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A perfluorous polyphenyl dendritic shell for the protection of a photosensitizing porphyrazine core

Patricia Löser, Andreas Winzenburg and Rüdiger Faust*

Institute for Chemistry and CINSaT – Center for Interdisciplinary Nanostructure Science and Technology, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Supporting Information

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General

All chemicals were used as supplied unless otherwise stated. Those not commercially available were synthesised as documented; the solvents were distilled from the appropriate drying agents under inert gas (argon) immediately prior to use. Thin layer chromatography was carried out on prefabricated TLC-Plates (Silica 60 F_{254}, Merck). Column chromatography was performed using silica gel 60M, 0.04-0.063 mm/230-400 mesh (Macherey Nagel). Gel-permeation chromatography was accomplished with Bio-beads S-X1 (40-80 µm, Bio-RAD) pre-swollen in THF. Melting point determinations (uncorrected) were carried out on a Melting Point M-565 (Büchi) apparatus. The syntheses of compounds **3** and **7** were carried out with the DISCOVER SP microwave from CEM (control software: Synergy). Nuclear magnetic resonance spectra were recorded on Varian spectrometers operating at either 400 or 500 MHz (^{1}H) at room temperature. Either, residual peaks from the respective deuterated solvent or, in case of ^{19}F-NMR spectroscopy, the ^{19}F-signal from trifluoroacetic acid served as internal references. MALDI-mass spectra were taken with a Bi-Flex IV (Bruker Daltonics) machine using 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enyliden]malononitrile) as matrix. High resolution mass spectra were obtained with the time-of-flight-mass spectrometer micrOTOF (Bruker Daltonics) equipped with a Apollo^{TM} "Ion Funnel" ESI ion source. EI/GC-mass spectra were taken with a DSQ II (single quadrupol GC-mass spectrometer with prefilter and turbomolecular pump 250 L/*s*) from Thermo Scientific. To take APCI-mass spectra the quadrupol ion trap mass spectrometer "Finnigan LCQ^{DECA}" from ThermoQest was used. IR-spectra were recorded with a Bio-RAD FTS-40A spectrometer featuring an ATR attachment.

Optical measurements:

All solvents were purchased as analytically pure. UV/Vis-spectra were recorded with a Lambda 40 spectrometer (Perkin Elmer). For the determination of the porphyrazine's resistance to photooxidation the sample was irradiated at wavelengths between 300 nm and 800 nm through glass fibre bundles inside the spectrometer at right angle to the probing beam. For this purpose, a 50 W halogen lamb (Osram) was used as the external light source. The relative resistance to photooxidation was explored by monitoring the intensity of the porphyrazine's *Q*-band over the period of 2 hours.

Measurement of the $^{1}O_2$-luminescence and determination of the $^{1}O_2$-quantum yield:

Compounds **1** and **2** were irradiated wavelength-selective between 320 nm-800 nm with a Xe arc lamp (model A 5000 from PTI). The excitation light was directed via fibre optics through a tempered cuvette device having an integrated magnetic stirrer from OceanOptics (CUV-

QPOD). For detection the monochromator Cornerstone™ 260i 1/4m from Newport Physics with a blazed grating (600 lines/mm, 1250 nm), a cooled InGaAs semiconductor diode detector, a chopper system and an Oriel Merlin™ digital lock-in radiometry system from Newport Physics was utilized. To eliminate high-order fluorescence in the range of 1270 nm a filter (780 nm cut-on, range 800 nm-2700 nm) was used.

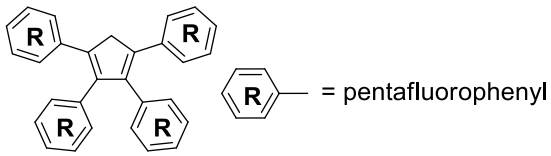
The $^1O_2$- quantum yields were determined in CCl_4 relative to ZnTPP.[1]

Cyclovoltammetric investigations:

The cyclovoltammetric measurements were carried out at room temperature in dichloromethane using 0.1 M tetrabutyl ammonium hexafluoro phosphate as a conducting salt and ferrocene as the internal reference. A platinum working- and counter electrode in combination with a Ag/AgCl reference electrode were used at a scan rate of 100 mV/s. The data were taken with a computer controlled Princeton Applied potentiostat (Versa Stat II) and recorded with the Princeton PowerSuit (version 2.58).

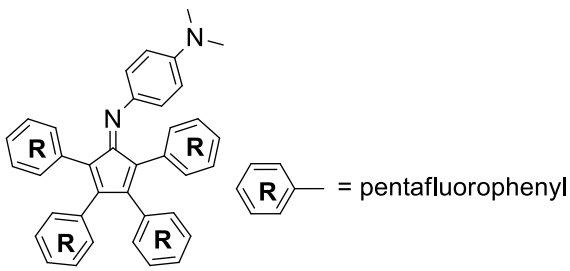
Syntheses

Tetrakis(pentafluorophenyl)cyclopentadiene (3)[2]



Sodium cyclopentadienide[3] (0.19 g, 2.13 mmol), hexafluorobenzene (2.38 g, 12.78 mmol, 1.48 mL) and sodium hydride (0.31 g, 12.78 mmol) were stirred in 11 mL diglyme in an argon atmosphere under microwave irradiation (1. 80 °C, 1.5 min, 0 bar internal pressure, 200 W; 2. 160 °C, 4 h, 8 bar internal pressure, 300 W; 35 mL vial). After cooling, the mixture was transferred to a flask and the solvents were removed *in vacuo*. The residue was taken up in THF (30 mL) and added to an aqueous solution of NH_4Cl (5 g in 200 mL). Further purification was achieved by filtration through celite (dichloromethane) to yield a brown solid (0.77 g, 1.065 mmol, 50%). Mp: 196 °C (Lit.:[2] 196-197 °C); ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 4.17 (s, 2H.) (Lit.:[2] δ_H (ppm): 4.17 (s, 2H)); EI/GC-MS: m/z (%): 730.37 (100) $[M]^+$, 711.37 (10) $[M-F]^+$, 563.32 (15) $[m-C_6F_5]^+$

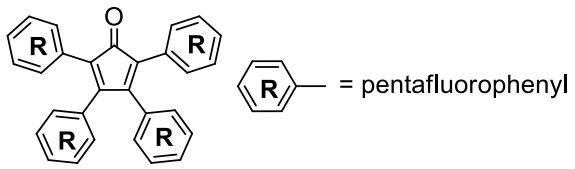
N,*N*-(p-dimethylaniline)-tetrakis(pentafluorophenyl)cyclopentadienimine (4)



A solution of **3** (2.7 g, 3.7 mmol) and *N*,*N*-dimethylnitrosoaniline (0.8 g, 5.5 mmol) in THF was stirred under reflux for 10 min. The solvent was evaporated under reduced pressure and the resulting solid purified by column chromatography on silica gel with petroleum ether/ dichloromethane 1:1 to yield a blue product (2.0 g, 2.4 mmol, 65%). Mp: degradation >360 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 6.77 (d, $^3J_{HH}$=9 Hz, 2H, $H_{arom.}$), 6.39 (d, $^3J_{HH}$=9 Hz, 2H, $H_{arom.}$), 2.97 (s, 6H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 157.87, 151.15, 144.84, 142.35, 139.16, 138.83, 136.34, 127.88, 125.41, 110.94, 107.41, 40.43; ^{19}F-NMR (376 MHz, $CDCl_3$): δ_F (ppm): -137.71, -138.80, -150.30, -152.37, -154.60, -159.69, -161.59; APCI-MS: m/z: 863.13 $[M+H]^+$, 848.13 $[M+H-CH_3]^+$; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 2927 (C-H), 2854 (C-H), 1654

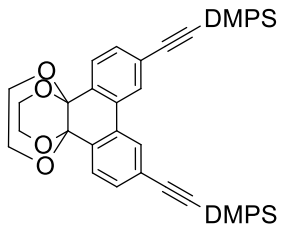
(C=C), 1609 ($ring_{arom.}$), 1488 ($ring_{arom.}$), 1442 (C-H-deform.), 1315 (C-N), 984 (C-F); UV/Vis (DCM): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 670, (5.00)

Tetrakis(pentafluorophenyl)cyclopentadienone (5)[4]



Compound **4** (2.0 g, 2.4 mmol) was stirred in a mixture of glacial acetic acid (100 mL) and concentrated sulphuric acid (1 mL) at 100 °C for 12 h. After cooling, the resulting precipitate was filtered, washed with methanol and purified by column chromatography (silica gel eluting with hexane) to yield a red solid (1.3 g, 1.7 mmol, 71%). Mp: 232 °C (Lit.:[4] 231.5-232 °C) ^{19}F-NMR (376 MHz, $CDCl_3$): δ_F (ppm): -136.81 (d, $^3J_{FF}$= 16.76 Hz, 4F, $F_{arom.}$); -137.08 (d, $^3J_{FF}$= 16.59 Hz, 4F, $F_{arom.}$); -146.70 (t, $^3J_{FF}$= 20.91 Hz, 2F, $F_{arom.}$); -148.89 (t, $^3J_{FF}$= 20.96 Hz, 2F, $F_{arom.}$); -157.71 - -157.86 (m, 4F, $F_{arom.}$); -159.31 - -159.46 (m, 4F, $F_{arom.}$) EI/GC-MS: m/z (%): 744.33 (18) $[M]^+$, 716.33 (15) $[M\text{-}CO]^+$, 358.25 (100) $[M\text{-}CO\text{-}C_{14}F_{10}]^+$, 289.22 (20) $[M\text{-}CO\text{-}C_{17}F_{13}]^+$, 258.22 (8) $[M\text{-}CO\text{-}C_{19}F_{17}]^+$

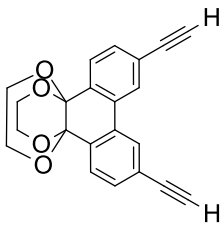
3,6-Bis(dimethylphenylsilylethinyl)phenanthrene-9,10-di-(ethyleneglycol)ketal



3,6-Dibromophenanthrene-9,10-diethyleneglycol)ketal[5] (5.0 g, 11 mmol), copper(I) iodide (62.9 mg, 0.3 mmol) tetrakis(triphenylphosphine)palladium(0), dimethylphenylsilylacetylene (4.3 g, 4.8 mL, 27.5 mmol), di-*iso*-propylamin (10 mL) and dioxane (100 mL) were heated in a Schlenk tube at 60 °C for 12 h in an argon atmosphere. After cooling to room temperature a saturated aqueous solution of NH_4Cl-EDTA was added and the resulting yellow precipitate was collected by filtration. The residue was purified by column chromatography on silica gel with dichloromethane. The product was precipitated from a concentrated solution in di-chloromethane with petroleum ether/ ethyl acetate (3:1) to yield a colourless product (5.4 g, 8.8 mmol, 76%). Mp: 212 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 8.00 (s, 2H, $H_{phenan.}$); 7.73-7.64 (m, 6H, $H_{arom.}$); 7.53, (d, $^3J_{HH}$=8 Hz, 2H, $H_{phenan.}$); 7.44-7.32 (m, 6H, $H_{arom.}$); 4.17 (br, 4H, H_{ketal}); 3.60 (br, 4H, H_{ketal}); 0.51 (s, 12H, H_{methyl});

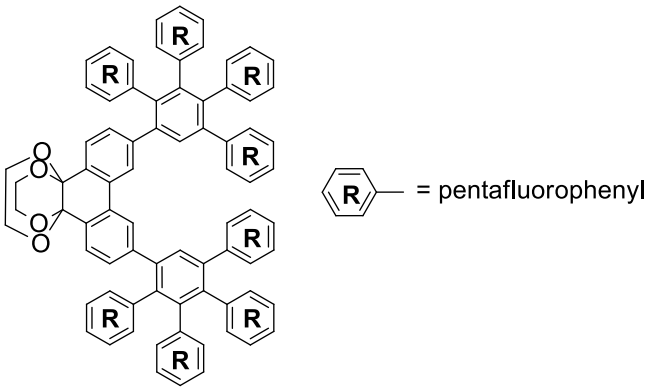
^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 137.0; 134.0; 133.5; 132.4; 129.7; 128.2; 127.8; 126.5; 125.0; 106.2 ($C_{ethinyl.}$); 93.7 ($C_{ethinyl.}$); 92.5 ($C_{quarternary, ketal}$); -0.74 (C_{methyl});
HR/ESI-MS: m/z: 613.2226 $[M+H]^+$, calculated for $[C_{38}H_{37}O_4Si_2]$= 613.2225;
UV/Vis ($CHCl_3$): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 261, (5.07); fluorescence ($CHCl_3$, excitation: 258 nm): λ_{max} (nm): 382; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3080 (aryl-H), 3048 (aryl-H), 2969 (CH), 2952 (CH), 2892 (CH), 2156 (C≡C)

3,6-Diethinylphenanthrene-9,10-di(ethylenglycol)ketal (6)



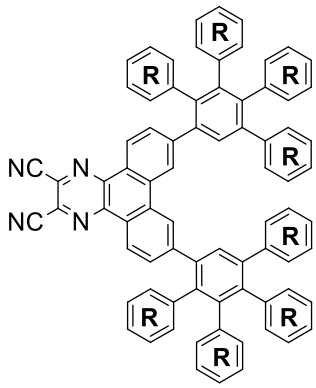
A mixture of 3,6-bis(dimethylphenylsilylethinyl)phenanthrene-9,10-di-(ethyleneglycol)ketal (3.0 g, 5.0 mmol) and potassium fluoride (1.2 g, 19.9 mmol) was stirred in tetrahydrofuran and methanol (2:1) (155 mL) at 30 °C for 12 h. After complete consumption of the starting material (TLC control, SiO_2, petroleum ether/ ethyl acetate- 3:1), dichloromethane (70 mL) was added. The mixture was extracted with water (2x50 mL), washed with saturated, aqueous solution of NaCl (1x25 mL) and dried over $NaSO_4$. Further purification was achieved by a filtration through silica gel (ethyl acetate) to obtain a colourless product (1.7 g, 4.9 mmol, 98%). Mp: degradation >263 °C, ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 8.02 (s, 2H, $H_{arom.}$); 7.72 (d, $^3J_{HH}$= 8.0 Hz, 2H, $H_{arom.}$), 7.55 (m, 2H, $H_{arom.}$), 4.24-4.14 (br, 4H, $H_{ketal.}$), 3.68-3.58 (br, 4H, $H_{ketal.}$), 3.16 (s, 2H, $H_{ethinyl.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 133.5, 132.5, 132.4, 127.7, 126.4, 123.9, 92.2 ($C_{quartär, ketal.}$), 83.0 ($C_{ethinyl.}$), 78.3 ($C_{ethinyl.}$), 62.3-60.3 (br, $C_{ketal.}$);
HR/ESI-MS: m/z: 345.1123 $[M+H]^+$, calculated for $[C_{22}H_{17}O_4]$= 345.1121;
UV/Vis ($CHCl_3$): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 252, (4.93); fluorescence ($CHCl_3$, excitation: 257 nm): λ_{max} (nm): 380; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3324 (acetylene-H), 3085 (aryl-H), 3052 (aryl-H), 2976 (CH), 2939 (CH), 2882 (CH), 2103 (C≡C)

3,6-Bis(2,3,4,5,-tetraperfluorophenyl-1-yl)phenanthren-9,10-di(ethylenglycol)ketal (7)



5 (0.44 g, 0.6 mmol) and **6** (0.08 g, 0.24 mmol) were stirred in 4 mL *o*-dichlorobenzene under microwave irradiation (1. 100 °C, 1.5 min, 0 bar internal pressure, 200 W; 2. 150 °C, 1.5 min, 1 bar internal pressure, 300 W; 3. 180 °C, 1 min, 2 bar internal pressure, 300 W; 4. 210 °C, 5 h, 3 bar internal pressure, 300 W; 35 mL vial). Afterward cooling, the solvent was removed by heating the reaction mixture under vacuum. Column chromatography of the crude product (SiO_2, petroleum ether/ dichloromethane- 1:1) furnished a colourless powder (0.38 mg, 0.21 mmol, 91%). Mp: 208 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 7.73 (s, 2H, $H_{arom.}$); 7.70-7.68 (m, 4H, $H_{arom.}$); 7.18, (d, $^3J_{HH}$=8.1 Hz, 2H, $H_{arom.}$); 4.21 (br, 4H, H_{ketal}); 3.59, (br, 4H, H_{ketal}); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 144.38; 144.13; 141.64; 139.33; 138.81; 137.77; 137.24; 135.27; 134.75; 133.77; 132.56; 131.89; 129.93; 129.79; 128.06; 127.87; 125.66; 123.06; 111.66; 111.43; 111.29, 110.96; 110.79; 110.60; 110.28; 110.14; 109.95; 109.77; 91.06; 60.33 (C_{ketal}); ^{19}F-NMR (376 MHz, $CDCl_3$): δ_F (ppm): -137.72- -137.78 (m, 4F, $F_{arom.}$); -138.45- -138.61 (m, 8F, $F_{arom.}$); -139.81- -139.87 (m, 4F, $F_{arom.}$); -149.22--149.43 (m, 4F, $F_{arom.}$); -150.11 (t, $^3J_{FF}$= 21.27 Hz; 2F, $F_{arom.}$);-150.78 (t, $^3J_{FF}$= 21.08 Hz, 2F, $F_{arom.}$); -159.41--159.61 (m, 8F, $F_{arom.}$); -159.80- -160.03 (m, 4F, $F_{arom.}$);-160.15- -160.29 (m, 4F, $F_{arom.}$); HR/ESI-MS: m/z: 1799.0326 $[M+Na]^+$, calculated for $[C_{78}H_{16}F_{40}NaO_4]$= 1799.0302; UV/Vis ($CH_3CN$): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 253, (4.30); fluorescence (CH_3CN, excitation: 253 nm): λ_{max} (nm): 391, 770; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 2950 (C-H), 2843 (C-H), 1654 (C=C), 1495 ($ring_{arom.}$), 1097 (C-F).

2,3-dicyano-7,10-bis(2,3,4,5-tetraperfluorophenyl-1-yl)dibenzo[*f,h*]chinoxaline (8)

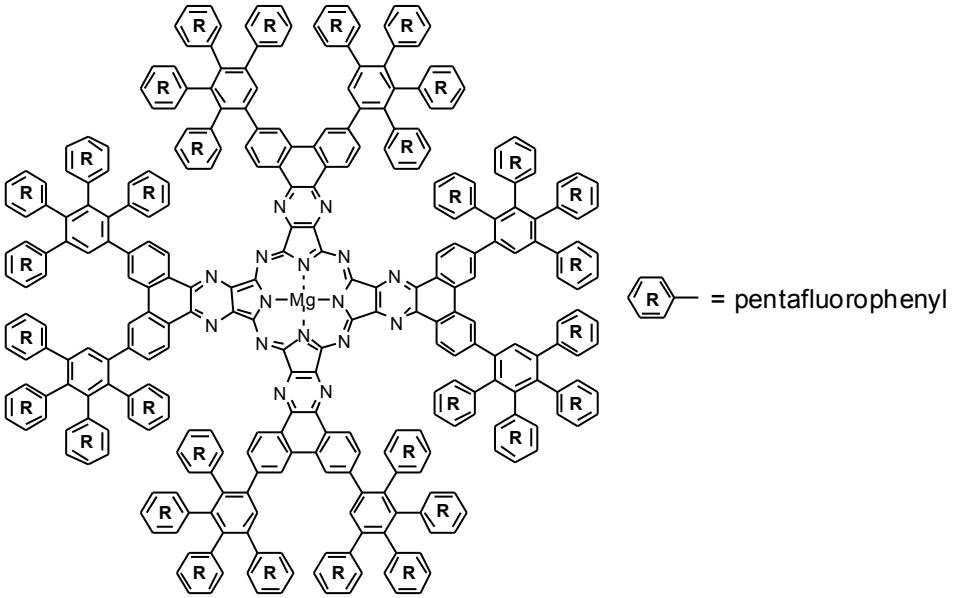


7 (50 mg, 28 µmol) and *p*-toluene sulphonic acid monohydrate (15 mg, 84 µmol) were heated in glacial acetic acid (2 mL) at 140 °C for 3 h until **7** was completely hydrolysed (TLC control, SiO_2, petroleum ether/ dichloromethane 1:1). After cooling to room temperature THF (2 mL) and diaminomaleonitrile (4.6 mg, 42 µmol) were added and the solution was stirred for 12 h. The crude product was dissolved in dichloromethane (8 mL) and extracted successively with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL), water (10 mL), and saturated aqueous NaCl (10 mL). After drying over $NaSO_4$, filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography (SiO_2, petroleum ether/ dichloromethane- 1:1) to obtain a yellow product (47 mg, 27 µmol, 96%).

