Electronic Supplementary Material (ESI) for Analyst.

Electronic supporting material

Absorption and Fluorescence:

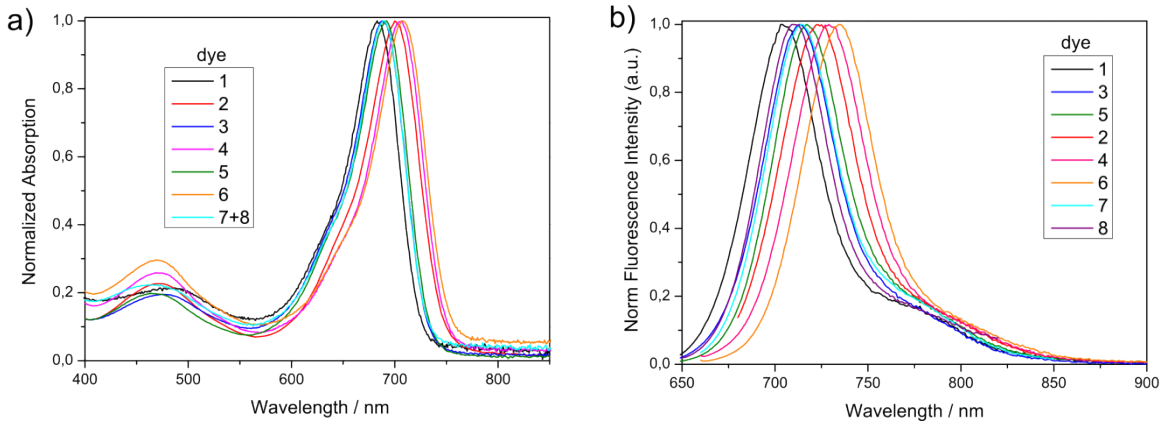


Figure S1. Normalized absorption (a) and fluorescence (b)of dyes (1-8)

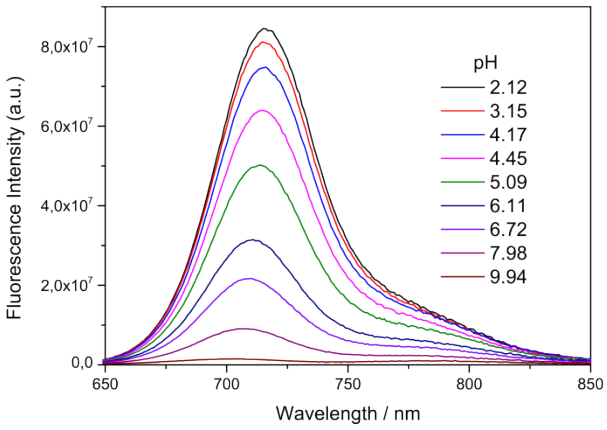


Figure S2. pH dependence of fluorescence emission of the novel broad-range pH sensor based on the mixture of dyes 1,2,3,5.

Table S1. Boltzmann equation

Model	Boltzmann
Equation	y = A2 + (A1-A2)/(1 + exp((x-x0)/dx))

Table S2. Parameters of the non-linear curve fit (Boltzmann) of broad-range sensor

A1	A2	x0	dx	R^2
7,57E+07	1,44E+06	5,14789	0,92544	0,99851

Leaching test

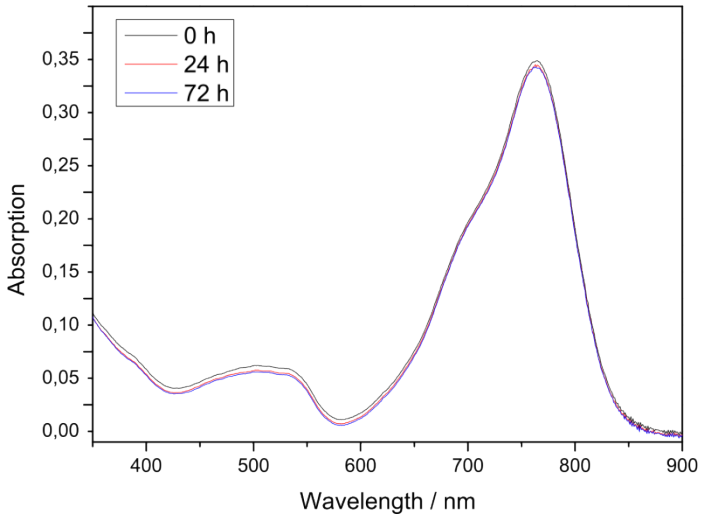


Figure S3. Absorption spectra of the broad-range sensor (dye 1,2,3,5) under continuous flushing with aqueous buffer (pH 9.2, IS 150mM). No leaching is observed.

Photostability

Photobleaching experiments of the broad-range pH sensor were performed by irradiating the samples with the light of a 642-nm high-power 10W LED array (~ 6300 µmol $s^{-1}m^{-2}$). In fact, continuous illumination for over 3 hours caused no changes in the absorption. This corresponds to ~72 000 000 measurements points if the sensor is read out with a phase fluorometer (Pyroscience oxygen meter) which equals the measurement time of 2.3 years (measurement frequency is set to one point per second).

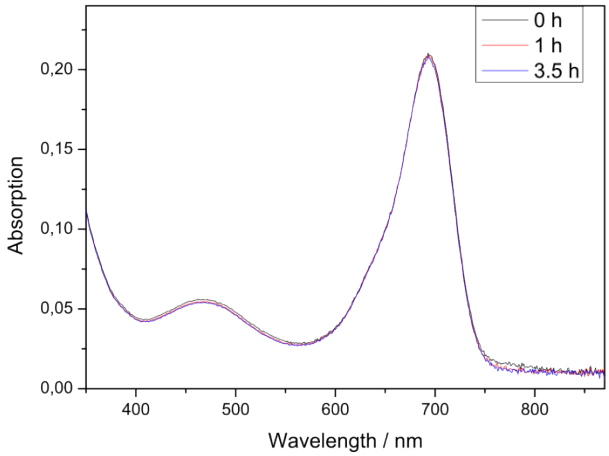
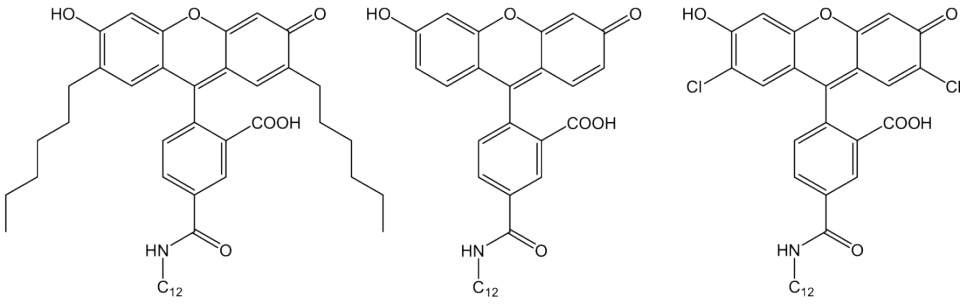


Figure S4. Absorption spectra of the broad-range sensor under continuous irradiation with a high-power LED.

Comparison with Fluorescein derivatives:

Figure S5 shows a broad-range pH sensor based on three lipophilic fluorescein derivatives. However, the pK_a determining functionalities have significant effect on the photostability of the indicator dyes respectively. Consequently, after irradiating the pH sensor with the light of high power 10 W LED array (λ_{max} 458nm, ~ 3900 µmol $s^{-1}m^{-2}$) for 30 minutes, the calibration curve is considerably altered due to photo-bleaching of the less photo-stable 2,7'dihexyl-fluorescein-octadodecylamide. This exemplifies that other classes of pH indicator dyes (here fluorescein) are not suitable for the development of a broad-range sensor due to different photo-degradation rates.



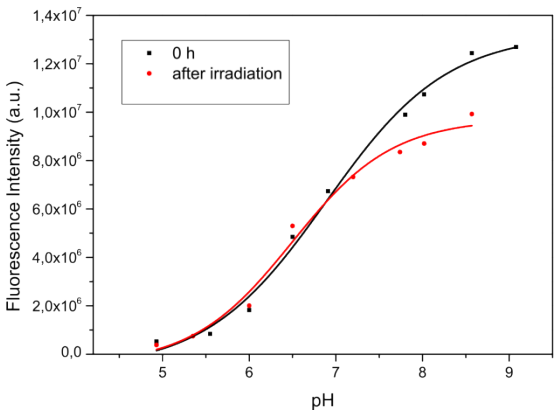


Figure S5 up: Chemical Structures of the used fluorescein derivatives. Below: calibration curve of the sensor before and after irradiation with blue LED.

Aggregation test

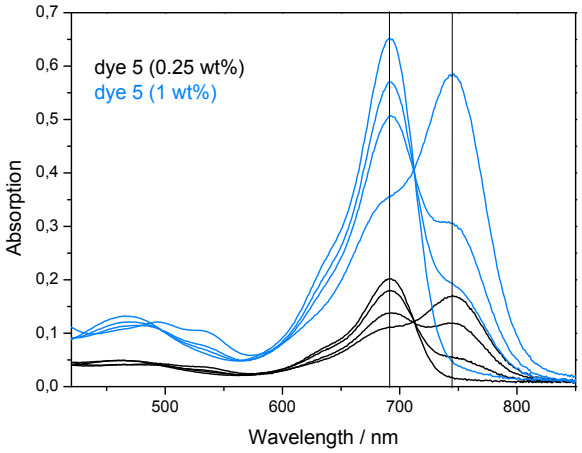


Figure S6 Absorption spectra of two pH sensors with different concentrations of dye (probe 5, 0.25 wt% and 1wt%, respectively), physically entrapped in hydrogel D4 at different pH. No aggregation is observed.

The new aza-BODIPY dyes exhibit pronounced hydrophobicity, which may favour aggregation when physically entrapped in hydrophilic host polymer. Thus, pH sensors with different dye concentrations (probe **5**, 0.25 wt% and 1wt%, respectively) were prepared and their potential aggregation at different pH was investigated via absorption measurements. No aggregation could be observed, even at high dye concentrations. The form of the absorption peaks is not changed and the absorption maxima of the (de)protonated form (690 nm and 745 nm, respectively) are not batho- or hypsochromically shifted. The isobestic point is observed and remains at 711 nm when increasing the dye concentration from 0.25 to 1wt% in D4. This indicates that the dyes are present in monomeric form in hydrogel D4.

Materials

4'-butoxyactophenone, 4'-acetylbenzoic acid, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, diisopropylethylamine, benzaldehyde and boron trifluoride diethyl etherate were purchased from TCI Europe (http://www.tcichemicals.com/en/eu/). 3',5' Dichloro-4'-hydroxyacetophenone was obtained from AApin Chemicals. (http://www.apinchemicals.com/) and 4'-hydroxychalcone was bought from ABCR (http://www.abcr.de/startseite/). 3'-Chloro-4'-hydroxyacetophenone, nitromethane, ammonium acetate, dodecylamine, 1-hydroxybenzotriazole hydrate, MOPS buffer and anhydrous sodium sulfate were purchased from Sigma Aldrich (http://www.sigmaaldrich.com/austria.html). Deuterated chloroform ($CDCl_3$) and dimethyl sulfoxide (DMSO-d_6) were obtained from Euriso-top (www.eurisotop.com). All other solvents (synthesis grade) as well as sodium chloride and the buffer salts (MES, HEPES, and CHES) were purchased from Carl Roth (www.roth.de). Silica-gel (0.04-0.063 mm) was bought from Acros (www.fishersci.com). Polyurethane hydrogel (Hydromed D4) was purchased from AdvanSource biomaterials (www.advbiomaterials.com). Poly-(ethylene glycol terephthalate) support (Mylar) was from Pütz (http://www.puetz-folien.com/wb/pages/englisch/home.php).

Methods

Absorption measurements were performed on a Cary 50 UV-VIS spectrophotometer from Varian, Palo Alto, United States (www.varianinc.com) at medium scan rate using baseline correction and an adequate blank sample.

Fluorescence spectra of dye solutions were recorded on a Hitachi-F-7000 spectrofluorometer (www.hitachi.com), equipped with a R980 photomultiplier and corrected for detector response. Fluorescence measurements for the pH sensors were performed on a Fluorolog3 spectrofluorimeter (Horiba J. Y., www.horiba.com) equipped with a NIR-sensitive photomultiplier R2658 from Hamamatsu (300-1050 nm). Relative fluorescence quantum yields were determined by using tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine as a standard (ϕ = 0.44, Fluka, www.sigmaaldrich.com) according to Demas and Crosby[1].

The pH of the buffer solution (acetate, MES, HEPES, CHES) was adjusted with a pH meter using a glass electrode (InoLab pH/ion, WTW GmbH & Co. KG, www.wtw.com). The pH meter was calibrated at 25°C with standard buffers of pH 7.01 and pH 4.01 (WTW GmbH & Co. KG, www.wtw.com). Ionic strength (IS = 150mM) of the buffers was adjusted by using sodium chloride as the background electrolyte.

The NMR spectroscopic experiments were performed on a 300 MHz instrument (Bruker) in DMSO-d_6 or $CDCL_3$ with TMS (tetramethylsilane) as a standard. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS and coupling constants *J* are stated in Hz.

