Electronic Supporting Information

for

A Boron Dipyrromethene Chiral-at-Boron and Carbon with a Bent Geometry: Synthesis, Resolution and Chiroptical Properties

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Table of Contents

General

F-BODIPY (**2**)[1] was synthesized following the literature. A 1.0 M *n*-hexane solution of BCl_3 was prepared from the neat reagent. All other chemicals and solvents used in this work were supplied commercially and used with no further purification unless noted otherwise. 1D and 2D NMR spectra were recorded on a Bruker Spectrospin Avance DPX 400 spectrometer using $CDCl_3$ as the solvent. High resolution NMR spectra were taken on an Agilent-Premium Compact (600 MHz, 14.1 Tesla). Chemical shifts values are reported in ppm from tetramethylsilane as internal standard. Spin multiplicities are reported as the following: s (singlet), d (doublet), dd (doublet of doublet), m (multiplet). HRMS data were acquired on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. UV-Vis Absorption spectra were taken on a Shimadzu UV-3101PC UV–VIS-NIR spectrophotometer. Fluorescence measurements were recorded on a Perkin–Elmer (Model LS 55) spectrofluorometer. Horiba Jobin-Yvon Time-Resolved Fluorometer, Fluorolog FL-1057, equipped with HORIBA NanoLED-495 light source, was used the fluorescence decay experiments. FT-IR spectra of compounds were obtained on a Perkin Elmer 100 model FTIR spectrometer (ATR). Chiral HPLC analytical resolutions were done on an Agilent Technologies Preparative HPLC-1260 Infinity II using a Chiralcel® OD-H column (0.46 cmØ×25 cm). Chiral HPLC semipreparative separations were done on an Agilent Technologies Preparative HPLC-1200 Series with a diode array detector (DAD) using a Kromasil® 10-Cellucoat column (1.0 cmØ×25 cm). LC-MS analyses were carried on a UPLC: Waters Acquity & MS: Waters SYNAPT G1 MS System equipped with ACQUITY UPLC BEH C18 1.7um column (1.0Ø×100 mm). Polarimetry measurements were recorded on an Rudoph Scientific Autopole III polarimeter. Electronic Circular Dichroism spectra were acquired on a JASCO J-1500 CD Spectrometers. Electrochemical studies were carried on a Gamry PCI4/300 Potentiostat/Galvanostat. X-ray data were collected on a four-circle Rigaku R-AXIS RAPID-S Diffractometer. For the detailed configuration of X-ray Diffractometer, see page S29. Flash grade silica gel (SiliaFlash Irregular Silica Gels, F60, 40–63 μm, 60 Å) was used for flash column chromatography (FCC) purifications. Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254), visualized by a handheld UV-Vis lamp. All organic extracts were dehydrated over either anhydrous Na_2SO_4 or $MgSO_4$ and concentrated by using rotary evaporator before being subjected to FCC. For all absorption and emission spectra recordings a quartz cell with 1.0 cm pathlength was used. The relative fluorescence quantum yields (Φ_{fl}) of the dye were calculated by taking aqueous alkaline solutions of fluorescein as the standard (λ_{ex} 490 nm in 0.1 N NaOH, $\Phi_{fl} = 0.85$ according to the literature).[1] Following equation was used to calculate Φ_{fl}:

$$\Phi_s = \Phi_r(\frac{m_s}{m_r})(\frac{n_s}{n_r})^2$$

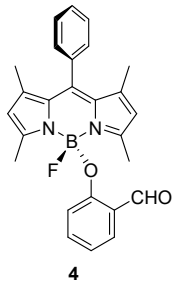
Where Φ denotes fluorescence quantum yield, m: gradient of the plot of integrated fluorescence intensity against absorbance, n: refractive index of solution, subscripts r and s denotes reference and sample, respectively. In fluorescence studies of Fig.1b and Table 1, the instrument parameters was set to followings: λ_{ex} 490 nm; slit widths: d_{ex} = 5.0 nm, d_{em} = 2.5 nm.

Acknowledgement

The authors thank Prof. Ahmet Önal and Elif Demir Arabacı of Middle East Technical University for CV analysis and Perihan Öztürk Düzenli of the same university for the help with CD measurements. M. I. thanks the Central Laboratory of Bingöl University.

