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Synergic Effect on Oxygen Reduction Reaction of Strapped Iron Porphyrins Polymerized around Carbon Nanotubes

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Supplementary information

Techniques. Mass spectra: ESI: *Micromass MS/ MS ZABSpec TOFF* spectrometer MALDI-TOF: *Microflex-LT Bruker Daltonics* were performed at the C.R.M.P.O. (University of Rennes 1). ^{1}H- and ^{13}C-NMR spectra were recorded on *BrukerAvance*500 or *BrukerAvance*300 spectrometers equipped with a TBI probe or a *BrukerAvance*300 spectrometer with a BBO probe. Spectra were referenced with residual solvent protons. UV/ Vis/NIR spectra were recorded on an Uvikon XL spectrometer or on a Perkin Elmer lambda900 UV/Vis/NIR spectrophotometer. FT-IR spectra were recorded on a

Bruker Alpha FT-IR spectrometer. Raman Spectra were recorded on a Horiba-Jobin Yvon LabRAM ARAMIS spectrometer with excitation at 532 nm or on a Renishaw Invia spectrometer using an excitation wavelength of 476 nm. For the SEM analyses: nanotube hybrids dispersed in THF were drop-casted on freshly cleaned Si/SiO_2 surfaces and immediately dried by N_2 blow drying. The samples were investigated with a Hitachi S-4500 Scanning Electron Microscope. For TEM analyses, the samples dispersed, in *iso*-propanol, were drop-casted on copper grids covered with Lacey carbon films and imaged with an aberration corrected TEM Titan Ultimate working at 80kV. For X-ray photoelectron spectroscopy (XPS) a Kratos Analytical Axis Ultra DLD, using an Al Kα source monochromatized at 1486.6 eV was used.

Materials. Chemicals were purchased from Aldrich and were used as received. Solvents were purchased form Aldrich or VWR and were used as received. THF (K/benzophenone, N_2) was distilled before use. MWNT commercial grade NC3100 (>95%) were purchased from Nanocyl and purified according literature procedure.[1]

Synthesis.

1. Synthesis of the MWNT-FeP hybrids 9 and 10 and preparation of MWNT-FeP(11)

MWNT-FeP (9) and MWNT-FeP (10). Purified **MWNT** (10 mg) were dispersed in *N*-methylpyrrolidone (NMP) (100 mL), then **FeP(9)** or **FeP(10)** (9 mg) was added and the mixture was gently sonicated and then let sit for 30 min. Then a freshly prepares solution of copper (I) chloride (30 mg, 0.30 mmol) in NMP (5 mL), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) (120 μL) were added and the reaction was stirred at room temperature for 24h under an atmosphere of oxygen. After reaction, the suspension of nanotube materials were purified by filtration through PTFE membrane (0.2 μm) and washing with NMP (to remove unbound porphyrins), water, NH_4Cl solution (to remove the copper catalyst) and then with again water and NMP. The buckypaper was

redispersed in NMP then refiltred, washed with NMP, water, acetone and CH_2Cl_2 and dried under vacuum.

MWNT-FeP (11). A mixture of purified **MWNT** (9 mg) and porphyrin **FeP(11)**(9 mg) in dry THF (10 ml) was homogenized using a sonic bath (Fisherbrand, 37kHz, power 100%) for 15 min. The THF was gently evaporated with a steam of N_2 and the mixtures were dried under vacuum.

2. Synthesis of iron catalysts 9 and 10 bearing propargyloxy groups at their periphery.

4-(prop-2-ynyloxy) benzaldehyde 1. To a solution of corresponding 4-hydroxy benzaldehyde (10 g, 0.08 mol) in DMF (100 mL) under vigorous stirring condition, K_2CO_3 (13.2 g, 1.2 equiv.) was added and the reaction was hold for another 10-15 minutes. Propargyl bromide (6.6 mL, 1.1 equiv.) was added at once. The reaction mixture was kept under stirring for 16 hours. The reaction was monitored by TLC. The reaction mixture was taken in a separating funnel and quenched by water. Water and diethyl ether were added. The organic layer was separated, washed with saturated brine solution. The organic solution was dried over anhydrous $MgSO_4$ and evaporated to dryness when a light yellow liquid appeared. The liquid was dissolved in the minimum amount of Et_2O and the small amount of hexane is slowly added on the top of Et_2O solution. After one hour the compound was crystallized from the solution. Yield: 87 % (11.4 g). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 9.86 (1H, s, CHO), 7.81 (2H, d, *J* = 8.78 Hz, aro_2), 7.05 (2H, d, *J* = 8.78 Hz, aro_3), 4.75 (2H, d, *J* = 2.39 Hz, alp_1), 2.59 (1H, t, ^3J = 2.39 Hz, alp_3). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 190.7, 162.3, 131.8, 130.5, 115.1, 77.6, 76.49, 56.0. ESI-HRMS: 183.0416 $[M+Na]^+$ for $C_{10}H_8O_2Na$, found 183.0418, calcd m/z = 215.0678 $[M+Na+CH_3OH]^+$ for $C_{11}H_{12}O_3Na$, found 215.0675.

5-(5-{prop-2-yn-1-yloxy}-2-nitrophenyl) dipyrromethane 2. In a two neck round bottom flask equipped with a stir bar and a gas inlet, compound **1** (10 g, 48.7 mmol) was charged with pyrrole (81 mL, 25 equiv.). The reaction mixture was degassed for 15 min in argon under dark at room temperature, then TFA (0.1 equiv.) was added. The solution was stirred for 30 min then the reaction mixture was quenched by Et_3N. The excess pyrrole was recovered under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 and directly loaded on a silica gel chromatography column. The desired compound eluted with 20% ethyl acetate-hexane was obtained in 51% yield (7.9 g). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 8.14 (2H, NH_{pyr}), 8.01 (1H, d, *J* = 9.15 Hz, aro_3), 6.92 (1H, dd, ^2J = 9.15 Hz, ^4J = 2.81 Hz, aro_4), 6.82 (1H, d, *J* = 2.81 Hz, aro_6), 6.70 (2H, m, Pyr_3), 6.35 (1H, s, CH_α), 6.14 (2H, m, Pyr_2), 5.88 (2H, m, Pyr_1), 4.66 (2H, d, *J* = 2.42 Hz, alp_1), 2.53 (1H, t, ^3J = 2.42 Hz, alp_3). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 160.9, 142.2, 140.8, 130.7, 127.4, 117.6, 117.1, 113.3, 108.6, 107.4, 77.1, 76.7, 56.1, 39.3. ESI-HRMS: calcd m/z = 344.1005 $[M+Na]^+$ for $C_{18}H_{15}N_3O_3Na$, found 344.1002.

2-nitro-5-(prop-2-yn-1-yloxy) benzaldehyde 3. To a solution of corresponding 5-hydroxy-2-nitrobenzaldehyde (25 g, 0.15 mol) in DMF (250 mL) under vigorous stirring condition, K_2CO_3 (24.7 g, 1.2 equiv.) was added and the reaction was hold for another 10-15 minutes. Propargyl bromide (12.4 mL, 1.1 equiv.) was added at once. The reaction mixture was kept under stirring for 16 hours. The reaction was monitored by TLC. The reaction mixture was taken in a separating funnel and quenched by water. Water and diethyl ether were added. The organic layer was separated, washed with saturated brine solution. The organic solution was dried over anhydrous $MgSO_4$ and evaporated to dryness when a pale yellow liquid appeared. The pale yellow liquid was dissolved in the minimum amount of Et_2O and the small amount of hexane is slowly added on the top of Et_2O solution. After one hour the compound was crystallized from the solution. Yield: 86 % (25.8 g). ^{1}H

NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 10.46 (1H, s, CHO), 8.16 (1H, d, *J* = 9.04 Hz, aro_3), 7.41 (1H, d, *J* = 2.80 Hz, aro_6), 7.24 (1H, dd, ^2J = 9.04 Hz, ^4J = 2.80 Hz, aro_4), 4.84 (2H, d, *J* = 2.45 Hz, alp_1), 2.60 (1H, t, ^3J = 2.31 Hz, alp_3). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 188.2, 161.7, 142.9, 134.1, 127.2, 119.3, 114.5, 77.3, 76.5, 56.6. ESI-HRMS: calcd m/z = 206.0447 $[M+H]^+$ for $C_{10}H_8NO_4$, found 206.0446, calcd m/z = 228.0267 $[M+Na]^+$ for $C_{10}H_7NO_4Na$, found 228.0268.

5,15-bis-(5-{prop-2-yn-1-yloxy}-2-nitrophenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-porphyrin 4. Dipyrromethane **2** (2 g, 6.2 mmol) and 4-(prop-2-ynyloxy) benzaldehyde **1** (990 mg, 6.2 mmol) were dissolved in freshly prepared distilled CH_2Cl_2 (600 mL) in a 1 L round-bottomed flask containing molecular sieves, degassed with a stream of argon for 15 min. Then BF_3-Et_2O (180 µL, 0.1 equiv.) was added slowly over 30 s. The reaction was stirred at room temperature with the progress of the reaction was monitored by TLC and MALDI. After 16 hours, DDQ (6.2 mmol) was added, and the reaction mixture was stirred at room temperature for further 1 h. The complete reaction mixture was quenched by triethylamine and evaporated under reduced pressure to give a black solid which was dissolved in CH_2Cl_2. The mixture of atropisomers αβ and αα dinitroporphyrin were purified by silica gel column chromatography using DCM as eluent. In this step, the two atropisomers were not separated due to the close polarity of the two compounds. Yield: 34 % (970 mg). ESI-HRMS: calcd m/z = 921.2667 $[M+H]^+$ for $C_{56}H_{37}N_6O_8$, found 921.2668, calcd m/z = 943.2486 $[M+Na]^+$ for $C_{56}H_{36}N_6O_8Na$, found 943.2488. UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 424 (305), 520 (28.6), 556 (19), 596 (17), 652 (14.4).

5,15-bis-(5-{prop-2-yn-1-yloxy}-2-aminophenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-porphyrin 5. The atropisomers of αβ and αα dinitroporphyrin **4** (2 g, 2.17 mmol) were taken in a 2 L conical flask along with a reducing agent $SnCl_2.2H_2O$ (10 equiv.) and concentrated HCl (100 mL) was

added slowly to the ethanol mixture of porphyrin. The resulting green solution was stirred for 2 days at RT. After completion of the reaction, it was quenched by aqueous KOH solution at 0 ^{0}C under ice. The resulting violet solution was washed several times with water and $CHCl_3$. The organic layers were collected and dried over $MgSO_4$. Yield: 80 % (1.5 g).

In a 1 L two necks round bottom flask equipped with a stir bar and a condenser, 200 g of silica (60 µm) were added to toluene (400 mL). The reaction mixture was heated to 80 ^{0}C and degassed with argon during 45 min. Then 1.5 g of the atropisomers was dissolved in toluene and added to the silica gel. The mixture was stirred overnight at 80 ^{0}C and loaded once cooled to room temperature over a silica gel chromatography. After evaporation of the solvent, the compound was dissolved in minimum amount of DCM and purified by column chromatography. The two atropisomers were separated on a silica gel chromatography eluted with DCM/MeOH (αβ 0.3%, αα 0.6%). Yield: αα (1 gm, 66%), αβ (0.5 gm, 34%). ^{1}H NMR of αα-isomer (DMSO-d_6, 298 K, 500.13 MHz): δ 8.88 (4H, d, *J* = 4.54 Hz, βpyr), 8.83 (4H, d, *J* = 4.27 Hz, βpyr), 8.15 (2H, d, *J* = 7.93 Hz, aro_9), 8.12 (2H, d, *J* = 7.93 Hz, $aro_{9'}$), 7.44 (6H, aro_8, $aro_{8'}$, aro_5), 7.24 (2H, dd, ^2J = 9.07 Hz, ^4J = 2.83 Hz, aro_3), 7.09 (2H, d, *J* = 9.07 Hz, aro_2), 5.10 (4H, d, *J* = 2.20 Hz, $alp_{1'}$), 4.79 (4H, d, *J* = 2.27 Hz, alp_1), 4.24 (4H, s, NH_2), 3.75 (2H, t, ^3J = 2.37 Hz, $alp_{3'}$), 3.57 (2H, t, *J* = 2.27 Hz, alp_3), -2.82 (2H, s, NH_{int}). ^{13}C NMR of αα-isomer (DMSO-d_6, 298 K, 500.13 MHz): δ 157.6, 148.2, 143.5, 135.7, 135.6, 134.4, 126.4, 121.6, 119.4, 117.8, 116.8, 116.1, 113.7, 80.4, 79.9, 79.0, 78.5, 56.8, 56.2. ESI-HRMS: calcd m/z = 861.3183 $[M+H]^+$ for $C_{56}H_{40}N_6O_4$, found 861.3180. UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 421 (316), 519 (24), 554 (13), 591 (11.4), 650 (9).

α-5,15-bis-(5-{prop-2-yn-1-yloxy}-2-[{3-chloromethyl}benzoylamido]-phenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-porphyrin 6. In a 250 mL two neck round bottom flask equipped with a stir bar was charged with **5** (700 mg, 0.82 mM); dry DCM (200 mL), and NEt_3 (300 µL, 2.5 equiv.), After

cooling in an ice bath, 3-(chloromethyl)benzoyl chloride (290 µL, 2.5 equiv.) was added dropwise under argon atmosphere. The reaction mixture was allowed to stir for three hours. Then the reaction was quenched by water and separated the organic layer. The solvent was removed under vacuum. The resulting solid was dissolved in CH_2Cl_2 and directly loaded on a silica gel chromatography column. The expected compound eluted with 0.1% DCM/MeOH, was obtained in 97% yield (930 mg). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 8.93 (8H, βpyr), 8.73 (2H, d, *J* = 9.31 Hz, $aro_{2'}$), 8.12 (2H, d, *J* =7.99 Hz, aro_9), 8.03 (2H, d, *J* = 7.99 Hz, $aro_{9'}$), 7.81 (2H, d, *J* = 2.90 Hz, $aro_{5'}$), 7.54 (2H, dd, ^2J = 9.31 Hz, ^4J = 2.97 Hz, $aro_{3'}$), 7.42 (2H, s, NHCO), 7.38 (2H, d, *J* = 8.16 Hz, aro_8), 7.35 (2H, d, *J* = 8.16 Hz, $aro_{8'}$), 6.73 (2H, d, *J* = 7.85 Hz, aro_4), 6.50 (2H, d, *J* = 7.45 Hz, aro_6), 6.52 (2H, t, *J* = 7.75, aro_5), 6.31 (2H, bs, aro_2), 4.98 (4H, d, *J* = 2.39 Hz, alp_1), 4.89 (4H, d, *J* = 2.25 Hz, $alp_{1'}$), 3.31 (4H, s, $CH_{2\ bz}$), 2.69 (2H, t, *J* = 2.52 Hz, alp_3), 2.60 (2H, t, *J* = 2.41 Hz, $alp_{3'}$), -2.65 (2H, s, NH_{int}). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 164.7, 157.7, 153.0, 137.1, 135.7, 135.6, 134.9, 134.5, 133.5, 133.1, 130.7, 128.3, 126.1, 126.0, 122.5, 121.5, 120.7, 116.2, 113.5, 113.4, 113.3, 78.5, 78.4, 77.2, 76.0, 56.4, 56.1, 44.3. ESI-HRMS: calcd m/z = 1165.3241 $[M+H]^+$ for $C_{72}H_{51}N_6O_6{}^{35}Cl_2$, found 1165.3245, calcd m/z = 1187.3061 for $[M+Na]^+$, found 1187.3054. UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 425 (382), 519 (15.2), 557 (7), 594 (5.5), 650 (4.2).

α-5,15-bis-(5-{prop-2-yn-1-yloxy}-{2,2-(3,3-[2,2-(ditertbutylxycarbonyl)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-porphyrin 7a. A mixture of potassium tert-butoxide (290 mg, 10 equiv.) and diterbutyl malonate (290 µL, 5 equiv.) in dry THF (20 mL) was stirred at RT for 30 min. The resulting mixture was added to a solution of porphyrin **6** (300 mg, 0.25 mM) in THF (100 mL) and was maintained for stirring 8h. The reaction was monitored in every hour by TLC and MALDI. After 8h of stirring the reaction was completed and quenched by water. After removal of THF in the rotary evaporator, the product was separated by DCM. The

solvent was removed under vacuum and purified by column chromatography eluted with CH_2Cl_2. The expected compound was obtained in 50% yield (170 mg). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz,): δ 8.95 (2H, d, *J* = 9.22 Hz, $aro_{2'}$), 8.91 (4H, d, *J* = 4.84 Hz, βpyr), 8.88 (4H, d, *J* = 4.83 Hz, βpyr), 8.16 (2H, d, *J* = 8.66 Hz, aro_9), 8.06 (2H, d, *J* = 8.72 Hz, $aro_{9'}$), 7.87 (2H, s, NHCO), 7.79 (2H, d, *J* = 2.99 Hz, $aro_{5'}$), 7.67 (2H, d, *J* = 7.85 Hz, aro_6), 7.54 (2H, dd, ^2J = 9.22 Hz, ^4J = 2.99 Hz, $aro_{3'}$), 7.38 (2H, d, *J* = 8.62 Hz, aro_8), 7.34 (2H, d, *J* = 8.22 Hz, $aro_{8'}$), 6.99 (2H, t, *J* = 7.70 Hz, aro_5), 6.82 (2H, d, *J* = 7.70 Hz, aro_4), 4.97 (4H, d, *J* = 2.37 Hz, alp_1), 4.94 (2H, s, aro_2), 4.88 (4H, d, *J* = 2.33 Hz, $alp_{1'}$), 2.69 (2H, t, ^3J = 2.37 Hz, alp_3), 2.58 (2H, t, ^3J = 2.33 Hz, $alp_{3'}$), 1.60 (4H, s, $CH_{2\ bz}$), -0.27 (18H, s, $CH_{3\ tBu}$), -2.48 (2H, s, NH_{int}). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz,): δ 167.7, 164.4, 157.6, 152.7, 136.4, 136.2, 135.2, 134.7, 133.7, 133.3, 132.9, 132.8, 128.2, 127.1, 125.6, 122, 121.5, 120.6, 116.2, 113.4, 113.3, 80.3, 78.5, 78.4, 76, 75.9, 59.9, 56.5, 56.1, 42, 26. ESI-HRMS: calcd m/z = 1309.5069 $[M+H]^+$ for $C_{83}H_{69}N_6O_{10}$, found 1309.5070, calcd m/z = 1331.4889 for $[M+Na]^+$, found 1331.4873. UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 424 (340), 516 (20), 556 (9), 595 (7), 650 (5).

α-5,15-bis-(5-{prop-2-yn-1-yloxy}-{2,2-(3,3-[2,2-(diethoxycarbonyl)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-porphyrin 7b. Sodium metal (120 mg, 10 equiv.) was added to the absolute alcohol (15 mL) in a small round bottom flask and stirred for few minutes until the complete consumption of Na. Diethyl malonate (785 µL, 10 equiv.) was added to this solution at room temperature and stirred for half an hour. The resulting mixture was added to a solution of porphyrin **6** (0.5 mmol, 600 mg, 1 equiv.) in CH_2Cl_2 (200 mL) and the solution was turned immediately from violet to green. After 2h of stirring the reaction was quenched by H_2O, the organic layer was separated and removed under vacuum. The desired product was purified on a silica gel chromatography column eluted with 0.1% CH_2Cl_2/MeOH. The expected compound was obtained in 80% yield (515 mg). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 9.03 (2H, d, *J* = 9.28 Hz,

$aro_{2'}$), 8.95 (4H, d, *J* = 4.83 Hz, βpyr), 8.92 (4H, d, *J* = 4.83 Hz, βpyr), 8.22 (2H, d, *J* = 8.08 Hz, aro_9), 8.02 (2H, d, *J* = 8.72 Hz, $aro_{9'}$), 8.01 (2H, s, NHCO), 7.71 (2H, d, *J* = 2.98 Hz, $aro_{5'}$), 7.68 (2H, d, *J* = 7.83 Hz, aro_6), 7.55 (2H, dd, ^2J = 9.23 Hz, ^4J=3 Hz, $aro_{3'}$), 7.40 (2H, d, *J* = 8.62 Hz, aro_8), 7.35 (2H, d, *J* = 8.22 Hz, $aro_{8'}$), 6.98 (2H, t, *J* = 7.63 Hz, aro_5), 6.73 (2H, d, *J* = 7.63 Hz, aro_4), 4.98 (4H, d, *J* = 2.29 Hz, alp_1), 4.96 (2H, bs, aro_2), 4.87 (4H, d, *J* = 2.33 Hz, $alp_{1'}$), 2.69 (2H, t, ^3J = 2.43 Hz, alp_3), 2.58 (2H, t, ^3J = 2.32 Hz, $alp_{3'}$), 1.72 (4H, s, $CH_{2\ bz}$), 1.29 (4H, bs, $CH_{2\ ester}$), -0.51 (6H, t, ^3J = 7.16 Hz, $CH_{3\ ester}$), -2.44 (2H, s, NH_{int}). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 167.6, 164.2, 157.6, 152.7, 135.9, 135.8, 135.1, 134.7, 133.8, 133.4, 132.9, 132.3, 128.2, 127.3, 125.7, 121.8, 121.3, 120.5, 116.1, 113.5, 113.4, 78.5, 78.4, 76.0, 75.9, 59.9, 58.8, 56.4, 56.1, 42.4, 12.0. ESI-HRMS: calcd m/z = 1253.4443 $[M+H]^+$ for $C_{79}H_{61}N_6O_{10}$, found 1253.4446, calcd m/z = 1275.4263 $[M+Na]^+$ for $C_{79}H_{60}N_6O_{10}Na$, found 1275.4253. UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 425 (344), 518 (20.6), 557 (9.8), 594 (7.6), 650 (5.6).

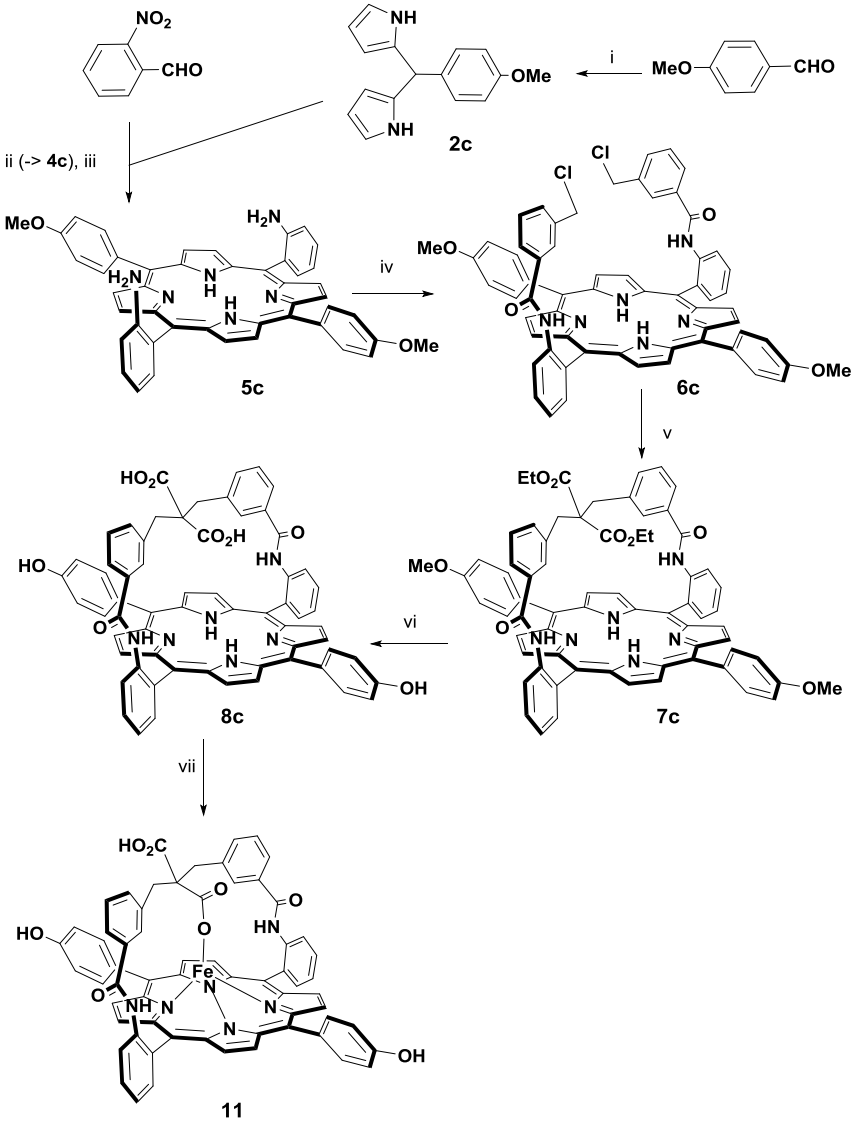
α-5,15-bis-(5-{prop-2-yn-1-yloxy}-{2,2-(3,3-[2,2-(diethoxycarbonyl)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-iron(III) porphyrin 10. 100 mg (0.19 mmol) portion of porphyrin **7b** was dissolved in 10 mL of dry, degassed THF in the schlenk flask in the glove box. Then four equivalent of $FeBr_2$ was added into the solution along with 50 µL of 2,6-leutidine acting as a base. The solution was heated for ~12 hours at 70°C under an argon atmosphere. The reaction was monitored by UV-visible spectroscopy and once complete, the product was purified by column chromatography eluted with 0.3% DCM/MeOH. The desired compound was obtained in 90% yield (93 mg). HR-MS (ESI-MS): calcd m/z = 1306.3558 $[M^{+\cdot}]$ for $C_{79}H_{58}FeN_6O_{10,}$ found 1306.3561**.** UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 419 (238), 514 (19), 572 (14), 615 (5.2).

α-5,15-bis-(5-{prop-2-yn-1-yloxy}-{2,2-(3,3-[2,2-(dicarboxylic acid)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-porphyrin 8. Compound **7a** (150 mg, 0.11 mmol) was dissolved in THF (50 mL), 1 mL concentrated HCl was added. After two days of stirring at 60 ^{0}C, the mixture was cooled to RT and the solvent was removed under reduced pressure. Then the compound was dissolved in DCM and washed with water in several times. The organic layer was separated and concentrated under vacuum. The expected compound was purified by column chromatography eluted with 1.5% DCM/MeOH, 0.1% acetic acid. The expected compound was obtained in 60% yield (80 mg). ^{1}H NMR (DMSO-d_6, 298 K, 500.13 MHz,): δ 8.88 (4H, d, *J* = 4.14 Hz, βpyr), 8.79 (4H, d, *J* = 4.38 Hz, βpyr), 8.62 (2H, s, NHCO), 8.22 (2H, d, *J* = 7.81 Hz, aro$_9$), 8.15 (2H, d, *J* = 8.94 Hz, aro$_{2'}$), 8.04 (2H, d, *J* = 2.88 Hz, aro$_{5'}$), 7.99 (2H, d, *J* = 7.95 Hz, aro$_9$), 7.55 (2H, dd, ^{2}J = 8.92 Hz, ^{4}J = 2.93 Hz, aro$_{3'}$), 7.42 (2H, d, *J* = 8.41 Hz, aro$_8$), 7.38 (2H, d, *J* = 8.60 Hz, aro$_{8'}$), 7.23 (2H, d, *J* = 7.73 Hz, aro$_6$), 6.91 (2H, t, ^{3}J = 7.74 Hz, aro$_5$), 6.73 (2H, d, *J* = 7.78 Hz, aro$_4$), 5.08 (4H, d, *J* = 2.37 Hz, alp$_1$), 5.06 (4H, d, *J* = 2.26 Hz, alp$_{1'}$), 4.60 (2H, s, aro$_2$), 3.76 (2H, t, ^{3}J = 2.31 Hz, alp$_3$), 3.74 (2H, t, ^{3}J = 2.37 Hz, alp$_{3'}$), 1.26 (4H, s, $CH_{2\ bz}$), -2.74 (2H, s, NH_{int}). ^{13}C NMR (DMSO-d_6, 298 K, 500.13 MHz,): δ 171.6, 166, 157.6, 158.9, 137, 135.8, 135.5, 134.9, 134.5, 133.2, 131.7, 127.9, 127, 126.7, 126.3, 121.7, 119.9, 115.5, 113.7, 113.6, 79.8, 79.2, 79.1, 79, 59.3, 56.4, 56.2, 40.3. ESI-HRMS: calcd m/z = 1195.3672 $[M-H]^-$ for $C_{75}H_{51}N_6O_{10}$, found 1195.3669, calcd m/z = 1133.3668 $[M-CO_2-H_2O-H]^+$ for $C_{74}H_{49}N_6O_7$, found 1133.3665. UV-vis (DMF): λ/nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 426 (330), 522 (14), 559 (9.4), 592 (9), 645 (5.2).

α-5,15-bis-(5-{prop-2-yn-1-yloxy}-{2,2-(3,3-[2,2-(dicarboxylic acid)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-{prop-2-yn-1-yloxy}-phenyl)-iron(III)porphyrin 9. A 80 mg (0.06 mmol) of porphyrin **8** was dissolved in 10 mL of dry, degassed THF in the glove box. Then excess amount of $FeBr_2$ was added into the solution along with 30 µL of 2,6-lutidine acting as a base. The

solution was stirred for ~36 hours at RT in order to avoid any decarboxylation reaction under an argon atmosphere. The reaction was monitored by UV-visible spectroscopy and once complete, the product was purified by column chromatography eluted with 0.6% DCM/MeOH, 0.1% acetic acid. The desired compound was obtained in 90% yield (75 mg). HR-MS (ESI-MS): calcd m/z = 1250.2932 $[M+H]^+$ for $C_{75}H_{50}FeN_6O_{10,}$ found 1250.2937**.** UV-vis ($CHCl_3$): λ/nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 418 (240), 515 (22).

3. Synthesis of iron catalyst 11 lacking propargyloxy groups at its periphery.



(4-methoxyphenyl)-dipyrromethane 2c. In a two neck round bottom flask equipped with a stir bar and a gas inlet, 4-methoxy benzaldehyde (92.8 mmol, 11.3 mL) and pyrrole (161.2 mL, 25 equiv.)

were mixed. The reaction mixture was degassed for 15 minutes in argon under dark at room temperature, and then TFA (707 µL, 0.1 equiv.) was added. The solution was stirred for further half an hour. The reaction was monitored by TLC, after that the reaction mixture was quenched by Et_3N. The excess pyrrole was recovered under reduced pressure. The resulting solid was dissolved in CH_2Cl_2 and directly loaded on a silica gel chromatography column. The desired compound eluted with 70% CH_2Cl_2-cyclohexane was obtained in 50% yield (11.65 g, 46.17 mmol). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 7.90 (2H, pyr_{NH}), 7.18 (2H, d, *J* = 8.61 Hz, aro_2), 6.91 (2H, d, *J* = 8.61 Hz, aro_3), 6.71 (2H, m, pyr_4), 6.22 (2H, m, pyr_3), 5.97 (2H, m, pyr_2), 5.44 (1H, CH_α), 3.84 (3H, s, OMe). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 158.5, 134.3, 132.9, 129.4, 117.2, 114, 108.3, 107.2, 55.3, 43.2. ESI-HRMS: calcd m/z = 275.1154 $[M-H+Na]^+$ for $C_{16}H_{16}N_2NaO$, found 275.1159.

5,15-bis-(2-nitrophenyl)-10,20-bis-(4-methoxyphenyl)-porphyrin 4c. 4-methoxyphenyldipyrro-methane **2c** (7.9 mmol, 2 g) and 2-nitrobenzaldhyde (1.19 g, 1 equiv.) were dissolved in freshly prepared distilled CH_2Cl_2 (600 mL) in a 1 L round-bottomed flask containing molecular sieves, degassed with a stream of Ar for 15 min. Then BF_3-Et_2O (110 µL, 0.1 equiv.) was added slowly over 30 s. The reaction was stirred at room temperature and monitored by TLC and MALDI. After 2 hours, DDQ (2.7 g, 1.5 equiv.) was added, and the reaction mixture was stirred at room temperature for a further 1 h. The complete reaction mixture was quenched by Et_3N and evaporated under reduced pressure to give a black solid which was dissolved in CH_2Cl_2. The mixture of two atropisomers *i.e.* αβ and αα-bis-2-nitrophenylporphyrin were purified by silica gel column chromatography using CH_2Cl_2 as eluent. The atropisomers could not be separated by the usual method of column chromatography on silica gel due to the same polarity. Overall yield: 600 mg (20 %).