Preparation of optical sensor

A “cocktail” containing an indicator (0.25 mg), hydrogel D4 (100 mg) in 700 µl EtOH/H_2O (9:1 v/v), and tetrahydrofuran (300 µl) was knife-coated on a dust-free PET support to obtain a ~2.5 µm thick sensing layer after solvent evaporation.

The “cocktail” for the broad-range pH sensor was prepared similarly from a mixture of indicator **1**, **2**, **3**, **4** (0.05 mg respectively, total Σ 0.20 % w/w), hydrogel D4 (100mg) and dissolved in 700 µl EtOH/H_2O (9:1 v/v) and tetrahydrofuran (300 µl). Subsequently it was knife-coated in the same way as mentioned above.

Experimental Section

1-(3-chloro-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one and 1–(4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one were synthesized according to Jokic et al.[2] 1-(4-butoxyphenyl)-4-nitro-3-phenylbutan-1-one was prepared according to literature procedure[3] The synthesis of the new aza-BODIPYs were performed in a routine step route, starting from diaryl α,β-unsaturated ketones (chalcones) which were prepared by Claisen-Schmidt condensation from the corresponding acetophenone and benzaldehyde. Michael-addition of nitromethane to these chalcones provide the 1,3-diaryl-4-nitrobutan-1-ones. Condensation with ammonium acetate at elevated temperature gave a mixture of azadipyrromethene dyes which were separated via chromatography. Carboxy-functionalized compounds (1, 3, 5) were modified with dodecylamine by using EDC (1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide) as carboxyl activating agent in order to yield an amide bond. Attachment of dodecylamine was performed prior to complexation reaction which avoids solubility problems. Finally, complexation reaction with boron trifluoride gave the new aza-BODIPYs in moderate yield.

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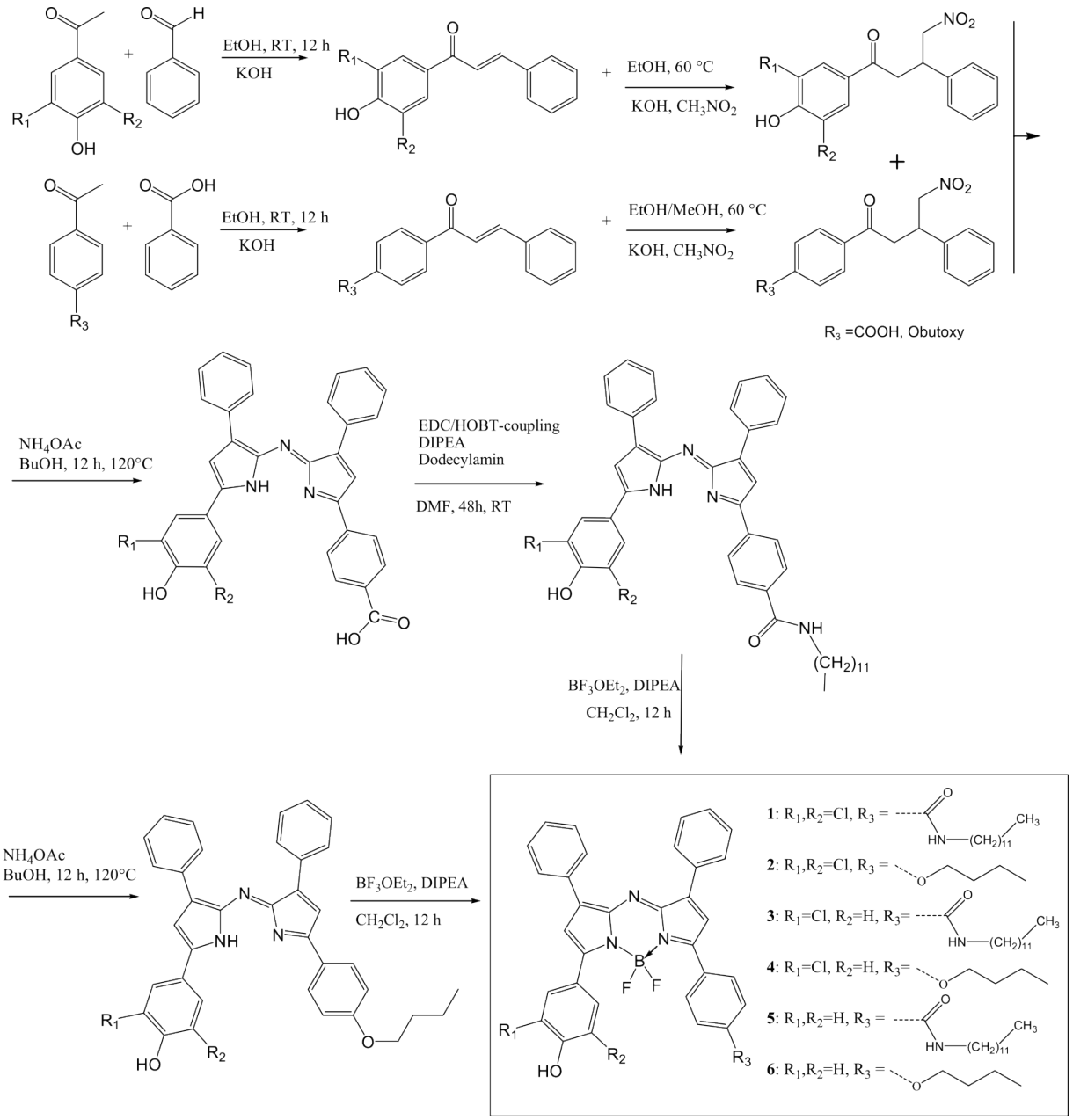


Figure S 7 Synthetic pathway of dye 1-6

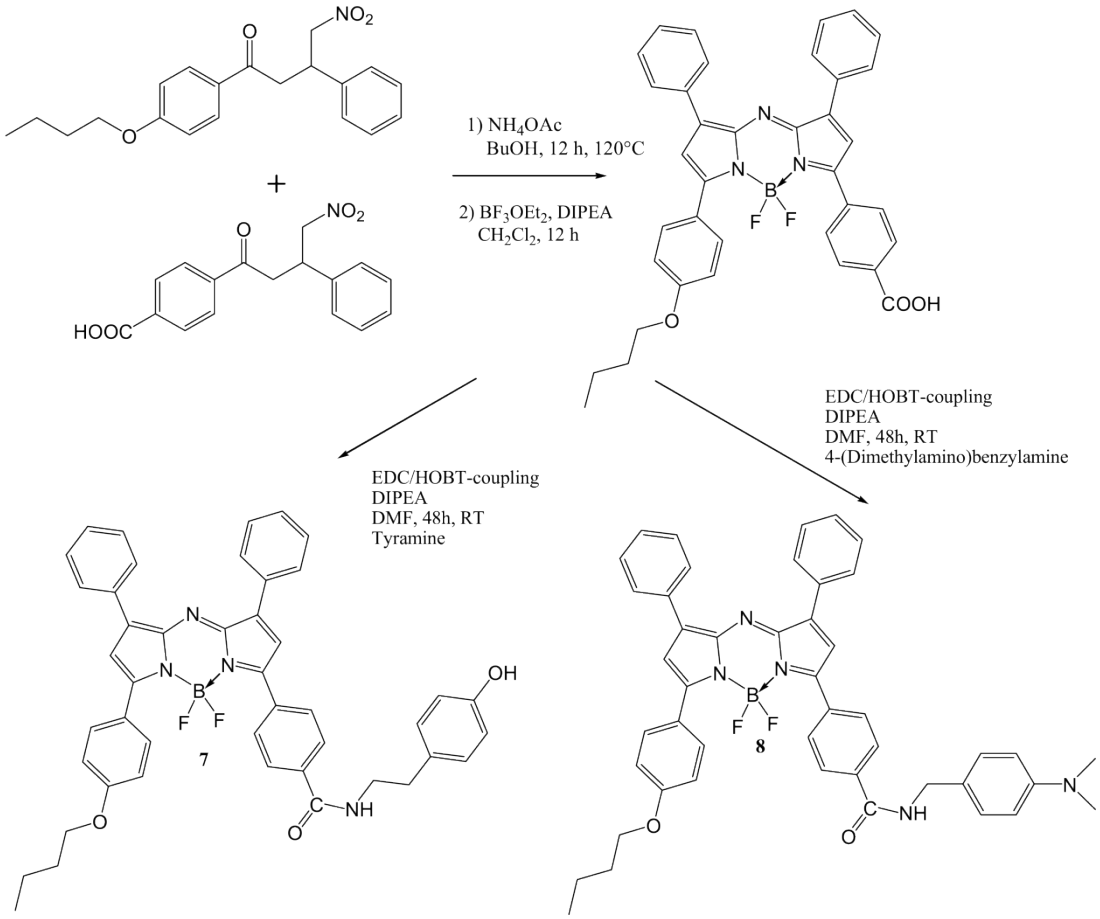


Figure S 8 Synthetic pathway of dye 7 and 8

Synthesis of compound 1

*4-(7-(3,5-dichloro-4-hydroxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide **(1)***

1-(3,5-dichloro-4-hydroxyphenyl)-3-phenylprop-2-en-1-one

3, 5 Dichloro-4-hydroxyacetophenone (1 eq, 2.01 g, 9.8 mmol), benzaldehyde (1 eq, 997 µl, 9.8 mmol) and potassium hydroxide (3 eq, 1.65 g, 29.4 mmol in 8 ml H_2O) were dissolved in ethanol (20ml) and stirred at room temperature for 12 hours. During the course of the reaction the product partly precipitates from the reaction mixture. Then, the reaction solution was acidified with hydrochloric acid (1M) and the resulting light yellow precipitate was isolated by filtration and washed with water. The precipitate was dried under reduced pressure and was used for the next step without further purification (2.85 g).

1-(3,5-dichloro-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (**1a**)

After 1-(3-chloro-4-hydroxyphenyl)-3-phenylpropenone (1 eq, 3.10 g, 120 mmol) was dissolved in ethanol/methanol (5:1 v/v, 60 ml), nitromethane (20 eq, 1.96 ml, 239 mmol) and potassium hydroxide (1.3 eq, 0.87 g, 15.6 mmol) were added and the reaction was heated at 65 °C for three hours. After cooling, the solvent was removed in vacuum and the resulting oily residue was acidified with hydrochloric acid (0.1 M) and was partitioned between ethyl acetate and water in a separating funnel. The organic layer was separated, dried over sodium sulfate and the solvent evaporated under reduced pressure. The obtained product was used for the next step without purification (3.37g, 88.0 %)

4-((E)-3-phenylacryloyl) benzoic acid

A solution of 4- acetylbenzoic acid (1 eq, 2.50 g, 15 mmol) and benzaldehyde (1 eq, 1.55 ml, 15 mmol) and potassium hydroxide (3 eq, 2.56 g, 47 mmol in 8 ml H_2O) in ethanol (100ml) was stirred at room temperature for 12 hours. During the course of the reaction the product partly precipitated from the reaction mixture. Then, the reaction solution was acidified with hydrochloric acid (1M) and the solid was collected on a filter and washed with distilled water to afford the title compound in quantitative yields (3.8 g).

4-(4-nitro-3-phenylbutanoyl) benzoic acid (**1b**)

4-((E)-3-phenylacryloyl) benzoic acid (1 eq, 3.80 g, 15.1 mmol) was dissolved in methanol (175 ml) nitromethane (20 eq, 16 ml, 301 mmol) and potassium hydroxide (1.3 eq, 1.10 g, 19.6 mmol) were added and the reaction was heated under reflux for 6 hours. After cooling to room temperature, the solvent was removed in vacuom. The resulting oily residue was acidified with 0.1 N HCl and was partitioned between ethyl acetate and distilled water in a

separating funnel. The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. (3.27 g, 67.6 %)

(Z)-4-(5-((5-(3,5-dichloro-4-hydroxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)benzoic acid (**1c**)

Coumpound **1a** (1 eq, 1.55 g, 4.4 mmol) and compound **1b** (1 eq, 1.37 g, 4.4 mmol) and ammonium acetate (35 eq, 17.10 g, 222 mmol) were dissolved in butanol (35 ml) and heated under reflux for 12 hours while stirring. After cooling, the solvent was removed under reduced pressure. The obtained solid was washed with water three times and the crude product was purified by column chromatography on silica-gel eluting with a MeOH/CH_2Cl_2 mixture. After eluting the symmetrical by-product with 2% MeOH/CH_2CL_2 the final product was obtained by gradually increasing the polarity to 12-18% MeOH/CH_2Cl_2 and the solvent evaporated under vacuum. The final product was recrystallised from hexane/tetrahydrofuran mixture (1:1) and dried in an oven at 60 °C. (231 mg, 8 %) For the calculation, the theoretical yield of the asymmetrical product is set as 100%.