Procedure for the synthesis of *B*C**-BODIPY

A 50 mg of BODIPY (**2**) placed in a 10 mL vial was dissolved in HPLC grade dichloromethane (5 mL) and to that 1.0 equiv BCl_3 (154 μL, 1.0 M in *n*-hexane) was added dropwise while stirring with a magnetic bar at rt. To another vessel (25 mL round-bottomed flask) containing a magnetic bar was added 3.60 equiv caesium carbonate (179 mg, 550 μmol), 3.25 equiv salicylaldehyde (61 mg, 500 μmol), and anhydrous DMF (3 mL) and left to stir at rt. After stirring both vessels for about an hour, the former solution was poured over the latter, and the resultant mixture was left to stir for an additional hour. To this dark-colored mixture, 50 mL dichloromethane was added and the resulting mixture was washed repeatedly with water (3 × 50 mL). After a final wash with brine (25 mL), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated using a rotary evaporator. The residue was purified by silica gel flash column chromatography (FCC) using DCM as the eluent. Chromatography gave the product (*B*C**-BODIPY) as an orange-red solid (11 mg, 18% yield). mp = 214–217 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 4H), 7.24 – 7.19 (m, 1H), 7.11 – 7.06 (m, 1H), 7.02 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.78 (td, *J* = 7.4, 0.9 Hz, 1H), 5.98 (s, 1H), 5.88 (s, 1H), 5.45 (bs, 1H), 3.51 (dd, *J* = 18.5, 6.3 Hz, 1H), 2.95 (d, *J* = 18.5 Hz, 1H), 2.53 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 155.9, 154.2, 151.7, 144.1, 142.81, 142.29, 134.9, 131.5, 129.82, 129.01, 128.90, 128.81, 128.34, 128.19, 128.08, 127.97, 125.3, 120.9, 118.25, 118.17, 118.10, 70.3, 35.6, 29.7, 14.9, 13.9. HRMS (APCI negative) $C_{26}H_{22}BN_2O_2$ calcd for $[M - H]^-$ 405.1774, found 405.1786. Δ= 2.90 ppm. IR (neat) ν 3052, 2955, 2922, 2885, 1607, 1581, 1548, 1538, 1514, 1500, 1488, 1426, 1406, 1380, 1361, 1348, 1329, 1308, 1282, 1243, 1217, 1191, 1153, 1051 cm^{-1}. $[\alpha]_D^{20} - 567.9°$ (c 4.05×10^{-3}, $CHCl_3$) for fast-eluting enantiomer, 99.5% ee, (−)-*B*C**-BODIPY; $[\alpha]_D^{20} + 617.3°$ (c 4.05×10^{-3}, $CHCl_3$) for slow-eluting enantiomer, 98.5% ee, (+)-*B*C**-BODIPY. HPLC (Chiralcel® OD-H column, 98:2 *n*-hexanes:2-propanol, 1 mL/min, 505 nm): t_{R1} = 8.38 and t_{R2} = 11.42 min. UV-vis: λ_{abs} 508 nm ($CHCl_3$). Fluorescence: λ_{em} 521 nm ($CHCl_3$), Φ_{fl} = 0.013 (λ_{ex} 490 nm, $CHCl_3$). ECD for (+)-*B*C**-BODIPY ($CHCl_3$) λ_{ext} 508 nm ($\Delta\varepsilon + 22.13$); ECD for (−)-*B*C**-BODIPY ($CHCl_3$) λ_{ext} 508 nm ($\Delta\varepsilon - 18.41$).



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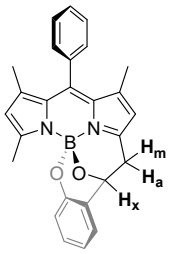
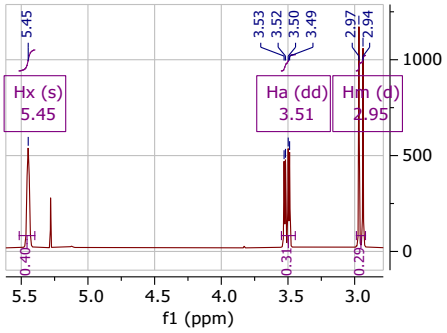
The minor product (**4**) was isolated as an orange solid in 3% chemical yield. mp = 185–189 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.69 (s, 1H), 7.76 (dd, J = 7.7, 1.8 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.34 – 7.20 (m, 3H), 6.83 (dd, J = 13.4, 5.9 Hz, 1H), 6.32 (d, J = 8.4 Hz, 1H), 5.93 (s, 2H), 2.44 (s, 6H), 1.40 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.4, 159.89, 159.83, 155.9, 143.7, 141.8, 135.7, 134.7, 131.5, 129.24, 129.23, 129.14, 127.97, 127.85, 127.80, 121.78, 121.76, 119.5, 117.2,14.83, 14.81, 14.5. HRMS (APCI negative) $C_{26}H_{24}BFN_2O_2$ calcd for $[M\cdot]^-$ 426.1914, found 426.19200 Δ= 1.22 ppm.

