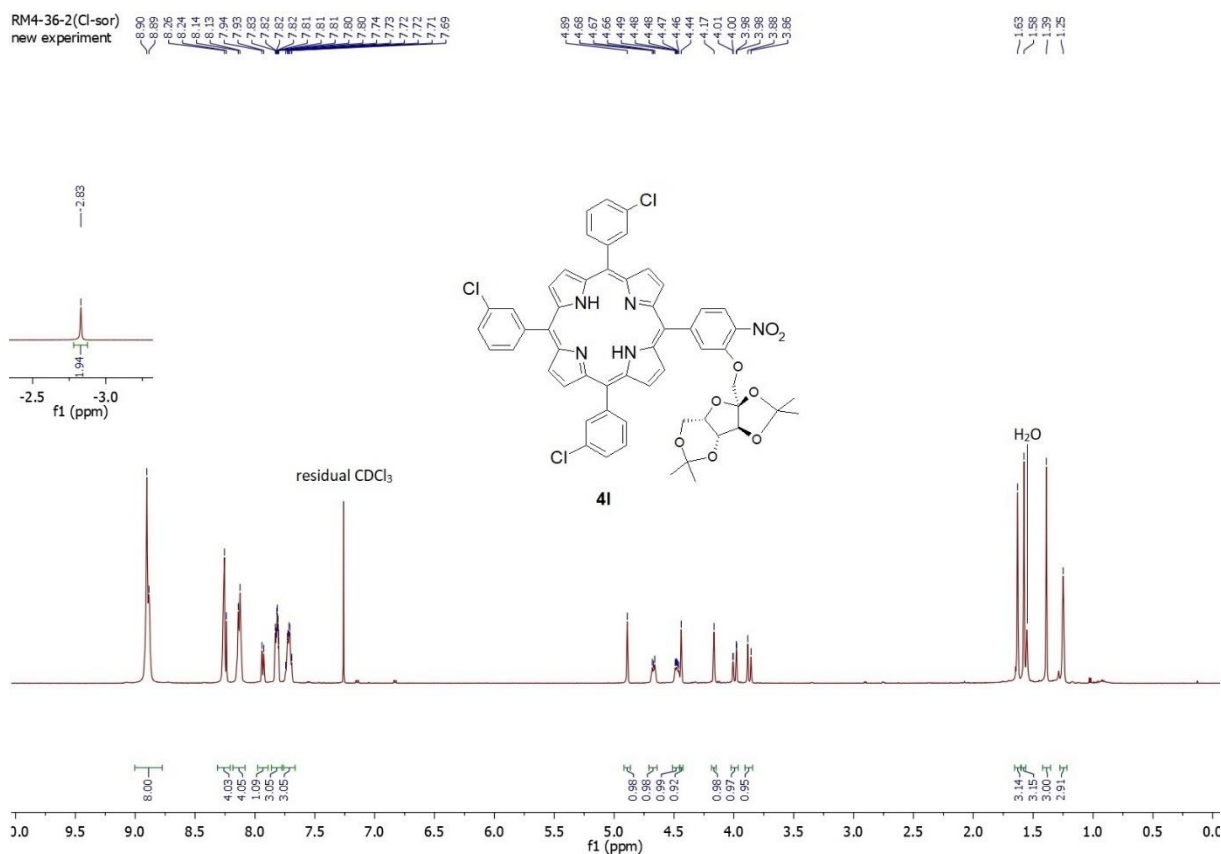
rm4-62-5(Cl-ryb)
new experiment



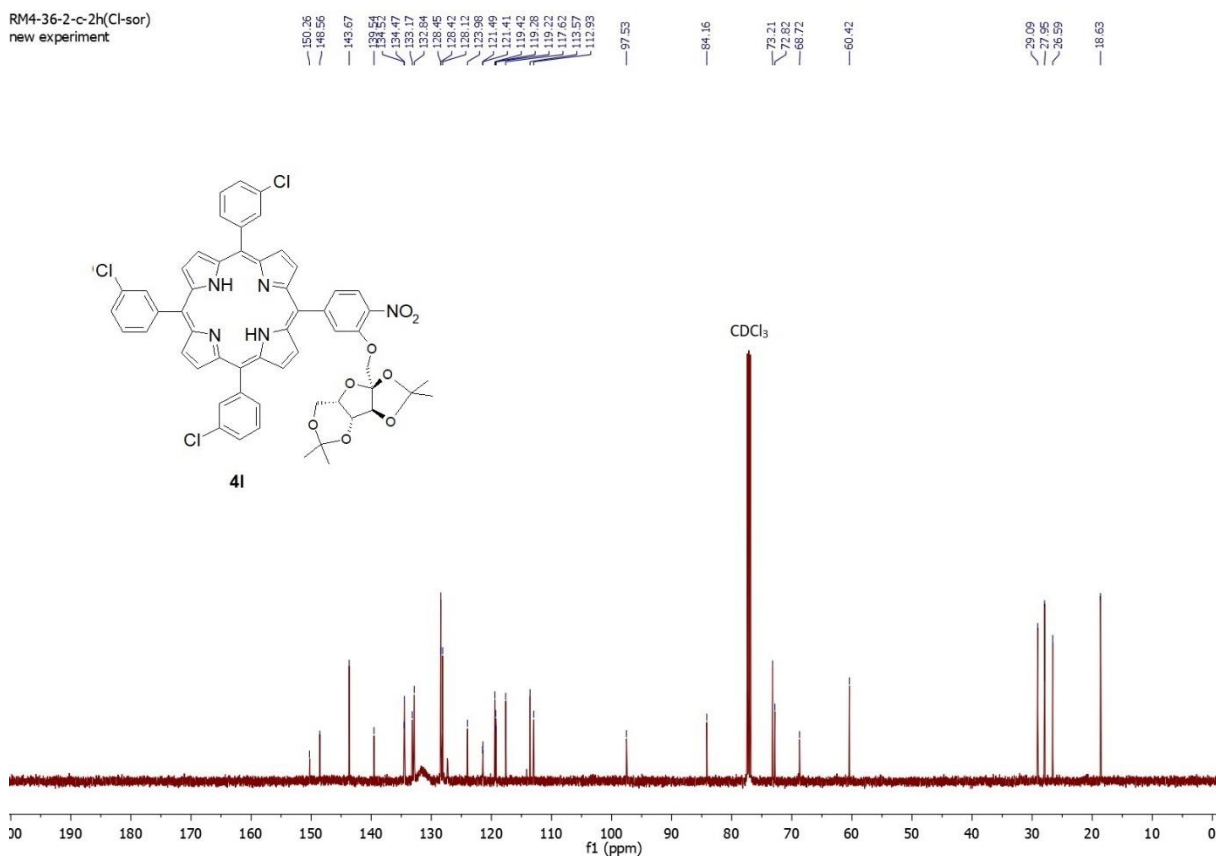
UV-VIS spectrum of **4k**



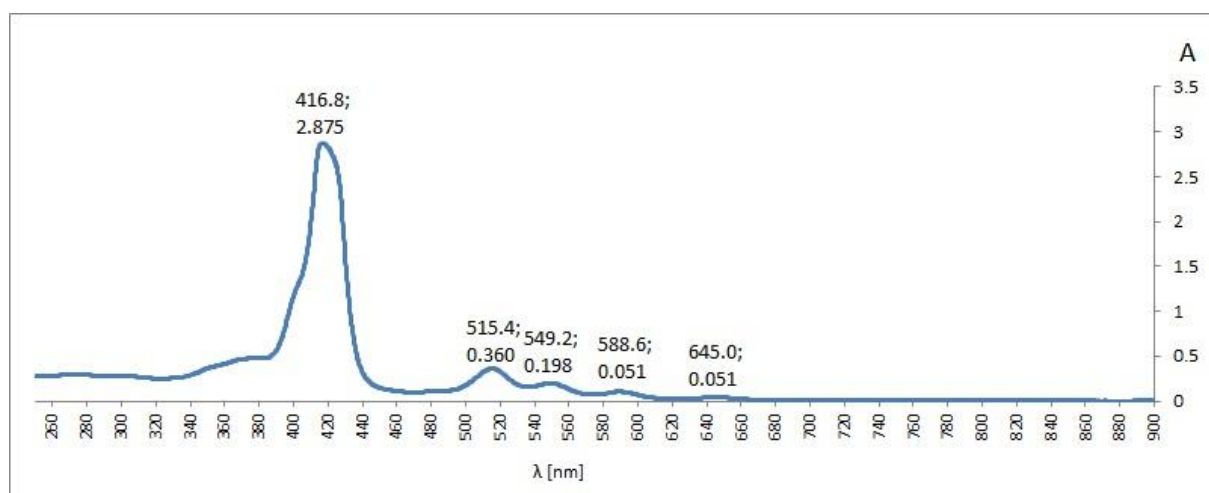