α-5,15-bis-(2-aminophenyl)-10,20-bis-(4-methoxyphenyl)-porphyrin 5c. αβ and αα atropisomers of the dinitroporphyrin **4c** (5.2 mmol, 4 g) were dissolved in the mixture of CH_2Cl_2-MeOH (100 mL), taken in a 2 L conical flask along with a reducing agent $SnCl_2.2H_2O$ (11.8 g, 10 equiv.) and concentrated HCl (200 mL) was added slowly to the mixture. The resulting green solution was stirred for 2 days at RT. After completion of the reaction (monitored by MALDI), it was quenched by aqueous KOH solution at 0 °C under ice. The resulting violet solution was washed several times with water and $CHCl_3$. The organic layers were collected and dried over $MgSO_4$. Yield: 2.95 g (80 %).

Atropisomerization. In a 1 L two necks round bottom flask equipped with a stir bar and a condenser, 200 g of silica (60 µm) were added to toluene (400 mL). The reaction mixture was heated to 80°C and degassed with argon during 45 min. Then 2.9 g of the αβ and αα atropisomers of the bis-2-aminophenylporphyrin obtained previously were dissolved in toluene and added to the silica gel mixture in toluene. After evaporation of the solvent, the compound was dissolved in minimum amount of CH_2Cl_2 and purified by column chromatography. The two atropisomers were separated on a silica gel chromatography eluted with CH_2Cl_2/MeOH (αβ 0.2%, αα 0.5%). Yield: **5c** αα (1.9 g, 66%), αβ (0.9 g, 34%). It is worth to note that the atropisomer αα **5c** remains contaminated with by-products resulting from scrambling reactions not separable by silica gel flash chromatography and has not been fully characterized.

α-5,15-bis-(2-[{3-chloromethyl}benzoylamido]-phenyl)-10,20-bis-(4-methoxyphenyl)-porphyrin 6c. A 500 mL two neck round bottom flask equipped with a stirrer and cooled in an ice bath was charged with compound **5c** (0.99 mmol, 700 mg), dry CH_2Cl_2 (300 mL) and NEt_3 (350 µL, 2.5 equiv.). 3-(chloromethyl)benzoyl chloride (420 µL, 3 equiv.) was then added dropwise under argon atmosphere. The reaction mixture was allowed to stir for three hours. Then the reaction was quenched by water and the organic layer was separated. The solvent was removed under vacuum.

The resulting solid was dissolved in CH_2Cl_2 and directly loaded on a silica gel chromatography column. The expected compound eluted with 0.2% CH_2Cl_2/MeOH, was obtained in 90% yield (902 mg). ^{1}H NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 8.93 (4H, d, *J* = 4.81 Hz, βpyr), 8.87 (4H, d, βpyr), 8.93 (2H, d, *J* = 8.06 Hz, $aro_{2'}$), 8.13 (2H, d, *J* =7.49 Hz, $aro_{5'}$), 8.11 (2H, d, *J* = 7.60 Hz, aro_9), 8.02 (2H, d, *J* = 7.60 Hz, $aro_{9'}$), 7.91 (2H, t, ^3J = 8.06 Hz, $aro_{3'}$), 7.63 (2H, s, NHCO), 7.59 (2H, t, *J* = 7.49 Hz, $aro_{4'}$), 7.28 (4H, bs, aro_8, $aro_{8'}$), 6.73 (2H, d, *J* = 7.68 Hz, aro_4), 6.55 (2H, d, *J* = 7.90 Hz, aro_6), 6.49 (2H, t, *J* = 7.68, aro_5), 6.33 (2H, s, aro_2), 4.09 (6H, s, OMe), 3.30 (4H, s, $CH_{2\ bz}$), -2.61 (2H, s, NH_{int}). ^{13}C NMR ($CDCl_3$, 298 K, 500.13 MHz): δ 164.7, 159.7, 138.7, 137.1, 135.7, 135.6, 134.9, 134.7, 133.6, 131.7, 130.8, 129.9, 128.4, 126.2, 126.1, 123.2, 120.9, 120.7, 113.7, 112.5, 112.4, 55.6, 44.3. ESI-HRMS: calcd m/z = 1009.3030 $[M+H]^+$ for $C_{62}H_{47}N_6O_4{}^{35}Cl_2$, found 1009.3031, calcd m/z = 973.3263 $[M-HCl+H]^+$ for $C_{62}H_{46}N_6O_4{}^{35}Cl$, found 973.3268. UV-vis (DMF): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 426 (364), 521 (14), 558 (8), 599 (4), 652 (3.4).

α-5,15-bis-({2,2-(3,3-[2,2-(diethoxycarbonyl)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-methoxyphenyl)-porphyrin 7c. Sodium metal (182 mg, 10 equiv.) was added to the absolute alcohol (20 mL) in a small round bottom flask and stirred for few minutes until the complete consumption of Na. Diethyl malonate (1.2 mL, 10 equiv.) was added to this solution at room temperature and stirred for half an hour. The resulting mixture was added to a solution of porphyrin **6c** (0.79 mol, 800 mg, 1 equiv.) in CH_2Cl_2 (600 mL) and the solution was turned immediately from violet to green. After 2h of stirring the reaction was quenched by H_2O, the organic layer was separated and removed under vacuum. The desired product was purified on a silica gel chromatography column eluted with 0.3% CH_2Cl_2/MeOH. The expected compound was obtained in 80% yield (702 mg). ^{1}H NMR ($CDCl_3$, 298 K, 500 MHz): δ 9.15 (2H, d, *J* = 8.39 Hz, $aro_{2'}$), 8.93 (4H, d, *J* = 4.58 Hz, βpyr), 8.86 (4H, d, *J* = 4.58 Hz, βpyr), 8.22 (2H, s, NHCO), 8.19 (2H, bs, aro_9),

8.01 (2H, d, $2H_l$, *J* = 7.54 Hz, $aro_{5'}$), 7.98 (2H, bs, $aro_{9'}$), 7.91 (2H, t, ^3J = 7.70 Hz, $aro_{3'}$), 7.70 (2H, d, $2H_h$, *J* = 7.98 Hz, aro_6), 7.55 (2H, t, ^3J = 7.70 Hz, $aro_{4'}$), 7.31 (4H, bs, aro_8, $aro_{8'}$), 6.98 (2H, t, ^3J = 7.90 Hz, aro_5), 6.74 (2H, d, *J* = 7.90 Hz, aro_4), 4.99 (2H, s, aro_2), 4.08 (6H, s, OCH_3), 1.70 (4H, s, $CH_{2\ bz}$), 1.23 (4H, bs, $CH_{2\ ester}$), -0.55 (6H, t, *J* = 6.58 Hz, $CH_{3\ ester}$), -2.40 (2H, s, NH_{int}). ^{13}C NMR ($CDCl_3$, 298 K, 500 MHz): δ 167.5, 164.4, 159.6, 138.8, 135.9, 135.2, 134.9, 133.8, 133.7, 132.4, 131.2, 129.9, 128.2, 127.4, 125.9, 122.8, 120.7, 119.7, 113.7, 112.5, 59.9, 58.8, 55.5, 42.5, 11.9. ESI-HRMS: calcd m/z = 1097.4232 $[M+H]^+$ for $C_{69}H_{57}N_6O_8$, found 1097.4234, calcd m/z = 1119.4051 $[M+Na]^+$ for $C_{69}H_{56}N_6O_8Na$, found 1119.4047. UV-vis (DMF): λ/nm (10^{-3} ε, $dm^3\ mol^{-1}\ cm^{-1}$): 425 (380), 520 (15.8), 558 (8.2), 596 (4.4), 653 (3.4).

α-5,15-bis-({{2,2-(3,3-[2,2-(dicarboxylic acid)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-hydroxyphenyl)-porphyrin 8c. Boron tribromide (2.5 mL, 50 equiv.) was added to compound **7c** (0.54 mmol, 600 mg) was dissolved in DCM (100 mL). After 12 h of stirring at RT, the reaction was completed. The mixture was quenched by water. The precipitated compound was filtered and the green solid was washed with water at pH =7. The product was purified by silica gel chromatography column and eluted with $CHCl_3$/MeOH/AcOH (90/9/1). Yield: 80% (440 mg). ^{1}H NMR (DMSO-d_6, 298 K, 500.13 MHz): δ 9.92 (2H, s, OH), 8.84 (4H, d, *J* = 4.55 Hz, βpyr), 8.77 (4H, d, *J* = 4.55 Hz, βpyr), 8.59 (2H, s, NHCO), 8.37 (4H, bs, $aro_{2'}$, $aro_{5'}$), 8.12 (2H, bs, aro_9), 7.92 (2H, t, ^3J = 7.92 Hz, $aro_{3'}$), 7.84 (2H, d, *J* = 6.25 Hz, $aro_{9'}$), 7.75 (2H, t, ^3J = 7.60 Hz, aro_4), 7.24 (2H, d, *J* = 8.04 Hz, aro_6), 7.16 (4H, bs, aro_8, $aro_{8'}$), 6.90 (2H, t, ^3J = 7.49 Hz, aro_5), 6.72 (2H, d, *J* = 7.77 Hz, aro_4), 4.57 (2H, s, aro_2), 1.19 (4H, s, $CH_{2\ bz}$), -2.70 (2H, bs, NH_{int}). ^{13}C NMR (DMSO-d_6, 298 K, 500 MHz): δ 171.5, 165.7, 157.8, 139.2, 136.2, 135.9, 135.7, 135.3, 134.9, 134.8, 132.1, 132, 129.7, 128.1, 126.8, 126.4, 124.6, 124.3, 120.7, 115.3, 114.3, 59.3, 40.49. ESI-HRMS: calcd m/z = 1013.3293 $[M+H]^+$ for $C_{63}H_{45}N_6O_8$, found 1013.3288, calcd m/z = 1035.3112 $[M-H+Na]^+$ for $C_{63}H_{43}N_6NaO_8$, found

1035.3102. UV-vis (DMF): λ/nm (10^{-3} ε, $dm^3\,mol^{-1}\,cm^{-1}$): 428 (344), 522 (19), 560 (12), 599 (7.6), 655 (6).

α-5,15-bis-({{2,2-(3,3-[2,2-(dicarboxylic acid)propane-1,3-diyl]-dibenzoyl-amido]-diphenyl)-10,20-bis-(4-hydroxyphenyl)-iron(III) porphyrin 11. A free-base solution of porphyrin **8c** in THF in the presence of an excess of iron bromide and 2,6-lutidine was heated at reflux overnight inside a glove box. During this process, some decarboxylation reaction was observed and **11** was obtained in roughly equal proportions with its decarboxylated counterpart as indicated by TLC analysis. The resulting mixture was taken out of the glove box, washed with HCl (1M), and dried. There were easily separated by silica gel chromatography using a gradient of MeOH in $CHCl_3$ (from 0.2% to 2.2 %) and identified by MALDI-TOF mass spectrometry (**11**: 37%, $[M + H]^+$ 1066.41).

X-ray crystallographic study.

($C_{75}H_{48}FeN_6O_{10}$); *M* = 1249.04. APEXII, Bruker-AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), *T* = 150(2) K; monoclinic *P* $2_1/c$ (I.T.#14), a = 16.0673(8), b = 15.0517(6), c = 29.0440(14) Å, β = 104.175(2) °, *V* = 6810.1(5) $Å^3$. *Z* = 4, *d* = 1.218 $g.cm^{-3}$, μ = 0.283 mm^{-1}. The structure was solved by dual-space algorithm using the *SHELXT* program,[1] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-2014*).[2] The contribution of the disordered solvents to the structure factors was calculated by the *PLATON* SQUEEZE procedure[3] and then taken into account in the final *SHELXL-2014<:I> least-square refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on* F^2 *with 15532 unique intensities and 840 parameters converged at* $\omega R(F^2) = 0.2756$ *(R(F) = 0.1065) for 8594 observed reflections with* $I > 2\sigma(I)$.

[1] G. M. Sheldrick, *Acta Cryst.*, 2015, **A71** 3-8.

[2] G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8

[3] A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9-18

Structural data

Empirical formula	$C_{75}H_{48}FeN_6O_{10}$
Formula weight	*1249.04*
Temperature	*150(2) K*
Wavelength	*0.71073 Å*
Crystal system, space group	*monoclinic, P* $2_1/c$
Unit cell dimensions	*a = 16.0673(8) Å, α = 90 °*
	b = 15.0517(6) Å, β = 104.175(2) °
	c = 29.0440(14) Å, γ = 90 °
Volume	$6810.1(5)\ Å^3$
Z, Calculated density	*4, 1.218* $(g.cm^{-3})$
Absorption coefficient	$0.283\ mm^{-1}$

F(000)	*2584*
Crystal size	*0.600 x 0.220 x 0.190 mm*
Crystal color	*black*
Theta range for data collection	*2.945 to 27.484 °*
h_min, h_max	*-20, 19*
k_min, k_max	*-19, 17*
l_min, l_max	*-37, 37*
Reflections collected / unique	*51054 / 15532 [R(int)^{a} = 0.0547]*
Reflections [I>2σ]	*8594*
Completeness to theta_max	*0.994*
Absorption correction type	*multi-scan*
Max. and min. transmission	*0.948 , 0.840*
Refinement method	*Full-matrix least-squares on F^2*
Data / restraints / parameters	*15532 / 59 / 840*
^{b}Goodness-of-fit	*1.018*
Final R indices [I>2σ]	*R1^{c} = 0.1065, wR2^{d} = 0.2756*
R indices (all data)	*R1^{c} = 0.1747, wR2^{d} = 0.3234*
Largest diff. peak and hole	*1.555 and -1.085 e^{-}.Å^{-3}*

$^{a}R_{int} = \sum |F_o^2 - < F_o^2 >| / \sum [F_o^2]$

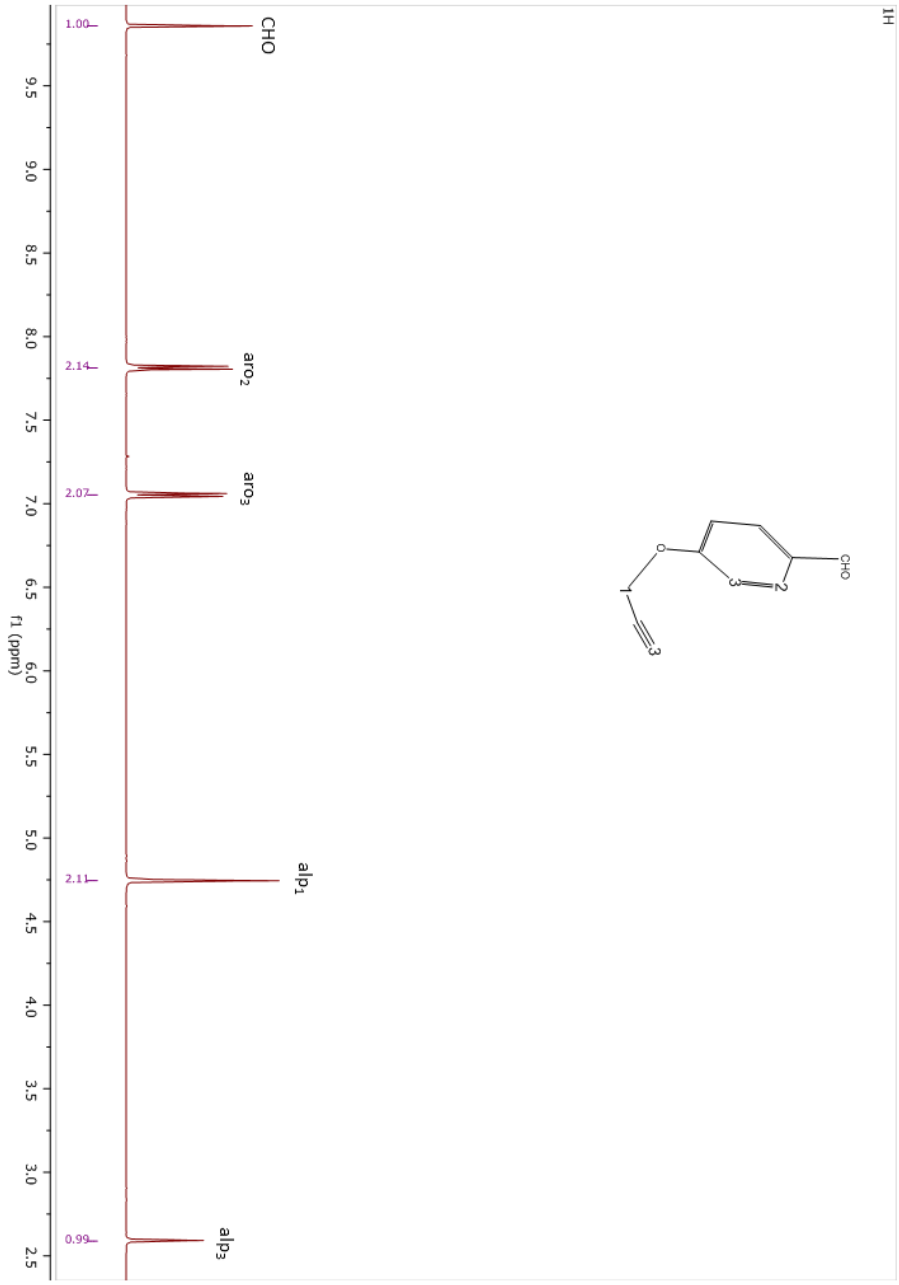
$^{b}S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

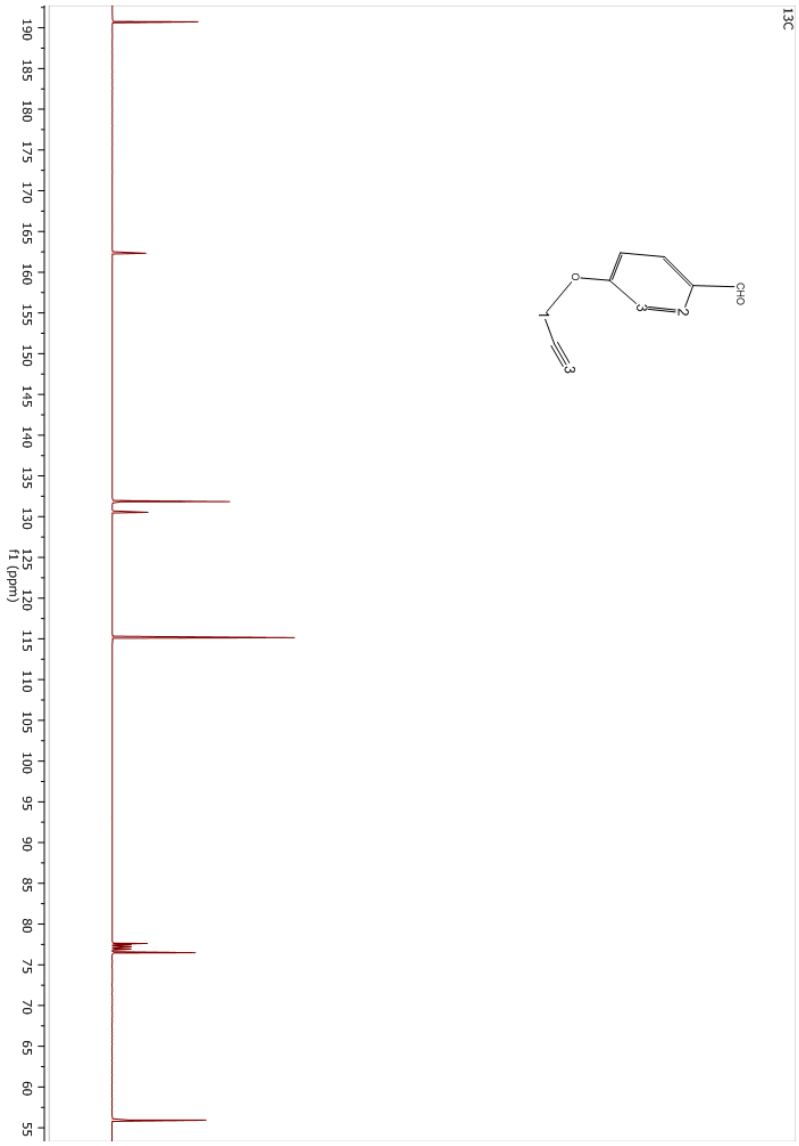
$^{c}R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

$^{d}wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + aP^2 + bP]$ where $P = [2F_c^2 + MAX(F_o^2, 0)] /3$

NMR (^{1}H, ^{13}C, 2D), HRMS and UV-vis. data




13C
CHO
O
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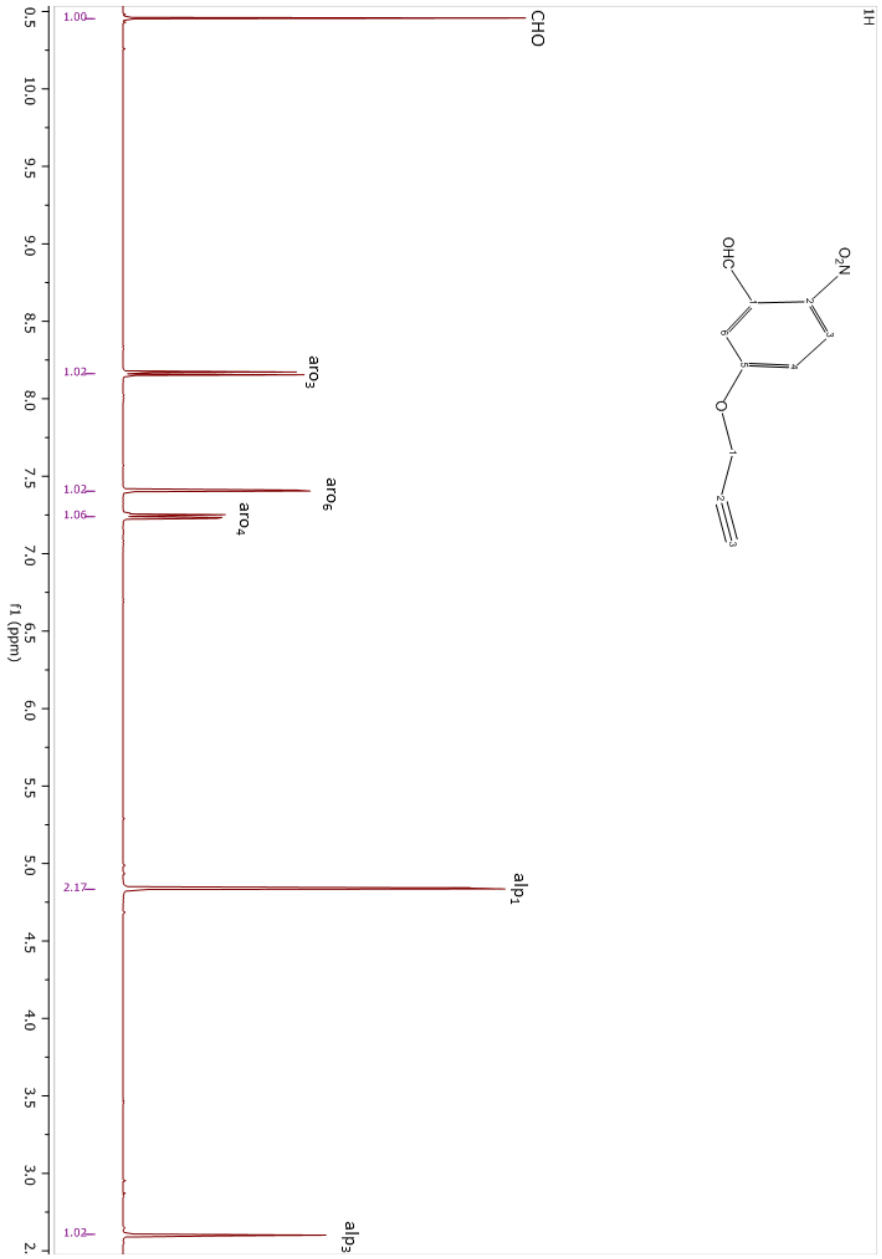
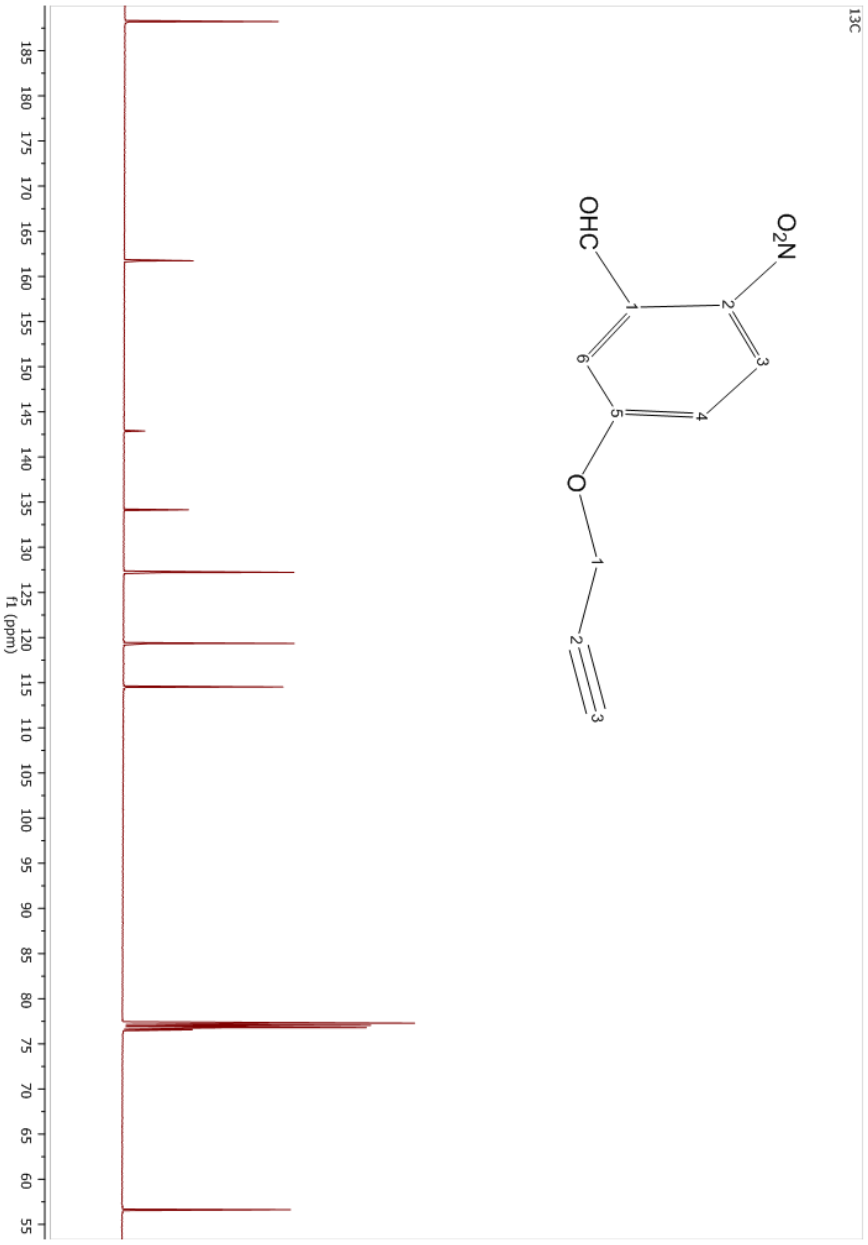
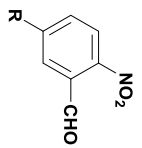
2
3
f1 (ppm)


1H
CHO
aro3
aro5
aro4
alp1
alp3
1.00
1.02
1.02
1.06
2.17
1.02
f1 (ppm)
OHC
O2N


13C
O2N
OHC
O
f1 (ppm)

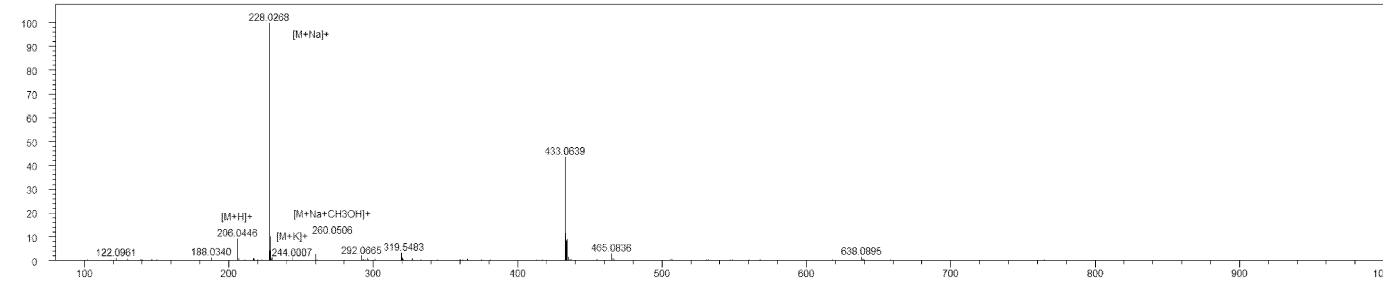
R = propargyloxy



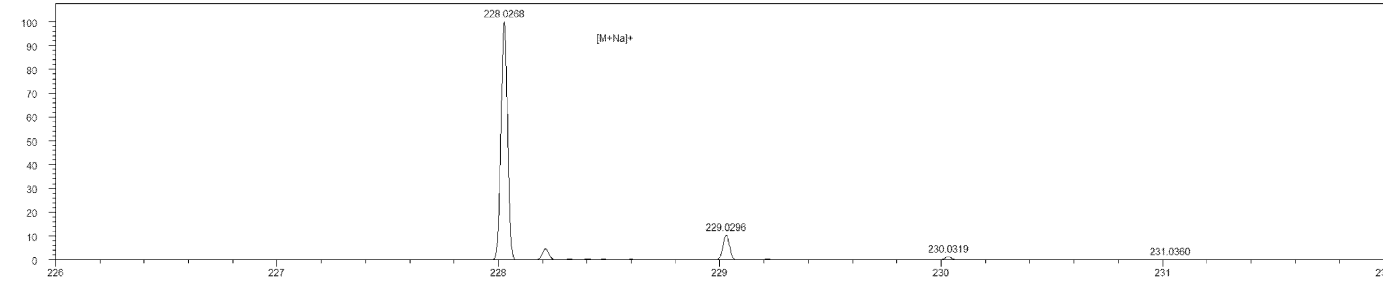
Rapport d'analyse de l'échantillon 2

Spectre et traitement réalisés au Centre régional de mesures physiques de l'Ouest - Université de Rennes 1

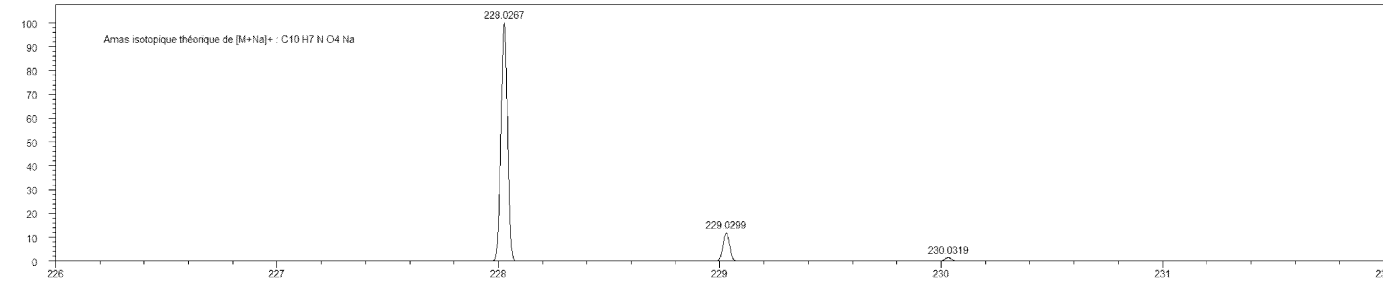
Instrument : Agilent 6510 Fichier : ESI_6322_MS_06.d Date/Heure : 2017-01-05 / 16:33:28 Scans : (60 : 117) de m/z 80 à 1000 Lockmass : 102
Description : P. DAS 2 TD Solvant : CH2Cl2

