Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Two-Color Emissive Probes for Click Reactions

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1. BODIPY derivatives and azides used for click reactions

Visualizing click reactions on BODIPYs, α-, β- and γ-ethynyl BODIPY were converted to the three different triazole products. Reaction monitoring was established in ensemble measurements. Out of these experiments, the compound with ideal optical characteristics for microscopy experiments was choosen, α-ethynyl BODIPY (**6**) (figure S1).

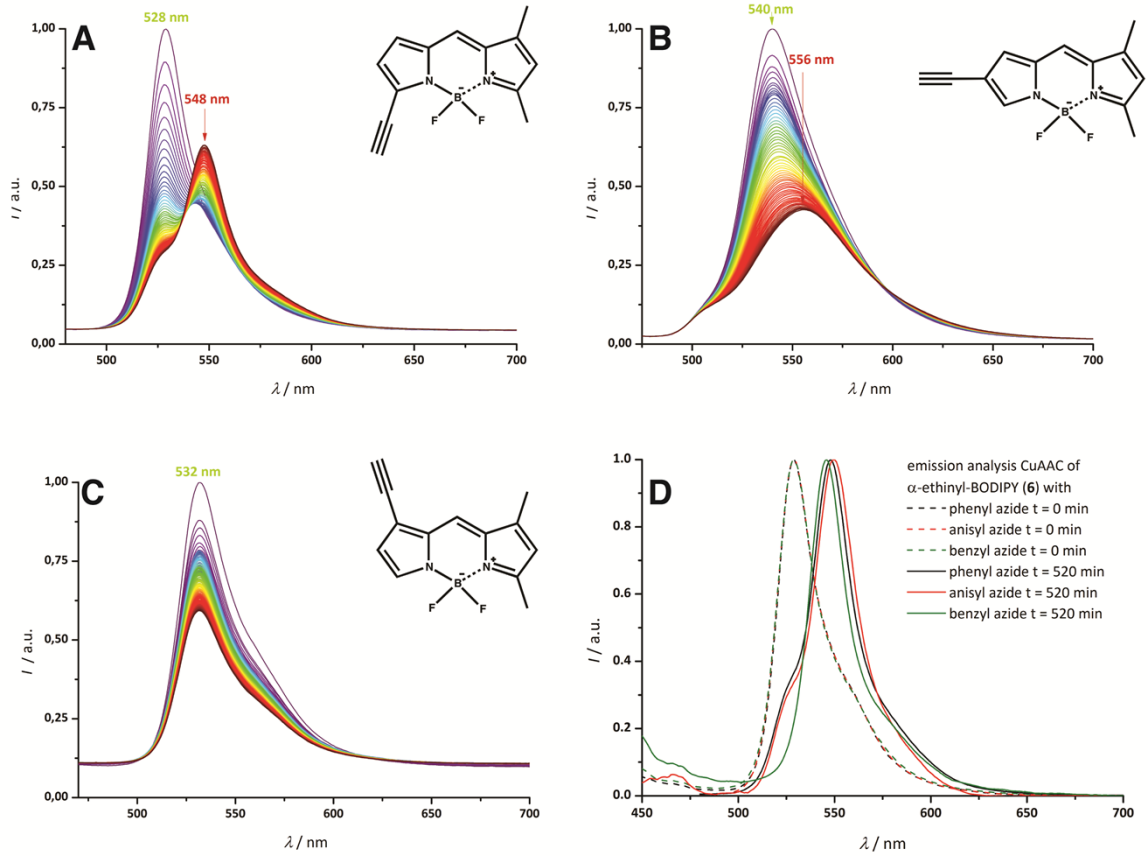


figure S1: *Reaction monitoring of different derivatised alkyne BODIPY dyes in CuAAC with phenyl azide and optical comparison of different used azide moieties. Spectra are collected every five minutes over a period of 11 hours.* ***A****: α-derivative;* ***B****: β-derivative;* ***C****: γ-derivative;* ***D****: comparison of starting compound and triazole product.*

2. Background signal in microscopy experiments

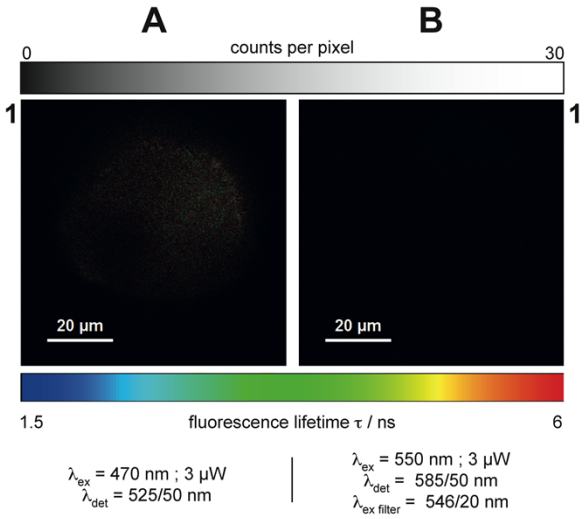


figure S2: Immobilized azide agarose beads without any fluorophore, before figure 3: **A**: minor background fluorescence in green detection channel; **B**: no background fluorescence in orange detection channel.

3. Comparison of alkyne-BODIPY and click transformation

The alkyne BODIPY compounds (**6**) – (**8**) could not be crystalized because of decomposition in solid state. The identification of these compounds was only possible using mass spectroscopy and the typical ^{1}H-NMR shift of the aromatic alkyne moiety, normally localized about δ = 3.10 ppm.

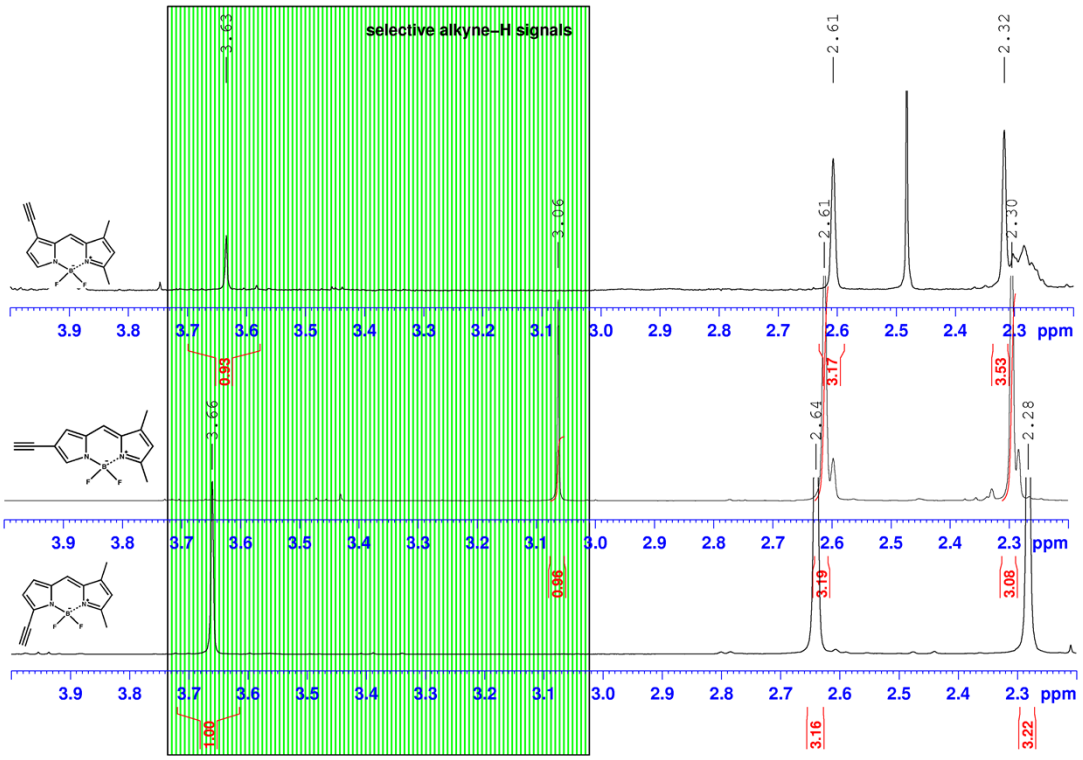


figure S3: *Compendium of α, β and γ-ethynyl BODIPY alkyne-H signals.*

All alkyne-H signals show a typical chemical shift for aromatic triple bond moieties (figure S3).[1] Comparing the α-ethynyl BODIPY (**6**) signal range with click product (**9b**), alkyne-H signal vanished (3.66 ppm) and the methoxy group signal emerges (3.89 ppm). These changes in chemical shift (0.23 ppm) and integration and the typical triazole-H formation at 8.83 ppm[2] show product formation (figure S4).

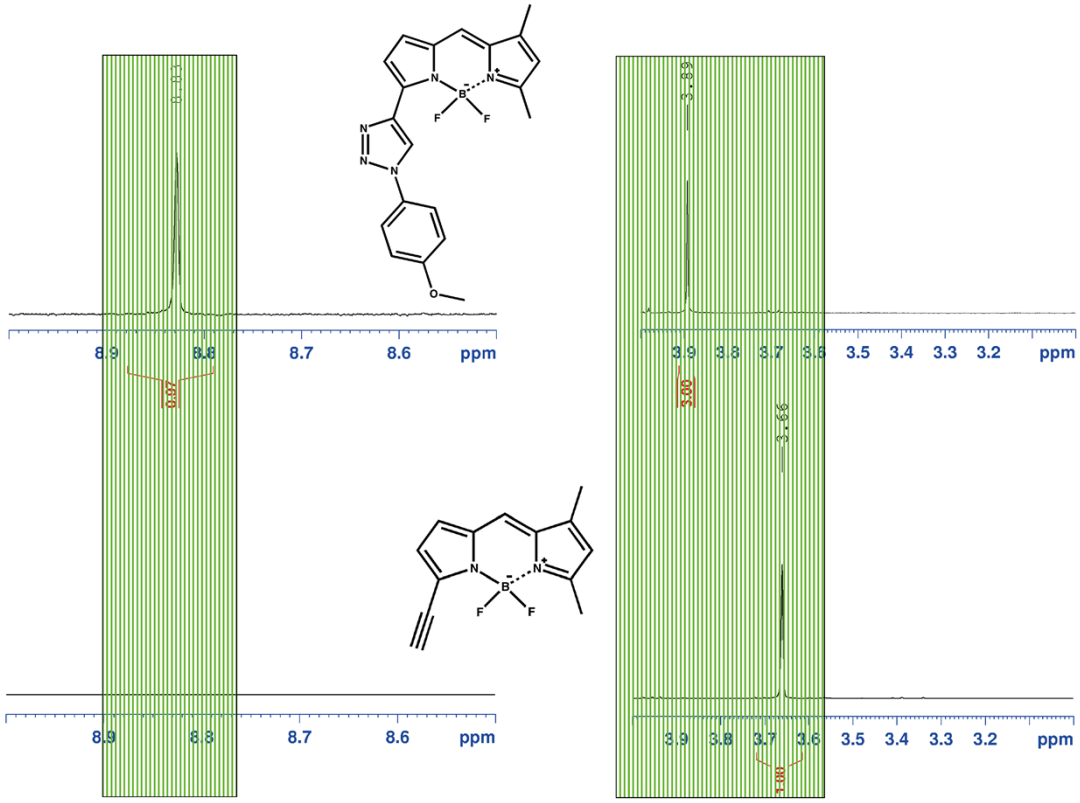


figure S4: *^{1}H-NMR comparison of characteristic signals of (**6**) and (**9b**).*

4. Influence of the copper moiety onto fluorescence in microscopy

In conversion FLIM images (figure 3), a reduction of fluorescence lifetime is detected. A quenching process, induced by different copper species and the changed environment could be the reason. Proving this assumption, a second FLIM experiment was conducted: unsubstituted 5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene-BODIPY[3] is used as lifetime tracer and phenylacetylene as triple-bond-compound for coupling (figure S5).

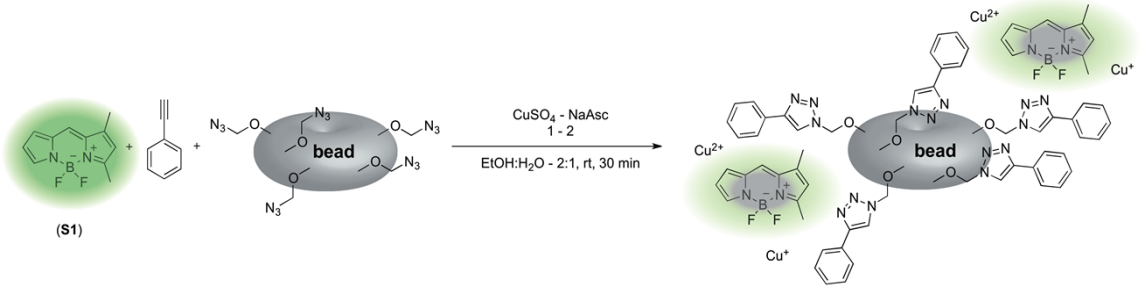


figure S5: *FLIM control experiment – molecular description*

In the reaction, phenylacetylene is connected on azide agarose in presence of the non-reactive BODIPY compound. The stepwise fluorescence lifetime development of the unreactive dye shows environmental change and quenching induced by Cu-species (figure S6, table S1).

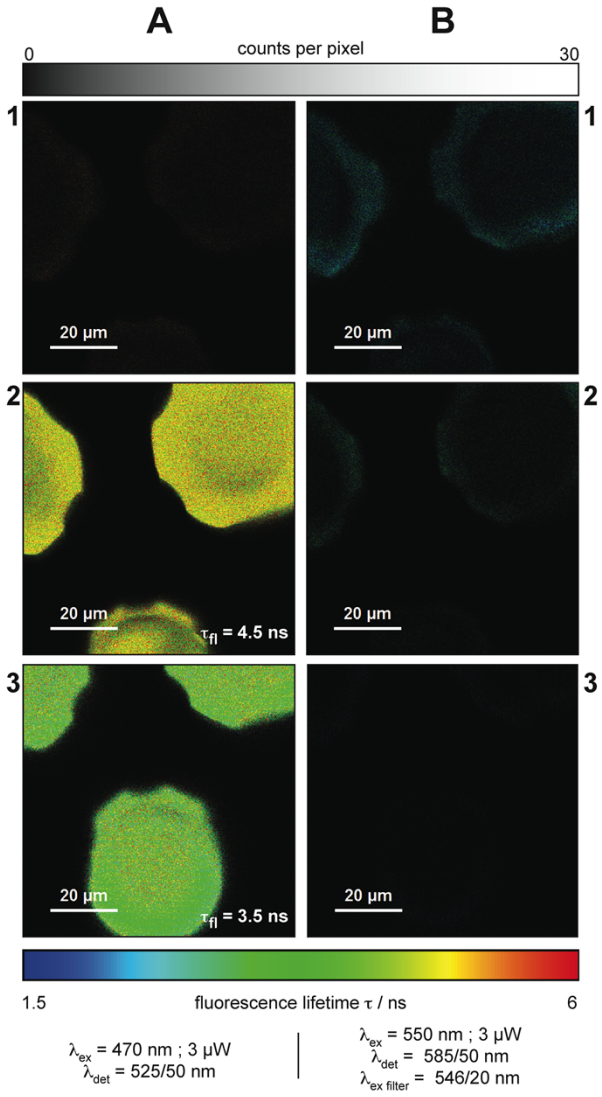
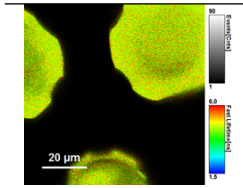
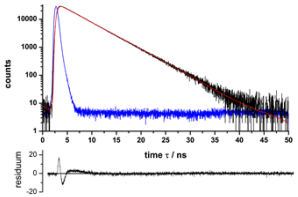
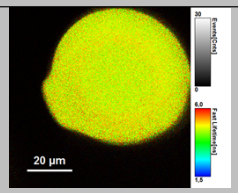
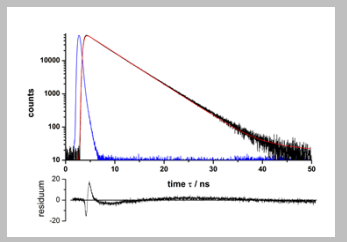
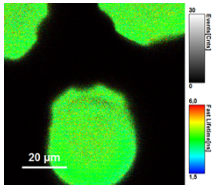
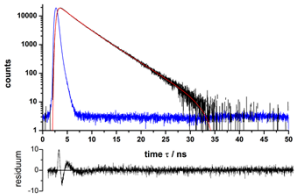
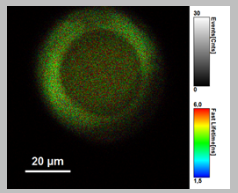
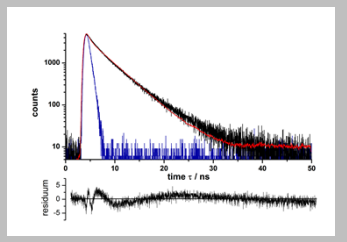
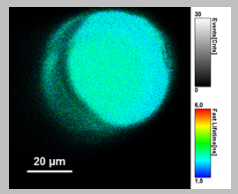
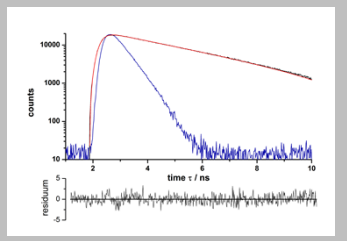


figure S6: *FLIM images showing the influences of environmental changes and copper onto fluorescence lifetime:* ***A****: excitation with λ_{ex} = 470 nm @ 20 MHz, emission filter λ_{det} = 525/50 nm only detection BODIPY;* ***B****: excitation with λ_{ex} = 550 nm @ 80 MHz, emission filter λ_{det} = 585/50 nm only showing background fluorescence of agarose.*

