Supplementary Material (ESI) for Medicinal Chemistry Communications

Glycosylated Porphyrin Derivatives and Their Photodynamic Activity in Cancer Cells

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Supporting Information

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Experimental Section

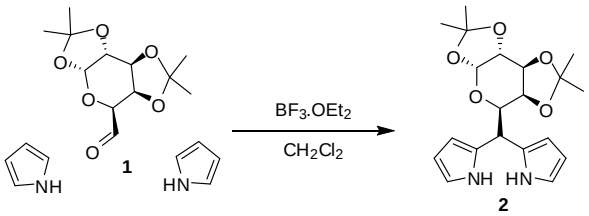
General method and materials

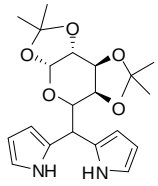
General: All the reactions were carried out in a flame or oven dried glassware under an argon or nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 nm). Analytical thin-layer chromatography was performed on E. Merck silica gel 60 F_{254} plates (0.25 mm). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using base solution of potassium permanganate. Porphyrinic compounds were visualized as green emerald spots by dipping in a solution of Ce(III)sulfate (1.0 g), ammonium molybdate (21.0 g), 96% sulfuric acid (31.0 mL), and distilled water (500 mL). IR spectra were recorded using FTIR Restige-21 (Shimadzu). NMR spectra were recorded at room temperature on 300 MHz Bruker ACF 300, 400 MHz Bruker DPX 400, 500 MHz Bruker AMX 500, and 400 MHz JEOL ECA 400 NMR spectrometers. The residual solvent signals were taken as the reference (7.26 ppm for 1H NMR spectra and 77.0 ppm for 13C NMR spectra in $CDCl_3$). Sometimes the TMS signal at 0.0 ppm was used an internal standard for 1H NMR spectra. Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal. HRMS (ESI) spectra were recorded on a Finnigan/MAT LCQ quadrupole ion trap mass spectrometer, coupled with the TSP4000 HPLC system and the Crystal 310 CE system.

Materials: All solvents were distilled under argon from the following drying agents immediately before use: Dichloromethane was distilled from calcium hydride. Technical grade solvents were used for chromatography and were distilled prior to use. All benzaldehyde were purchased from commercial suppliers and used without further purification. Sugar aldehyde was prepared galactose isopropylidene protection[1] followed by IBX oxidation[2]. $BF_3{\cdot}Et_2O$ solution and DDQ were purchased from commercial suppliers and used without further purification. Starting material dipyrryl methane unit (**2**) was prepared from condensation freshly distilled pyrrole with 1,2:3,4-di-*O*-isopropylidene-α-D-galacto-hexadialdo-1,5-pyranose (**1**) purified through silica gel column and perfectly dried prior to use.

Synthesis and spectral details of dipyrryl methane:

Synthesis of 1,2:3,4-di-*O*-isopropylidene-5,5-dipyrryl-6-deoxy-α-D-galactopyranose (2):

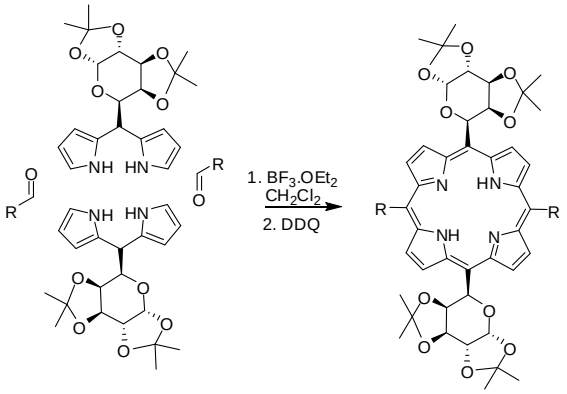




To a solution of freshly distilled pyrrole (1.35 mL, 19.38 mmol) and 1,2:3,4-di-*O*-isopropylidene-*α*-D-galacto-hexadialdo-1,5-pyranose (**1**) (1 g, 3.88 mmol) in CH_2Cl_2 (100 mL) at ambient temperature with stirring under N_2 was added BF_3·ethereal solution (48 μL, 0.39 mmol). After 3 h stirring, the bright orange reaction mixture was quenched by addition of a saturated aqueous $NaHCO_3$ solution (10 mL) and then diluted with CH_2Cl_2 (100 mL). The organic layer was separated, washed with water (2x50 mL). Then the combined organic layer were dried ($MgSO_4$), filtered, evaporated, and purified by flash chromatography (7:3 hexane/EtOAc) to give 913 mg (63%) of **2** as a white solid; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.83 (s, 1H, NH), 8.49 (s, 1H, NH), 6.71-6.69 (m, 2H, Py-CH), 6.15-6.13 (m, 2H, Py-CH), 6.09 (d, J = 1.1 Hz, 1H, Py-CH), 6.02 (s, 1H, Py-CH), 5.65 (d, J = 5.0 Hz, 1H, Sug-CH), 4.55 (dd, J_1 = 8.0 Hz, J_2 = 2.3 Hz), 4.48 (d, J = 10.0 Hz, 1H, Sug-CH), 4.32 (dd, J_1 = 5.0 Hz, J_2 = 2.3 Hz, 1H, Sug-CH), 4.13 (dd, J_1 = 10.0 Hz, J_2 = 1.3 Hz, 1H), 3.91 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, Sug-CH), 1.55 (s, 3H, -CH_3), 1.51 (s, 3H, -CH_3), 1.35 (s, 6H, -CH_3); **^{13}C NMR** (75MHz, $CDCl_3$): δ 131.0, 129.6, 116.6, 116.5, 109.1, 108.8, 108.1, 107.7, 107.6, 107.0, 96.9, 71.6, 70.8, 70.7, 70.3, 38.1, 25.9, 25.8, 24.8, 24.5; **IR** (neat): ν_{max} 3417, 1643, 1384, 1213, 717 cm^{-1}; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{20}H_{27}N_2O_5$: 375.1920, found: 375.1917.

Synthesis of sugar porphyrin conjugates & spectral details:

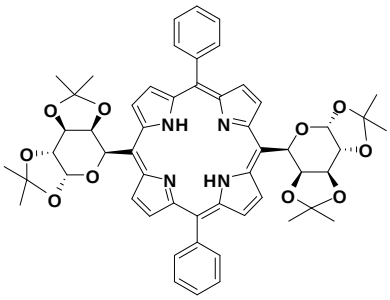
General procedure:



3. R=Ph
4. R=2,6-OMePh
5. R=4-OMePh
6. R=4-SMePh
7. R=4-OCF_3
8. R=C_6F_5
9. R=4-ClPh
10.R=4-NO_2Ph
11.R= thiophen-3-yl
12.R=Sugar

To a solution of 1,2:3,4-di-*O*-isopropylidene-5,5-dipyrryl-6-deoxy-α-D-galactopyranose **(2)** (200 mg, 0.53 mmol) in 250 mL of CH_2Cl_2 were added sequentially aromatic aldehyde (0.53 mmol) and BF_3·ethereal solution (6.7 μL, 0.05 mmol) while a stream of pure argon was passing. The reaction vessel was carefully shielded from light, and stirring was continued for 3 h. Then, triethylamine (7.4 μL, 0.05 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (132.90 mg, 0.59 mmol) were added, and the reaction mixture was stirred at room temperature for an additional 3 h. The solvent was evaporated under vacuum, and the resulting dark-violet solid was purified by column chromatography on silica gel to give porphyrin compound as a purple solid (5-16% yields).

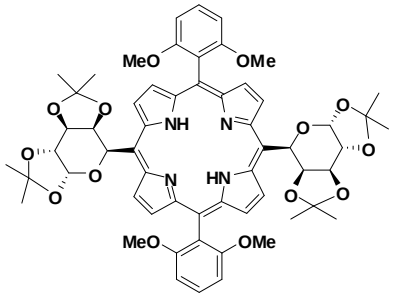
5,15-[Bis(phenyl)]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)] porphyrin (3):



Prepared according to general procedure using benzaldehyde; Purple solid; (58 mg, 12% yield); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.69 (d, J = 4.2 Hz, 4H, H-β), 8.82 (d, J = 4.8 Hz, 4H, H-β), 8.19 (d, J = 6.3 Hz, 4H, Ph-CH), 7.79-7.72 (m, 4H, Ph-CH), 7.68 (s, 2H, H-5'), 6.26 (d, J = 5.1 Hz, 2H, H-1'), 5.21 (d, J = 1.2 Hz, 2H, H-4'), 5.14 (d, J = 1.8 Hz, 2H, H-3'), 4.79 (dd, J_1 = 5.0 Hz, J_2 = 2.0 Hz, 2H, H-2'), 1.86 (s, 6H, -CH_3), 1.7 (s, 6H, -CH_3), 1.55 (s, 6H, -CH_3), 1.19 (s, 6H, -CH_3), -2.67 (s, 2H, NH); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 162.3, 143.3, 134.5, 131.7, 129.6,

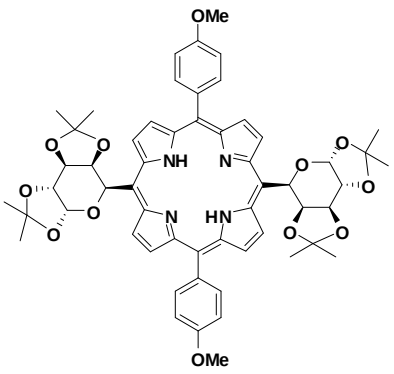
127.5, 126.3, 119.4, 113.7, 109.6, 109.0, 97.8, 71.9, 71.4, 26.8, 25.9, 25.1, 23.4; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{54}H_{55}N_4O_{10}$: 919.3918, found: 919.3948; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 406 (4.478), 516 (4.136), 549 (3.749), 589 (3.672), 644 (3.549); **IR** (neat): ν_{max} 3437, 2989, 1732, 1597, 1483, 1382, 1064, 802 cm^{-1}.

5,15-[Bis(2,6-dimethoxyphenyl)]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6 yl)]porphyrin (4):



Prepared according to general procedure using 2,6-dimethoxybenzaldehyde; Purple solid; (72 mg, 13% yield); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.59 (s, 4H, H-*β)*, 8.77 (d, J = 4.8 Hz, 4H, H-*β*), 7.72 (t, J = 8.5 Hz, 2H, Ph-CH), 7.64 (s, 2H, H-5'), 7.01-6.99 (m, 4H, Ph-CH), 6.23 (d, J = 4.9 Hz, 2H, H-1'), 5.26 (d, J = 7.8 Hz, 2H, H-4'), 5.8 (dd, J_1 = 7.8 Hz, J_2 = 1.9 Hz, 2H, H-3'), 4.76 (dd, J_1 = 4.9 Hz, J_2 = 2.0 Hz, 2H, H-2'), 3.49 (s, 12H,-OCH_3), 1.84 (s, 6H, -CH_3), 1.70 (s, 6H, -CH_3), 1.52 (s, 6H, -CH_3), 1.21 (s, 6H, -CH_3), -2.48 (s, 2H, NH); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.6, 146.5, 145.2, 130.7, 129.8, 129.5, 121.3, 112.3, 111.3, 109.4, 108.9, 104.2, 97.7, 76.6, 71.9,71.8, 71.4, 56.0, 26.8,25.9, 25.1, 23.4; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{58}H_{63}N_4O_{14}$: 1039.4341, found: 1039.4347; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 412 (4.533), 516 (4.205), 546 (3.607) 590 (3.768), 644 (3.526); **IR** (neat): ν_{max} 3435, 2927, 1633, 1469, 1382, 1249, 1109, 1064 cm^{-1}.

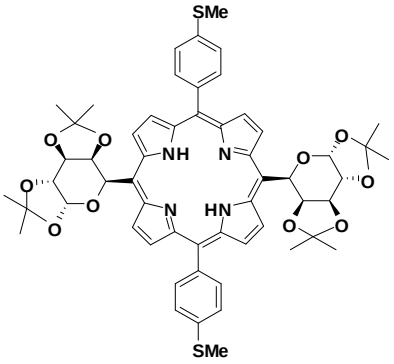
5,15-[Bis(4-methoxyphenyl)]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]porphyrin (5):



Prepared according to general procedure using 4-methoxybenzaldehyde; Purple solid; (41 mg, 8% yield); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.67 (s, 4H, H-*β*), 8.84 (d, J = 4.6 Hz, 4H, H-*β*), 8.08 (d, J = 8.0 Hz, 4H, Ph-CH), 7.66 (s, 2H, H-5'), 7.24 (d, J = 7.6 Hz, 4H, Ph-CH), 6.25 (d, J = 4.8 Hz, 2H, H-1'), 5.21 (d, J = 7.8 Hz, 2H, H-4'), 5.12 (d, J = 6.7 Hz, 2H, H-3'), 4.78 (d, J = 3.1 Hz, 2H, H-2'), 4.08 (s, 6H,-CH_3), 1.85 (s, 6H, -CH_3), 1.68 (s, 6H, -CH_3), 1.53 (s, 6H, -CH_3), 1.17 (s, 6H, -CH_3), -2.69 (s, 2H, NH); **^{13}C NMR**

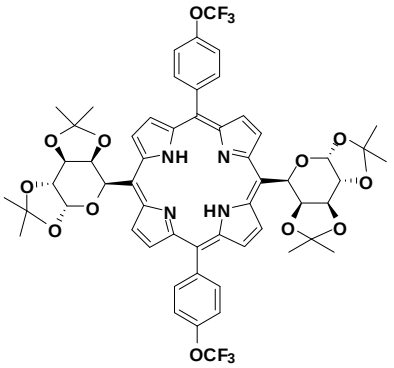
(125 MHz, $CDCl_3$): δ 159.3, 135.7, 135.5, 119.2, 113.5, 112.0, 111.8, 109.6, 109.0, 97.8, 71.9, 71.4, 55.6, 26.8, 25.9, 25.1, 23.4. **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{56}H_{59}N_4O_{12}$: 979.4129, found: 979.4128; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 414 (4.494), 518 (3.514), 550 (3.412), 590 (3.160), 646 (2.890). **IR** (neat): ν_{max} 3435, 2922, 1643, 1462, 1379, 1247, 1174, 1066 cm^{-1}.

5,15-[Bis(4-(methylthio)phenyl]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]porphyrin (6):



Prepared according to general procedure using 4-(methylthio)benzaldehyde; Purple solid; (37 mg, 7% yield); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.70 (d, J = 3.6 Hz, 4H, H-β), 8.86 (d, J = 4.9 Hz, 4H, H-β), 8.11 (d, J = 8.1 Hz, 4H, Ph-CH), 7.69 (s, 2H, H-5'), 7.64 (d, J = 8.3 Hz, 4H, Ph-CH), 6.27 (d, J = 5.0 Hz, 2H, H-1'), 5.22 (d, J = 8.2 Hz, 2H, H-4'), 5.15 (d, J = 7.8 Hz, 2H, H-3'), 4.80 (dd, J_1 = 5.0 Hz, J_2 = 1.8 Hz, 2H, H-2'), 2.78 (s, 6H,-CH_3), 1.87 (s, 6H, -CH_3), 1.71 (s, 6H, -CH_3), 1.56 (s, 6H, -CH_3), 1.20 (s, 6H, -CH_3), -2.69 (s, 2H, NH); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.0, 138.0, 135.1, 134.8, 131.6, 129.6, 125.2, 124.2, 118.8, 113.7, 109.6, 109.0, 107.0, 105.1, 97.8, 71.9, 71.3, 26.7, 25.8, 25.1, 23.3, 15.92; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{56}H_{59}N_4O_{10}S_2$: 1011.3673, found: 1011.3665; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 414 (4.540), 518 (4.282), 550 (3.817), 591 (3.796), 645 (3.653); **IR** (neat): ν_{max} 3439, 2924, 1643, 1456, 1382, 1257, 1163, 1066 cm^{-1}.

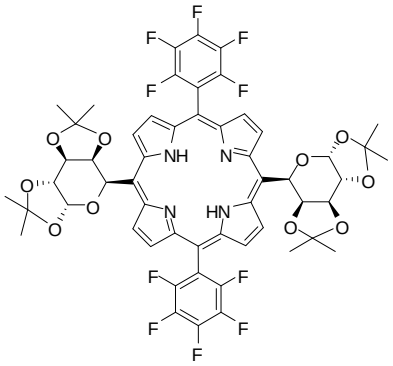
5,15-[Bis(4-trifluromethoxyphenyl)]-10*α*,20*β*[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]porphyrin (7):



Prepared according to general procedure using 4-trifluromethoxybenzaldehyde; Purple solid; (29 mg, 5% yield); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.71 (s, 4H, H-β), 8.77 (d, J = 4.8 Hz, 4H, H-β), 8.20 (d, J = 8.2 Hz, 4H, Ph-CH), 7.67 (s, 2H, H-5'), 7.60 (d, J = 7.9 Hz, 4H, Ph-CH), 6.25 (d, J = 4.9 Hz, 2H, H-1'), 5.20 (dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 2H, H-4'), 5.13 (dd, J_1 = 7.8 Hz, J_2 = 1.9 Hz, 2H, H-3'), 4.79 (dd, J_1 =5.0 Hz, J_2 = 2.0 Hz,

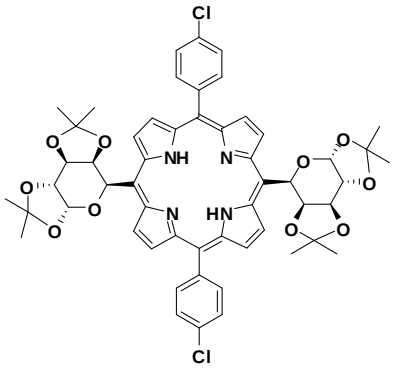
2H, H-2'), 1.85 (s, 6H, -CH_3), 1.69 (s, 6H, -CH_3), 1.53 (s, 6H, -CH_3), 1.18 (s, 6H, -CH_3), -2.73 (s, 2H, NH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8, 141.9, 135.5, 130.1, 129.2, 117.9, 114.2, 109.7, 109.1, 97.8, 71.9, 71.3, 26.8, 25.9, 25.1, 23.4; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{56}H_{53}N_4O_{12}F_6$: 1087.3564, found: 1087.3545; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 403 (4.538), 516 (4.211), 550 (3.827), 591 (3.757), 645 (3.487); **IR** (neat): ν_{max} = 3435, 2922, 1643, 1382, 1257, 1066, 804 cm^{-1}.