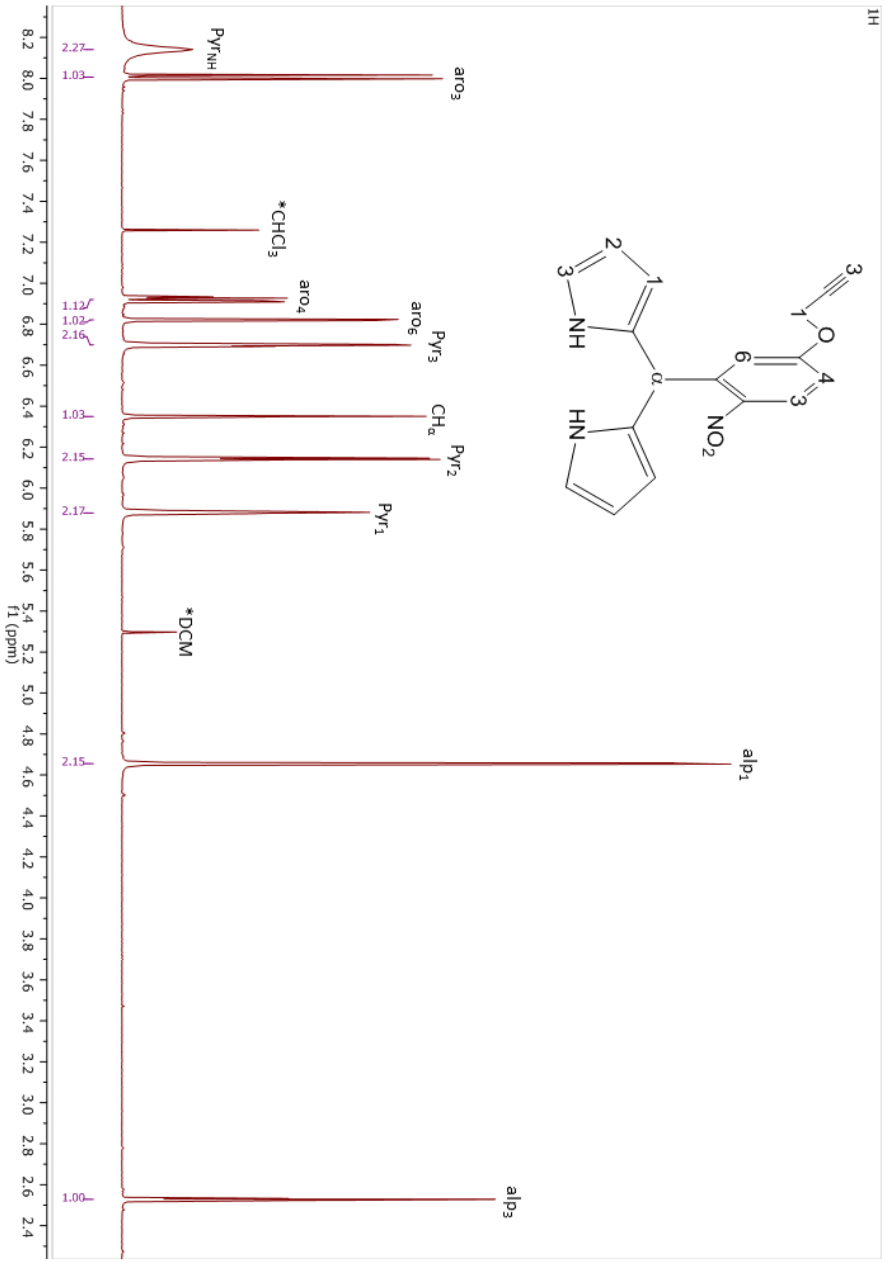


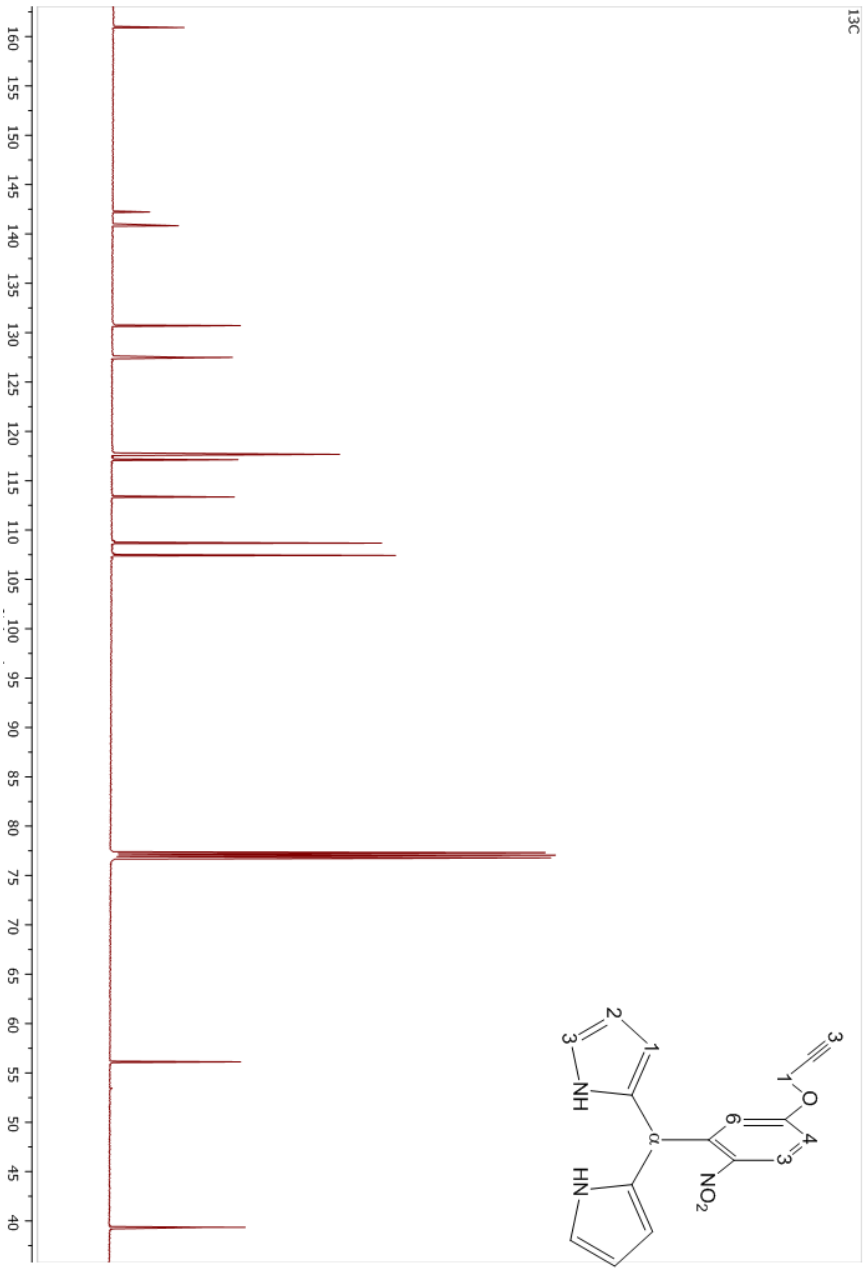
Instrument : Agilent 6510 Fichier : ESI_6322_MS_06.d Date/Heure : 2017-01-05 / 16:33:28 Scans : (60 : 117) de m/z 226 à 232 Lockmass : 102
Description : P. DAS 2 TD Solvant : CH2Cl2



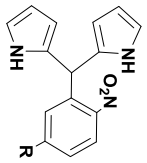
Séparation : 10 Seuil : 0.01 mmu Charge : 1 Résolution : 7000
Formule brute : C10 H7 N O4 Na




1H
PyrNH
aro3
*CHCl3
aro4
aro6
Pyr3
CHα
Pyr2
Pyr1
*DCM
alp1
alp3
2.27
1.03
1.12
1.02
2.16
1.03
2.15
2.17
2.15
1.00
NH
HN
α
NO2
O
f1 (ppm)


13C
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
NH
HN
α
O
NO2

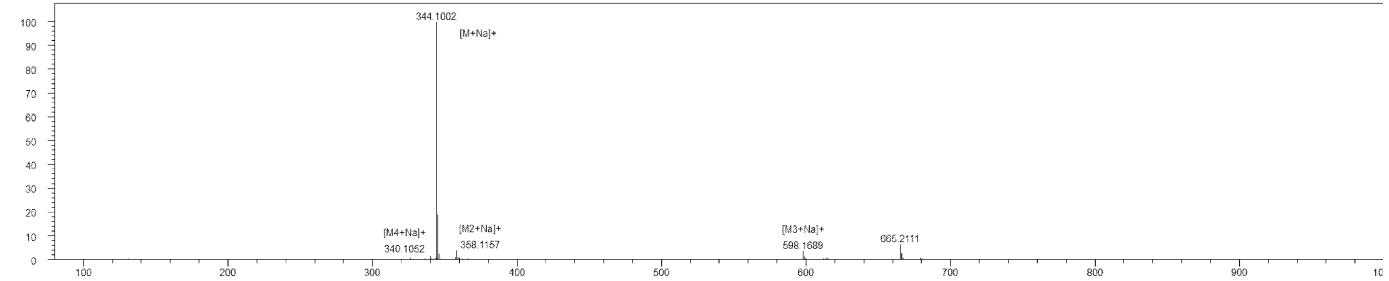
R = propargyloxy



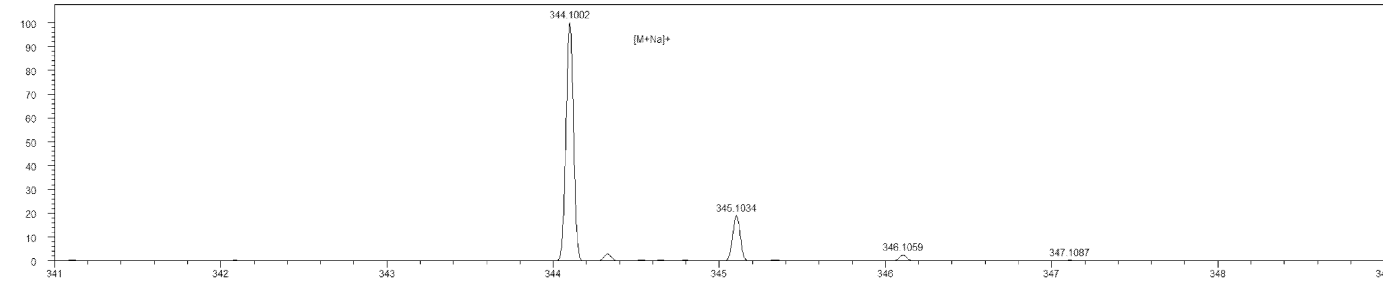
Rapport d'analyse de l'échantillon 3

Spectre et traitement réalisés au Centre régional de mesures physiques de l'Ouest - Université de Rennes 1

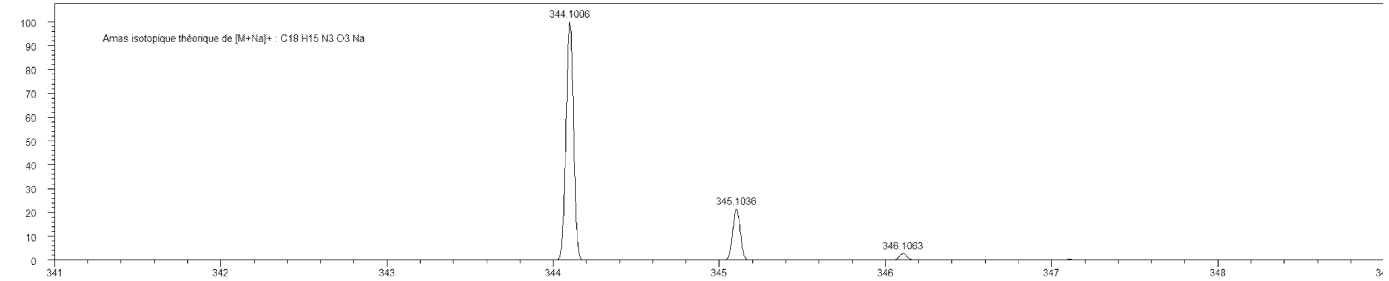
Instrument : Agilent 6510 Fichier : ESI_6362_MS_01.d Date/Heure : 2017-01-16 / 18:08:10 Scans : (1 : 119) de m/z 80 à 1000 Lockmass : 553
Description : P. DAS 3 TD Solvant : CH3OH/CH2Cl2 (80/20)

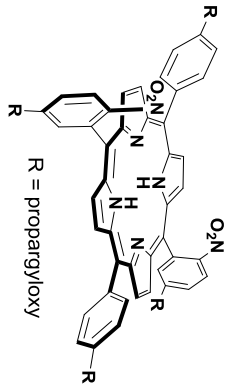


Instrument : Agilent 6510 Fichier : ESI_6362_MS_01.d Date/Heure : 2017-01-16 / 18:08:10 Scans : (1 : 119) de m/z 341 à 349 Lockmass : 553
Description : P. DAS 3 TD Solvant : CH3OH/CH2Cl2 (80/20)



Séparation : 10 Seuil : 0.01 mmu Charge : 1 Résolution : 7000
Formule brute : C18 H15 N3 O3 Na



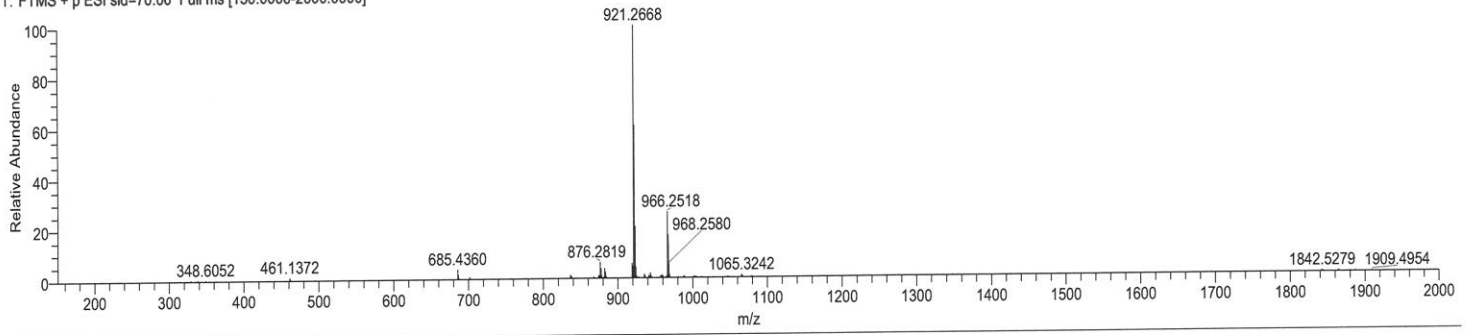


CRMPO
P. DAS 4 PJ Solvant : CH3COCH3 (+ 0.1% acide formique)
C:\Xcalibur\Data\ESI_6323_MS_03

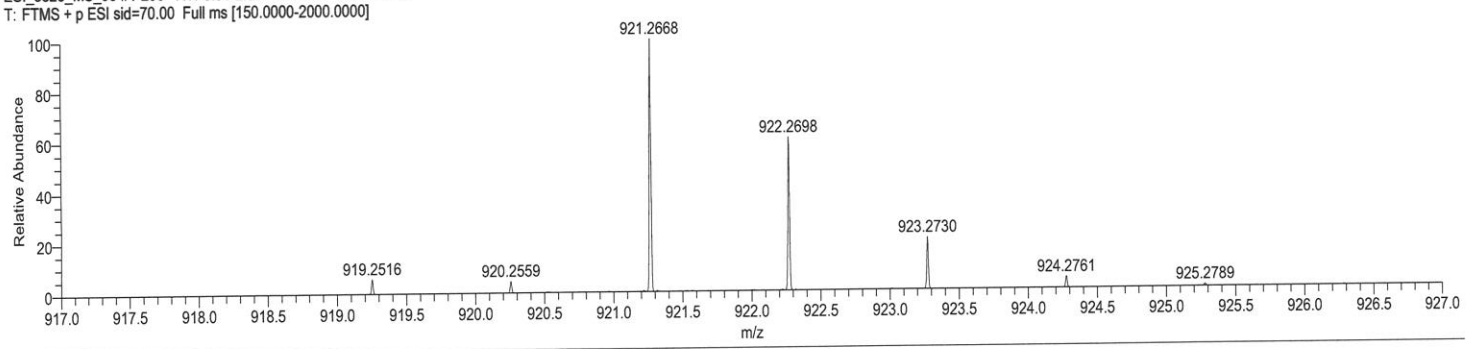
Rapport d'analyse
01/06/17 20:17:04

Thermo Fisher Scientific Q-Exactive

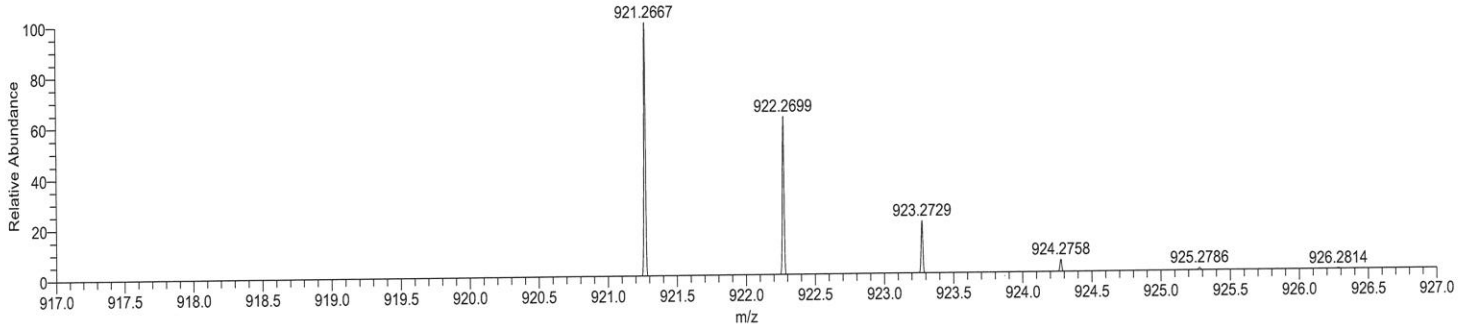
ESI_6323_MS_03 #1-230 RT: 0.01-2.01 AV: 230 NL: 5.47E8
T: FTMS + p ESI sid=70.00 Full ms [150.0000-2000.0000]

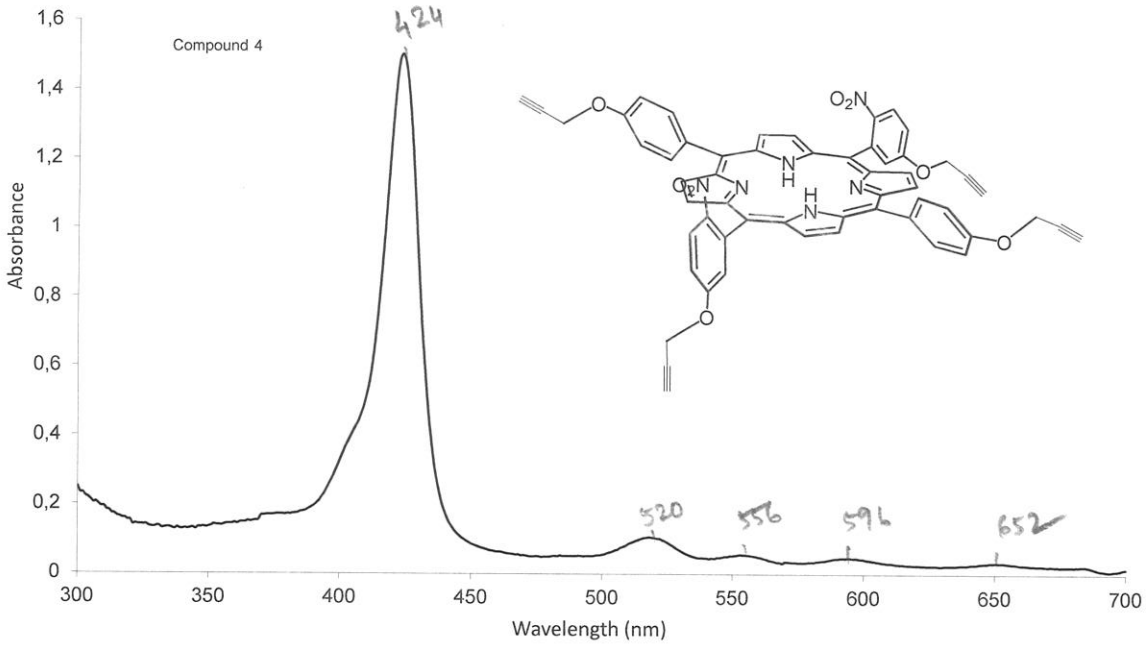


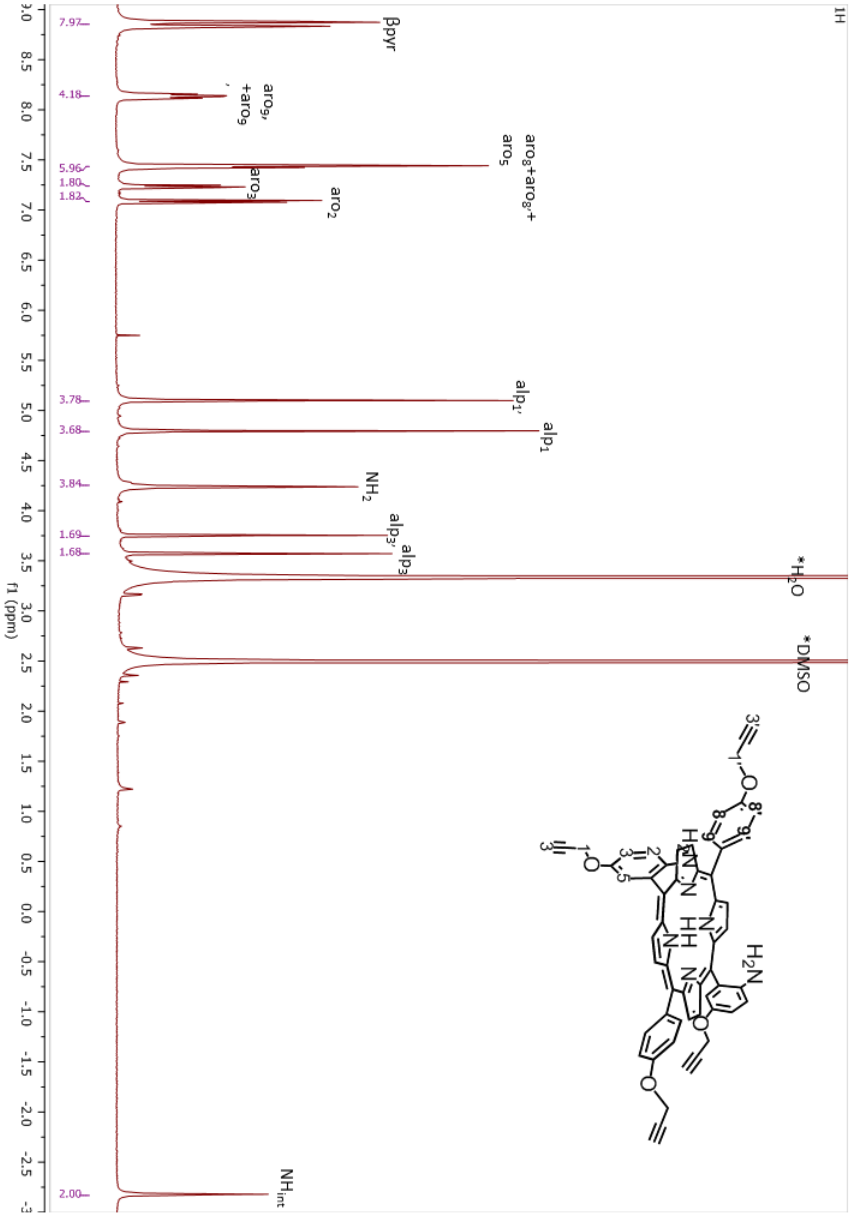
ESI_6323_MS_03 #1-230 RT: 0.01-2.01 AV: 230 NL: 5.47E8
T: FTMS + p ESI sid=70.00 Full ms [150.0000-2000.0000]

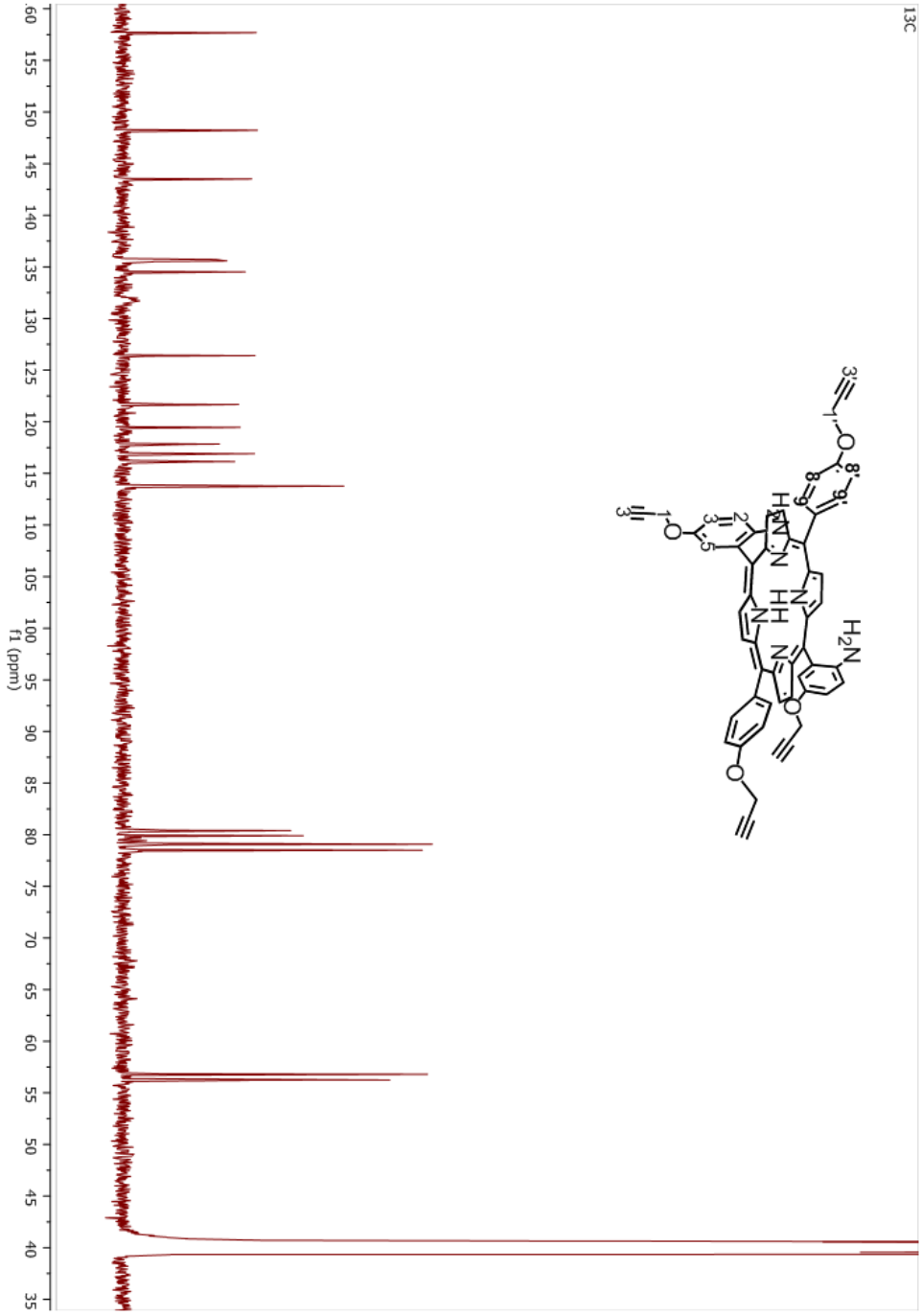


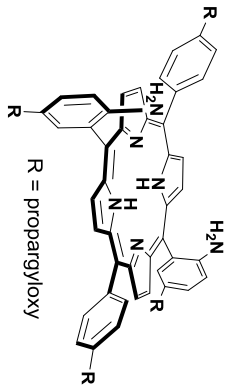
C56H36N6O8 +H: C56 H37 N6 O8 p(gss, s/p:40) Chrg 1...