(Z)-4-(5-((5-(3,5-dichloro-4-hydroxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)-N-dodecylbenzamide (**1d**)

A solution of **1c** (1 eq, 231 mg, 0.4 mmol), 1-hydroxybenzotriazole hydrate (1.2 eq, 64.8 mg 0.48 mmol), 1-(3-dimethylaminopropyl)3-ethylcarbodiimide hydrochloride (EDC, 1,2 eq, 91,8 mg, 0.48 mmol) dodecylamine (1 eq, 74.0 mg, 0.4 mmol) and diisopropylethylamine (DIPEA, 5 eq, 333 µl, 2 mmol) in DMF was stirred at room temperature for 48 hours. Then the product was precipitated by adding saturated NaCl solution and collected by centrifugation. The crude solid was purified by column chromatography on silica gel, eluting with 2.5 % EtOH/CH_2Cl_2. The fractions were united and the solvent was removed under reduced pressure and the resulting blue solid was recrystallized from hexane/tetrahydrofuran. (32 mg, **19.8** %)

4-(7-(3,5-dichloro-4-hydroxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide (**1**)

1d (1 eq, 25 mg, 0.035 mmol) was dissolved in dry CH_2Cl_2 (20 ml) N,N-diisopropylethylamine (DIPEA, 10 eq, 0.35 mmol 61 µl) and boron trifluoride diethyl etherate (15 eq, 0.53 mmol, 65 µl) were added under inert atmosphere (N_2) and the solution was stirred at room temperature for 12 hours. The green-blue solution was shaken with water and dichloromethane three times and dried over sodium sulfate. The product was purified by column chromatography on silica gel using 2-4 % EtOH/ CH_2Cl_2 as eluent. The fractions containing the product were united and the solvent was removed under reduced pressure. Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a blue powder. (15 mg, 55.6 %)

^{1}H- NMR (300 MHz, $CDCl_3$) δ: 8.12-8.04 (m, 8H); 7.94-7.85 (m, 2H); 7.47-7.34 (m, 6H); 7.07 (s, 1H); 6.98 (s, 1H); 6.2 (t, *J* =5.3 Hz, 1H) 3.47 (1, *J* = 6.8 Hz, 2H); 1.67-1.58 (m, 3H); 1.36-1.27 (m, 18H); 0.88 (t, *J* = 5.8 Hz, 3H)

MALDI-TOF *m/z* found 792.2934 calculated 792.2988.

Synthesis of compound 2

*(Z)-4-(2-((5-(4-butoxyphenyl)-3-phenyl-1H-pyrrol-2-yl)imino)-3-phenyl-2H-pyrrol-5-yl)-2,6-dichlorophenol (**2a)***

Compound **1a** (1 eq, 1.16 g, 3.3 mmol) and 1-(4-butoxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 1.12 g, 3.3 mmol) were dissolved in butanol (30 ml). Ammonium acetate (35 eq, 17.10 g, 115 mmol) was added and the reaction solution was heated at 120 °C under reflux for 12 hours. After cooling to room temperature, the solvent was removed under reduced pressure. Afterwards the solid was redissolved in CH_2Cl_2 and washed with water three times. Then, the solid was purified by column chromatography on silica gel. After eluting the first symmetrical by-product with cyclohexane/dichloromethane (1:1 v/v), the product was eluted with dichloromethane and the solvent was removed under reduced pressure. Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the dye as blue powder. For the calculation, the theoretical yield of the asymmetrical product is set as 100 %. (526 mg, 26.6 %)

*4-(7-(4-butoxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-2,6-dichlorophenol (**2)***

Compound **2a** (1 eq, 526 mg, 0.87 mmol) was dissolved in CH_2Cl_2 (25 ml). *N,N*-diisopropylethylamine (DIPEA, 10 eq, 8.7 mmol, 1.51 ml) and boron trifluoride diethyl etherate (15 eq, 13.0 mmol, 1.59 ml) were added under N_2-atmosphere and the reaction solution was stirred at room temperature over night. Then, the green solution was washed with water three times. The product was purified by column chromatography (silica gel in cyclohexane). The product was obtained by gradually increasing the polarity of cyclohexane/CH_2Cl_2 (1:1.5 -1:3 v/v). Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a red-metallic solid. (162 mg, 30.8 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.15 (d *J* = 9.0 Hz, 2H); 8.06 (m, *J* = 8.6 Hz; 4H); 8.03 (s, 2H); 7.46 (t, *J* = 7.4 Hz, 6H); 7.16 (s, 1H); 7.03 (d, 2H); 6.90 (s, 1H); 4.12 (t, *J* = 7.86 Hz, 2H); 1.75 (q, 2H); 1.47 (q, 2H); 0.96 (t, *J* = 7.3 Hz, 3H)

MALDI-TOF *m/z* found 653.1664 calculated 653.1626

Synthesis of compound 3

*(Z)-4-(5-((5-(3-chloro-4-hydroxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)benzoic acid **(3a)***

1-(3-chloro-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 2.03 g, 6.3mmol) was dissolved in butanol (100 ml). Compound **1b** (1 eq, 1.99 g, 6.3 mmol) and ammonium acetate (35 eq, 17.10 g, 222 mmol) were added and the reaction solution was heated at 120 °C for 12 hours. After cooling to room temperature the solvent was removed under reduced pressure. Afterwards the solid was washed with water three times. The crude solid was purified by column chromatography on silica gel using CH_2Cl_2. After eluting impurities and symmetrical by-product with 5% MeOH/CH_2Cl_2, the final product was obtained by increasing the polarity of the eluent (10-12% MeOH/CH_2Cl_2). Afterwards the blue-black solid was recrystallized from hexane/tetrahydrofuran mixture. For the calculation, the theoretical yield of the asymmetrical product is set as 100 %. (359 mg, **10.4 %**)

*(Z)-4-(5-((5-(3-chloro-4-hydroxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)-N-dodecylbenzamide **(3b)***

3a (1 eq, 122 mg, 0.224 mmol) was dissolved in DMF (20 ml). N-hydroxysuccinimide (1.01 eq, 26.1 mg 0.227 mmol), dodecylamine (1.01 eq, 42.0 mg, 0.227 mmol) and 1-(3-dimethylaminopropyl)3-ethylcarbodiimide hydrochloride EDC (1.01 eq, 43.5 mg, 0.227 mmol) were added and the reaction solution was stirred at room temperature for 48 hours. Then, the dye was precipitated by adding saturated NaCl-solution and separated by centrifugation. The crude product was purified by column chromatography on silica gel, eluting with 2.5 % EtOH/CH_2Cl_2. Further purification was achieved by crystallization from hexane-THF mixture . (32 mg, **19.8 %)**

*4-(7-(3-chloro-4-hydroxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide **(3)***

3b (1 eq, 25 mg, 0.035 mmol) was dissolved in dry CH_2Cl_2 (20 ml) *N,N*-diisopropylethylamine (DIPEA, 10 eq, 0.35 mmol 61 µL) was added and the solvent wat stirred at room temperature. Boron trifluoride diethyl etherate (15 eq, 0.53 mmol, 65 µL) was added under N_2-atmosphere and the reaction solution was stirred overnight. The green-blue solution was partitioned with water and dichloromethane three times and dried over sodium sulfate. The crude solid was purified by column chromatography on silica gel in CH_2Cl_2. The product was obtained by gradually increasing the polarity to 2-4 % EtOH/ CH_2Cl_2. The fractions containing the product were united and the solvent was removed under reduced pressure. Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a blue powder. (15 mg, **55.6 %)**

^{1}H- NMR (300 MHz, $CDCl_3$) δ: 8.10-7.94 (m, 7H); 7.86-7.83 (d, *J* = 8.4 Hz, 2H); 7.45-7.43 (m, 6H); 7.14-7.11 (s, 1H); 7.03 (d, *J* = 7.4 Hz, 2H); 6.24 (t, *J* =5.5 Hz, 1H) 3.46 (m, 2H); 1.64-1.60 (m, 4H); 1.34-1.26 (m, 18H); 0.88 (t, *J* = 6.4 Hz, 3H)

MALDI-TOF: *m/z* found 758.3310, calculated 758.3378.

Synthesis compound 4

*(Z)-4-(2-((5-(4-butoxyphenyl)-3-phenyl-1H-pyrrol-2-yl)imino)-3-phenyl-2H-pyrrol-5-yl)-2-chlorophenol **(4a)***

1-(3-chloro-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 2.93 g, 9.16 mmol) and 4-butoxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 2.55 g, 7.46 mmol) were dissolved in 100 ml 2-propanol and ammonium acetate (35 eq, 20.12 g, 261 mmol) was added. Then the solution was heated at 110 °C and stirred over night. The next day, the solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 and washed with water three times. The crude solid was purified by column chromatography on silica gel, eluting with CH_2Cl_2/n-hexane (1:1 v/v). Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a red-metallic solid. (1.49 g, **35 %**).

^{1}H-NMR (300 MHz, DMSO-*d6*) : 8.07 (d, *J* = 6.7 Hz, 5H); 7.98 (d, *J* = 8.6 Hz, 2H); 7.89 - 7.82 (m, 1 H); 7.58 (s, 1 H); 7.53 (s, 1H); 7.42 (dt, *J* = 15.3 Hz,7.0 Hz, 6H); 7.18 (d, *J* = 8.5 Hz, 1H); 7.14 - 7.06 (m, 2H); 4.09 (t, *J* = 6.4 Hz, 2H); 1.75 (p, *J* = 6.5 Hz, 2H); 1.48 (h, *J* = 7.2 Hz, 2H); 0.97 (t, *J* = 7.3 Hz, 3H)

*4-(7-(4-butoxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-2-chlorophenol (**4**)*

Compound **4a** (1.41 g, 2.47 mmol) was dissolved in anhydrous CH_2Cl_2 under inert atmosphere (N_2). Afterwards *N'N*-diisopropylethylamine (DIPEA, 10 eq, 4.2 ml, 24.7 mmol) and BF_3 diethyl etherate (15 eq, 4.57 ml, 37.0 mmol) were added and the solution was stirred over night at room temperature. Then, the green solution was washed with water three times. The product was purified by column chromatography (silica gel in cyclohexane). The product was obtained by eluting with cyclohexane/CH_2Cl_2 (1:1 v/v). Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a red-metallic solid. 370 mg (**25 %**).

^{1}H NMR (300 MHz, DMSO-*d6*) δ: 8.23-8.15 (m, 7H); 8.04-8.01 (m, 1H); 7.64-7.45 (m, 9H); 7.16-7.1 (m, 3H); 4.12 (t, *J*= 6.4 Hz, 2H); 1.83-1.66 (m, 2H); 1.57-1.38 (m, 2H); 0.96 (t, *J*= 7.4 Hz, 3H)

MALDI-TOF *m/z* found 619.157 calculated 619.201

Synthesis of compound 5

*(Z)-4-(5-((5-(4-hydroxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)benzoic acid (**5a**)*

1–(4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 2 g, 7 mmol), compound **1b** (1 eq, 2.19 g, 7 mmol) and ammonium acetate (35 eq, 15.22 g, 245 mmol) were dissolved in butanol (100 ml) and the solution was heated under reflux at a temperature of 120 °C for 12 h while stirring. After the reaction was cooled down to room temperature the solvent was removed in vacuum. The obtained solid was washed with water three times. Then the raw product was purified by column chromatography by gradually increasing the polarity to 10-18% THF/CH_2Cl_2. The final product was recrystalized from hexane/tetrahydrofuran mixture and dried in the oven at 60 °C. For the calculation, the theoretical yield of the asymmetrical product is set as 100%. (300 mg, **12 %**)

^{1}H NMR (300 MHz, DMSO-*d6*) δ: 8.19-8.06 (m, 8H); 7.99-7.96 (d, J = 8.3 Hz, 2H); 7.87 (s 1H), 7.51-7.33 (m, 7H); 7.08-7.05 (d, J= 8.6 Hz, 2H)

Electron impact direct insertion time-of-flight (EI-DI-TOF) *m/z* [MH^+] found 510.184, calc 510.1818.