5,15-[Bis(pentaflurophenyl)]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]porphyrin (8):



Prepared according to general procedure using pentaflurobenzaldehyde; Purple solid; (64 mg, 11% yield); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.86 (s, 4H, H-*β*), 8.87 (d, J = 4.6 Hz, 4H, H-*β*), 7.72 (s, 2H, H-5'), 6.31 (d, J = 4.8 Hz, 2H, H-1'), 5.26 (d, J = 7.7 Hz, 2H, H-4'), 5.19 (d, J = 7.6 Hz, 2H, H-3'), 4.85 (d, J = 4.8 Hz, 2H, H-2'), 1.91 (s, 6H, -CH_3), 1.76 (s, 6H, -CH_3), 1.58 (s, 6H, -CH_3), 1.24 (s, 6H,-CH_3), -2.63 (s, 2H, -NH); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 147.9 (d, J = 58.6 Hz), 144.3 (t, J = 54.1 Hz), 139.6 (d, J = 86.3), 135.7, 131.6, 130.0, 117.6 (dt, J_1 = 39.0 Hz, J_2 = 3.6 Hz), 115.3, 109.8, 109.2, 101.5, 97.8, 77.3, 76.6, 71.9, 71.8, 71.3, 26.8, 25.9, 25.0, 23.4; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{54}H_{45}N_4O_{10}F_{10}$: 1099.2976, found: 1099.2979; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 405 (4.521), 513 (4.163), 543 (3.422), 586 (3.701), 640 (3.163); **IR** (neat): ν_{max} 3439, 2077, 1645, 1494, 1257, 1163, 1064 cm^{-1}.

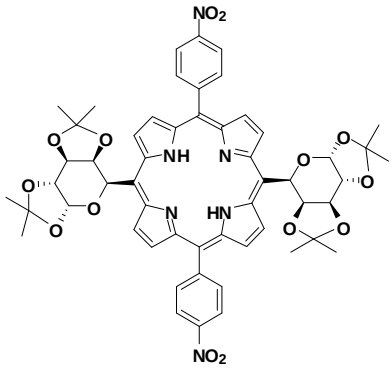
5,15-[Bis(4-chlorophenyl)]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]Porphyrin (9):



Prepared according to general procedure using 4-chlorobenzaldehyde; Purple solid; (36 mg, 7% yield); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.70 (s, 4H, H-*β*), 8.79 (d, J = 4.6 Hz, 4H, H-*β*), 8.10 (d, J = 7.0 Hz, 4H, Ph-CH), 7.72 (d, J = 7.0 Hz, 4H, Ph-CH), 7.66 (s, 2H, H-5'), 6.25 (d, J = 4.9Hz, 2H, H-1'), 5.20 (d, J = 7.7 Hz, 2H, H-4'), 5.13 (d, J = 7.8 Hz, 2H, H-3'), 4.79 (d,

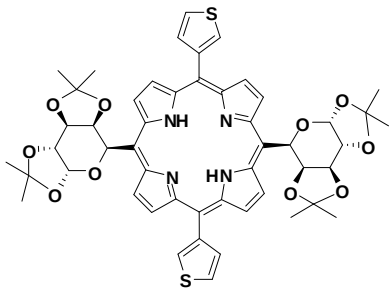
J = 4.9 Hz, 2H, H-2'), 1.85 (s, 6H, -CH_3), 1.69 (s, 6H, -CH_3), 1.52 (s, 6H, -CH_3), 1.18 (s, 6H, -CH_3), -2.74 (s, 2H, NH); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 141.7, 135.4, 134.0, 131.9, 130.2, 126.6, 117.9,114.0, 109.6, 109.0, 97.8, 71.9, 71.3, 26.7, 25.8, 25.1, 23.3; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{54}H_{53}N_4O_{10}Cl_2$: 987.3139, found: 919.3138; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 416 (4.480), 516 (3.453), 548 (3.051), 590 (2.979), 644 (2.723); **IR** (neat): ν_{max} 3439, 2922, 1714, 1643, 1462, 1379, 1068, 702 cm^{-1}.

5,15-[Bis(4-nitrophenyl)]-10*α*,20*β*-[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]porphyrin (10):



Prepared according to general procedure using 4-nitrobenzaldehyde; Purple solid; (32 mg, 6% yield); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.74 (d, *J* = 3.9 Hz, 4H, H-*β*), 8.72 (d, *J* = 4.9 Hz, 4H, H-*β*), 8.63 (d, *J* = 8.6 Hz, 4H, Ph-CH), 8.36 (d, *J* = 8.5 Hz, 4H, Ph-CH), 7.66 (s, 2H, H-5'), 6.25 (d, *J* = 5.0 Hz, 2H, H-1'), 5.18 (d, *J* = 9.5 Hz, 2H, H-4'), 5.14 (d, *J* = 1.8 Hz, 2H, H-3'), 4.80 (dd, J_1 = 5.0 Hz, J_2 = 1.8 Hz, 2H, H-2') 1.85 (s, 6H, -CH_3), 1.69 (s, 6H, -CH_3), 1.53 (s, 6H, -CH_3),1.19 (s, 6H, -CH_3), -2.72 (s, 2H, NH); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.0, 147.7, 135.0, 121.6, 116.8, 114.9, 109.7, 109.1, 97.8, 71.8, 71.8, 71.3, 26.7, 25.8, 25.0, 23.3. **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{54}H_{53}N_6O_{14}$: 1009.3620, found: 1009.3619; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 419 (4.506), 518 (3.577), 550 (3.103), 590 (3.106), 645 (2.811); **IR** (neat): ν_{max} 3439, 2958, 1714, 1643, 1519, 1462, 1066, cm^{-1}.

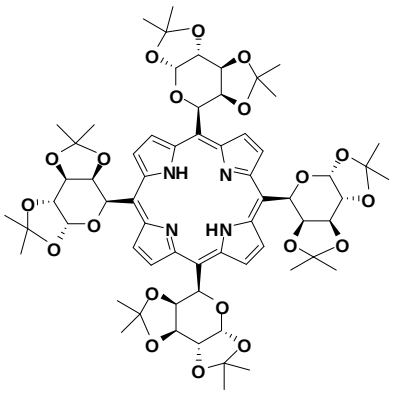
5,15-[Bis(3-thiophene)]-10*α*,20*β*–[bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)]porphyrin (11):



Prepared according to general procedure using 3-formyl thiophene; Purple solid; (24 mg, 5% yield); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.68 (d, *J* = 3.9 Hz, 4H, H-*β*), 8.94 (d, *J* = 4.9 Hz, 4H, H-*β*), 7.98-7.96 (m, 4H, Ar-CH), 7.70 (dd, J_1 = 4.8 Hz, J_2 = 3.0 Hz, 4H, H-*β*), 7.66 (d, *J* = 1.1 Hz, 2H, H-5'), 6.25 (d, *J* = 4.9 Hz, 2H, H-1'), 5.20 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 2H, H-

4'), 5.12 (dd, J_1 = 7.9 Hz, J_2 = 2.0 Hz, 2H, H-3'), 4.78 (dd, J_1 = 5.0 Hz, J_2 = 2.0 Hz, 2H, H-2'), 1.86 (s, 6H, -CH_3), 1.69 (s, 6H, -CH_3), 1.53 (s, 6H, -CH_3), 1.18 (s, 6H, -CH_3), -2.7 (s, 2H, NH); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 162.3, 143.3, 134.8, 131.4, 130.1, 128.1, 122.8, 113.8, 113.7, 109.6, 109.6, 109.0, 97.8, 76.5, 71.9, 71.3, 26.7, 25.9, 25.1, 23.3; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{50}H_{51}N_4O_{10}S_2$: 931.3047, found: 931.3044; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 412 (4.501), 518 (3.767), 550 (3.480), 591 (3.329), 646 (3.089); **IR** (neat): ν_{max} 3437, 2918, 1643, 1454, 1382, 1255, 1064 cm^{-1}.

5*α*,10*β*,15*α*,20*β*-Tetrakis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-yl)porphyrin (12):



Prepared according to general procedure with slight modification. Here, we used instead of aromatic aldehyde another 1,2:3,4-di-*O*-isopropylidene-**α**-D-galacto-hexadialdo-1,5-pyranose (**1**); Purple solid; (104 mg, 16% yield); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.81 (s, 8H), 7.77 (s, 4H, H-5'), 6.32 (d, J = 4.9 Hz, 4H, H-1'), 5.28 (d, J = 8.7 Hz, 4H, H-4'), 5.18 (dd, J_1 = 7.9 Hz, J_2 = 1.8 Hz, 4H, H-3'), 4.84 (dd, J_1 = 5.0 Hz, J_2 = 1.9 Hz, 4H, H-2'), 1.94 (s, 12H, -CH_3), 1.85 (s, 12H, -CH_3), 1.59 (s, 12H, -CH_3), 1.26 (s, 12H, -CH_3), -2.88 (s, 2H, NH); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 130.0, 112.5, 109.6, 109.0, 97.7, 76.6, 72.2, 71.9, 71.5, 26.9, 26.1, 25.1, 23.5; **HRMS** (ESI): m/z $(M+H)^+$ Calcd for $C_{64}H_{79}N_4O_{20}$: 1223.5288, found: 1223.5266; **UV–VIS** ($CHCl_3$) λ_{max} (log ε): 406 (4.519), 519 (4.017), 552 (3.381), 591 (3.591), 646 (3.437); **IR** (neat): ν_{max} 3441, 2989, 2073, 1643, 1382, 1255, 1064, cm^{-1}.

Biology Methods and Materials:

Cell Cultures:

Human cancer cell lines including HCT116 and HeLa were maintained in Dulbecco's Modified Eagle Medium (DMEM) containing 10% fetal bovine serum and 1% penicillin/streptomycin in a humidified 5% CO_2 incubator at 37 °C.

Photocytotoxicity Assay.

Cells were seeded onto 96-well plates at a density of about 2 x 10^4 cells per well and incubated in the dark in medium containing 5% serum together with compounds for 24 h at 37°C. Cells were rinsed with phosphate buffered saline (PBS) and then exposed to broad-spectrum green light (480-550 nm) generated by two layers of green cellophane-filtered 50 W halogen lamp using a dose rate of 13 mW/cm^2. Cell viability was determined using the CellTiter 96 Aqueous One Solution Reagent kit (Promega, Medison, WI) according to the manufacturer's instructions, 24 h after light exposure by measuring absorbance at 490 nm.

Intracellular Localization and Image Analysis.

Cells plated on coverslips in a 6-well plate were incubated with 1 μM of compound for 24 h. For intracellular localization in HeLa cells, cells incubated with compound for 24 h were loaded with 100 nM MitoTracker Deep Red (Molecular Probes) for 15 min or with 100 nM LysoTracker Red (Molecular Probes) for 1 h at 37 °C. The slides were washed three times with PBS and were visualized by at 60 x magnification on a Zeiss LSM META confocal laser scanning microscopy (Zeiss, Oberkochen, Germany).

Measurement of Apoptosis.

Apoptosis was performed as previously described from our group.[3] In brief, cells treated with 1 μM compound were incubated for 24 h and then illuminated. After 24 h, cells were collected and apoptosis was examined by using Annexin V-FLUOS staining kit (Roche, Penzberg, Germany). Cells were counter-stained with propidium iodide followed by fluorescence activated cell sorter (FACS) analysis on a flow cytometer (BD LDR II, BD Biosciences, San

Jose, CA). For visualization of apoptotic cells, cells were seeded on coverslips within a 6-well plate. After fixation in 3.7% paraformaldehyde, cells were washed with PBS and permeabilized with 0.2% Triton X-100, washed again with PBS, and mounted by ProLong Gold antifade reagent with DAPI (Molecular probes, Eugene, Oregon). The stained nuclei were observed and photographed under a fluorescence microscope (Nikon Inc., Melville, NY). Apoptosis was measured as the percentage of annexin V-positive and PI-negative cell population. For all experiments, at least 10,000 events were collected per sample.

Immunoblot Analysis.

Cells were resuspended in a lysis buffer (20 mM Tris-HCl, pH 7.5, 150 mM NaCl, 0.5% Triton X-100, 1 mM EDTA, 1 mM PMSF) containing protease inhibitors on ice for 40 min. The clear cell lysates were obtained after centrifuging for 15 min at 15,000 rpm. The lysates (30 μg of protein) were resolved by SDS-polyacrylamide gel electrophoresis (SDS-PAGE) and were transferred to nitrocellulose membranes. The membranes were blocked with 5% dry milk in TBS-T (20 mM Tris-HCl, pH 7.5, 140 mM NaCl, and 0.05% tween-20) and subsequently incubated with primary antibody followed by a goat anti-rabbit or goat anti-mouse IgG conjugated to horseradish peroxidase, and the immunoreactive bands were visualized by the SUPEX Western blotting detection kit (Neuronex, Korea)

1) J. B. Malcolm R. Banks, J. I. G. Cadogan, lan M. Dawson, Suneel Gaur, lan Gosney, Robert and K. J. G. a. P. K. G. H. Gould, *J . Chem. Soc., Chem. Commun.*, 1993, 1146.

2) J. T. Suri, S. Mitsumori, K. Albertshofer, F. Tanaka and C. F. Barbas, *J. Org. Chem,* 2006, **71**, 3822-3828.

3) a) B.-H. Choi, L. Feng and H. S. Yoon, *J. Biol. Chem.*, 2010**, 285**, 9770; b) B.-H. Choi, W. Kim, Q. C. Wang, D.-C. Kim, S. N. Tan, J. W. H. Yong, K.-T. Kim and Yoon, H. S. *Cancer Lett.* 2008**, 261**, 37.

NMR, UV, HRMS spectrum of sugar porphyrin conjugates

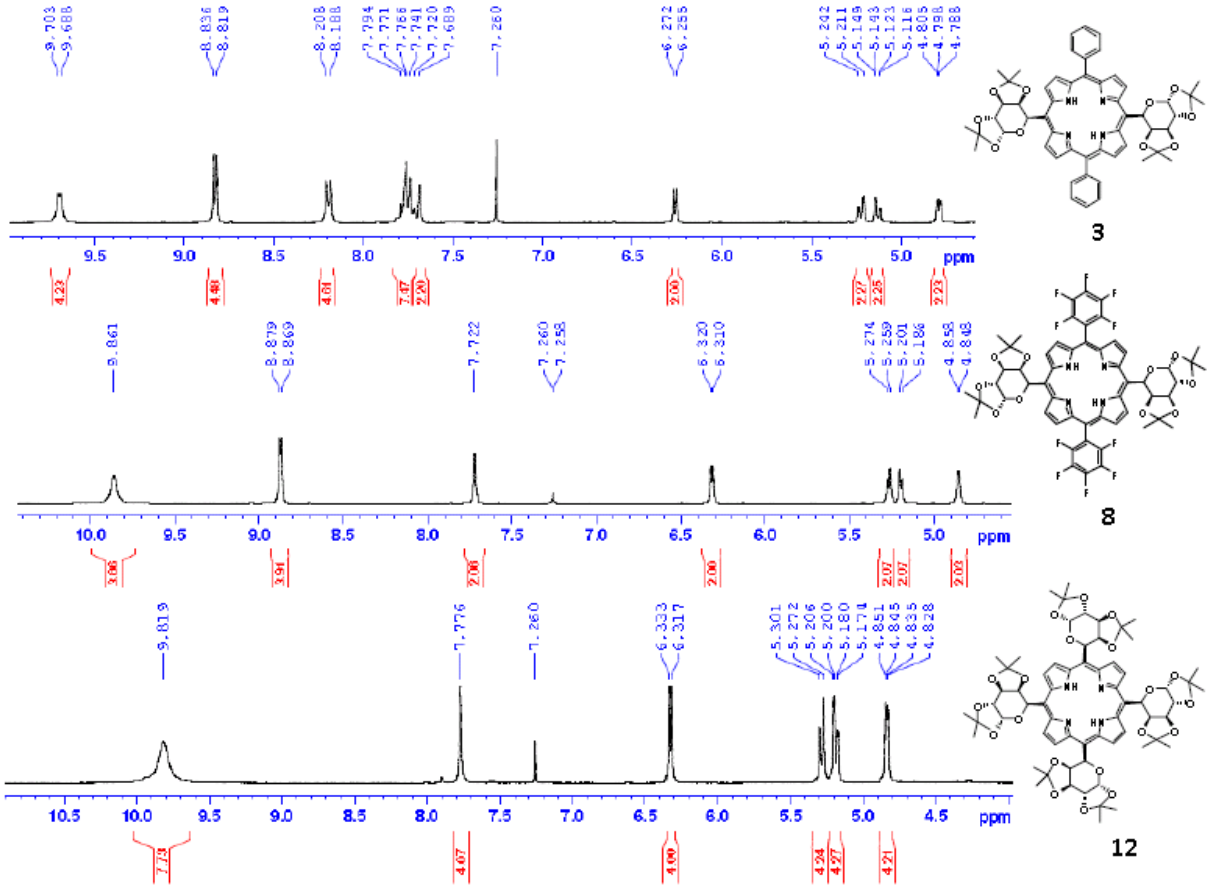
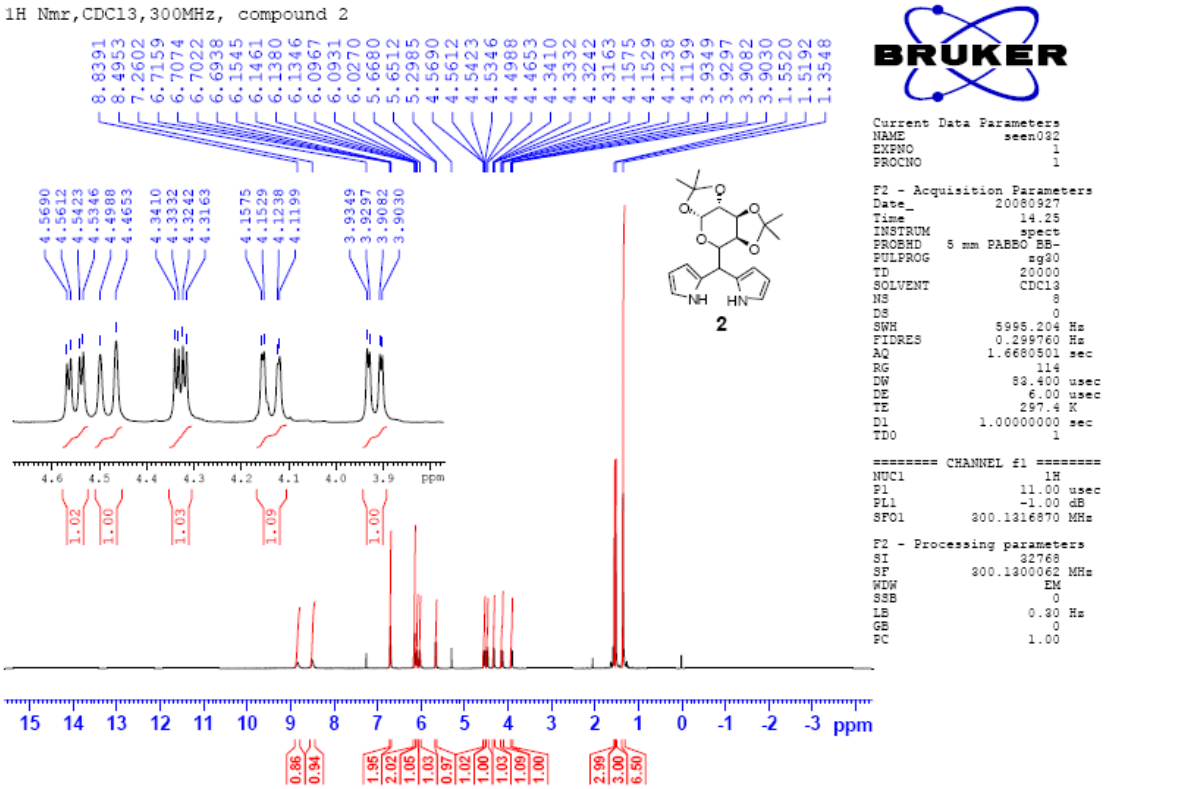