¹H NMR of **41**



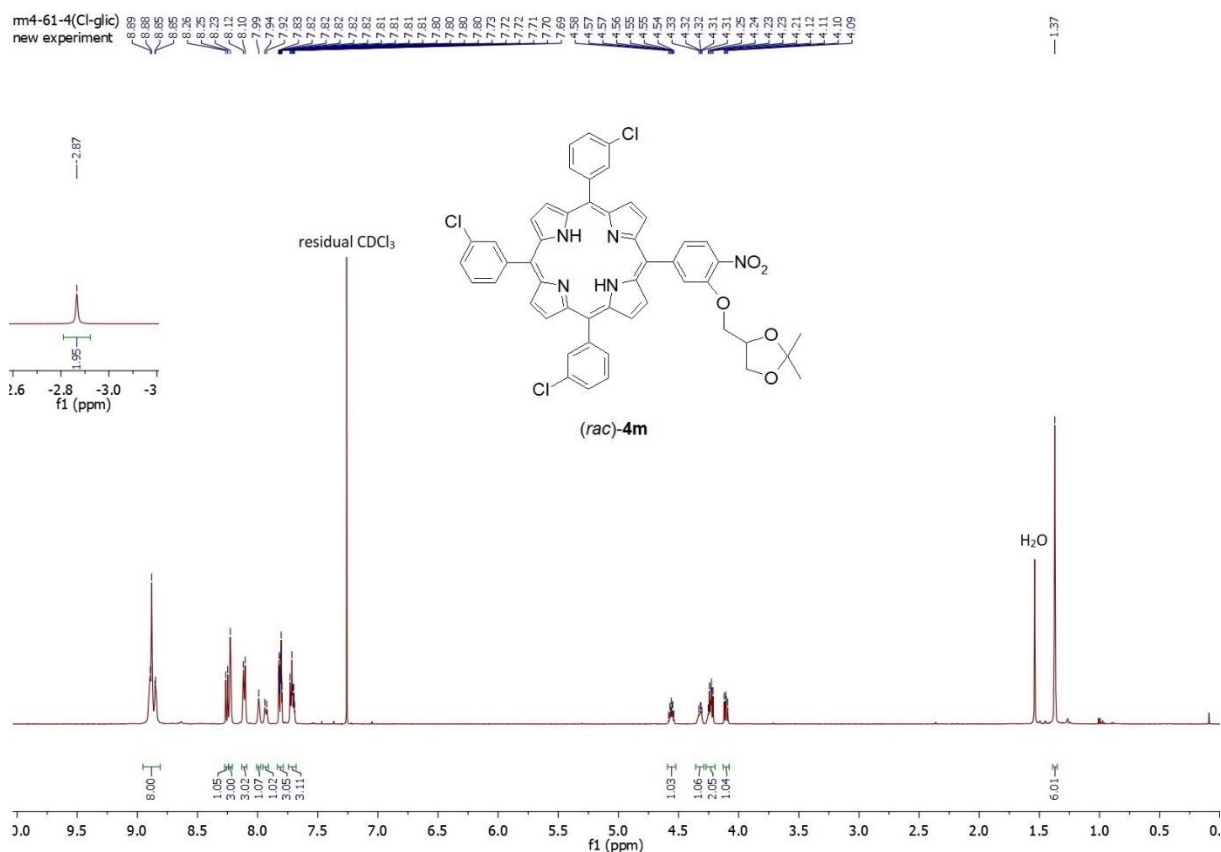
¹³C NMR of **41**



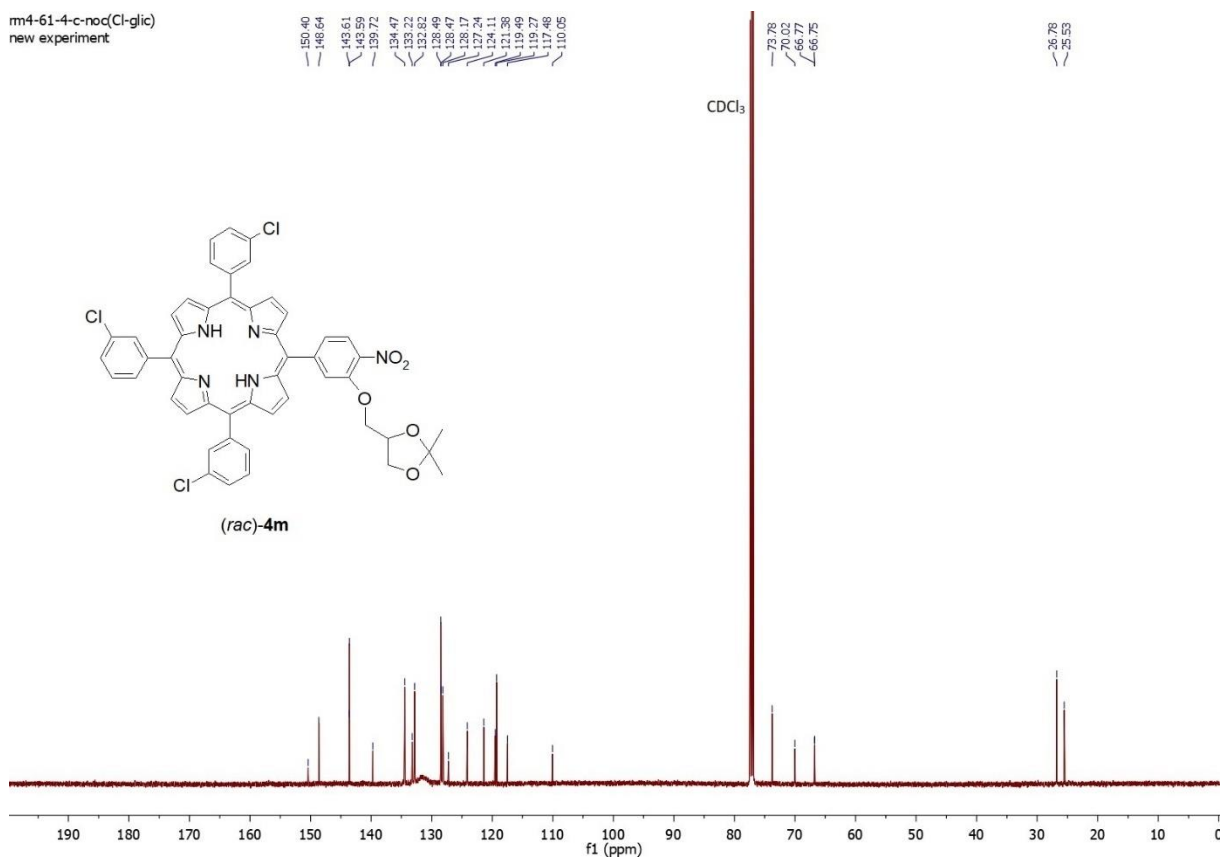
UV-VIS spectrum of **4l**



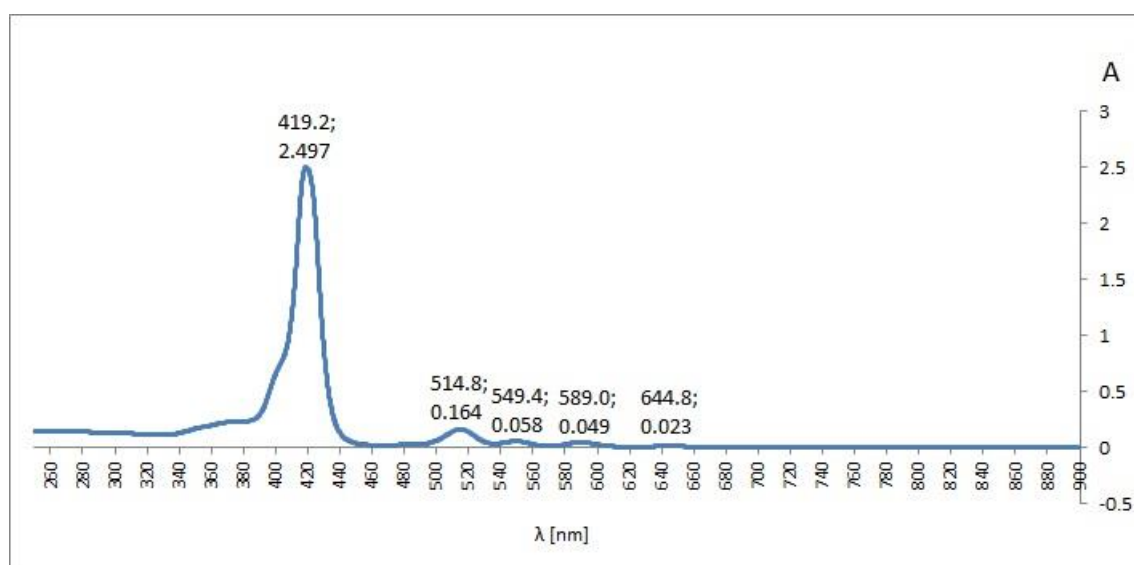