Quenching visualization was established with the same setup used for reaction monitoring. In figure S6-A1 and -B1 no chromophore was added, only background fluorescence of the agarose network is visible. Next (figure S6-2), a mixture of unsubstituted BODIPY (**S1**) and phenylacetylene is added. With an excitation wavelength λ_{ex} = 470 nm the green fluorescence of the BODIPY compound is detected (figure S6-A2). The fluorescence lifetime has already reduced about 1 ns because of the changed environment (table S1).[4] Adding the reactive cuprous ion, the transformation starts and the phenyltriazole is formed. Parallel to product formation, the lifetime of the chromophore reduced again about 1 ns (figure S6-A3, table S1). Using λ_{ex} = 550 nm, only background fluorescence is visible (figure S6-B3).

table S1: *fluorescence lifetime analysis of control experiment (figure S6) and reaction monitoring (figure 3).*

FLIM *control experiment* (figure S6)			**FLIM *reaction progress* (figure 3)**		
FLIM image	**τ_{fl} (over all pixels) / ns**	**lifetime histogram over all pixels reconvolution fit**	**FLIM image**	**τ_{fl} (over all pixels) / ns**	**lifetime histogram over all pixels reconvolution fit**
	4.5			<4.5>	
λ_{ex} = 470 nm, λ_{det} = 525/50 nm			λ_{ex} = 470 nm, λ_{det} = 525/50 nm		
	3.5			<3.5>	
λ_{ex} = 470 nm, λ_{det} = 525/50 nm			λ_{ex} = 470 nm, λ_{det} = 525/50 nm		
				3.2	
			λ_{ex} = 550 nm, λ_{det} = 585/50 nm		

Consequently, the fluorescence lifetime of chromophores changes twice:

- First, the lifetime reduces with transfer into the agarose matrix
- A second change results from the reaction conditions of CuAAC.

5. General Experimental

a. Chemicals and solvents

All chemicals and solvents were obtained from different suppliers (Sigma-Aldrich, Merck, Acros Organics, Alfa-Aesar, Apollo Scientific, TCI, Carbolution Chemicals, Combi Blocks, ABI). They were used without further purification. Solvents for spectroscopy investigations were used in HPLC or spectroscopic grade. Anhydrous solvents and pyrrole starting compounds were bought or prepared under literature-known procedures[5–11].

b. Analytical instruments and measurement techniques

i. NMR-spectra:

NMR spectra were recorded in deuterated solvents as noted in experimental procedures using a Bruker Avance 400 (400 MHz) spectrometer according (nucleus frequency see table S2).

table S2: *NMR nuclei and correlated frequency.*

Measured nucleus	Frequency / MHz
^{1}H	400.00
^{13}C	100.00
^{19}F	376.50

Chemical shifts were listed in parts per million (ppm) according to literature known deuterated solvent residual peaks[12,13]. Coupling constants (*J*) were specified in Hz. Fluorine spectra were calibrated using an internal, instrument-specific calibration factor of +179.91, estimated with fluorine standard.

ii. Crystal structures:

Crystal structures were measured at the Institute of Inorganic Chemistry, Saarland University (Dr. V. Huch) using X8 ApexII X-ray diffractometer. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1010897-1010900.

iii. UV-Vis and fluorescence spectra, lifetime measurement, quantum yields

All spectra were recorded in quartz cuvettes (3 mL content, 1 cm layer thickness, Hellma Analytics 117.11-FQS). UV-Vis spectra were recorded in a Jasco Spectrophotometer V-650 spectrometer, fluorescence spectra in a Jasco Spectrofluorometer FP-6500. The concentrations of all solutions were in the μmolar range.

Fluorescence lifetime measurements were conducted using a home-built TCSPC setup including a time-correlated single photon counting module (PicoQuant Picoharp 300). Excitation was established using a pulsed diode laser (LDH-P-C-470B 470 nm, Picoquant) containing a pulse width of 60-120 ps or a fiber laser (FemtoFiber pro TVIS, Toptica). Emission filters with a transmission range of 525/50, 546/20, 590/70 and 585/50 nm (all AHF Analysentechnik) were applied, with respect to the dye's fluorescence signal. A single-photon avalanche device was used (PDM 100ct SPAD, Micron Photo Devices) as detector. Analysis was done with reconvolution fit (PicoQuant Symphotime 64, Picoquant). Lifetime histograms were tail-fitted with Origin Pro 8.6G using exponential function.

Fluorescence quantum yields were estimated using cross calibration method with two references according to table S3:

table S3: *References for estimated QY.*

chromophore	**reference 1 - solvent**	**reference 2 - solvent**
α-Br-BODIPY (**1**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol
α -TMSAc-BODIPY (**4**)	Rhodamine 6G - ethanol	Atto 520 - water
α -Ethynyl-BODIPY (**6**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol
click product (**9b**)	Rhodamine 6G - ethanol	Atto 520 - water
β-I-BODIPY (**2**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol
β -Ethynyl-BODIPY (**7**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol
γ-Br-BODIPY (**3**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol
γ -TMSAc-BODIPY (**5**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol
γ -Ethynyl-BODIPY (**8**)	Rhodamine 123 - ethanol	Fluorescein – basic ethanol

c. Kinetic measurement technique

Kinetic measurements were established using self-manufactured, lockable quartz cuvettes (from type 3/GS/Q/10mm, Starna), designed by M. Wirtz and G. Berlin, Inorganic Chemistry, Saarland University. The measurements were done in a Jasco Spectrofluorometer FP-6500. Data were recorded over a period of 16 h every five minutes using front face excitation in a 30° angle.

For analysis, the product signal intensity was reduced about the relative starting compound ratio. Plotting signal maximum versus measurement time delivers the formation and decay kinetics. These curves were fitted with Origin Pro 8.6G using exponential function

$$y = y0 + \sum_{n=1}^{x} An * e^{(-(x-x0)/tn)}$$

d. Microscopy instrumentation

The azide functionalized agarose beads pictures were generated using fluorescence lifetime imaging. The setup components and picture recording specifications are listed in table S4.

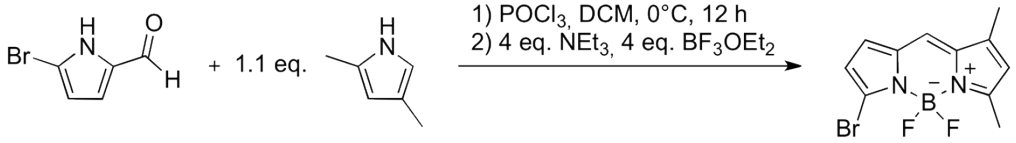
table S4: *Instrumentation for FLIM measurement.*

	green channel	orange channel
excitation		
laser	LDH-P-C-470B	Toptica FemtoFiber pro TVIS
wavelength	470 nm	550 nm
power	3 µW	3 µW
puls frequency	20 MHz	80 MHz
excitation filter		546/20
emission		
dichroitic mirror	F68-544HC Triple Line (AHF Analysentechnik)	
filter	525/50 (AHF Analysentechnik)	585/50 (AHF Analysentechnik)
detector	Perkin Elmer SPCM-AQR-14	
hardware		
microscope	Zeiss Axiovert 200	
objectiv	Zeiss C-Apochromat 63x/1.2 Water corrected for 170 µm cover slide	
TCSPC-system	PicoQuant Picoharp 300	
piezostage	PI E710.4CL	
laser driver	PicoQuant PDL808	
picture		
aquisition	PicoQuant Symphotime 64 Version	
size	80 µm x 80 µm	
pixel	512x512	
pixel dwell time	3.0 ms	

6. Synthetic procedures and characterization data

All oxygen and moister sensitive reactions were carried out under inert gas atmosphere. Glassware was oven-dried and used with Schlenk-technique methods. Reaction progress was controlled using Silica on TLC PET-foils with a layer thickness of 0.250 mm (pore size: 60 Å, Fluka Analytics). Compound screening was done by general column chromatography using silica gel, pore size of 0.040 – 0.063 mm as technical grade (Fluka - Analytics).

*a. Synthesis of 3-Bromo-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-Br-BODIPY (**1**)*



5.0 mmol (865.7 mg) 5-bromopyrrole carbaldehyde are dissolved in 250 mL dry dichloromethane. Then, 5.2 mmol (495.0 mg) 2,4-dimethylpyrrole and 5.0 mmol (768.0 mg) phosphorous oxychloride are added at 0°C. After stirring for 12 h, 30.0 mmol (4.5 mL) triethylamine brighten the dark red solution. 4.0 mL boron trifluoride diethyl etherate (48%) are added after stirring for additional 5 min. The reaction mixture is heated to reflux over 5 h. Subsequent to cooling to room temperature, saturated sodium hydrogen carbonate solution quenches the reaction. The phases are separated, the organic layer is washed three times with H_2O and dried over sodium sulfate. Quick filtration with silica gel and dichloromethane - petrol ether (1:1) delivers the crude product. Additional column chromatography using same solvent delivers a red crystalline solid (1270.4 mg, 4.2 mmol, 85%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.01 (s, 1 H), 6.75 (d, *J* = 3,9 Hz, 1 H), 6.34 (d, *J* = 3.9 Hz, 1 H), 6.13 (s, 1 H), 2.55 (s, 3 H), 2.20 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 163.8, 145.9, 136.4, 133.6, 126.8, 124.8, 123.0, 121.8, 115.8, 15.2, 11.3 ppm.

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -146.63 (q, *J* = 30.8 Hz, 2 F) ppm.

Crystal structure CCDC 1010897

HRMS (ESI)

chemical formula	calculated exact mass / Da	measured accurate mass / Da	Error / ppm
$C_{11}H_{11}{}^{10}B{}^{79}BrF_2N_2^+$	298.020303	298.02045	0.5
$C_{11}H_{11}{}^{11}B{}^{79}BrF_2N_2^+$	299.016671	299.01663	-0.1
$C_{11}H_{11}{}^{10}B{}^{81}BrF_2N_2^+$	300.018257	300.01841	0.5
$C_{11}H_{11}{}^{11}B{}^{81}BrF_2N_2^+$	301.014625	301.01475	0.4

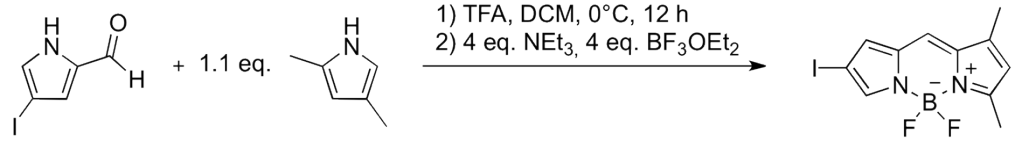
Absorbance and Emission: λ_{abs} = 506 nm, λ_{em} = 516 nm (DCM)

Lifetime: τ_{fl} = 6.5 ns (DCM)

Quantum Yield: Φ = 0.86 ±0.01 (DCM)

The spectra (see spectral data **7.a.i**) contain a second, not separable BODIPY fluorophore with identical optical properties, which doesn't affect further synthetic steps. This compound is identified as the corresponding chloride, originating from nucleophilic halogen exchange due to synthesis. ^{1}H-NMR shifts and mass spectra confirm 3-Chloro-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene.

*b. Synthesis of 5,7-Dimethyl-2-iodo-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - β-I-BODIPY (**2**)*



2.5 mmol (552.0 mg) 4-iodopyrrole carbaldehyde are dissolved in 20 mL dry dichloromethane. Then, 2.6 mmol (247.2 mg) 2,4-dimethylpyrrole and 0.1 mL of trifluoroacetic acid are added at 0°C. After stirring for 12 h, 10.0 mmol (2.0 mL) triethylamine brighten the dark red solution. 2.0 mL boron trifluoride diethyl etherate (48%) are added after stirring for additional 5 min. The reaction mixture was hold at 0°C. After 2 hours, the solvent was evaporated and subsequent column chromatography (dichloromethane : petrol ether – 1:1) isolates a red crystalline solid (340.0 mg, 1.0 mmol, 40%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.54 (s, 1 H), 7.11 (s, 1 H), 6.95 (s, 1 H), 6.21 (s, 1 H), 2.58 (s, 3 H), 2.26 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 165.4, 147.2, 141.9, 137.1, 133.4, 130.9, 123.3, 122.2, 99.9, 15.2, 11.3 ppm.

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -146.65 (q, *J* = 30.5 Hz, 2 F) ppm.

Crystal structure CCDC 1010898

HRMS (ESI)

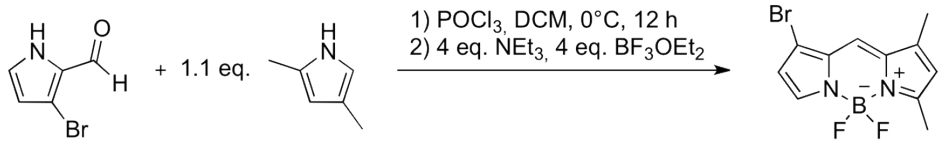
chemical formula	calculated exact mass / Da	measured accurate mass / Da	Error / ppm
$C_{11}H_{11}{}^{10}BF_2IN_2^+$	346.006439	346.0059	-1.6
$C_{11}H_{11}{}^{11}BF_2IN_2^+$	347.002807	347.00229	-1.5
$C_{10}{}^{13}CH_{11}{}^{11}BF_2IN_2^+$	348.006162	348.00558	-1.7

Absorbance and Emission: λ_{abs} = 509 nm, λ_{em} = 533 nm (DCM)

Lifetime: $\tau_{fl,1}$ = 3.3 ns, $\tau_{fl,2}$ = 0.6 ns (DCM)

Quantum Yield: Φ = 0.14 ±0.02 (DCM)

*c. Synthesis of 1-Bromo-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - γ-Br-BODIPY (**3**)*



This compound was synthesized analogously to the described method in **6.a**. A red, crystalline solid was yielded (340.0 mg, 1.0 mmol, 40%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.64 (s, 1 H), 7.37 (s, 1 H), 6.62 (s, 1 H), 6.36 (s, 1 H), 2.73 (s, 3 H), 2.45 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 167.0, 148.9, 139.4, 139.2, 132.7, 124.1, 123.9, 119.7, 117.0, 17.3, 13.4 ppm.