Proton NMR discussion of *B*C**-BODIPY on account of its chirality



	chemical shift (ppm)	coupling constant (*J*) (Hz)
H_m :	2.95	d, $^{2}J_{Ha\text{-}Hm}$ = 18.5 Hz
H_a :	3.51	dd, $^{2}J_{Ha\text{-}Hm}$ = 18.5 Hz, $^{3}J_{Ha\text{-}Hx}$ = 6.4 Hz
H_x :	5.45	s

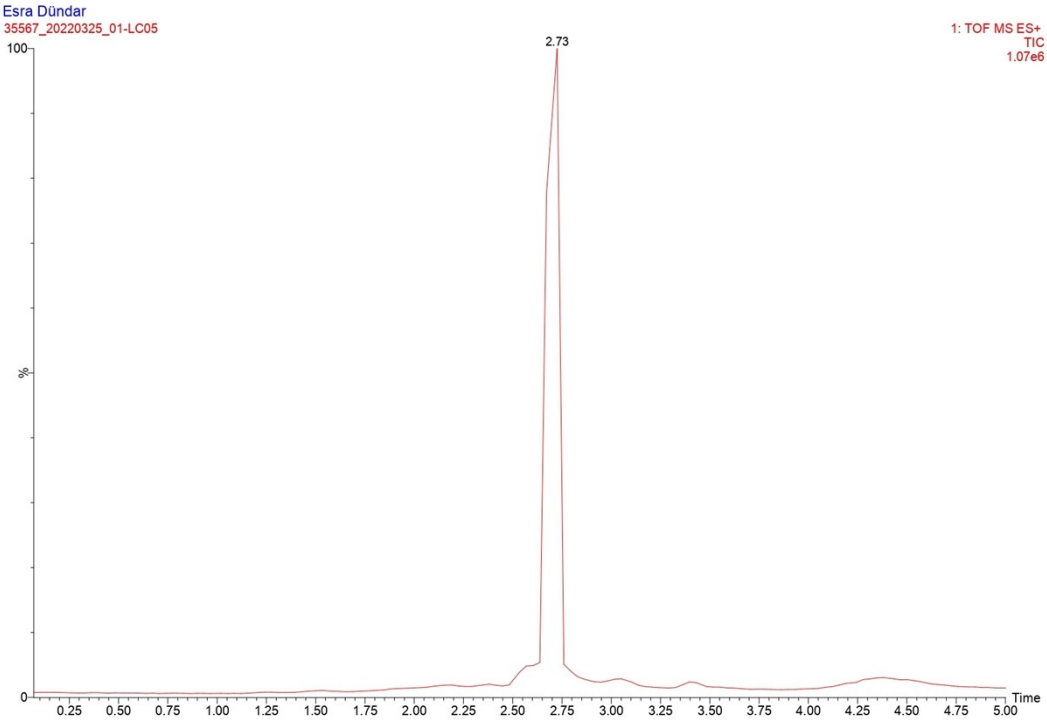


An AMX-type spin patterning is observed for the coupling of diastereotopic methylenic protons (δ_{Ha}: 3.51 ppm; δ_{Hm}: 2.95 ppm) with that of neighboring methynic (δ_{Hx}: 5.45 ppm). In other words, the generated asymmetric centers (B* and C*), or more inclusively, the thus generated chiral space, cause a significant chemical differentiation of the diastereotopic protons. The geminal homonuclear coupling ($^{2}J_{Ha\text{-}Hm}$ = 18.5 Hz) of diastereotopic protons and that of vicinal ($^{3}J_{Ha\text{-}Hx}$ = 6.4 Hz) is traceable from the cross-peaks in the ^{1}H-^{1}H COSY spectrum (see Fig. S6). There was no vicinal coupling between H_m and H_x ($^{3}J_{Hm\text{-}Hx}$), presumably because the dihedral angle is *ca*. 78°.