*(Z)-N-dodecyl-4-(5-((5-(4-hydroxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)benzamide (**5b**)*

5a (1 eq, 150 mg, 0.295 mmol) was dissolved in DMF (20 ml). N-hydroxysuccinimide (1.01 eq, 34 mg 0.297 mmol), dodecylamine (1.01 eq, 55 mg, 0.297 mmol) and EDC (1.01 eq, 57 mg, 0.297 mmol) were added and the reaction solution was stirred at room temperature for 48 hours. Then, the dye was precipitated by adding saturated NaCl solution and separated by centrifugation. The crude product was purified by column chromatography on silica gel, eluting with 2.5 % EtOH/CH_2Cl_2. Further purification was achieved by crystallization from hexane-THF mixture. (50 mg, **25 %**)

^{1}H NMR (300 MHz, DMSO-*d6*) δ: 8.57 (t, J= 6.0 Hz, 1H); 8.18-7.96 (m, 12H); 7.85 (s, 1H); 7.53-7.33 (m, 7H); 7.05 (d, J= 8.6 Hz, 3H); 1.56 (m, 2H); 1.36-1.22 (m, 20 H); 0.84 (m, 3H)

*4-(5,5-difluoro-7-(4-hydroxyphenyl)-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide **(5)***

5b (1 eq, 50 mg, 0.074 mmol) was dissolved in dry CH_2Cl_2 (20 ml) N,N-diisopropyletylamine (DIPEA, 10 eq, 0.74 mmol 122 µl) was added and stirred at room temperature. Afterwards boron trifluoride diethyl etherate (15 eq, 1.11 mmol, 139 µl) was added under N_2-atmosphere and the reaction solution was stirred overnight. The green-blue solution was partitioned with water and dichloromethane three times and dried over sodium sulfate. The crude solid was purified by column chromatography on silica gel in CH_2Cl_2. The product was obtained by gradually increasing the polarity from 2-4 % EtOH/ CH_2Cl_2. The fractions containing the product were united and the solvent was removed under reduced pressure. Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a blue powder. (29.7 mg, **55.6 %**)

^{1}H NMR (300 MHz, DMSO-*d6*) δ: 8.6-6.5 (m, 20H); 1.6-0.8 (m, 25H)

MALDI-TOF *m/z* found 724.368 calculated 724.376

Synthesis of compound 6

(Z)-4-(2-((5-(4-butoxyphenyl)-3-phenyl-1H-pyrrol-2-yl)imino)-3-phenyl-2H-pyrrol-5-yl)phenol **(6a)**

1–(4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 1.75 g, 6.15 mmol), 1-(4-butoxyphenyl)-4-nitro-3-phenylbutan-1-one (1 eq, 2.10 g, 6.15 mmol) and ammonium acetate (35 eq, 16.6 g, 215 mmol) were dissolved in butanol (100 ml) and heated under reflux at a temperature of 120 °C for 12 h while stirring. After the reaction was cooled down to room temperature the solvent was removed in vacuum. The obtained solid was washed with water three times. Then the raw product was purified by column chromatography, eluting with CH_2Cl_2/n-hexane (1:1 v/v). The final product was recrystalized from hexane/tetrahydrofuran mixture and dried in the oven at 60 °C. For the calculation, the theoretical yield of the asymmetrical product is set as 100%. (352 mg, **32 %**)

^{1}H NMR (300 MHz, DMSO-*d6*) δ: 8.09 (d, J= 7.3 Hz, 4H); 7.98 (d, *J* = 8.7 Hz, 4H); 7.59-7.35 (m, 8H); 7.18 (d, *J*=8.8 Hz, 2H); 7.02 (d, J= 8.6 Hz, 2H); 4.11 (t, *J*= 6.4 Hz,2H); 1.8-1.71 (m, 2H); 1.54 -1.4 (m, 2H); 0.97 (t, *J*= 7.3 Hz, 3H)

*4-(7-(4-butoxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)phenol (**6**)*

Compound 6c (1eq, 200 mg, 0.37 mmol) was dissolved in dry CH_2Cl_2 (20 ml) N,N-diisopropyletylamine (DIPEA, 10 eq, 3.7 mmol 618 µl) was added and stirred at room temperature. Afterwards boron trifluoride diethyl etherate (15 eq, 5.6 mmol, 702 µl) was added under N_2-atmosphere and the reaction solution was stirred overnight. The green-blue

solution was partitioned with water and dichloromethane in a separating funnel three times and dried over sodium sulfate. The crude solid was purified by column chromatography on silica gel in CH_2Cl_2. The product was obtained by gradually increasing the polarity to 2-4 % EtOH/ CH_2Cl_2. Further purification was achieved by crystallization from hexane/tetrahydrofuran to give the final product as a blue powder. (121 mg, **55.6 %**)

^{1}H NMR (300 MHz, DMSO-*d6*) δ: 8.17-8.12 (m, 8H); 7.63 (s, 1H); 7.57-7.43 (m, 7H); 7.13 (d, *J*= 8.8 Hz, 2H); 6.95 (d, 8.7Hz, 2H); 4.11 (t, J= 6.4 Hz, 2H); 1.74 (m, 2H), 1.47 (m, 2H; 0.96 (t, *J*= 7.4 Hz, 3H)

MALDI-TOF *m/z* found 585.180 calculated 585.240

Synthesis of compound 7

*(Z)-4-(5-((5-(4-butoxyphenyl)-3-phenyl-2H-pyrrol-2-ylidene)amino)-4-phenyl-1H-pyrrol-2-yl)benzoic acid **(7a)***

Compound **1b** (4.59 g, 14.67 mmol, 1eq) and 1-(4-butoxyphenyl)-4-nitro-3-phenylbutan-1-one (5.03 g, 14.67 mmol, 1 eq.) and ammonium acetate (41.6, 539 mmol, 35 eq.) were dissolved in butanol (100 ml) and stirred at 120 °C for 18 hours. The solvent of the blue mixture was removed by rotary evaporation and the residue was extracted with dichloromethane and H2O and the combined organic layers were concentrated under reduced pressure. The crude product was purified by column chromatography on silica-gel by eluting with 5 % THF/CH_2Cl_2. Finally the product was re-crystallized from hexane /tetrahydrofurane to obtain green-red shimmered crystals (1.083 g, **13 %**)

*3-(4-butoxyphenyl)-7-(4-carboxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide **(7b)***

Compound 7a (1.083 g, 1.914 mmol, 1eq.) was dissolved in dry dichloromethane (350 ml) under inert atmosphere by using nitrogen. Then, boron trifluoride diethyletherate (3.6 ml, 29.18 mmol, 15 eq.) and DIPEA (3.188 ml, 19.16 mmol, 10 eq.) were added with a syringe and the reaction was stirred for 21 hours at room temperature. Then, the grenn solution was partitioned between dichloromethane and H_2O in a separating funnel and the organic layer dried over sodium sulphate. The crude product was purified by column chromatography on silica-gel by eluting again with 5 % THF/CH_2Cl_2. Hexane and tetrahydrofurane was used for cristallization. (0.907 g, **77.2 %**)

^{1}H NMR (300 MHz, DMSO-d_6) δ:8.17-7.18 (m, 20H), 4.13 (t, *J* = 6.2 Hz, 2H), 1.79-1.69 (m, J = 6.6 Hz, 2H), 1.52-1.39 (m, *J*= 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

*3-(4-butoxyphenyl)-7-(4-((4-(dimethylamino)benzyl)carbamoyl)phenyl)-5,5-difluoro-1,9-diphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide **(7)***

Compound **7 b** (102.6 mg, 0.167 mmol, 1 eq.), EDC (40 mg, 0.208 mmol, 1.2 eq), 1-hydroxybenzotriazole hydrate (30.5 mg, 0.225 mmol 1.2 eq.) and 4-(dimethylamino)benzylamine (29.3 mg, 0.225 mmol, 1 eq.) were dissolved in DMF. Then *N,N*-diisopropylethylamine (140 µL, 0.841 mmol, 5 eq.) was added, the mixture was stirred at room temperature for 22 hours and the solvent was removed by rotary evaporation. The solvent was extracted with dichloromethane (100 ml) and H_2O (100 ml), dried over sodium sulphate and purified via column chromatography on silica gel by eluting with 2 % THF/ CH_2Cl_2. Hexane and tetrahydrofurane was used for crystallization. (0.097 g, **64.0 %**)

^{1}H NMR (300 MHz, Chloroform-d_6) δ: 8.14-8.03 (m, *J* = 14.3 Hz, 8H), 7.87-7.84 (d, *J* = 8.4 Hz, 2H), 7.48-7.40 (m, *J* = 7.3 Hz, 6H), 7.24 (s, 2H), 7.01-6.98 (d, *J* = 8.7 Hz, 3H), 6.75-6.72 (d, *J* = 8.7 Hz, 2H), 6.31 (t, *J* = 4.5 Hz, 1H), 4.57-4.55 (d, *J* = 5.2 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 2.95 (s, 6H), 1.84-1.75 (m, *J* = 6.6 Hz, 2H), 1.54-1.47 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

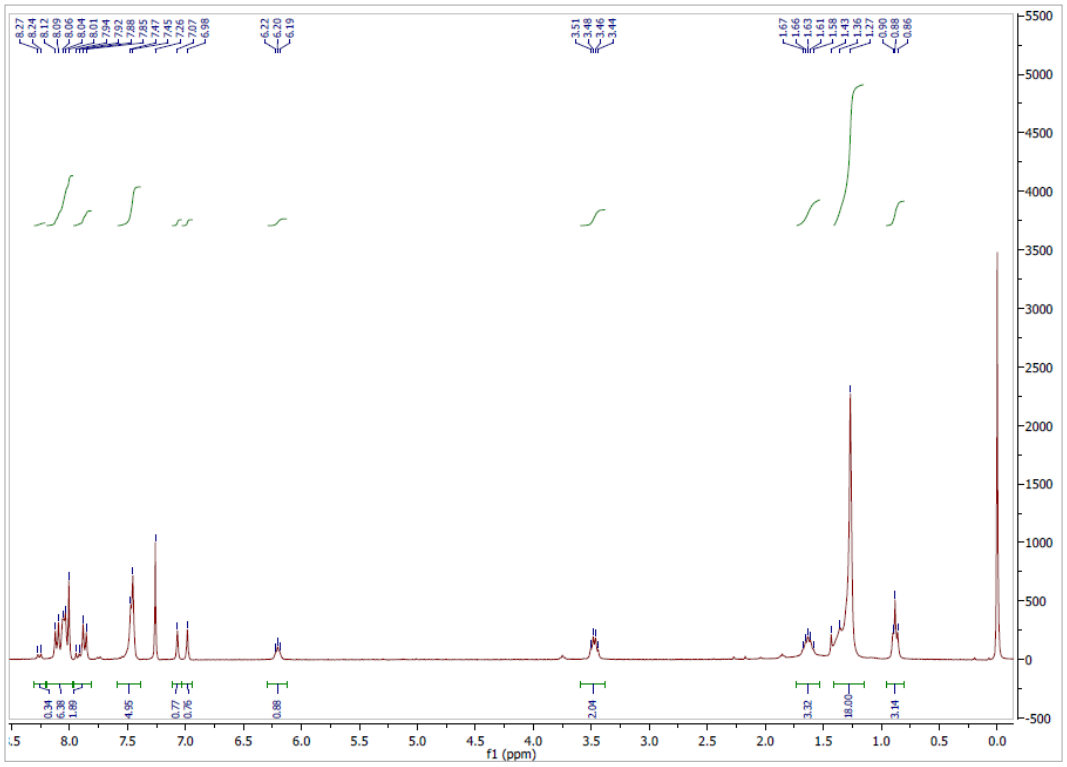
3-(4-butoxyphenyl)-5,5-difluoro-7-(4-((4-hydroxybenzyl)carbamoyl)phenyl)-1,9-diphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide **(8)**

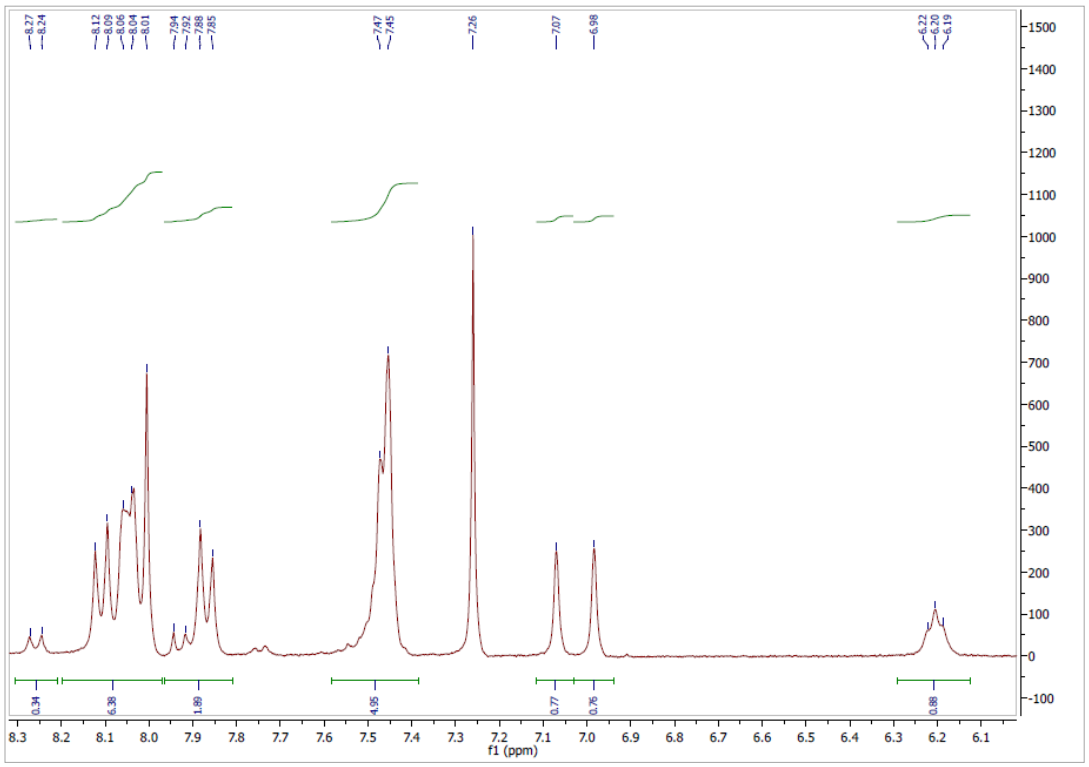
Compound **7 b** (50 mg, 0.08 mmol, 1 eq.), EDC (18.7 mg, 0.09 mmol, 1.2 eq), 1-hydroxybenzotriazole hydrate (13.2 mg, 0.09 mmol 1.2 eq.) and 4-hydroxyphenethylamine (11.2 mg, 0.08 mmol, 1 eq.) were dissolved in DMF. Then *N,N*-diisopropylethylamine (70 µL, 0.4 mmol, 5 eq.) was added, the mixture was stirred at room temperature over night. The solvent was extracted with dichloromethane (50 ml) and H_2O (50 ml), dried over sodium sulphate and purified via column chromatography on silica gel by eluting with 4 % THF/ CH_2Cl_2. Hexane and tetrahydrofurane was used for crystallization. (32.2 g, **54.0 %**)