¹H NMR of (*rac*)-4m



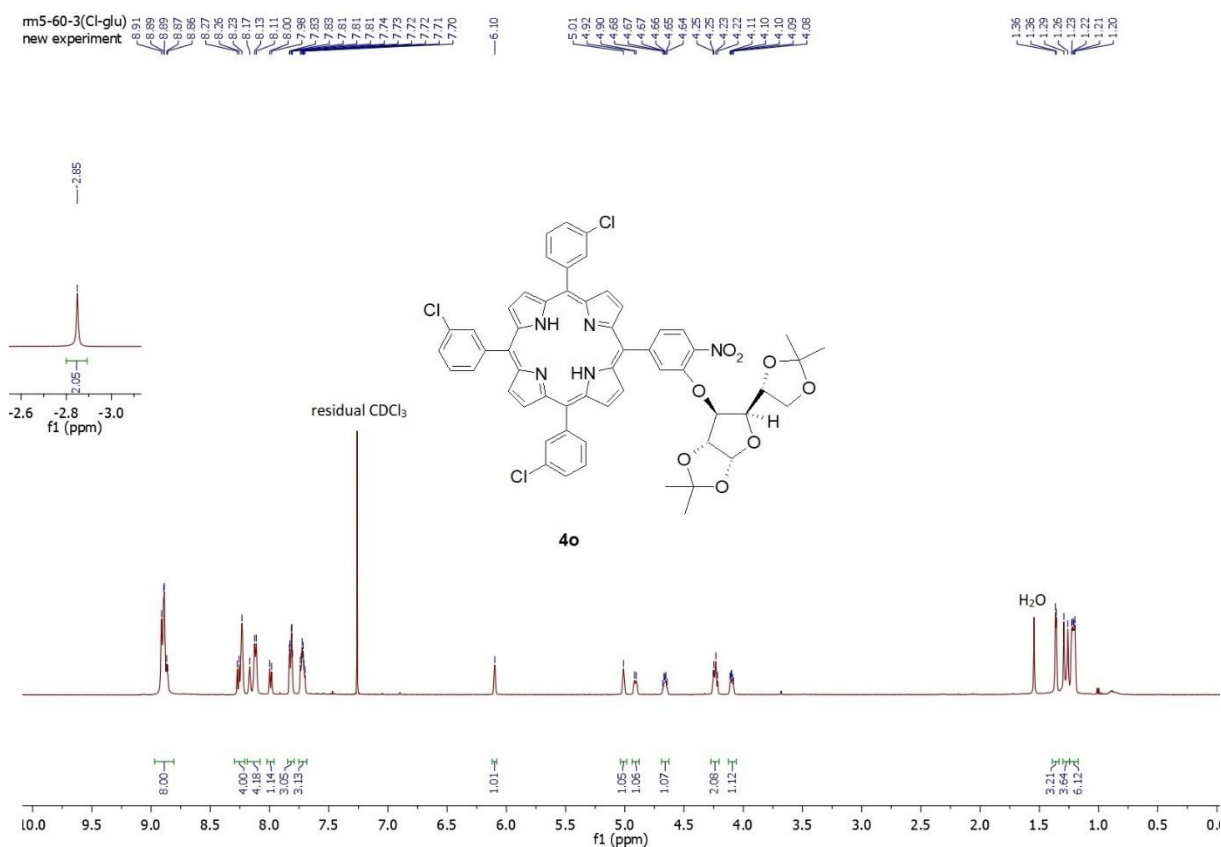
¹³C NMR of (*rac*)-4m



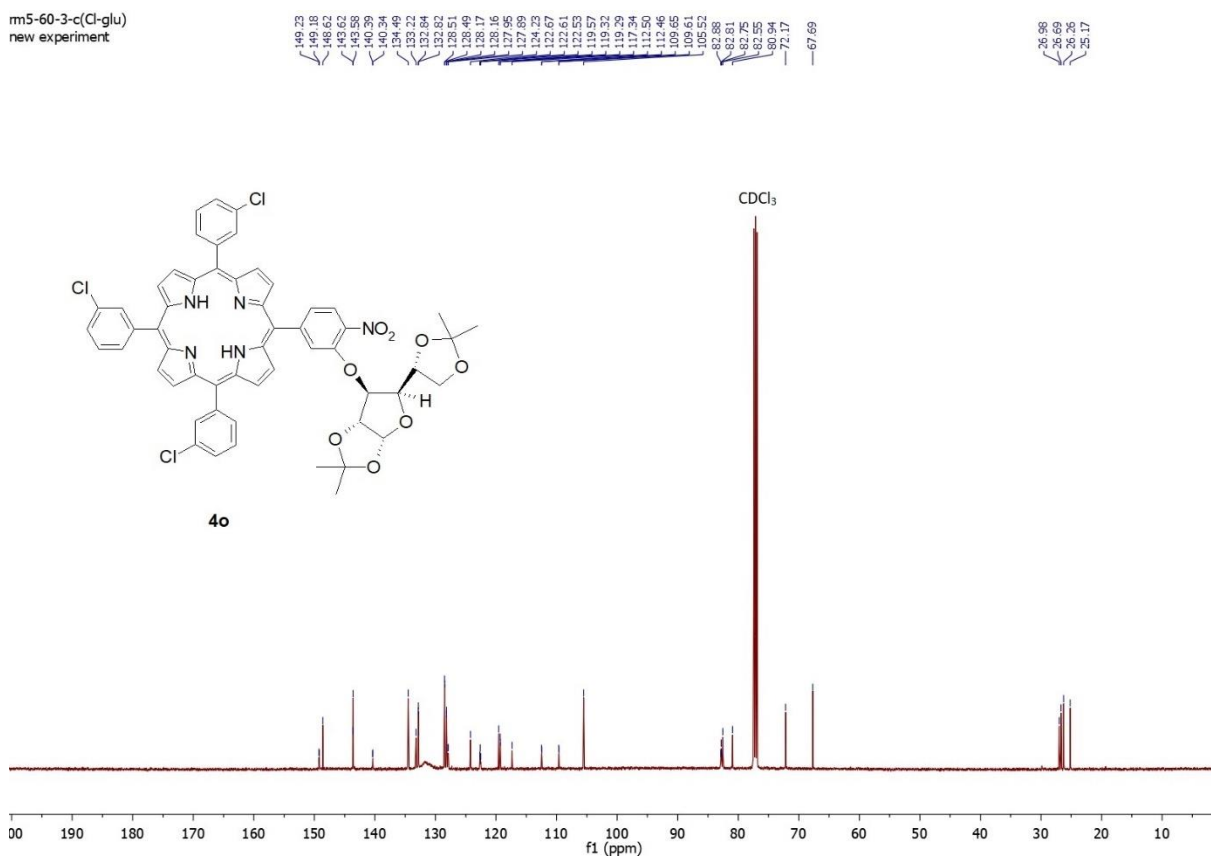
UV-VIS spectrum of (*rac*)-**4m**