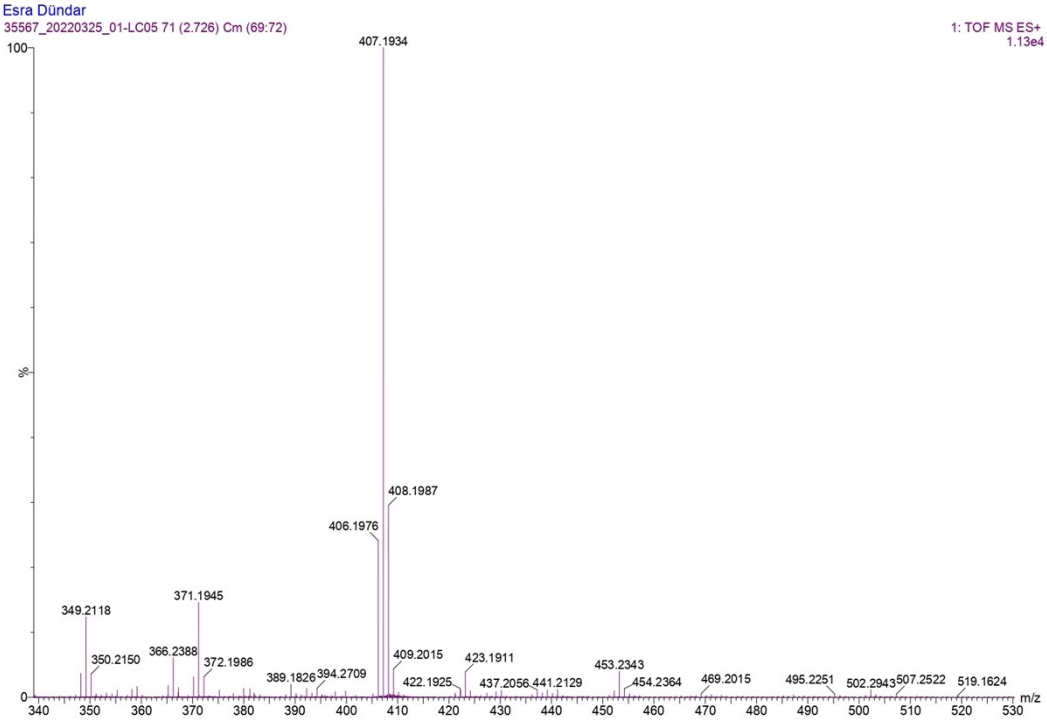
LC-MS analysis of *B*C**-BODIPY synthesis reaction

To decide the optimum time to quench the reaction, we took several aliquots of 1 mL from the reaction mixture at times t_1: 1min, t_2: 15 min, t_3: 30 min, and t_4: 60 min, extracted thrice with water, and ran LC-MS analysis. We observed no other molecules with the same mass of B*C*-BODIPY. The chromatograms shows that the reaction is almost instantaneous. However, we found 60 min. (1 h) as the optimum reaction time as it allows a smoother chromatographic separation.