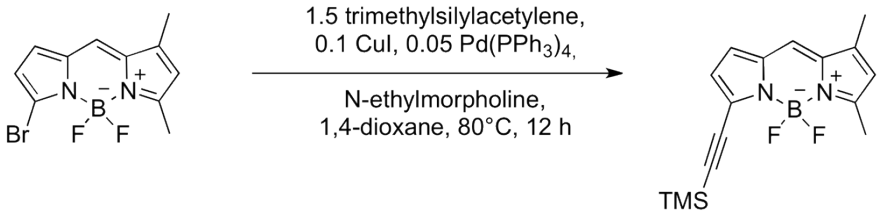
^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -146.765 (q, *J* = 30.7 Hz, 2 F) ppm.

Absorbance and Emission: λ_{abs} = 496 nm, λ_{em} = 506 nm (DCM)

Lifetime: τ_{fl} = <5.0> ns (DCM)

Quantum Yield: Φ = 0.34 ±0.01 (DCM)

*d. Synthesis of 5,7-Dimethyl-3-(trimethylsilyl-)ethynyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-TMSAc-BODIPY (**4**)*



1.00 mmol (300.0 mg) (**1**) and 1.50 mmol (147.1 mg) trimethylsilylacetylene are dissolved in 4.0 mL 1,4-dioxane. Then 4.0 mL N-ethylmorpholine, 0.05 mmol (57.8 mg) tetrakistriphenylpalladium(0) and 0.10 mmol (19.0 mg) CuI are added. The mixture is stirred for 12 h at 80°C. The solvent was evaporated and subsequent column chromatography (dichloromethane : petrol ether – 1 : 1 ; ethyl acetate : petrol ether – 1 : 4) yields a shiny pink solid (183 mg, 0.58 mmol, 58%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.02 (s, 1 H), 6.80 (d, *J* = 3.9 Hz, 1 H), 6.55 (d, *J* = 3.9 Hz, 1 H), 6.16 (s, 1 H), 2.61 (s, 3 H), 2.25 (s, 3H), 0.29 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 164.9, 146.9, 137.3, 137.2, 134.7, 122.0, 121.7, 120.4, 118.6, 102.3, 97.8, 15.3, 11.5, -0.1 ppm.

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -147.15 (q, *J* = 30.0 Hz, 2 F) ppm.

Crystal structure CCDC 1010899

HRMS (ESI)

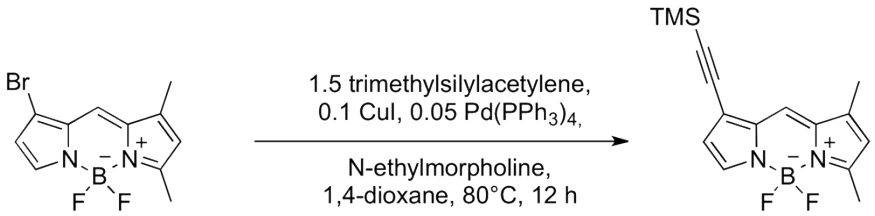
chemical formula	calculated exact mass / Da	measured accurate mass / Da	Error / ppm
$C_{16}H_{20}{}^{10}BF_2N_2Si^+$	316.149318	316.15028	3.0
$C_{16}H_{20}{}^{11}BF_2N_2Si^+$	317.145686	317.14662	2.9
$C_{15}{}^{13}CH_{20}{}^{11}BF_2N_2Si^+$	318.149041	318.15021	3.7

Absorbance and Emission: λ_{abs} = 529 nm, λ_{em} = 540 nm (DCM)

Lifetime: τ_{fl} = 5.3 ns (DCM)

Quantum Yield: Φ = 1.00 -0.02 (DCM)

*e. Synthesis of 5,7-Dimethyl-1-(trimethylsilyl-)ethynyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - γ-TMSAc-BODIPY (**5**)*



This compound is synthesized analogously to described method in **6.d**. A shiny pink solid (143 mg, 0.45 mmol, 45%) is obtained.

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.49 (s, 1 H), 7.27 (s, 1 H), 6.48 (d, *J* = 2.0 Hz, 1 H), 6.21 (s, 1 H), 2.60 (s, 3 H), 2.33 (s, 3H), 0.29 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 164.9, 146.9, 137.1, 134.7, 122.0, 121.7, 120.4, 118.7, 110.0, 102.3, 97.8, 15.3, 11.5, -0.1 ppm.

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -146.69 (q, *J* = 30.7 Hz, 2 F) ppm.

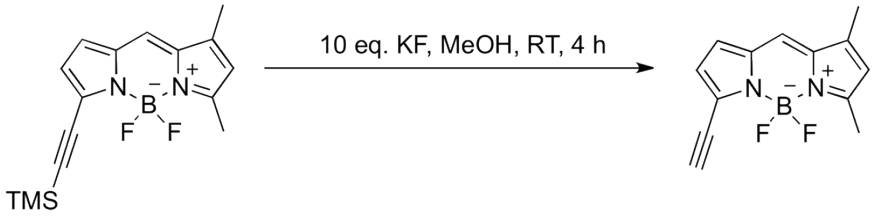
Crystal structure CCDC 1010900

Absorbance and Emission: λ_{abs} = 510 nm, λ_{em} = 520 nm (DCM)

Lifetime: τ_{fl} = 4.9 ns (DCM)

Quantum Yield: Φ = 0.92 ±0.04 (DCM)

*f. Synthesis of 3-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-ethynyl-BODIPY (**6**)*



1.00 mmol (316.2 mg) (**4**) is dissolved in 50.0 mL methanol and 10.0 mmol (580.9 mg) potassium fluoride is added. The solution is stirred at room temperature for 4 h. The solvent is evaporated and subsequent column chromatography (dichloromethane : petrol ether – 1 : 1) delivers a red, rapidly decomposing solid (127 mg, 0.52 mmol, 52%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.08 (s, 1 H), 6.82 (d, *J* = 3.8 Hz, 1 H), 6.61 (d, *J* = 3.9 Hz, 1 H), 6.01 (s, 1 H), 3.66 (s, 1 H), 2.64 (s, 3 H), 2.28 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 165.6, 146.4, 137.8, 133.2, 130.8, 125.2, 123.1, 122.3, 122.2, 110.0, 85.7, 14.3, 11.4 ppm.

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -146.81 (q, *J* = 30.6 Hz, 2 F) ppm.

HRMS (ESI)

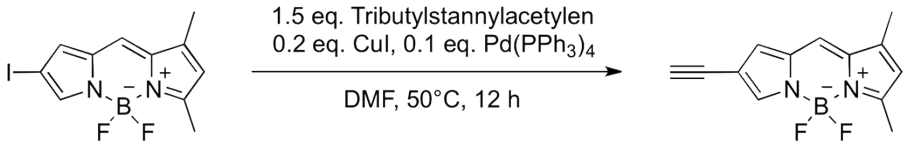
chemical formula	calculated exact mass / Da	measured accurate mass / Da	Error / ppm
$C_{13}H_{12}{}^{10}BF_2N_2^+$	244.109791	244.10911	-2.8
$C_{13}H_{12}{}^{11}BF_2N_2^+$	245.106159	245.10543	-3.0
$C_{12}{}^{13}CH_{12}{}^{11}BF_2N_2^+$	246.109514	246.10883	-2.8

Absorbance and Emission: λ_{abs} = 518 nm, λ_{em} = 529 nm (DCM)

Lifetime: τ_{fl} = 6.5 ns (DCM)

Quantum Yield: Φ = 0.89 ±0.02 (DCM)

*g. Synthesis of 2-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - β-ethynyl-BODIPY (**7**)*



1.00 mmol (345.3 mg) β-iodo-BODIPY (**2**) is dissolved in 10 mL DMF and 0.1 mmol (115.5 mg) tetrakistriphenylpalladium(0), 0.2 mmol (38.1 mg) CuI and 1.5 mmol (348.8 mg) tributylstannylacetylene are added and stirred at room temperature for 12 h. The solvent was evaporated and subsequent column chromatography (dichloromethane : petrol ether – 1 : 1) yields a red, rapidly decomposing solid (161.3 mg, 0.66 mmol, 66%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 7.72 (s, 1 H), 7.16 (s, 1 H), 6.97 (s, 1 H), 6.22 (s, 1 H), 3.06 (s, 1 H), 2.61 (s, 3 H), 2.29 (s, 3H).

^{13}C-NMR (100.0 MHz, $CDCl_3$, 298 K): δ = 165.9, 141.2, 137.8, 131.5, 127.4, 125.2, 124.4, 122.3, 110.1, 103.6, 78.3, 15.4, 11.5 ppm.

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -146.62 (q, *J* = 22.9 Hz, 2 F) ppm.

HRMS (ESI)

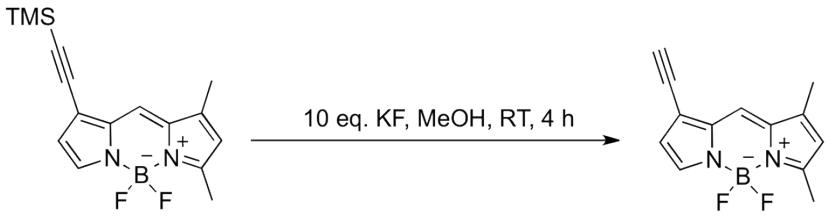
chemical formula	calculated exact mass / Da	measured accurate mass / Da	Error / ppm
$C_{13}H_{12}{}^{10}BF_2N_2^+$	244.109791	244.10899	-3.2
$C_{13}H_{12}{}^{11}BF_2N_2^+$	245.106159	245.10532	-3.4
$C_{12}{}^{13}CH_{12}{}^{11}BF_2N_2^+$	246.109514	246.10867	-3.4

Absorbance and Emission: λ_{abs} = 509 nm, λ_{em} = 536 nm (DCM)

Lifetime: τ_{fl} = 6.2 ns (DCM)

Quantum Yield: Φ = 0.84 ±0.04 (DCM)

*h. Synthesis of 1-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - γ-ethynyl-BODIPY (**8**)*



(**5**) is deprotected similarly to the procedure **6.f.** A red, rapidly decomposing solid (124 mg, 0.51 mmol, 51%) is obtained.

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 8.04 (s, 1 H), 7.43 (s, 1 H), 6.74 (s, 1 H), 6.25 (s, 1 H), 3.63 (s, 1 H), 2.61 (s, 3 H), 2.48 (s, 3H).

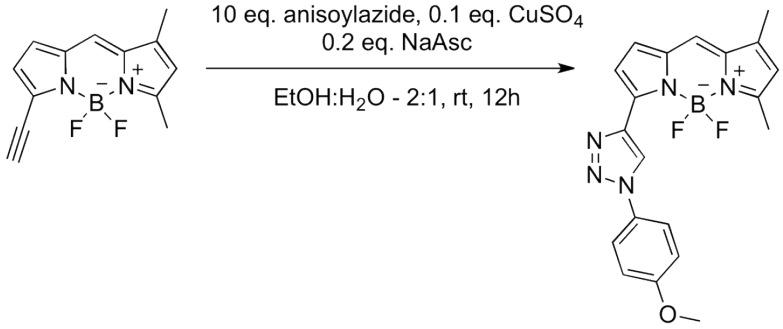
^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -147.36 (q, *J* = 30.3 Hz, 2 F) ppm.

Absorbance and Emission: λ_{abs} = 510 nm, λ_{em} = 519 nm (DCM)

Lifetime: τ_{fl} = 4.4 ns (DCM)

Quantum Yield: Φ = 0.87 ±0.05 (DCM)

*i. Synthesis of 3-(Methoxyphenyl)triazoyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene – click product (**9b**)*



Triazole formation is achieved using 0.5 mmol (123.6 mg) α-ethynyl-BODIPY (**6**) and 5.0 mmol (50 µl) of a 1 M anisyl azide solution in *tert.* butyl methyl ether. Both components were dissolved in 20 mL ethanol. $CuSO_4$ and sodium ascorbate are mixt in 10 mL water and are added to the reaction mixture after catalyst formation. After 12 h at room temperature, the solvent is removed under vacuum and column chromatography (dichloromethane) delivers a purple solid (0.1 mmol, 39.3 mg, 20%).

^{1}H-NMR (400.0 MHz, $CDCl_3$, 298 K):

δ = 8.83 (s, 1H), 7.74 (d, *J* = 8.9 Hz, 1 H), 7.36 (d, *J* = 4.2 Hz, 1 H), 7.17 (s, 1H), 7.06 (d, *J* = 8.9 Hz, 1 H), 6.17 (s, 1H), 3.89 (s, 3H), 2.63 (s, 3H), 2.30 (s, 3H)

^{19}F-NMR (376.5 MHz, $CDCl_3$, 298 K): δ = -145.91 ppm

HRMS (ESI)

chemical formula	calculated exact mass / Da	measured accurate mass / Da	Error / ppm
$C_{21}H_{20}{}^{10}BF_2N_4O^+$	393.16975	393.16833	-3.6
$C_{21}H_{20}{}^{11}BF_2N_4O^+$	394.166118	394.1647	-3.6
$C_{20}{}^{13}CH_{20}{}^{11}BF_2N_4O^+$	395.169473	395.1681	-3.5

Absorbance and Emission: λ_{abs} = 544 nm, λ_{em} = 555 nm (DCM)

Lifetime: τ_{fl} = 6.1 ns (DCM)

Quantum Yield: Φ = 0.73 ±0.05 (DCM)

7. Spectral data

a. NMR-spectra

i. 3-Bromo-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-Br-BODIPY (**1**)