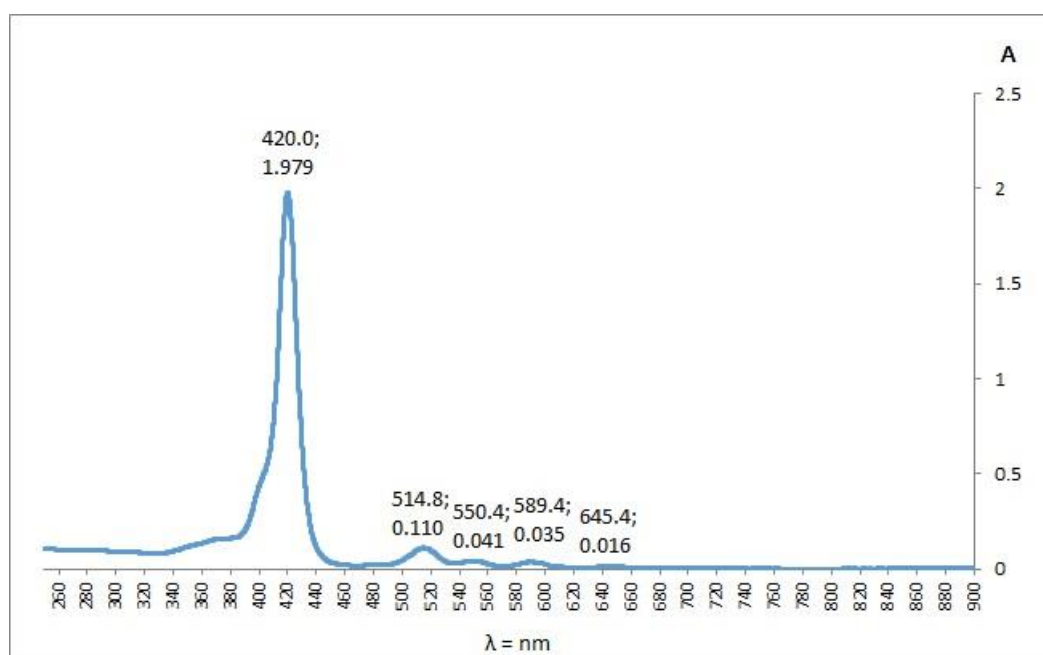
¹H NMR of **4o**



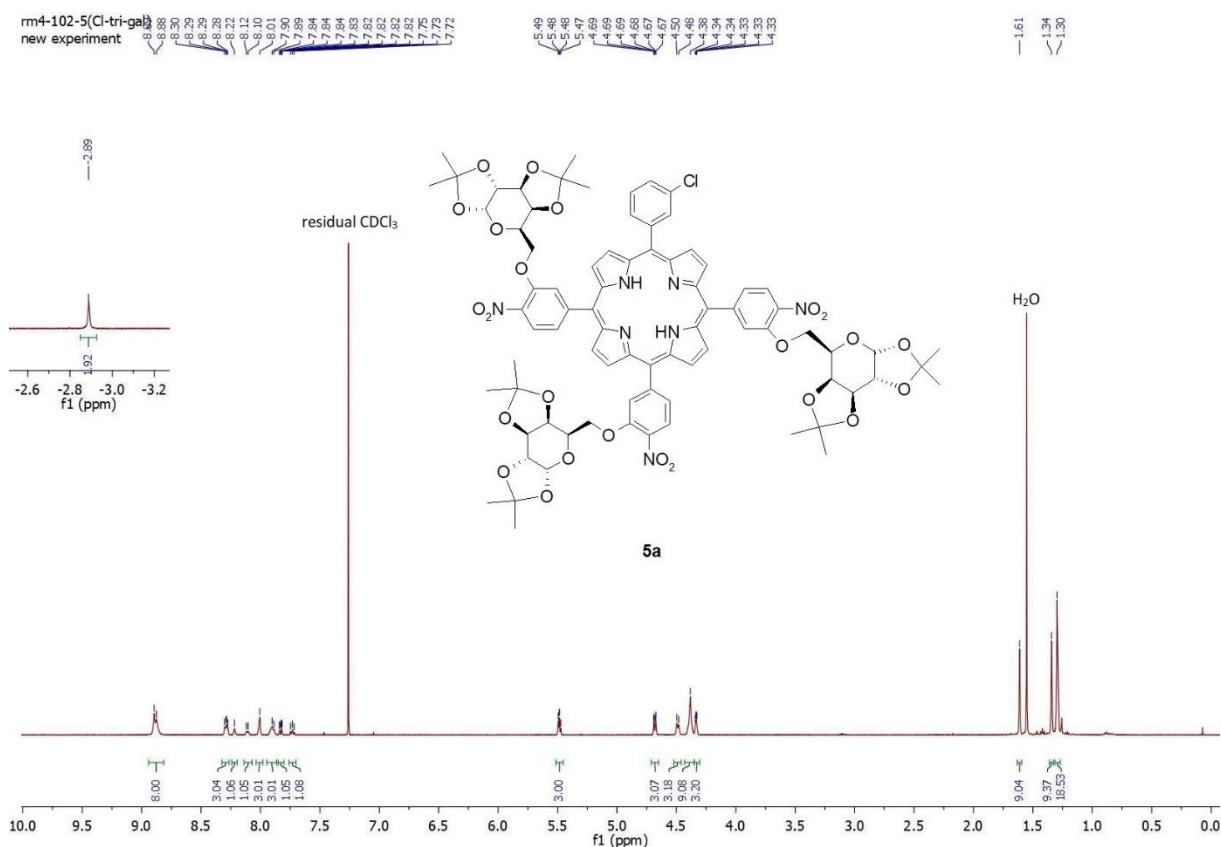
¹³C NMR of **4o**



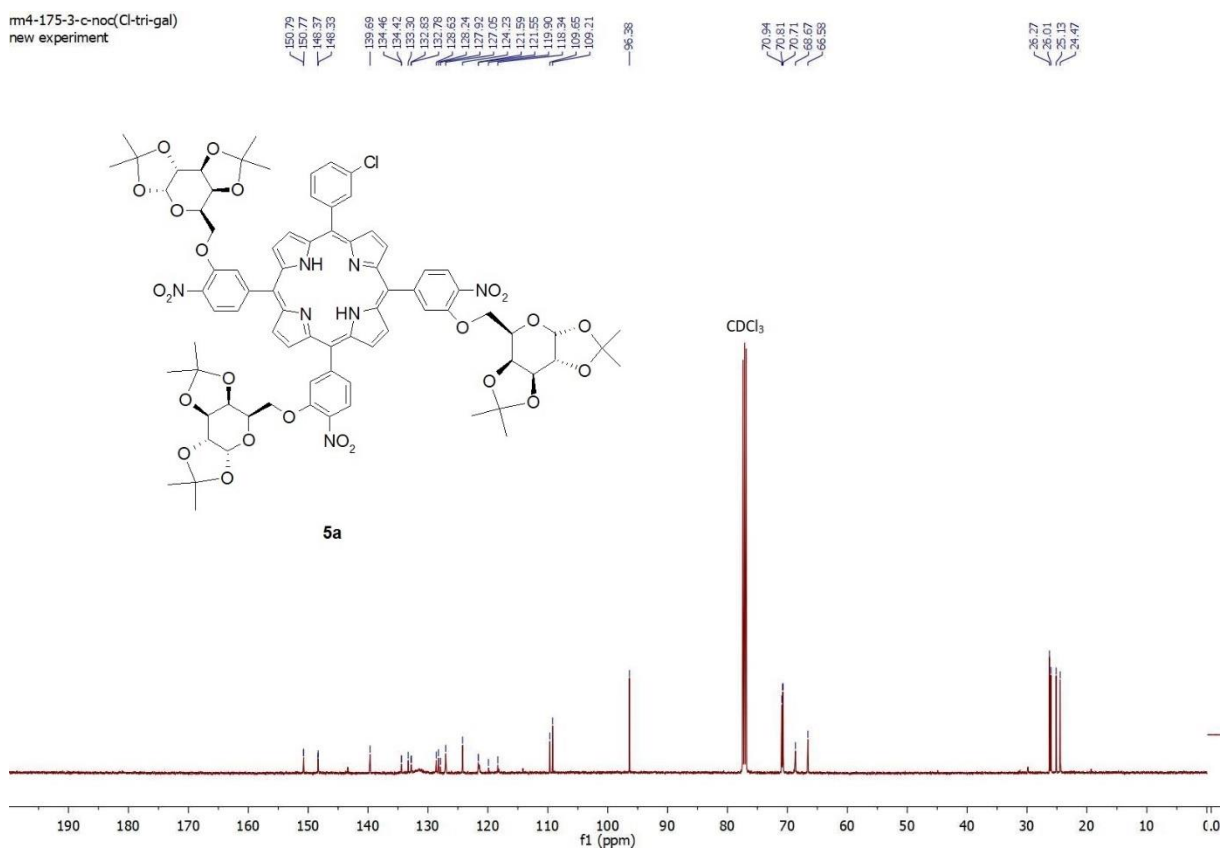
UV-VIS of **4o**



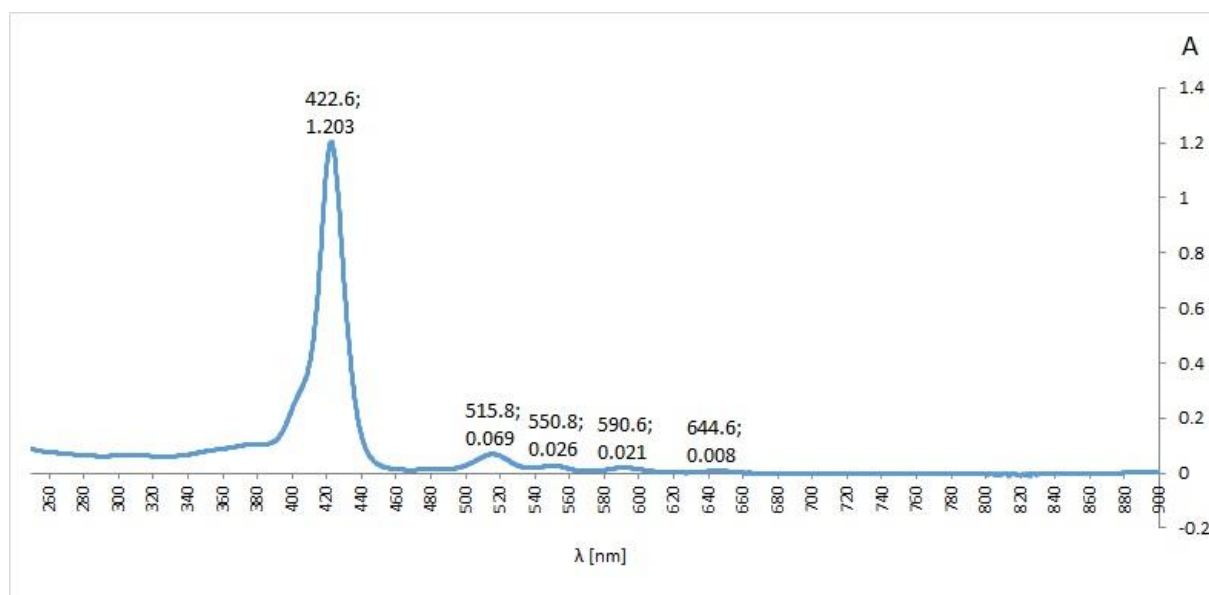