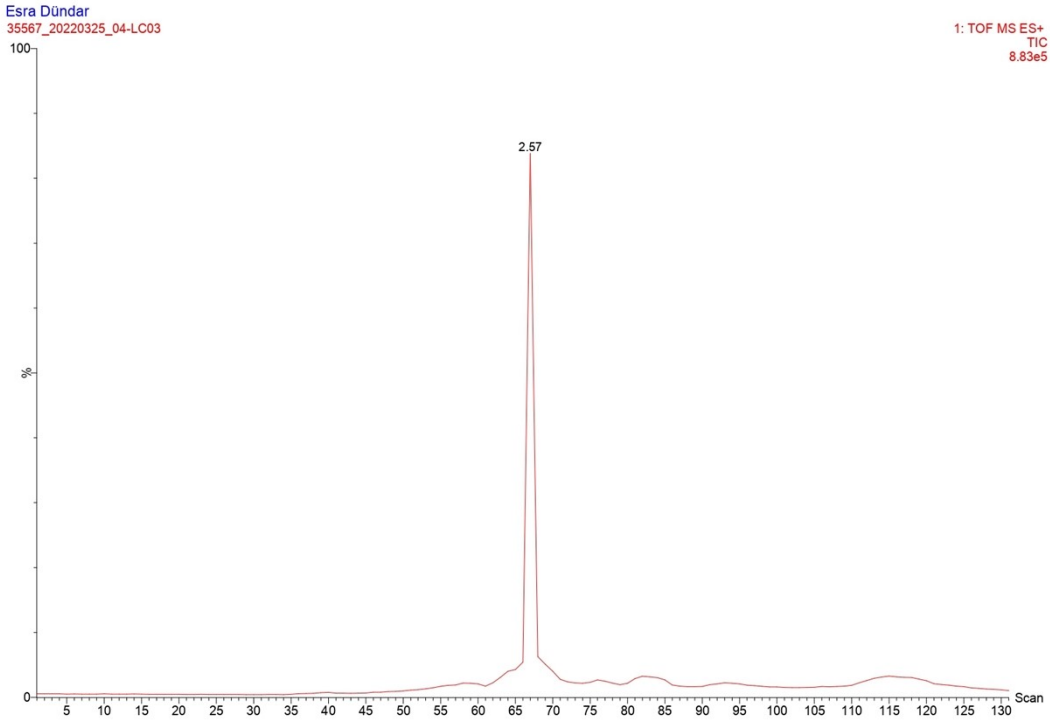
LCMS chromatogram of t_1: 1min



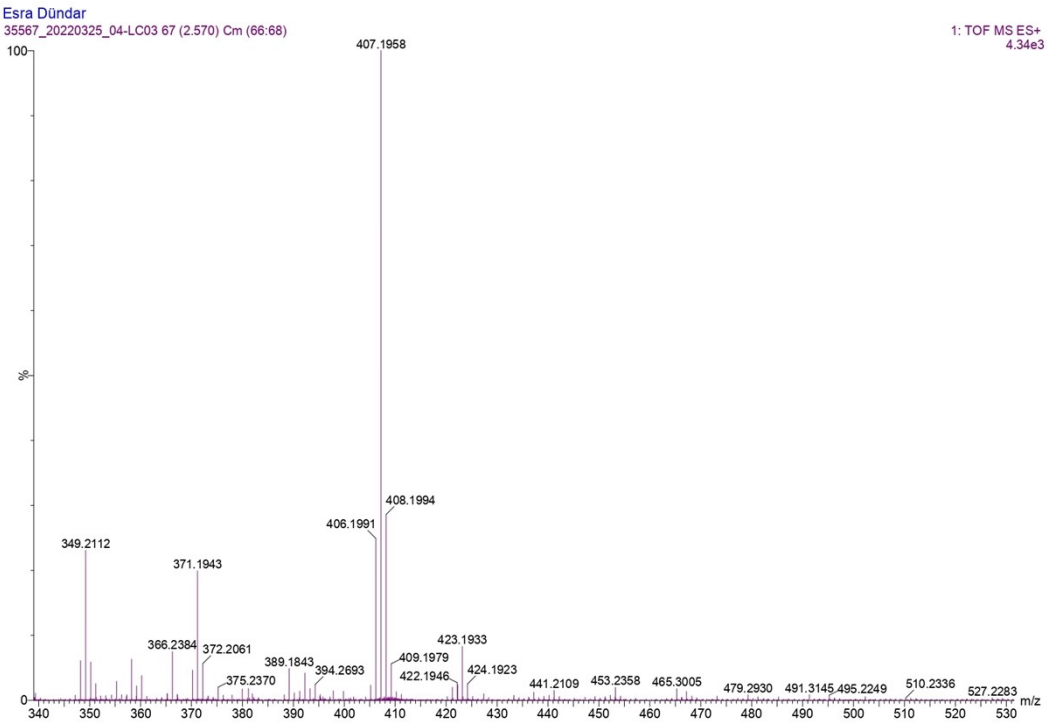
LCMS mass spectrum of t_1: 1min



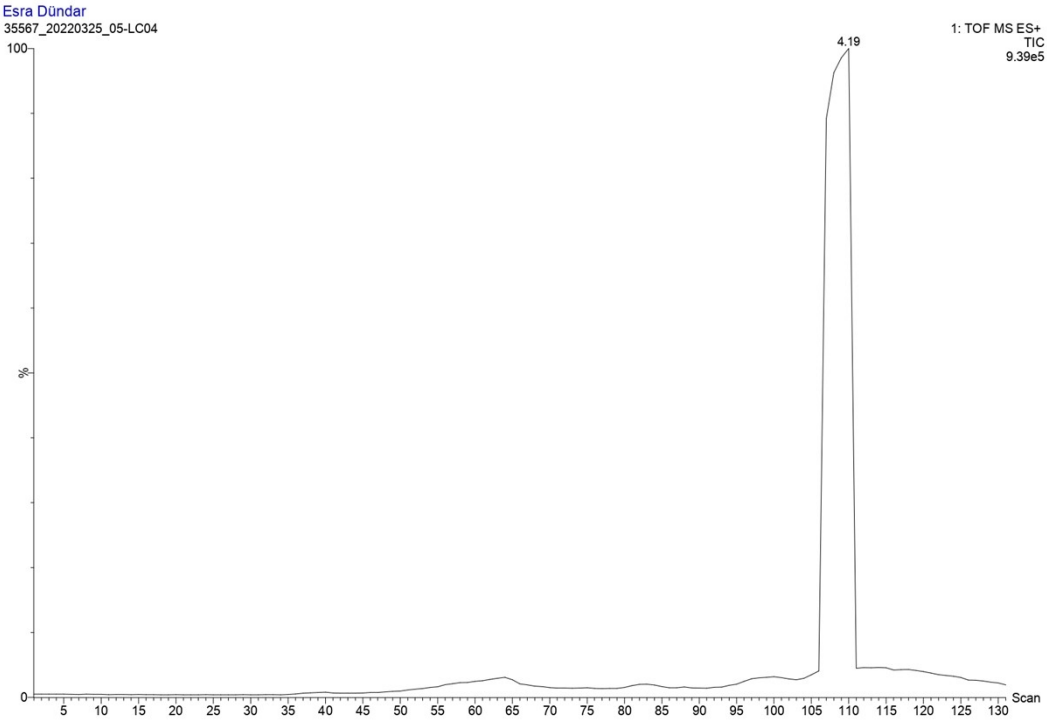
LCMS chromatogram of t_4: 60min

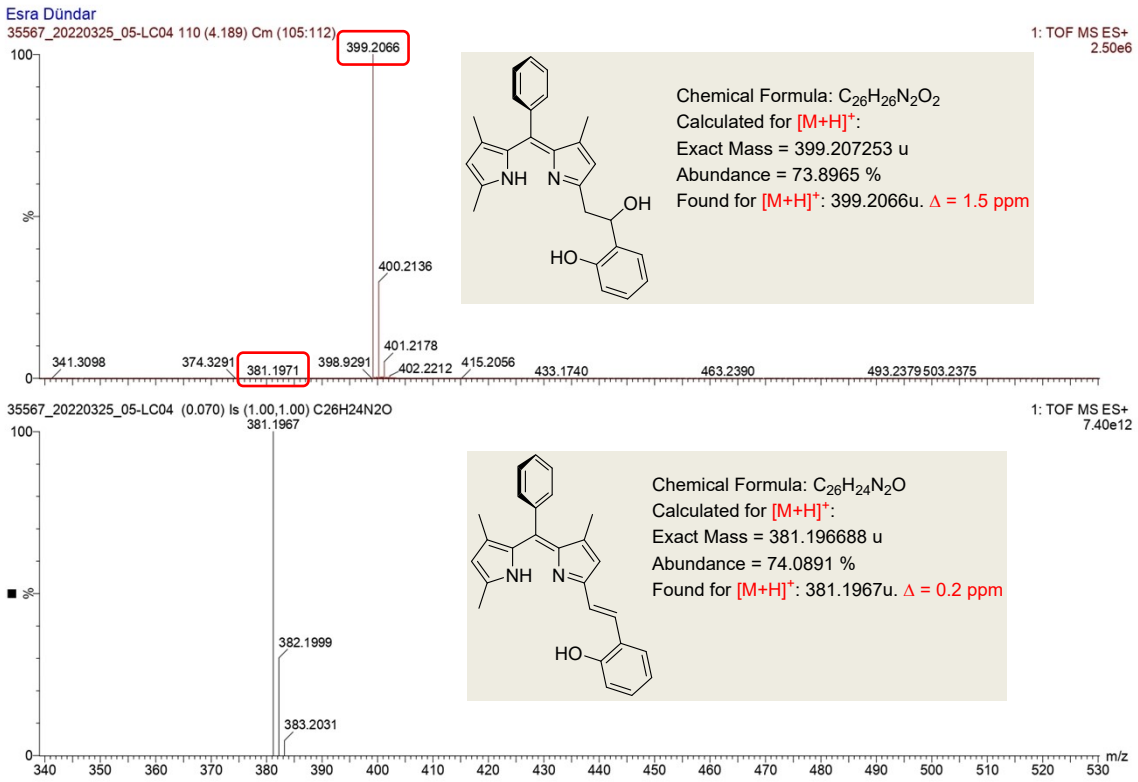


LCMS mass spectrum of t_4: 60min



LC-MS results of chemical stability experiment: *B*C**-BODIPY with TFA