Fig. 1S. Partial ^{1}H NMR spectra of compound **3**, **8** and **12**

Furthermore, comparative NMR diagram illustrates that the partial ^{1}H NMR spectra of compounds **3**, **8** and **12**, thereby evidencing the diagnostic signals. For compounds **3** and **8,** two types of *β, β*' pyrrole protons appeared in the most deshielded aromatic region, but compound **12** displayed single peak. Compound **3** displayed Ar-H signal next to the *β,β*' pyrrole proton, but it disappeared in compound **8** due to the replacement of Ar-H by Ar-F. For all the compounds, sugar H-5' appeared in the deshielded region due to ring-current obtained by highly conjugated aromatic system. Successively, anomeric proton followed by the sugar methelene protons appears towards the shielded region. This picture further evidencing compounds **3** & **8** possess C_2-symmetry where as compound **12** shows highly D_2 symmetry.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6.1461
6.1380
6.1346
6.0967
6.0931
6.0270
5.6680
5.6512
5.2985
4.5690
4.5612
4.5423
4.5346
4.4988
4.4653
4.3410
4.3332
4.3242
4.3163
4.1575
4.1529
4.1238
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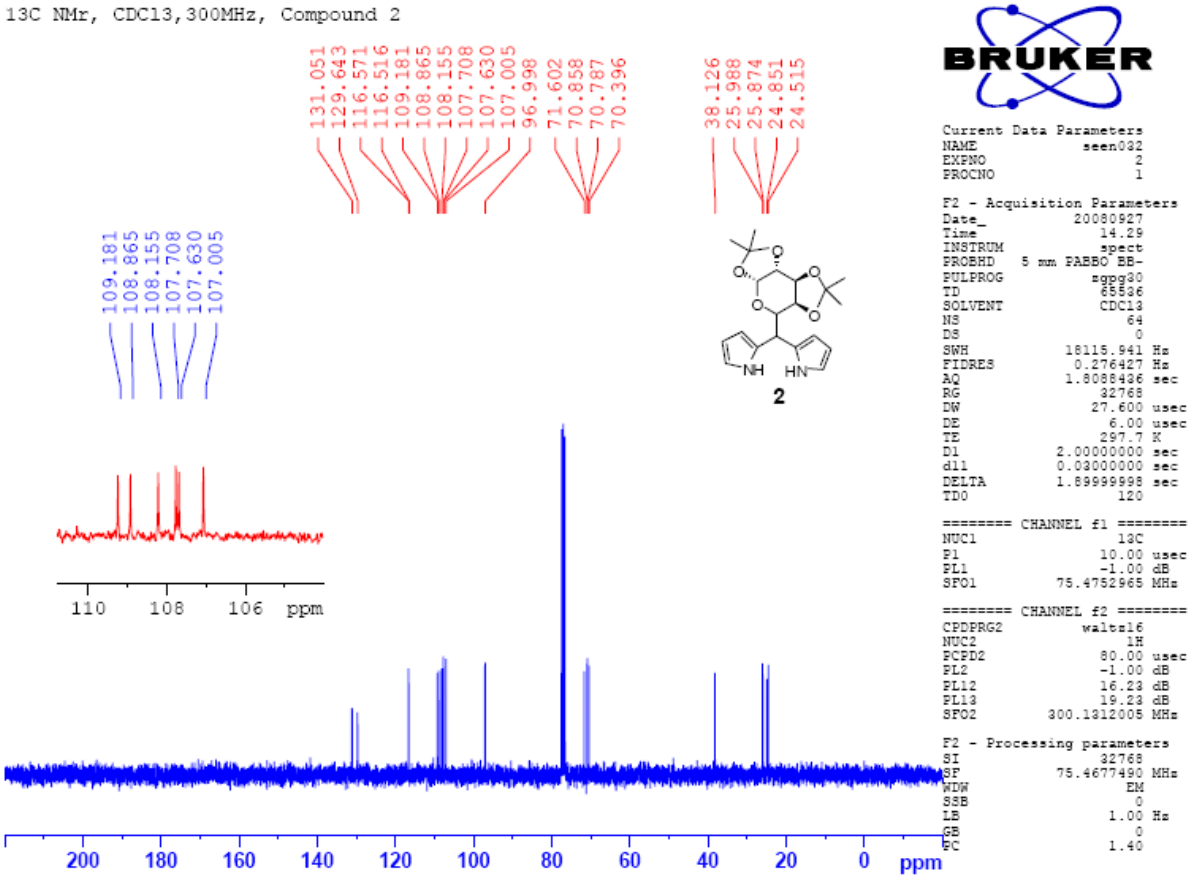
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HN
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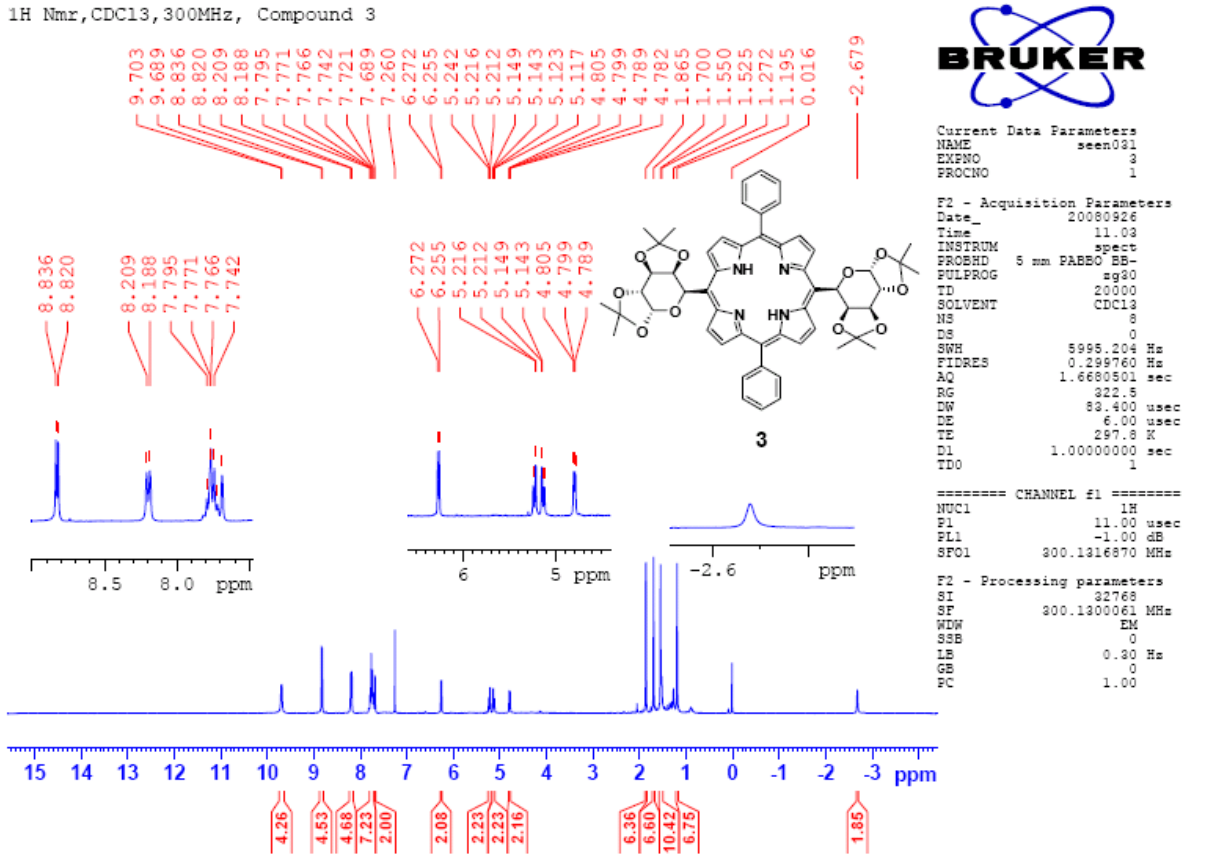
ppm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8.836 8.820 8.209 8.188 7.795 7.771 7.766 7.742
6.272 6.255 5.216 5.212 5.149 5.143 4.805 4.799 4.789
3
8.5 8.0 ppm
6 5 ppm
-2.6 ppm
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
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BRUKER
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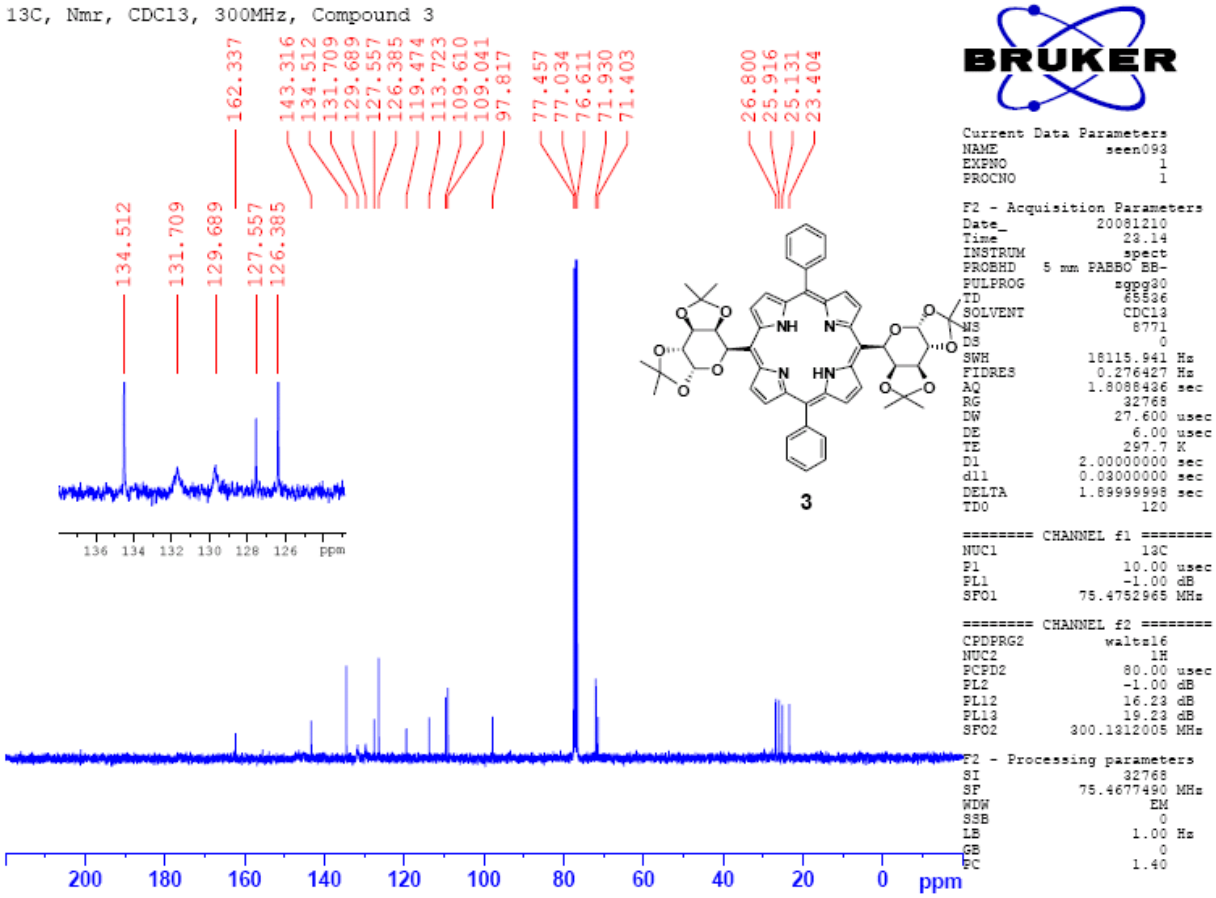
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PL13 19.23 dB
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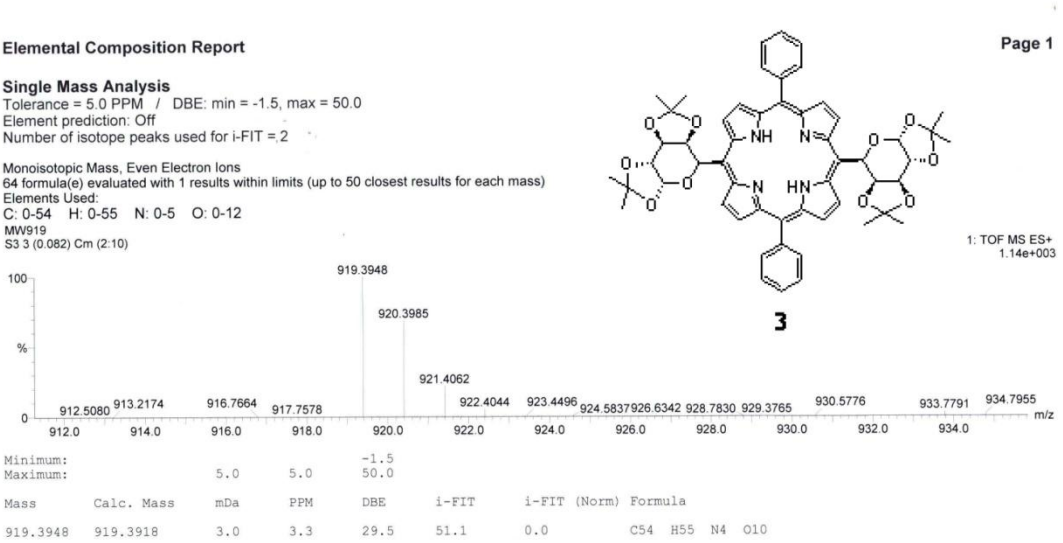
Elemental Composition Report
Page 1
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Number of isotope peaks used for i-FIT = 2
Monoisotopic Mass, Even Electron Ions
64 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
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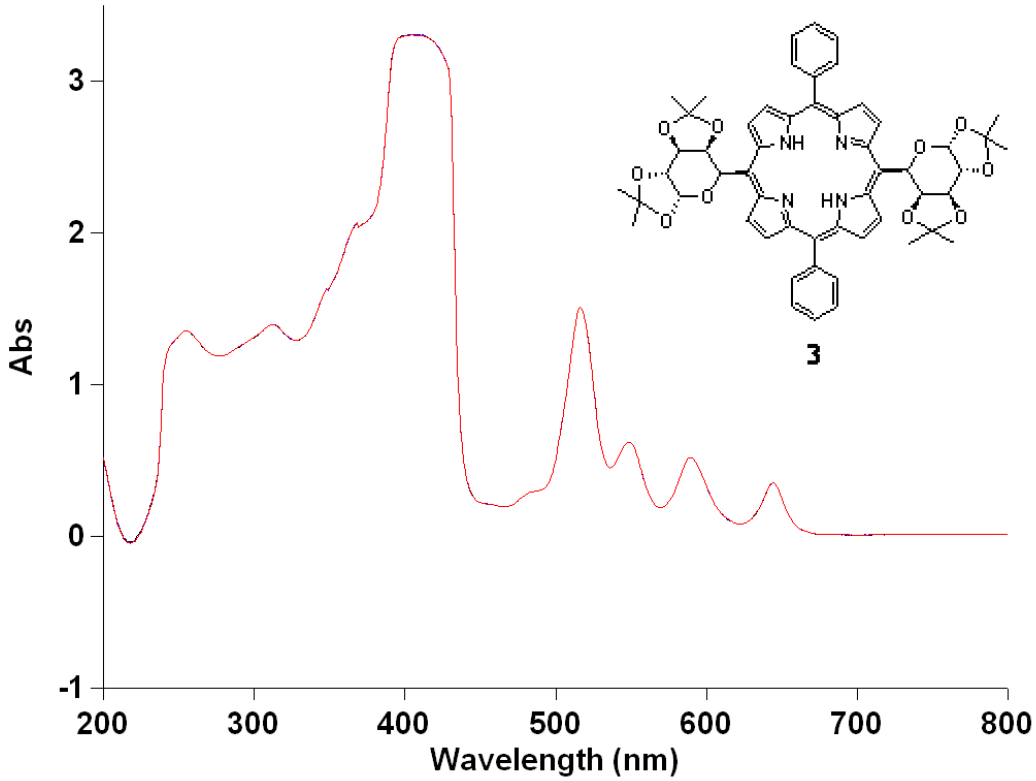
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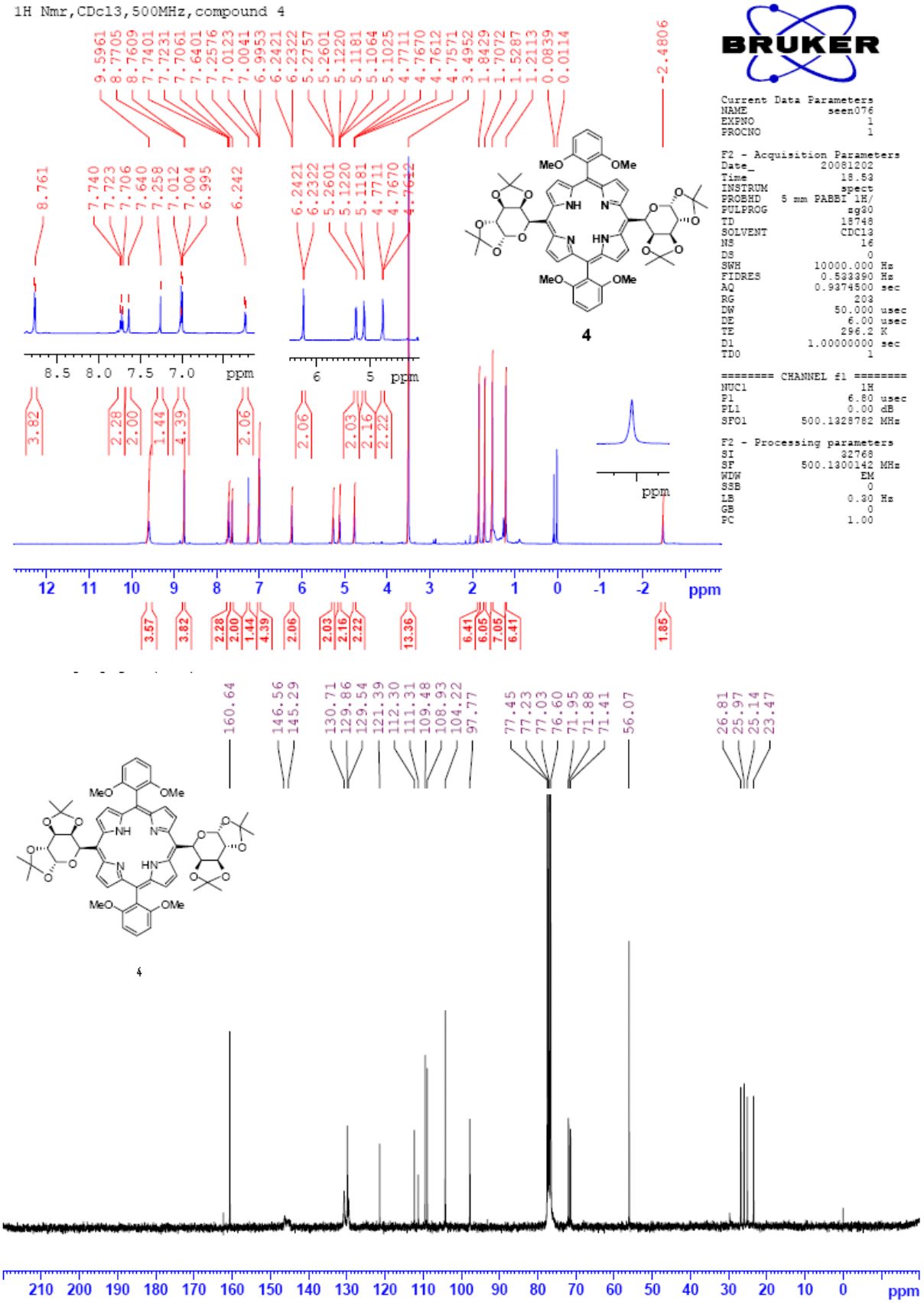
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5.1064
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2.06
2.03
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ppm
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HN
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77.23
77.03
76.60
71.95
71.88
71.41
56.07
26.81
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25.14
23.47
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NH
N
HN
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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Elemental Composition Report Page 1