¹H NMR of **5a**



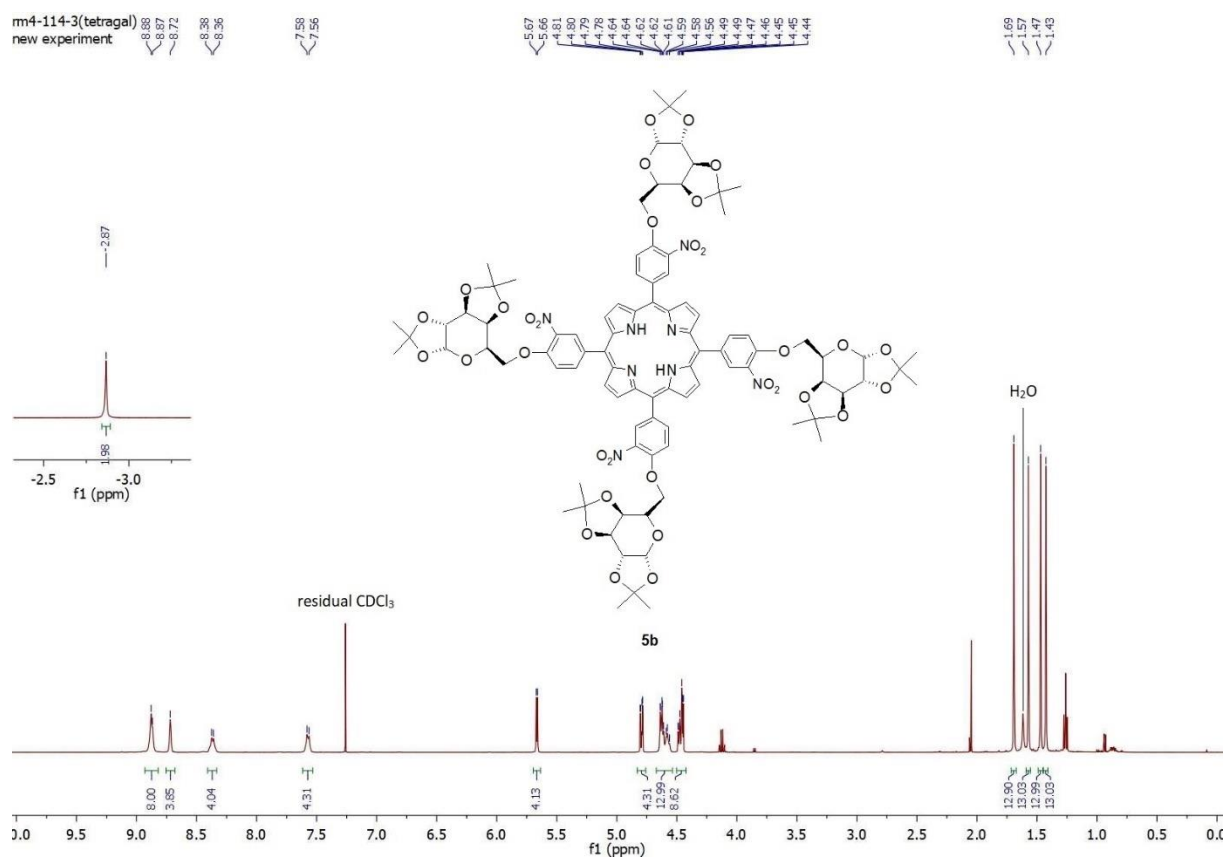
¹³C NMR of **5a**



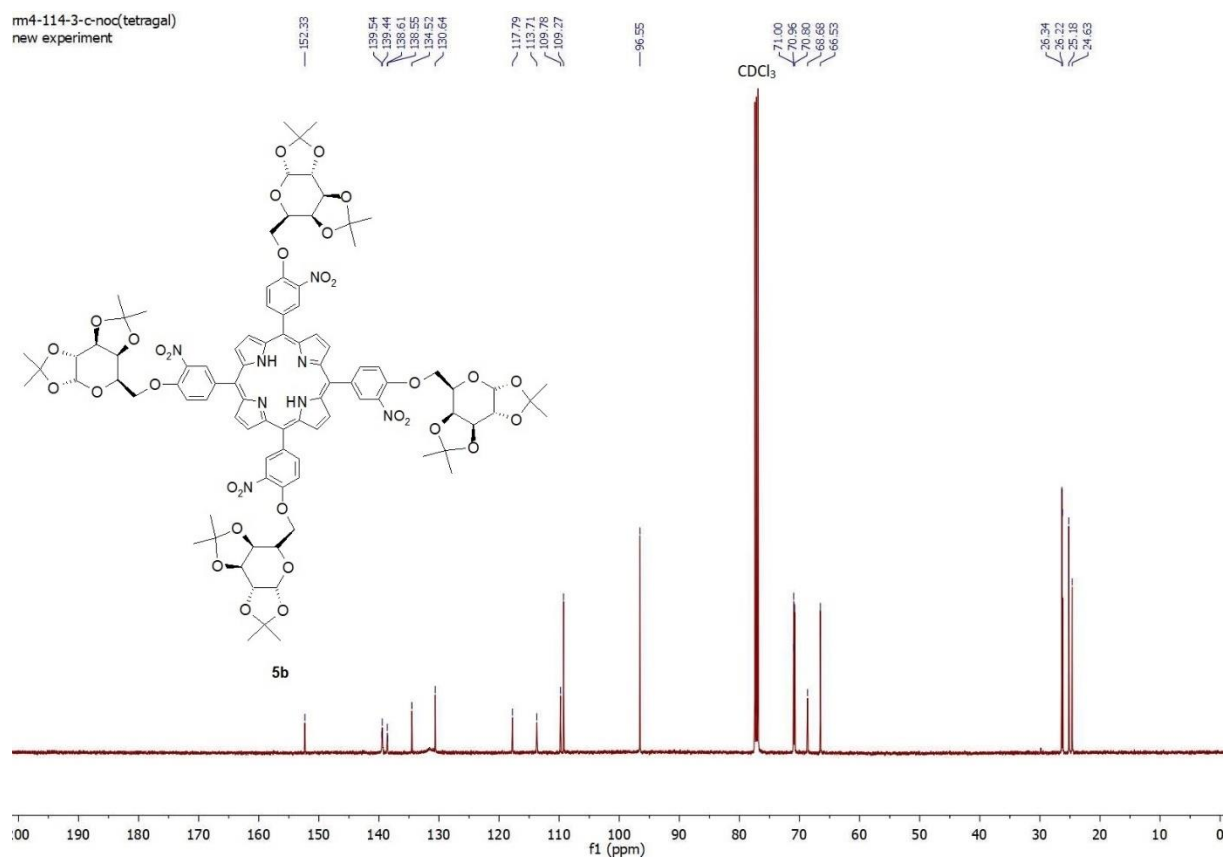
UV-VIS spectrum of **5a**



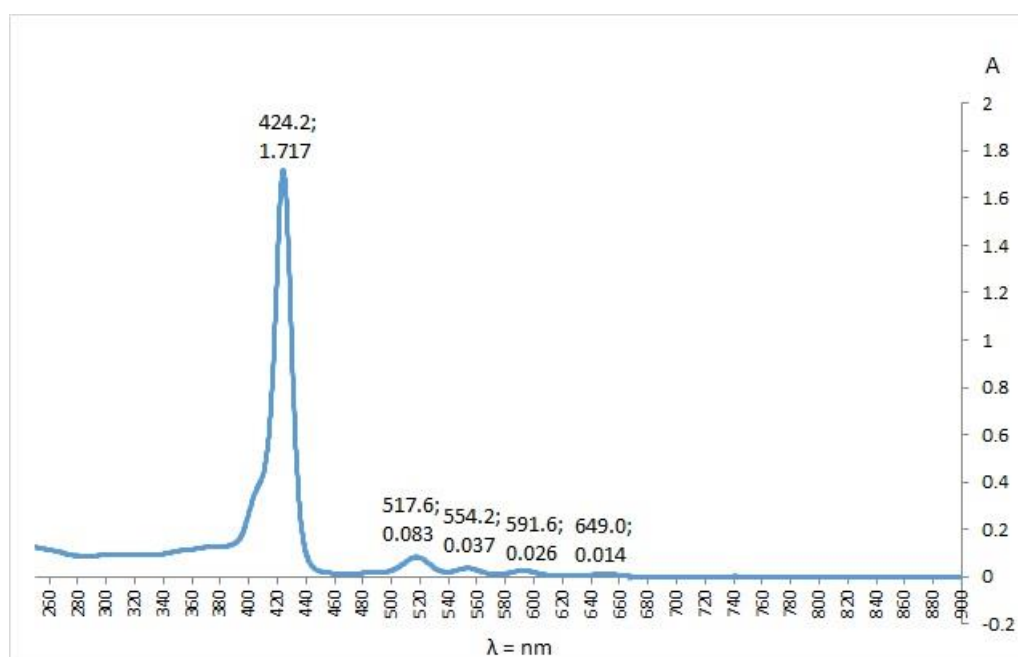