Reports of chiral HPLC resolution

I. Resolution of racemic *B*C**-BODIPY

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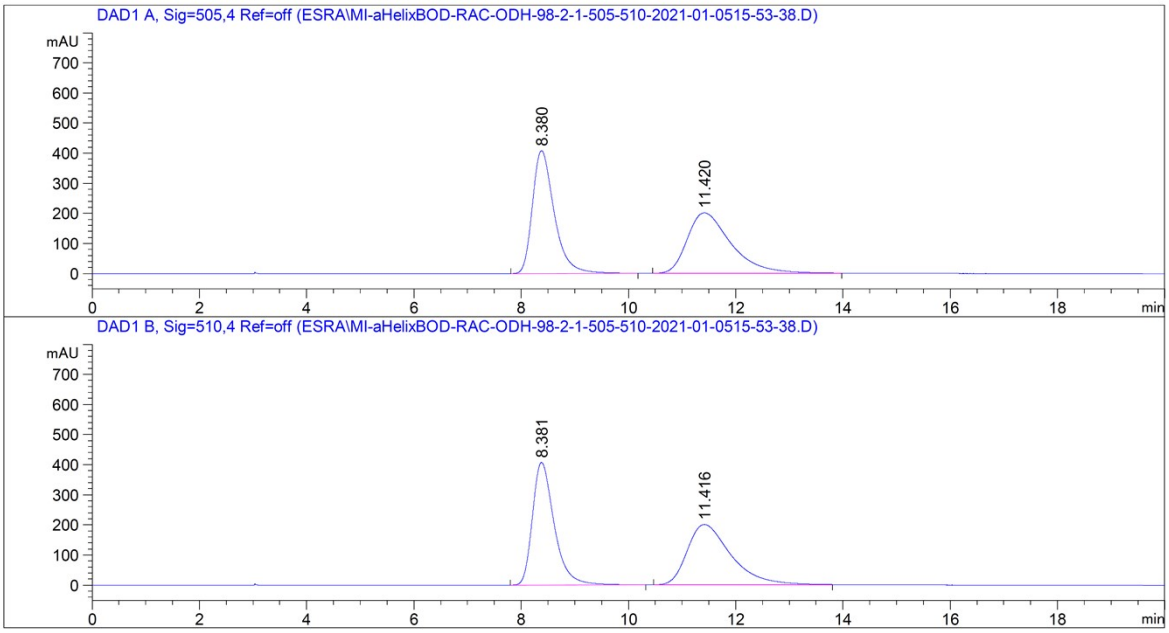


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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   1   8.380 BB    0.4214 1.15027e4   408.04095  50.3403
   2  11.420 BB    0.6654 1.13472e4   200.62273  49.6597

Totals :                  2.28499e4   608.66368
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Signal 2: DAD1 B, Sig=510,4 Ref=off

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1	8.381	BB	0.4249	1.15018e4	407.37750	50.4564
2	11.416	BB	0.6799	1.12937e4	200.26288	49.5436
Totals :				2.27955e4	607.64038	

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II. Chromatograms of fast-eluting enantiomer