Mp: degradation > 360 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 9.13 (d, $^3J_{HH}$= 8.38 Hz, 2H, $H_{arom.}$); 8.45 (s, 2H, $H_{arom.}$); 7.85 (s, 2H, $H_{arom.}$); 7.60 (d, $^3J_{HH}$= 8.44 Hz, 2H, $H_{arom.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 144.91; 144.74; 142.80; 142.51; 142.27; 140.70; 138.71; 138.59; 138.46; 138.09; 136.70; 136.56; 136.46; 136.11; 134.55; 132.54; 131.36; 131.18; 130.79; 129.96; 129.02; 127.60; 127.54; 123.33; 113.36; 112.24; 111.50; 110.80; 110.66; ^{19}F-NMR (376 MHz, $CDCl_3$): δ_F (ppm): -137.91- -137.96 (m, 4F, $F_{arom.}$); -138.59- -138.63 (m, 8F, $F_{arom.}$); -139.73- -139.79 (m, 4F, $F_{arom.}$); -148.63- -148.87 (m, 4F, $F_{arom.}$); -149.11 (t, $^3J_{FF}$= 20.72 Hz, 2F, $F_{arom.}$); -150.30 (t, $^3J_{FF}$= 20.50 Hz, 2F, $F_{arom.}$); -159.13- -159.19 (m, 8F, $F_{arom.}$); -159.61- -159.74 (m, 8F, $F_{arom.}$); HR/ESI-MS: m/z: 1783.0006 $[M+Na]^+$, calculated for $[C_{78}H_8F_{40}N_4Na]$= 1783.0002;

UV/Vis (CH_3CN): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 250, (4.69), 311, (4.56), 358 (sh), (3.96); fluorescence (CH_3CN, excitation: 311 nm): λ_{max} (nm): 487; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 2950 (C-H), 1654 (C-H), 1654 (C=C), 1497 ($ring_{arom.}$), 1102 (C-F)

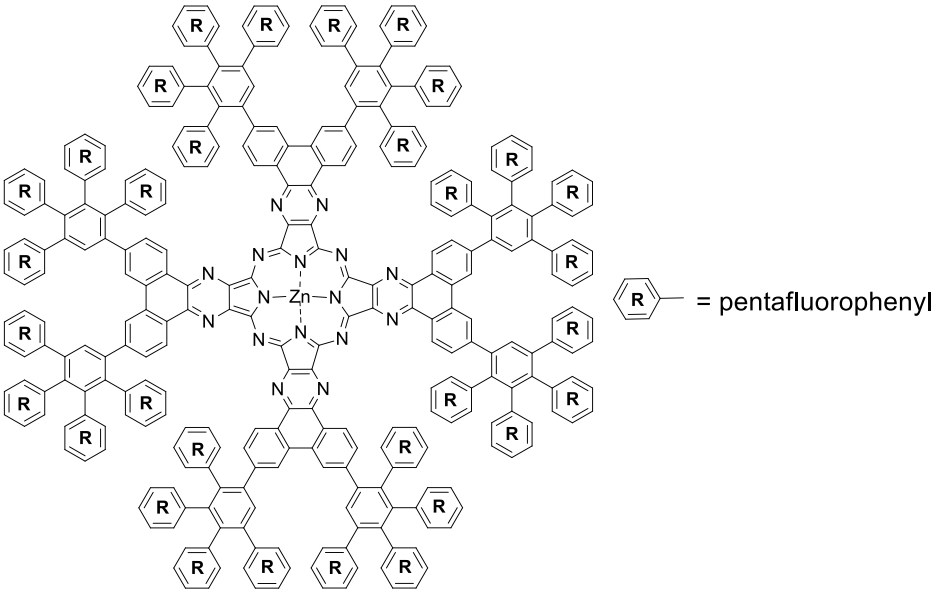
[Tetra-(7,10-bis(2,3,4,5-tetraperfluorophenyl-1-yl)dibenzo[*f*,*h*]chinoxalino)porphyrazinato]magnesium(II) (1-Mg)



Magnesium turnings (6.9 mg, 0.3 mmol) and a small crystal of iodine were heated for 3 h in *n*-butanol (3.5 mL) at 160 °C in an argon atmosphere. Then **8** (50 mg, 28 µmol) was dissolved in a minmal amount of *o*-dichlorobenzene and was added to the refluxing solution of magnesium butanolate. The reaction mixture was stirred for a further 3 h at 160 °C, then cooled to room temperature and poured into a methanolic solution of NH_4Cl. The resulting green precipitate was filtered and washed successively with methanol, water and again with methanol. For further purification the crude product was filtered through silica gel (first washing with petroleum ether/dichloromethane- 1:1, second washing with THF) followed by a gelpermeation chromatography (THF). Finally, the substance was filtered through silica gel again (1. petroleum ether/dichloromethane- 1:1, 2. THF) to yield a green solid (32 mg, 4.52 µmol, 64%). Mp: 321 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 10.34 (d, $^3J_{HH}$= 8.55 Hz, 8H, $H_{arom.}$); 8.75 (s, 8H, $H_{arom.}$); 8.09 (s, 8H, $H_{arom.}$); 7.87 (d, $^3J_{HH}$= 8.14 Hz, 8H, $H_{arom.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 144.05; 143.90; 143.61; 141.91; 140.52; 139.63; 137.58; 137.07; 135.55; 135.09; 133.60; 131.52; 131.26; 131.03; 130.11; 129.50; 128.68; 128.20; 128.12; 127.51; 126.70; 126.68; 122.12; 111.31; 110.67; 109.91; ^{19}F-NMR (376 MHz, $CDCl_3$): δ_F (ppm): -137.92- -137.96 (m, 16F, $F_{arom.}$); -138.53- -138.57 (m, 32F, $F_{arom.}$); -139.72- -139.77 (m, 16F, $F_{arom.}$); -148.83- -148.99 (m, 16F, $F_{arom.}$); -149.22- -149.31 (m, 8F, $F_{arom.}$); -150.41- -150.50 (m, 8F, $F_{arom.}$); -159.20- -159.24 (m, 32F, $F_{arom.}$); -159.76- -159.79 (m, 32F, $F_{arom.}$); MALDI-MS: m/z: 7068 $[M]^+$;

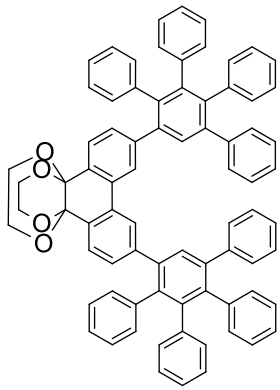
UV/Vis (CH_3CN): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 243, (4.43), 295 (sh), (4.03); 375, (4.23); 641 (sh), (3.51); 675 (sh), (3.55); 712, (4.44); fluorescence (CH_3CN, excitation: 375 nm): λ_{max} (nm): 486, 700; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3068 (aryl-H), 2952 (C-H), 728 (C-F), 697 (C-F)

[Tetra-(7,10-bis(2,3,4,5-tetraperfluorophenyl-1-yl)dibenzo[*f*,*h*]chinoxalino)porphyrazinato]zinc(II) (1)



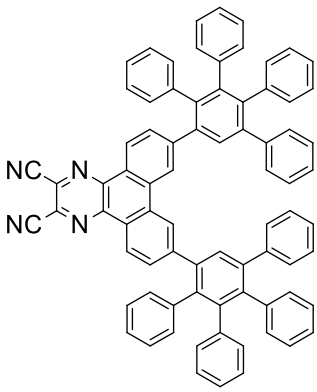
A mixture of **1-Mg** (13 mg, 1.8 µmol) and *p*-toluene sulphonic acid monohydrate (3.5 mg, 18 mmol) was stirred in THF at room temperature (7 mL) for 2 h followed by the addition of zinc acetate dihydrate (6 mg, 27 µmol) and continuous stirring overnight. After that chloroform (10 mL) was added and the organic phase was extracted with water (3x10 mL) and saturated aqueous NaCl solution (1x10 mL). For further purification the product was filtered through silica gel (tetrahydrofuran) to obtain a green solid (11 mg, 1.5 µmol, 86%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H (ppm): 10.34 (d, $^{3}J_{HH}$= 8.0 Hz, 8H, $H_{arom.}$); 8.77 (s,8H, $H_{arom.}$); 8.09 (s, 8H, $H_{arom.}$); 7.89 (d, $^{3}J_{HH}$= 7.80 Hz, 8H, $H_{arom.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 145.50; 145.05; 144.64; 142.98; 141.53; 140.68; 138.10; 136.10; 134.79; 134.59; 132.36; 132.05; 131.31; 131.19; 130.33; 129.70; 129.34; 129.20; 128.52; 127.71; 127.48; 123.49; 123.12; 112.46; 111.81; 110.89; ^{19}F-NMR (376 MHz, $CDCl_3$): δ_F (ppm): -137.86- -137.95 (m, 16F, $F_{arom.}$); -138.52- -138.56 (m, 32F, $F_{arom.}$); -139.66- -139.72 (m, 16F, $F_{arom.}$); -148.82- -148.94 (m, 16F, $F_{arom.}$); -149.21- -149.26 (m, 8F, $F_{arom.}$); -150.45- -150.49 (m, 8F, $F_{arom.}$); -159.17- -159.22 (m, 32F, $F_{arom.}$); -159.70- -159.75 (m, 32F, $F_{arom.}$); MALDI-MS: m/z: 7144 $[M+Cl]^-$; UV/Vis (CH_3CN): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 298, (4.78), 376, (4.99); 642 (sh), (4.30); 679 (sh), (4.33); 712, (5.24); fluorescence (CH_3CN, excitation: 376 nm): λ_{max} (nm): 450, 707; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 2961 (C-H), 2922 (C-H), 2852 (C-H), 737 (C-F), 687 (C-F)

3,6-bis(2,3,4,5,-tetraphenyl-1-yl)phenanthren-9,10-di(ethylenglycol)ketal (7a)



Tetraphenylcyclopentadienone (1.192 g, 3.1 mmol) and **6** (0.08 g, 0.24 mmol) were stirred in *o*-dichlorobenzene at 210 °C for 4 d. After cooling to room temperature the solvent was removed *in vacuo*. The crude product was purified by column chromatography (SiO_2 eluting with dichloromethan). For further purification the product was dissolved in chloroform and precipitated with methanol to yield a colourless powder (1.241 g, 1.2 mmol, 91%). Mp: degradation > 310 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm): 7.68 (d, $^4J_{HH}$= 1.4 Hz, 2H, $H_{arom.}$); 7.58 (s, 2H, $H_{arom.}$); 7.44 (d, $^3J_{HH}$= 8.0 Hz, 2H, $H_{arom.}$); 7.17 (m, 10H, $H_{arom.}$); 7.03 (dd, $^3J_{HH}$= 8.1 Hz, $^4J_{HH}$= 1.4 Hz, 2H, $H_{arom.}$); 6.93 (m, 6H, $H_{arom.}$); 6.88-6.80 (m, 18H, $H_{arom.}$); 6.79-6.72 (m, 6H, $H_{arom.}$); 4.27-4.03 (br, 4H, $H_{ketal.}$); 3.73-3.49 (br, 4H, $H_{ketal.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 143.3, 141.8, 141.6, 140.8, 140.2, 139.94, 139.87, 139.6, 139.5, 139.1, 132.4, 131.53, 131.50, 131.47, 131.43, 130.5, 130.4, 129.9, 127.6, 127.1, 126.9, 126.6, 126.3, 125.8, 125.61, 125.58, 125.29, 125.27, 92.6 ($C_{ketal., quarter.}$); HR/ESI-MS: m/z: 1163.3227 $[M+Ag]^+$, calculated for $[C_{78}H_{56}AgO_4]$= 1163.3224; UV/Vis ($CHCl_3$): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 257, (5.03); fluorescence (CH_3CN, excitation: 376 nm): λ_{max} (nm): 450, 707; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3068 (aryl-H), 3055 (aryl-H), 3024 (aryl-H), 2960 (C-H), 2937 (C-H), 2872 (C-H).

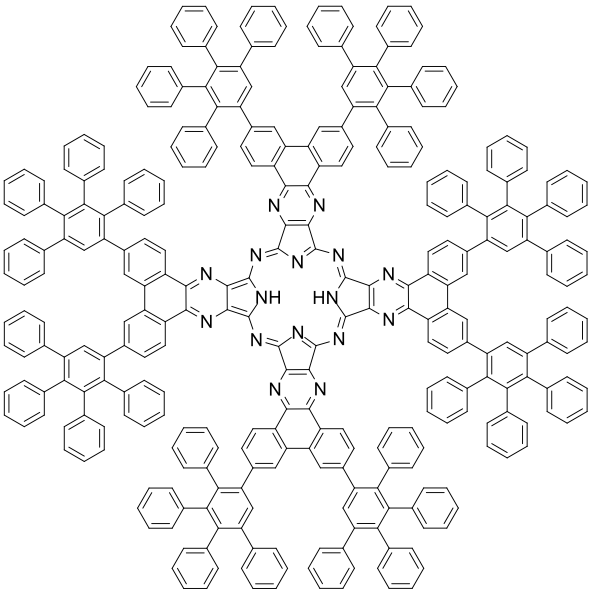
2,3-dicyano-7,10-bis(2,3,4,5-tetraphenyl-1-yl)dibenzo[*f,h*]chinoxaline (8a)



7a (320 mg, 300 µmol) and *p*-toluene sulphonic acid monohydrate (173 mg, 910 µmol) were heated in glacial acetic acid (22 mL) at 140 °C for 3 h until **7a** was completely hydrolysed (TLC control, SiO_2, petroleum ether/ dichloromethane 1:1). After cooling to room temperature THF (20 mL) and diaminomaleonitrile (33 mg, 300 µmol) were added and the solution was stirred at room temperature for 12 h. The solvent was evaporated under reduced pressure and the crude product was dissolved in chloroform and precipitated with methanol to obtain a yellow solid (253 mg, 240 µmol, 81%).

Mp: degradation > 310 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm): 8.83 (d, $^3J_{HH}$= 8.3 Hz, 2H, $H_{arom.}$); 8.46 (s, 2H, $H_{arom.}$); 7.76 (s, 2H, $H_{arom.}$); 7.50 (d, $^3J_{HH}$= 8.4 Hz, 2H, $H_{arom.}$); 7.33-7.21 (m, 8H, $H_{arom.}$); 7.06-6.83 (m, 32H, $H_{arom.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 146.7 ($C_{C=N,\ chinox.}$), 142.5, 142.2, 141.4, 141.2, 140.4, 139.8, 139.6, 139.43, 139.40, 139.36, 132.8, 131.5, 131.4, 131.3, 130.8, 129.9, 129.5, 127.7, 127.3, 127.0, 126.7, 126.5, 126.0, 125.8, 125.5, 125.2, 124.6, 113.8 ($C_{nitrile}$); HR/ESI-MS: m/z: 1147.2929 $[M+Ag]^+$, calculated for $[C_{78}H_{48}N_4Ag]$= 1147.2924; UV/Vis ($CHCl_3$): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 252, (5.05); 349, (4.66); 409 (sh), (4.27); fluorescence ($CHCl_3$, excitation: 349 nm): λ_{max} (nm): 479; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3112 (aryl-H), 3081 (aryl-H), 3057 (aryl-H), 3024 (aryl-H).

Tetra-(7,10-bis(2,3,4,5-tetraphenyl-1-yl)dibenzo[*f*,*h*]chinoxalino)porphyrazine (2a)

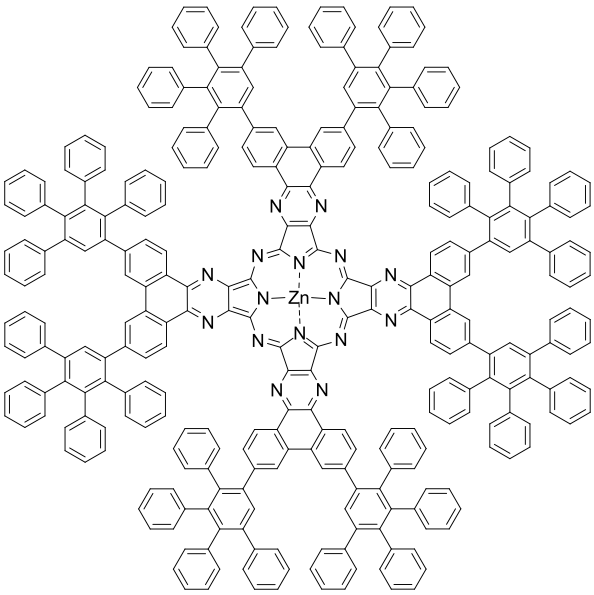


Magnesium turnings (6.9 mg, 0.3 mmol) and a small crystal of iodine were heated for 3 h in *n*-butanol (3.5 mL) at 160 °C under argon. **8a** (25 mg, 24 µmol) was dissolved in the minimum amount of *o*-dichlorobenzene and the solution was added to the refluxing magnesium butanolate solution. The reaction mixture was stirred for 3 h at 160 °C, then cooled to room temperature and poured into a methanolic solution of NH_4Cl. The resulting green precipitate was filtered and washed successively with methanol, water and again with methanol. For further purification the crude product was filtered through silica gel (washing first with chloro-

form, then with THF). A concentrated solution of the crude product in THF was submitted to gel permeation chromatography (THF). The isolated product fraction was filtered through silica again (1. chloroform 2. THF). Evaporation of the solvent left a green product (12 mg, 2.9 µmol, 48%). Mp: degradation > 400 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm): 10.06 (d, $^{3}J_{HH}$= 8.2 Hz, 8H, $H_{arom.}$); 8.70 (s, 8H, $H_{arom.}$); 7.90 (s, 8H, $H_{arom.}$); 7.73 (d, $^{3}J_{HH}$= 8.3 Hz, 8H, $H_{arom.}$); 7.29 (m, 16H, $H_{arom.}$); 7.25-7.17 (m, 32H, $H_{arom.}$); 7.06 (m, 16H, $H_{arom.}$); 6.99 (m, 34H, $H_{arom.}$); 6.94 (m, 48H, $H_{arom.}$); 6.89 (m, 32H, $H_{arom.}$); 6.80 (m, 8H, $H_{arom.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 146.08; 145.58; 144.56; 142.58; 142.55; 142.11; 141.98; 141.97; 141.62; 141.60; 140.67; 140.61; 140.42; 140.33; 140.18; 140.16; 140.13; 140.03; 139.98; 139.89; 132.82; 132.25; 132.17; 131.99; 131.88; 131.86; 130.83; 130.53; 130.42; 128.21; 128.16; 127.82; 127.68; 127.50; 127.45; 127.24; 127.18; 126.94; 126.72; 126,67; 126.50; 126.22; 125.96; 124.83; 110.46;

MALDI-MS: m/z: 4168 $[M+H]^+$; UV/Vis ($CHCl_3$): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 706, (5.49); 698 (sh), (5.14); 674 (sh), (4.74); 651 (sh), (4.54); 637, (4.67); 627 (sh), (4.60); 510, (4.82); 476, (4.80); 445 (sh), (4.84); 393, (5.19); 343, (5.07); fluorescence ($CHCl_3$, excitation: 393 nm): λ_{max} (nm): 469, 712; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3051 (aryl-H), 3020 (aryl-H), 2945 (C-H), 2877 (C-H).