Compound 4
424
520
556
596
652
Absorbance
Wavelength (nm)
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
300
350
400
450
500
550
600
650
700
O2N
N
H
O


1H
βpyr
aro9'
+aro9
aro8+aro8'+
aro5
aro3
aro2
alp1'
alp1
NH2
alp2
alp3
*H2O
*DMSO
NHint
H2N
f1 (ppm)


13C
f1 (ppm)
H2N



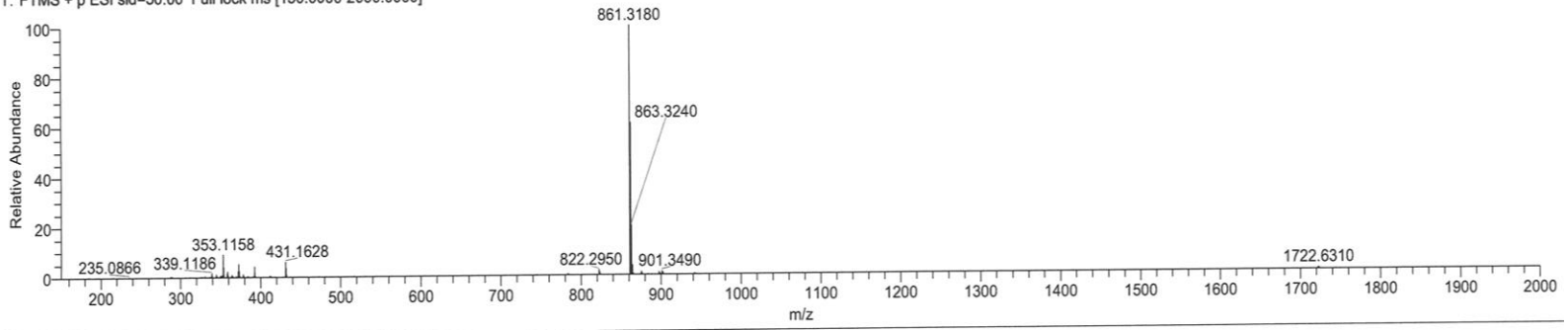
CRMPO
P. DAS 5 PJ Solvant : CH3COCH3
C:\Xcalibur\Data\ESI_6324_MS_02

Rapport d'analyse

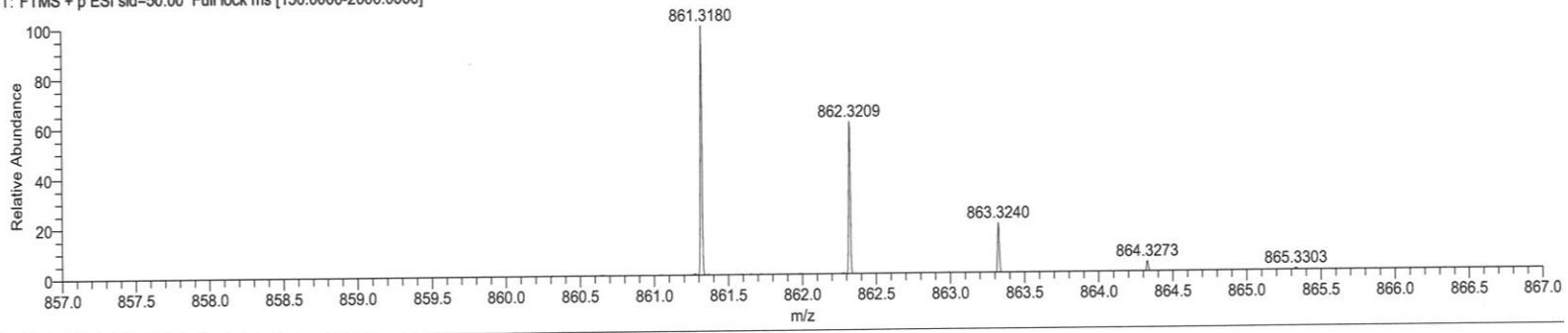
01/05/17 16:50:37

Thermo Fisher Scientific Q-Exactive

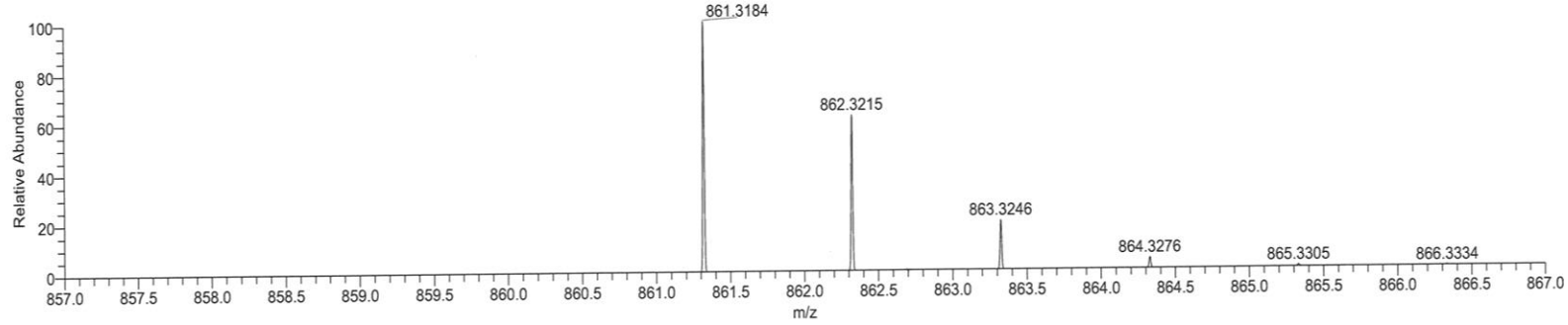
ESI_6324_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 2.11E8
T: FTMS + p ESI sid=50.00 Full lock ms [150.0000-2000.0000]

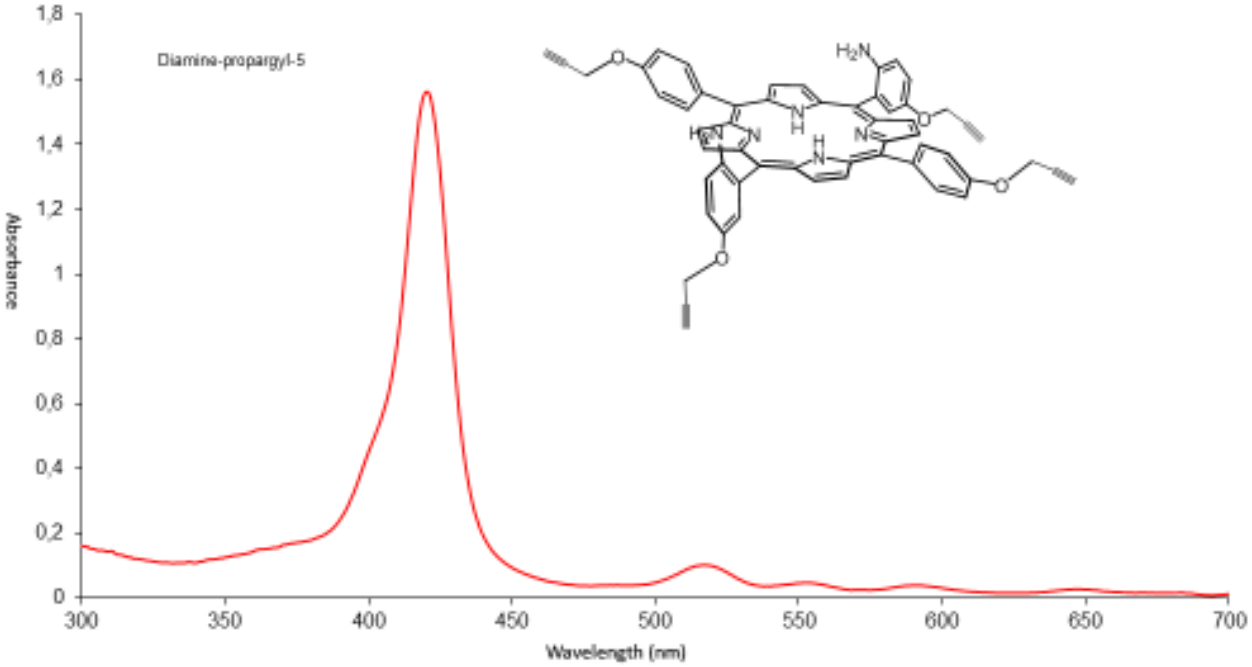


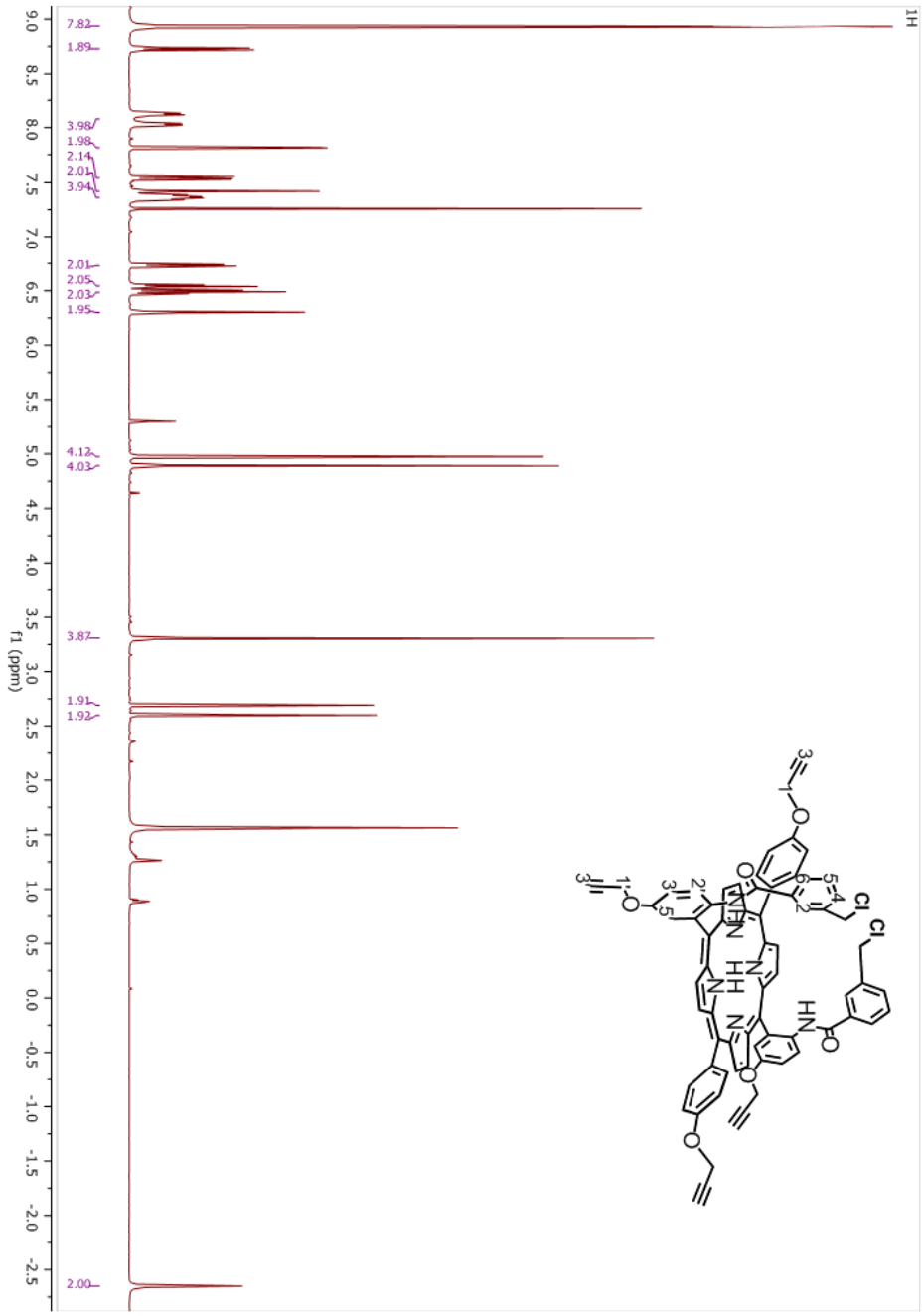
ESI_6324_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 2.11E8
T: FTMS + p ESI sid=50.00 Full lock ms [150.0000-2000.0000]

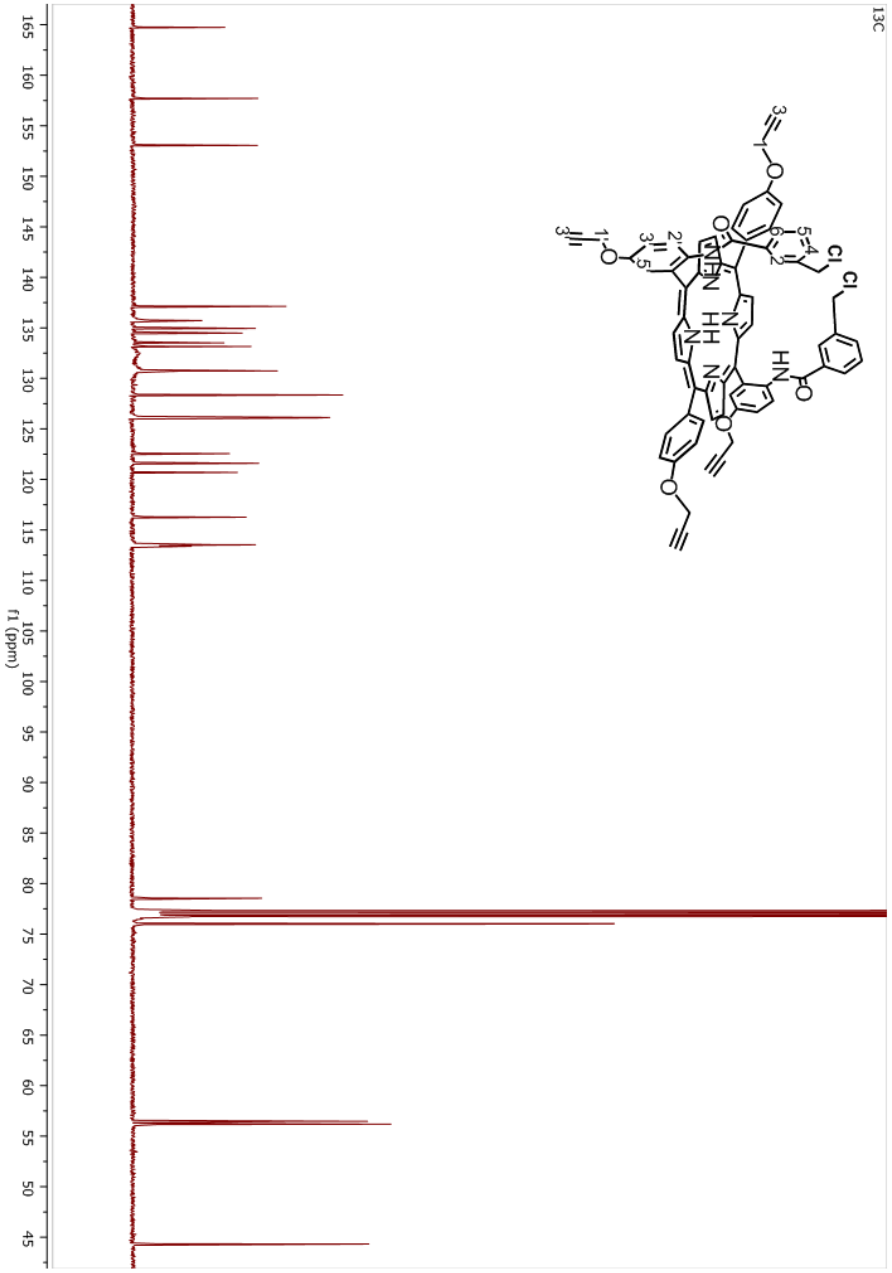


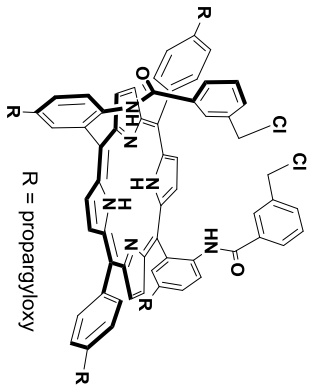
C56H40N6O4 +H: C56 H41 N6 O4 p(gss, s/p:40) Chrg 1...




Diamine-propargyl-5
Absorbance
Wavelength (nm)
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
300
350
400
450
500
550
600
650
700
H2N
N
H
HN
N
N
H
N
O
O
O
O


1H
7.82
1.89
3.98
1.98
2.14
2.01
3.94
2.01
2.05
2.03
1.95
4.12
4.03
3.87
1.91
1.92
2.00
f1 (ppm)
Cl
Cl
HN
NH
N
O


13C
f1 (ppm)
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45

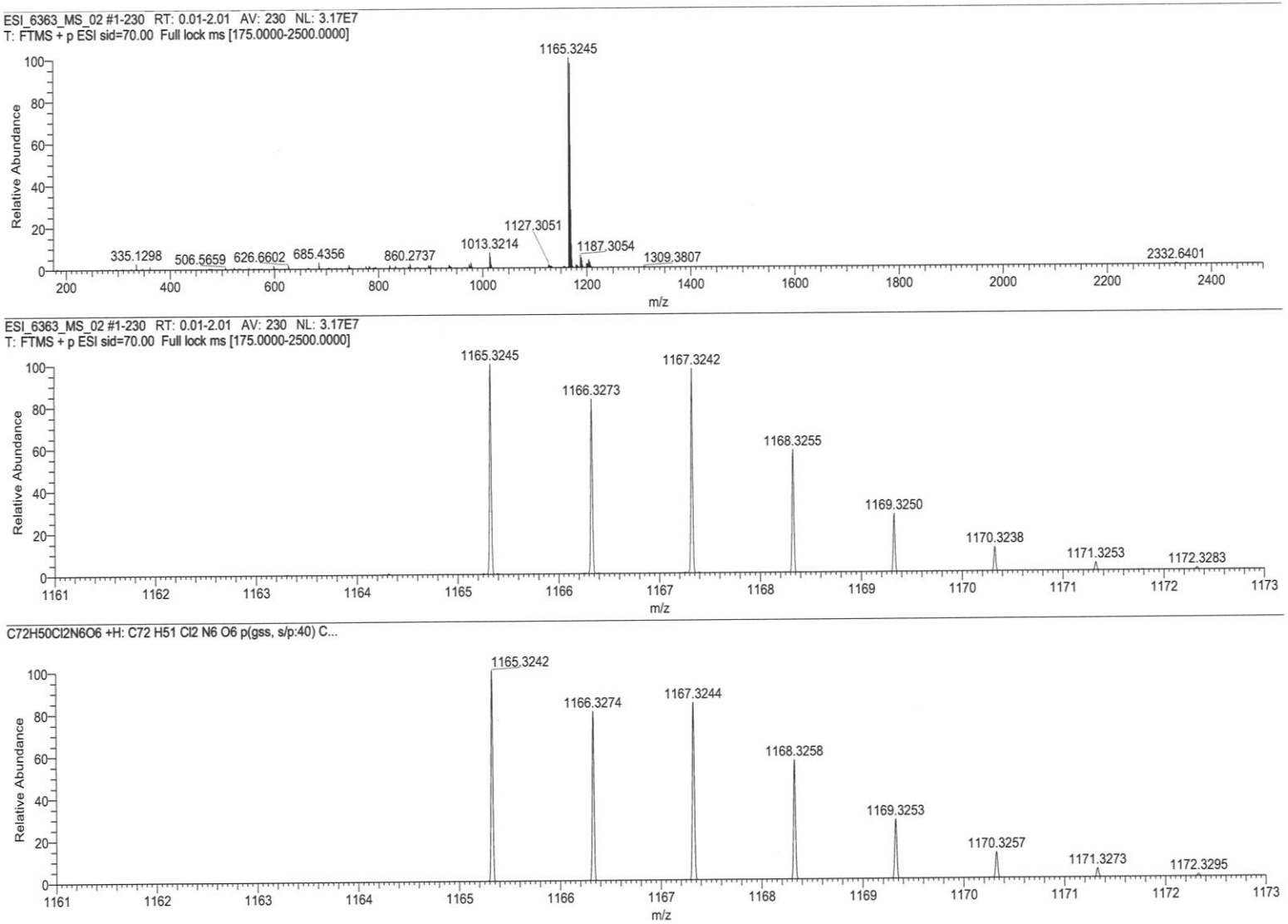


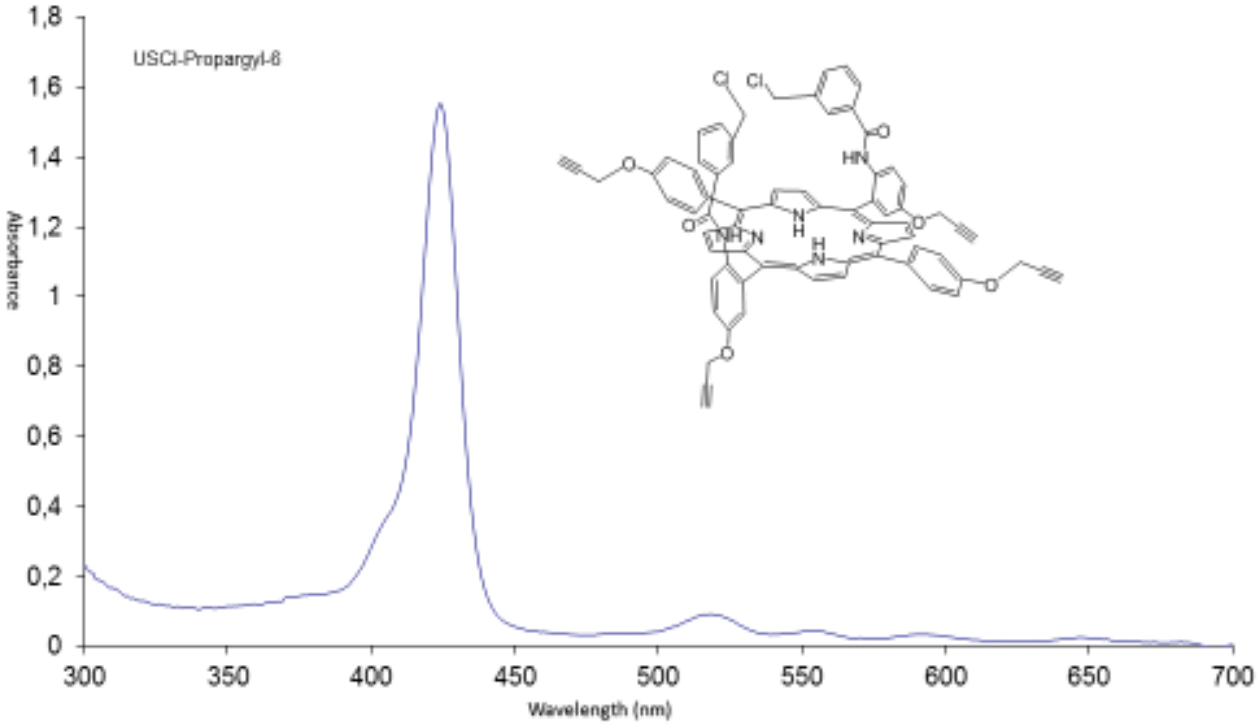
CRMPO
P. DAS 6 PJ Solvant : CH3COCH3
C:\Xcalibur\Data\ESI_6363_MS_02

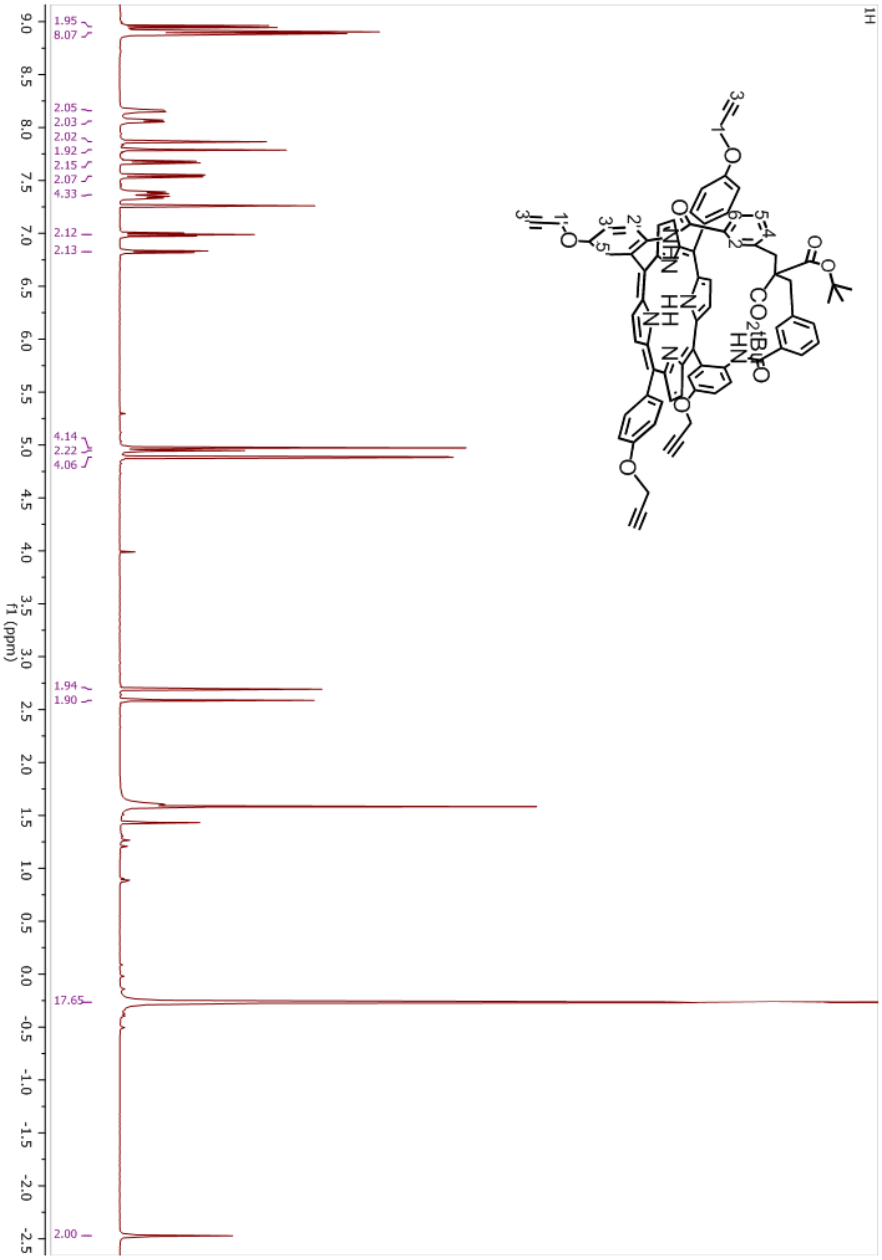
Rapport d'analyse

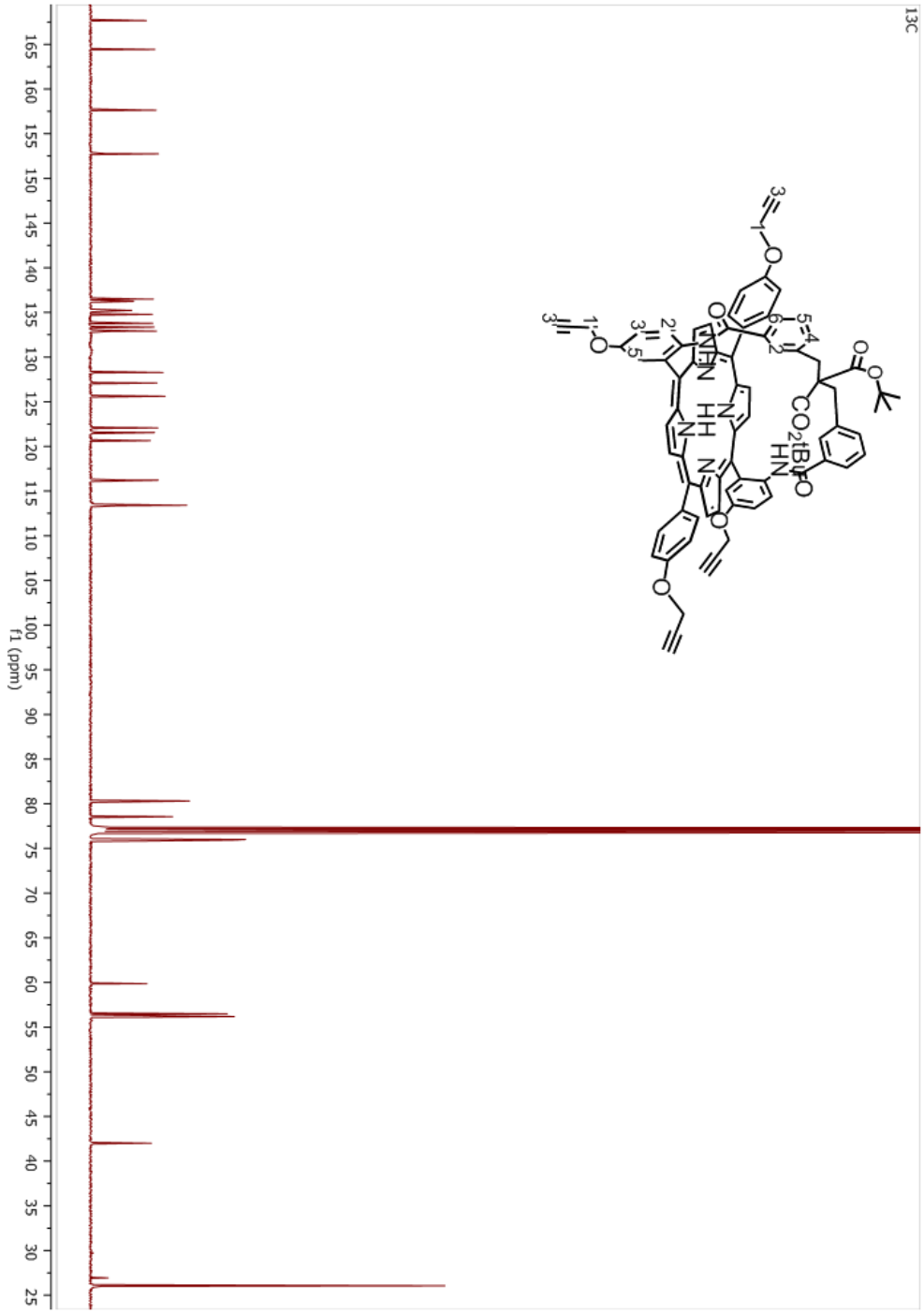
01/19/17 11:51:25

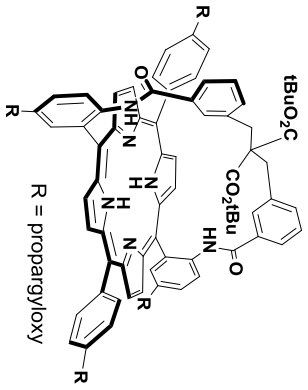
Thermo Fisher Scientific Q-Exactive




USCI-Propargyl-8
Absorbance
Wavelength (nm)
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
300
350
400
450
500
550
600
650
700
Cl
Cl
HN
O
O
NH
N
N
H
H
N
N
O
O
O

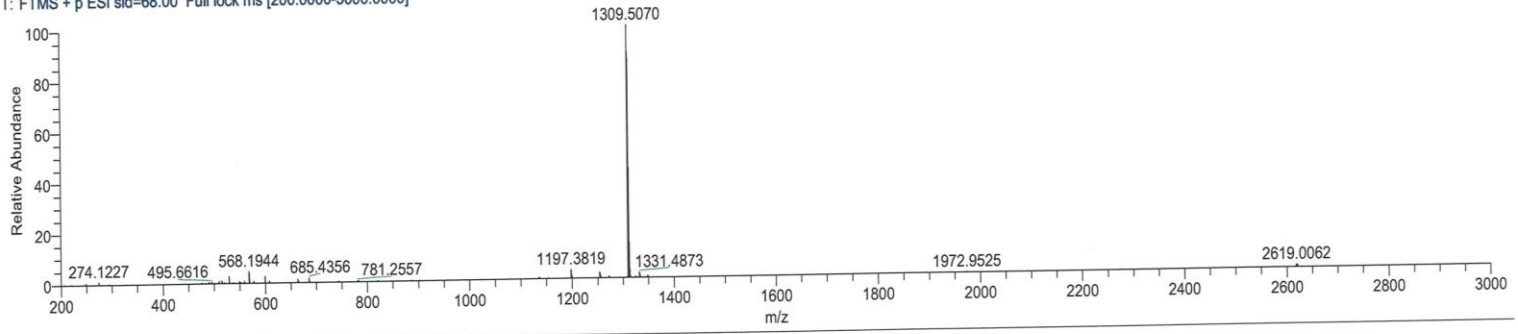

1H
f1 (ppm)
1.95
8.07
2.05
2.03
2.02
1.92
2.15
2.07
4.33
2.12
2.13
4.14
2.22
4.06
1.94
1.90
17.65
2.00
CO2tBu
HN
NH
N


13C
f1 (ppm)
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25

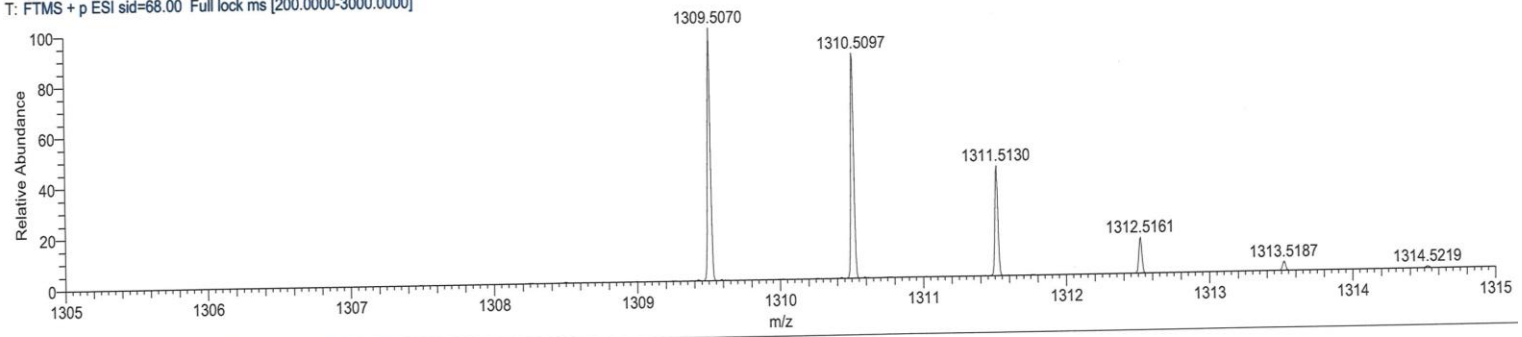


CRMPO
Rapport d'analyse
Thermo Fisher Scientific Q-Exactive
P. DAS 8 PJ Solvant : CH2Cl2 (+ 0.1% acide formique)
C:\Xcalibur\Data\ESI_6364_MS_02
01/24/17 16:51:12