Figure S7: *^{1}H-NMR (**1**).*

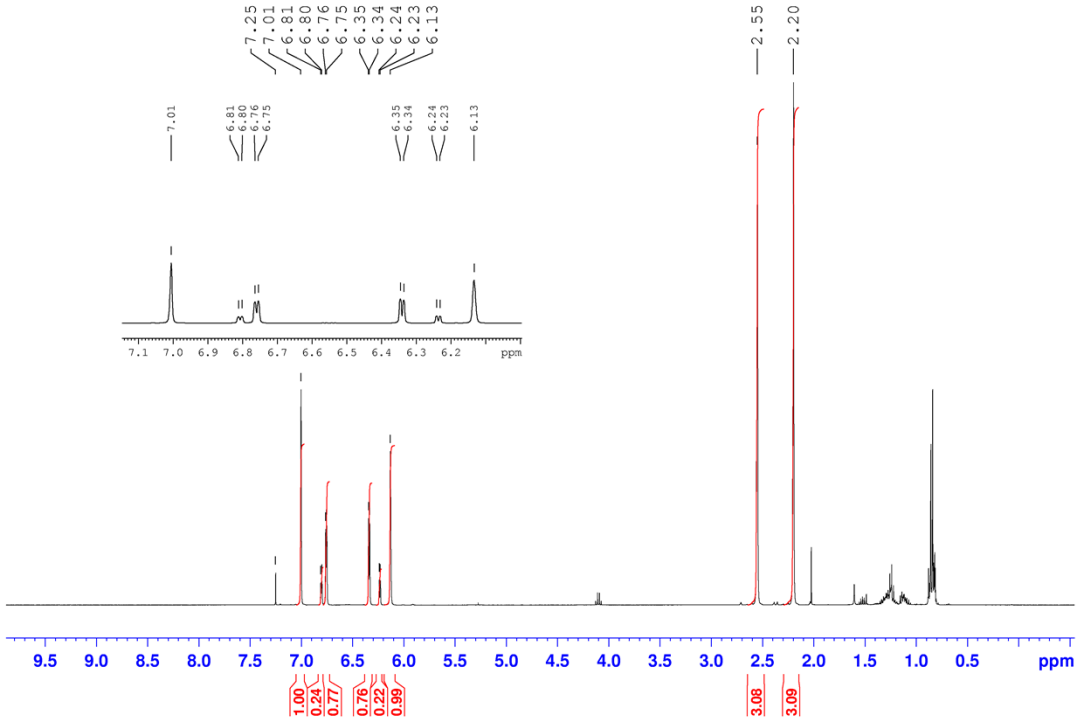


Figure S8: *^{13}C-NMR (**1**).*

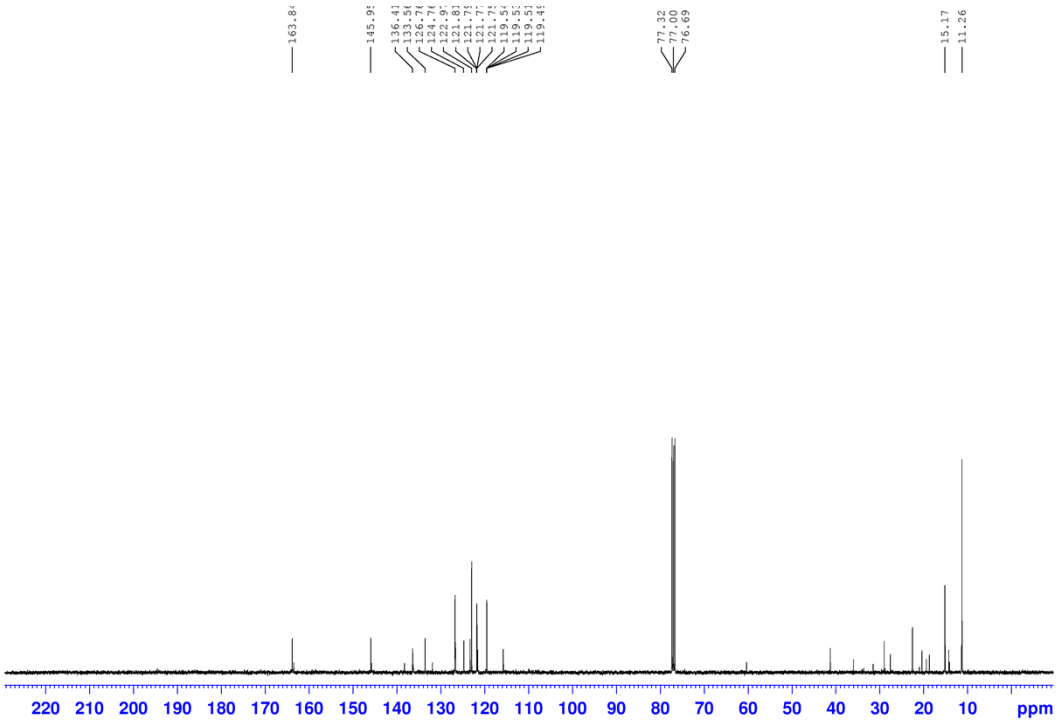
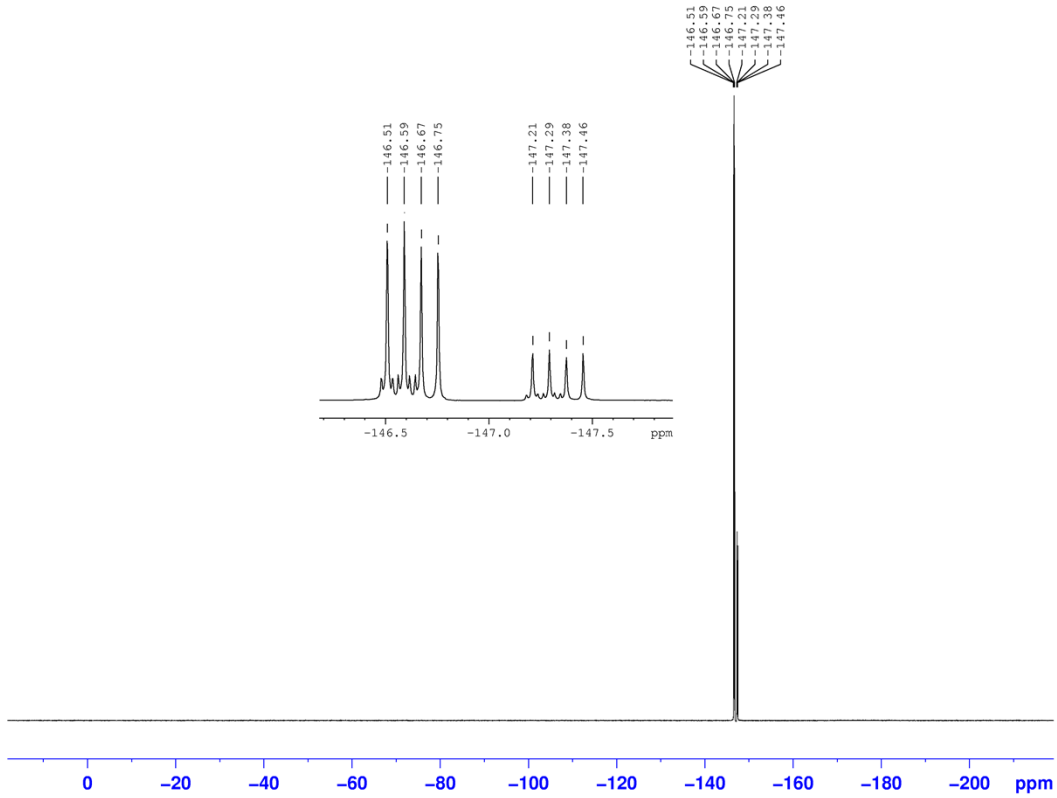


Figure S9: *^{19}F-NMR (**1**).*



ii. 1,3-Dimethyl-2-iodo-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - β-I-BODIPY (**2**)

Figure S10: *^{1}H-NMR (**2**).*

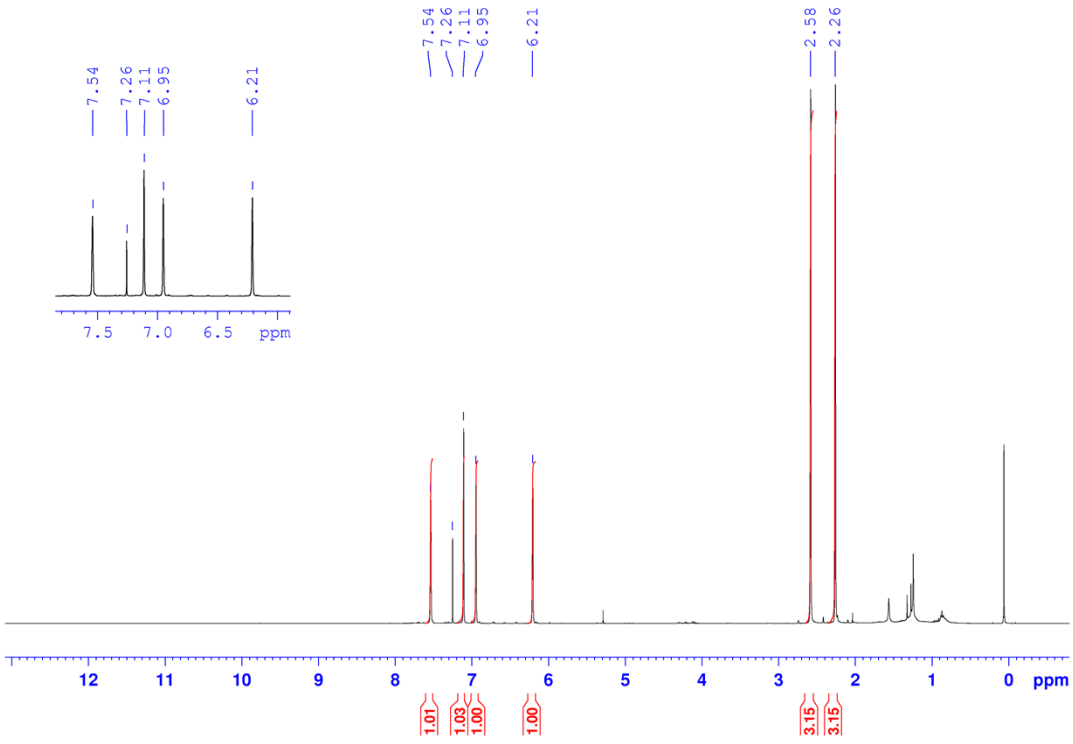


Figure S11: *^{13}C-NMR (**2**).*

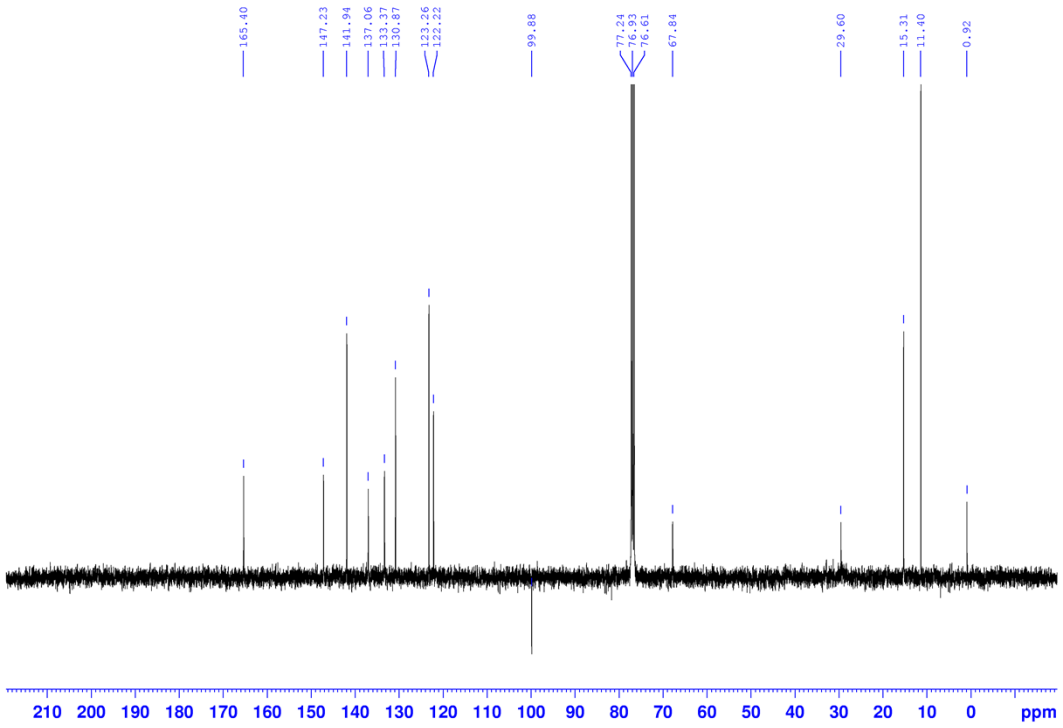
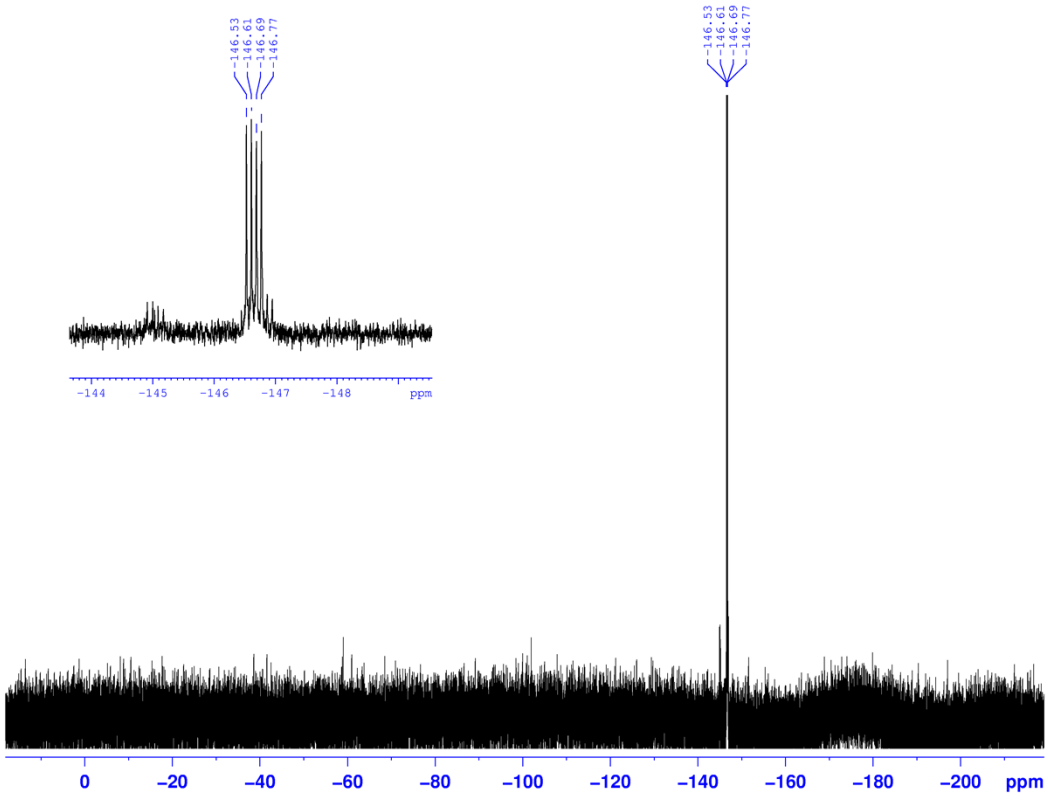


Figure S12: *^{19}F-NMR (**2**).*



iii. 1-Bromo-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - γ-Br-BODIPY (**3**)