[Tetra-(7,10-bis(2,3,4,5-tetraphenyl-1-yl)dibenzo[*f*,*h*]chinoxalino)porphyrazinato]zinc(II) (2)



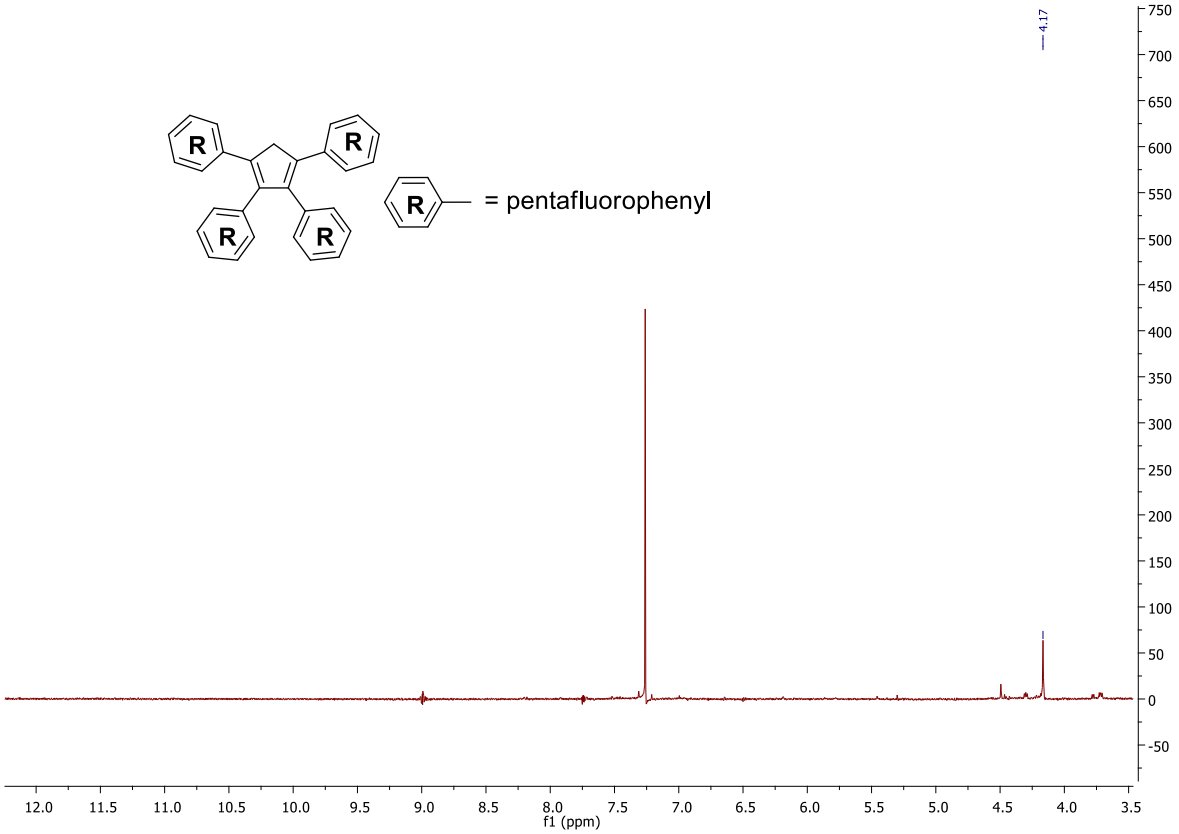
A mixture of **2a** (74.6 mg, 17.9 µmol) and *p*-toluene sulphonic acid monohydrate (34.0 mg, 17.9 mmol) was stirred in THF at room temperature (30 mL) for 2 h. After the addition of zinc acetate dihydrate (58.9 mg, 26.8 mmol) the mixture was stirred overnight. Chloroform (50 mL) was added and the organic phase was washed with water (3x50 mL) and saturated aqueous NaCl (1x50 mL). For further purification the product was filtered through silica gel

(THF) to obtain a green solid (73.6 mg, 17.4 µmol, 97%); ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H (ppm): 10.06 (d, $^{3}J_{HH}$= 8.2 Hz, 8H, $H_{arom.}$); 8.68 (s, 8H, $H_{arom.}$); 7.90 (s, 8H, $H_{arom.}$); 7.72 (d, $^{3}J_{HH}$= 8.5 Hz, 8H, $H_{arom.}$); 7.29 (m, 16H, $H_{arom.}$); 7.24-7.19 (m, 32H, $H_{arom.}$); 7.06 (m, 16H, $H_{arom.}$); 6.98 (m, 34H, $H_{arom.}$); 6.94 (m, 48H, $H_{arom.}$); 6.91 (m, 32H, $H_{arom.}$); 6.81 (m, 8H, $H_{arom.}$); ^{13}C-NMR (126 MHz, $CDCl_3$): δ_C (ppm): 146.10; 145.60; 144.55; 142.58; 142.55; 142.12; 141.98; 141.60; 140.67; 140.60; 140.42; 140.34; 140.18; 140.16; 140.14; 140.07; 140.03; 139.97; 139.89; 132.83; 132.18; 131.99; 131.88; 131.86; 130.83; 130.53; 130.42; 128.20; 128.16; 127.83; 127.68; 127.50; 127.45; 127.24; 127.18; 126.94; 126.73; 126.50; 126.22; 125.96; 125.28; 124.83; 110.46;

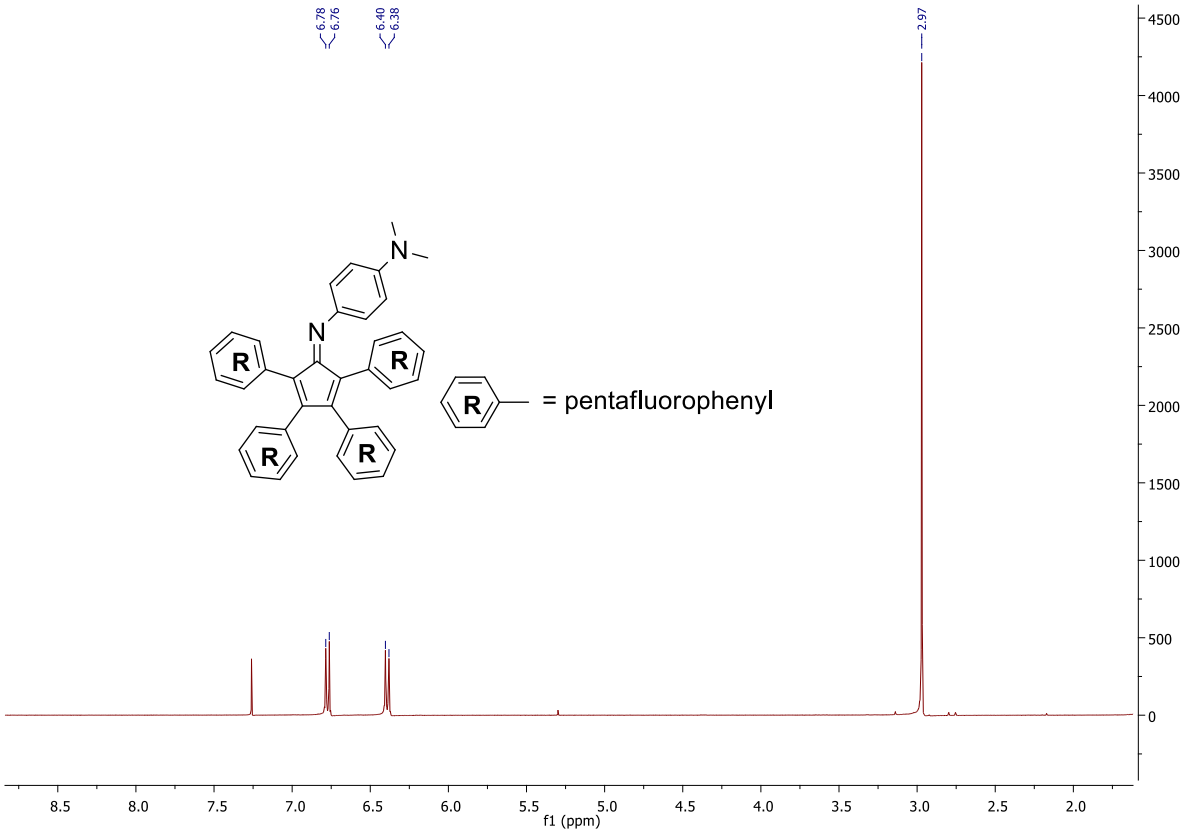
MALDI-MS: m/z: 4230 $[M]^+$; UV/Vis (CCl_4): λ_{max} (nm), (log ε_λ ($M^{-1}cm^{-1}$)): 264, (5.65), 392, (5.27); 457, (4.95); 673, (4.94); 697, (4.94); 772, (4.88); fluorescence (CCl_4, excitation: 392 nm): λ_{max} (nm): 491, 709; IR (ATR): $\tilde{\nu}_{max}$ (cm^{-1}): 3050 (aryl-H), 3019 (aryl-H), 2915 (C-H), 2848 (C-H).

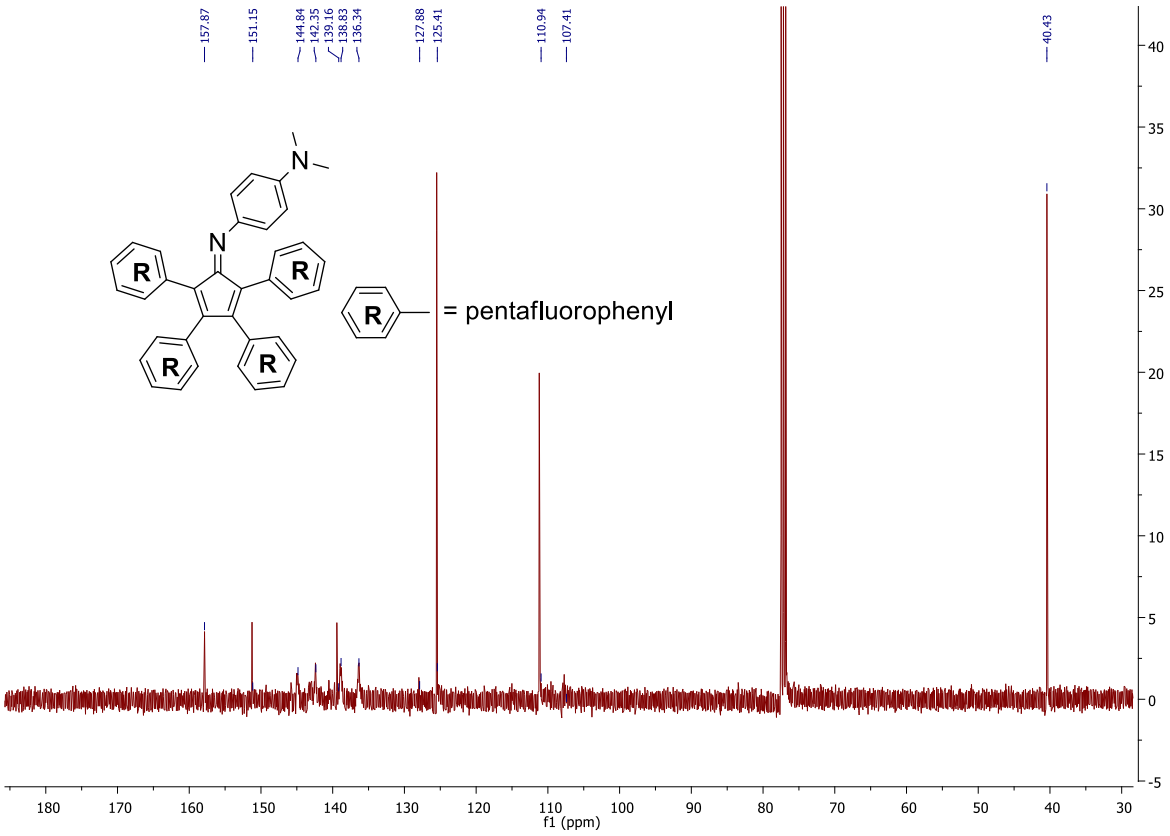
NMR spectra

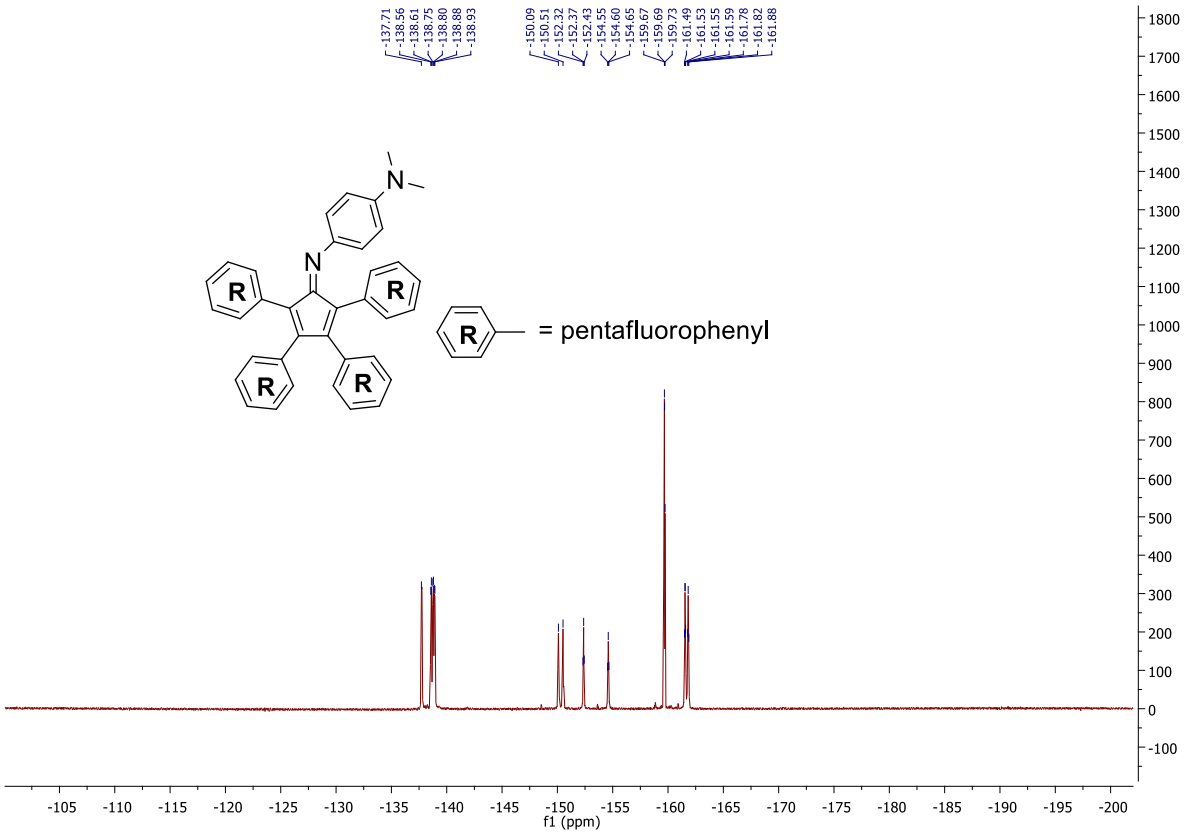
Compound **3**



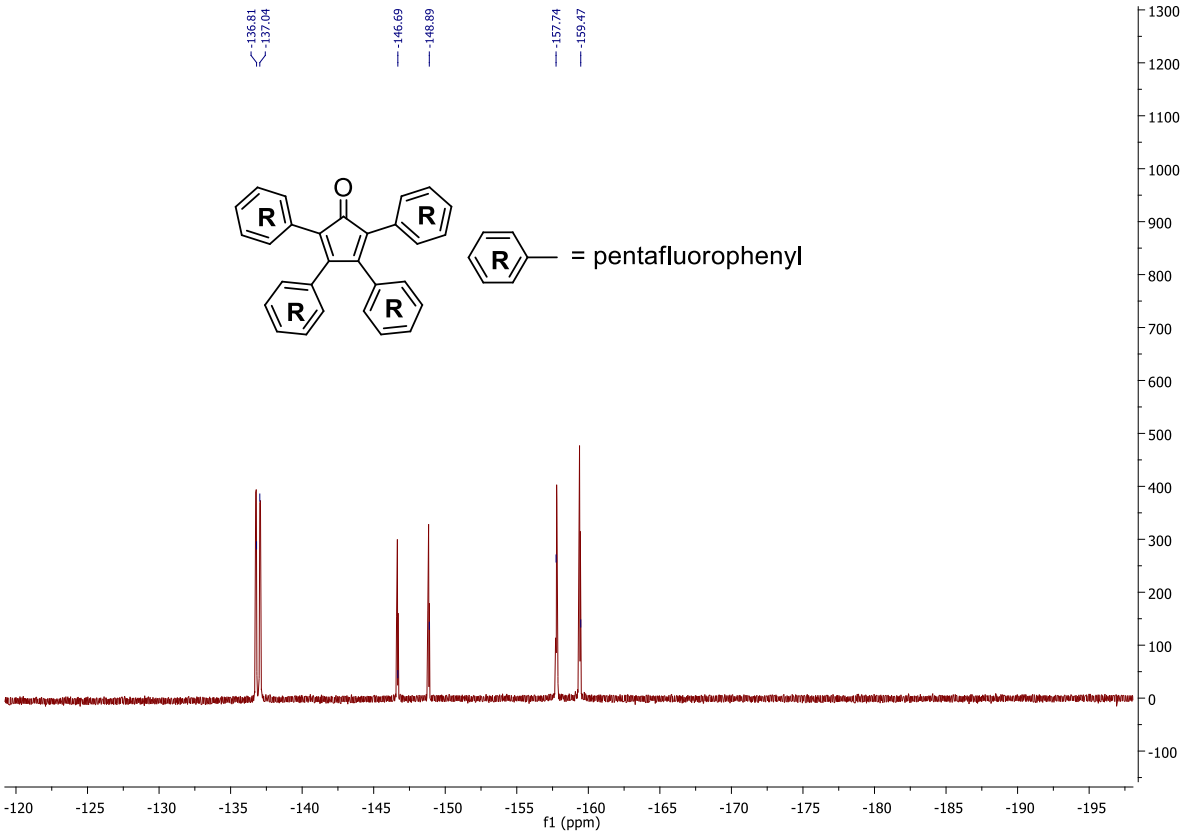
Compound **4**



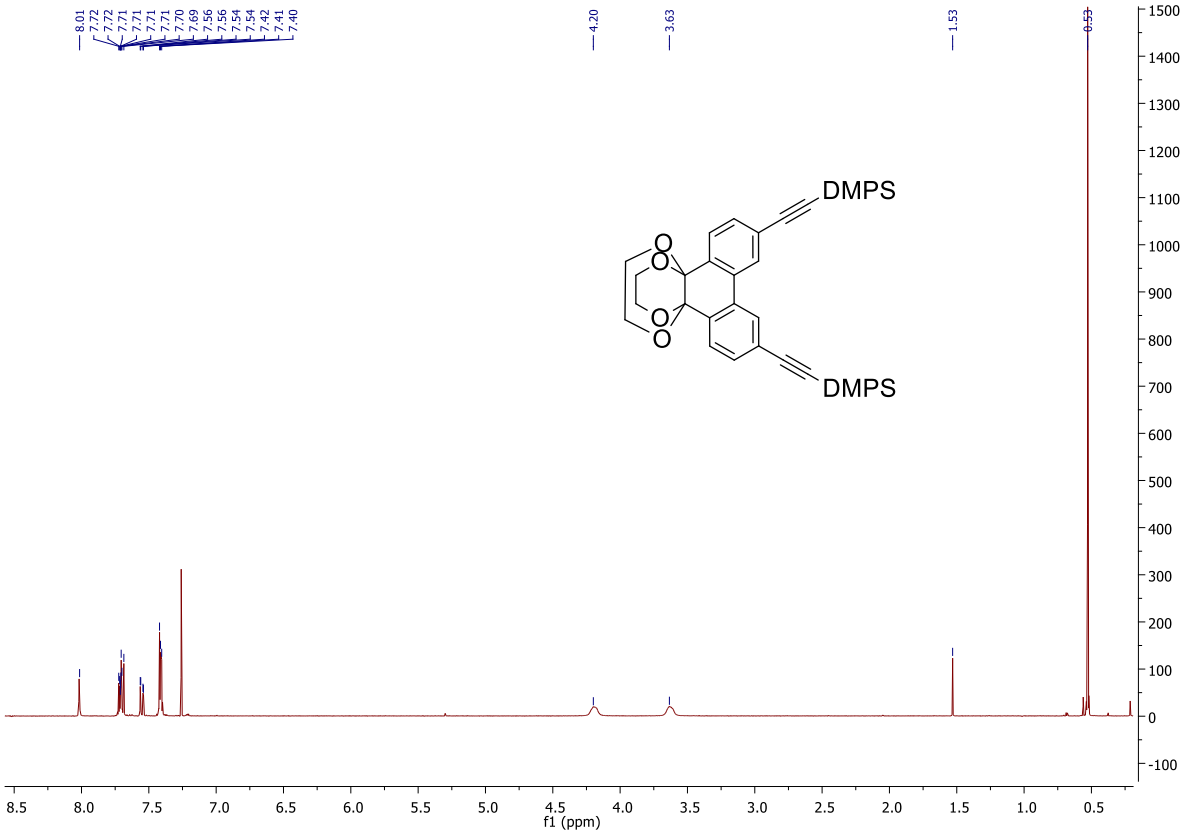

157.87
151.15
144.84
142.35
139.16
138.83
136.34
127.88
125.41
110.94
107.41
40.43
N
N
R
R
R
R
R
= pentafluorophenyl
f1 (ppm)

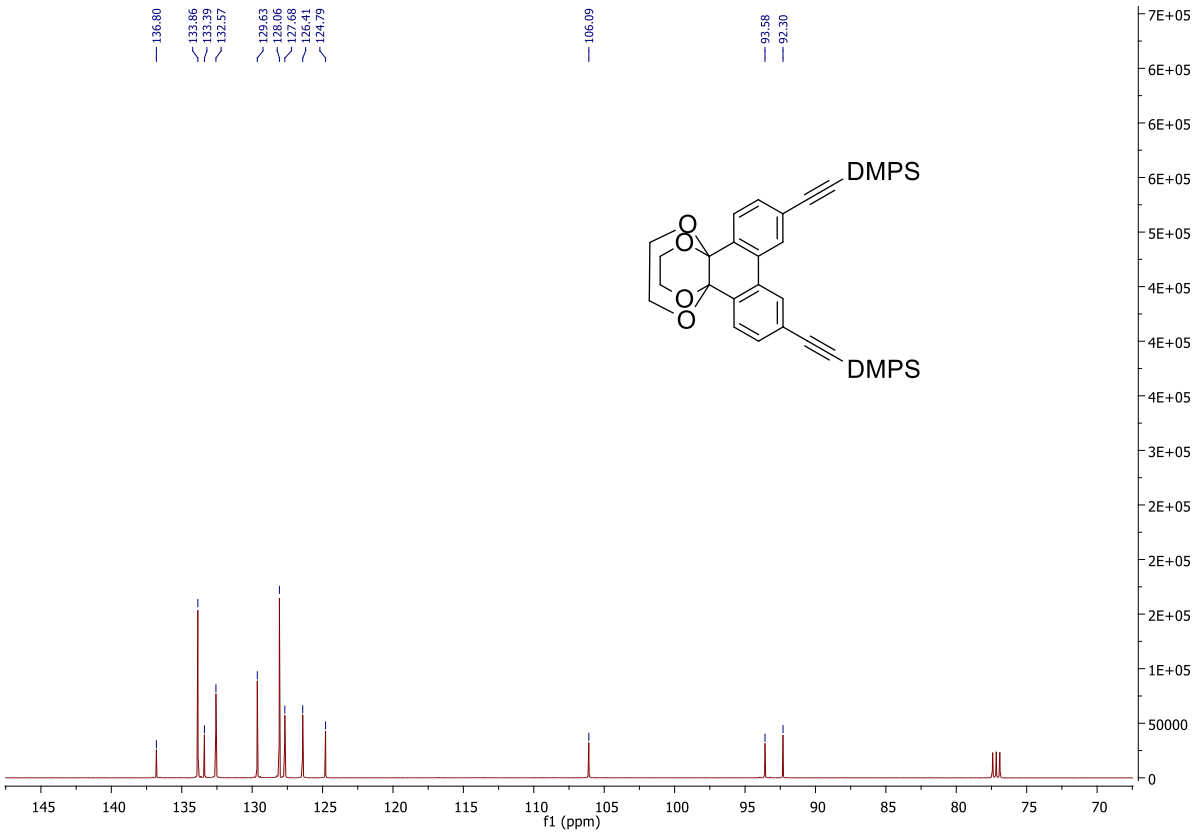

-137.71
-138.56
-138.61
-138.75
-138.80
-138.88
-138.93
-150.09
-150.51
-152.32
-152.37
-152.43
-154.55
-154.60
-154.65
-159.67
-159.69
-159.73
-161.49
-161.53
-161.55
-161.59
-161.78
-161.82
-161.88
N
N
R
R
R
R
R
= pentafluorophenyl
f1 (ppm)