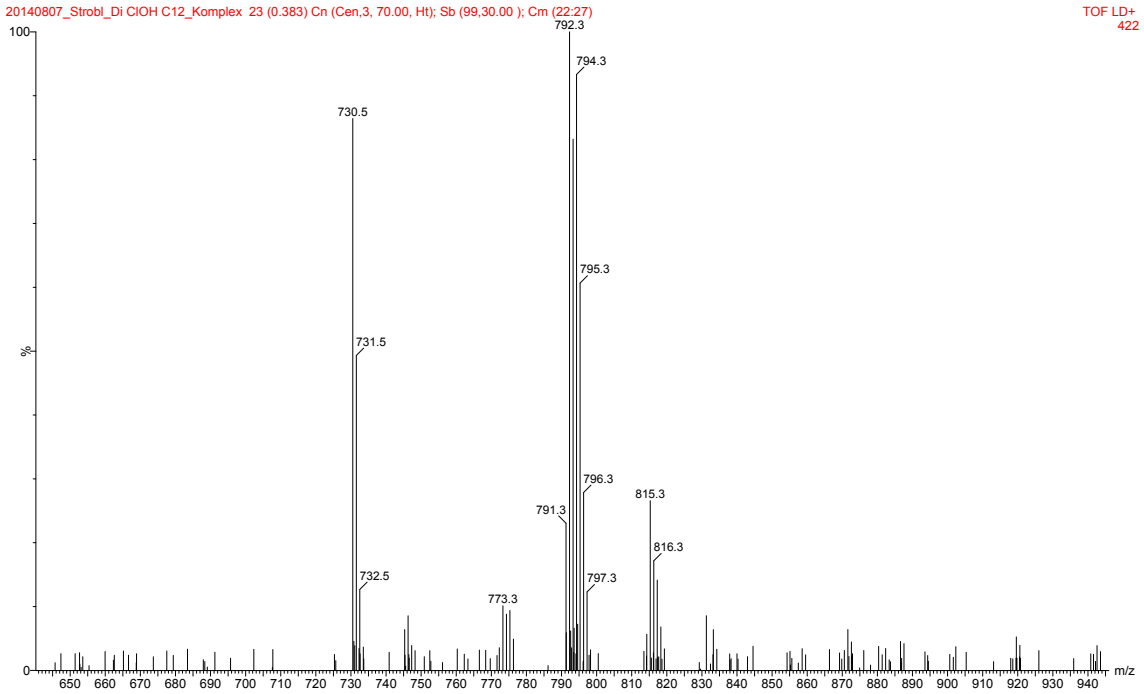
^{1}H NMR (300 MHz, Chloroform-d_6) δ: 8.14-8.03 (m, 8H), 7.78-7.75 (m,2H), 7.51-7.37 (m, 6H), 7.14-7.09 (m, 3H), 7.01-6.97 (m, 4H), 4.07-4.03 (t, 2H), 3.73-3.66 (m, 2H), 2.87 (t, 2H), 1.81-1.76 (m, 2H), 1.55-1.47 (m, 2H), 1.02-0.97 (t, *J* = 7.4 Hz, 3H)

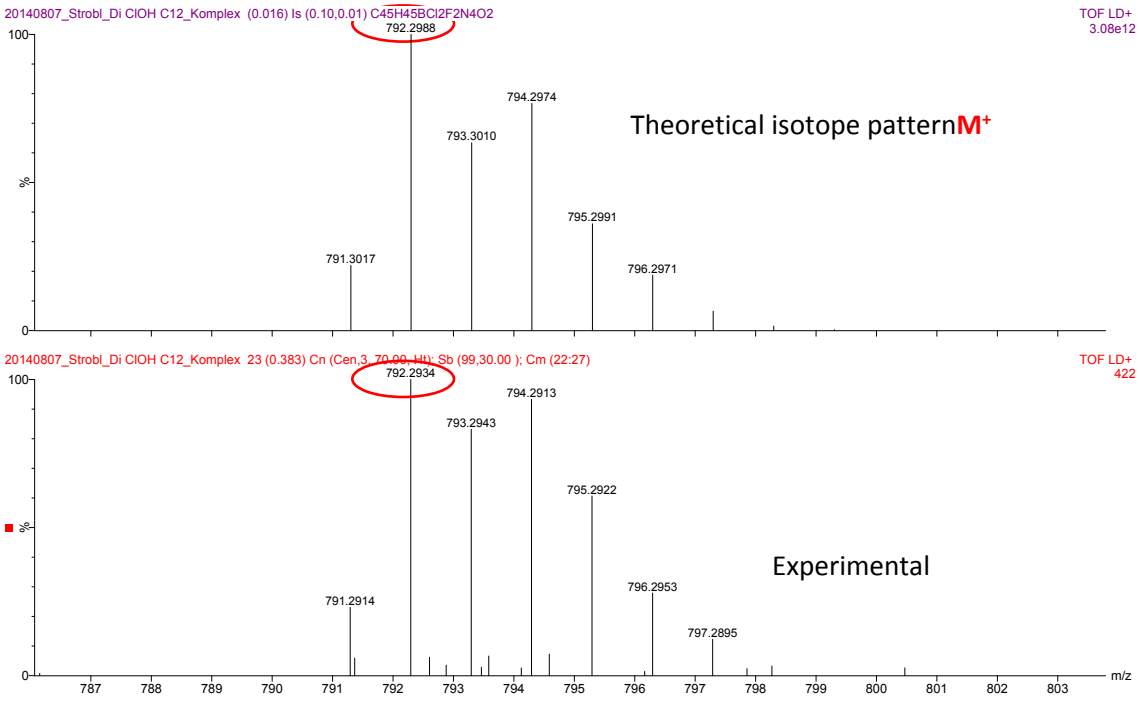
Compound 1

4-(7-(3,5-dichloro-4-hydroxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide



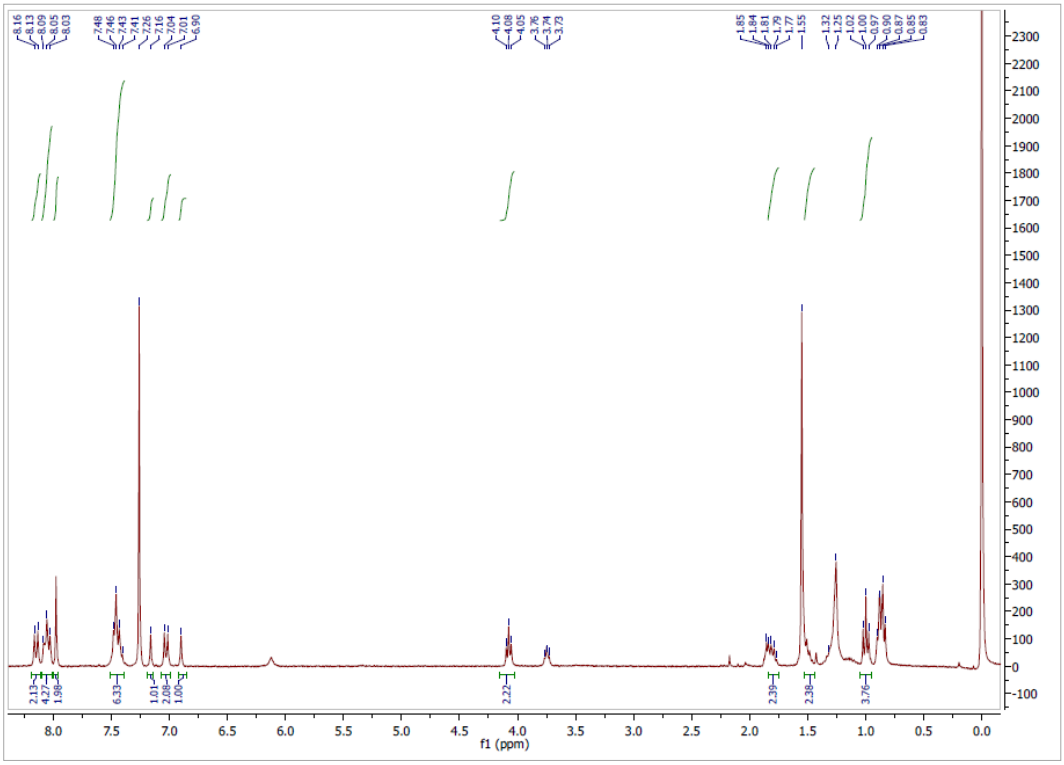


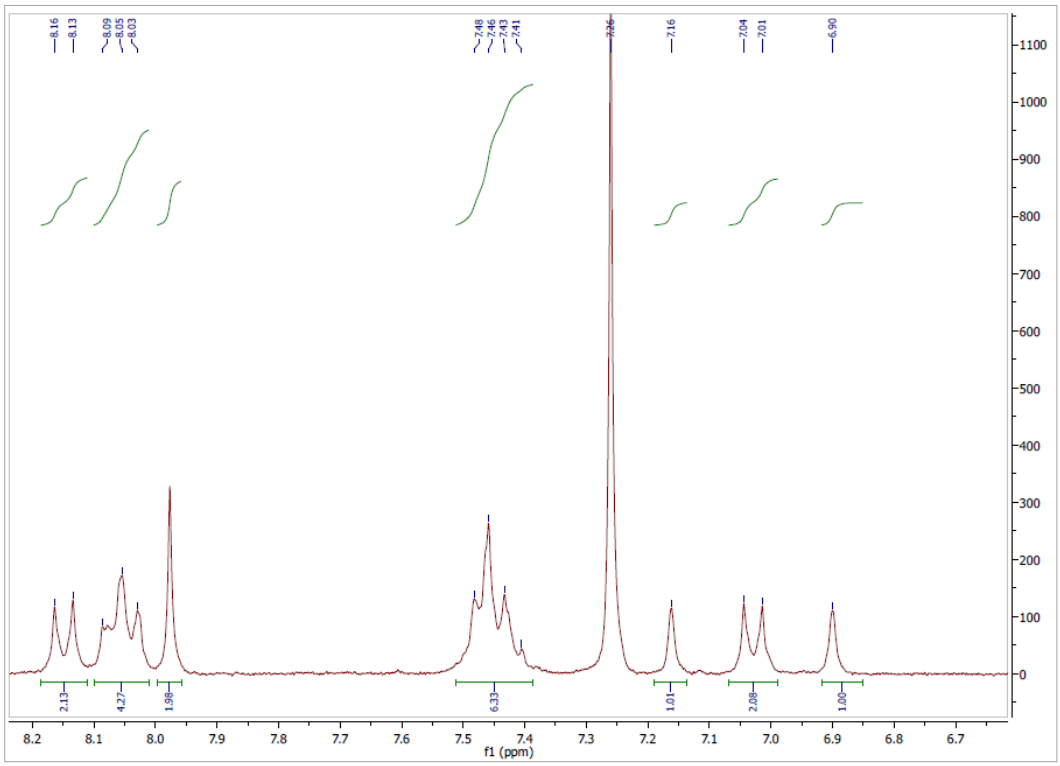

20140807_Strobl_Di ClOH C12_Komplex 23 (0.383) Cn (Cen,3, 70.00, Ht); Sb (99,30.00); Cm (22:27)
TOF LD+
422
100
%
0
792.3
794.3
730.5
795.3
731.5
796.3
815.3
791.3
816.3
732.5
797.3
773.3
650 660 670 680 690 700 710 720 730 740 750 760 770 780 790 800 810 820 830 840 850 860 870 880 890 900 910 920 930 940
m/z


20140807_Strobl_Di ClOH C12_Komplex (0.016) Is (0.10,0.01) C45H45BCl2F2N4O2
TOF LD+
3.08e12
100
%
0
792.2988
794.2974
793.3010
795.2991
791.3017
796.2971
Theoretical isotope pattern M+
20140807_Strobl_Di ClOH C12_Komplex 23 (0.383) Cn (Cen,3, 70.00, Ht); Sb (99,30.00); Cm (22:27)
TOF LD+
422
100
%
0
792.2934
794.2913
793.2943
795.2922
791.2914
796.2953
797.2895
Experimental
787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803
m/z

Compound 2

*4-(7-(4-butoxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-2,6-dichlorophenol (**2**)*