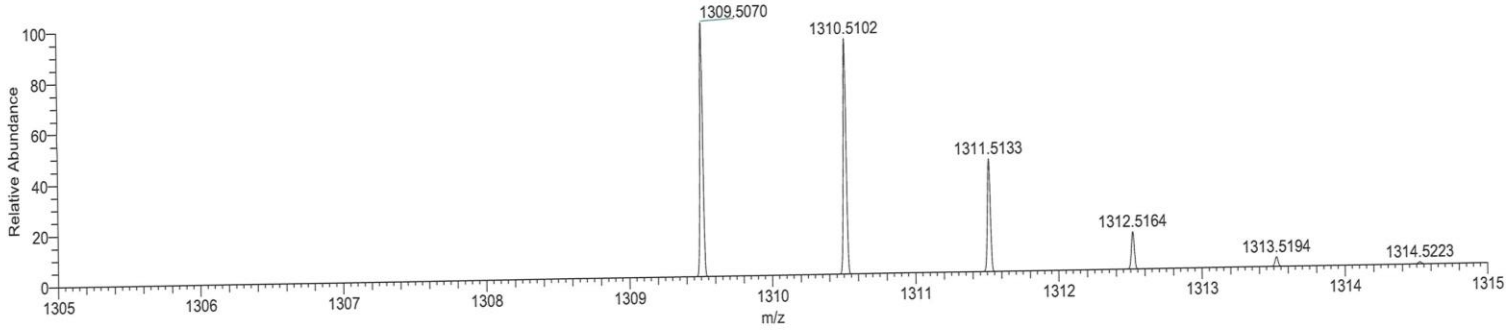
ESI_6364_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.33E7
T: FTMS + p ESI sid=68.00 Full lock ms [200.0000-3000.0000]

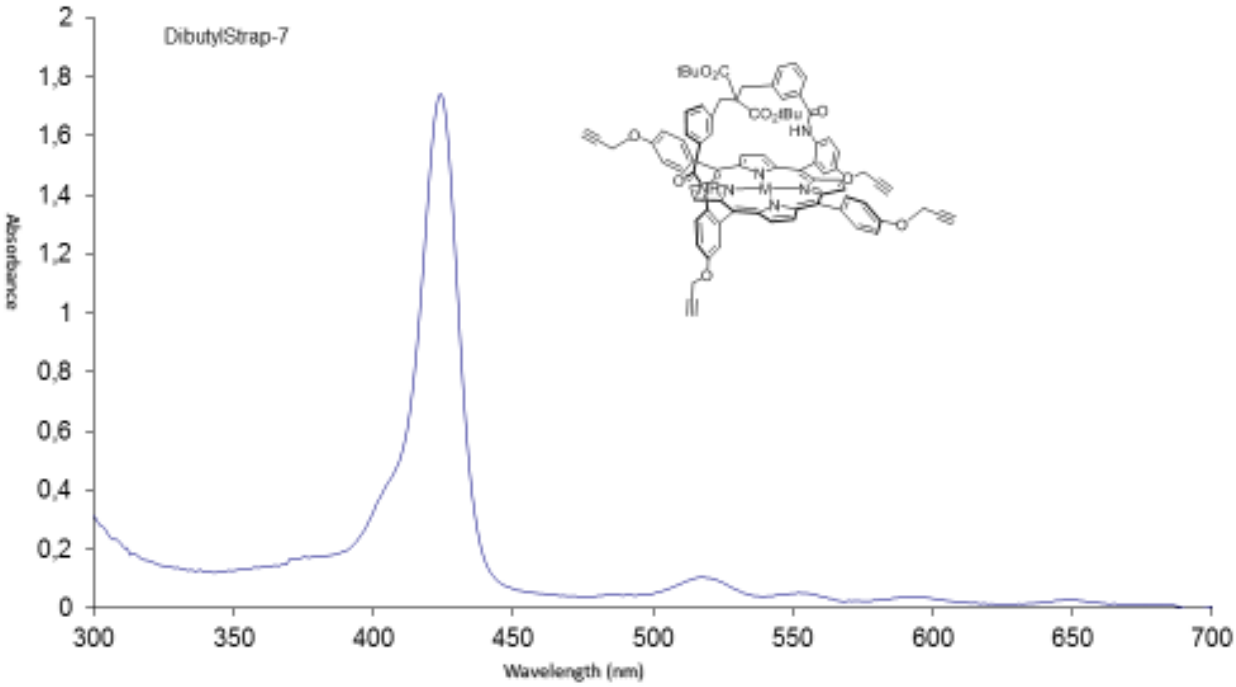


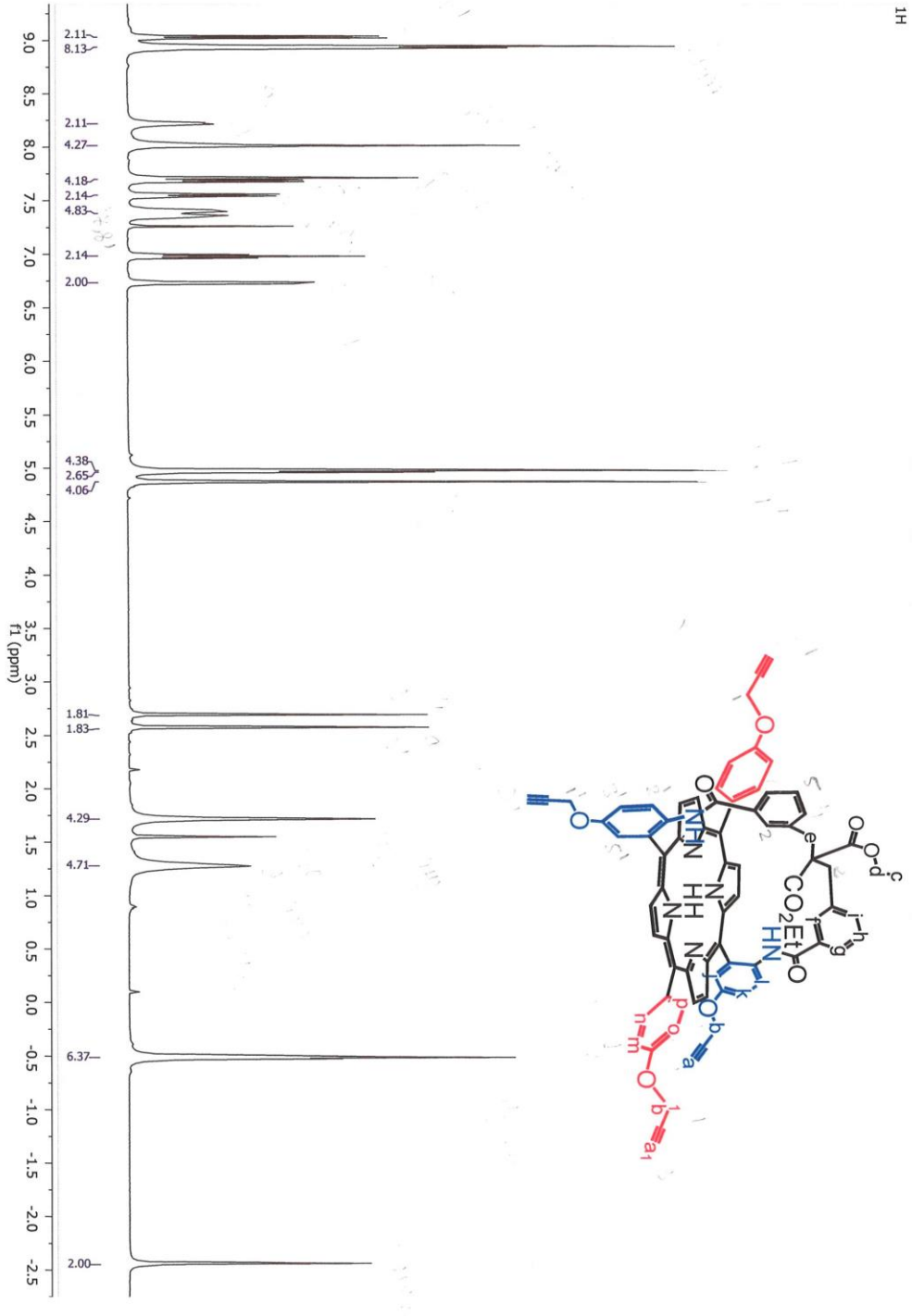
ESI_6364_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.33E7
T: FTMS + p ESI sid=68.00 Full lock ms [200.0000-3000.0000]

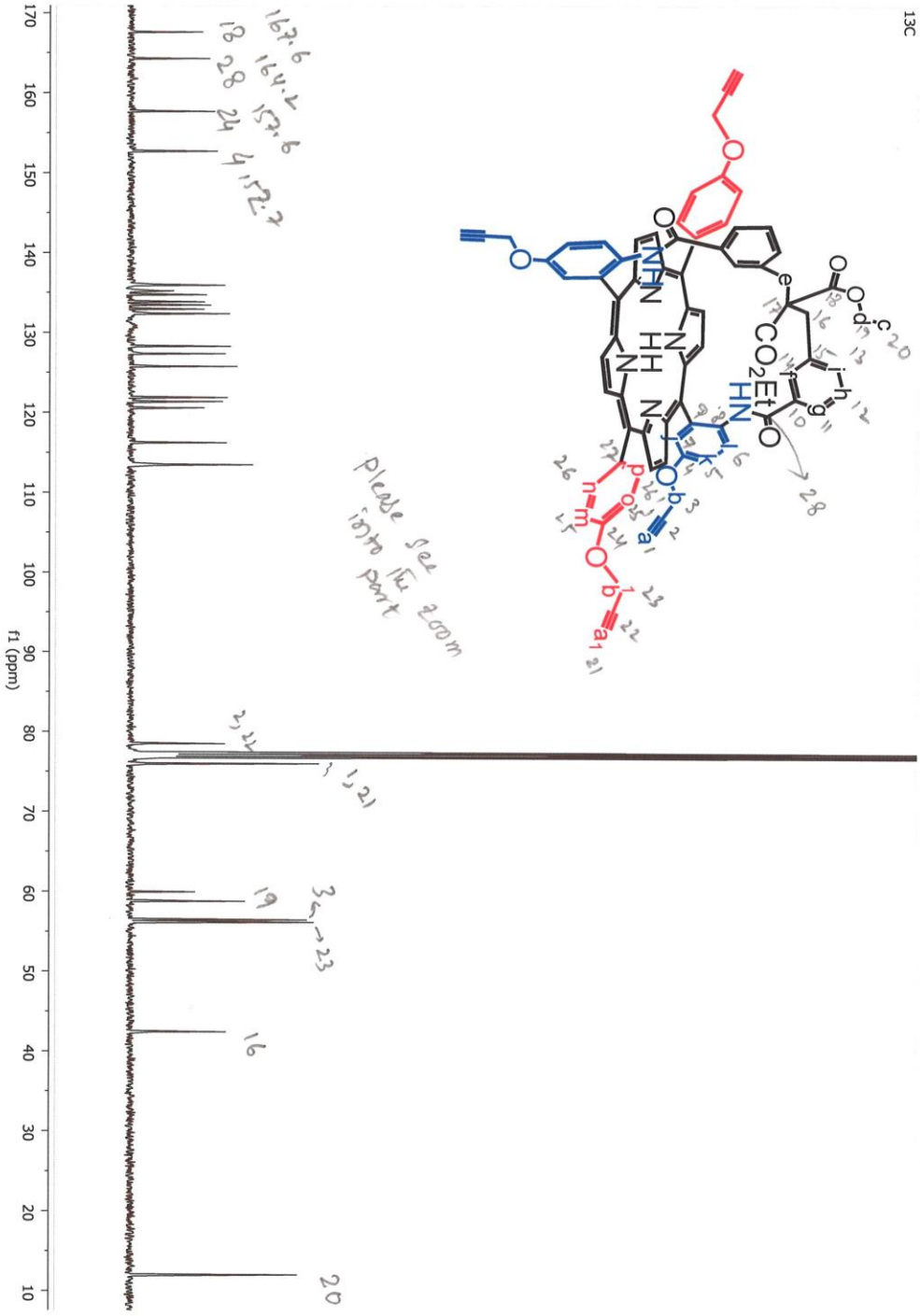


C83H68N6O10 +H: C83 H69 N6 O10 p(gss, s/p:40) Chrg 1...




DibutylStrap-7
Absorbance
Wavelength (nm)
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
300
350
400
450
500
550
600
650
700


1H
f1 (ppm)
2.11
8.13
2.11
4.27
4.18
2.14
4.83
2.14
2.00
4.38
2.65
4.06
1.81
1.83
4.29
4.71
6.37
2.00
CO2Et
HN
NH
N


13C
f1 (ppm)
167.6
164.2
153.6
122.7
please see zoom into the part

7b

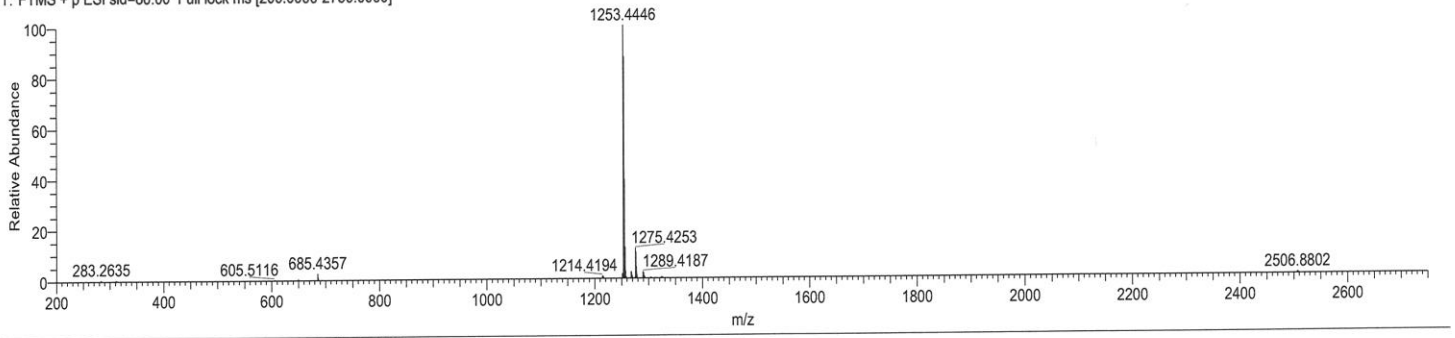
CRMPO
P. DAS 7 PJ Solvant : CH3COCH3
C:\Xcalibur\Data\ESI_6325_MS_01

Rapport d'analyse

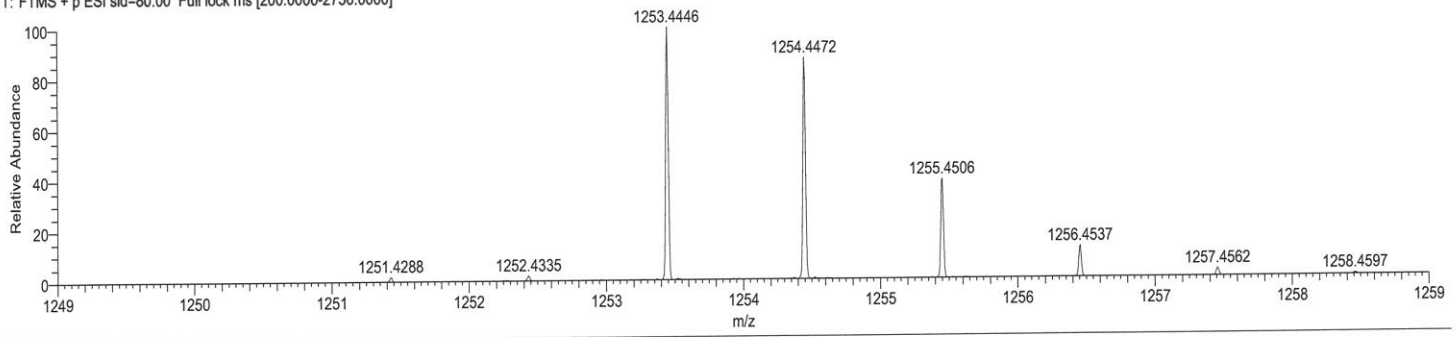
01/05/17 19:40:09

Thermo Fisher Scientific Q-Exactive

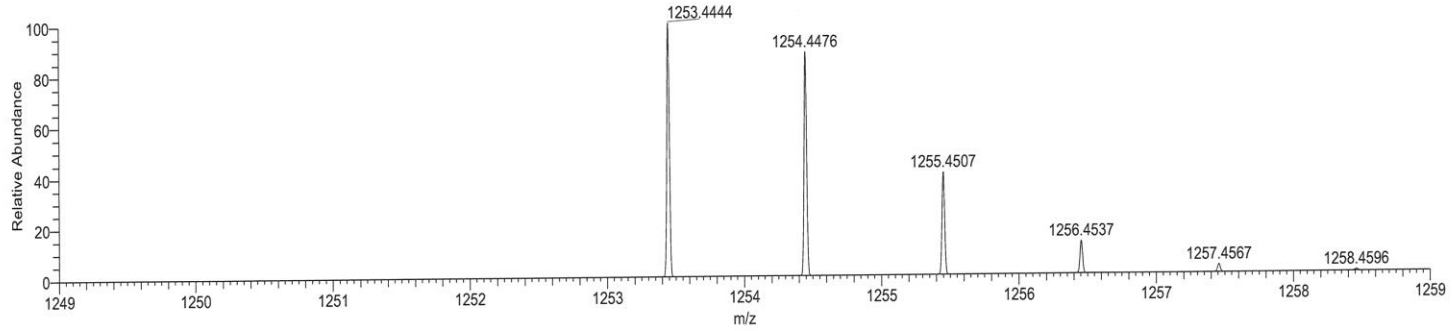
ESI_6325_MS_01 #1-230 RT: 0.01-2.01 AV: 230 NL: 6.88E6
T: FTMS + p ESI sid=80.00 Full lock ms [200.0000-2750.0000]

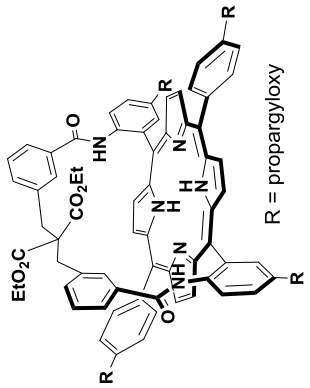


ESI_6325_MS_01 #1-230 RT: 0.01-2.01 AV: 230 NL: 6.88E6
T: FTMS + p ESI sid=80.00 Full lock ms [200.0000-2750.0000]



C79H60N6O10 +H: C79 H61 N6 O10 p(gss, s/p:40) Chrg 1...



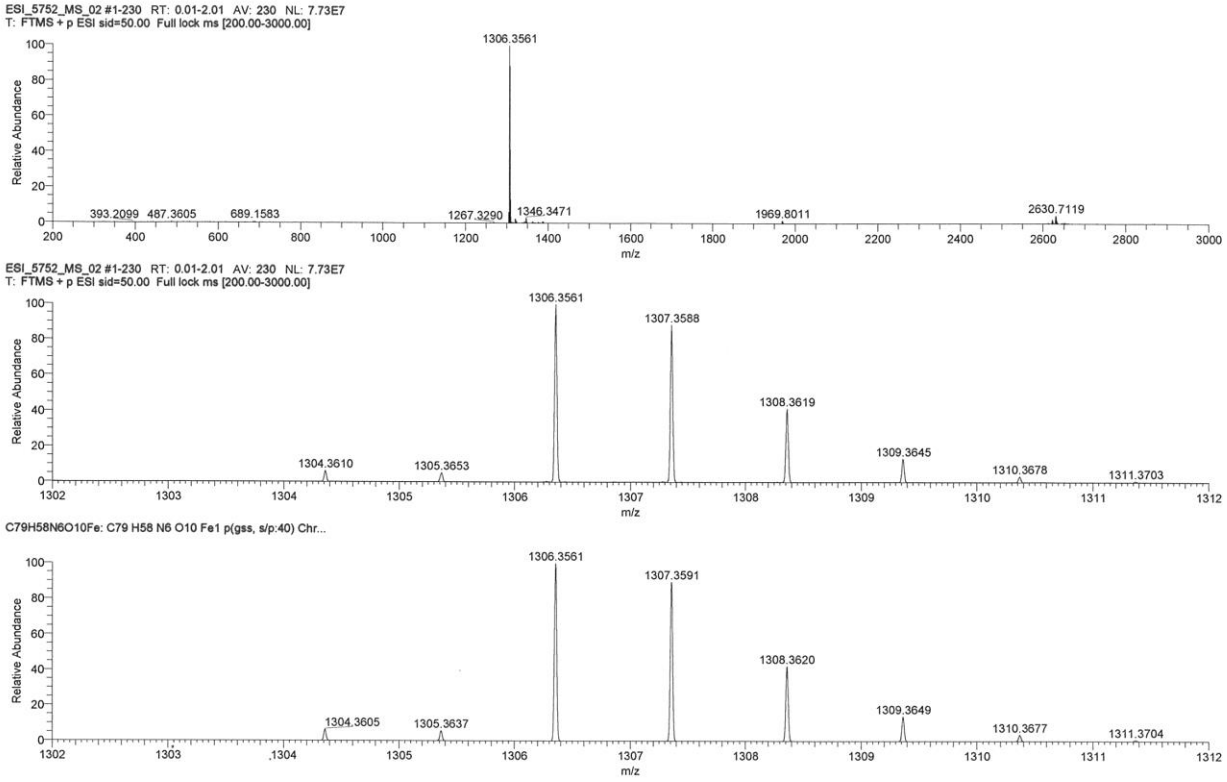


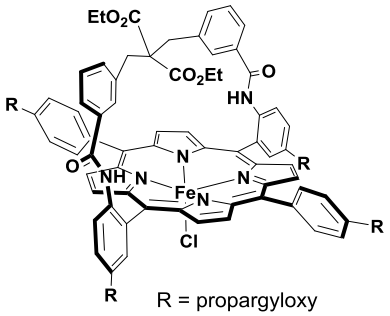
CRMPO
S. LE GAC PD E PJ Solvant : CH3COCH3
C:\Xcalibur\Data\ESI_5752_MS_02

Rapport d'analyse

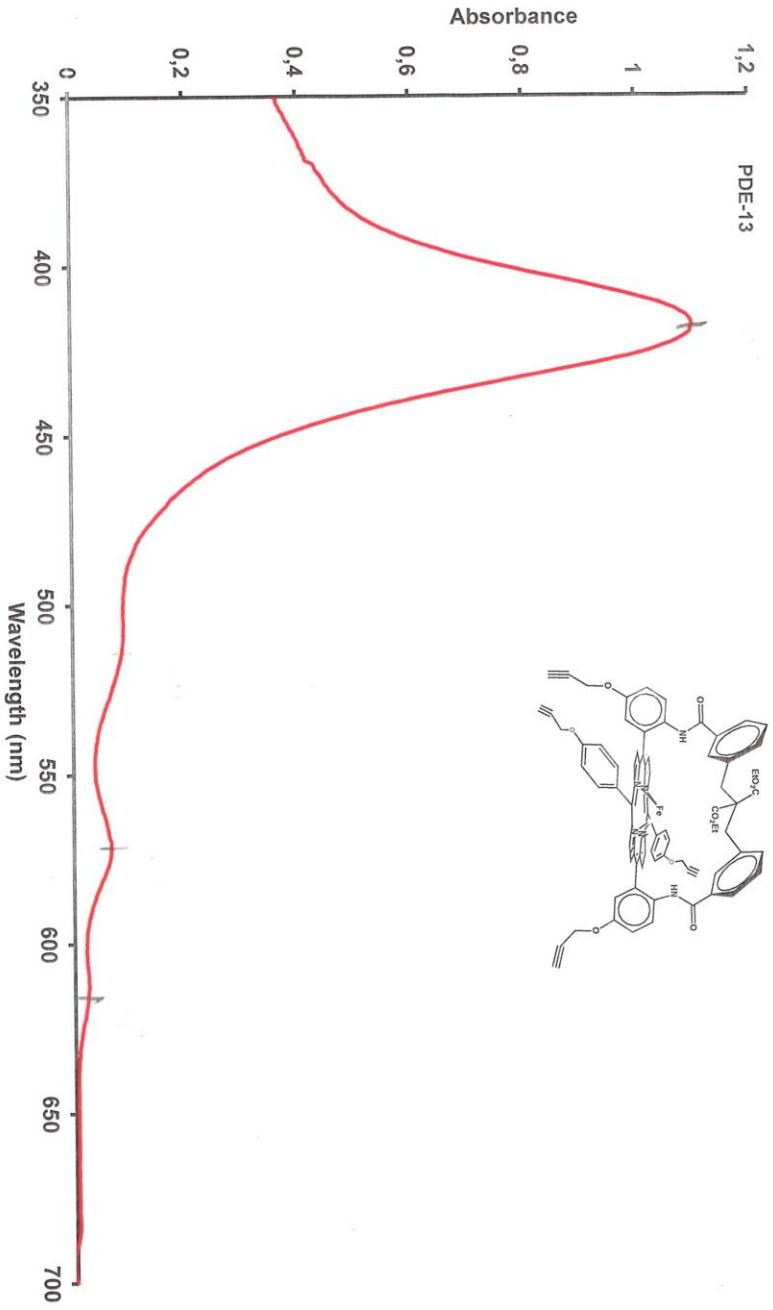
07/19/16 10:19:38

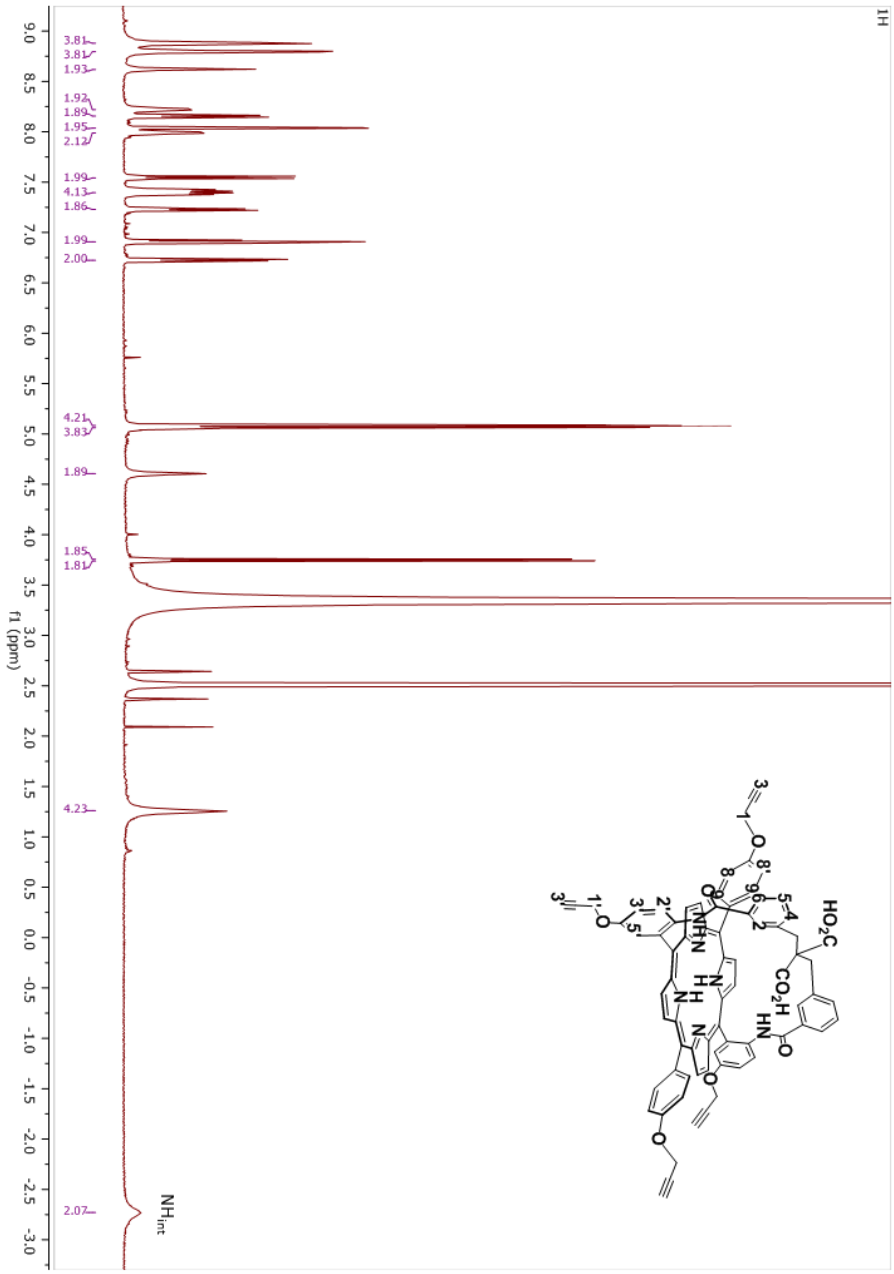
Thermo Fisher Scientific Q-Exactive

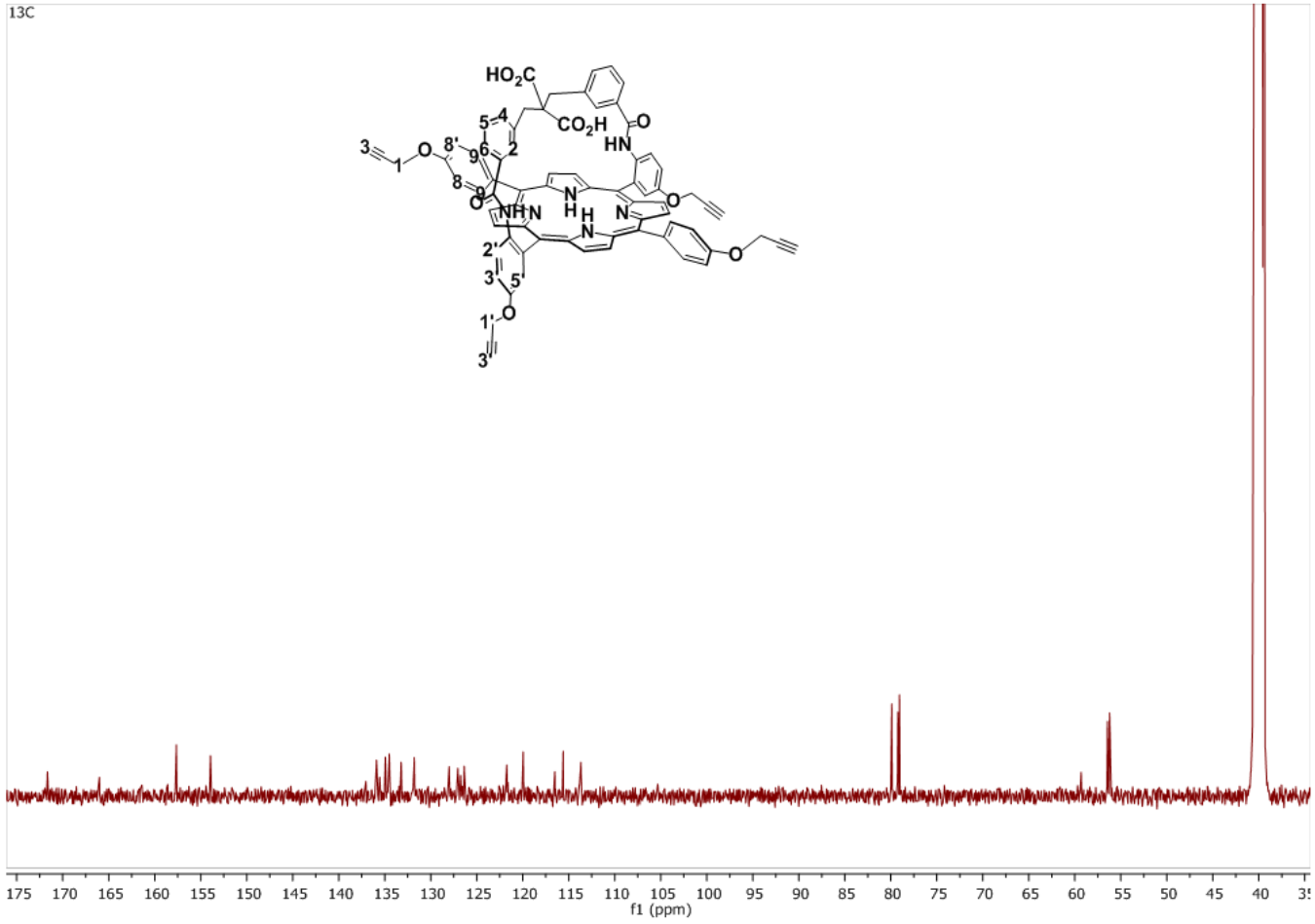


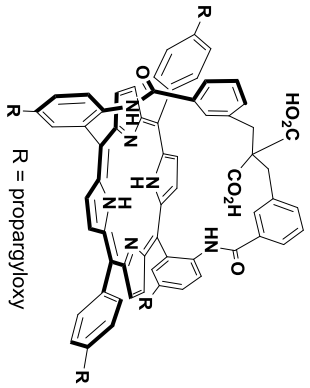


R = propargyloxy


Absorbance
0
0,2
0,4
0,6
0,8
1
1,2
PDE-13
350
400
450
500
550
600
650
700
Wavelength (nm)
NH
HN
Fe
EtO2C
CO2Et