Compound **5**

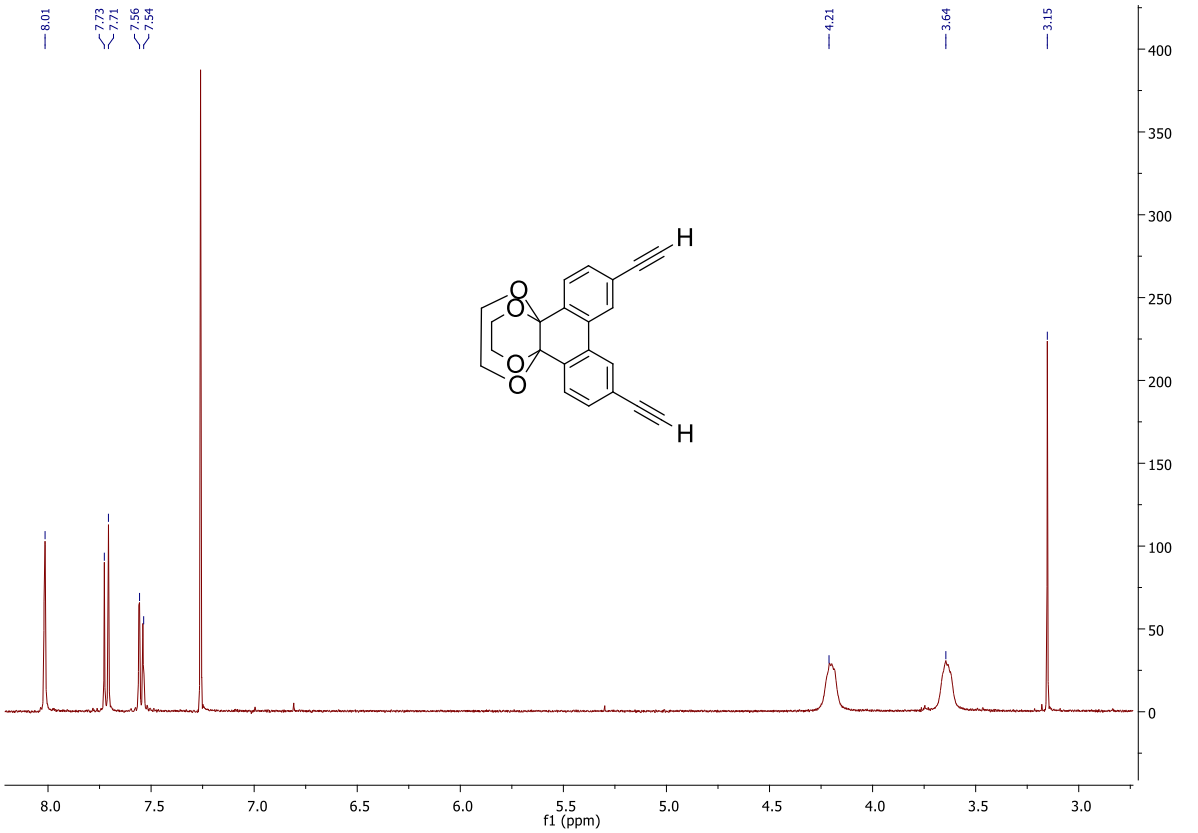


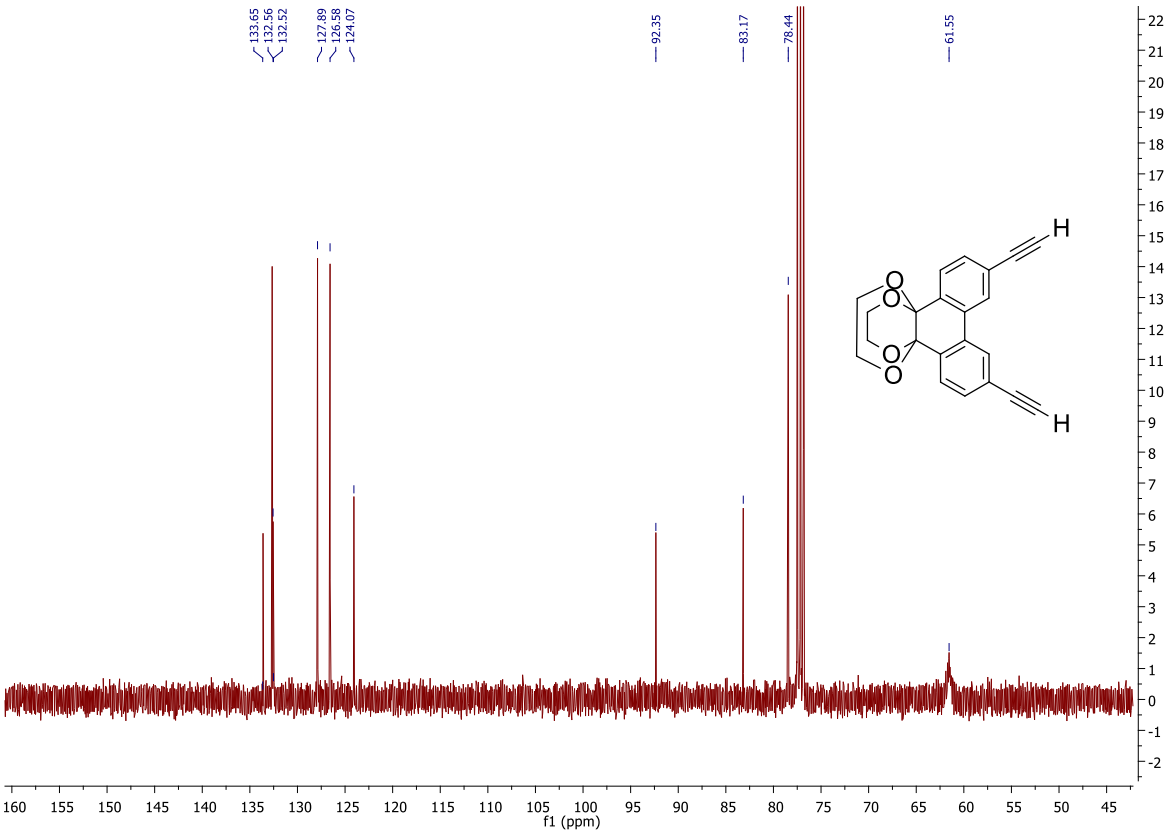
DMPS-ketal



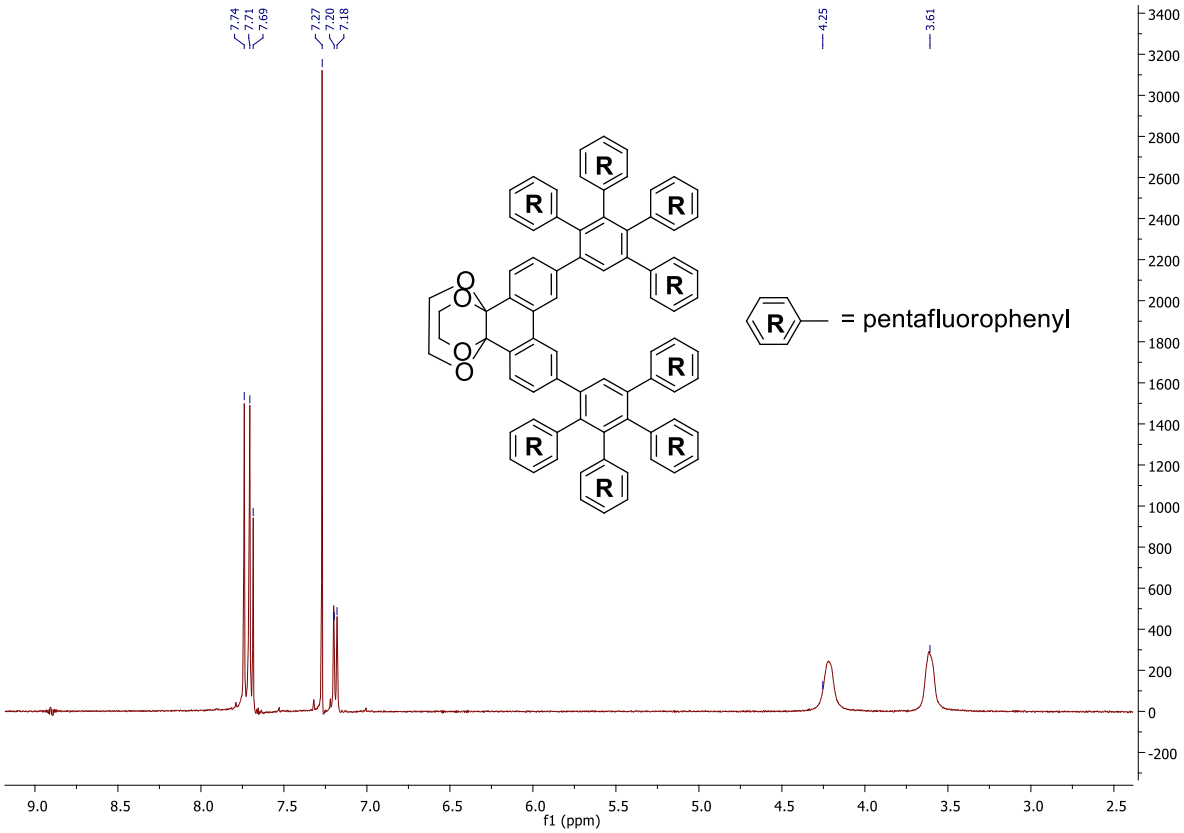

136.80
133.86
133.39
132.57
129.63
128.06
127.68
126.41
124.79
106.09
93.58
92.30
DMPS
DMPS
O
O
O
O
f1 (ppm)

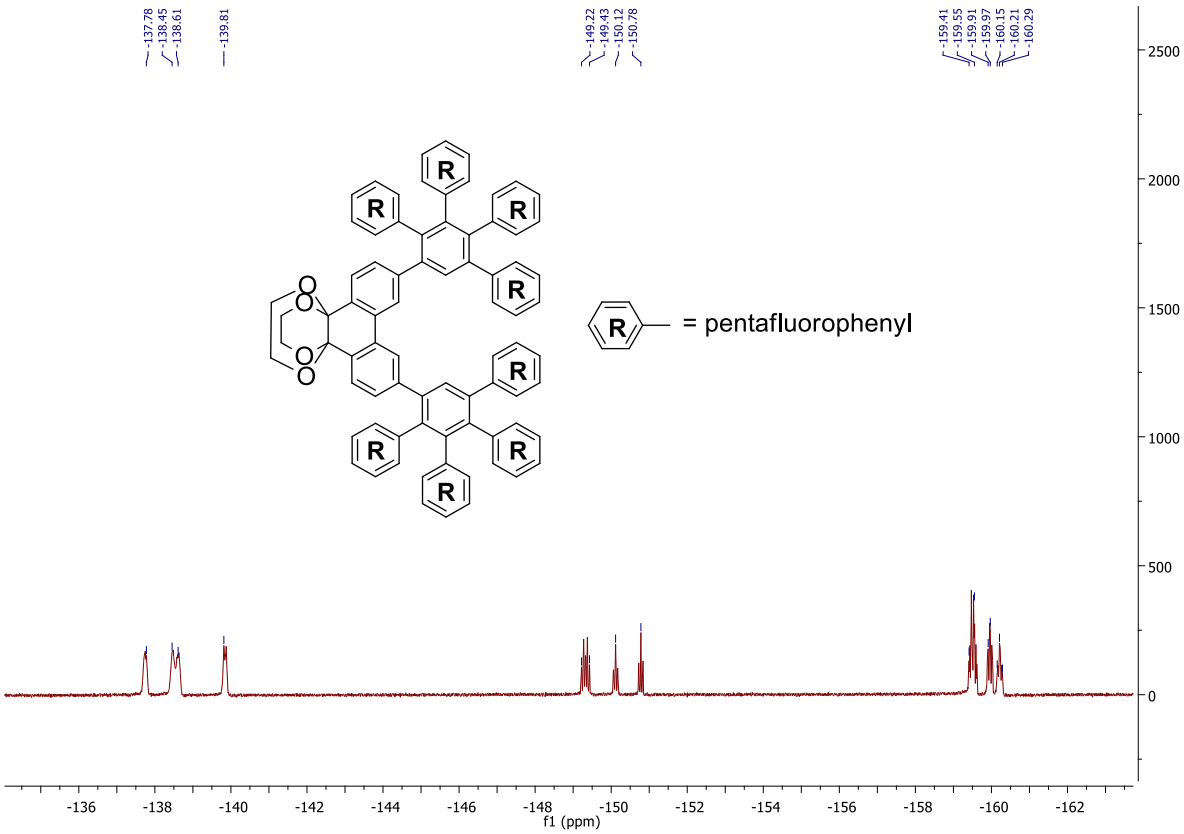
Compound **6**

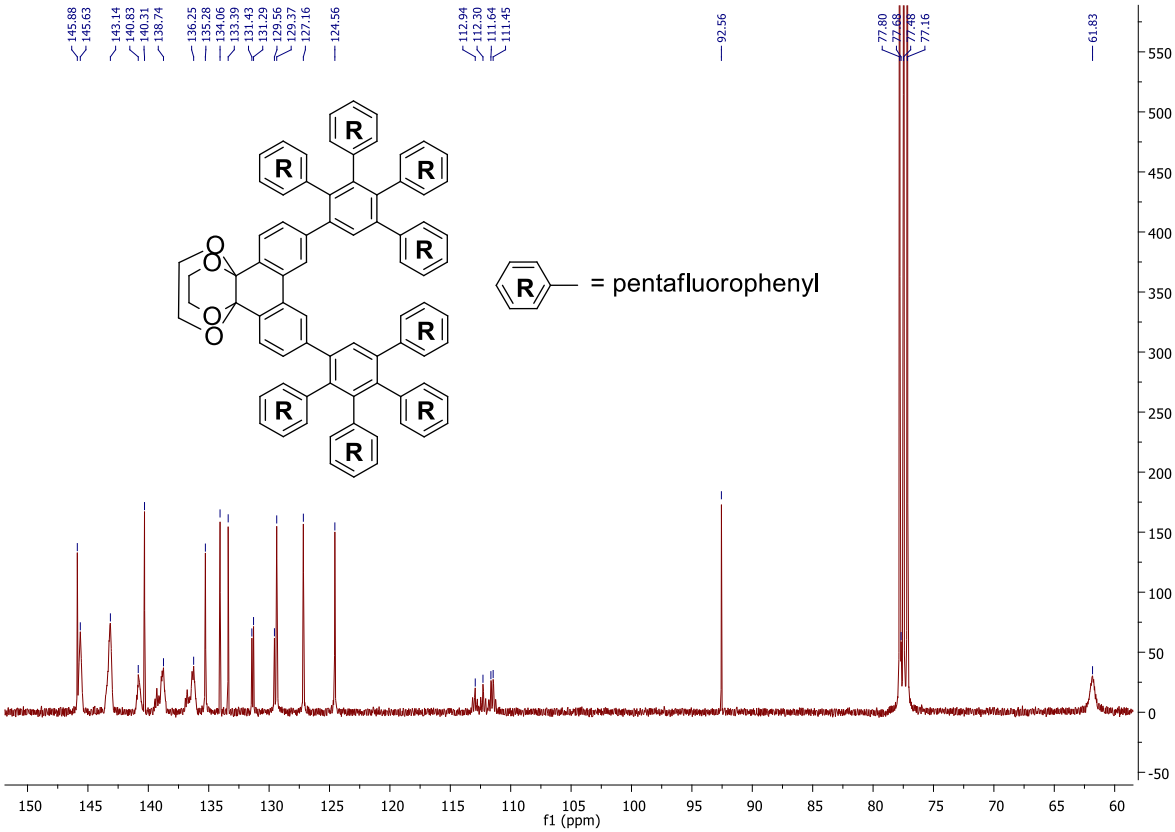

8.01
7.73
7.71
7.56
7.54
4.21
3.64
3.15
H
H
O
O
O
O
f1 (ppm)


133.65
132.56
132.52
127.89
126.58
124.07
92.35
83.17
78.44
61.55
H
H
O
O
O
O
f1 (ppm)

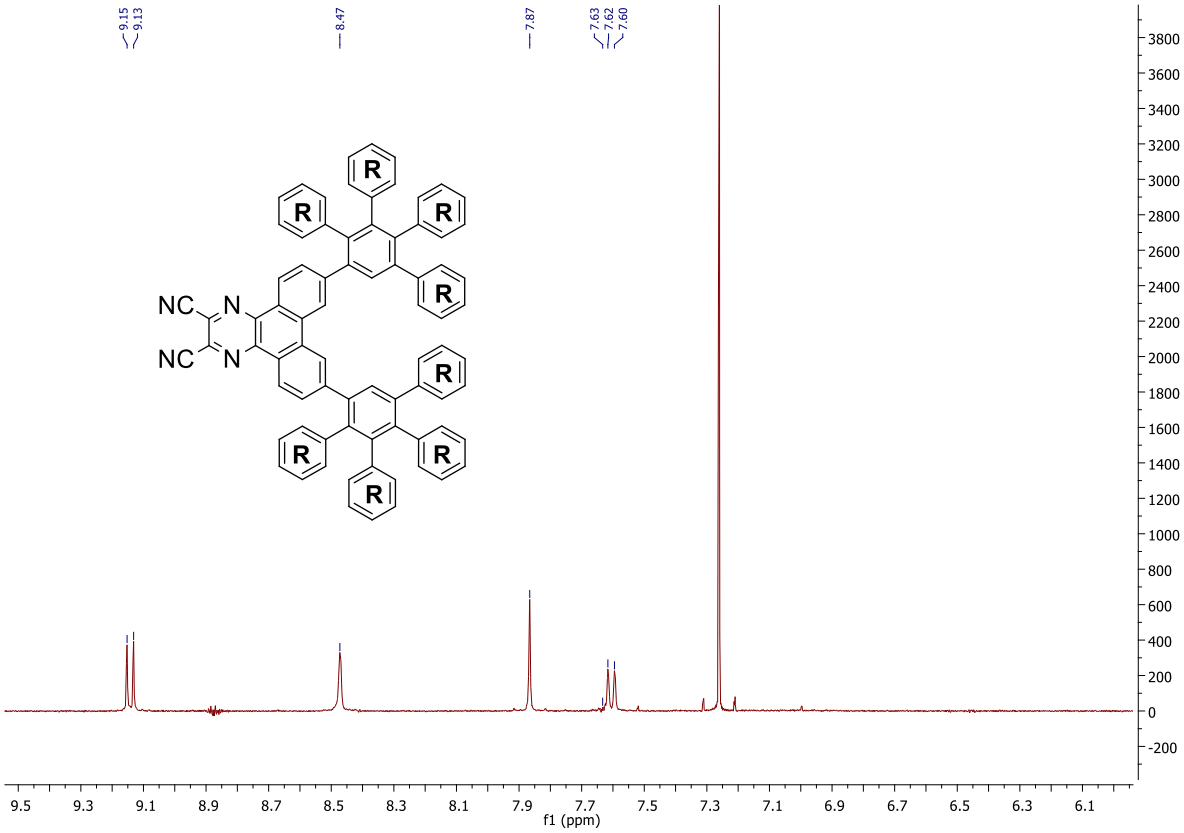
Compound **7**

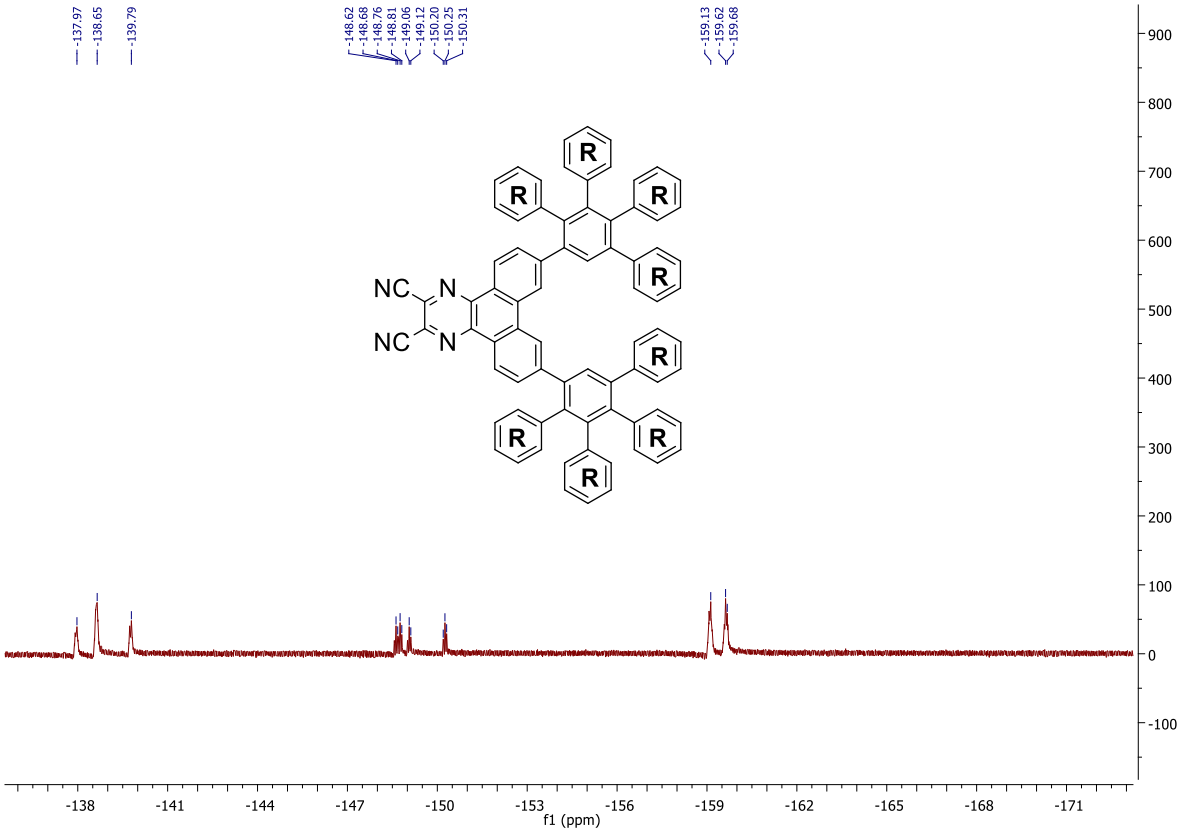

7.74
7.71
7.69
7.27
7.20
7.18
4.25
3.61
R
= pentafluorophenyl
O
O
O
O
f1 (ppm)