¹H NMR spectrum of **5b**



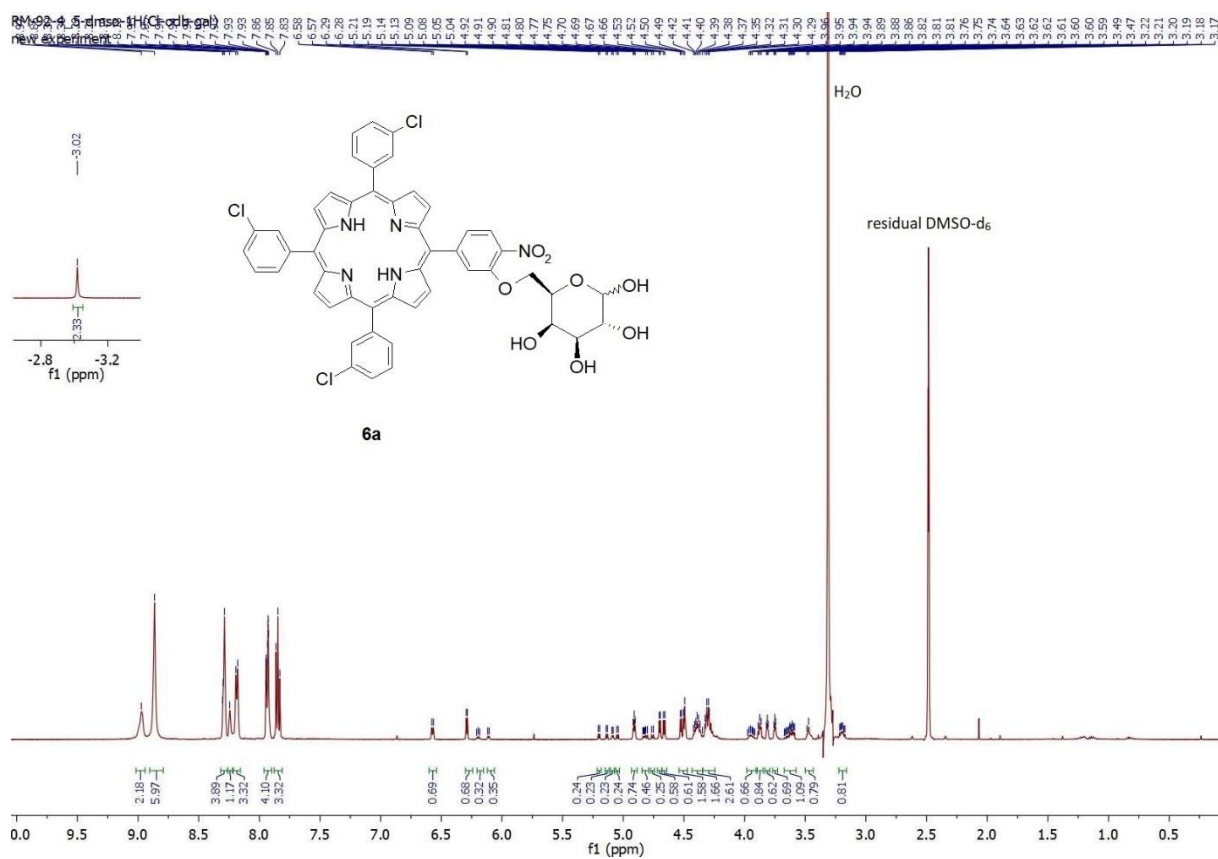
¹³C NMR spectrum of **5b**



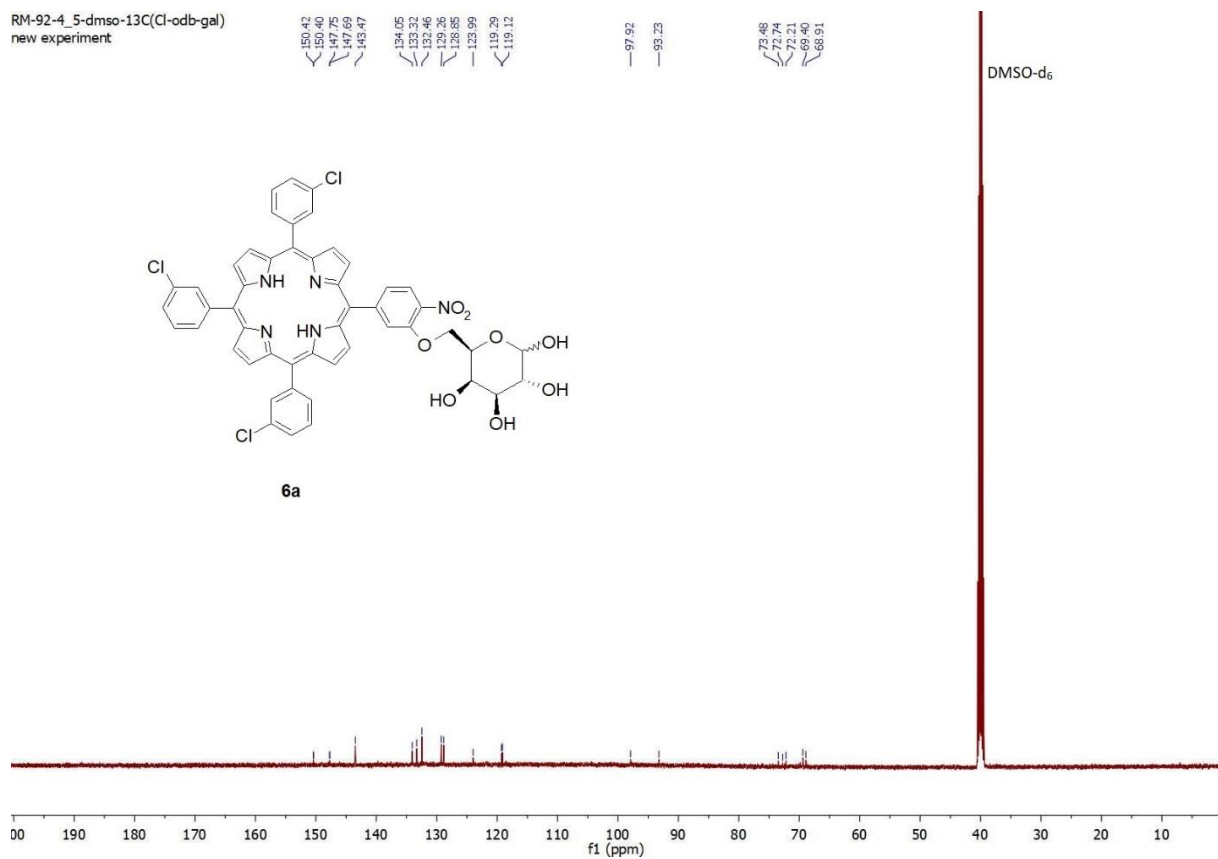
UV-VIS spectrum of **5b**