Figure S13: *^{1}H-NMR (**3**).*

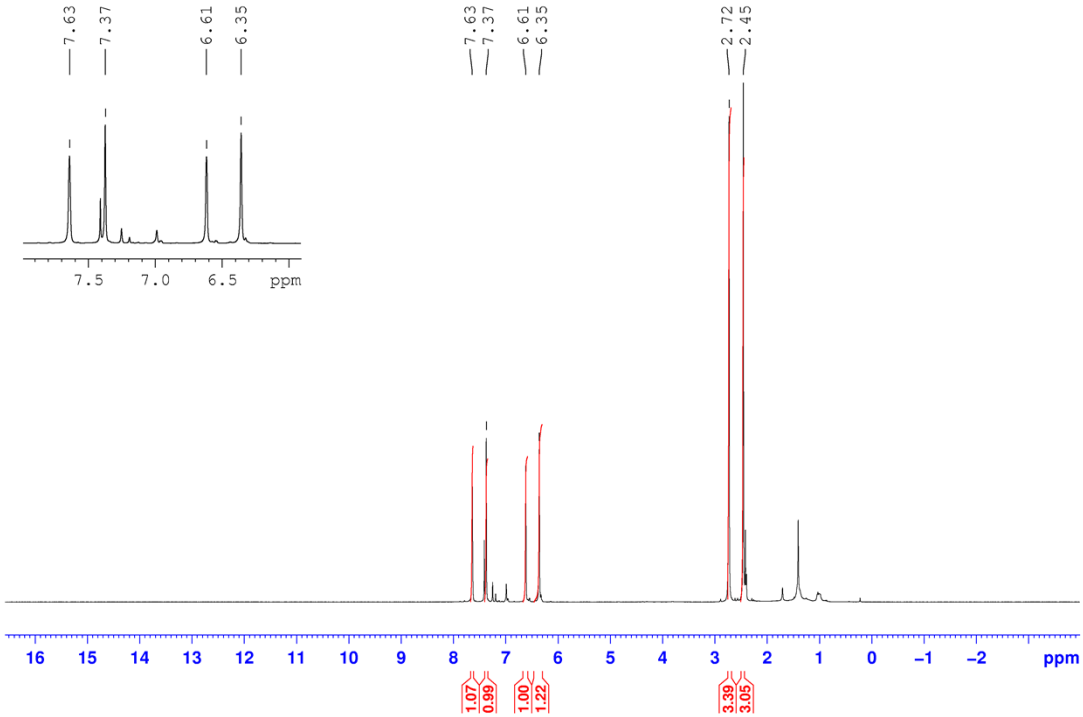


Figure S14: *^{13}C-NMR (**3**).*

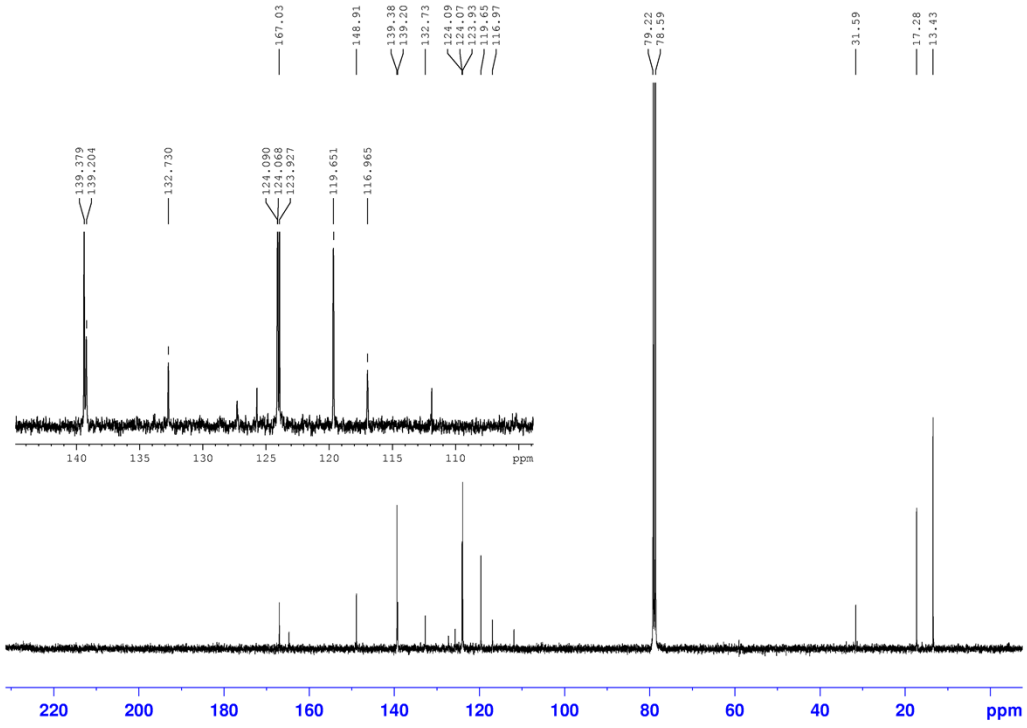
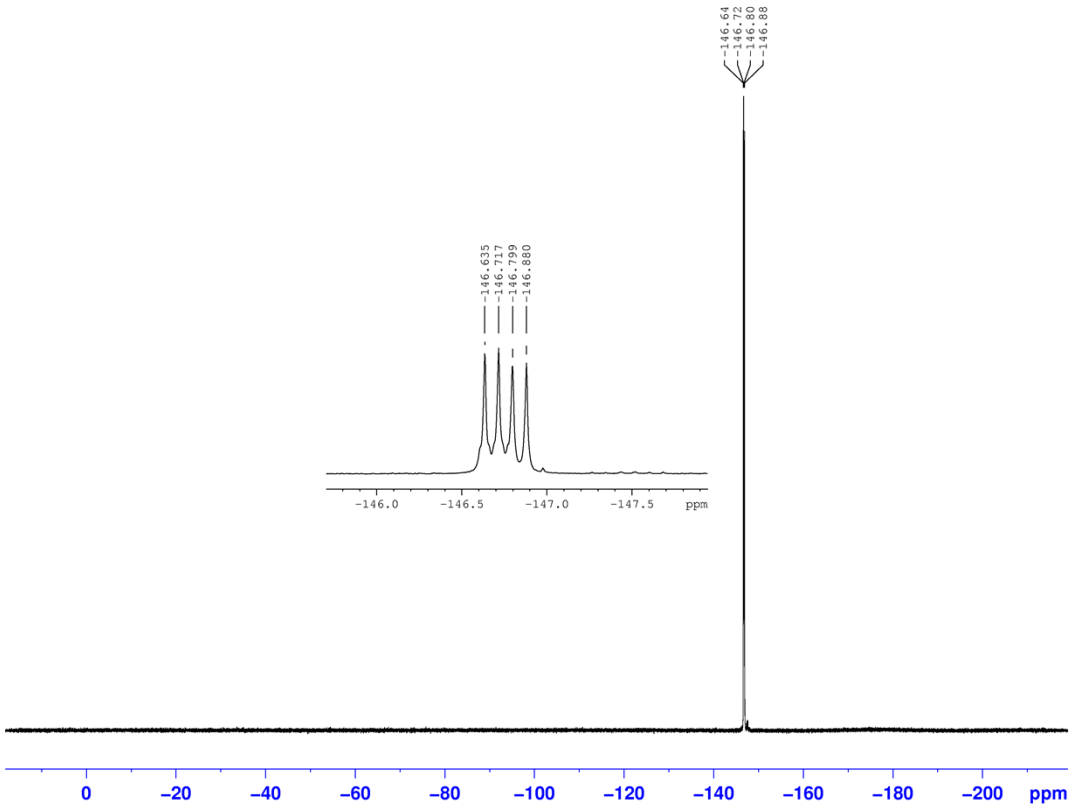


Figure S15: *[19]F-NMR (**3**).*



iv. 1,3-Dimethyl-3-(trimethylsilyl)ethynyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene _ -_ α-TMSAc-BODIPY (**4**)

Figure S16: *[1]H-NMR (**4**).*

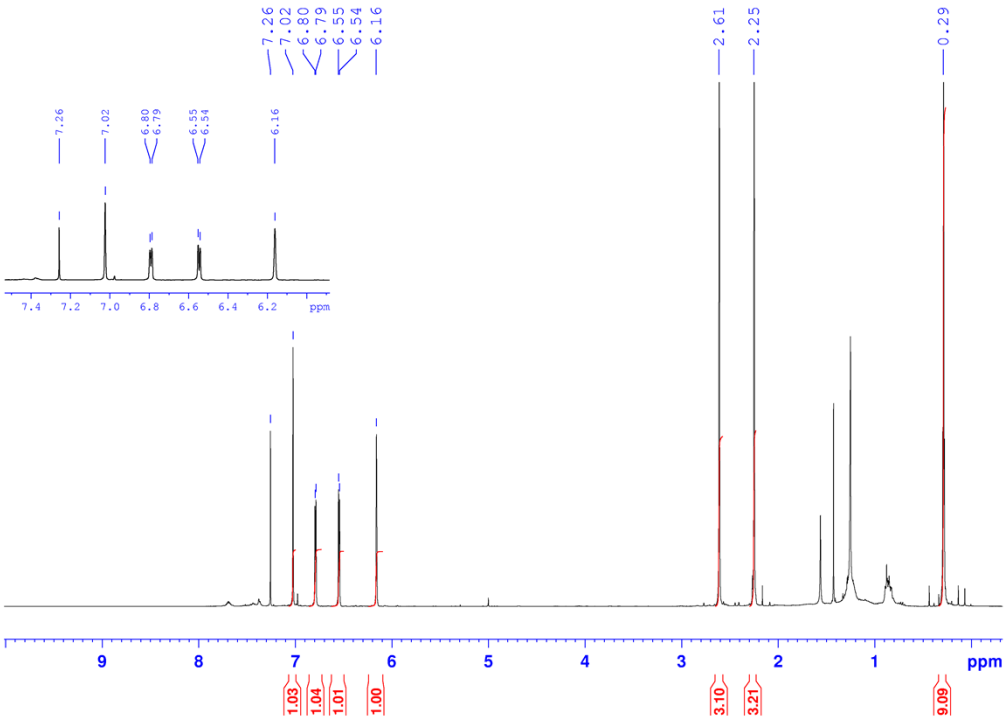


Figure S17: *^{13}C-NMR (**4**).*

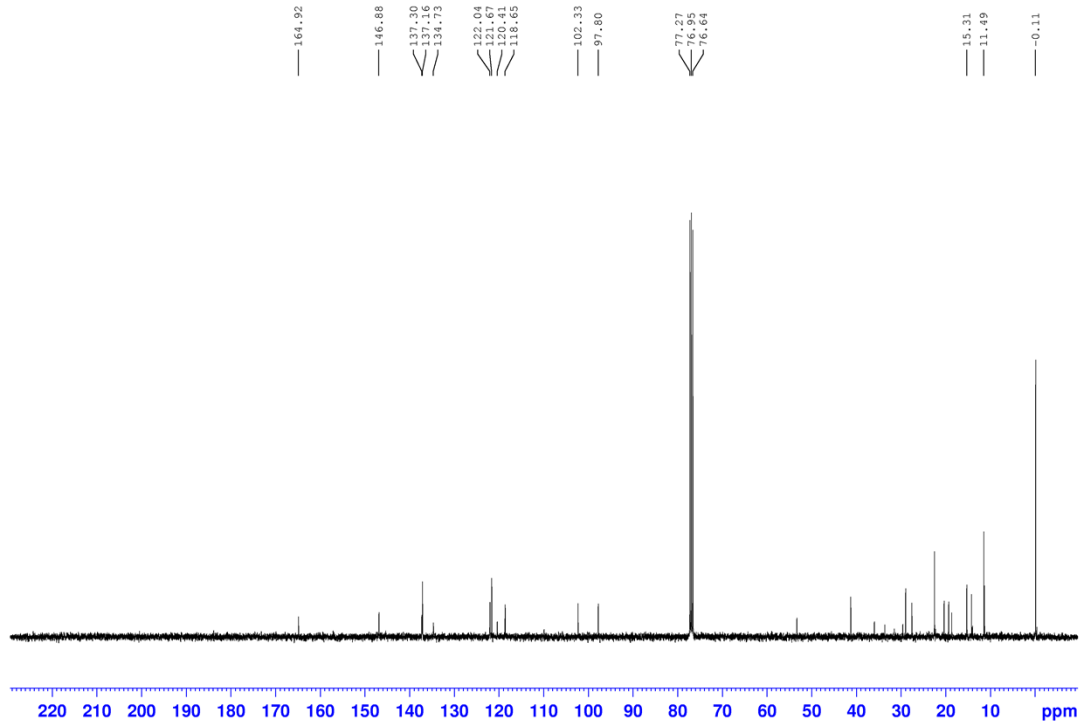
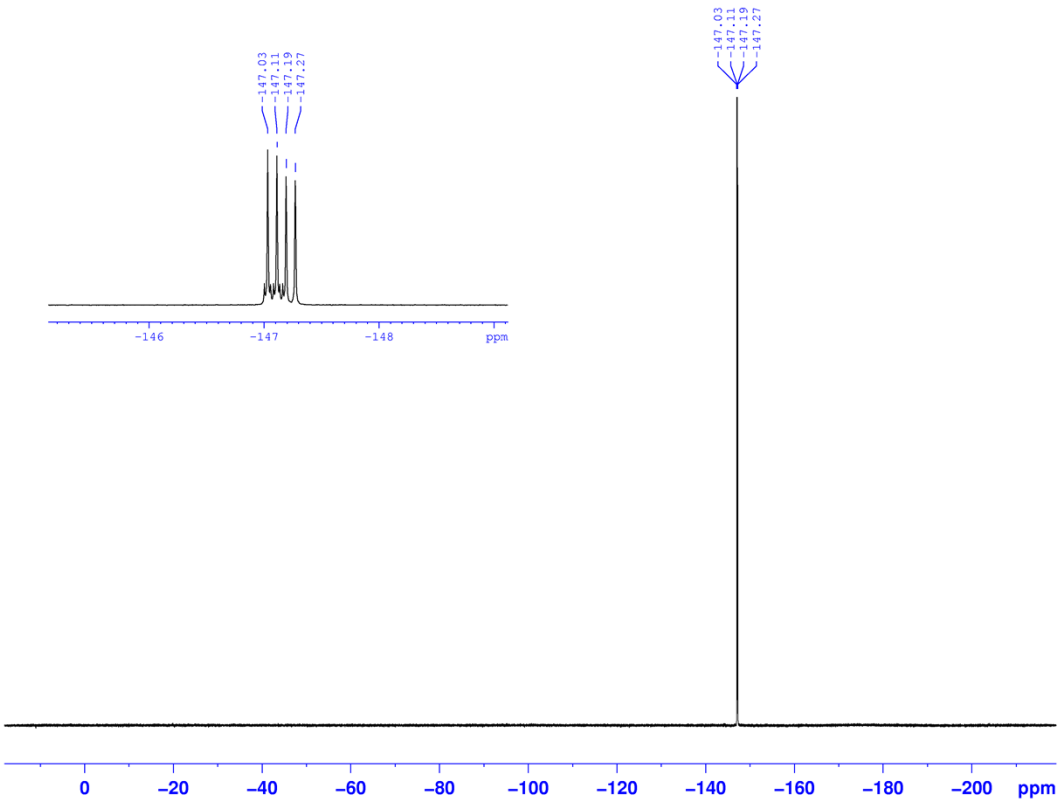


Figure S18: *^{19}F-NMR (**4**).*



v. 5,7-Dimethyl-1-(trimethylsilyl)ethynyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene _-_ γ-TMSAc-BODIPY (**5**)