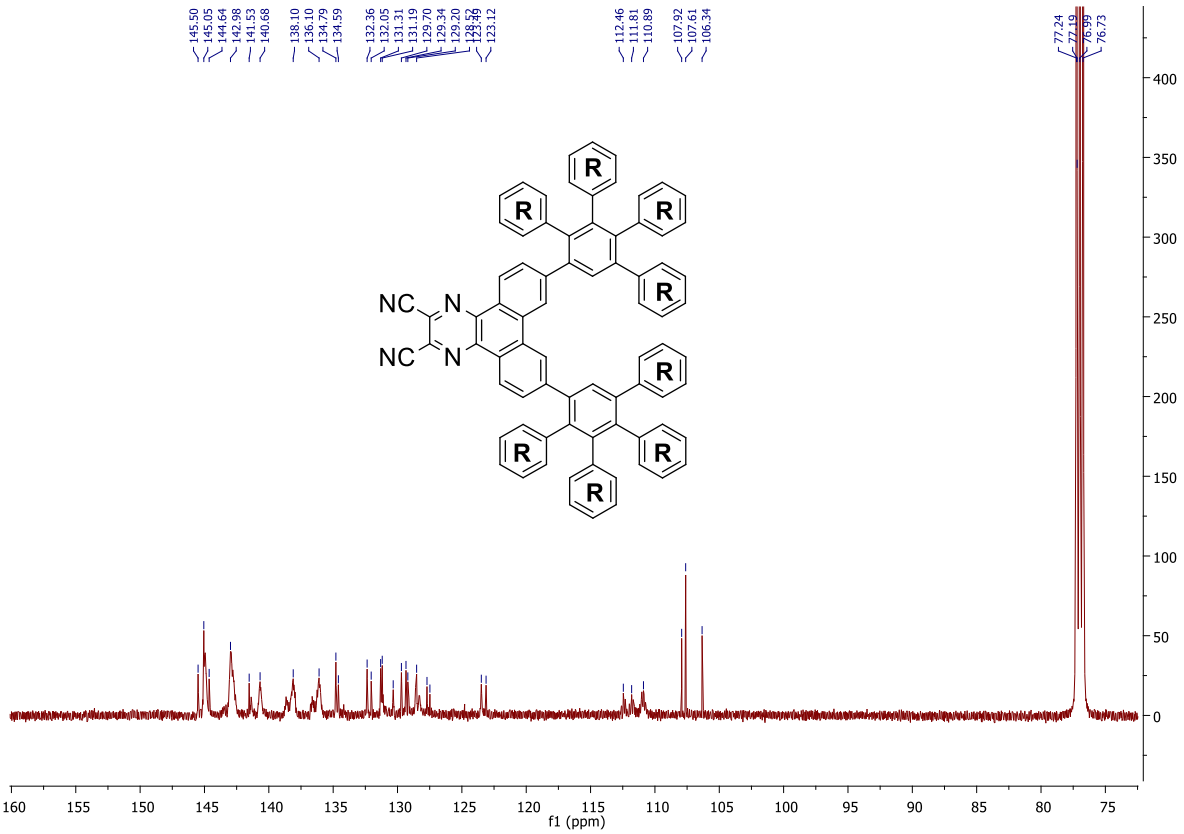

-137.78
-138.45
-138.61
-139.81
-149.22
-149.43
-150.12
-150.78
-159.41
-159.55
-159.91
-159.97
-160.15
-160.21
-160.29
= pentafluorophenyl
f1 (ppm)


145.88
145.63
143.14
140.83
140.31
138.74
136.25
135.28
134.06
133.39
131.43
131.29
129.56
129.37
127.16
124.56
112.94
112.30
111.64
111.45
92.56
77.80
77.68
77.48
77.16
61.83
= pentafluorophenyl
f1 (ppm)

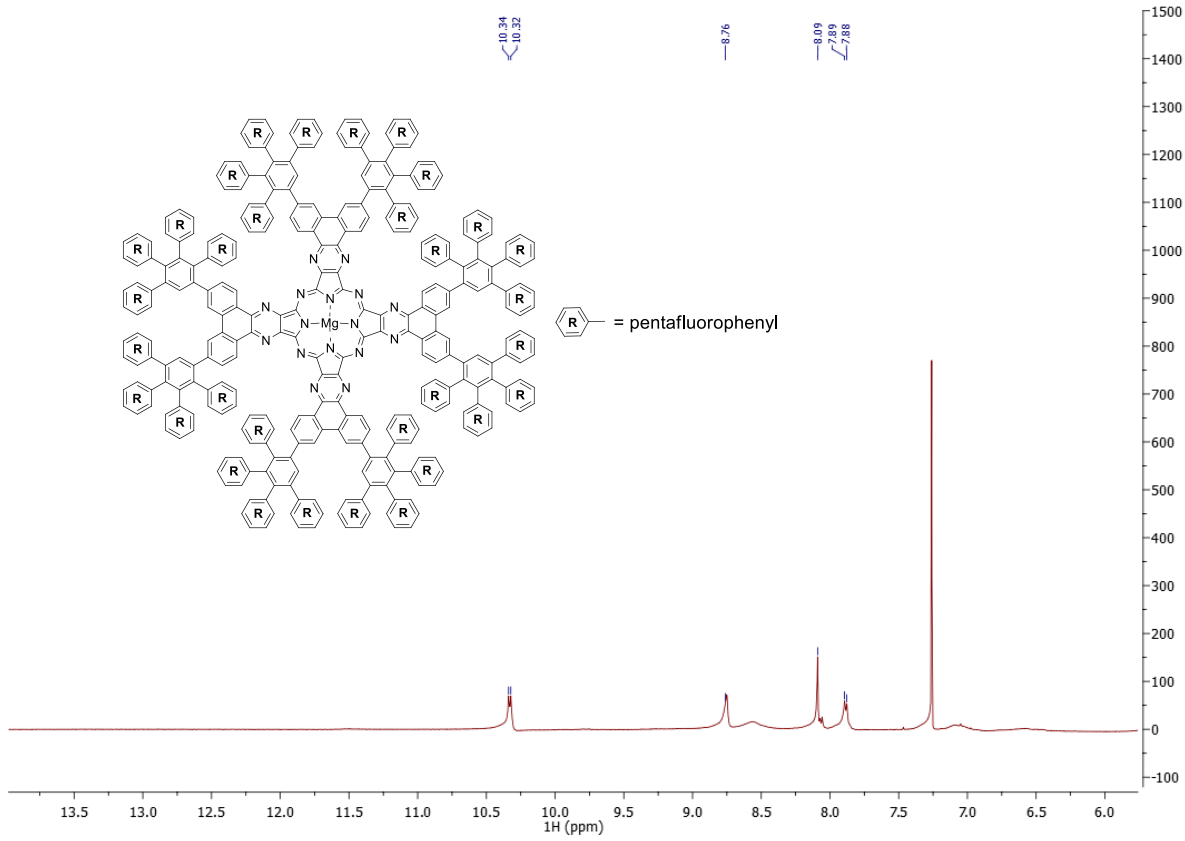
Compound **8**

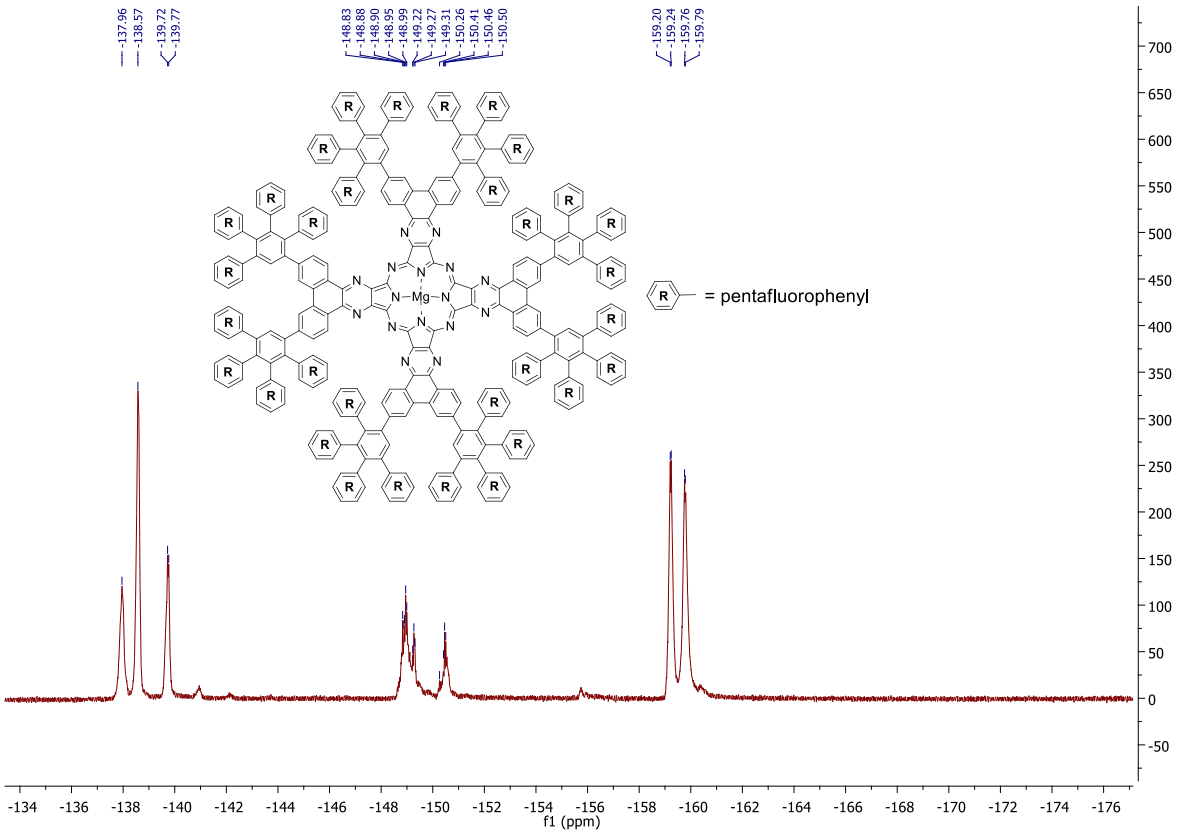

9.15
9.13
8.47
7.87
7.63
7.62
7.60
NC
N
NC
N
R
f1 (ppm)

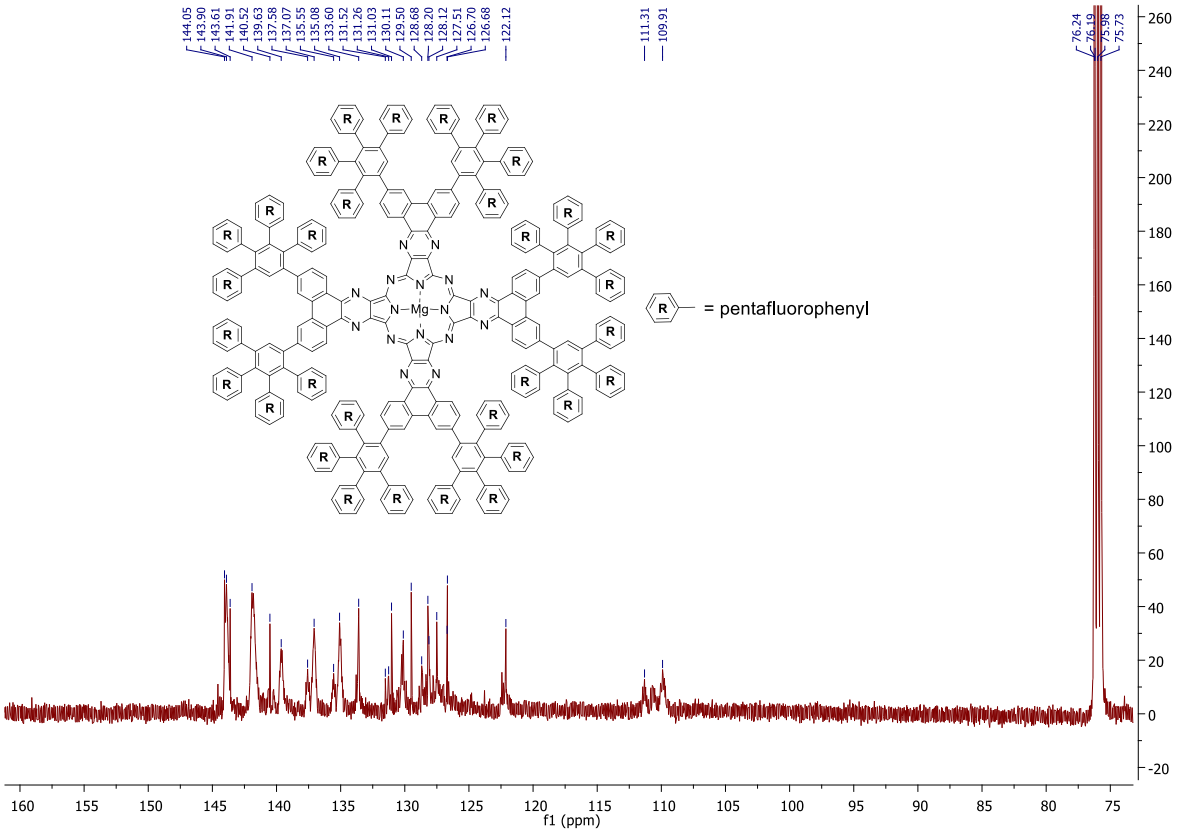

-137.97
-138.65
-139.79
-148.62
-148.68
-148.76
-148.81
-149.06
-149.12
-150.20
-150.25
-150.31
-159.13
-159.62
-159.68
NC
N
NC
N
R
f1 (ppm)