1H
3.81
3.81
1.93
1.92
1.89
1.95
2.12
1.99
4.13
1.86
1.99
2.00
4.21
3.83
1.89
1.85
1.81
4.23
2.07
NHint
f1 (ppm)
HO2C
CO2H
HN
O
NH
N


13C
HO2C
CO2H
HN
O
NH
N
H
N
N
H
N
O
O
O
O
O
1
2
3
4
5
6
8
8'
9
9'
1'
2'
3'
5'
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)



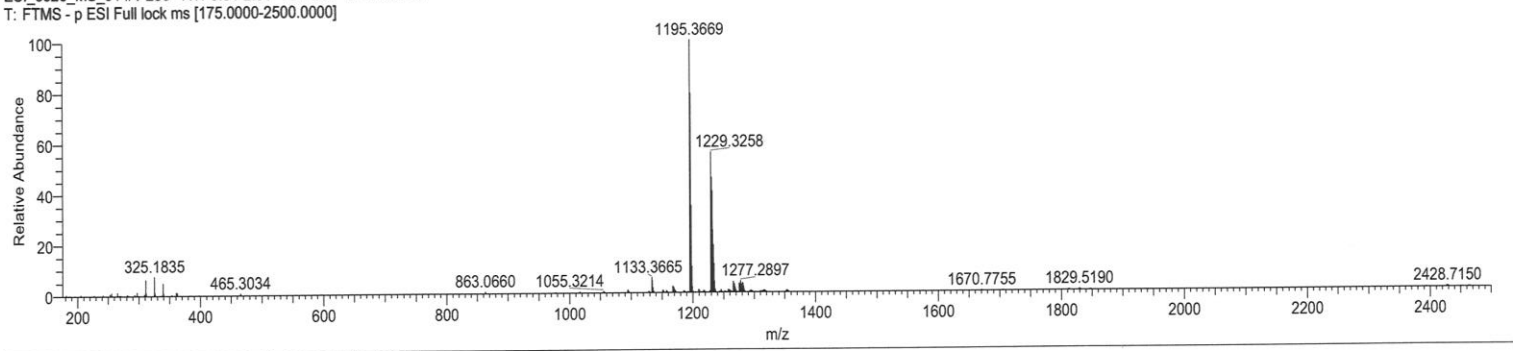
CRMPO
P. DAS 9 PJ Solvant : CH3COCH3
C:\Xcalibur\Data\ESI_6326_MS_01

Rapport d'analyse

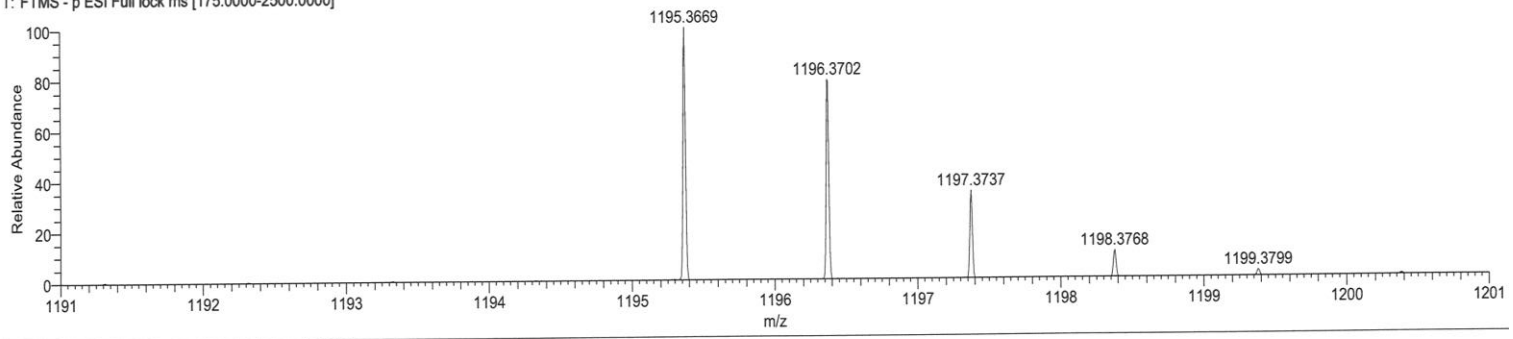
01/06/17 15:01:04

Thermo Fisher Scientific Q-Exactive

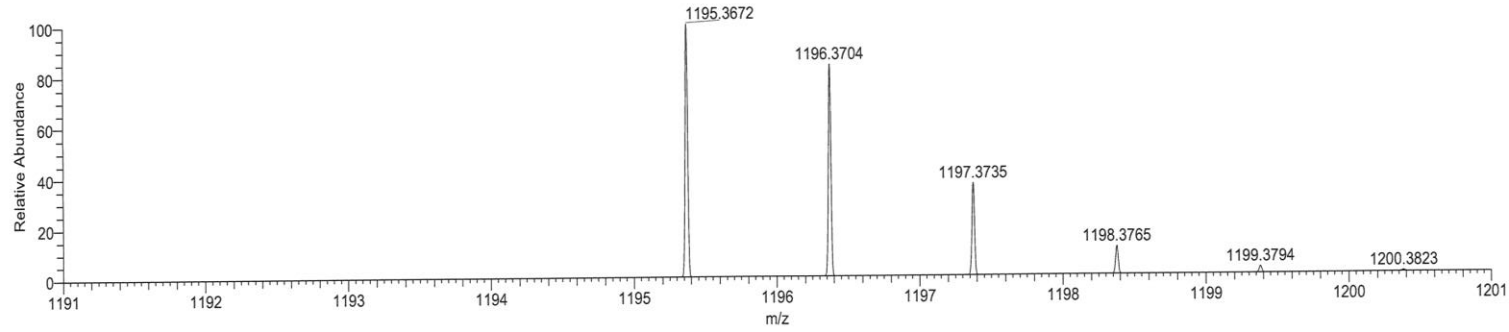
ESI_6326_MS_01 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.37E6
T: FTMS - p ESI Full lock ms [175.0000-2500.0000]

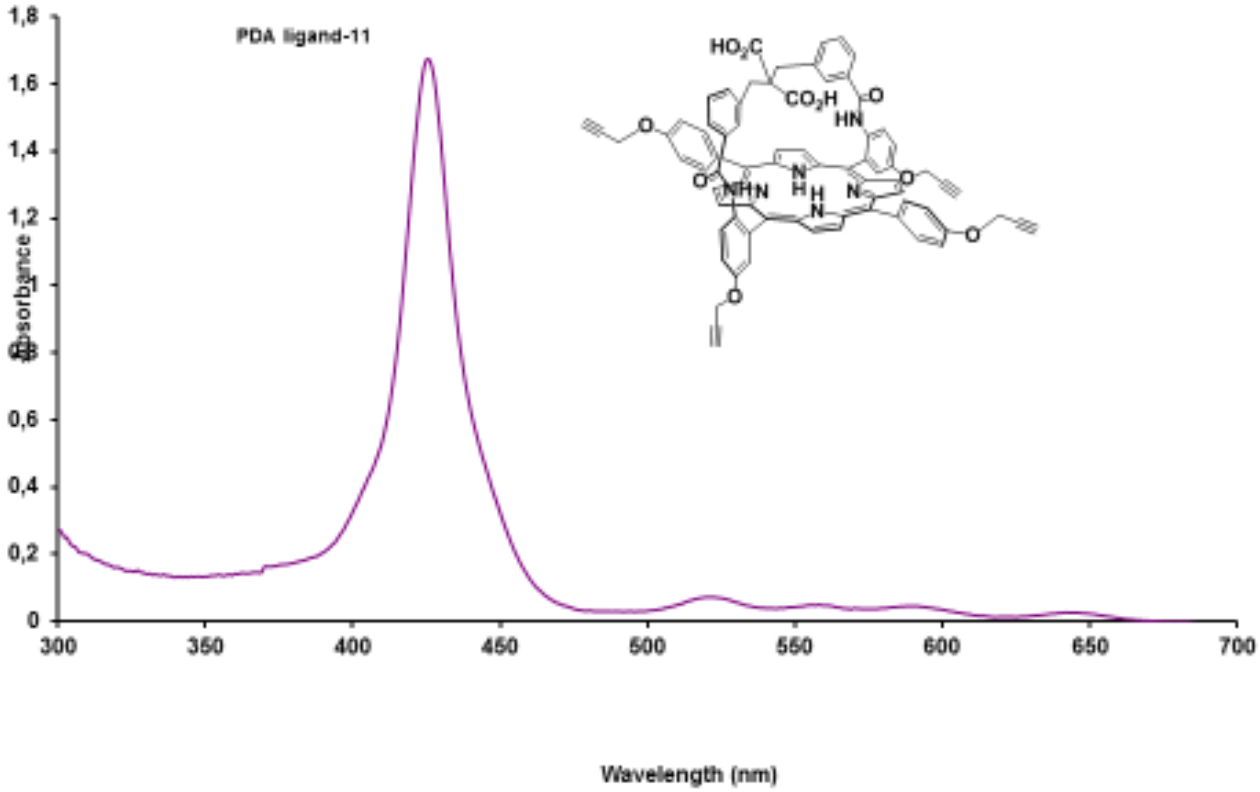


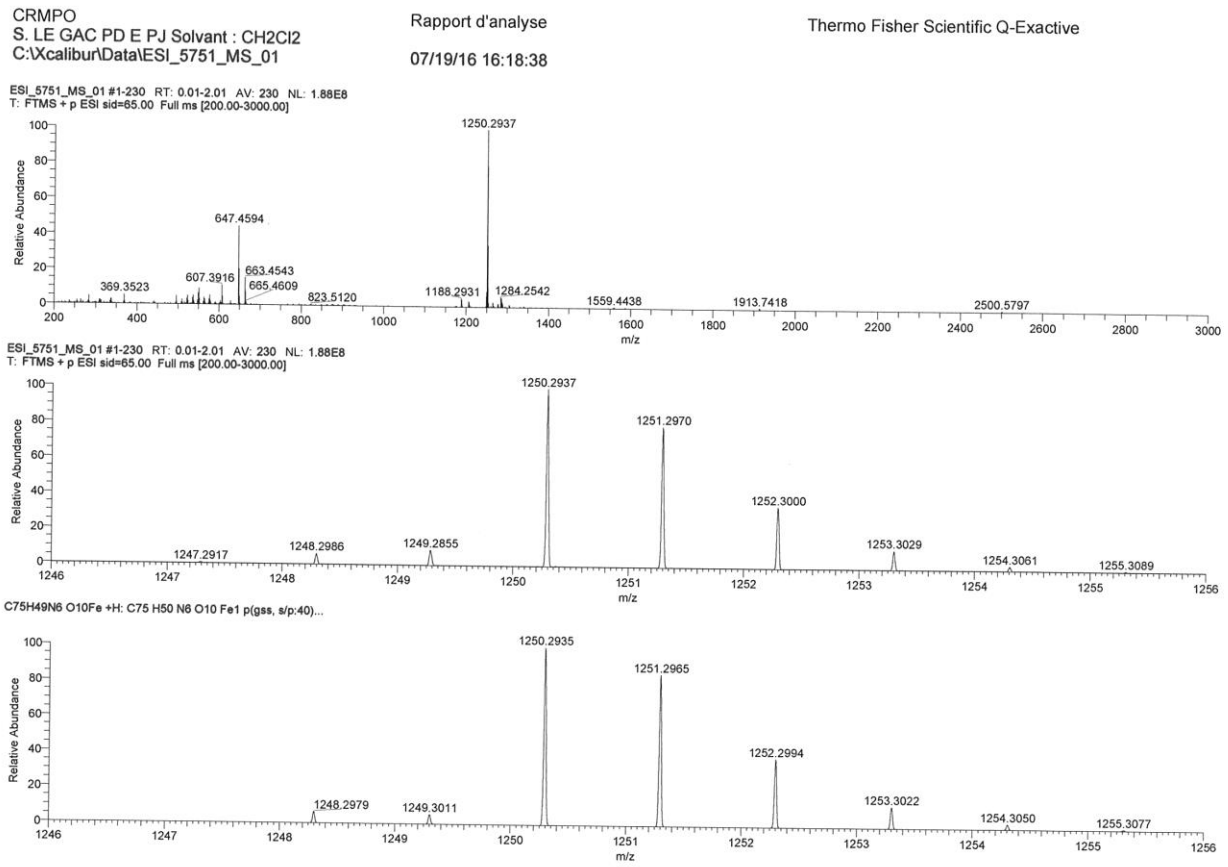
ESI_6326_MS_01 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.37E6
T: FTMS - p ESI Full lock ms [175.0000-2500.0000]

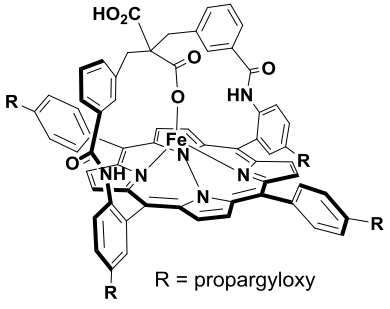


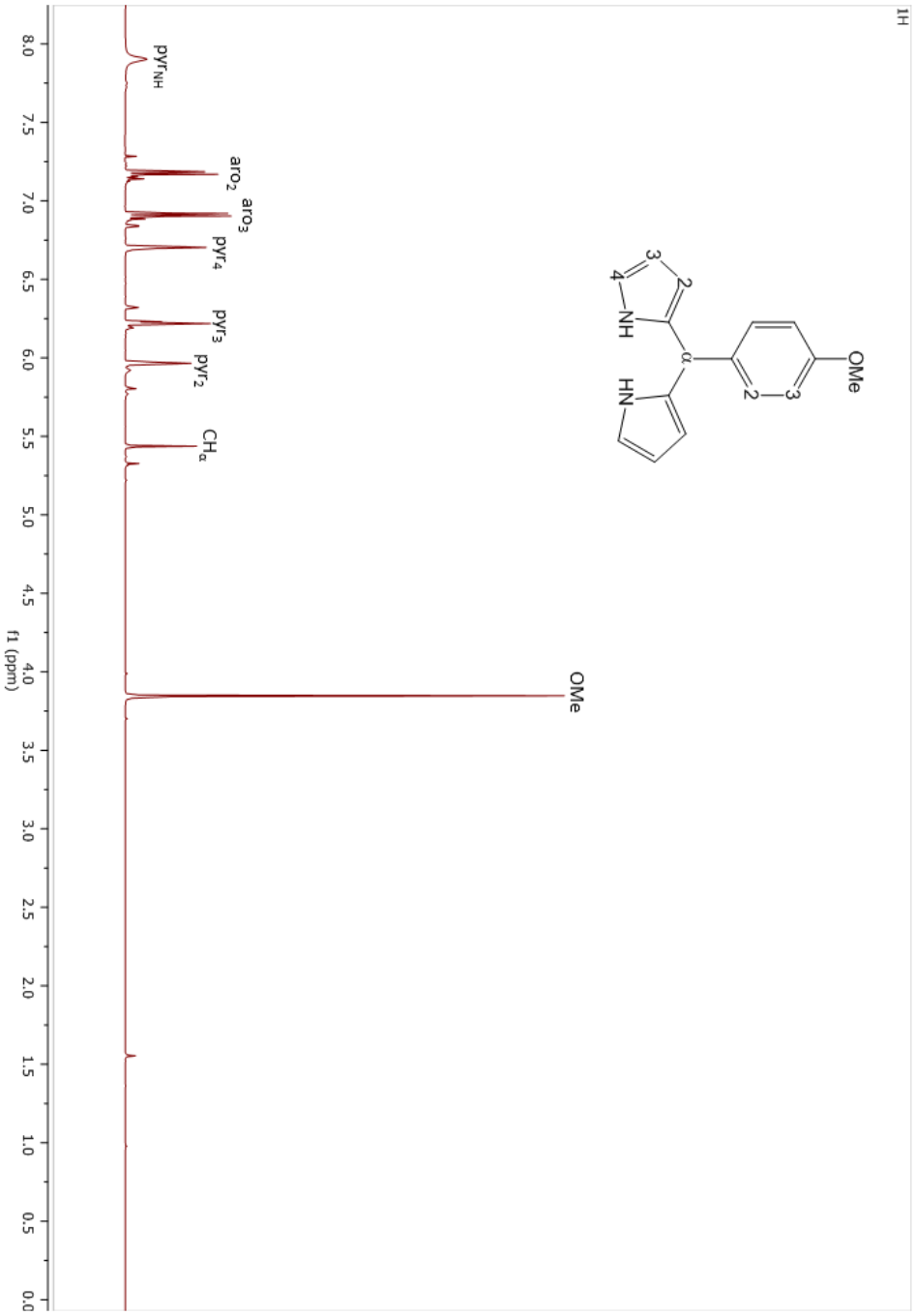
C75H52N6O10 +H: C75 H51 N6 O10 p(gss, s/p:40) Chrg -...

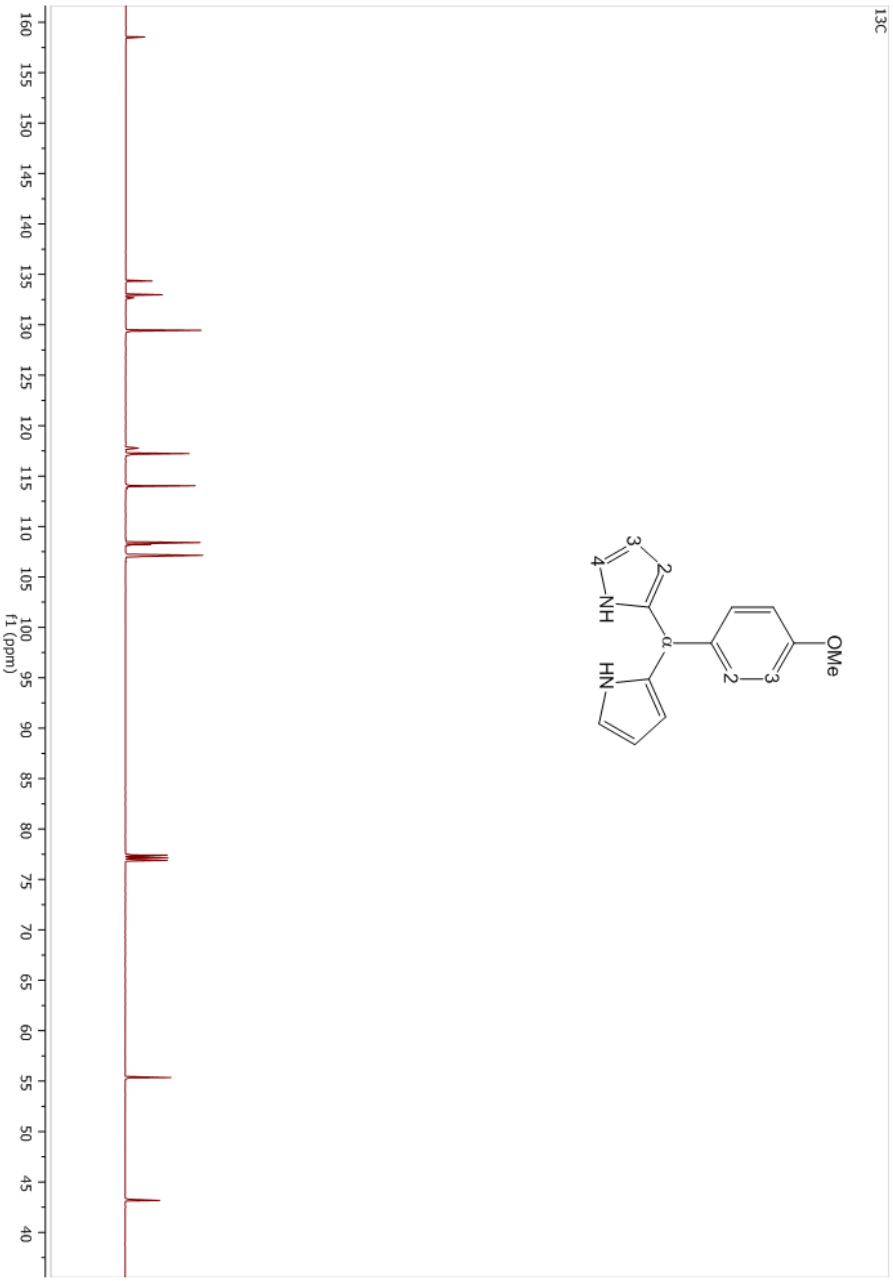



PDA ligand-11
Absorbance
Wavelength (nm)
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
300
350
400
450
500
550
600
650
700
HO2C
CO2H
HN
O
NH
N
H


CRMPO
S. LE GAC PD E PJ Solvant : CH2Cl2
C:\Xcalibur\Data\ESI_5751_MS_01
Rapport d'analyse
07/19/16 16:18:38
Thermo Fisher Scientific Q-Exactive
ESI_5751_MS_01 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.88E8
T: FTMS + p ESI sid=65.00 Full ms [200.00-3000.00]
Relative Abundance
m/z
1250.2937
647.4594
607.3916
663.4543
665.4609
369.3523
823.5120
1188.2931
1284.2542
1559.4438
1913.7418
2500.5797
ESI_5751_MS_01 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.88E8
T: FTMS + p ESI sid=65.00 Full ms [200.00-3000.00]
1250.2937
1251.2970
1252.3000
1247.2917
1248.2986
1249.2855
1253.3029
1254.3061
1255.3089
C75H49N6 O10Fe +H: C75 H50 N6 O10 Fe1 p(gss, s/p:40)...
1250.2935
1251.2965
1252.2994
1248.2979
1249.3011
1253.3022
1254.3050
1255.3077


HO2C
O
O
HN
O
O
R
Fe
N
NH
N
N
N
R
R
R
R = propargyloxy

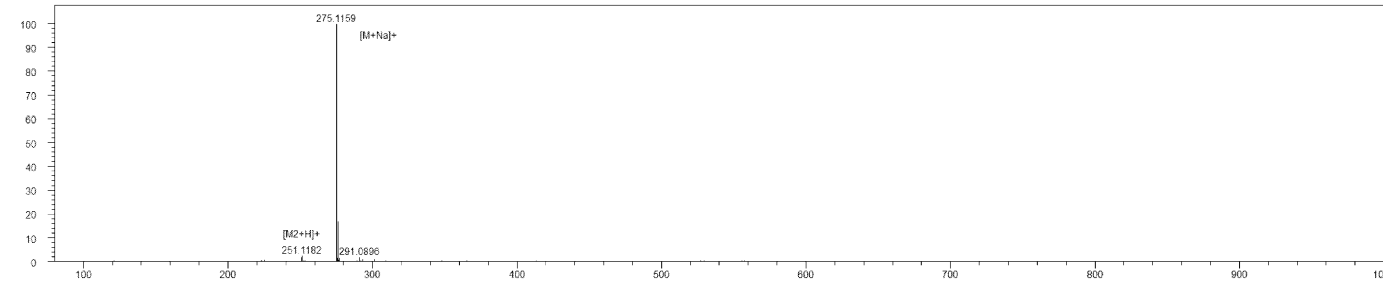

1H
pyrNH
aro2
aro3
pyr4
pyr3
pyr2
CHα
OMe
OMe
NH
HN
α
f1 (ppm)


13C
OMe
NH
HN
α
f1 (ppm)

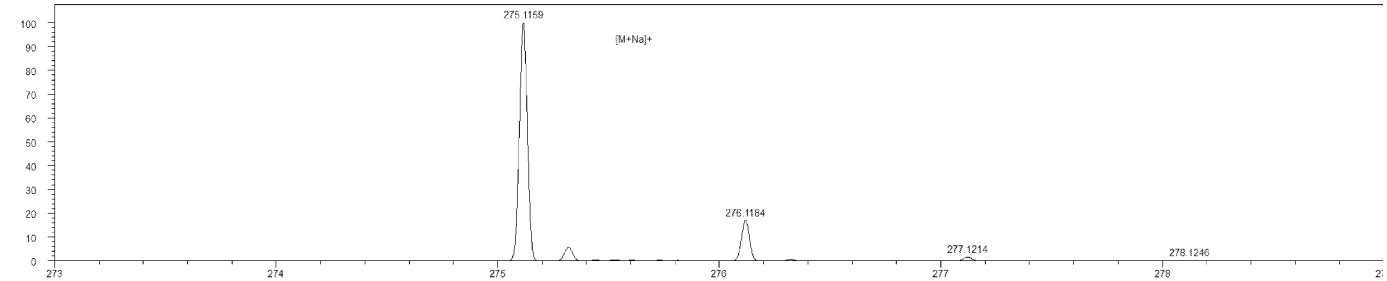
Rapport d'analyse de l'échantillon 18

Spectre et traitement réalisés au Centre régional de mesures physiques de l'Ouest - Université de Rennes 1

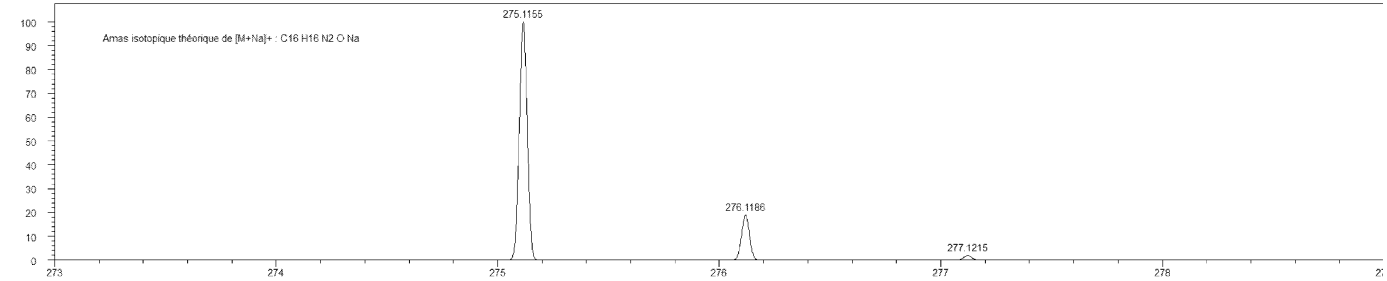
Instrument : Agilent 6510 Fichier : ESI_6979_MS_01.d Date/Heure : 2017-06-02 / 12:56:17 Scans : (1 : 119) de m/z 80 à 1000 Lockmass : 455
Description : P. DAS 18 TD Solvant : CH3OH

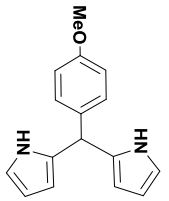


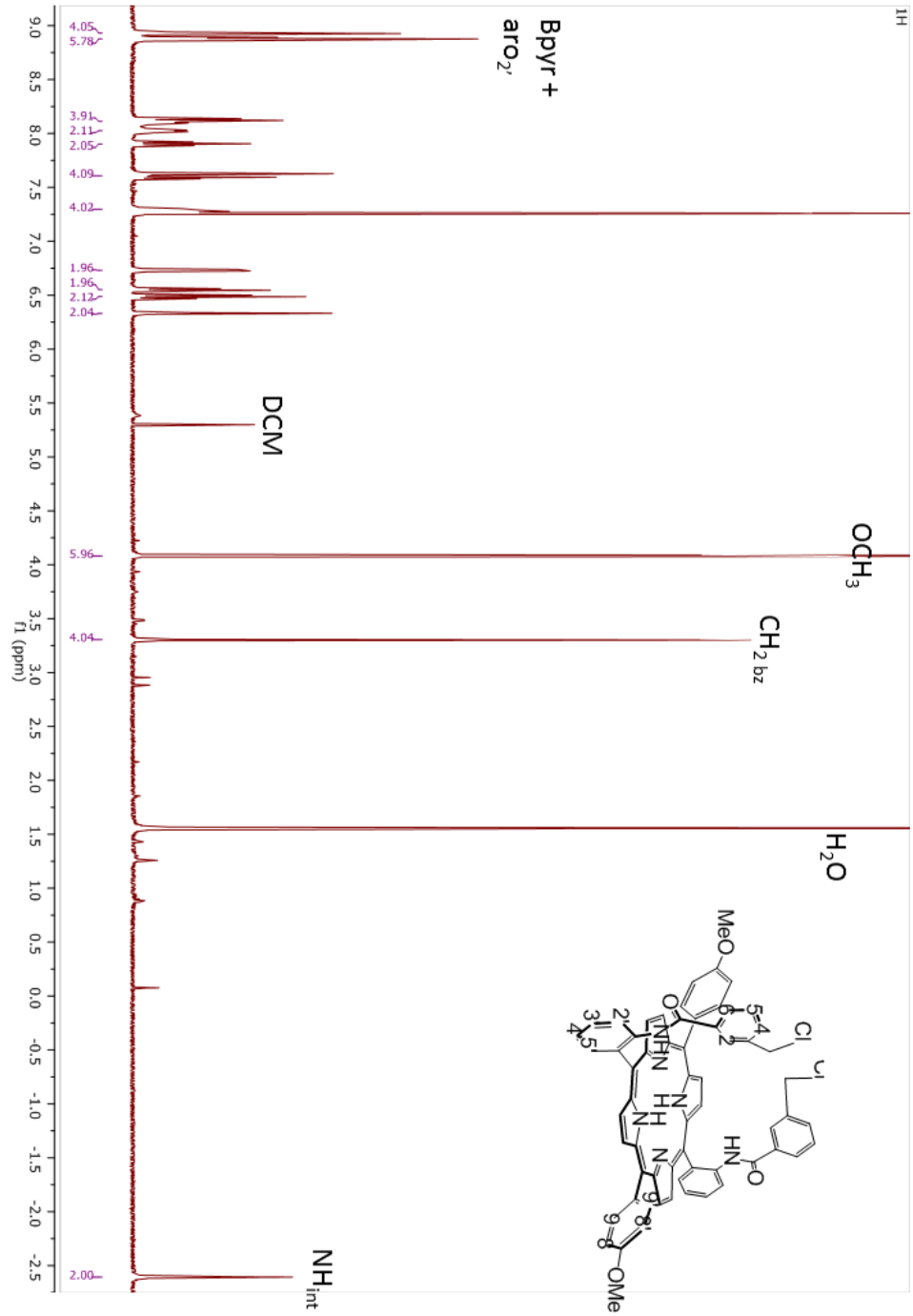
Instrument : Agilent 6510 Fichier : ESI_6979_MS_01.d Date/Heure : 2017-06-02 / 12:56:17 Scans : (1 : 119) de m/z 273 à 279 Lockmass : 455
Description : P. DAS 18 TD Solvant : CH3OH