Figure S19: *^{1}H-NMR (**5**).*

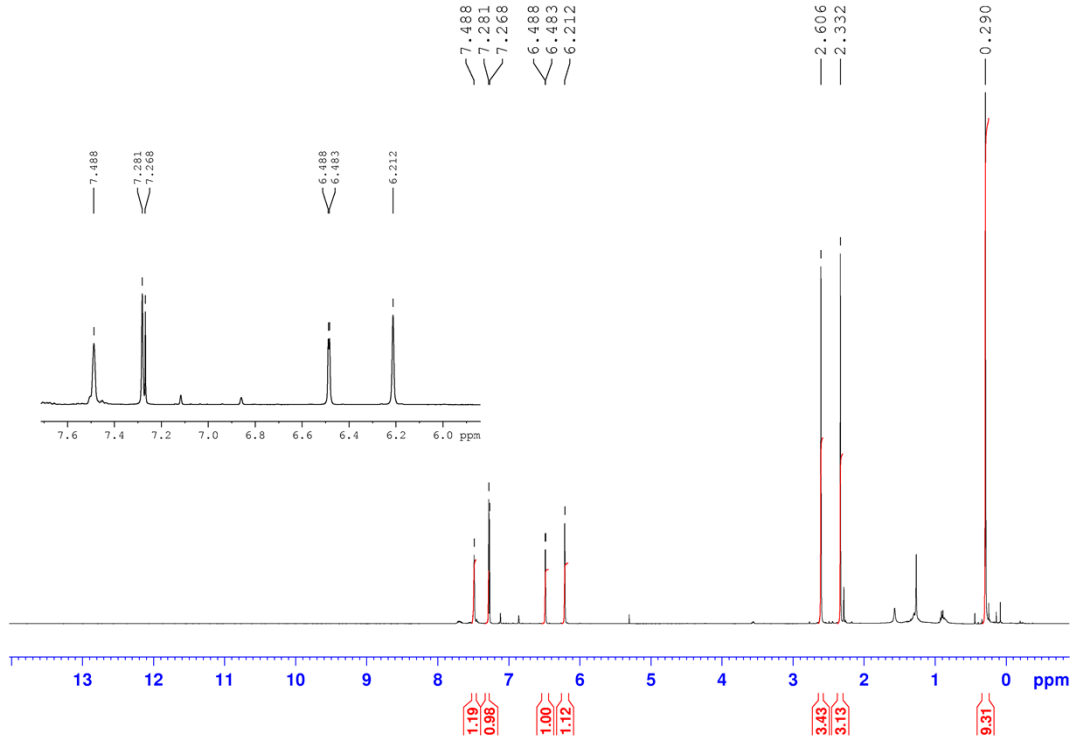


Figure S20: *^{13}C-NMR (**5**).*

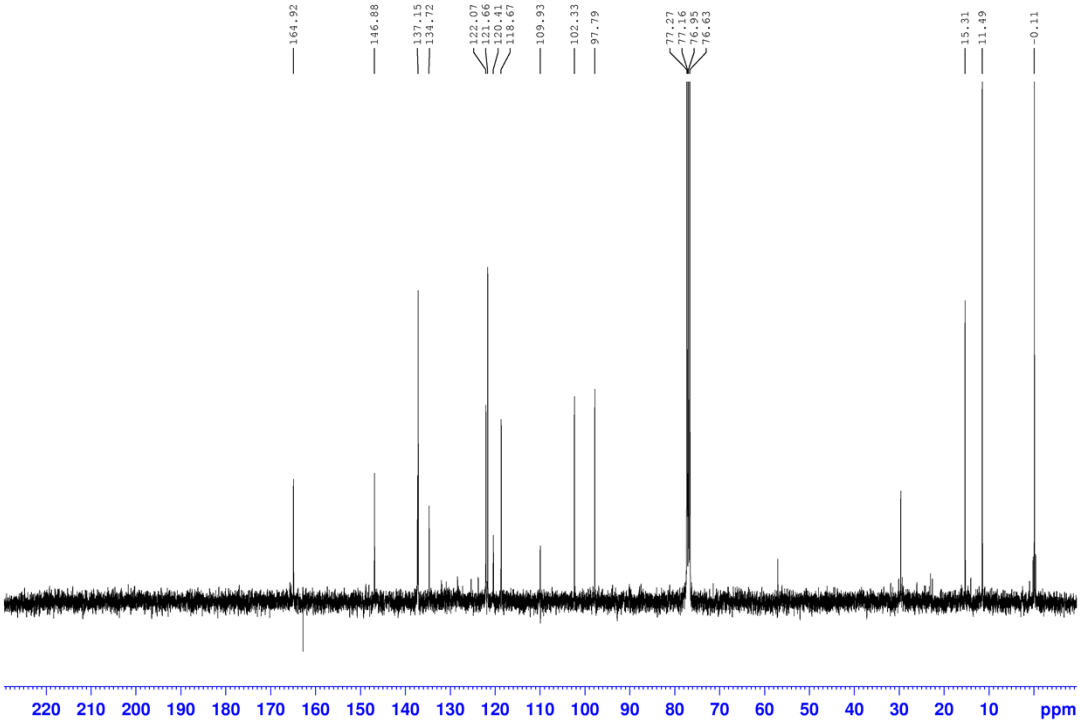
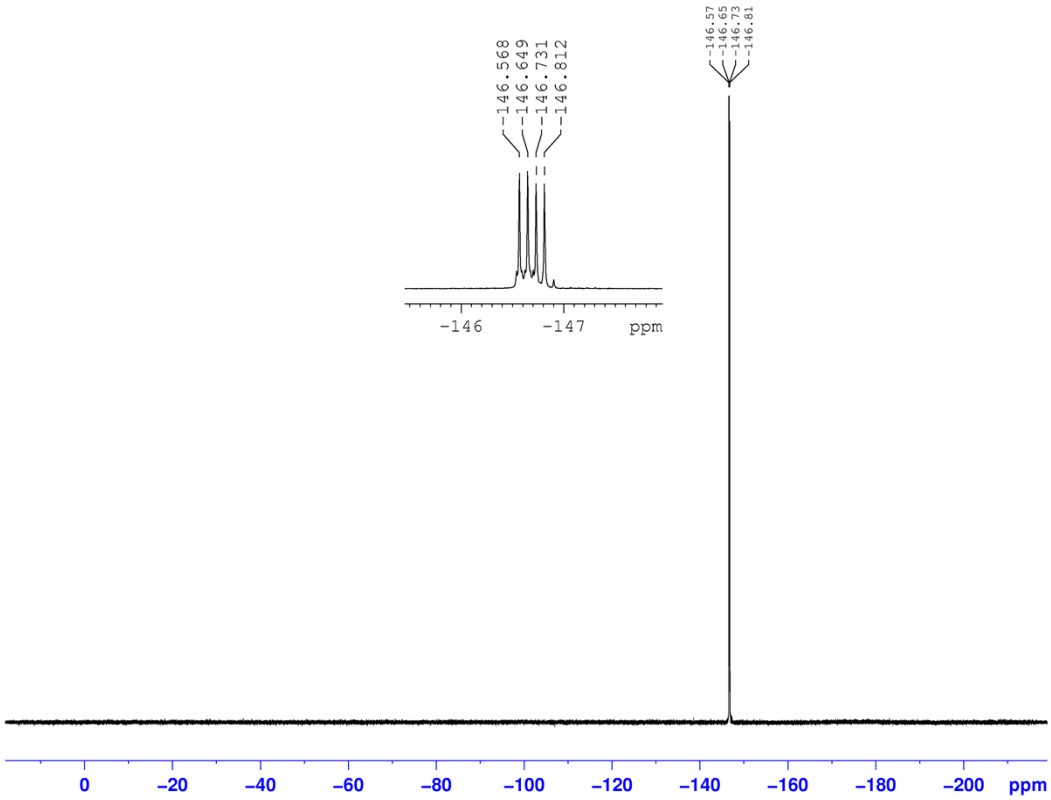


Figure S21: *[19]F-NMR (**5**).*



vi. 3-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-ethynyl-BODIPY (**6**)

Figure S22: *[1]H-NMR (**6**).*

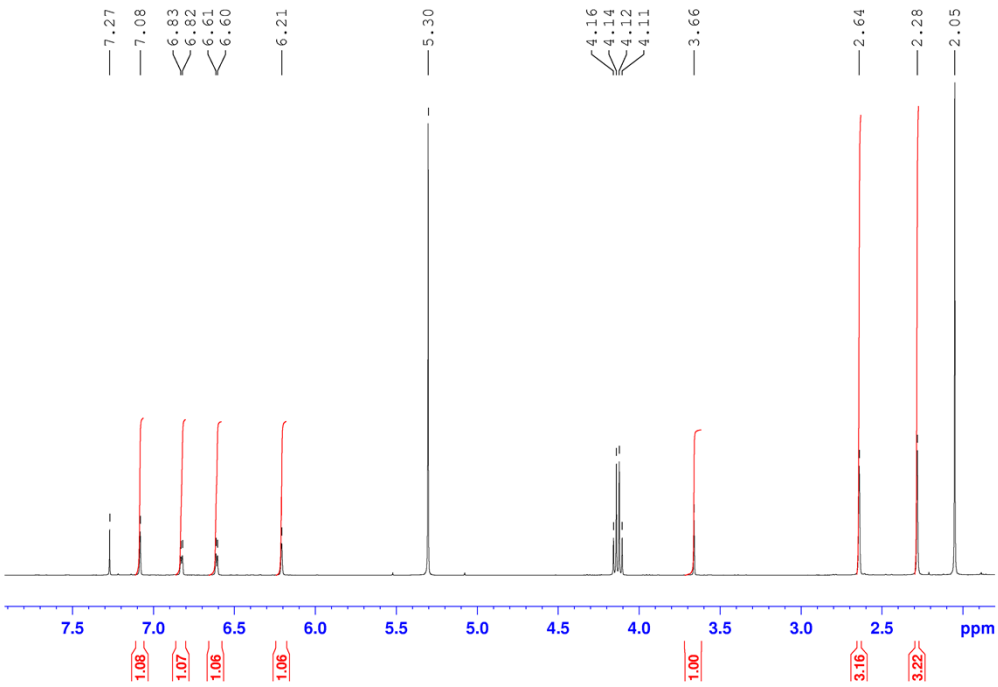


Figure S23: *^{13}C-NMR (**6**).*

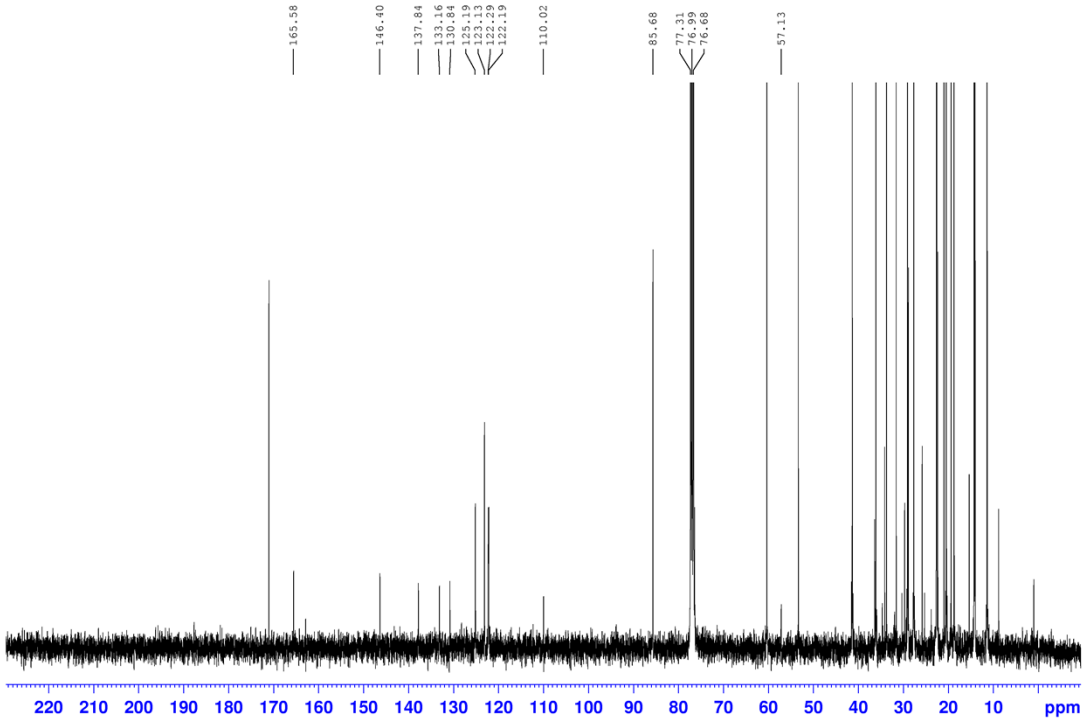
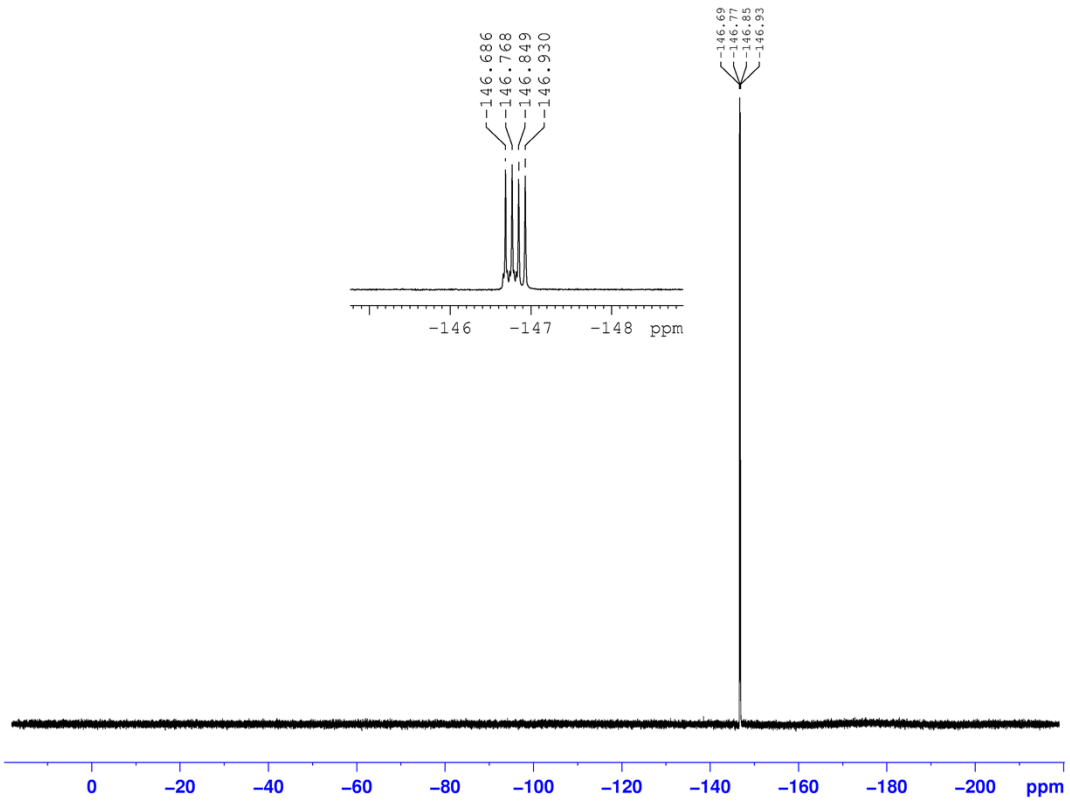


Figure S24: *^{19}F-NMR (**6**).*



vii. 2-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - β-ethynyl-BODIPY (**7**)