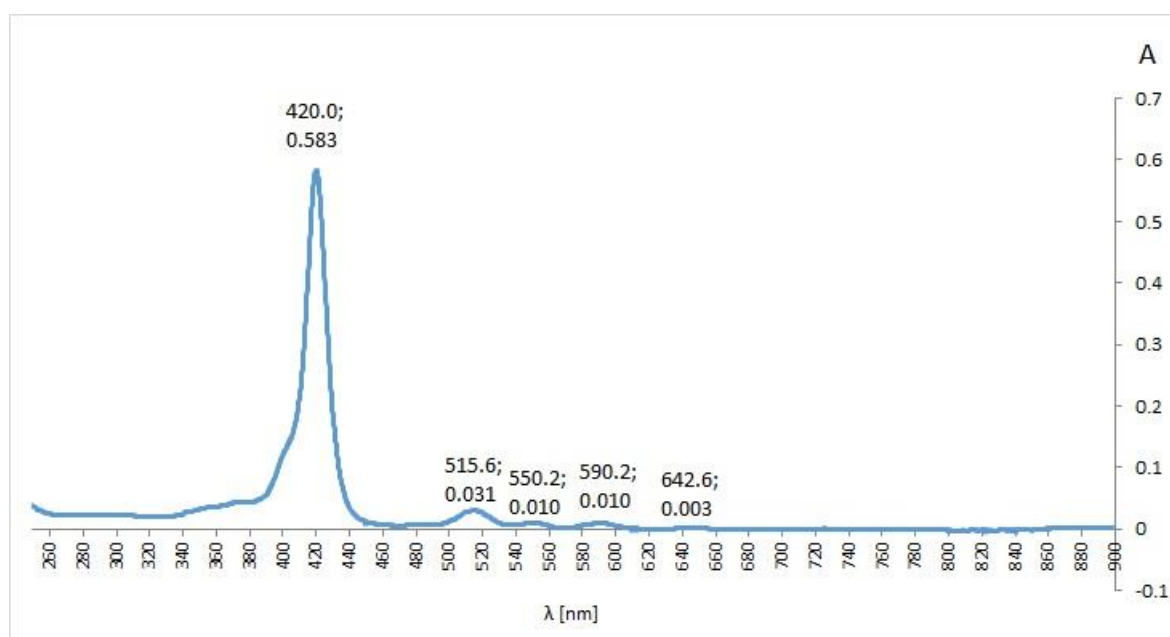
¹H NMR of **6a**



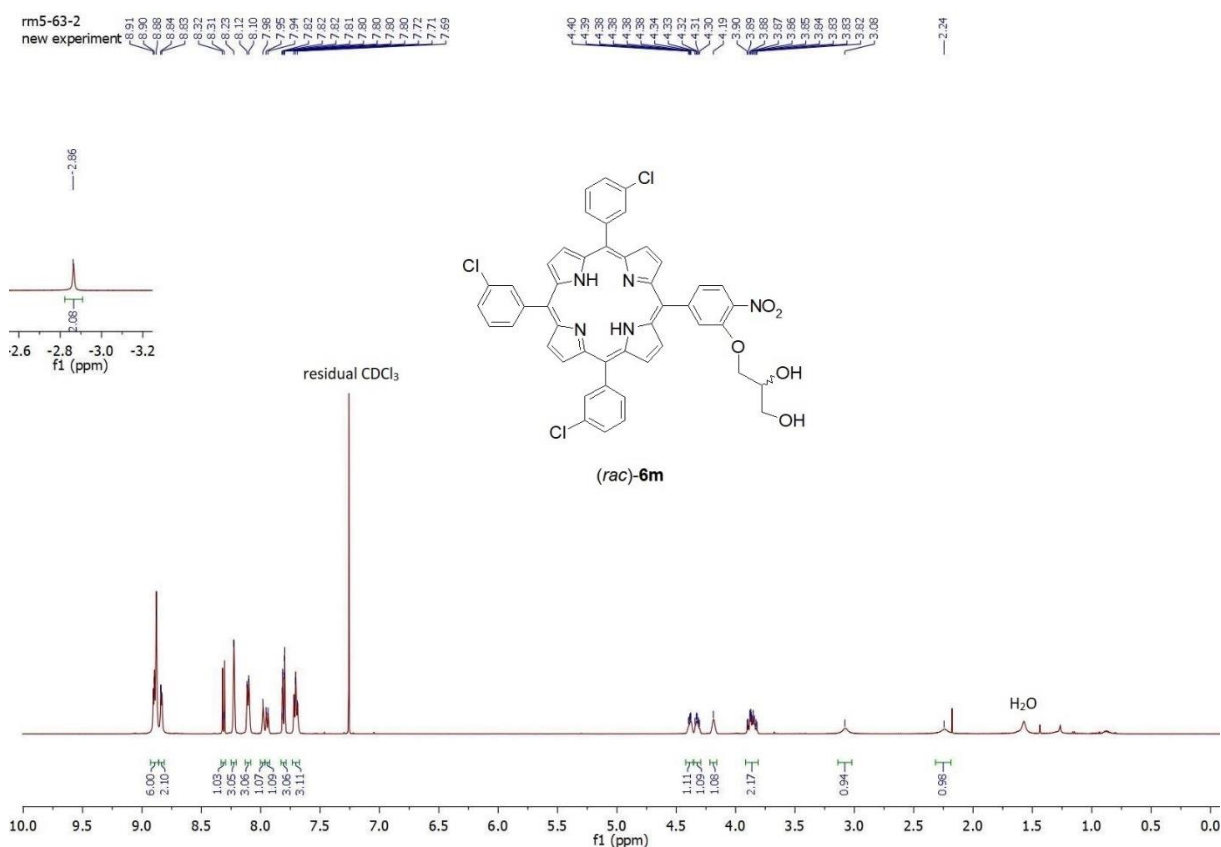
¹³C NMR of **6a**



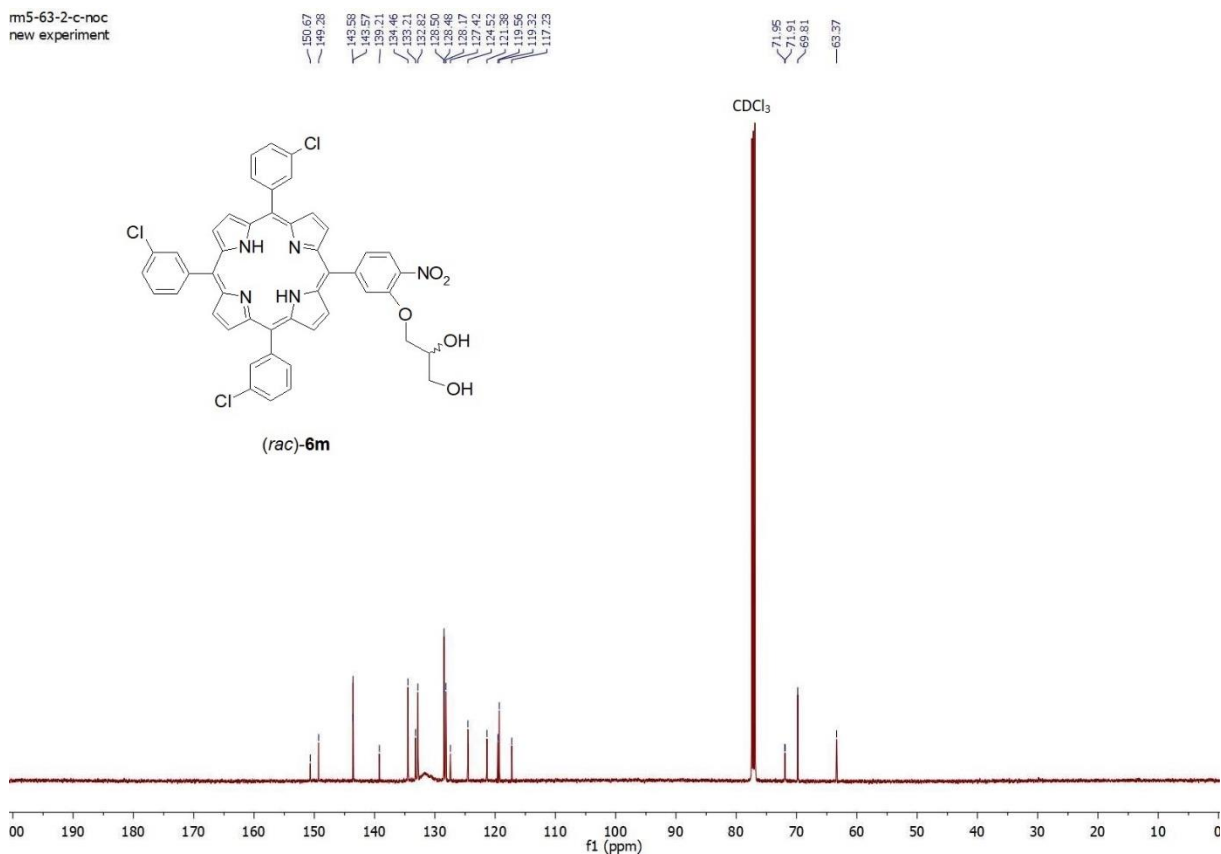
UV-VIS of **6a**