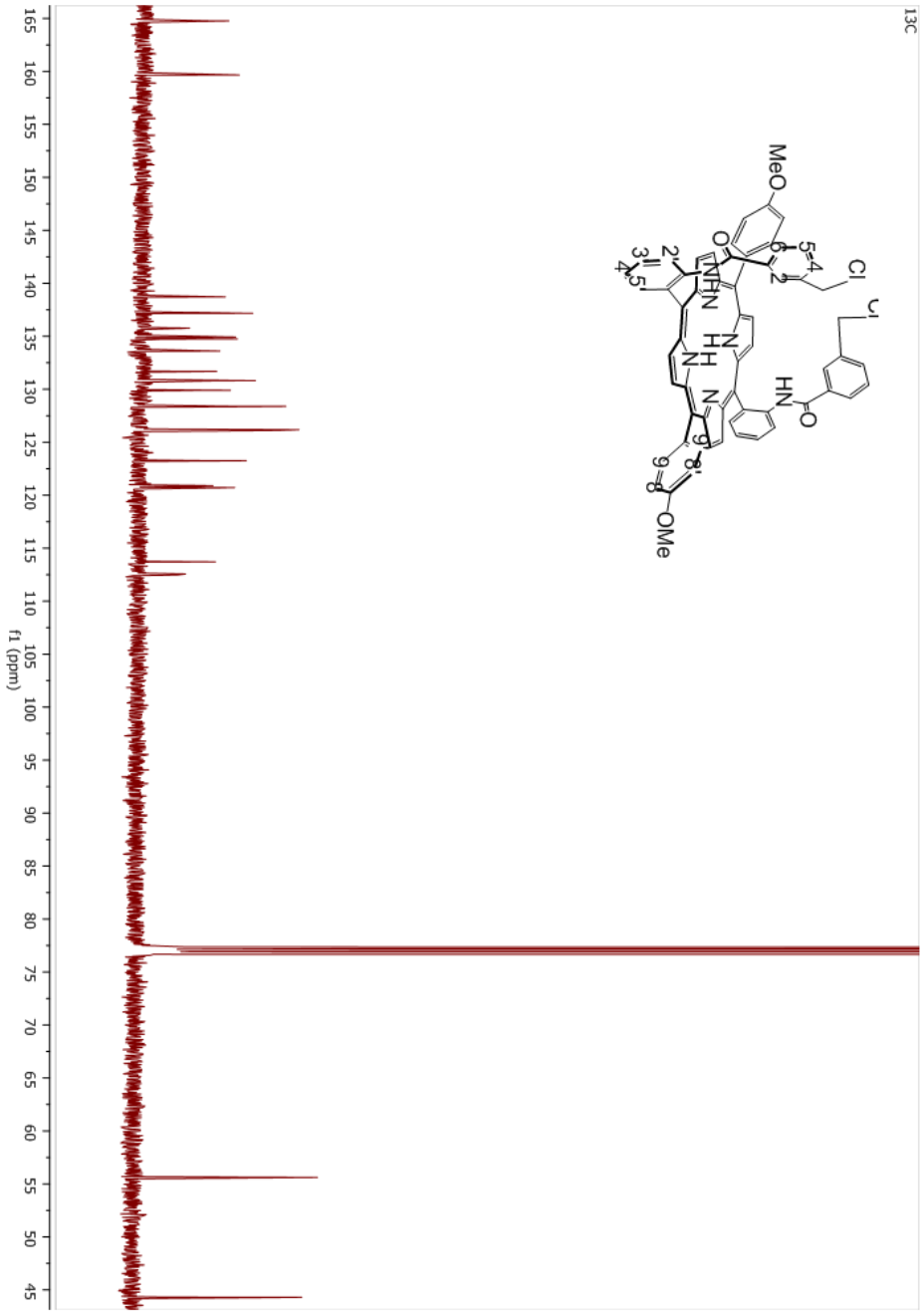


Séparation : 10 Seuil : 0.01 mmu Charge : 1 Résolution : 7000
Formule brute : C16 H16 N2 O Na





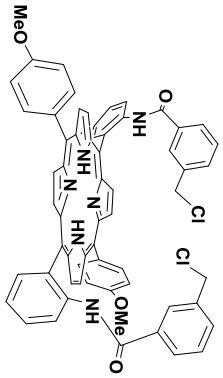

1H
Bpyr +
aro2'
DCM
OCH3
CH2 bz
H2O
NHint
MeO
Cl
HN
OMe
f1 (ppm)


13C
MeO
Cl
Cl
HN
O
OMe
f1 (ppm)

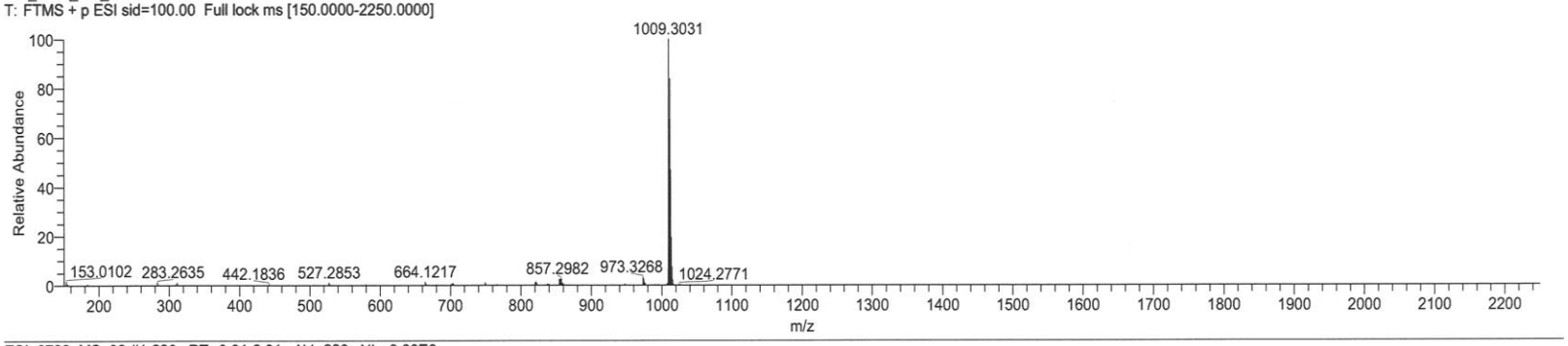
CRMPO Rapport d'analyse Thermo Fisher Scientific Q-Exactive

P. DAS 21 PJ Solvant : CH2Cl2 (+ 0.1% acide formique)

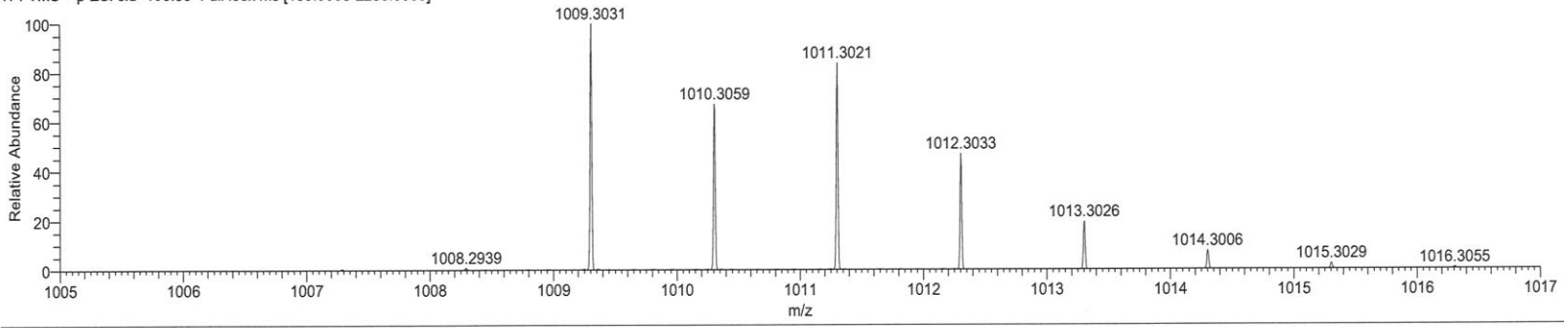
C:\Xcalibur\Data\ESI_6762_MS_02 04/13/17 10:17:41



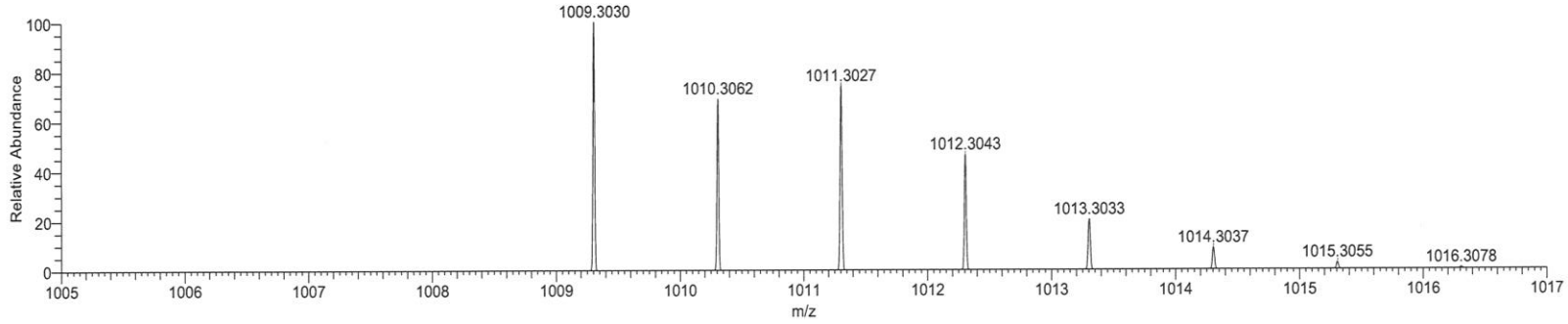
ESI_6762_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 3.60E6
T: FTMS + p ESI sid=100.00 Full lock ms [150.0000-2250.0000]

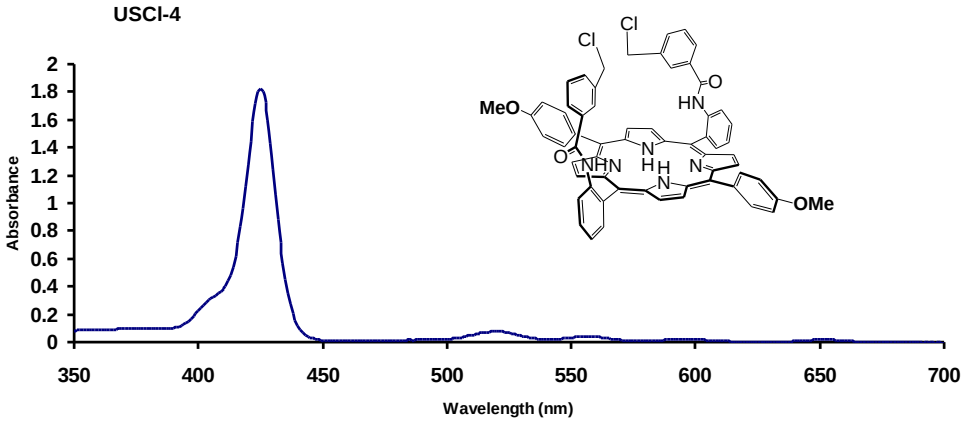


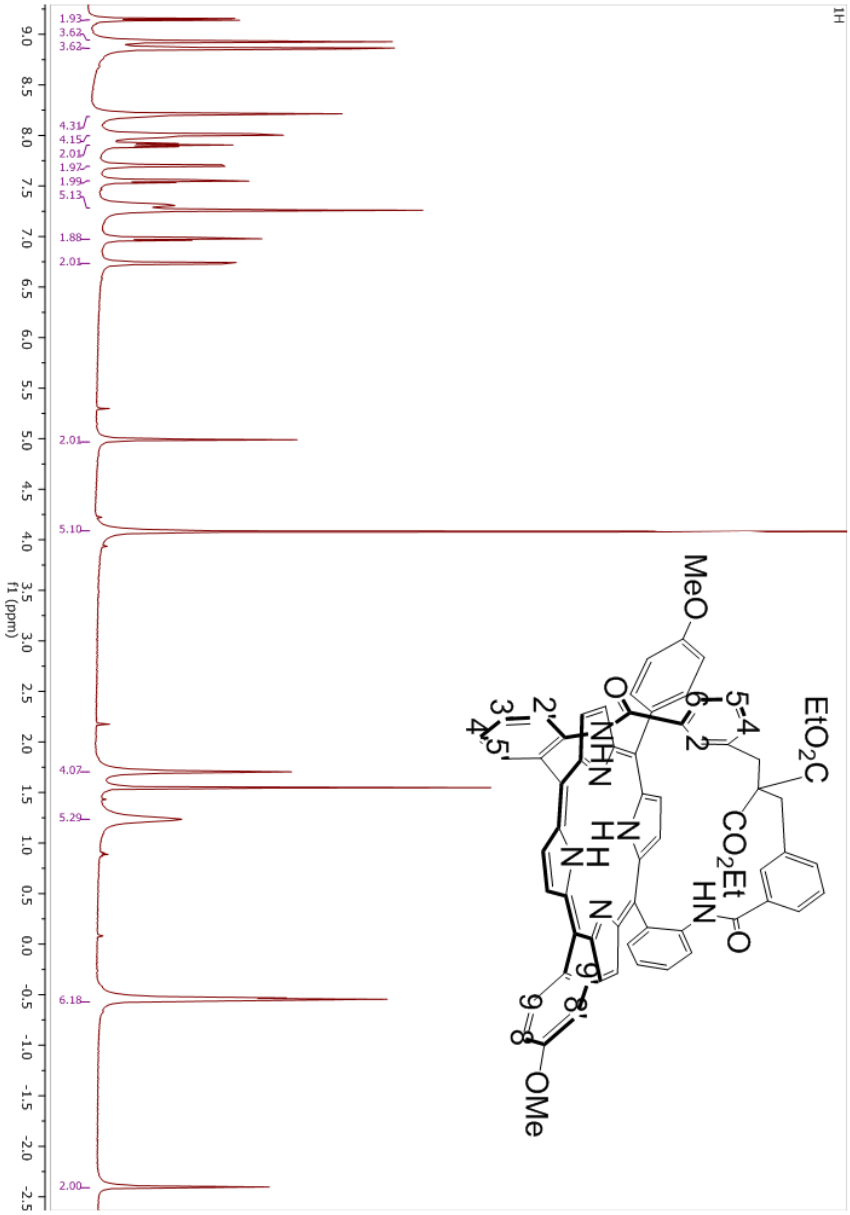
ESI_6762_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 3.60E6
T: FTMS + p ESI sid=100.00 Full lock ms [150.0000-2250.0000]

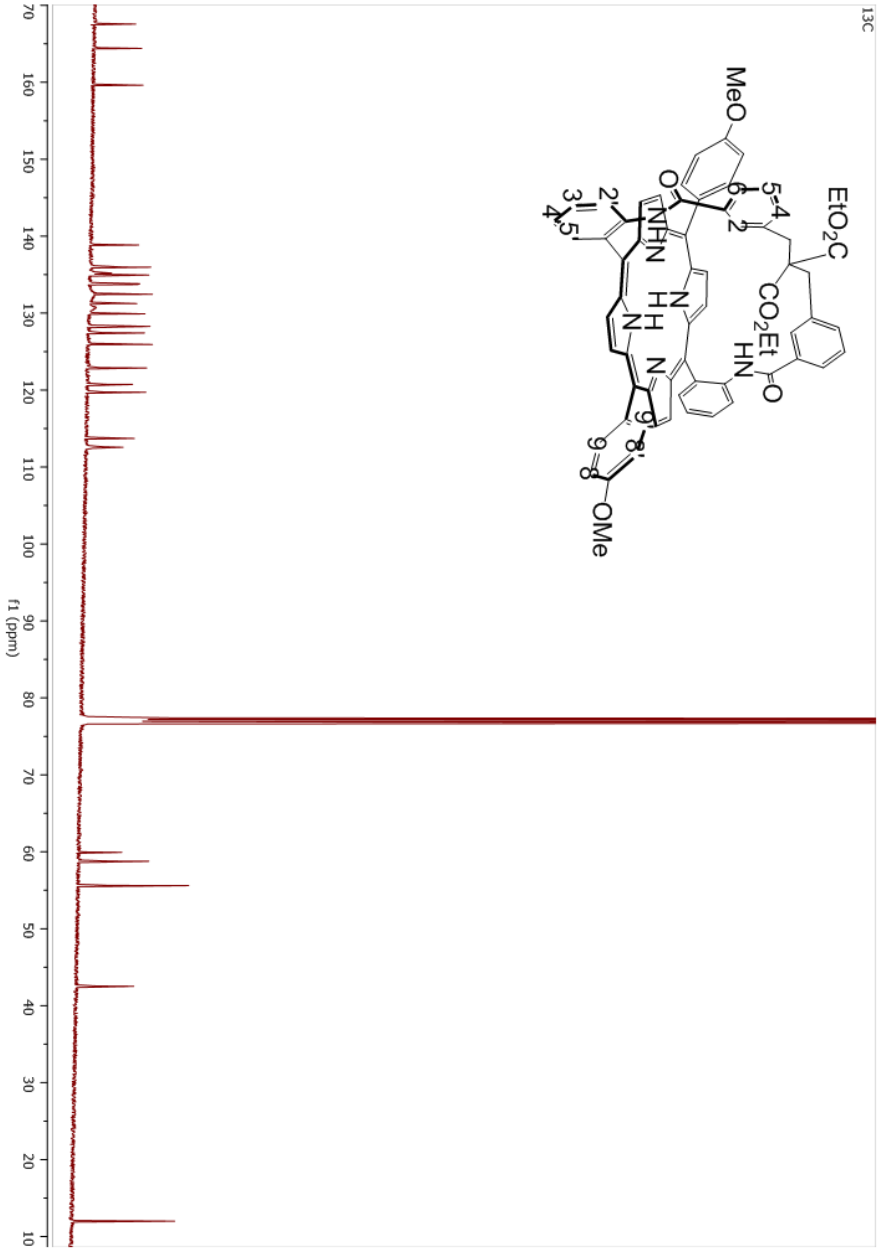


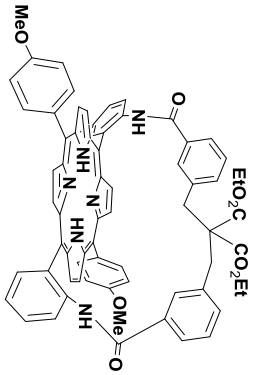
C62H46Cl2N6O4 +H: C62 H47 Cl2 N6 O4 p(gss, s/p:40) C...




USCl-4
Absorbance
Wavelength (nm)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
350
400
450
500
550
600
650
700
Cl
Cl
O
HN
MeO
O
NH
N
H
N
H
N
N
OMe


1H
1.93
3.62
3.62
4.31
4.15
2.01
1.97
1.99
5.13
1.88
2.01
2.01
5.10
4.07
5.29
6.18
2.00
f1 (ppm)
MeO
O
NH
N
H
N
N
H
N
2'
3'
4'
5'
6
2
5
4
EtO2C
CO2Et
HN
O
9'
8'
9
8
OMe


13C
MeO
EtO2C
CO2Et
HN
O
NH
N
H
N
OMe
f1 (ppm)

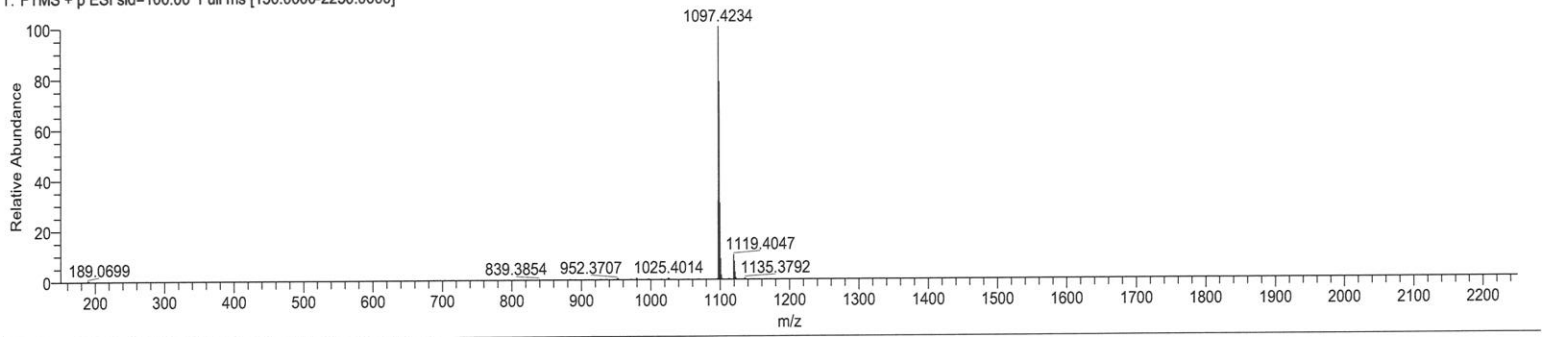


CRMPO
P. DAS 22 PJ Solvant : CH2Cl2/CH3OH (95/5)
C:\Xcalibur\Data\ESI_6763_MS_02

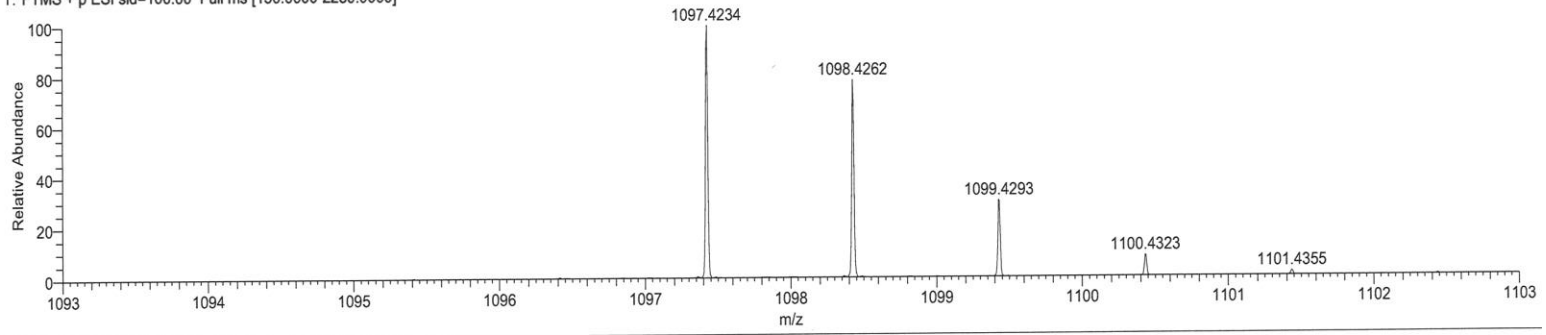
Rapport d'analyse
04/12/17 12:41:49

Thermo Fisher Scientific Q-Exactive

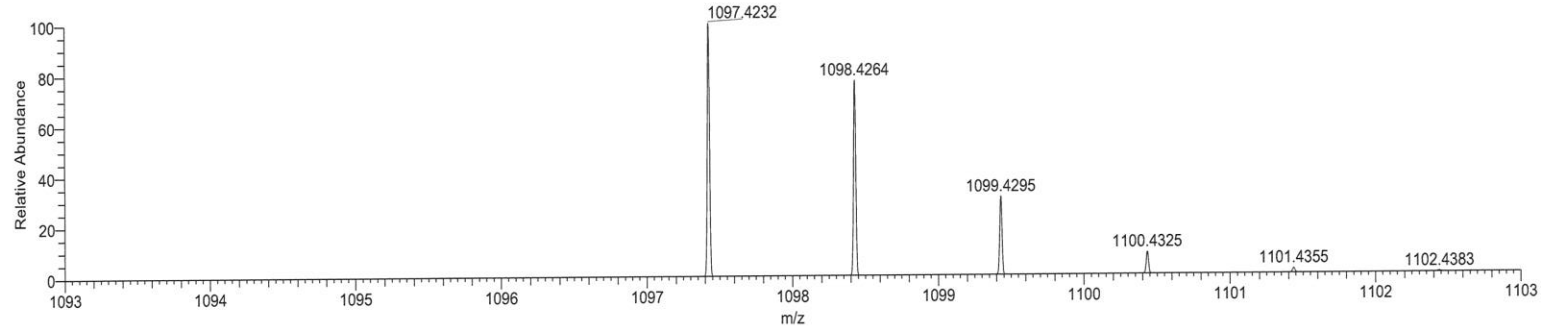
ESI_6763_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.91E7
T: FTMS + p ESI sid=100.00 Full ms [150.0000-2250.0000]

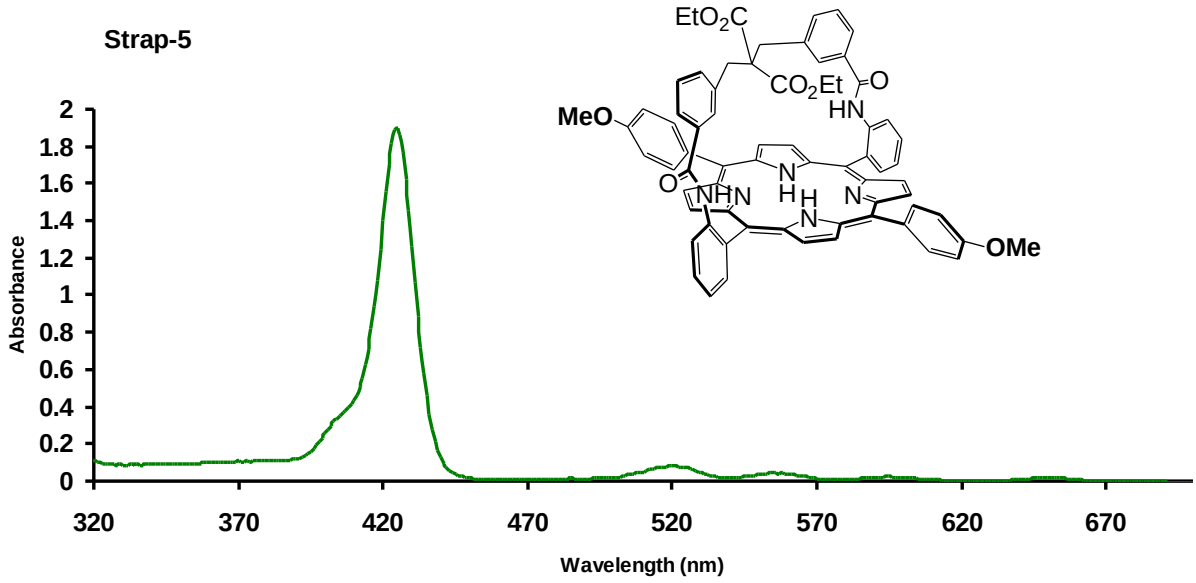


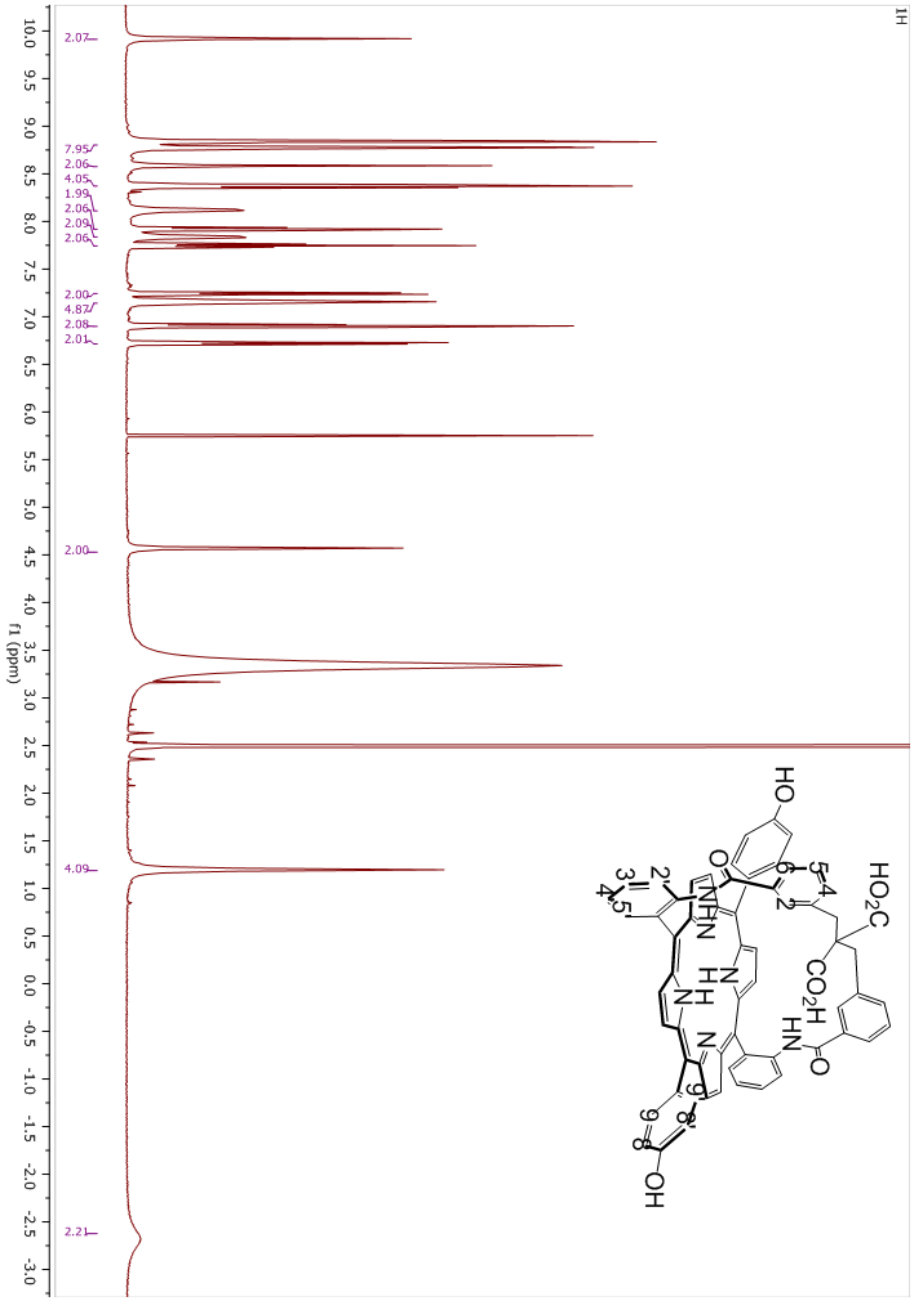
ESI_6763_MS_02 #1-230 RT: 0.01-2.01 AV: 230 NL: 1.91E7
T: FTMS + p ESI sid=100.00 Full ms [150.0000-2250.0000]

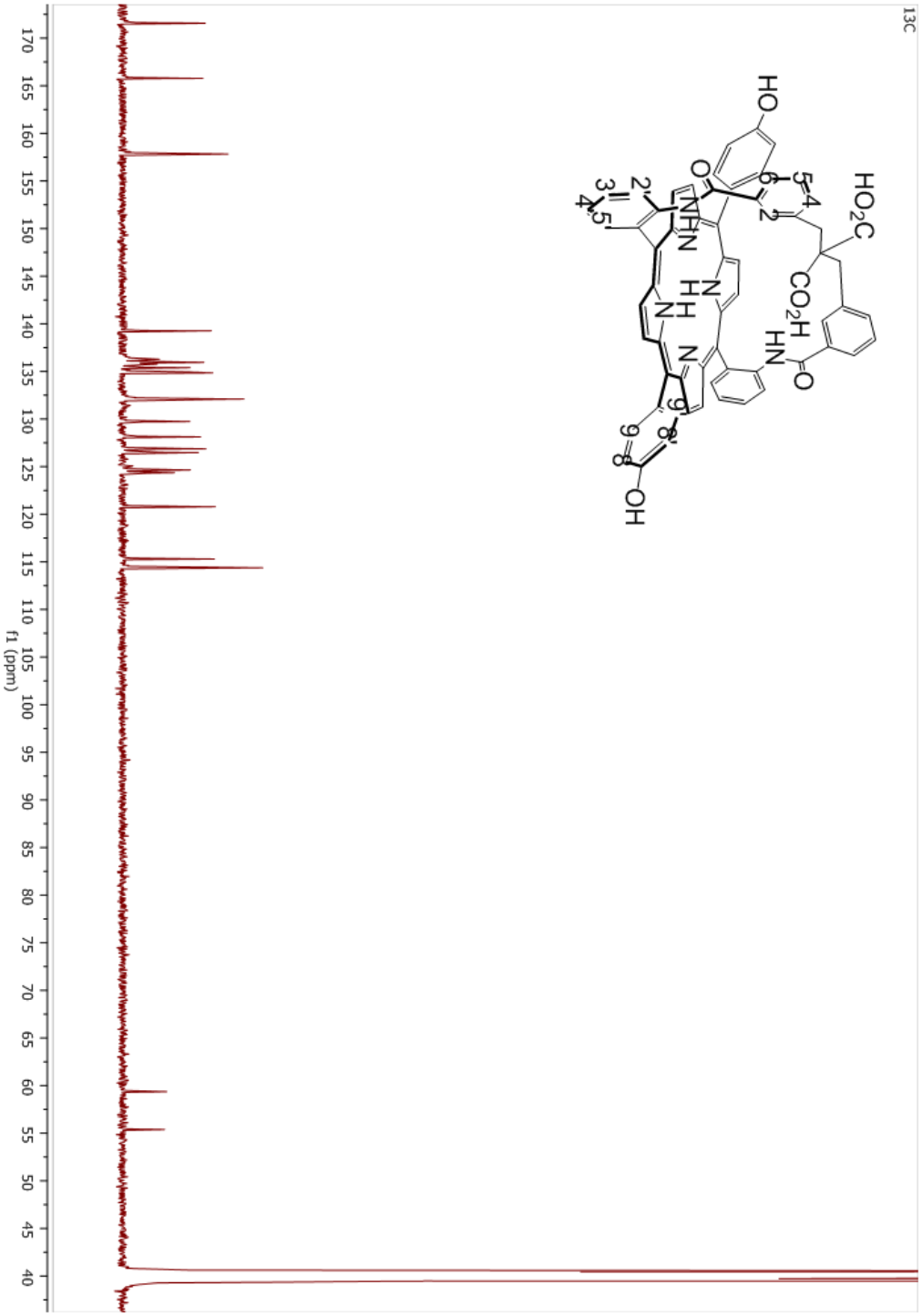


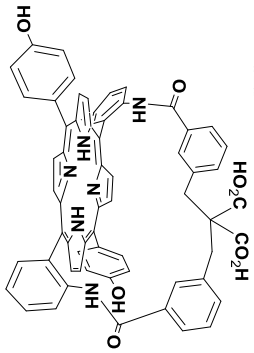
C69H56N6O8 +H: C69 H57 N6 O8 p(gss, s/p:40) Chrg 1...