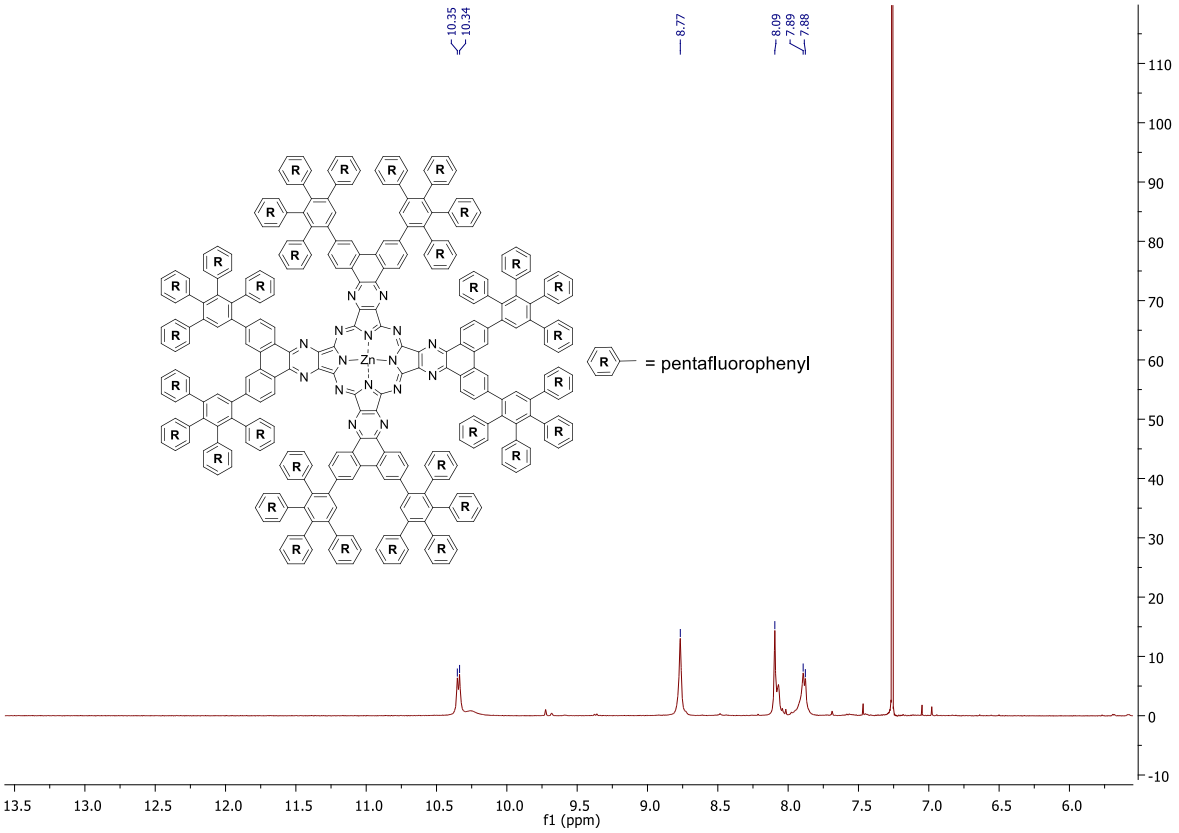
Compound **1-Mg**

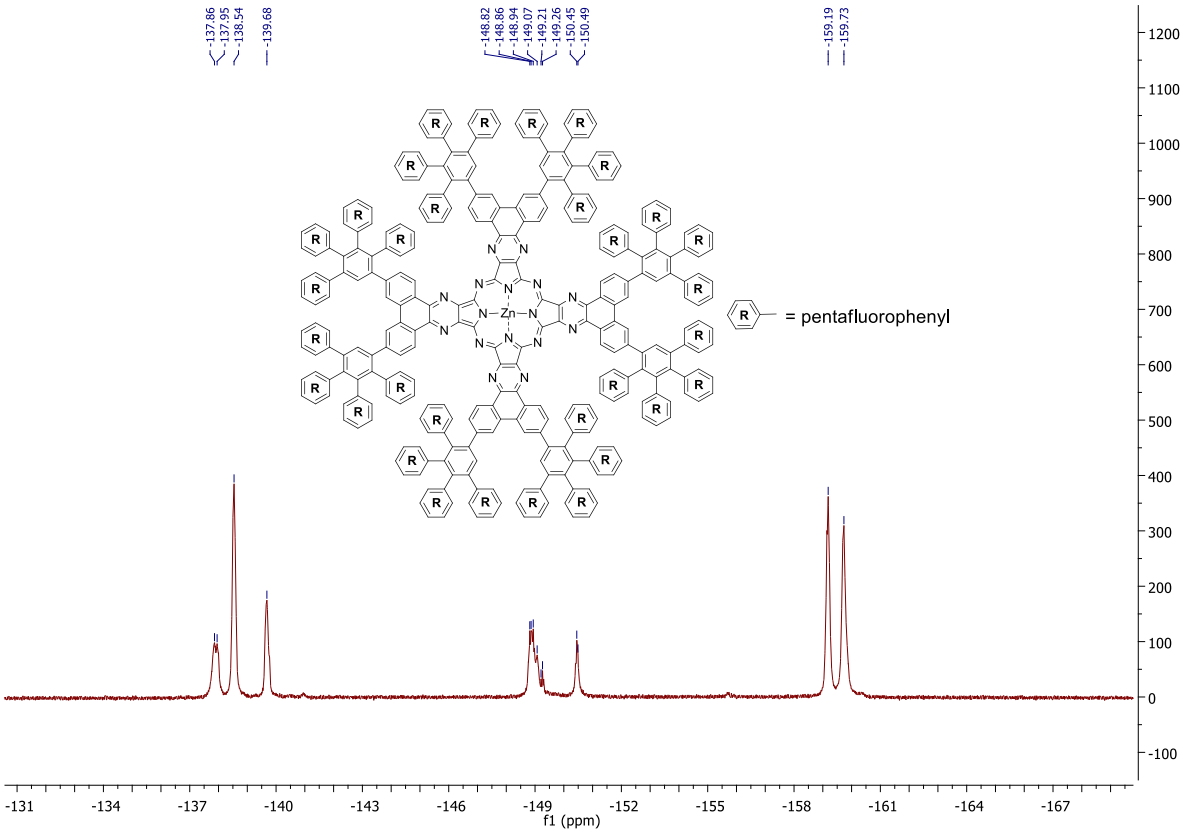


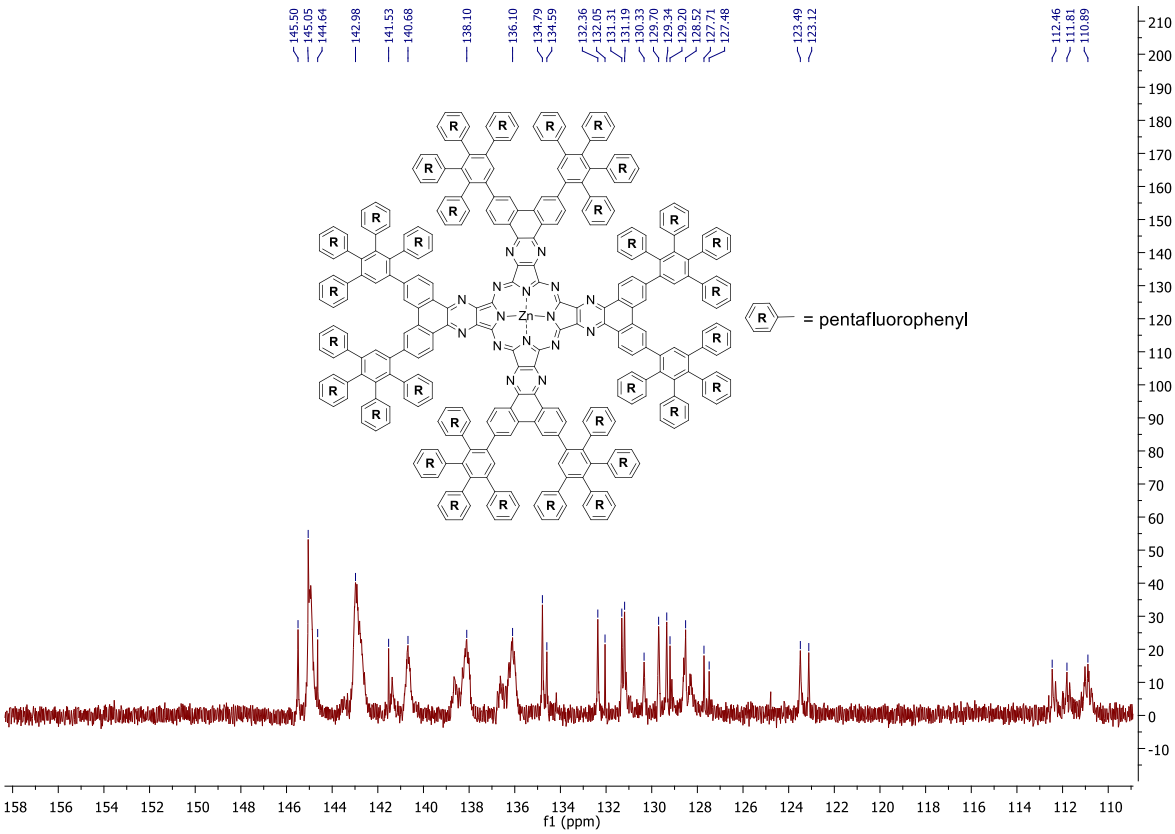

-137.96
-138.57
-139.72
-139.77
-148.83
-148.88
-148.90
-148.95
-148.99
-149.22
-149.27
-149.31
-150.26
-150.41
-150.46
-150.50
-159.20
-159.24
-159.76
-159.79
= pentafluorophenyl
f1 (ppm)


144.05
143.90
143.61
141.91
140.52
139.63
137.58
137.07
135.55
135.08
133.60
131.52
131.26
131.03
130.11
129.50
128.68
128.20
128.12
127.51
126.70
126.68
122.12
111.31
109.91
76.24
76.19
75.98
75.73
= pentafluorophenyl
f1 (ppm)

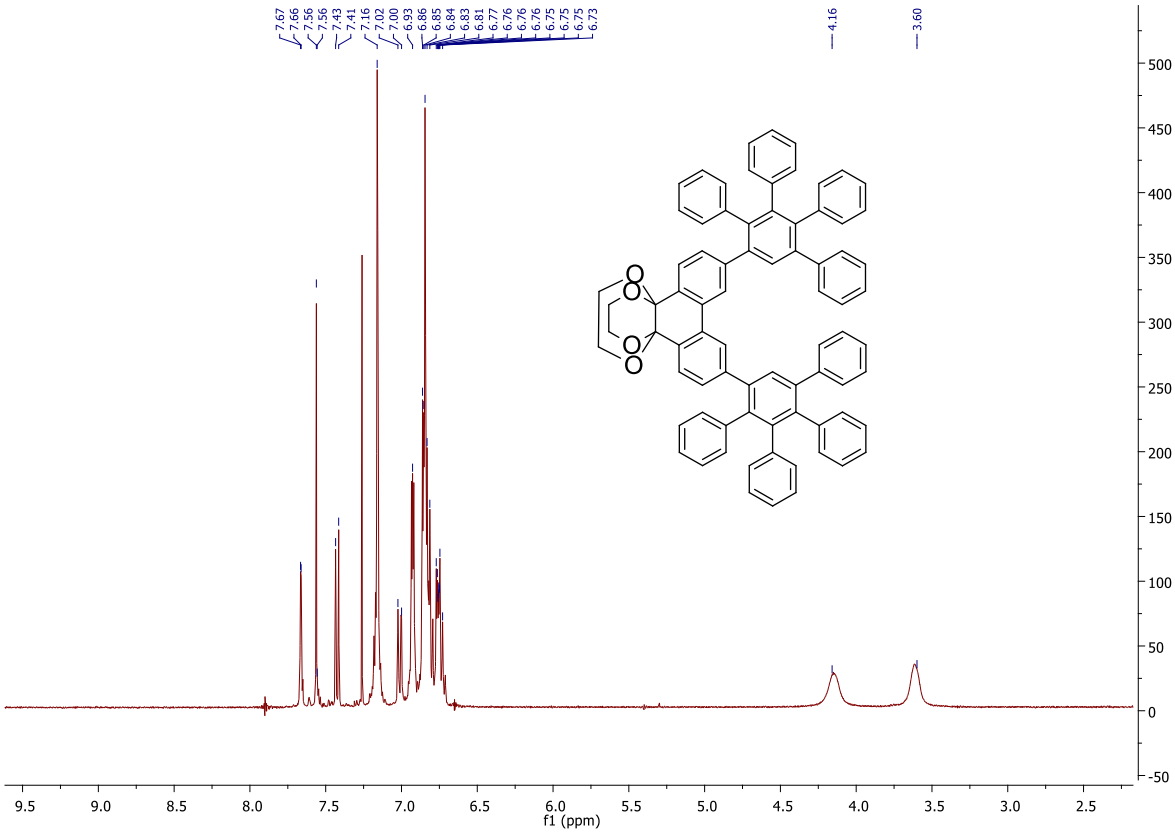
Compound **1**

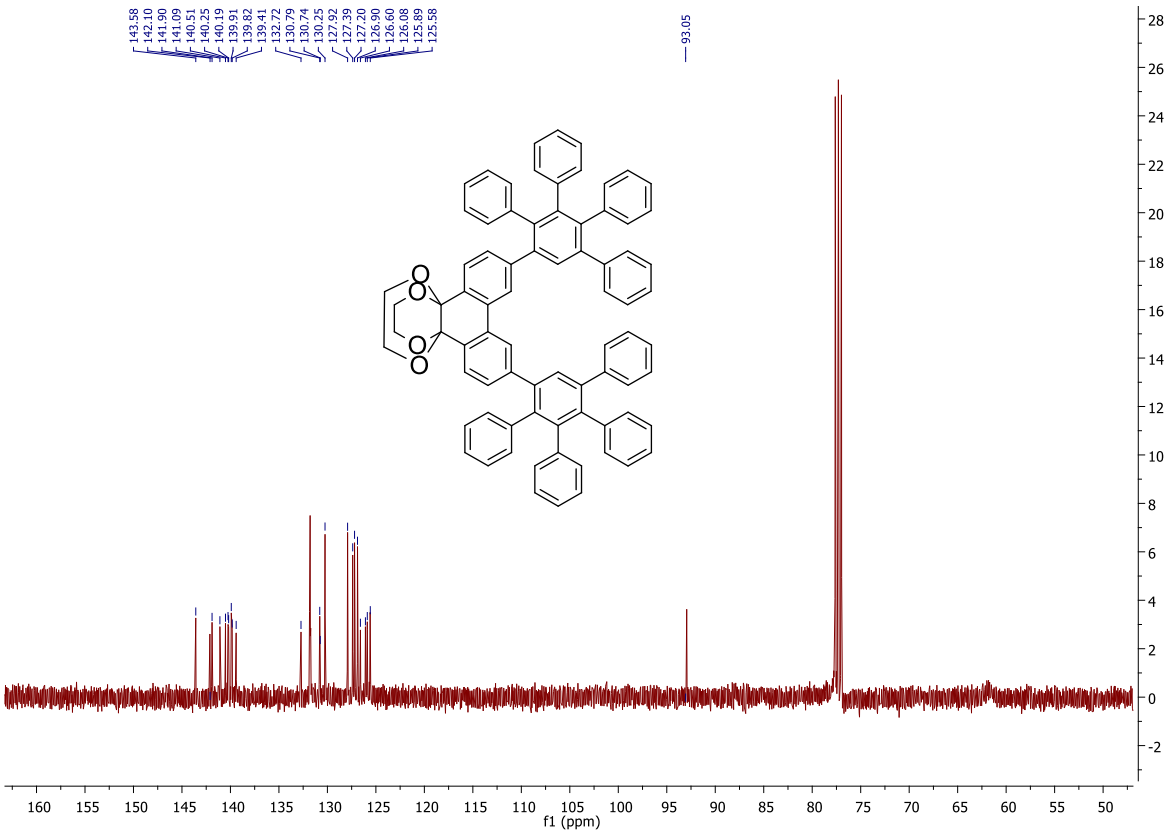

10.35
10.34
8.77
8.09
7.89
7.88
= pentafluorophenyl
f1 (ppm)


-137.86
-137.95
-138.54
-139.68
-148.82
-148.86
-148.94
-149.07
-149.21
-149.26
-150.45
-150.49
-159.19
-159.73
= pentafluorophenyl
f1 (ppm)

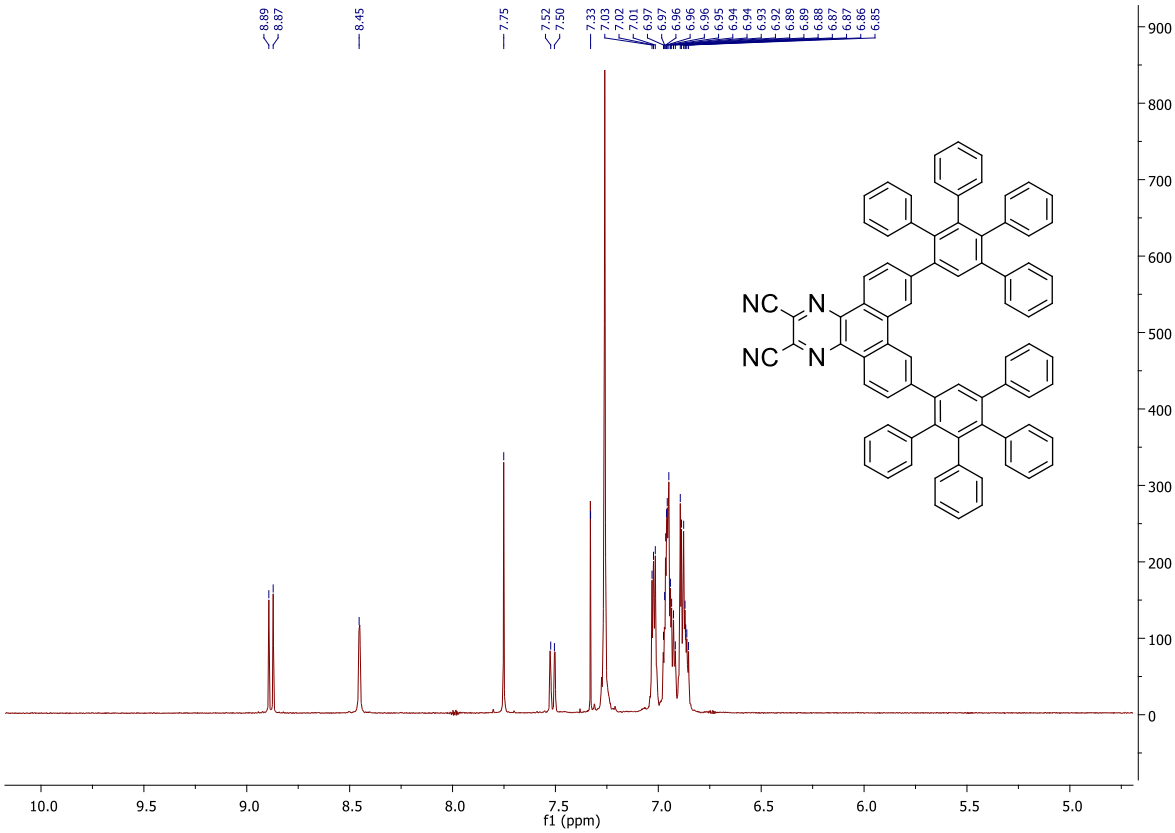

145.50
145.05
144.64
142.98
141.53
140.68
138.10
136.10
134.79
134.59
132.36
132.05
131.31
131.19
130.33
129.70
129.34
129.20
128.52
127.71
127.48
123.49
123.12
112.46
111.81
110.89
= pentafluorophenyl
f1 (ppm)

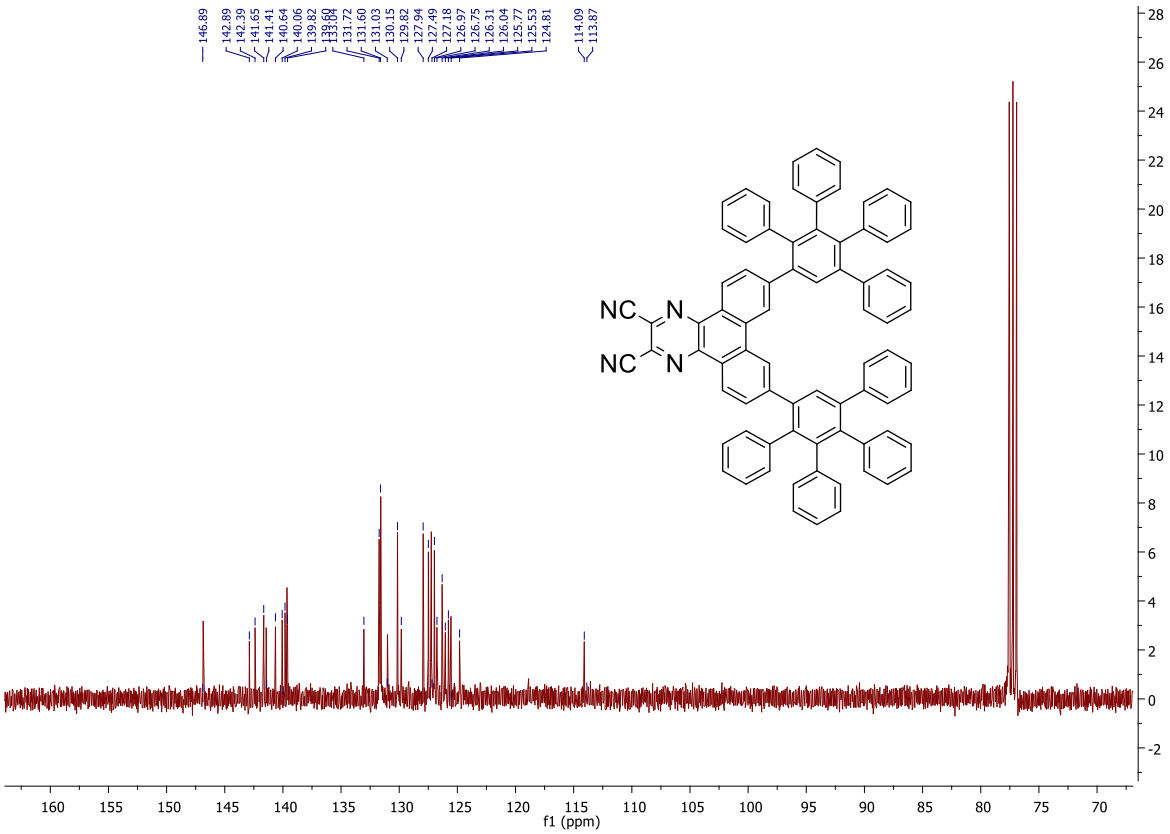
Compound **7a**


7.67
7.66
7.56
7.55
7.43
7.41
7.16
7.02
7.00
6.93
6.86
6.85
6.84
6.83
6.81
6.77
6.76
6.76
6.76
6.75
6.75
6.75
6.73
4.16
3.60
f1 (ppm)

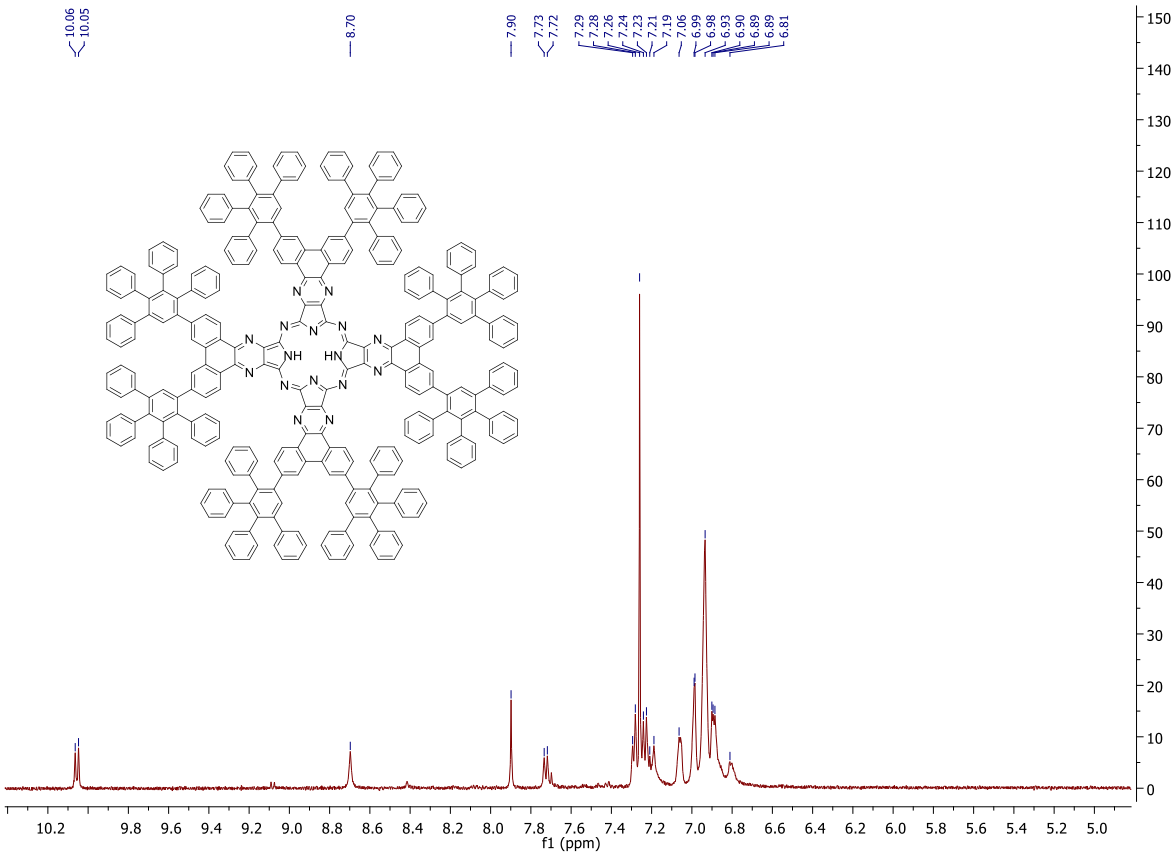

143.58
142.10
141.90
141.09
140.51
140.25
140.19
139.91
139.82
139.41
132.72
130.79
130.74
130.25
127.92
127.39
127.20
126.90
126.60
126.08
125.89
125.58
93.05
f1 (ppm)