Single Mass Analysis
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Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
61 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
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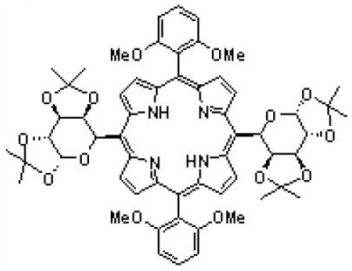

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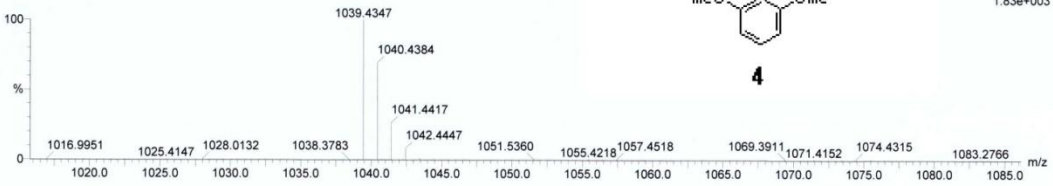

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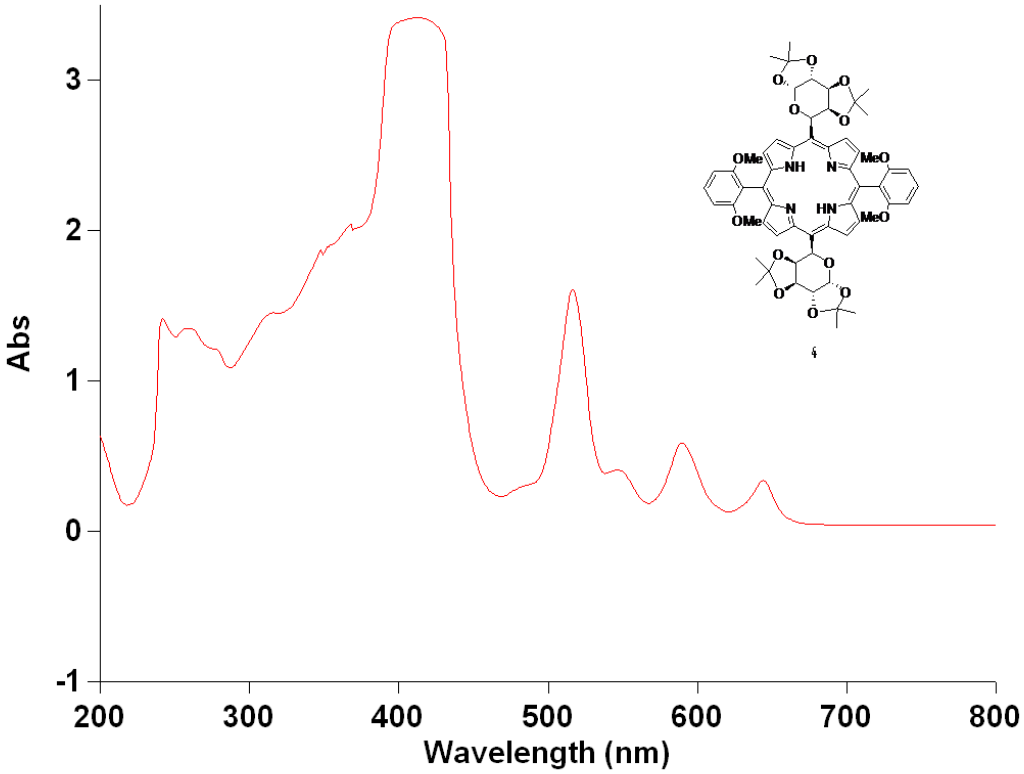
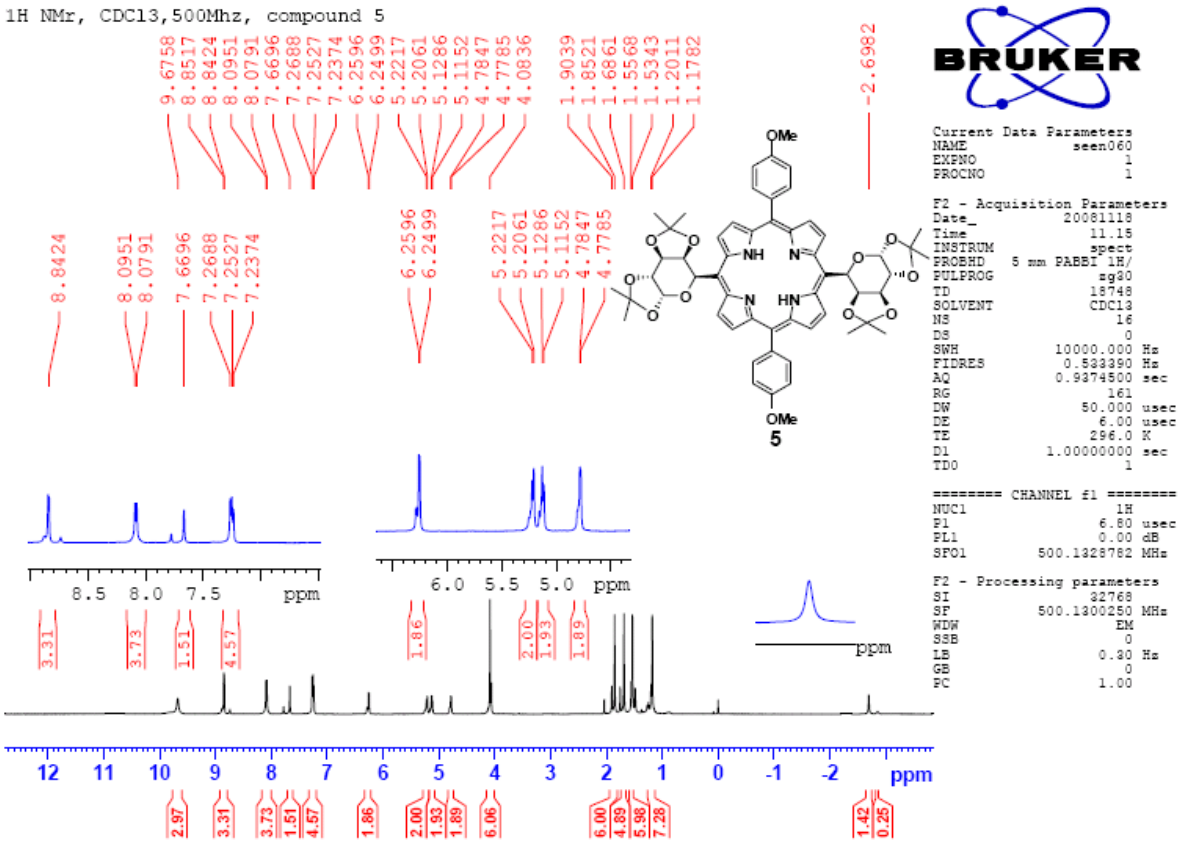


6

1H NMr, CDCl3,500Mhz, compound 5



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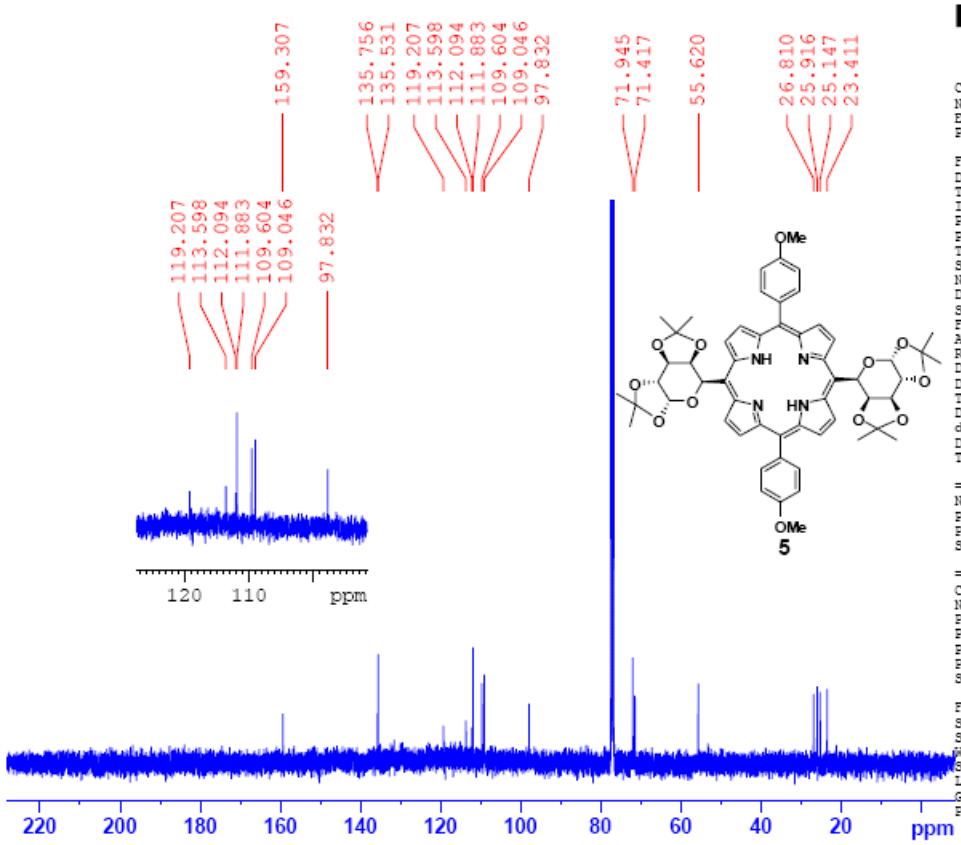
RG                       161
DW                    50.000 usec
DE                     6.00 usec
TE                    296.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     6.80 usec
PL1                    0.00 dB
SFO1              500.1328782 MHz

F2 - Processing parameters
SI                        32768
SF                500.1300250 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                      1.00
```

13CNmr, CDCl3,500MHz, Compound 5



BRUKER

```
Current Data Parameters
NAME                 seen060
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_               20081118
Time                   11.30
INSTRUM                spect
PROBHD     5 mm PABBI 1H/
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       188
DS                         4
SWH                29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      2050
DW                    16.800 usec
DE                     10.00 usec
TE                    296.6 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     14.50 usec
PL1                    -2.00 dB
SFO1              125.7716224 MHz