Strap-5
Absorbance
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
320
370
420
470
520
570
620
670
Wavelength (nm)
EtO2C
CO2Et
O
HN
MeO
O
NH
N
N
H
H
N
N
OMe


1H
2.07
7.95
2.06
4.05
1.99
2.06
2.09
2.06
2.00
4.87
2.08
2.01
2.00
4.09
2.21
f1 (ppm)
HO
HO2C
CO2H
HN
O
NH
N
OH


13C
HO
HO2C
CO2H
HN
O
NH
N
HO
OH
f1 (ppm)

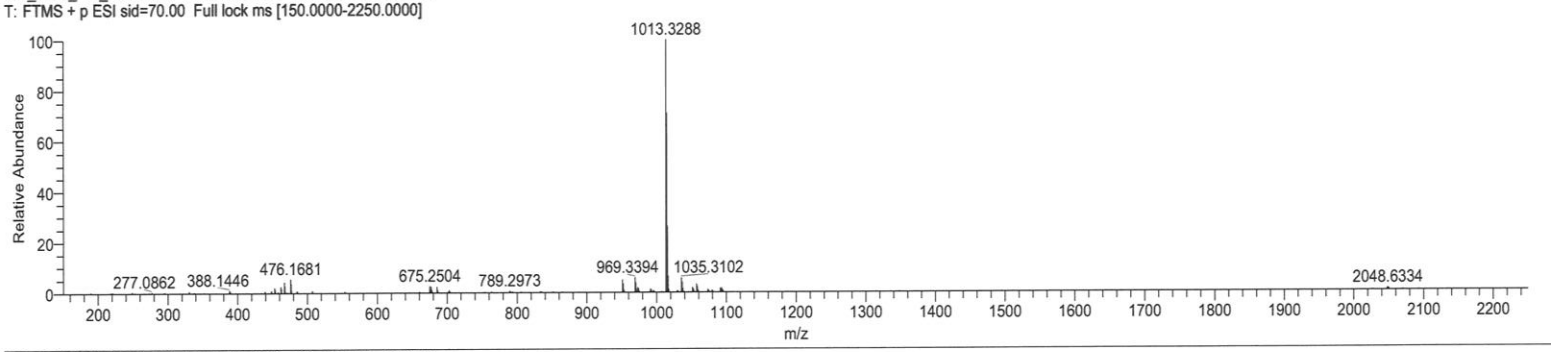


CRMPO
P. DAS 23 PJ Solvant : CH2Cl2/CH3COCH3 (95/5) (+ 0.1% acide formique)
C:\Xcalibur\Data\CRMPO\ESI_6980_MS_03

Rapport d'analyse
06/07/17 18:51:28

Thermo Fisher Scientific Q-Exactive

ESI_6980_MS_03 #1-230 RT: 0.01-2.01 AV: 230 NL: 5.69E8
T: FTMS + p ESI sid=70.00 Full lock ms [150.0000-2250.0000]



ESI_6980_MS_03 #1-230 RT: 0.01-2.01 AV: 230 NL: 5.69E8
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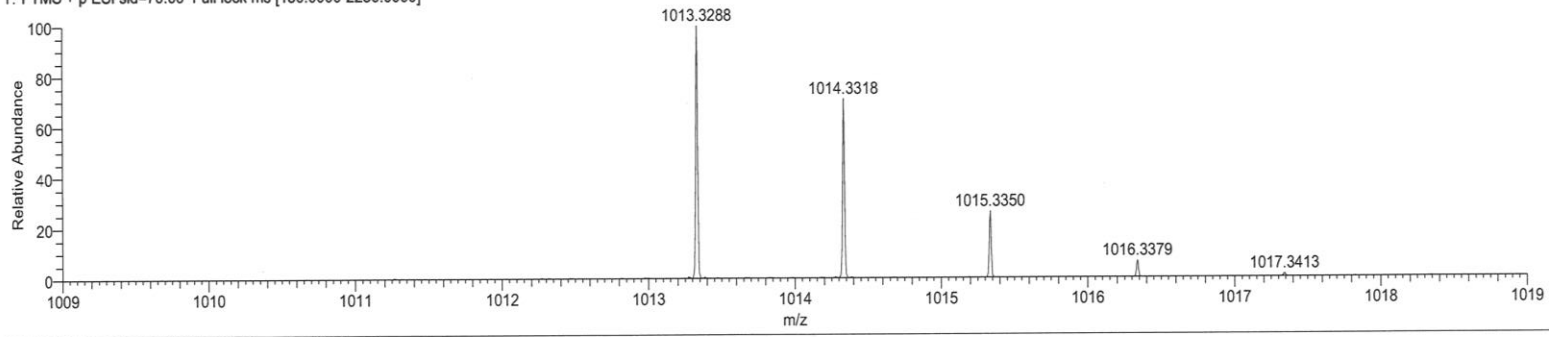
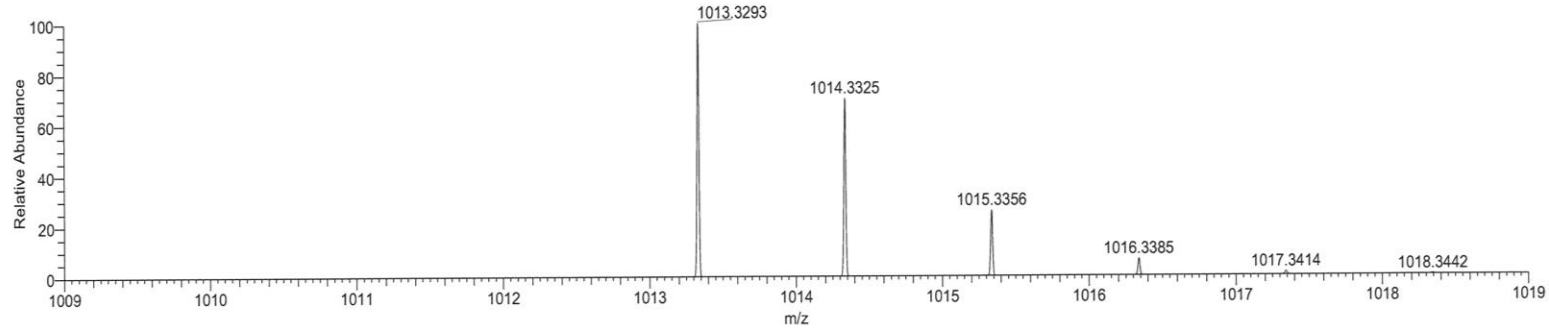
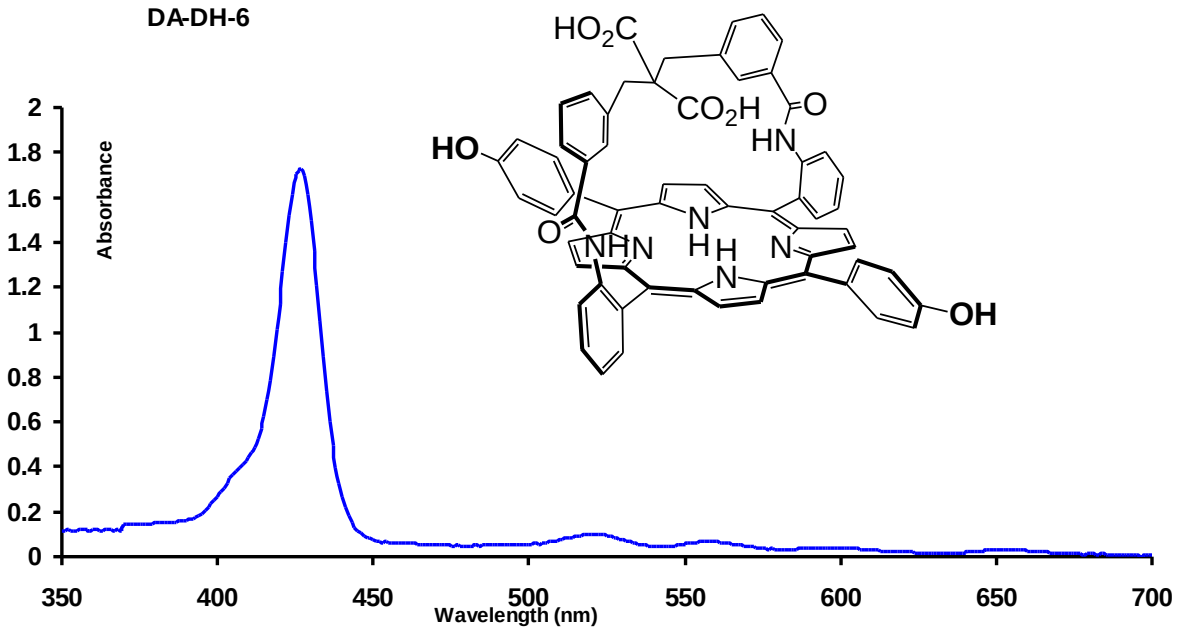


C63H44N6O8 +H: C63 H45 N6 O8 p(gss, s/p:40) Chrg 1...




DA-DH-6
Absorbance
Wavelength (nm)
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1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
350
400
450
500
550
600
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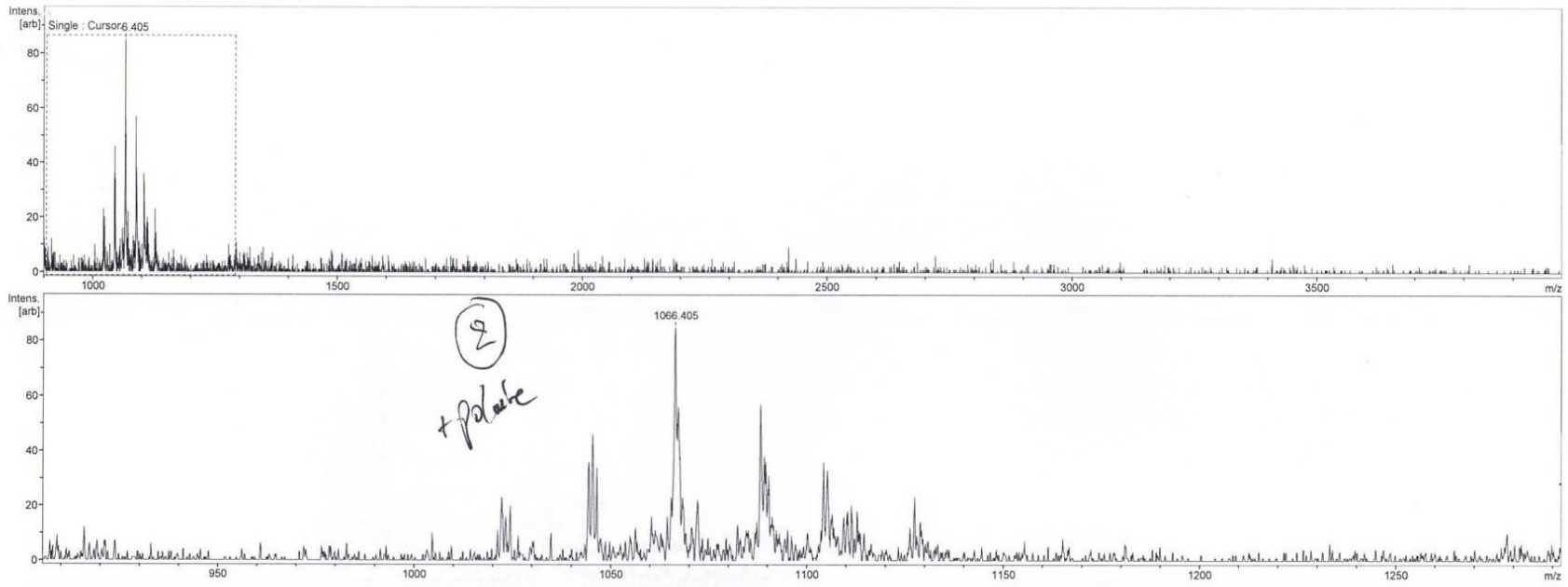
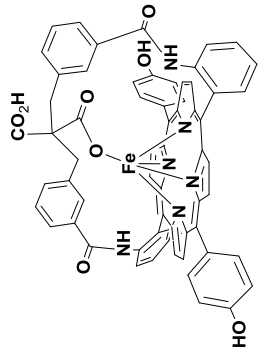
HN
HO
O
NH
HN
N
H
H
N
N
OH



Bruker Daltonics flexControl

Display Screenshot - Generated On 2015-04-01 17h17m20s



Electrochemical experiments.

Sample preparation.

3mg of each mixture (**MWNT-FeP(9)**, **MWNT-FeP(10)** or **MWNT-FeP(11)**) were dispersed in 750 µl of ethanol and 75 µl of Nafion solution (5% in alcohol). The mixtures were homogenized using a sonic bath until they formed homogenous inks. For the **MWNT** ink, the same procedure was followed but without adding porphyrins. For the reference **FeP(9)** inks, 3 mg of porphyrins were directly dispersed in 750 µl of ethanol and 75 µl of Nafion solution (5% in alcohol)

Electrode preparation. Before each measurement, the glassy carbon (GC) disk (5 mm, 0.196 cm^2) used as rotating electrode was polished with aqueous dispersions of synthetic diamonds (1 µm), then rinsed and sonicated with water. 5 µl of the catalyst inks were deposited by drop-casting onto the GC disk, then dried in air. For pH 6, a new ink was deposited onto the GC disk for each rotation step.

Electrochemical measurements. The instrument used was a VSP bipotentiostat (Bio-Logic SAS). The electrochemical tests were carried out in pH 10, 8 and 6 (phosphate buffers) solution in a three electrode glass cell, thermostated at 25°C. A ‘‘CE to Ground’’ connection with a saturated KCl Ag/AgCl electrode as reference and a graphite plate as counter electrode was used. As working electrode, a Pine rotating ring disk electrode (RRDE) with catalyst-loaded GC disk (0.196 cm^2) and Pt ring (0.110 cm^2) was controlled by a speed control unit from Princeton Applied Research Model 636 Electrode Rotator. The voltammograms were recorded at 5 $mV.s^{-1}$ in stationary conditions (with various rotating rates: 0, 400, 800, 1200, 1600, and 2000 rpm) in O_2-saturated solutions. An average current was calculated from the forward and backward scans. All potentials reported in this paper refer to that of the Ag/AgCl electrode. H_2O_2 production was monitored in the RRDE configuration at 400 rpm with a CV at the GC disk (5 $mV.s^{-1}$). The collection coefficient of the RRDE (0.20) was

measured using the one-electron $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple, according to the manufacturer's instructions.

Figures.

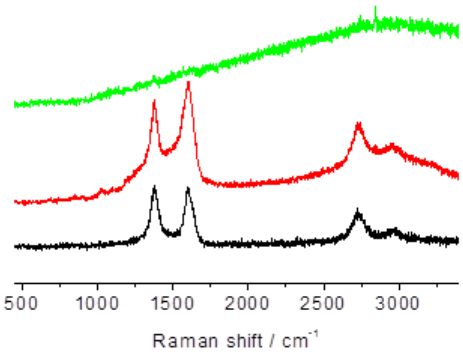


Fig. S1 Raman spectra recorded with excitation at 476 nm of **MWNT** (black), **MWNT-FeP(9)** (red) and porphyrin **9** (green).

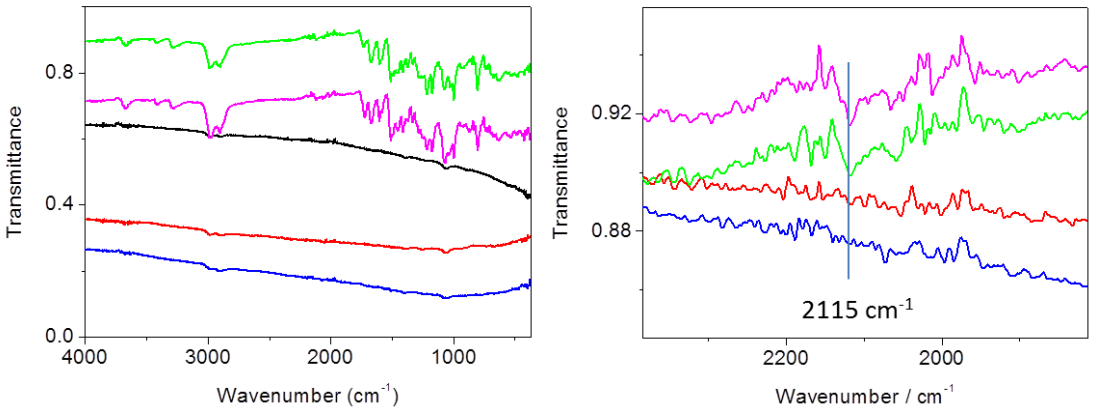


Fig. S2 Infrared spectra of **FeP(9)** (green), **FeP(10)** (pink), **MWNT** (black), **MWNT-FeP(9)** (red) and **MWNT-FeP(10)** (blue); on the left: full spectra and on right close-up of the 2100 cm^{-1} region. Very weak peaks at 2115 cm^{-1} corresponding to the C≡C stretching are discernable only in **FeP(9)** and **FeP(10)** and not in MWNT-porphyrin hybrids.

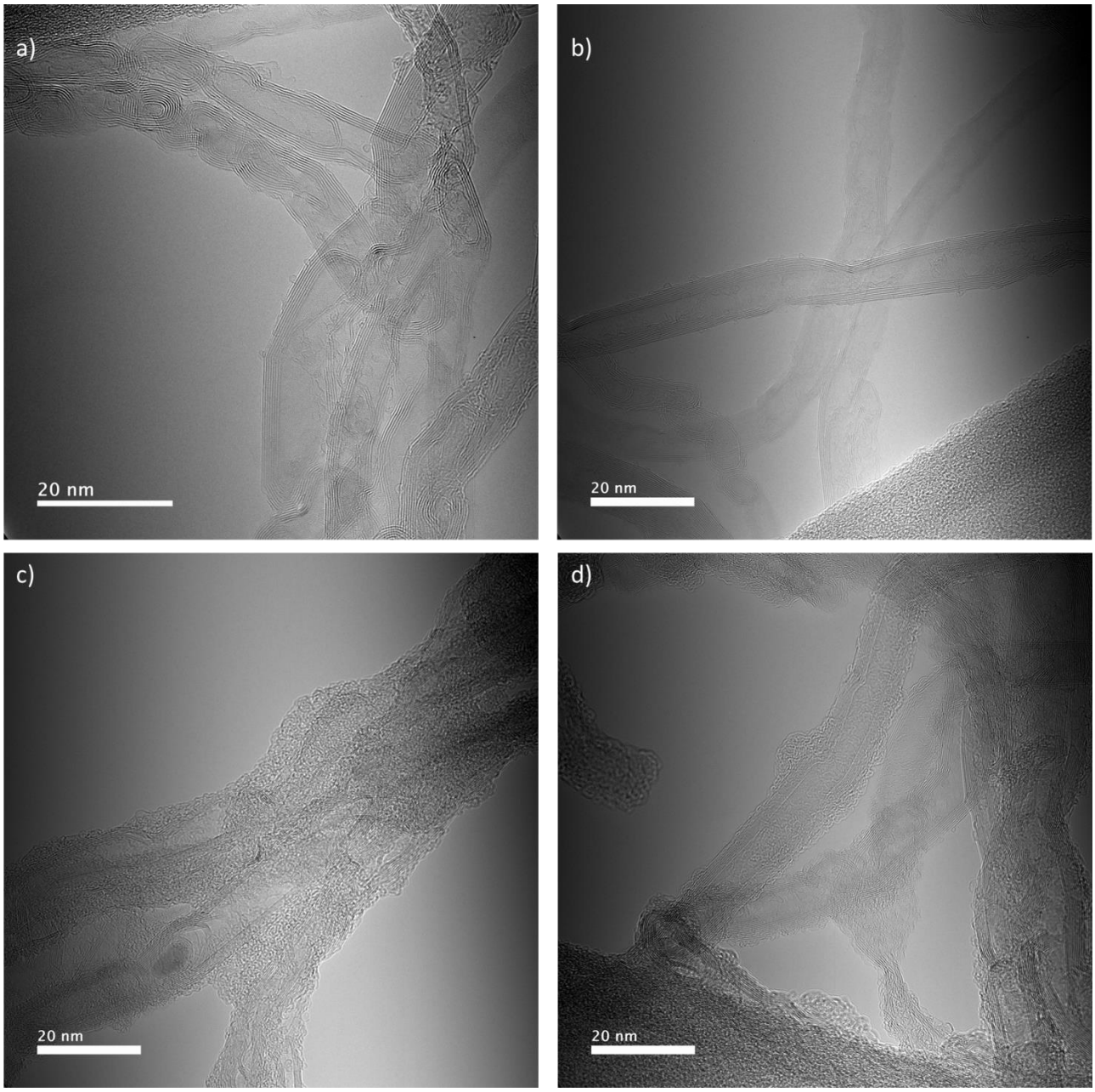


Fig. S3 TEM images of purified MWNT (a-b) and additional images for **MWNT-FeP (9)** (c-d)

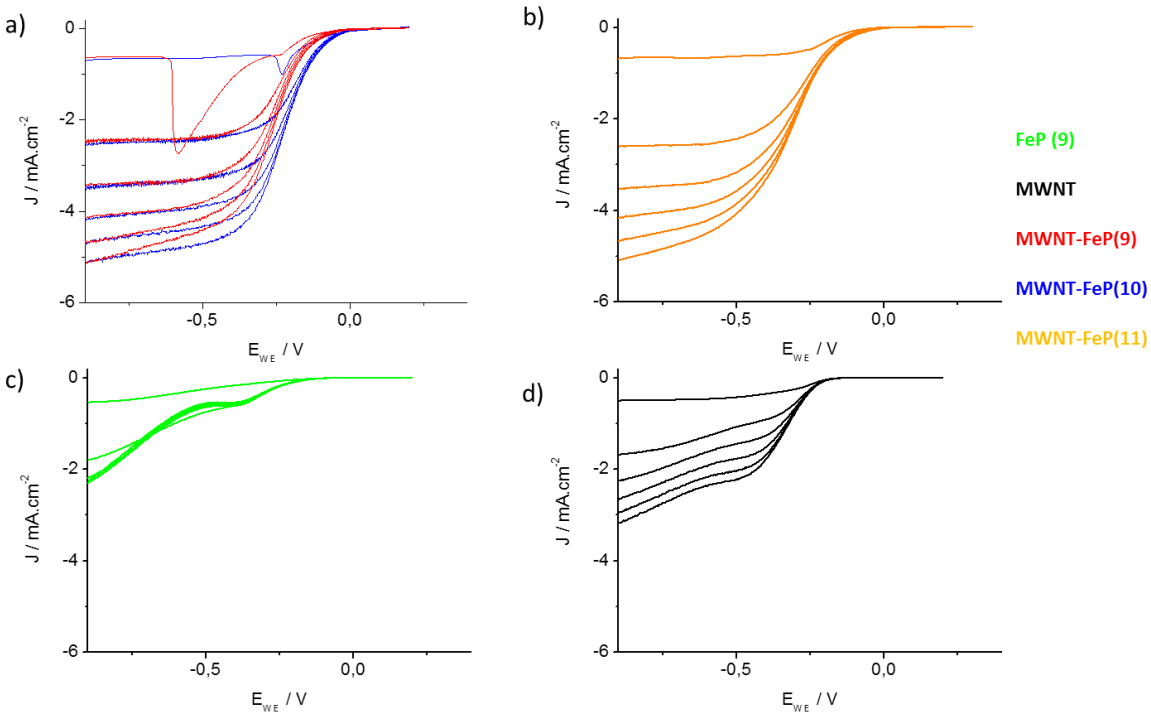


Fig. S4. Polarization curves at different rotation rates (0, 400, 800, 1200, 1600 and 2000 rpm) recorded for ORR in O_2-saturated at pH 10 (phosphate buffer solution) (scan rate = 5 mV/s, room temperature) on GC with predeposited **FeP(9)** (green) (c) **MWNT-FeP(11)** (orange) (b) and **MWNT** (black) (d). (a) Comparison between, **MWNT-FeP(9)** (red) and **MWNT-FeP(10)** (blue)

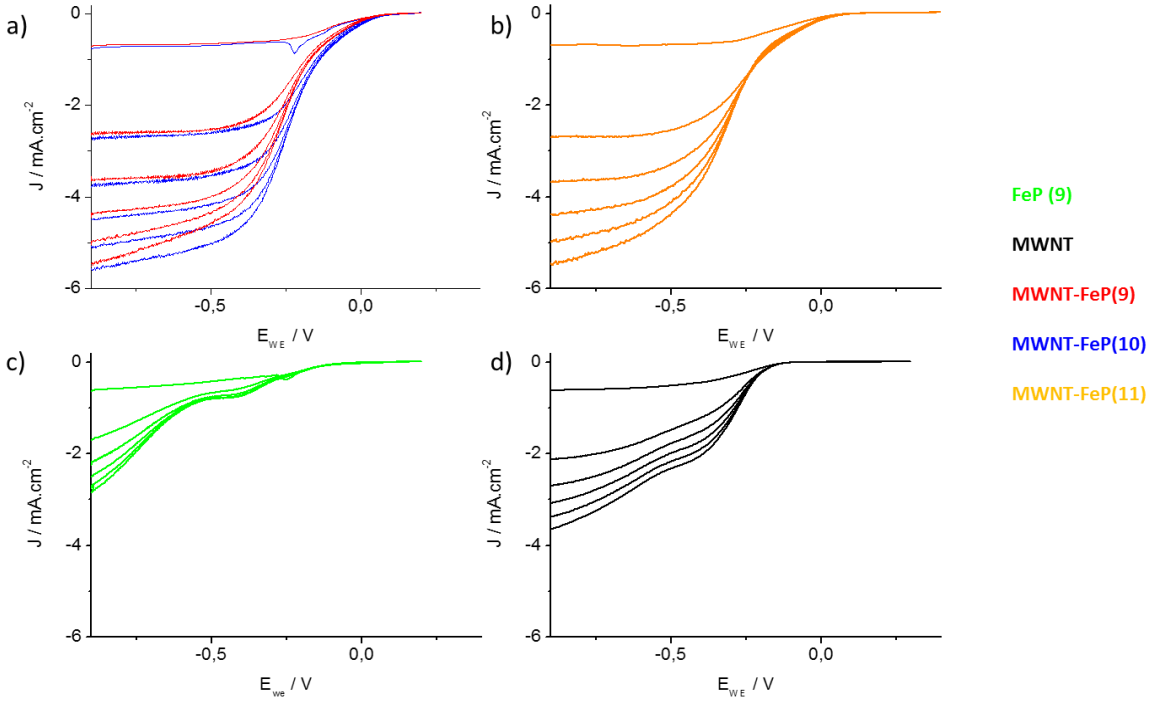


Fig. S5 Polarization curves at different rotation rates (0, 400, 800, 1200, 1600 and 2000 rpm) recorded for ORR in O_2-saturated at pH 8 (phosphate buffer solution) (scan rate = 5 mV/s, room temperature) on GC with predeposited **FeP(9)** (green) (c) **MWNT-FeP(11)** (orange) (b) and **MWNT** (black) (d). (a) Comparison between, **MWNT-FeP(9)** (red) and **MWNT-FeP(10)** (blue)

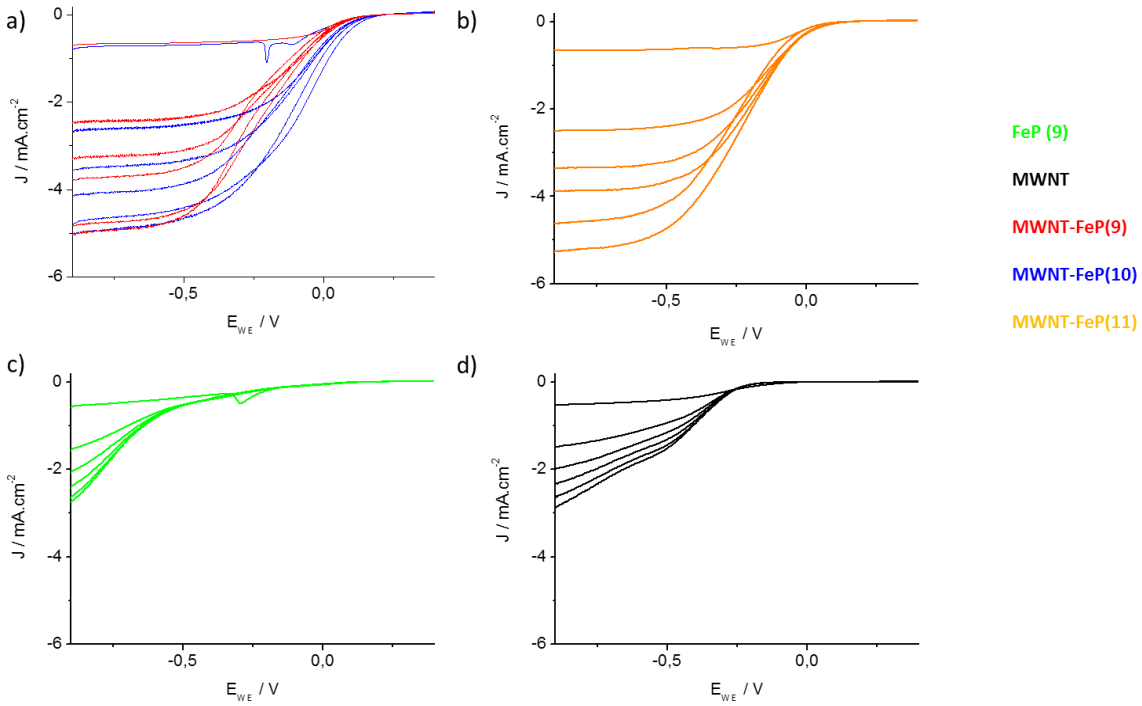


Fig. S6 Polarization curves at different rotation rates (0, 400, 800, 1200, 1600 and 2000 rpm) recorded for ORR in O_2-saturated at pH 6 (phosphate buffer solution) (scan rate = 5 mV/s, room temperature) on GC with predeposited **FeP(9)** (green) (c) **MWNT-FeP(11)** (orange) (b) and **MWNT** (black) (d). (a) Comparison between, **MWNT-FeP(9)** (red) and **MWNT-FeP(10)** (blue).

Reference List

1. I. Hijazi, T. Bourgeteau, R. Cornut, A. Morozan, A. Filoramo, J. Leroy, V. Derycke, B. Jousselme and S. Campidelli, *J. Am. Chem. Soc.*, 2014, **136**, 6348.