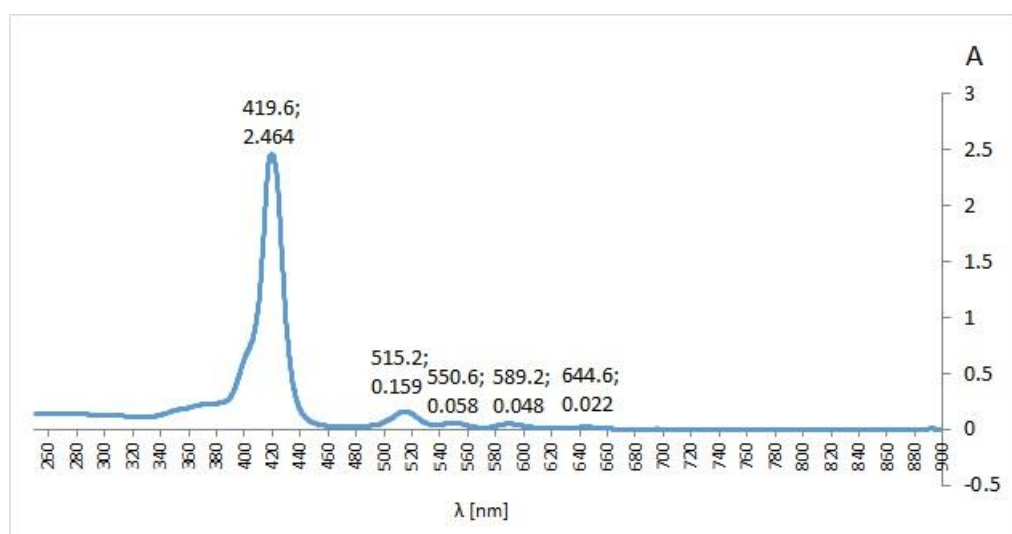
¹H NMR of (rac)-6m



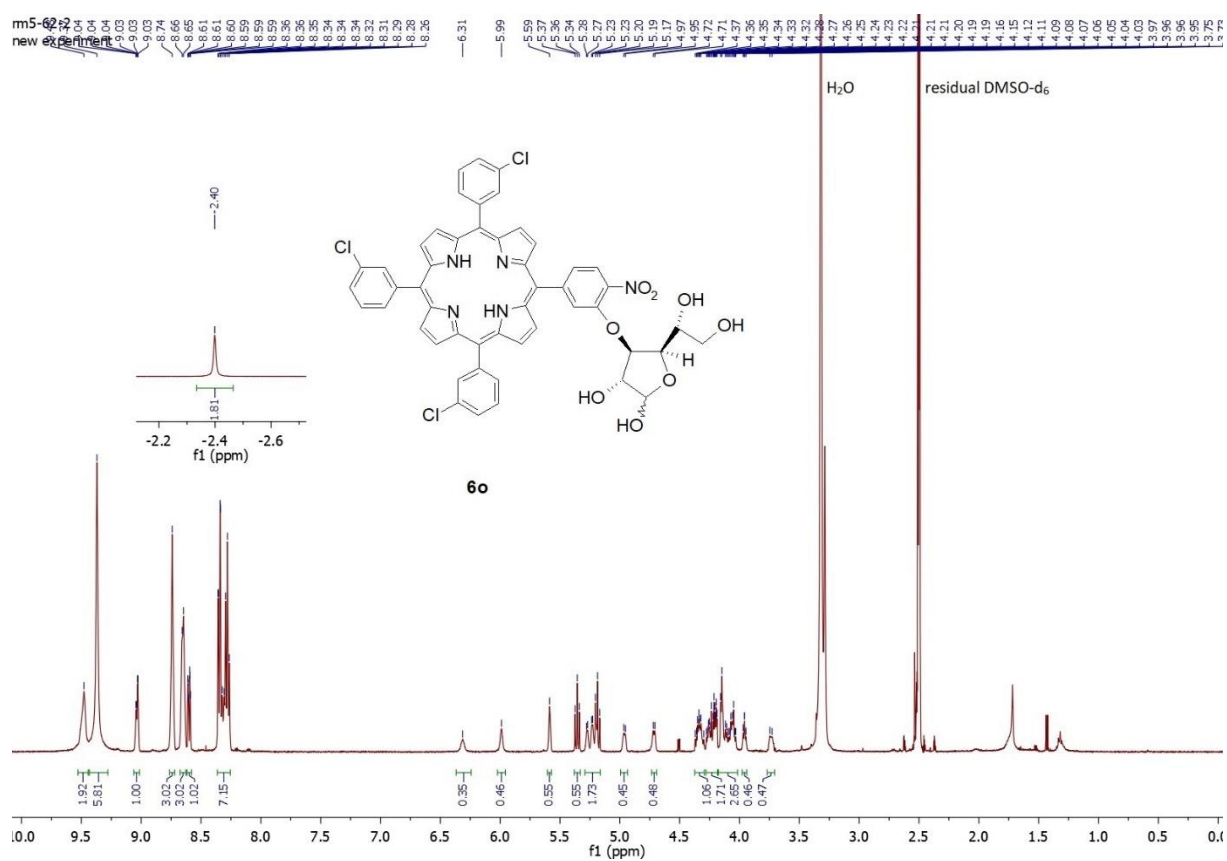
¹³C NMR of (rac)-6m



UV-VIS of (*rac*)-**6m**



¹H NMR of **6o**



UV-VIS of **6o**