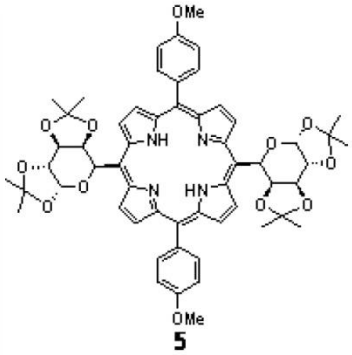
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   21.41 dB
PL13                   22.00 dB
SFO2              500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                125.7577890 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                      1.40
```

Elemental Composition Report Page 1

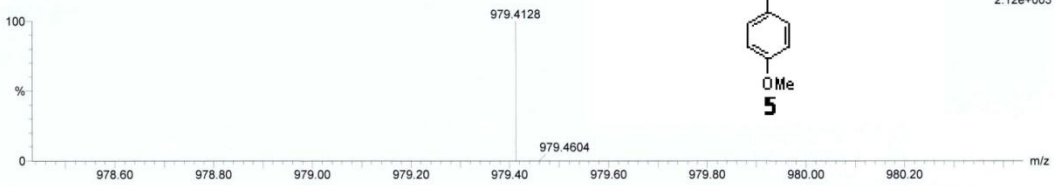
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
101 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-56 H: 0-59 N: 0-4 O: 0-12 S: 0-1
MW978
2-snv 3 (0.083) Cm (2:9)

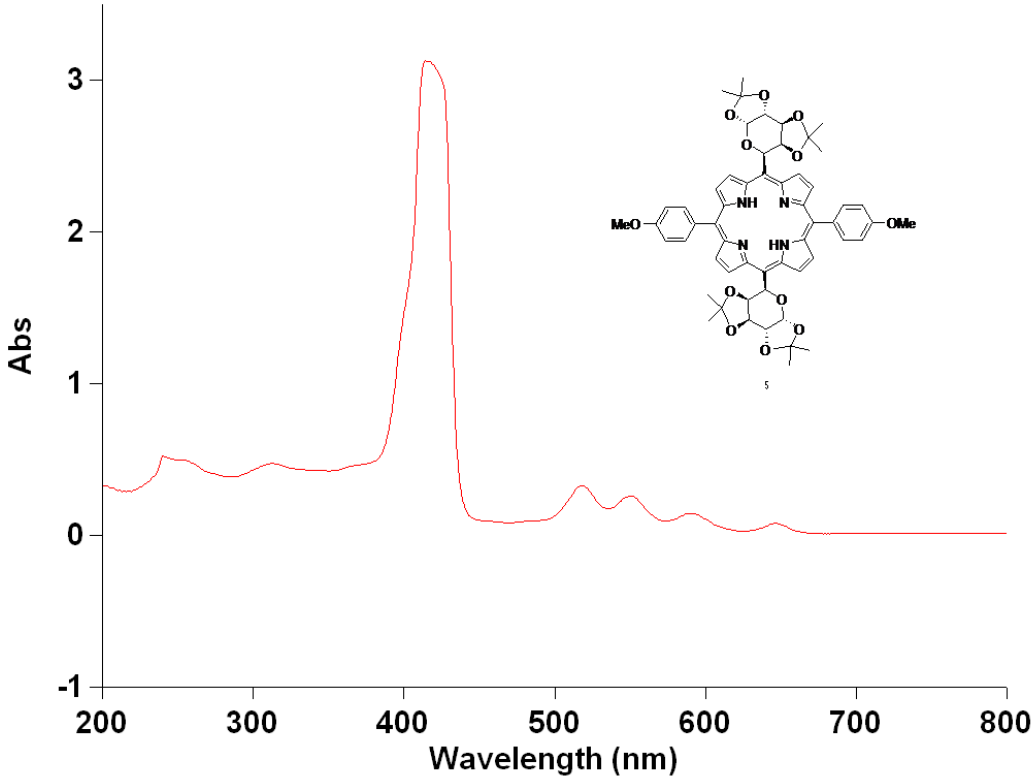


5

1: TOF MS ES+
2.12e+003

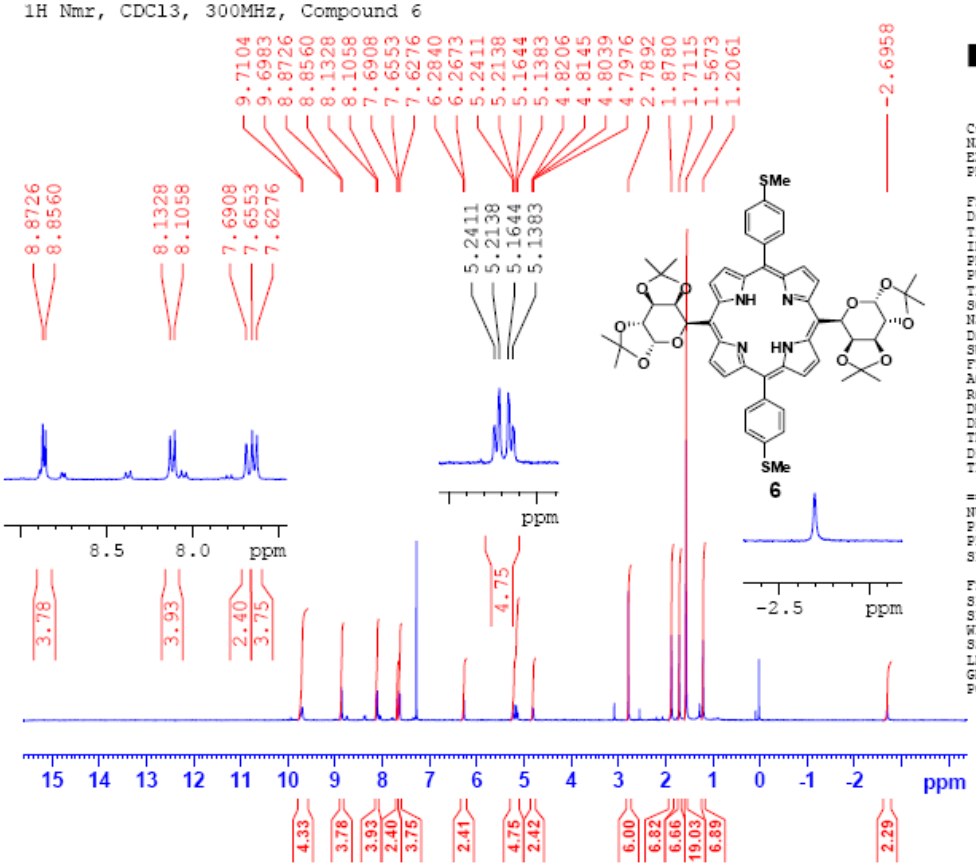


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
979.4128	979.4129	-0.1	-0.1	29.5	28.9	0.0	C56 H59 N4 O12



5

1H Nmr, CDCl3, 300MHz, Compound 6



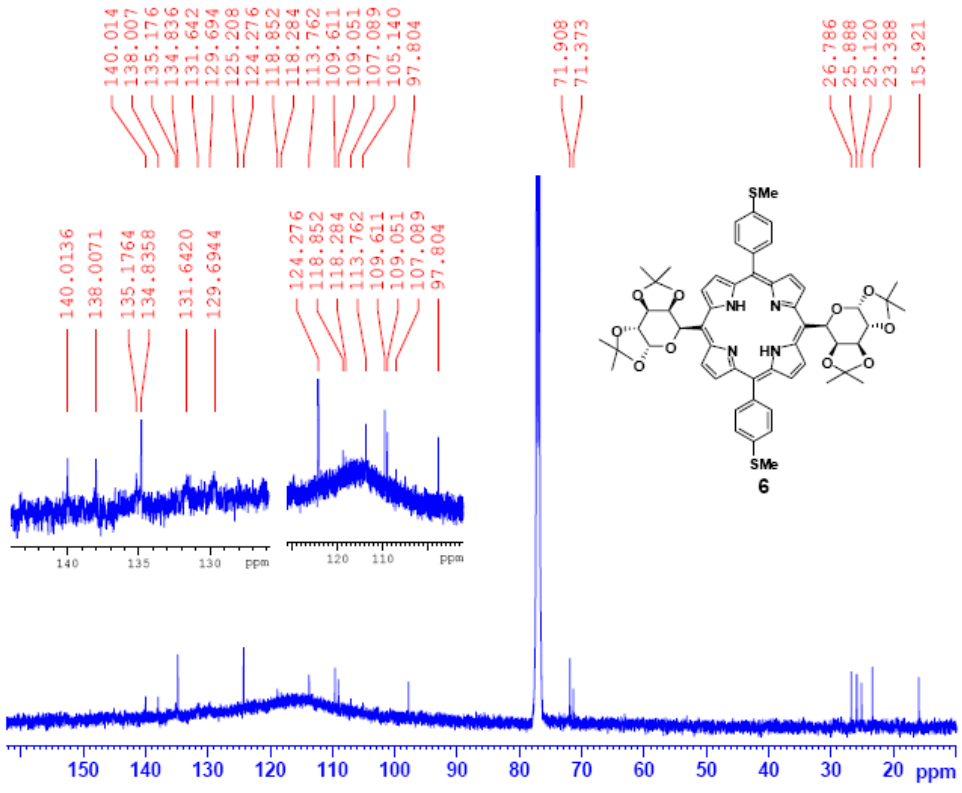

```
Current Data Parameters
NAME                 seen114
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20081227
Time                    9.53
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    20000
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                5995.204 Hz
FIDRES             0.299760 Hz
AQ                 1.6680501 sec
RG                     456.1
DW                    83.400 usec
DE                     6.00 usec
TE                    297.0 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1                    -1.00 dB
SFO1          300.1316870 MHz

F2 - Processing parameters
SI                        32768
SF                300.1300000 MHz
WDW                       EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

13C NMr, CDCl3, 500Mhz, compound 6




```
Current Data Parameters
NAME                 seen112
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20090105
Time                   21.47
INSTRUM                spect
PROBHD    5 mm PABBI 1H/
PULPROG             sgpg30
TD                     65536
SOLVENT               CDCl3
NS                     12204
DS                         4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                 1.1010548 sec
RG                      2050
DW                    16.800 usec
DE                    10.00 usec
TE                    296.0 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     14.50 usec