Figure S25: *^{1}H-NMR (**7**).*

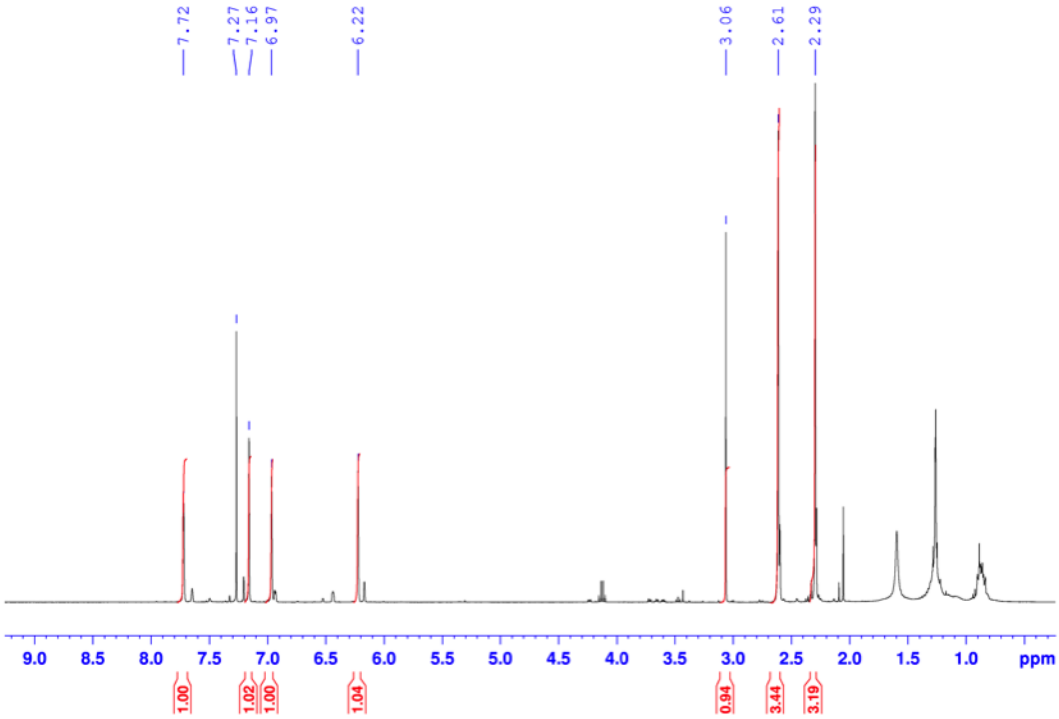


Figure S26: *^{13}C-NMR (**7**).*

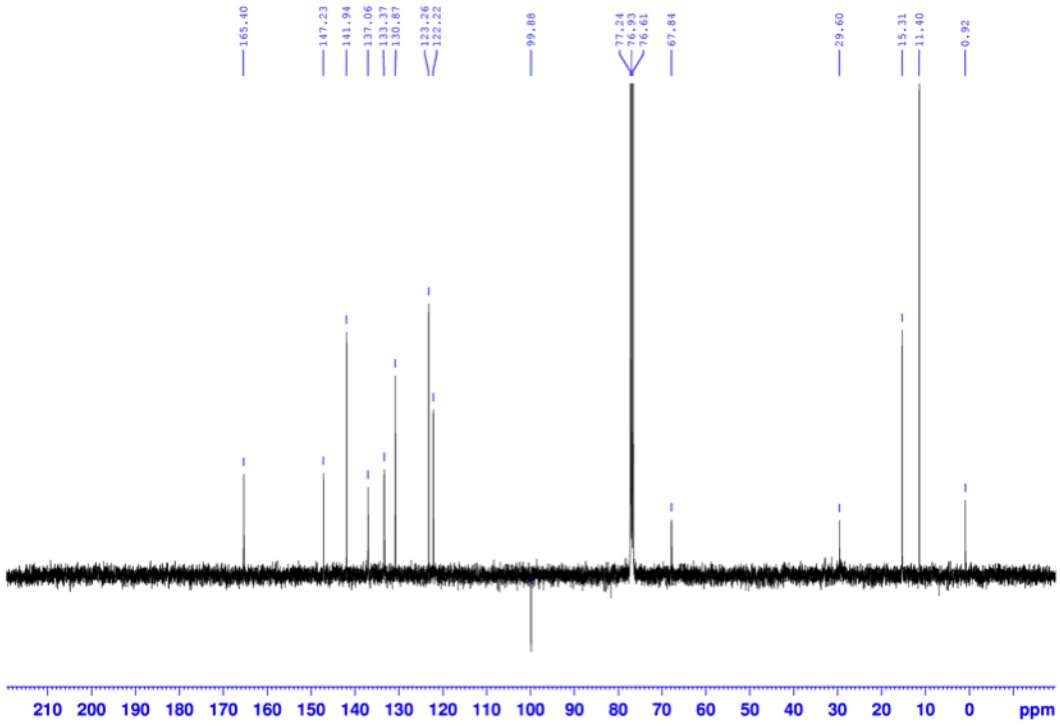
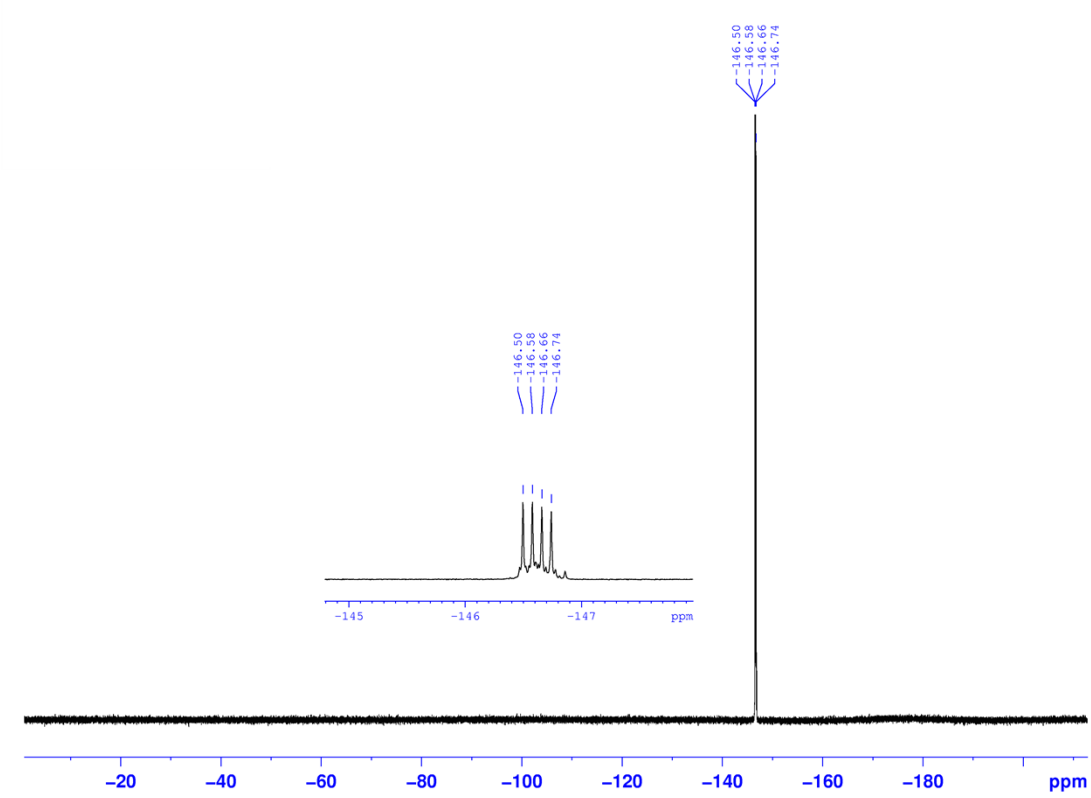


Figure S27: *[19]F-NMR (**7**).*



viii. 1-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - γ-ethynyl-BODIPY (**8**)

Figure S28: *[1]H-NMR (**8**).*

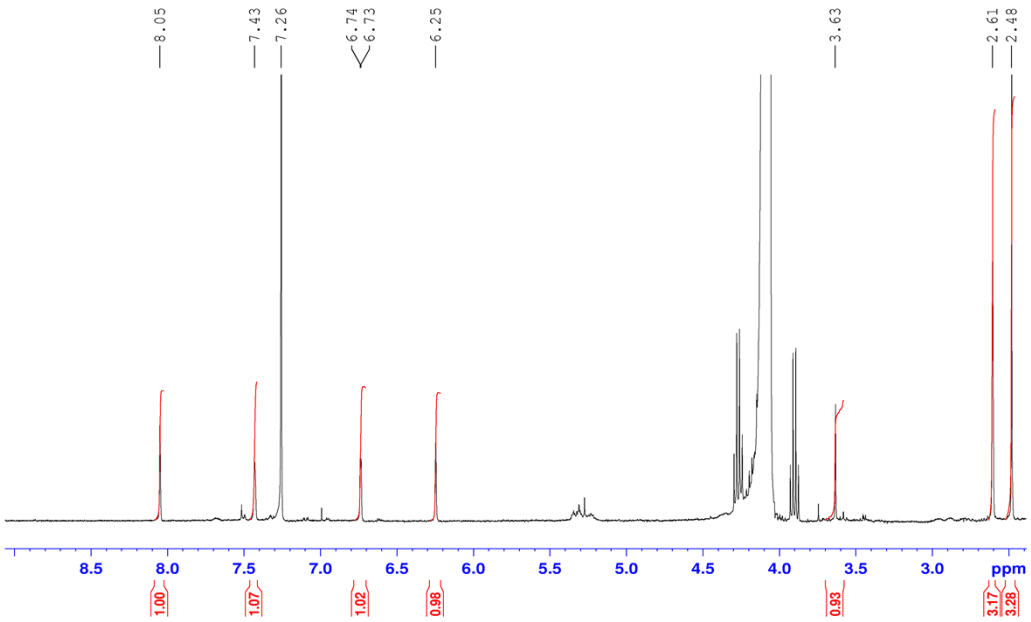
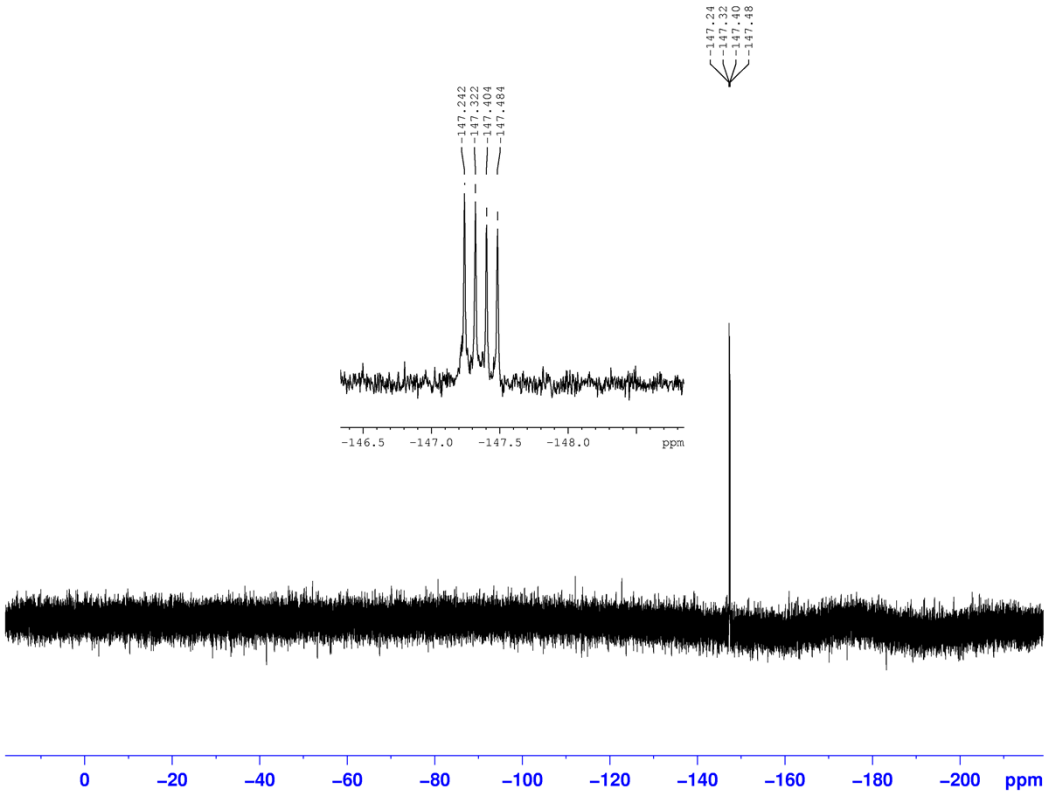


Figure S29: *[19]F-NMR (**8**).*



ix. 3-(Methoxyphenyl)triazol-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene_ _ – _ _click product (**9b**)

Figure S30: *[1]H-NMR (**9b**).*

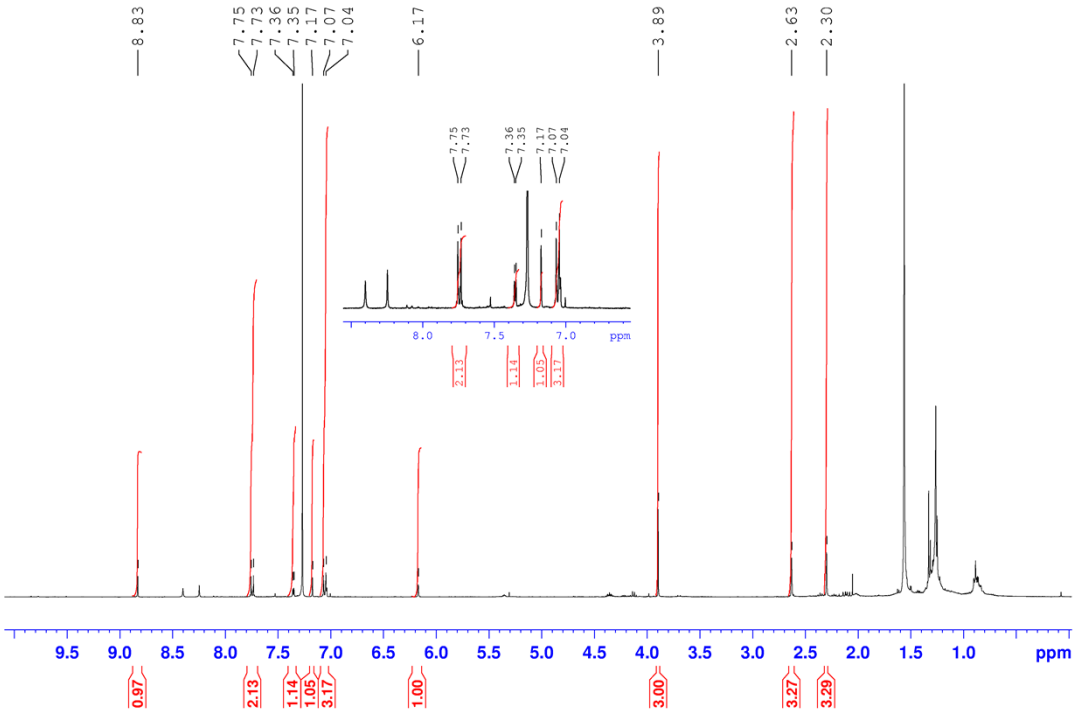
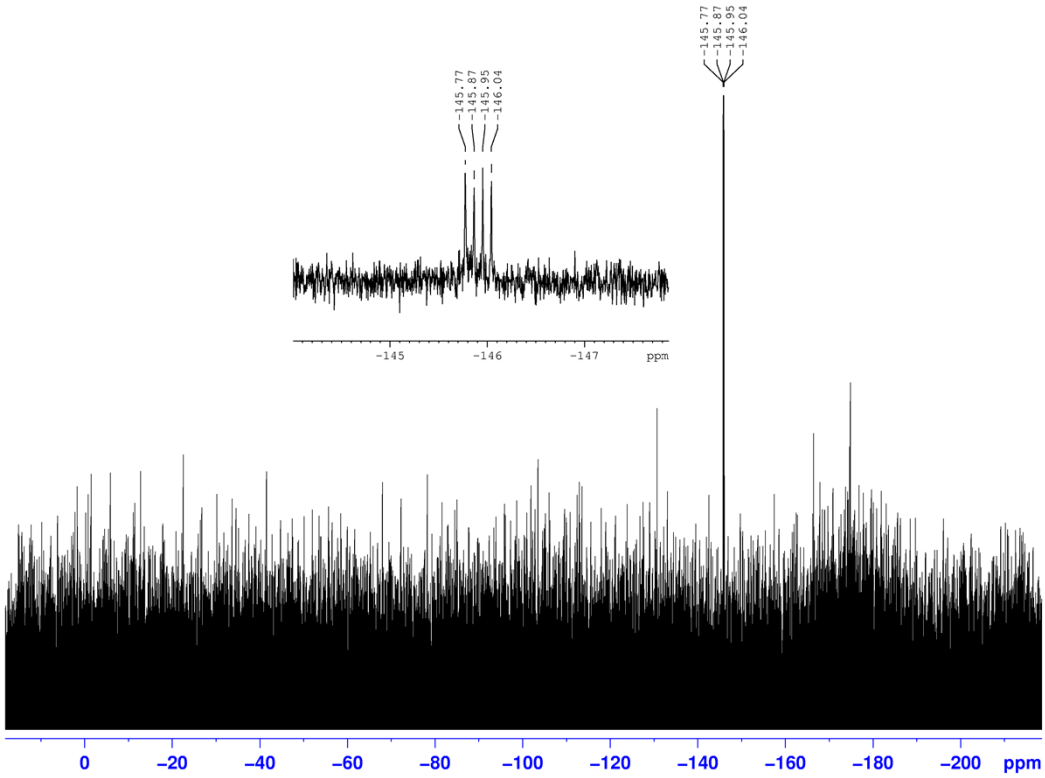