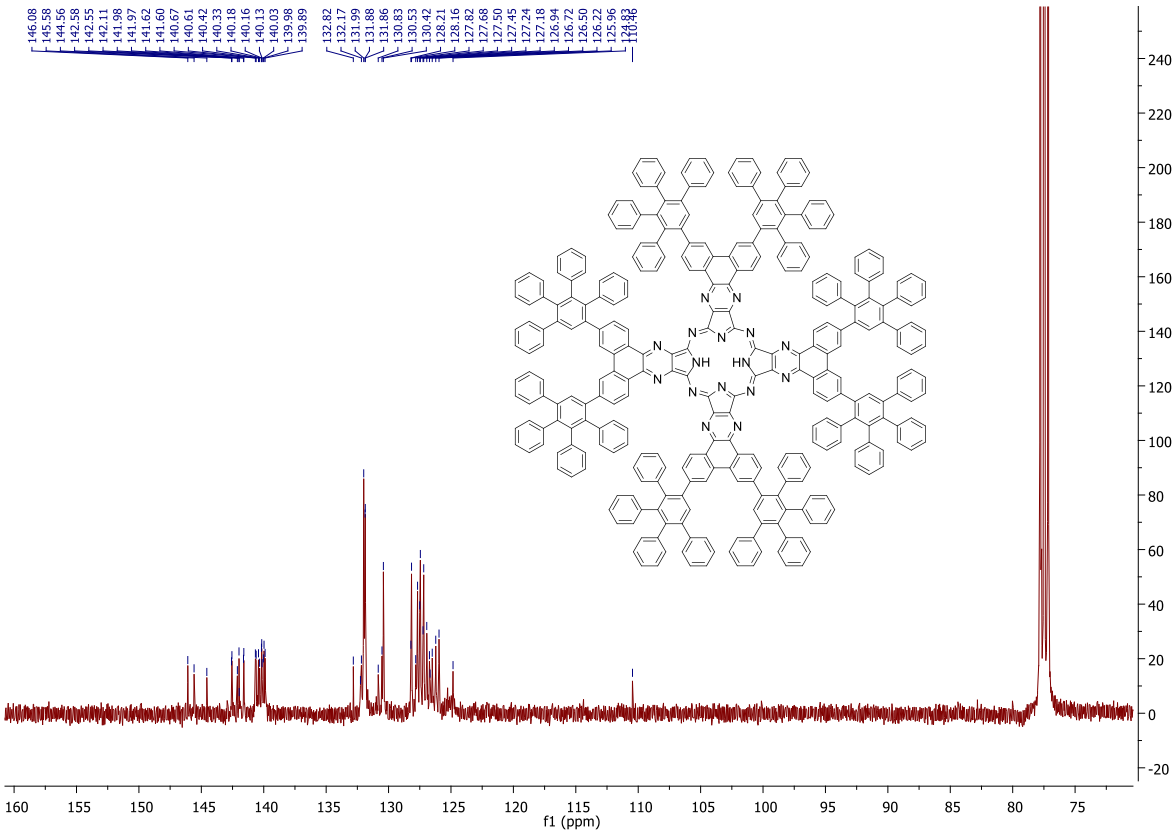
Compound **8a**


8.89
8.87
8.45
7.75
7.52
7.50
7.33
NC
N
NC
N
f1 (ppm)

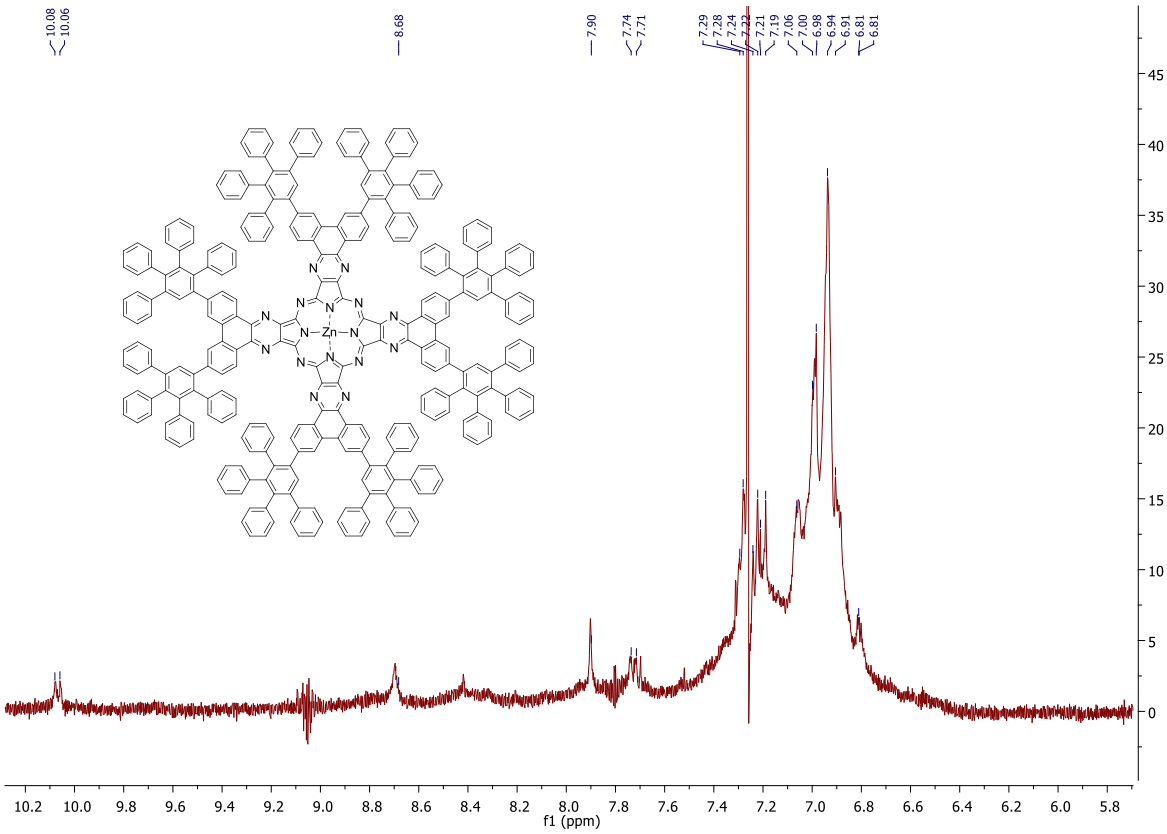

146.89
142.89
142.39
141.65
141.41
140.64
140.06
139.82
131.72
131.60
131.03
130.15
129.82
127.94
127.49
127.18
126.97
126.75
126.31
126.04
125.77
125.53
124.81
114.09
113.87
NC
N
NC
N
f1 (ppm)

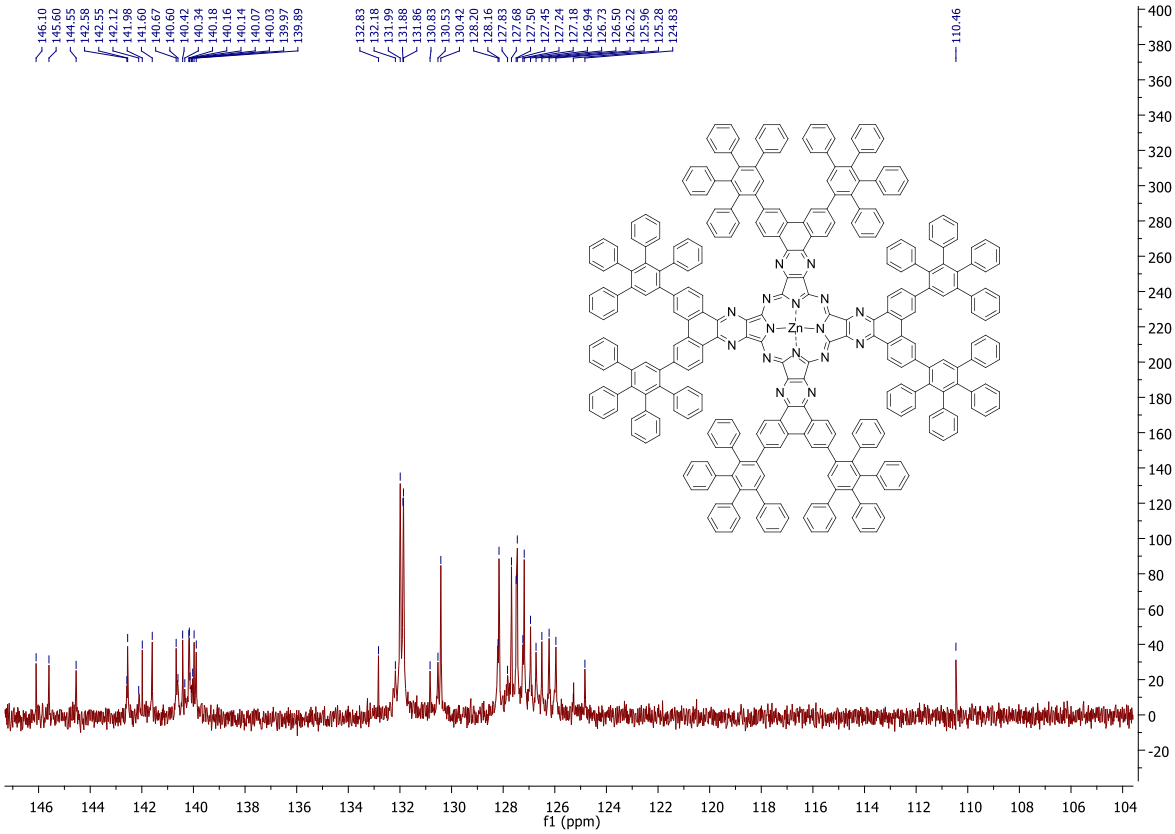
Compound **2a**


10.06
10.05
8.70
7.90
7.73
7.72
7.29
7.28
7.26
7.24
7.23
7.21
7.19
7.06
6.99
6.98
6.93
6.90
6.89
6.89
6.81
NH
HN
f1 (ppm)


146.08
145.58
144.56
142.58
142.55
142.11
141.98
141.97
141.62
141.60
140.67
140.61
140.42
140.33
140.18
140.16
140.13
140.03
139.98
139.89
132.82
132.17
131.99
131.88
131.86
130.83
130.53
130.42
128.21
128.16
127.82
127.68
127.50
127.45
127.24
127.18
126.94
126.72
126.50
126.22
125.96
110.48
f1 (ppm)

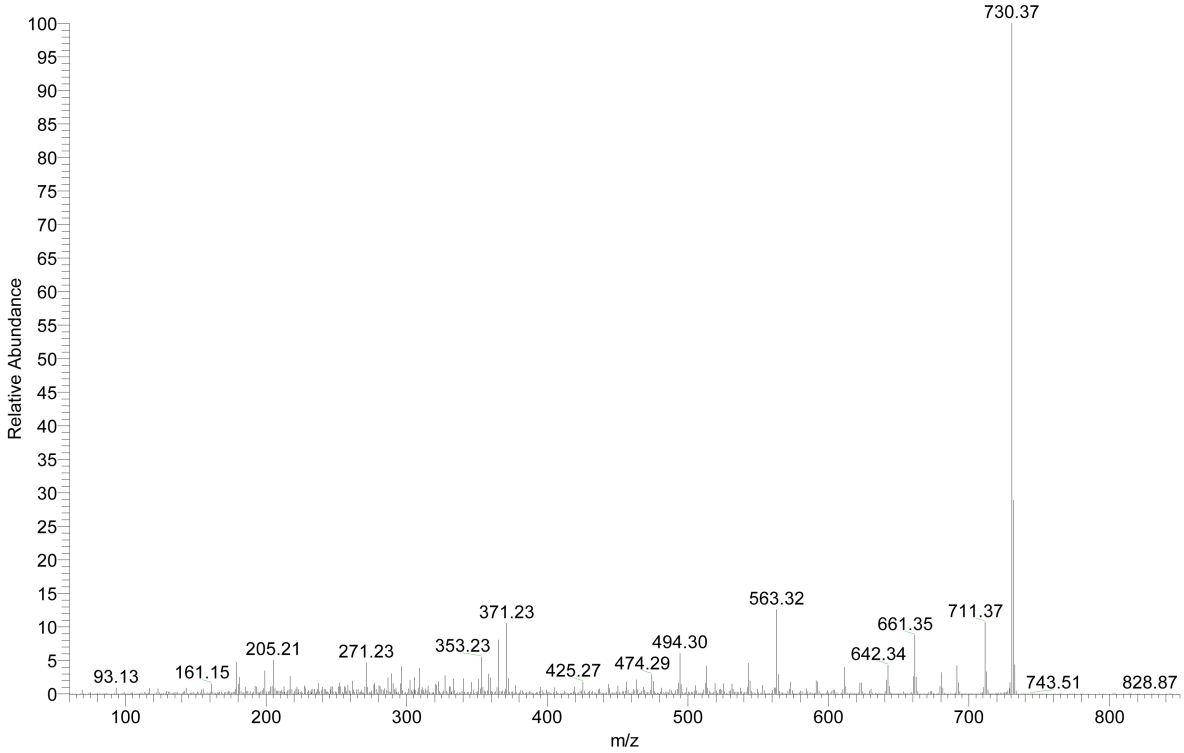
Compound **2**


10.08
10.06
8.68
7.90
7.74
7.71
7.29
7.28
7.24
7.22
7.21
7.19
7.06
7.00
6.98
6.94
6.91
6.81
6.81
f1 (ppm)

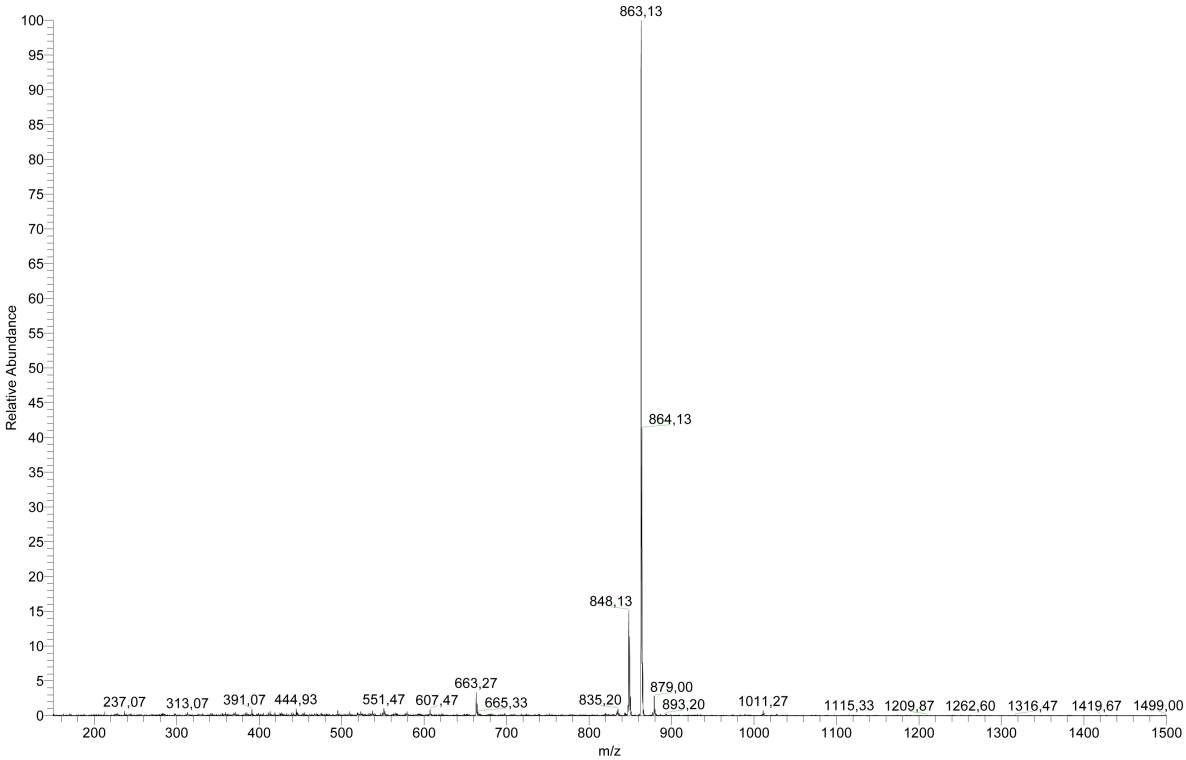

146.10
145.60
144.55
142.58
142.55
142.12
141.98
141.60
140.67
140.60
140.42
140.34
140.18
140.16
140.14
140.07
140.03
139.97
139.89
132.83
132.18
131.99
131.88
131.86
130.83
130.53
130.42
128.20
128.16
127.83
127.68
127.50
127.45
127.24
127.18
126.94
126.73
126.50
126.22
125.96
125.28
124.83
110.46
Zn
f1 (ppm)