PL1                    -2.00 dB
SFO1          125.7716224 MHz

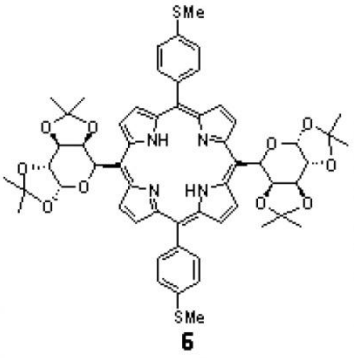
======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   21.41 dB
PL13                   22.00 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                125.7577890 MHz
WDW                       EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Elemental Composition Report Page 1

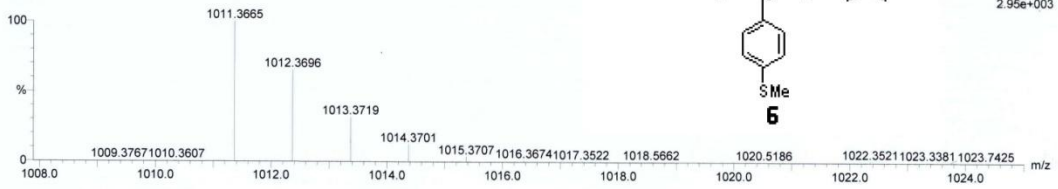
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
144 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-56 H: 0-59 N: 0-4 O: 0-10 S: 0-2
MW1011
SNV-9 5 (0.120) Cm (5:10)

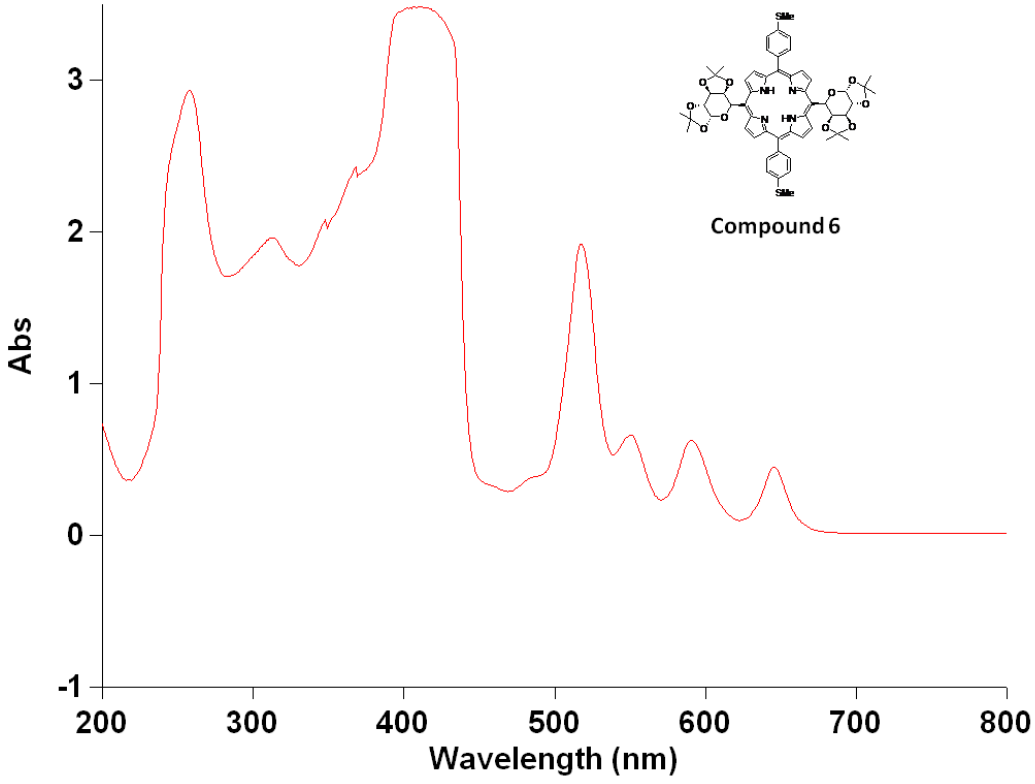


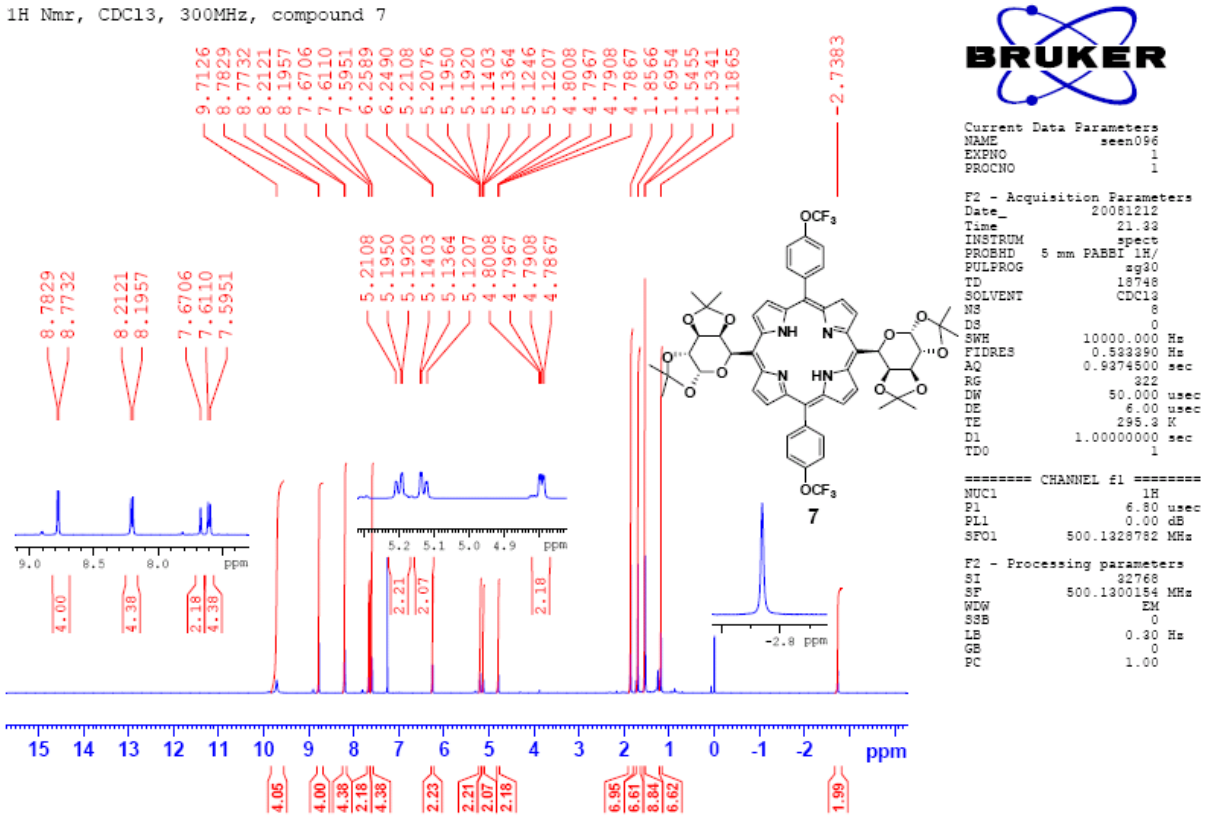
6

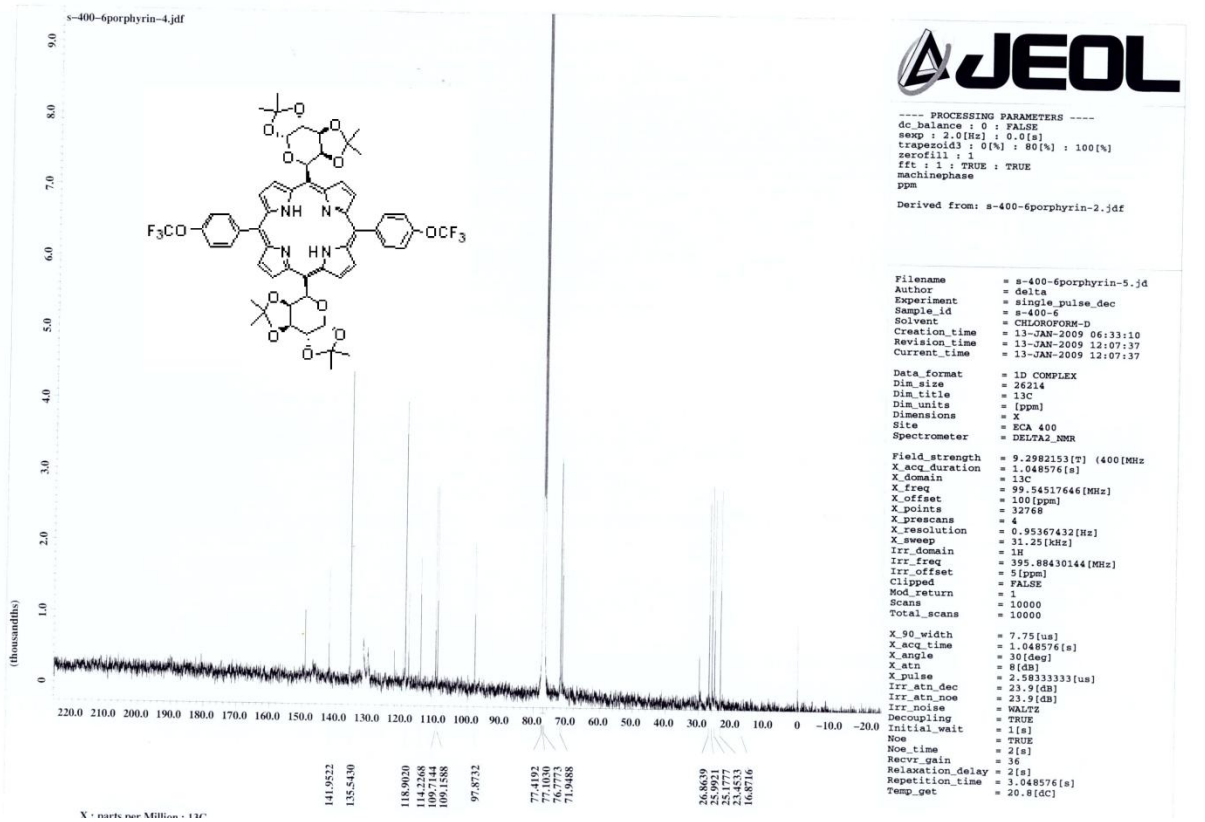
1: TOF MS ES+
2.95e+003



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1011.3665	1011.3673	-0.8	-0.8	29.5	78.3	0.0	C56 H59 N4 O10 S2




1H Nmr, CDCl3, 300MHz, compound 7
X
BRUKER
Current Data Parameters
NAME seen096
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081212
Time 21.33
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 18748
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.533390 Hz
AQ 0.9374500 sec
RG 322
DW 50.000 usec
DE 6.00 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 6.80 usec
PL1 0.00 dB
SFO1 500.1328782 MHz
F2 - Processing parameters
SI 32768
SF 500.1300154 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OCF3
NH
N
HN
7
ppm

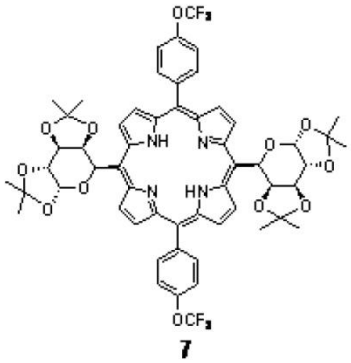

s-400-6porphyrin-4.jdf
JEOL
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: s-400-6porphyrin-2.jdf
F3CO
OCF3
NH
N
HN
(thousandths)
X : parts per Million : 13C

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

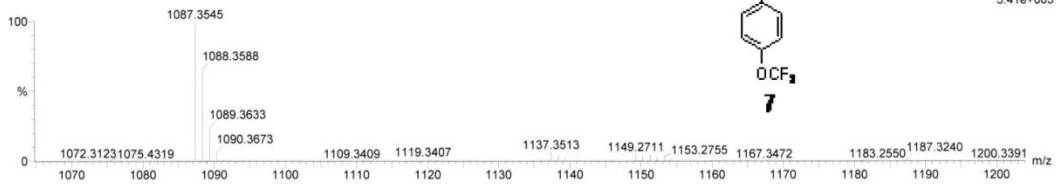
Monoisotopic Mass, Even Electron Ions
423 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-56 H: 0-53 N: 0-4 O: 0-12 F: 0-6

MW1086
SNV-11 5 (0.119) Cm (5:12)

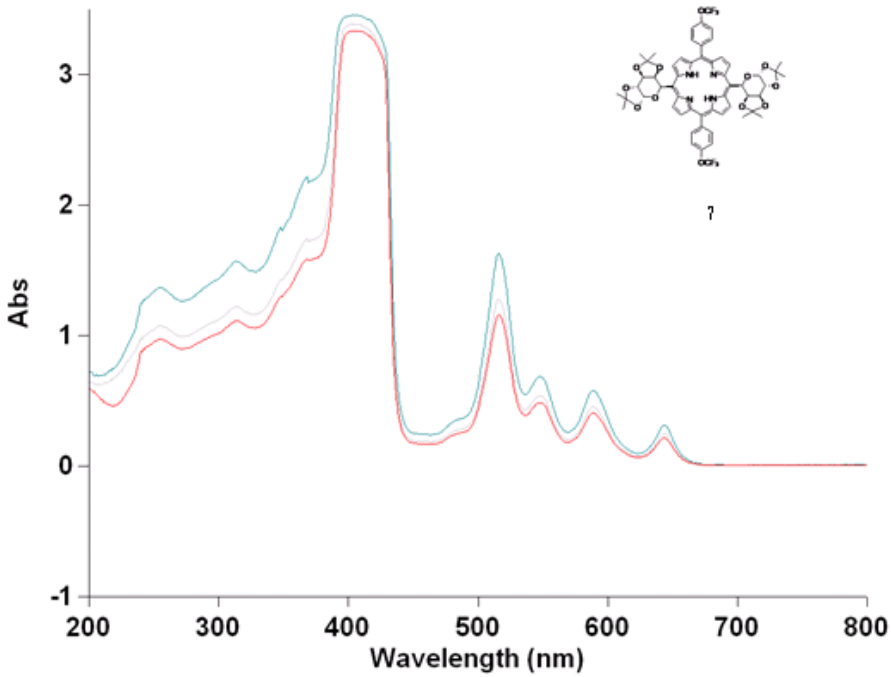


7

1: TOF MS ES+
5.41e+003

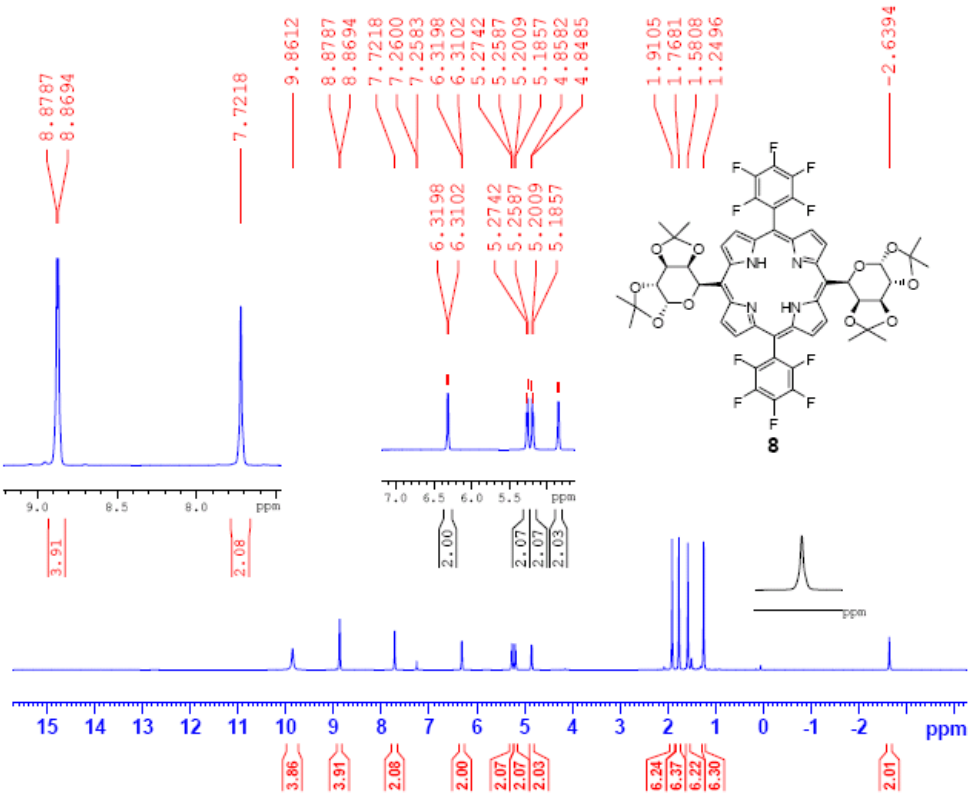


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
1087.3545	1087.3564	-1.9	-1.7	29.5	100.2	0.0	C56 H53 N4 O12 F6	



7

1H Nmr, 500MHz, CDCl3, compound 8



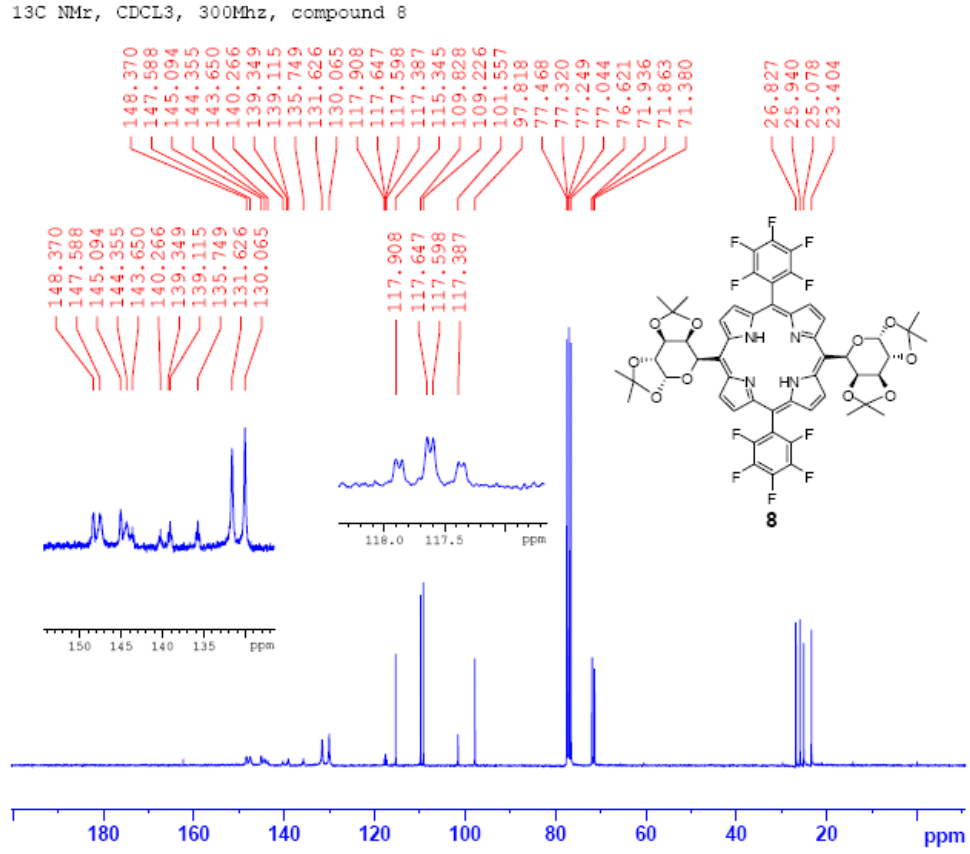