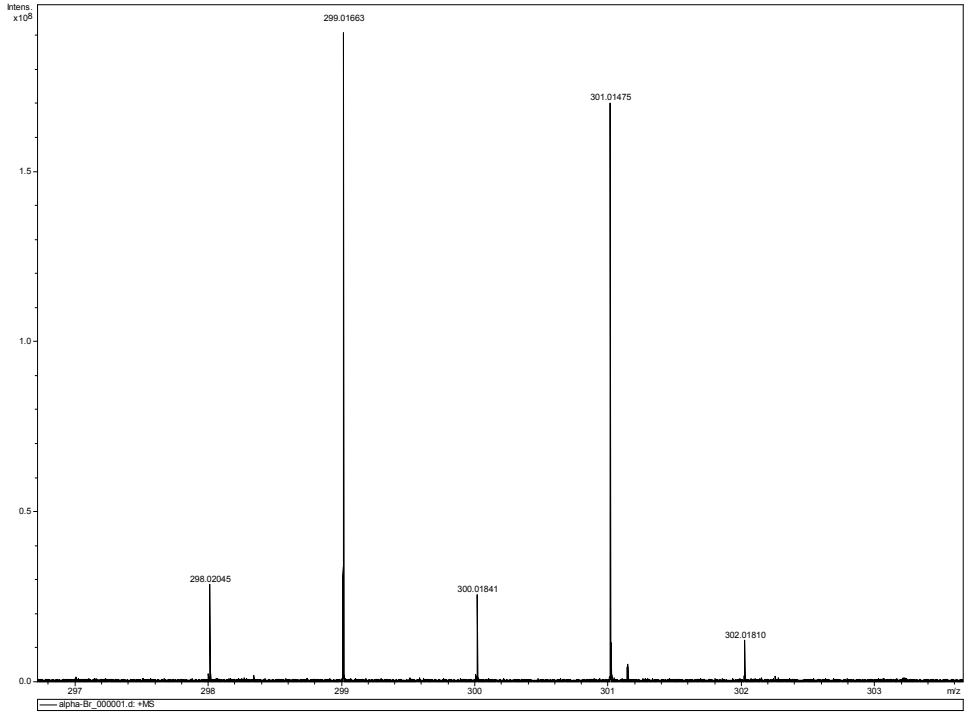
Figure S31: *^{19}F-NMR (**9b**).*



b. Mass spectra

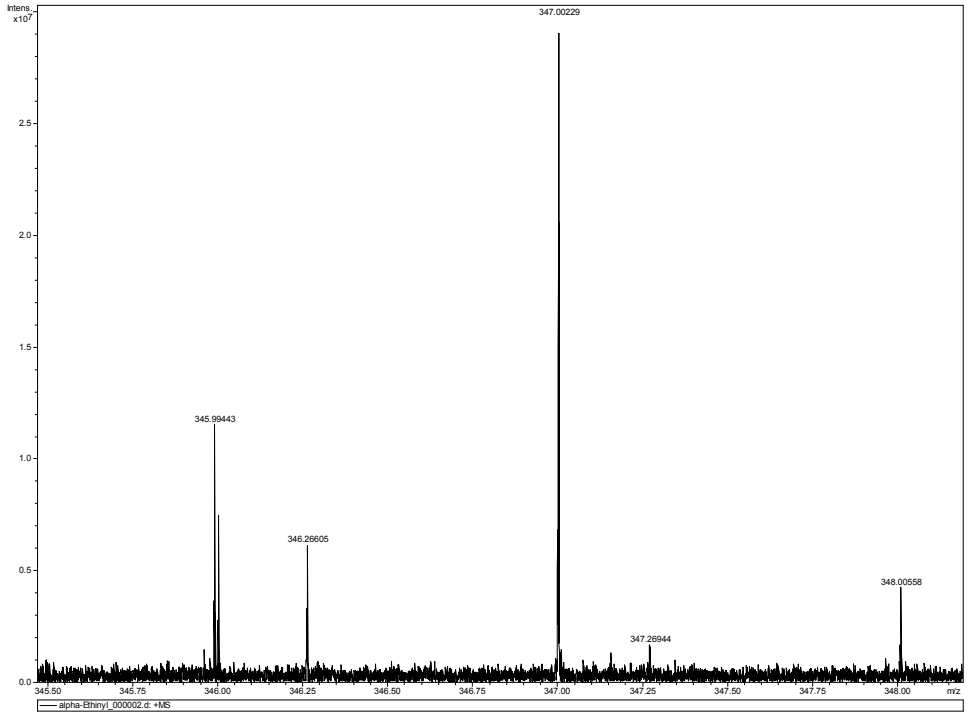
i. 3-Bromo-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-Br-BODIPY (**1**)

Figure S32: *mass spectra (**1**).*



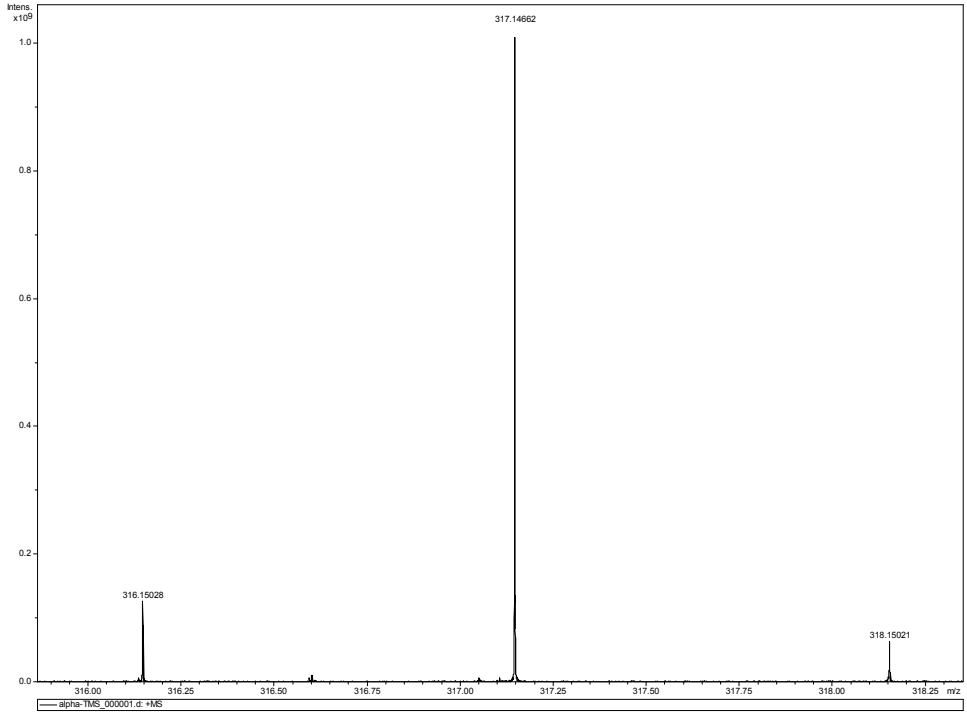
ii. 1,3-Dimethyl-2-iodo-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - β-I-BODIPY (**2**)

Figure S33: *mass spectra (**2**).*



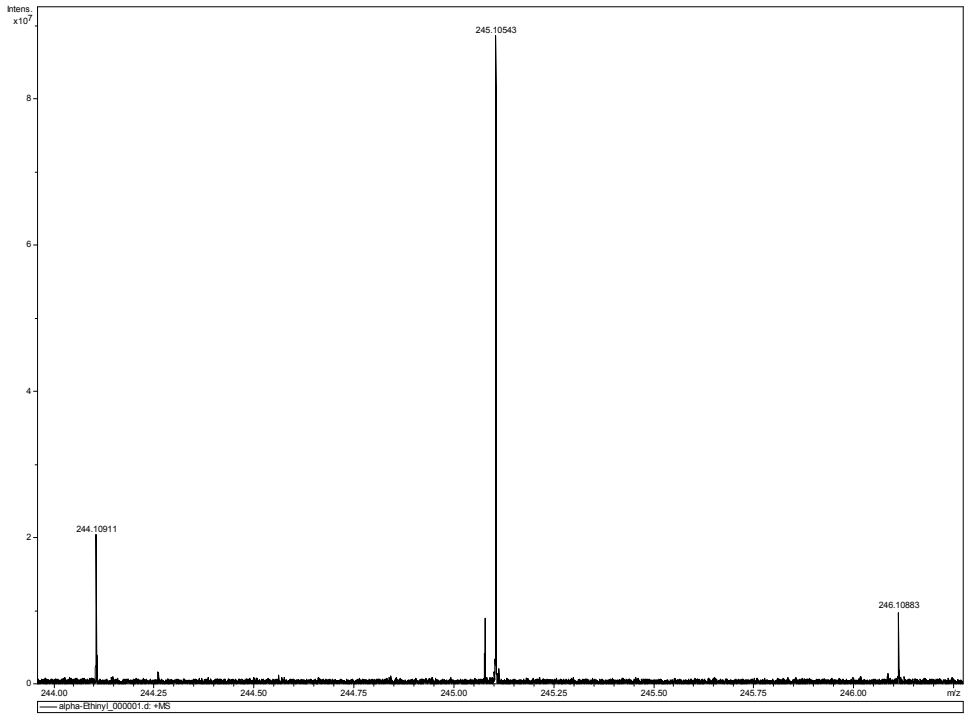
iii. 5,7-Dimethyl-3-(trimethylsilyl)ethynyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene _ -_ α-TMSAc-BODIPY (**4**)

Figure S34: *mass spectra (**4**).*



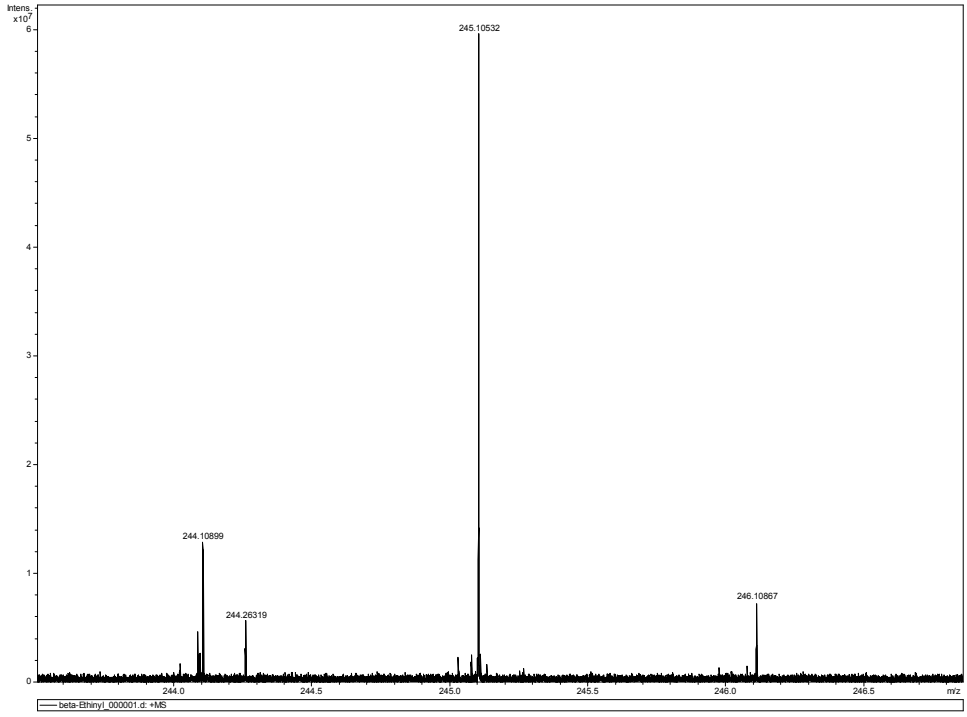
iv. 3-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - α-ethynyl-BODIPY (**6**)

Figure S35: *mass spectra (**6**).*



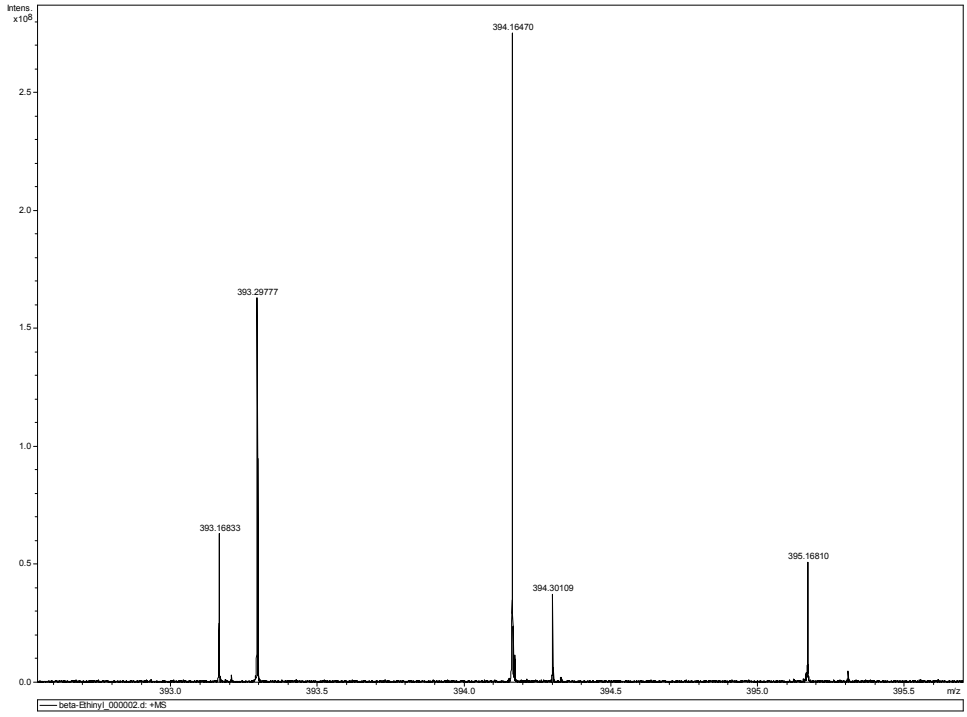
v. 2-Ethynyl-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene - β-ethynyl-BODIPY (**7**)

Figure S36: *mass spectra (**7**).*



vi. 3-(Methoxyphenyl)triazol-5,7-dimethyl-4,4´-difluoro-bora-3a,4a-diaza-(s)-indacene_ _ – _ _click product (**9b**)

Figure S37: *mass spectra (**9b**).*



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