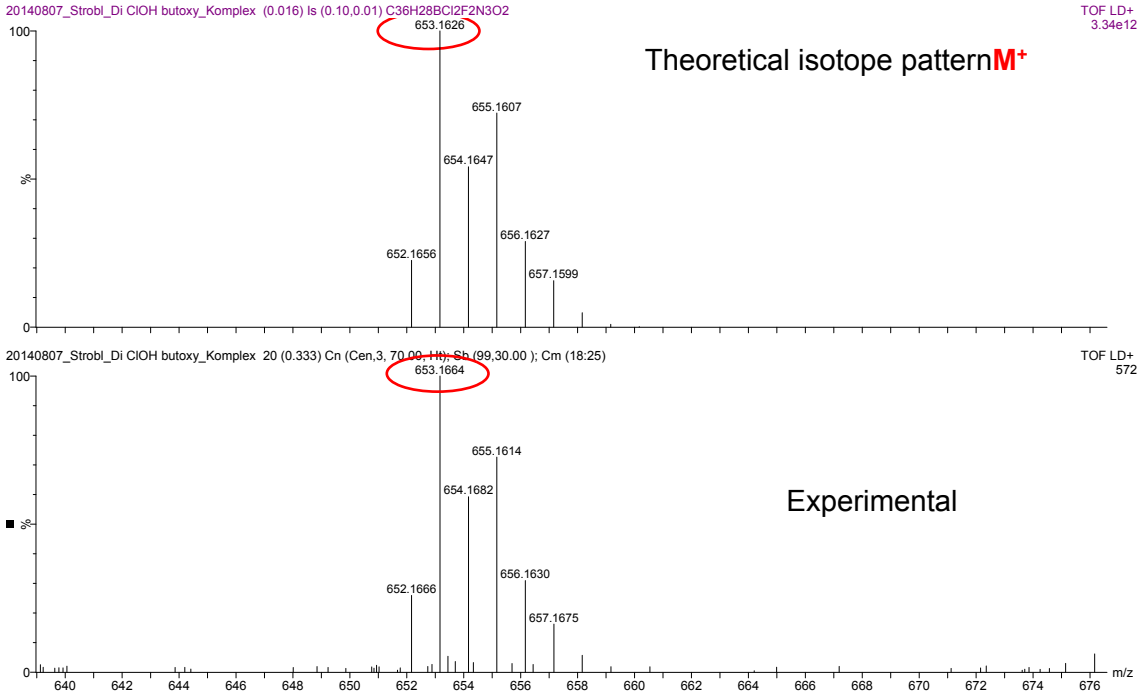
20140807_Strobl_Di ClOH butoxy_Komplex 20 (0.333) Cn (Cen,3, 70.00, Ht); Sb (99,30.00); Cm (18:25)

TOF LD+

100

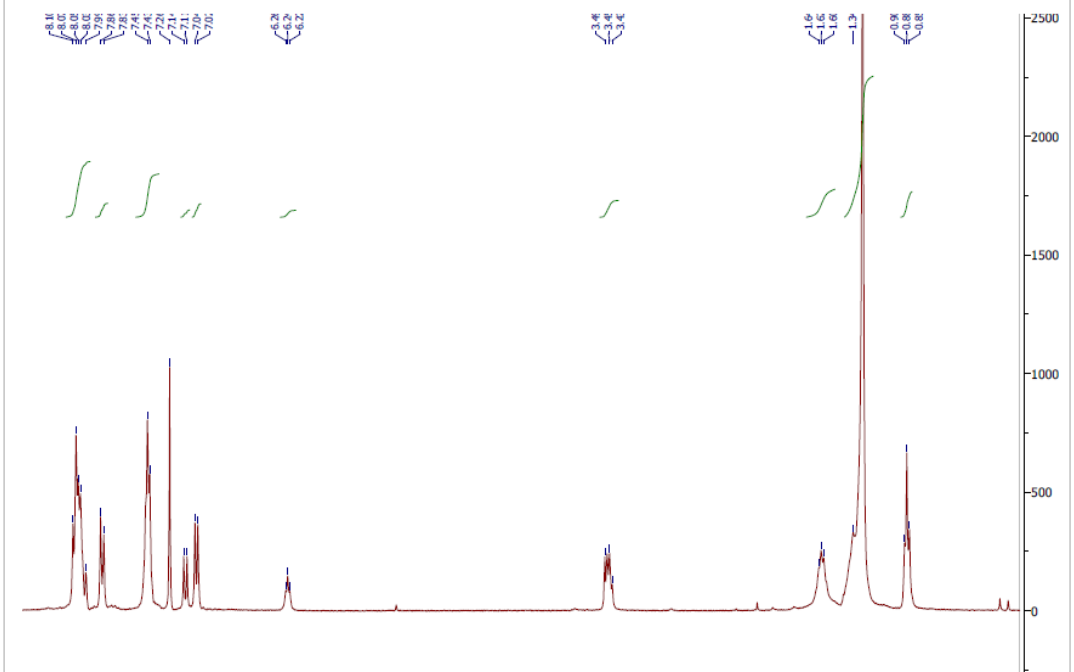
653.2

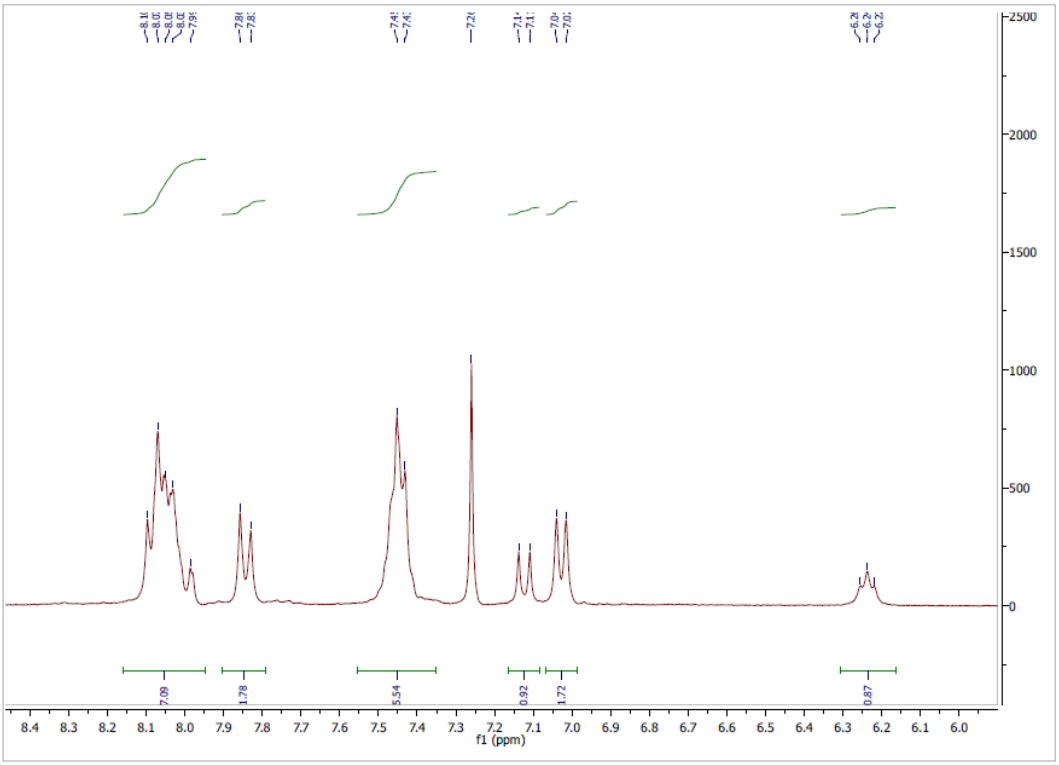
572

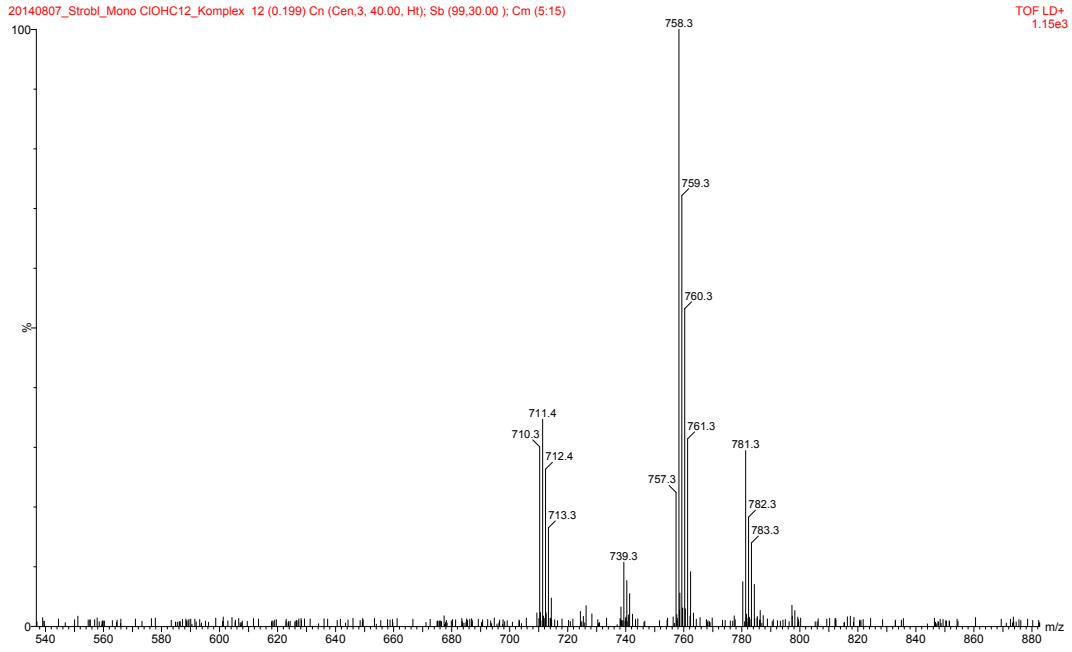


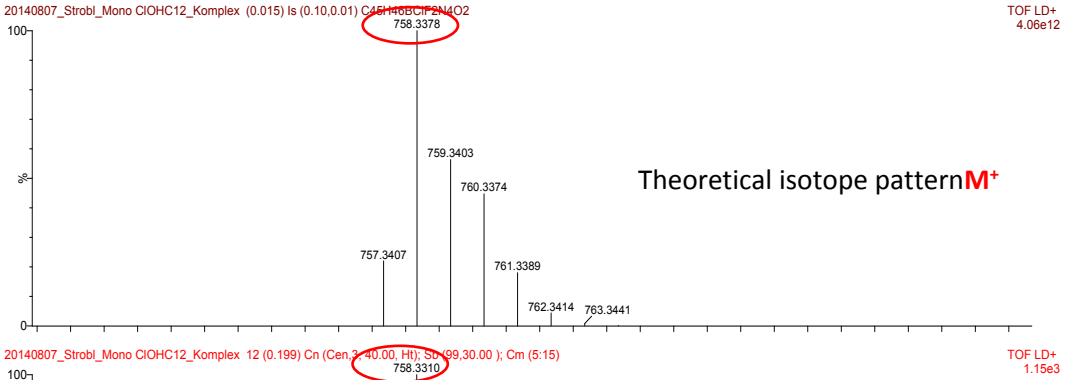
Compound 3

4-(7-(3-chloro-4-hydroxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide ***(3)***