Mass spectra

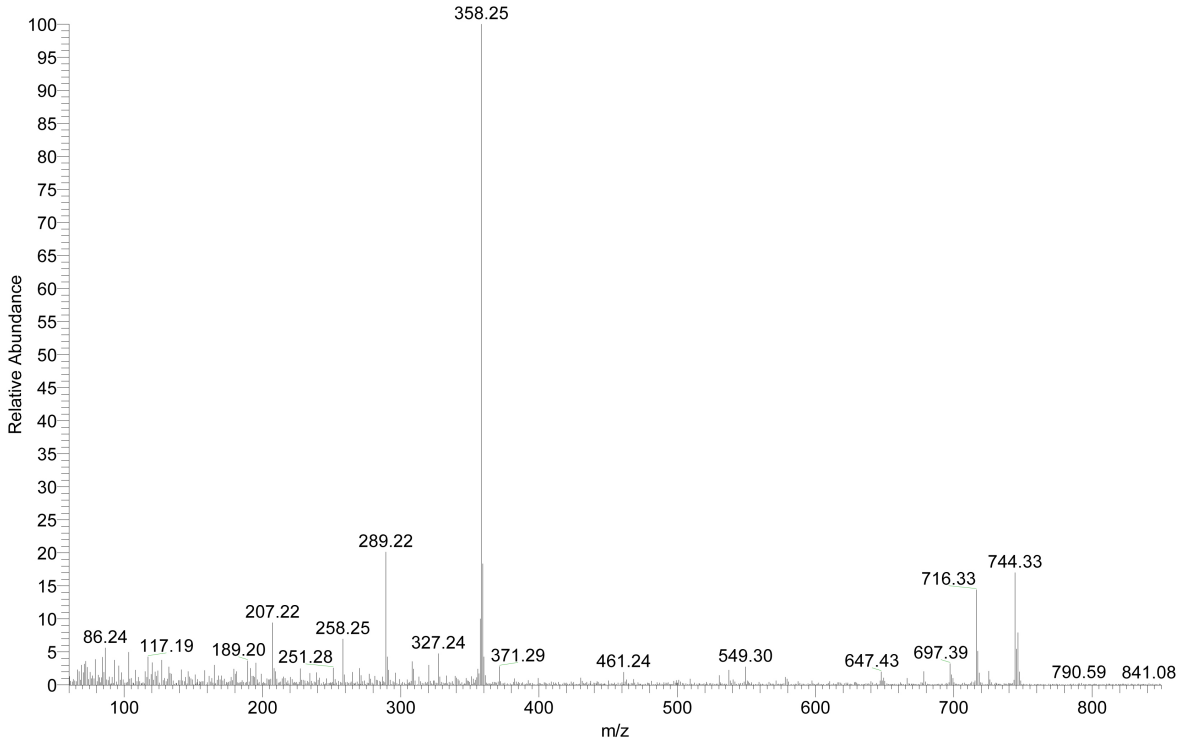
Compound **3**



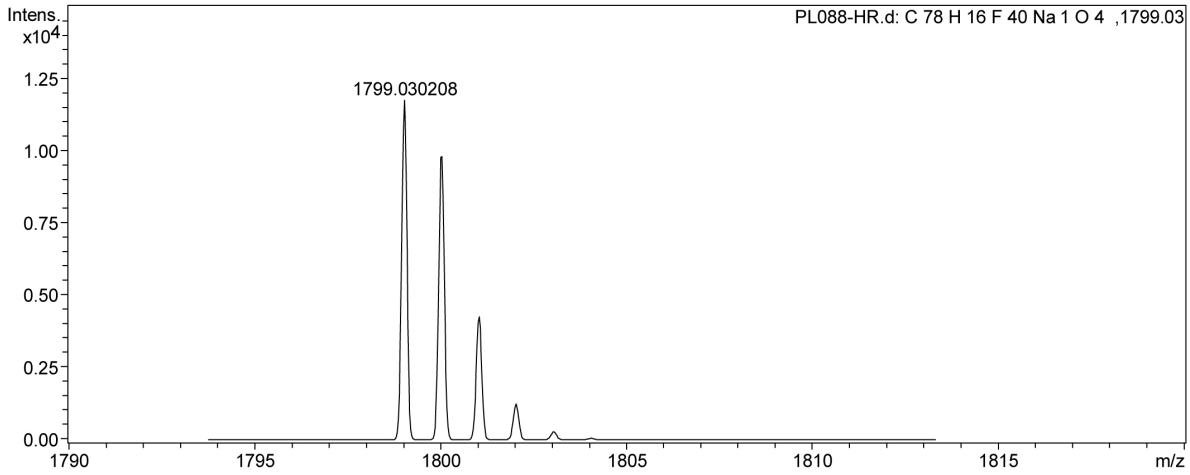
Compound **4**



Compound **5**

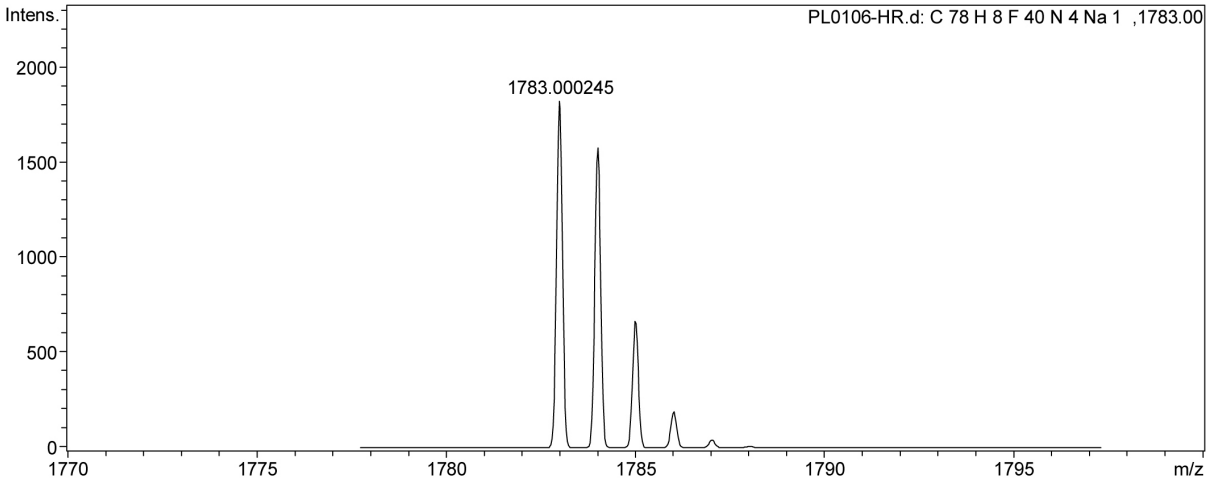


Compound **7**



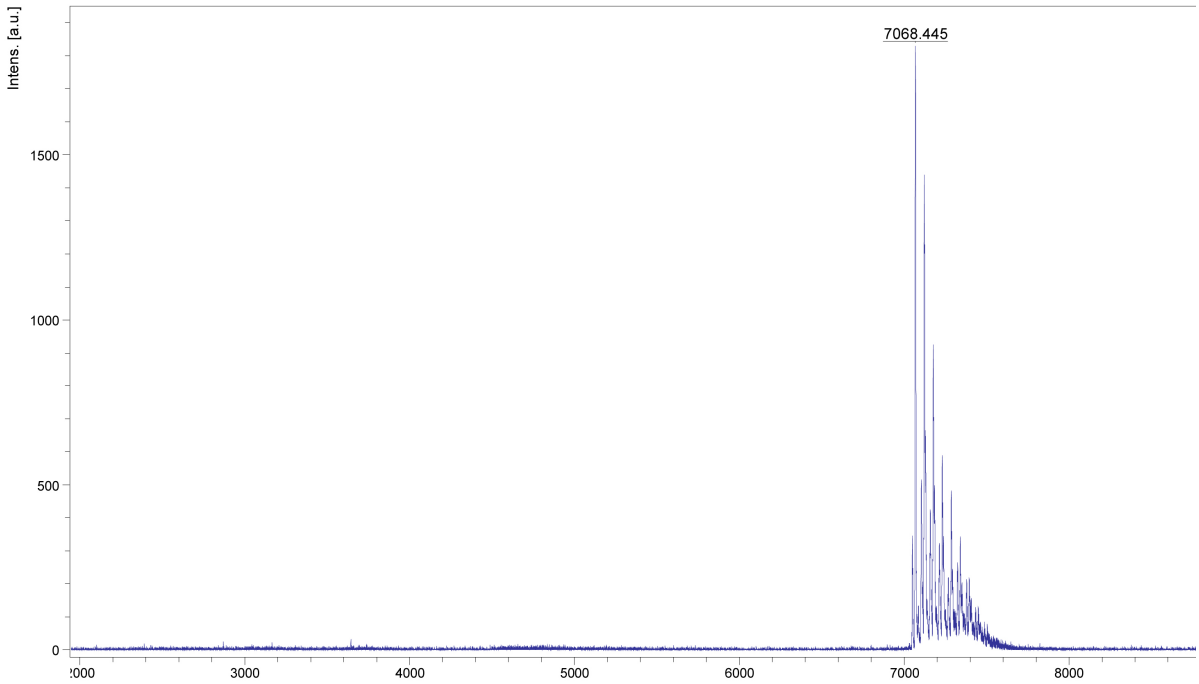
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 78 H 16 F 40 Na 1 O 4	0.01	1799.030208	-1.31	-0.80	50.50	ok	even

Compound **8**

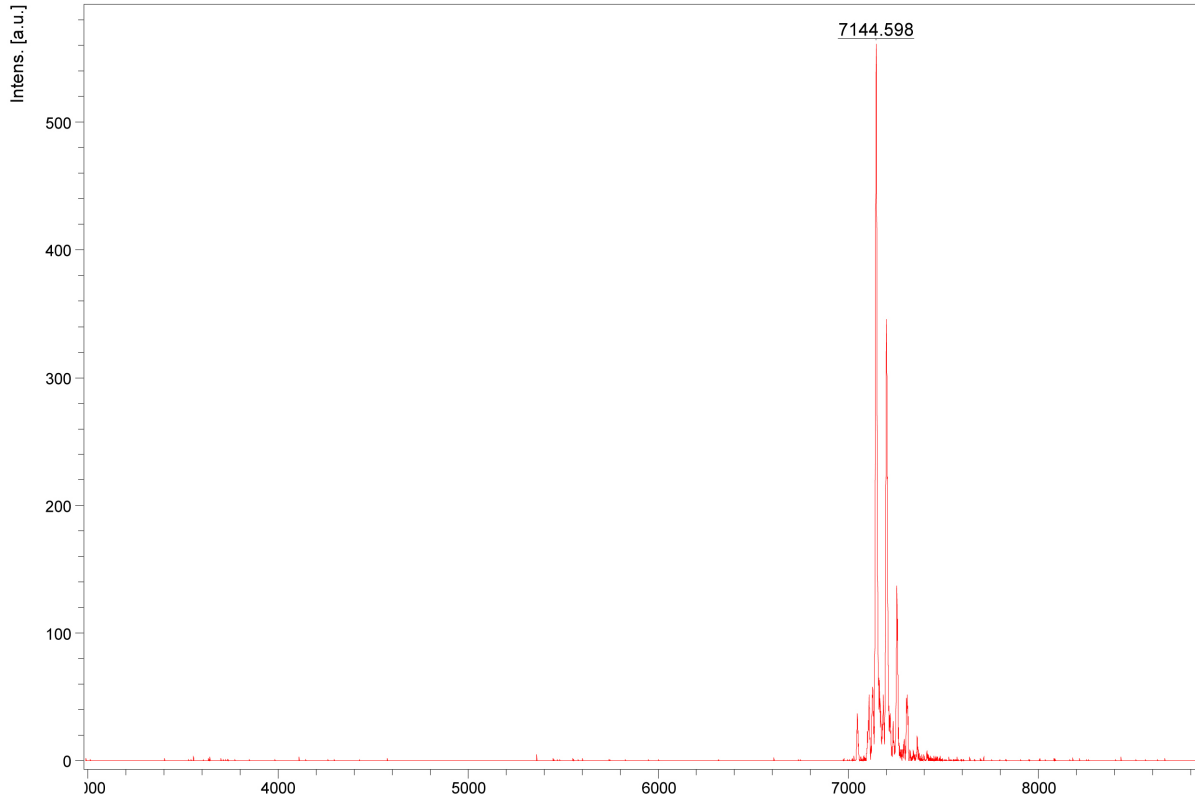


Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 78 H 8 F 40 N 4 Na 1	0.01	1783.000245	-0.22	-0.69	56.50	ok	even

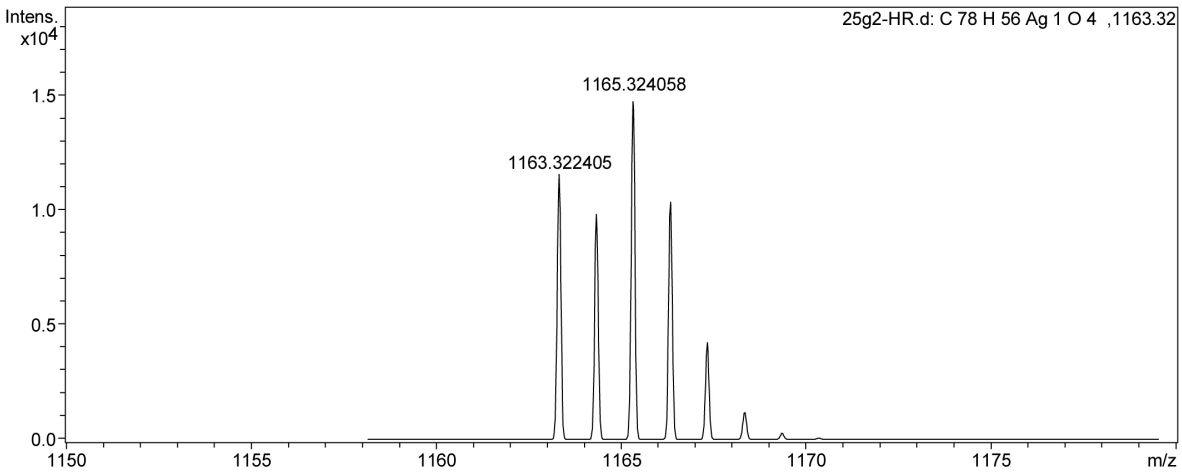
Compound **1-Mg**



Compound **1**

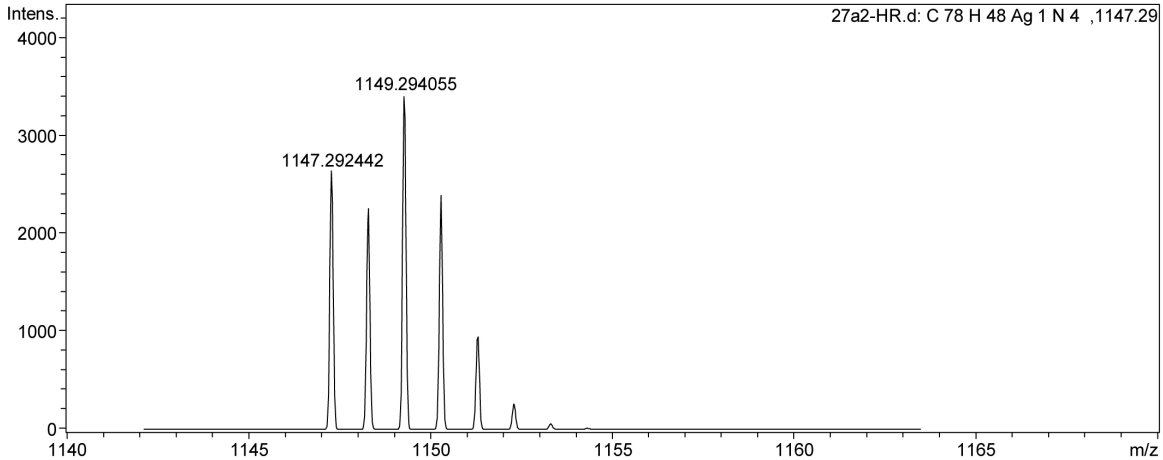


Compound **7a**



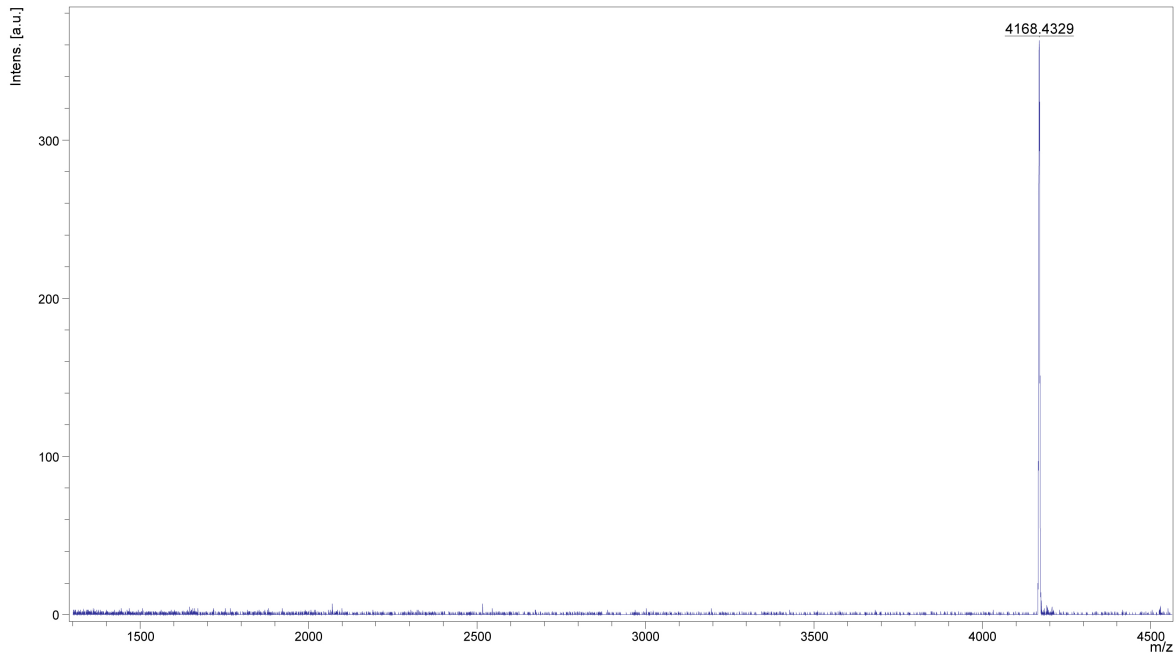
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 78 H 56 Ag 1 O 4	0.02	1163.322405	-0.24	-0.01	50.50	ok	even

Compound **8a**

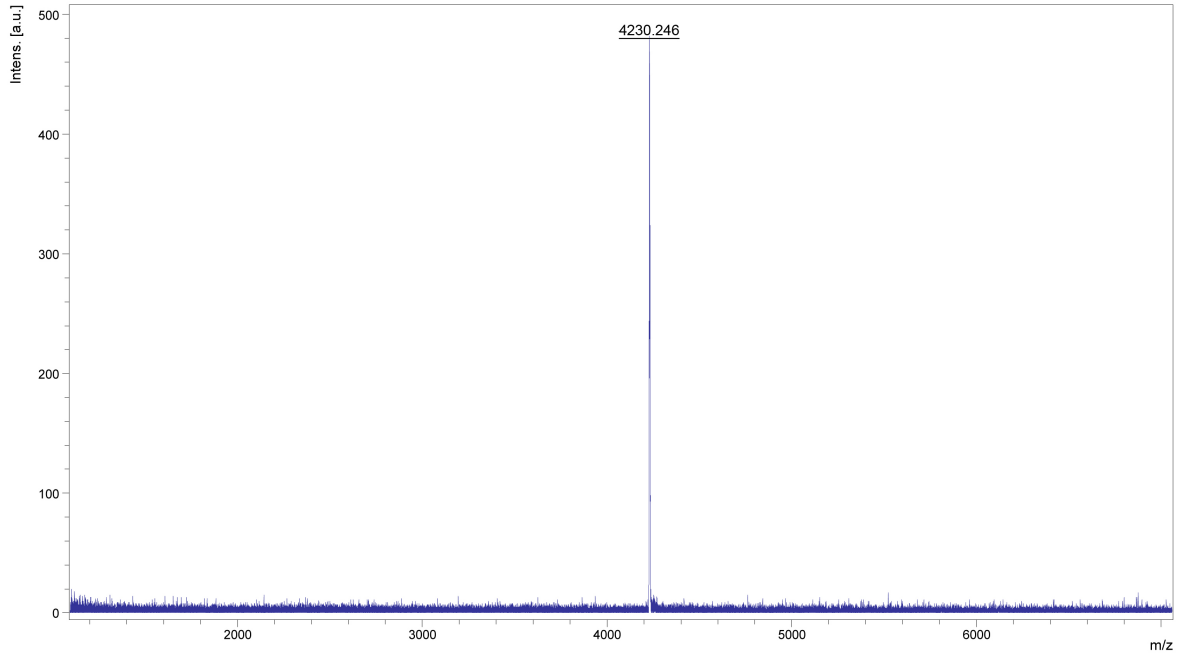


Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	rdb	N Rule	e⁻
C 78 H 48 Ag 1 N 4	0.02	1147.292442	-0.43	-0.37	56.50	ok	even

Compound **2a**



Compound **2**


Intens. [a.u.]
500
400
300
200
100
0
4230.246
2000
3000
4000
5000
6000
m/z

Cyclovoltammograms

Fluorinated Pc (**1**):

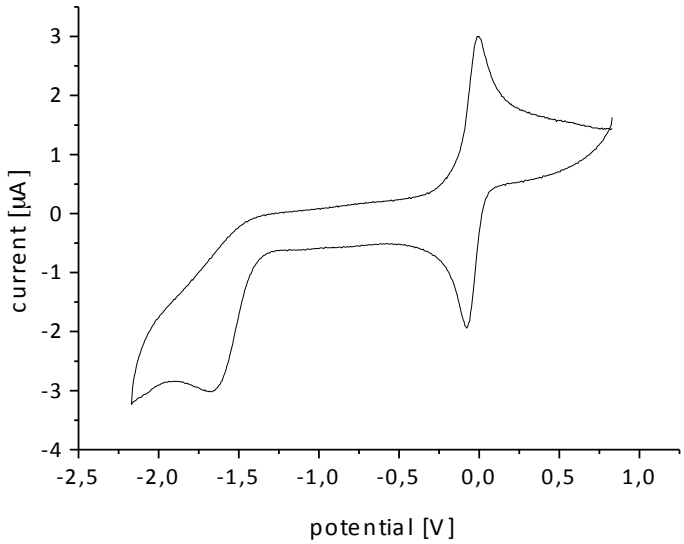


Fig. 1: Cyclovoltammogram of **1** in DCM with tetrabutylammonium hexafluorophosphate as conducting salt and ferrocene as internal reference.

Unfluorinated model compound (**2**):

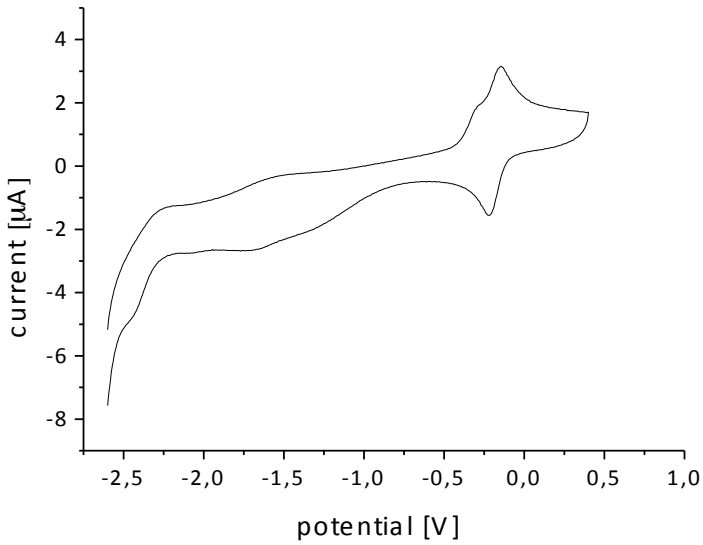


Fig. 2: Cyclovoltammogram of **2** in DCM with tetrabutylammonium hexafluorophosphate as conducting salt and ferrocene as internal reference.

References

1. F. Wilkinson, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113.
2. M. P. Thornberry, C. Slebodnick, P. A. Deck and F. R. Fronczek, *Organometallics*, 2001, **20**, 920.
3. T. K. Panda, M. T. Gamer and P. W. Roesky, *Organometallics*, 2003, **22**, 877.
4. R. Bauer, D. Liu, A. V. Heyen, F. D. Schryver, S. D. Feyter and K. Müllen, *Macromolecules*, 2007, **40**, 4753.
5. Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, C. Yu-Hung, L. B. Alemany, T. Sasaki, J.-F. Morin, J. M. Guerrero, K. F. Kelly and J. M. Tour, *J. Am. Chem. Soc.*, 2006, 128, 4854