```
Current Data Parameters
NAME      pyridyl(isoindole)
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20081201
Time                  14.20
INSTRUM               spect
PROBHD    5 mm PABBI 1H/
PULPROG               zg30
TD                   18748
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES               0.533390 Hz
AQ                0.9374500 sec
RG                      57
DW                   50.000 usec
DE                    6.00 usec
TE                   295.9 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    6.80 usec
PL1                   0.00 dB
SFO1          500.1328782 MHz

F2 - Processing parameters
SI                   32768
SF            500.1300139 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

13C NMr, CDCL3, 300Mhz, compound 8



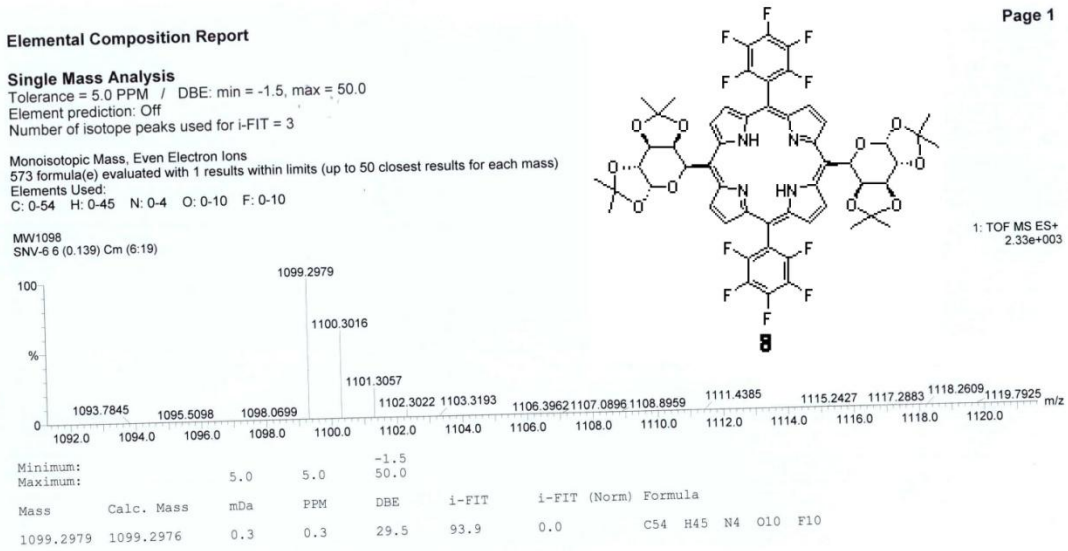

```
Current Data Parameters
NAME                  seen082
EXPNO                       3
PROCNO                      1

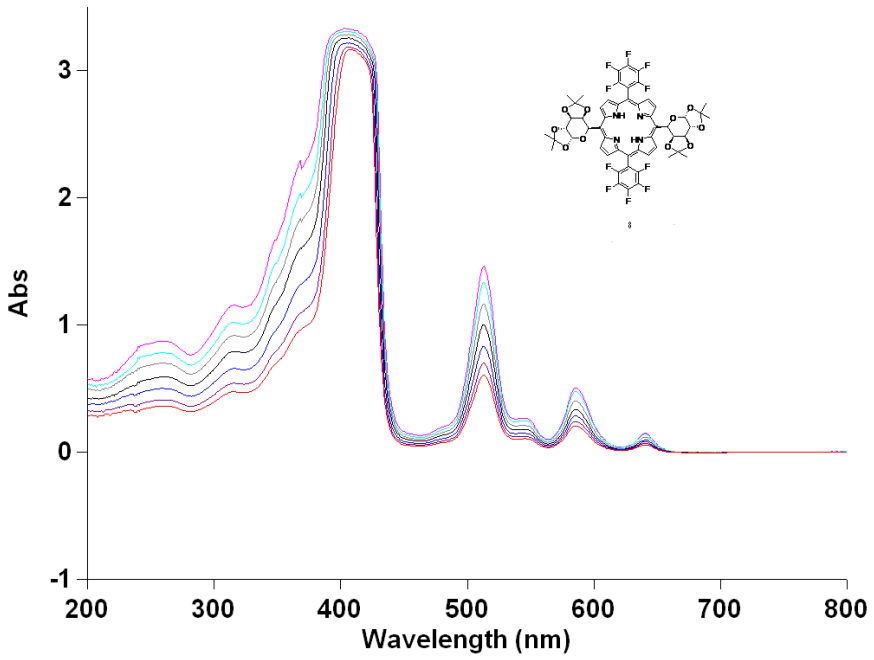
F2 - Acquisition Parameters
Date_              20081204
Time                  22.46
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    9033
DS                       0
SWH             18115.941 Hz
FIDRES               0.276427 Hz
AQ                1.8088436 sec
RG                      32768
DW                   27.600 usec
DE                    6.00 usec
TE                   297.8 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     120

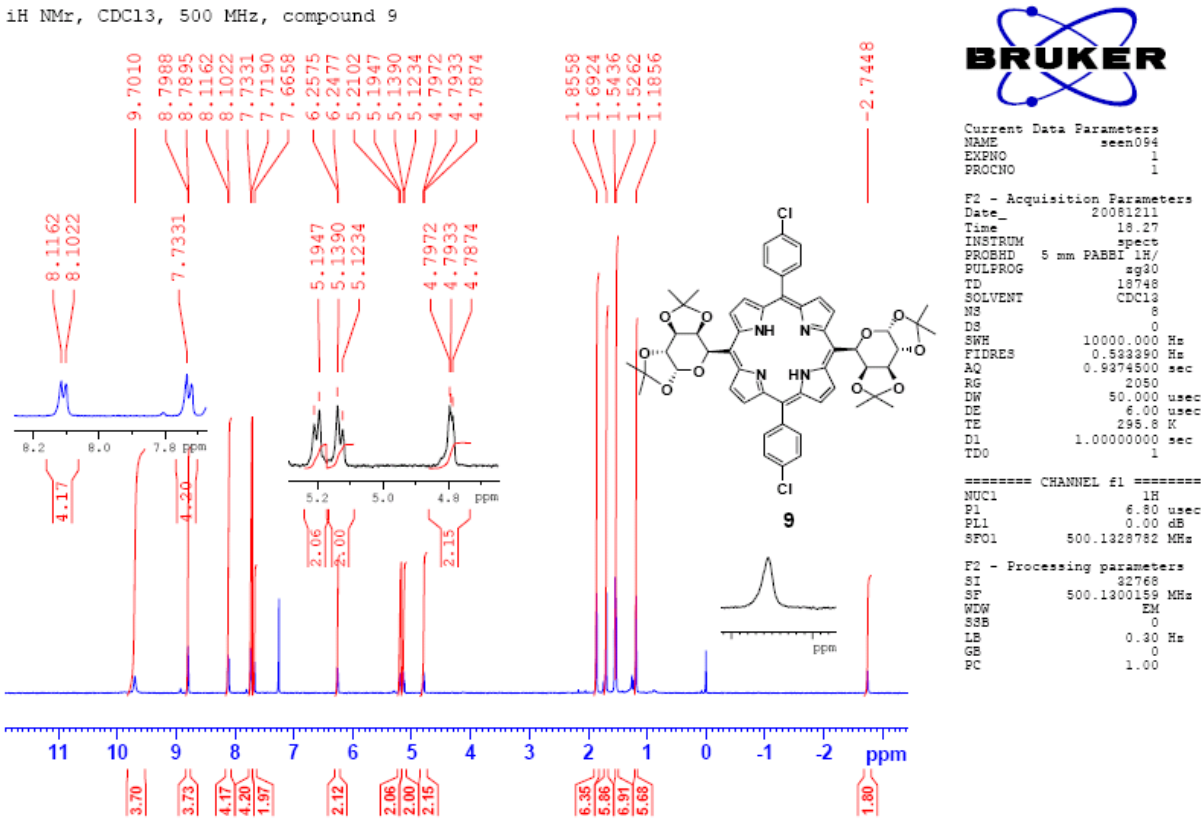
======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                  -1.00 dB
SFO1          75.4752965 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.23 dB
PL13                 19.23 dB
SFO2          300.1312005 MHz

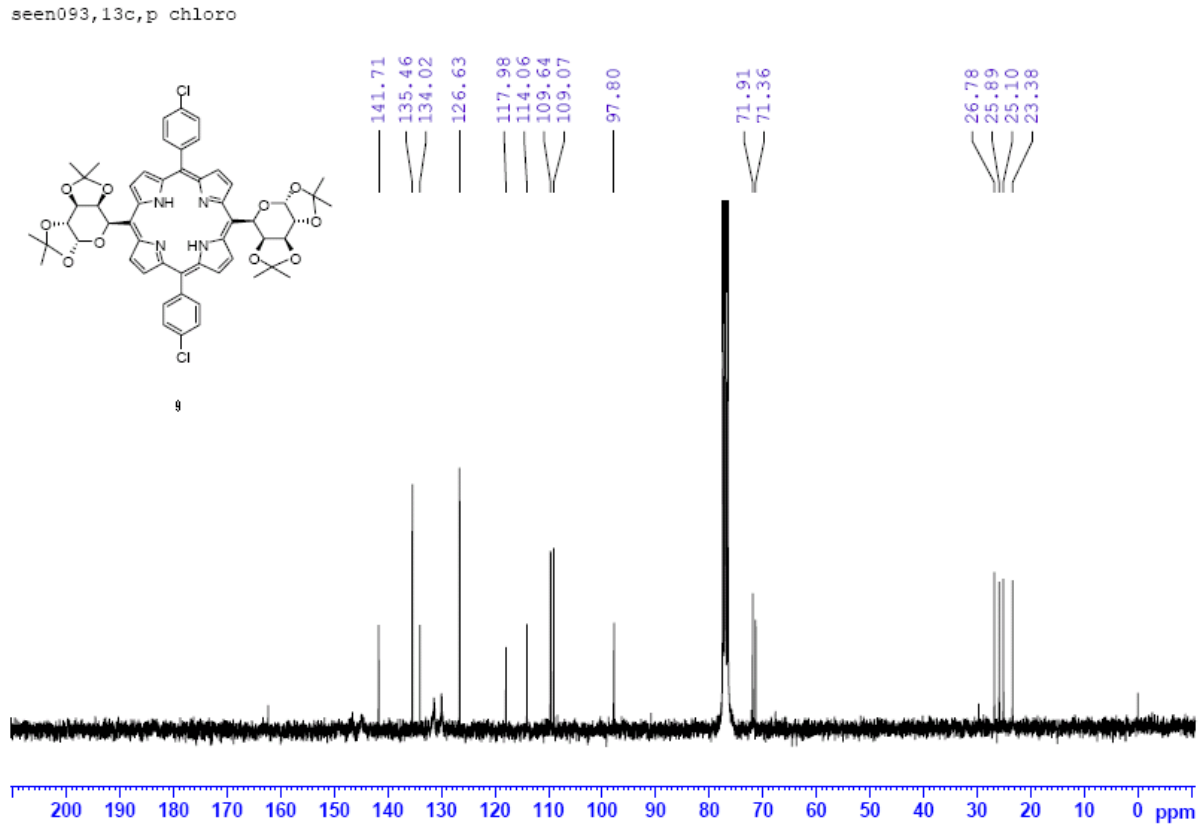
F2 - Processing parameters
SI                   32768
SF            75.4677490 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```


Elemental Composition Report
Page 1
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
573 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-54 H: 0-45 N: 0-4 O: 0-10 F: 0-10
MW1098
SNV-6 6 (0.139) Cm (6:19)
1: TOF MS ES+
2.33e+003
1099.2979
1100.3016
1101.3057
1093.7845
1095.5098
1098.0699
1102.3022
1103.3193
1106.3962
1107.0896
1108.8959
1111.4385
1115.2427
1117.2883
1118.2609
1119.7925
m/z
Minimum: -1.5
Maximum: 5.0 5.0 50.0
Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula
1099.2979 1099.2976 0.3 0.3 29.5 93.9 0.0 C54 H45 N4 O10 F10


Abs
Wavelength (nm)


iH NMr, CDCl3, 500 MHz, compound 9
9.7010
8.7988
8.7895
8.1162
8.1022
7.7331
7.7190
7.6658
6.2575
6.2477
5.2102
5.1947
5.1390
5.1234
4.7972
4.7933
4.7874
1.8558
1.6924
1.5436
1.5262
1.1856
-2.7448
9
ppm

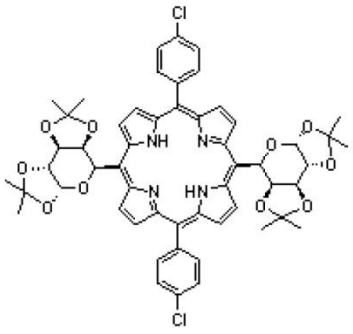
Current Data Parameters
NAME seen094
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081211
Time 18.27
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 18748
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.533390 Hz
AQ 0.9374500 sec
RG 2050
DW 50.000 usec
DE 6.00 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 6.80 usec
PL1 0.00 dB
SFO1 500.1328782 MHz
F2 - Processing parameters
SI 32768
SF 500.1300159 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


seen093,13c,p chloro
141.71
135.46
134.02
126.63
117.98
114.06
109.64
109.07
97.80
71.91
71.36
26.78
25.89
25.10
23.38
9
ppm

Elemental Composition Report Page 1

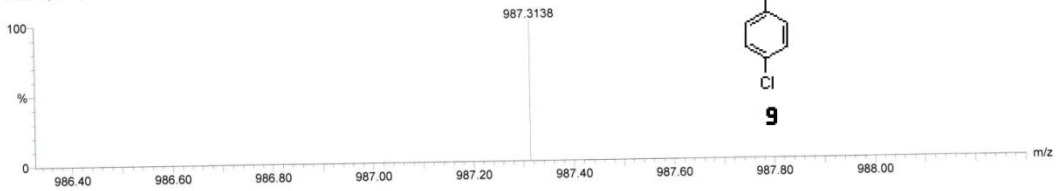
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
273 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-54 H: 0-53 N: 0-4 O: 0-10 S: 0-1 Cl: 0-2
MW986
1-snv 4 (0.101)

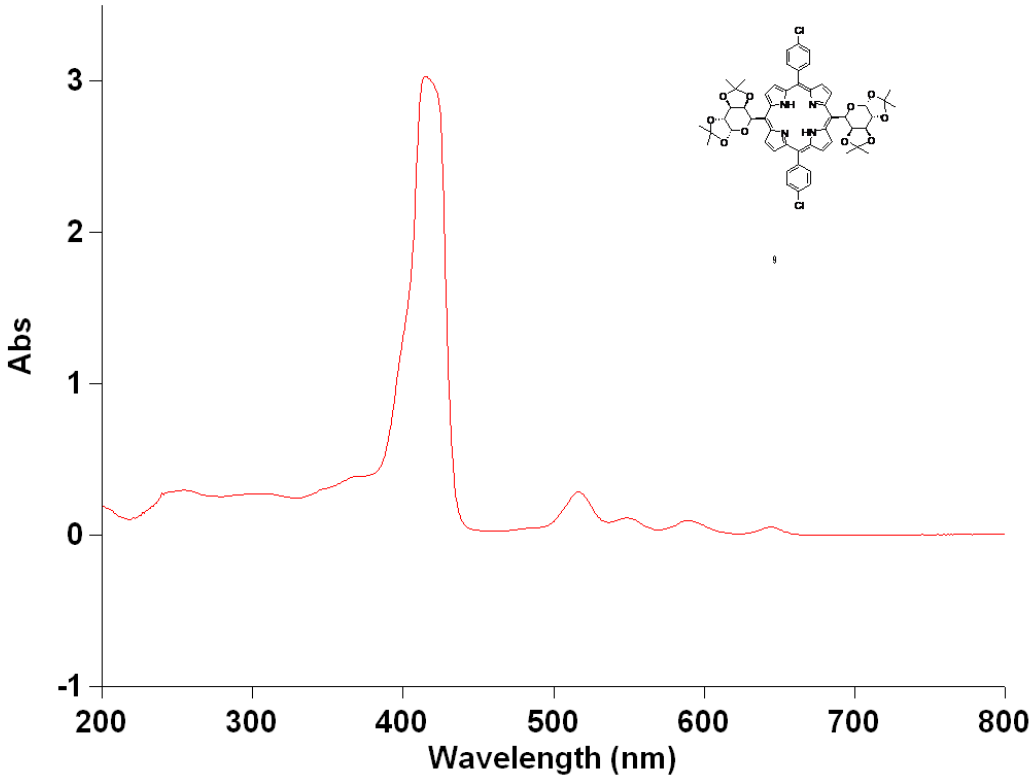


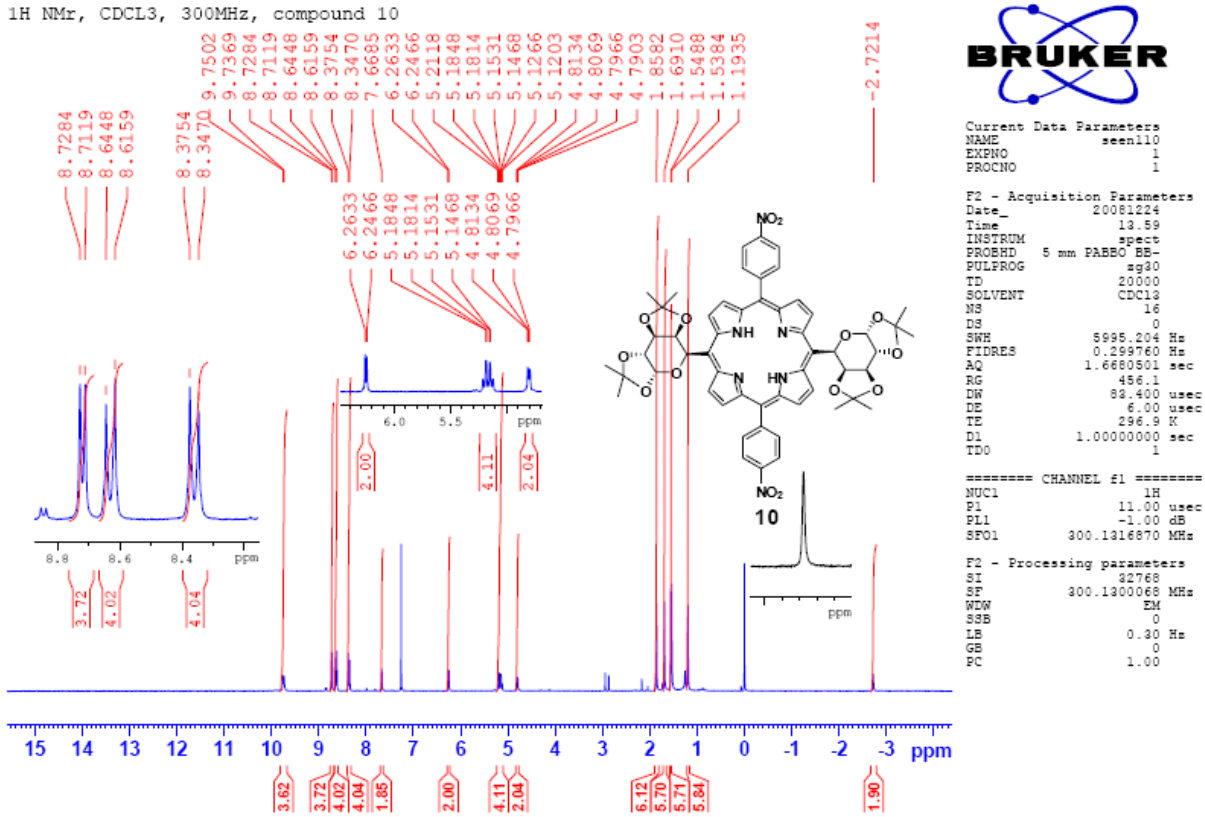
9

1: TOF MS ES+
8.38e+002



Minimum:		5.0	5.0	-1.5			
Maximum:				50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
987.3138	987.3139	-0.1	-0.1	29.5	25.4	0.0	C54 H53 N4 O10 Cl2



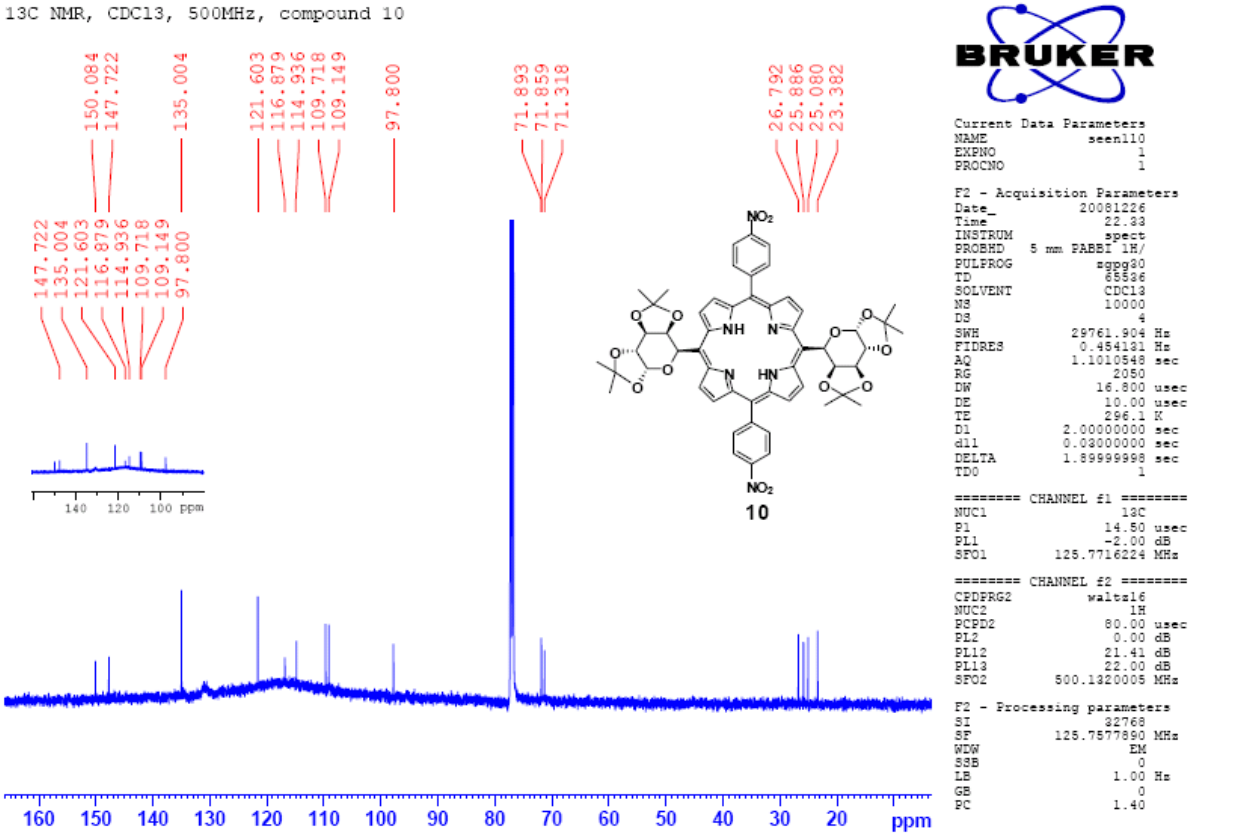



```
Current Data Parameters
NAME                  seen110
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20081224
Time                  13.59
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    20000
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                5995.204 Hz
FIDRES                0.299760 Hz
AQ                 1.6680501 sec
RG                     456.1
DW                    83.400 usec
DE                     6.00 usec
TE                    296.9 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      11.00 usec
PL1                     -1.00 dB
SFO1              300.1316870 MHz

F2 - Processing parameters
SI                      32768
SF                300.1300068 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```




```
Current Data Parameters
NAME                  seen110
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20081226
Time                  22.33
INSTRUM                spect
PROBHD   5 mm PABBI 1H/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    10000
DS                        4
SWH               29761.904 Hz
FIDRES                0.454131 Hz
AQ                 1.1010548 sec
RG                     2050
DW                   16.800 usec
DE                    10.00 usec
TE                    296.1 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      14.50 usec
PL1                     -2.00 dB
SFO1              125.7716224 MHz

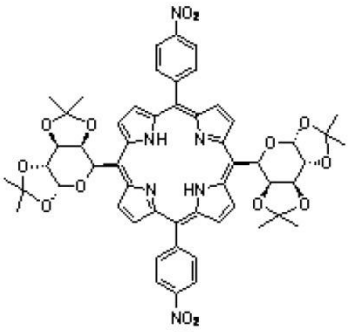
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   21.41 dB
PL13                   22.00 dB
SFO2              500.1320005 MHz

F2 - Processing parameters
SI                      32768
SF                125.7577890 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                       1.40
```

Elemental Composition Report Page 1

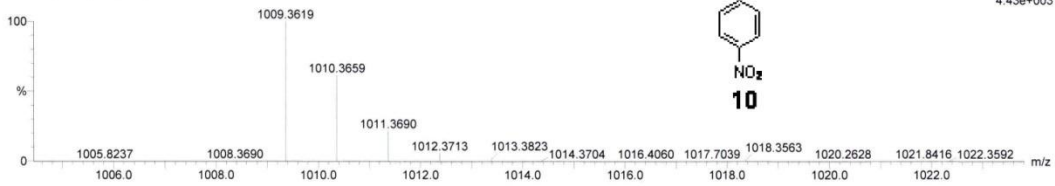
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
91 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-54 H: 0-53 N: 0-6 O: 0-14
MW1008
SNV-8 3 (0.082) Cm (3:13)