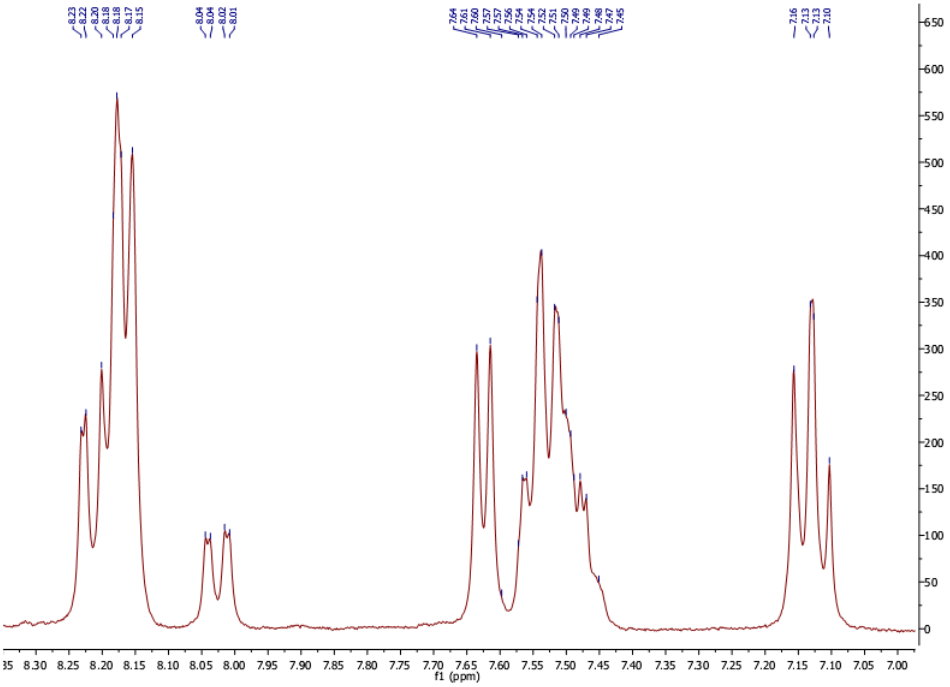

f1 (ppm)
7.09
1.78
5.54
0.92
1.72
0.87

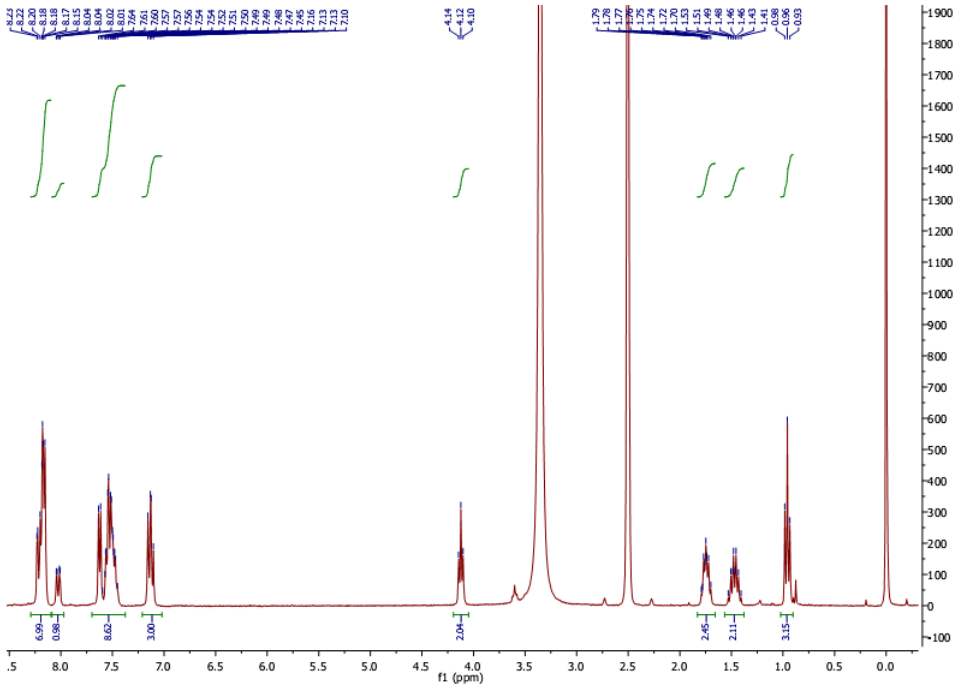

20140807_Strobl_Mono ClOHC12_Komplex 12 (0.199) Cn (Cen,3, 40.00, Ht); Sb (99,30.00); Cm (5:15)
TOF LD+
1.15e3
758.3
759.3
760.3
761.3
711.4
710.3
712.4
713.3
757.3
739.3
781.3
782.3
783.3
m/z

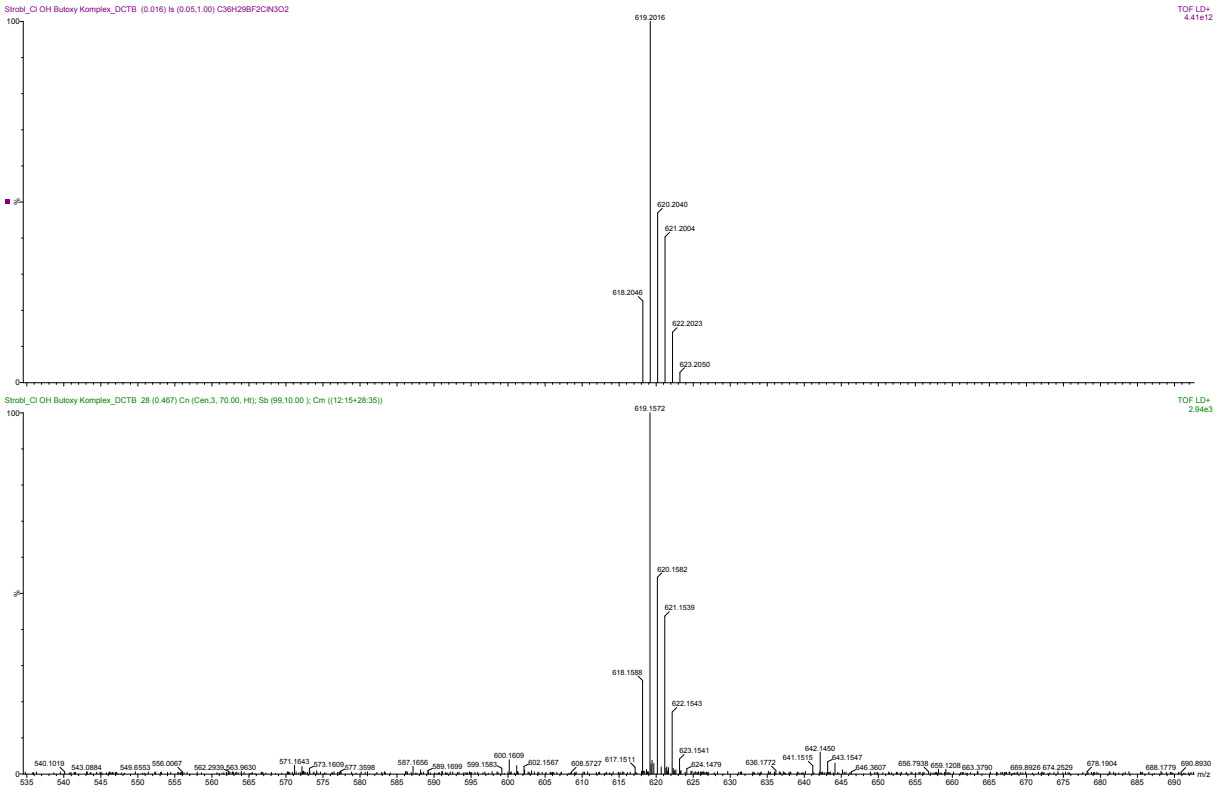

20140807_Strobl_Mono ClOHC12_Komplex (0.015) Is (0.10,0.01) C45H46ClF2N4O2
TOF LD+
4.06e12
758.3378
759.3403
760.3374
757.3407
761.3389
762.3414
763.3441
Theoretical isotope pattern M+
20140807_Strobl_Mono ClOHC12_Komplex 12 (0.199) Cn (Cen,3, 40.00, Ht); Sb (99,30.00); Cm (5:15)
TOF LD+
1.15e3
758.3310

Compound 4

*4-(7-(4-butoxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-2-chlorophenol (**4**)*

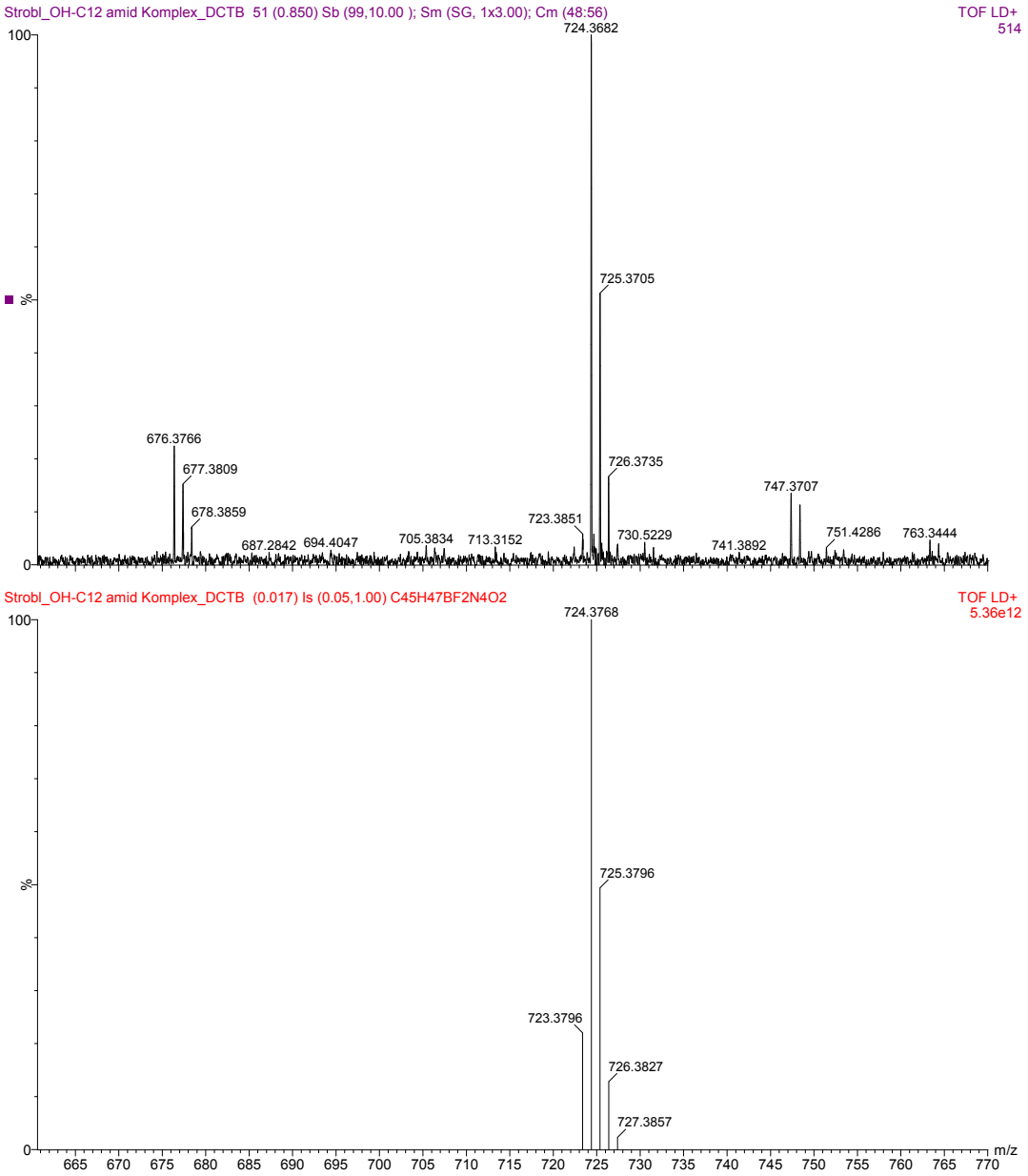



f1 (ppm)


Strobl_Cl OH Butoxy Komplex_DCTB (0.016) Is (0.05,1.00) C36H29BF2ClN3O2
TOF LD+
4.41e12
619.2016
620.2040
621.2004
618.2048
622.2023
623.2050
Strobl_Cl OH Butoxy Komplex_DCTB 28 (0.467) Cn (Cen,3, 70.00, Ht); Sb (99,10.00); Cm ((12:15+28:35))
TOF LD+
2.94e3
619.1572
620.1582
621.1539
618.1588
622.1543
623.1541
m/z

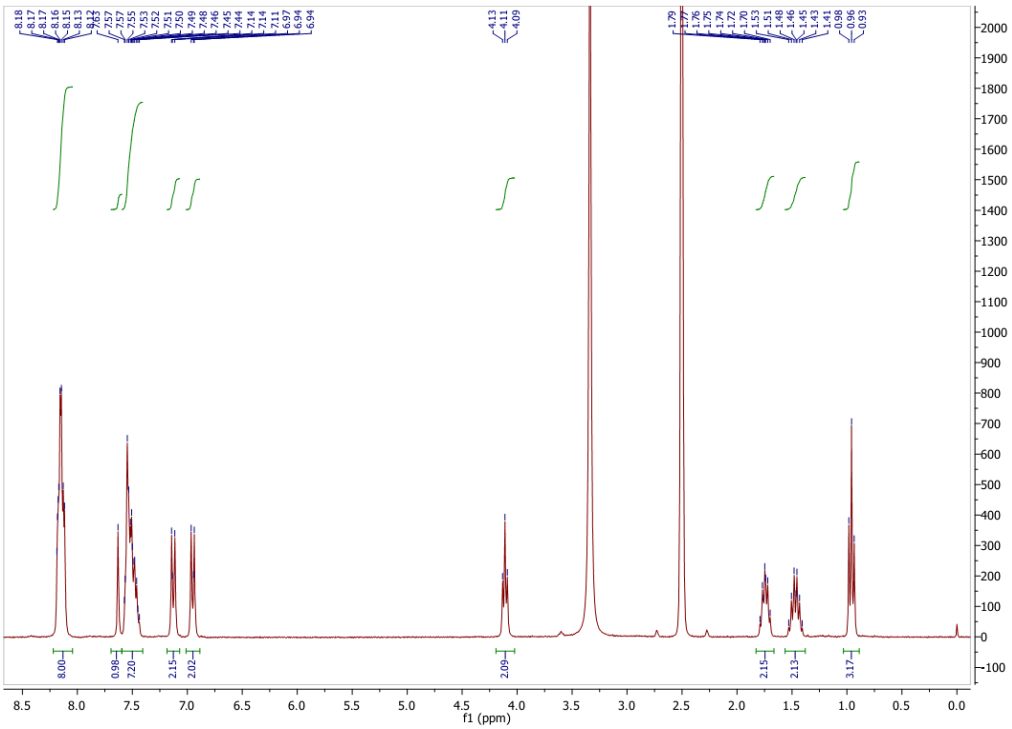
Compound 5

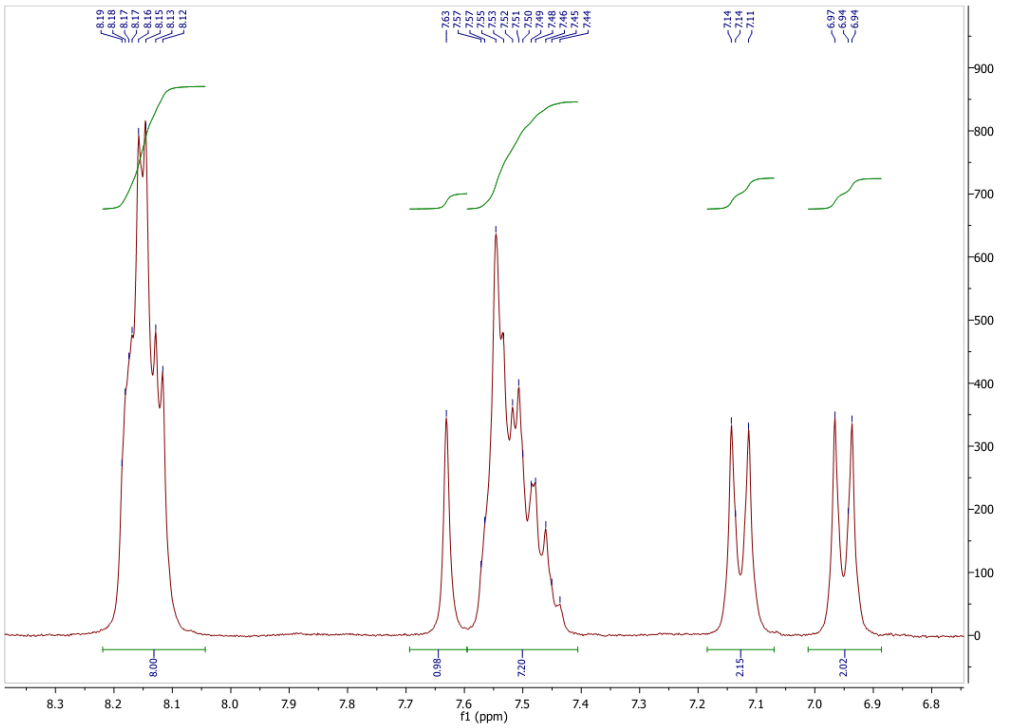
4-(5,5-difluoro-7-(4-hydroxyphenyl)-1,9-diphenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)-N-dodecylbenzamide ***(5)***

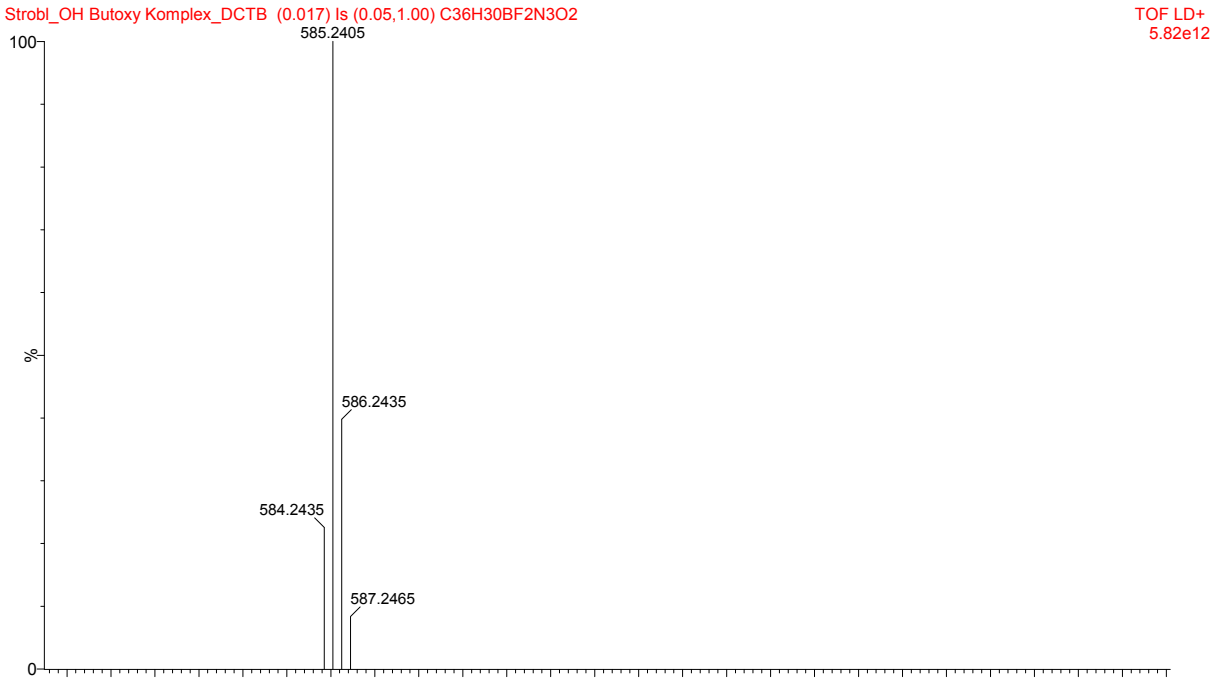


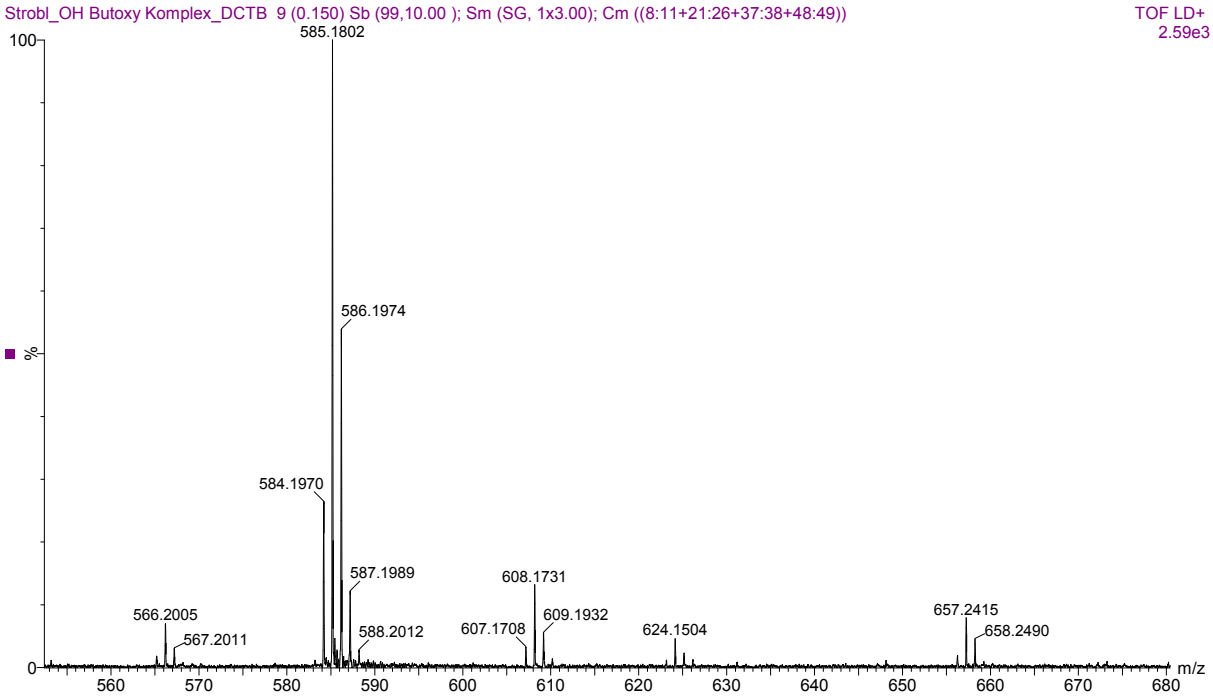
Compound 6

*4-(7-(4-butoxyphenyl)-5,5-difluoro-1,9-diphenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-3-yl)phenol (**6**)*


f1 (ppm)

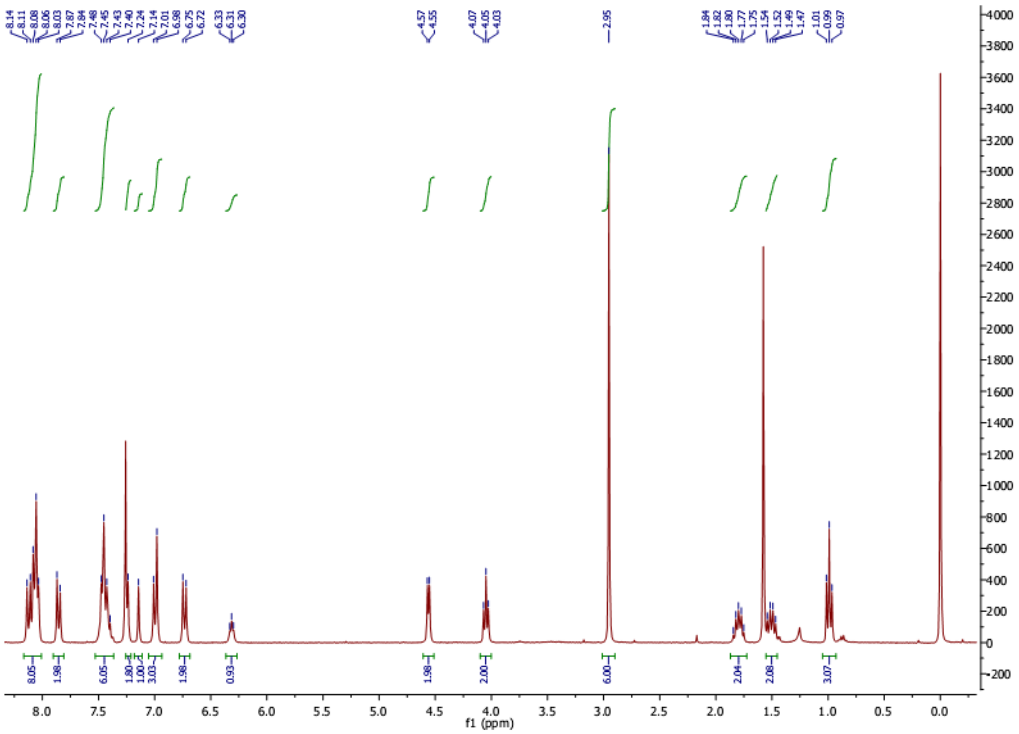

f1 (ppm)

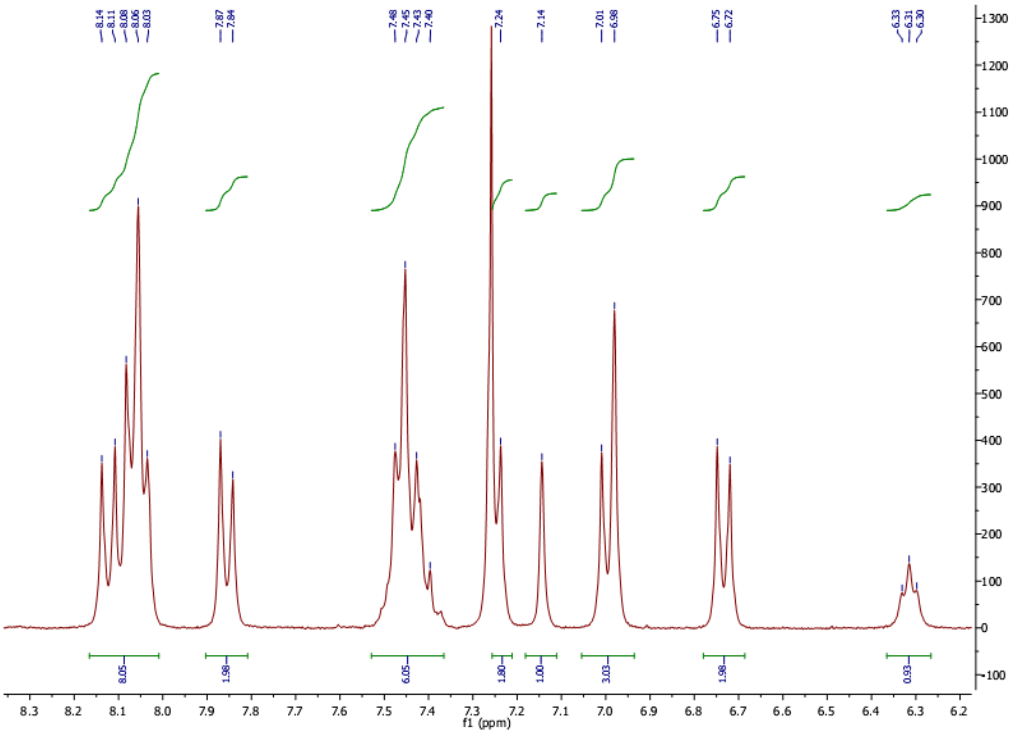

Strobl_OH Butoxy Komplex_DCTB (0.017) Is (0.05,1.00) C36H30BF2N3O2
TOF LD+
5.82e12
100
%
0
585.2405
586.2435
584.2435
587.2465


Strobl_OH Butoxy Komplex_DCTB 9 (0.150) Sb (99,10.00); Sm (SG, 1x3.00); Cm ((8:11+21:26+37:38+48:49))
TOF LD+
2.59e3
100
%
0
585.1802
586.1974
584.1970
587.1989
608.1731
566.2005
567.2011
588.2012
607.1708
609.1932
624.1504
657.2415
658.2490
560
570
580
590
600
610
620
630
640
650
660
670
680
m/z

Compound 7

3-(4-butoxyphenyl)-7-(4-((4-(dimethylamino)benzyl)carbamoyl)phenyl)-5,5-difluoro-1,9-diphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide ***(7)***





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