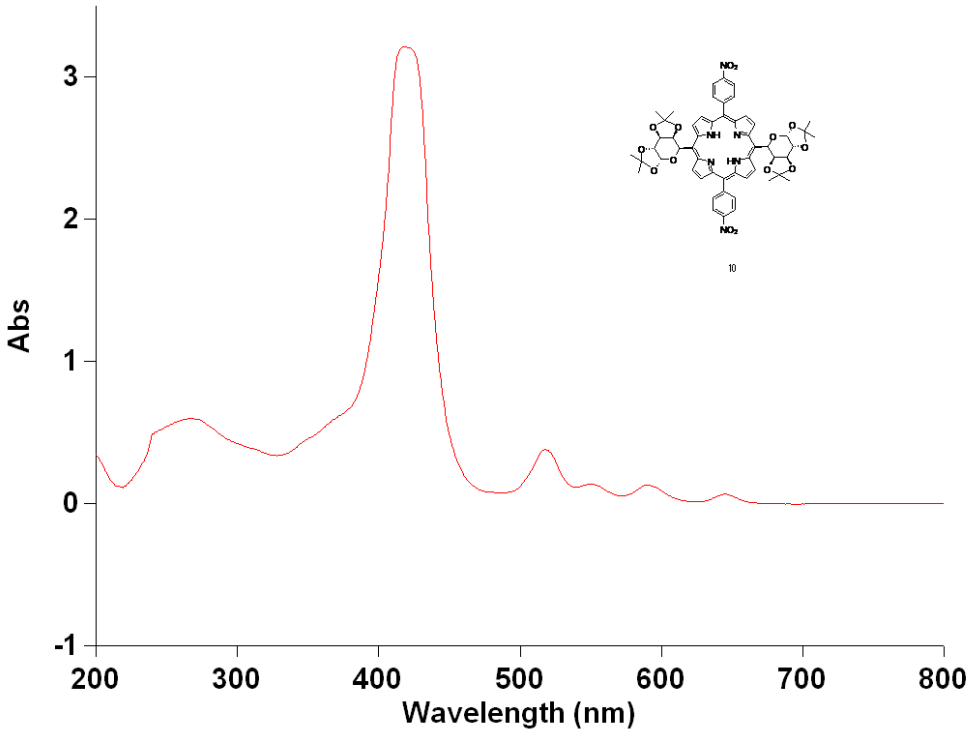


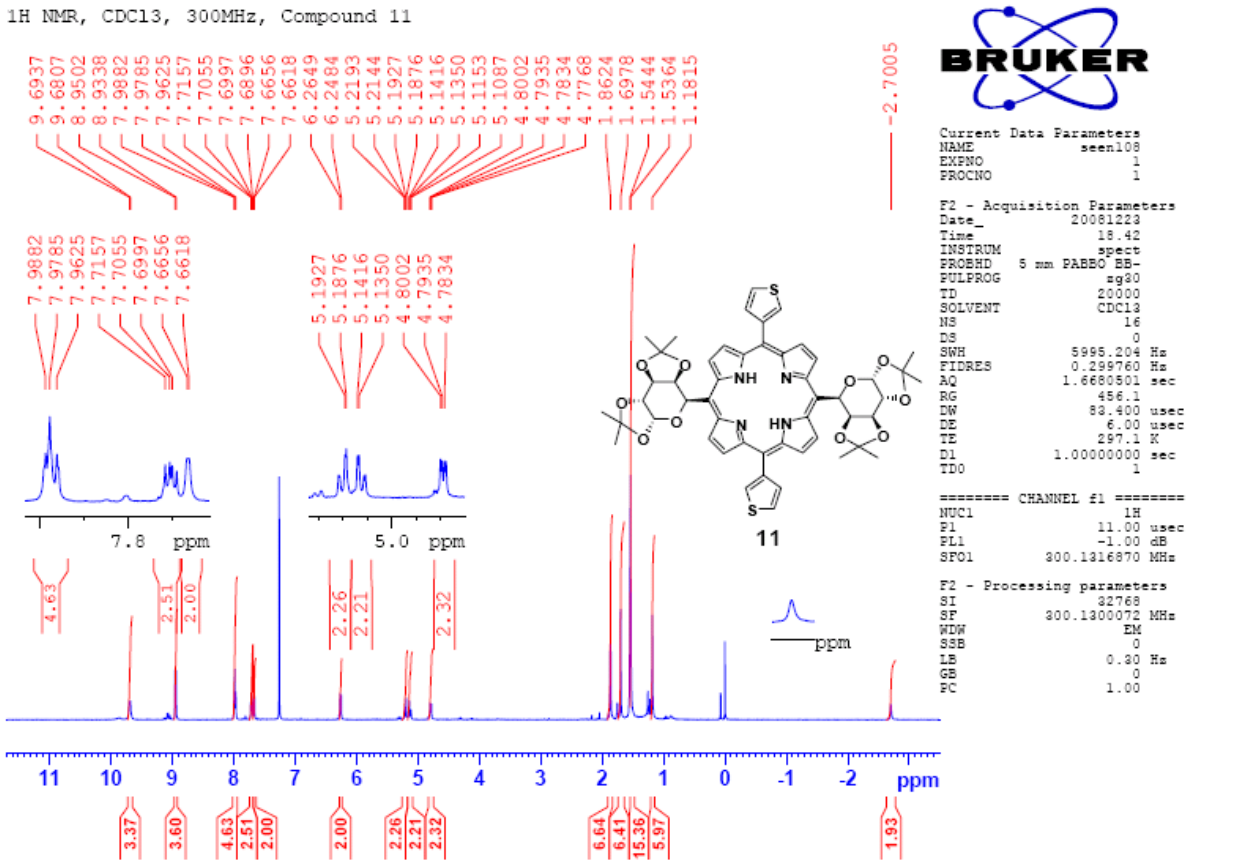
10

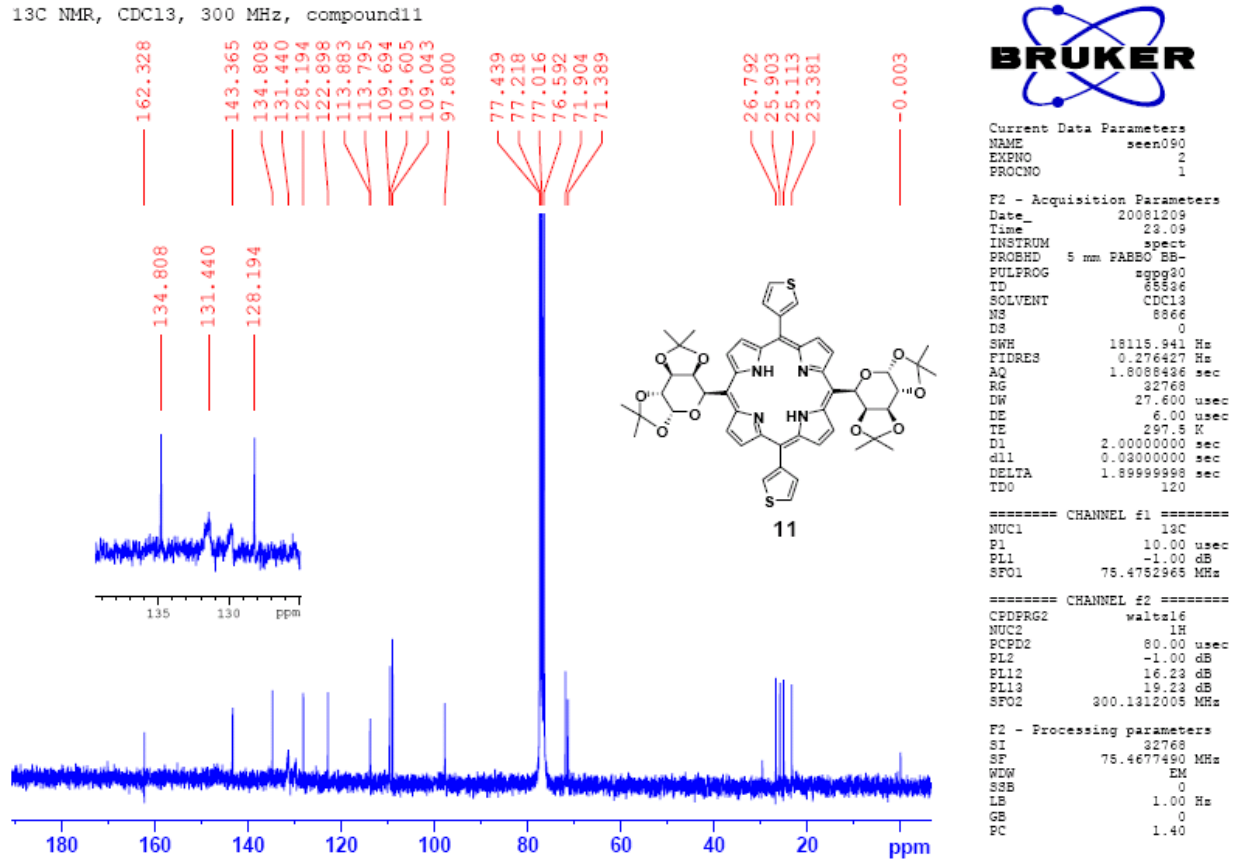
1: TOF MS ES+
4.43e+003



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1009.3619	1009.3620	-0.1	-0.1	31.5	107.6	0.0	C54 H53 N6 O14




1H NMR, CDCl3, 300MHz, Compound 11
9.6937
9.6807
8.9502
8.9338
7.9882
7.9785
7.9625
7.7157
7.7055
7.6997
7.6896
7.6656
7.6618
6.2649
6.2484
5.2193
5.2144
5.1927
5.1876
5.1416
5.1350
5.1153
5.1087
4.8002
4.7935
4.7834
4.7768
1.8624
1.6978
1.5444
1.5364
1.1815
-2.7005
7.8 ppm
5.0 ppm
11
ppm
4.63
2.51
2.00
2.26
2.21
2.32
3.37
3.60
4.63
2.51
2.00
2.00
2.26
2.21
2.32
6.64
6.41
15.36
5.97
1.93
Current Data Parameters
NAME seen108
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081223
Time 18.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 20000
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.299760 Hz
AQ 1.6680501 sec
RG 456.1
DW 83.400 usec
DE 6.00 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -1.00 dB
SFO1 300.1316870 MHz
F2 - Processing parameters
SI 32768
SF 300.1300072 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

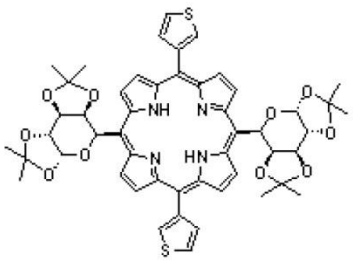

13C NMR, CDCl3, 300 MHz, compound11
162.328
143.365
134.808
131.440
128.194
122.898
113.883
113.795
109.694
109.605
109.043
97.800
77.439
77.218
77.016
76.592
71.904
71.389
26.792
25.903
25.113
23.381
-0.003
135 130 ppm
11
Current Data Parameters
NAME seen090
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20081209
Time 23.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 8866
DS 0
SWH 18115.941 Hz
FIDRES 0.276427 Hz
AQ 1.8088436 sec
RG 32768
DW 27.600 usec
DE 6.00 usec
TE 297.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 120
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -1.00 dB
SFO1 75.4752965 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 16.23 dB
PL13 19.23 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

n

Elemental Composition Report Page 1

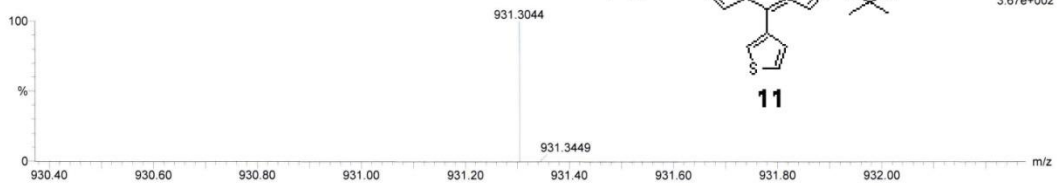
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
144 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-50 H: 0-51 N: 0-4 O: 0-10 S: 0-2
MW930
3-snv 6 (0.139) Cm (6:36)

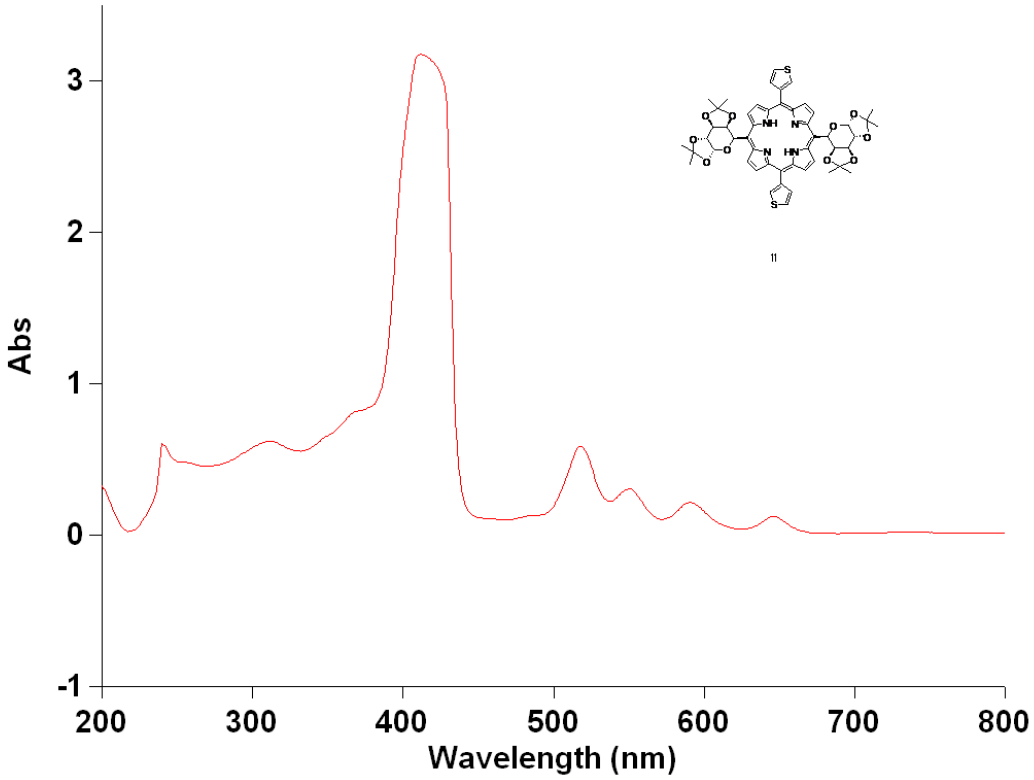


11

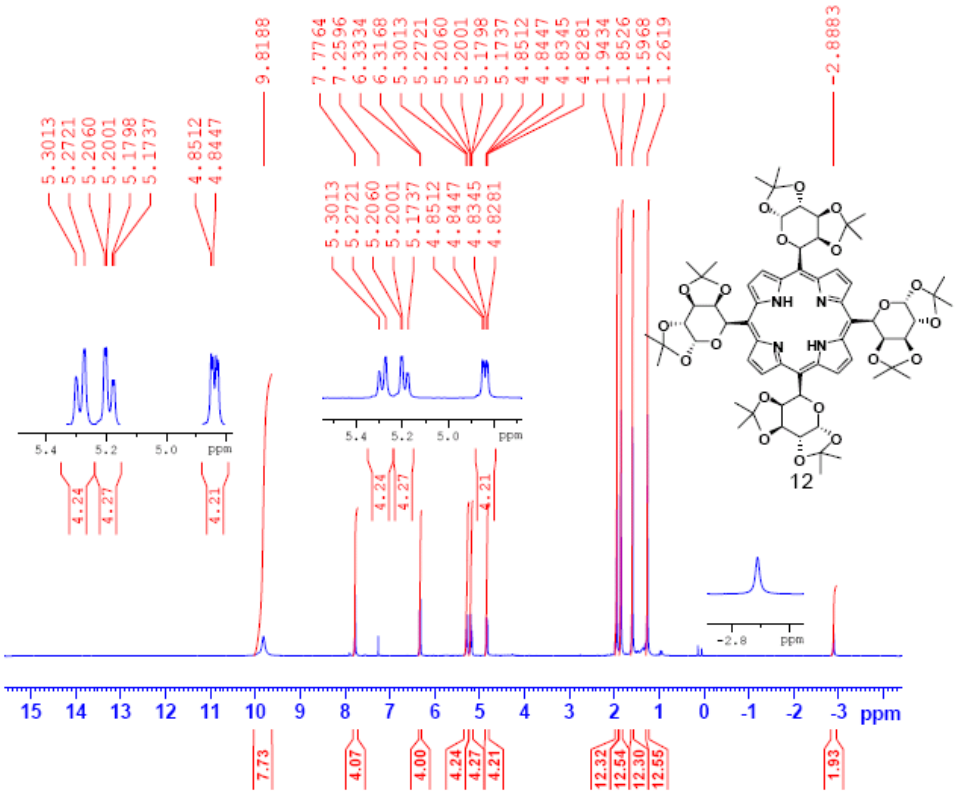
1: TOF MS ES+
3.67e+002



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
931.3044	931.3047	-0.3	-0.3	27.5	24.6	0.0	C50 H51 N4 O10 S2



1H NMR, CDCL3, 300MHz, compound 12



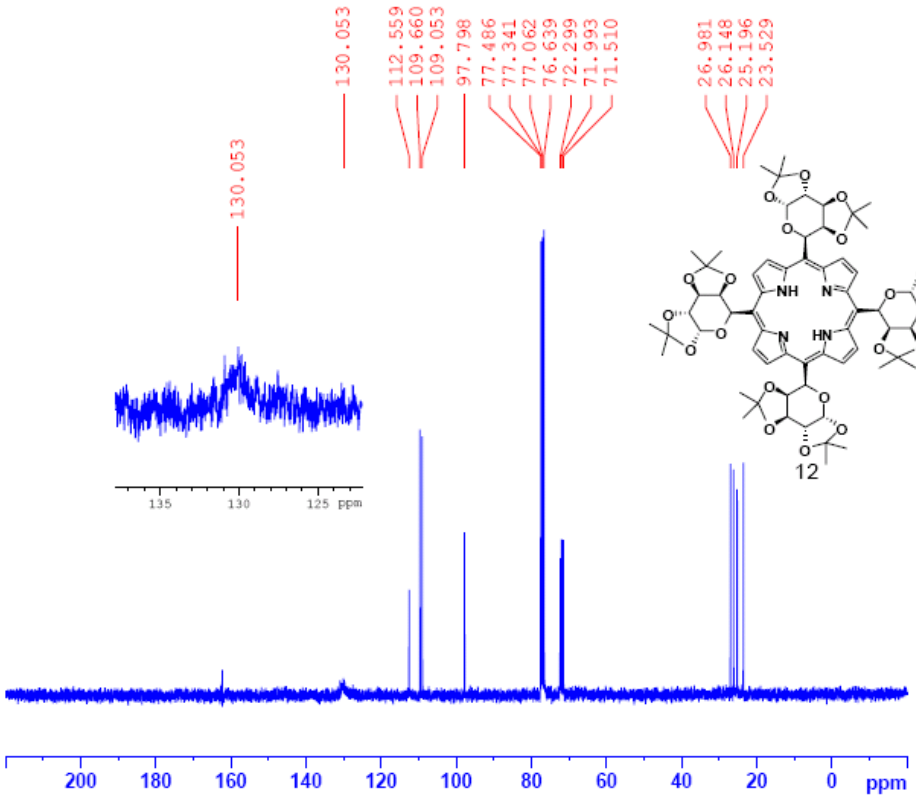

```
Current Data Parameters
NAME                  seen071
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20081129
Time                   13.58
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    20000
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                5995.204 Hz
FIDRES             0.299760 Hz
AQ                 1.6680501 sec
RG                       64
DW                   83.400 usec
DE                    6.00 usec
TE                   297.2 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.00 usec
PL1                   -1.00 dB
SFO1           300.1316870 MHz

F2 - Processing parameters
SI                        32768
SF                300.1300062 MHz
WDW                          EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

13C NMR, CDCL3, 300MHz, compound 12




```
Current Data Parameters
NAME                  seen071
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20081129
Time                   14.09
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      278
DS                        0
SWH               18115.941 Hz
FIDRES             0.276427 Hz
AQ                 1.8088496 sec
RG                   18390.4
DW                   27.600 usec
DE                    6.00 usec
TE                   297.9 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                     120

======== CHANNEL f1 ========
NUC1                     13C
P1                    10.00 usec
PL1                   -1.00 dB
SFO1           75.4752965 MHz

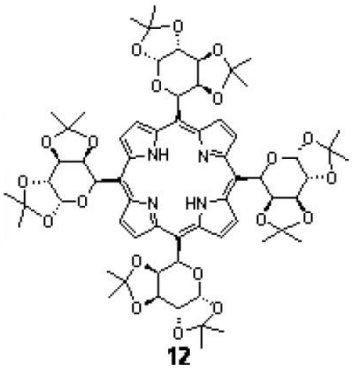
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 80.00 usec
PL2                   -1.00 dB
PL12                  16.23 dB
PL13                  19.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                75.4677490 MHz
WDW                          EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

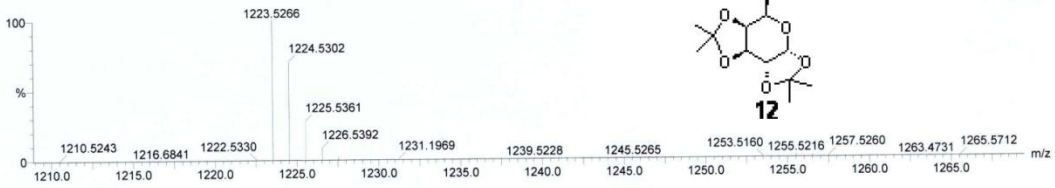
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
91 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-64 H: 0-79 N: 0-4 O: 0-20
MW1222
SNV-10 3 (0.083) Cm (3:11)



1: TOF MS ES+
1.38e+004



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1223.5266	1223.5288	-2.2	-1.8	27.5	158.2	0.0	C64 H79 N4 O20