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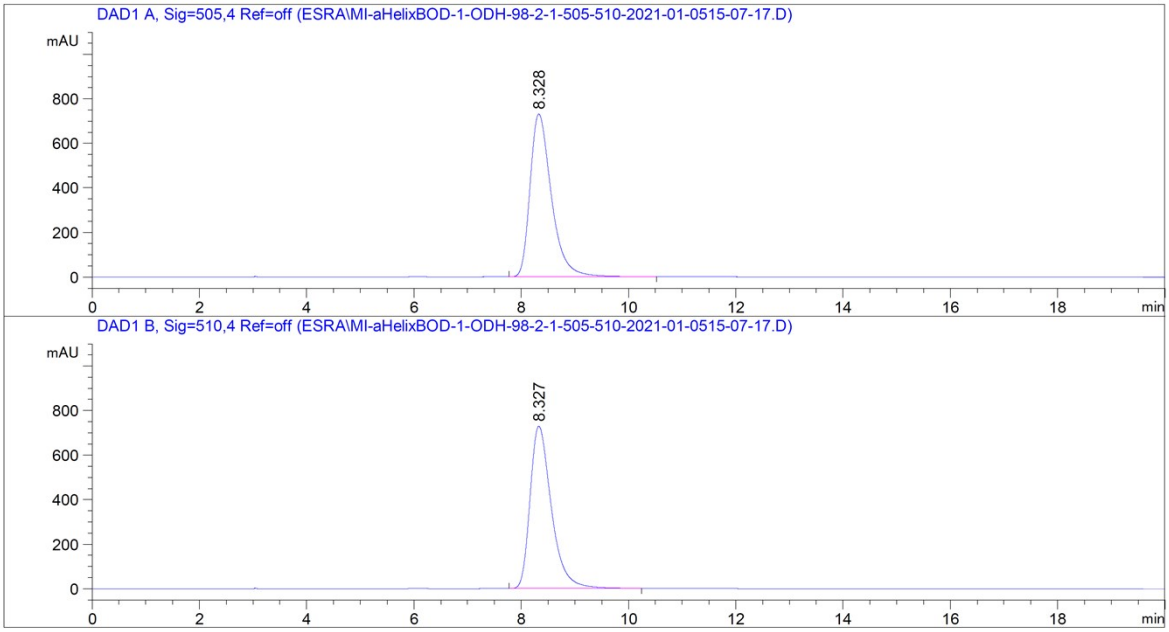


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Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=505,4 Ref=off

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Totals :                  2.02058e4   731.17596
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III. Chromatograms of slow-eluting enantiomer

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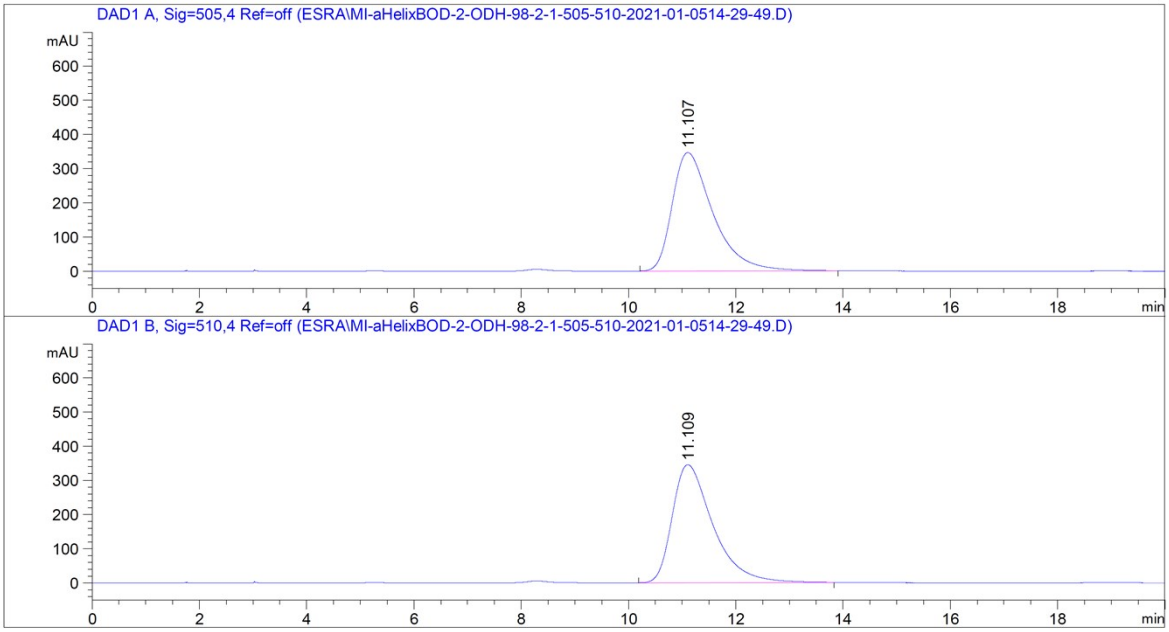


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Use Multiplier & Dilution Factor with ISTDs


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   1  11.107 BB    0.6856 1.82133e4   346.56940 100.0000

Totals :                  1.82133e4   346.56940
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Configurational stability test: chiral HPLC reports

I. Heating fast-eluting enantiomer for 1h at 50 °C.

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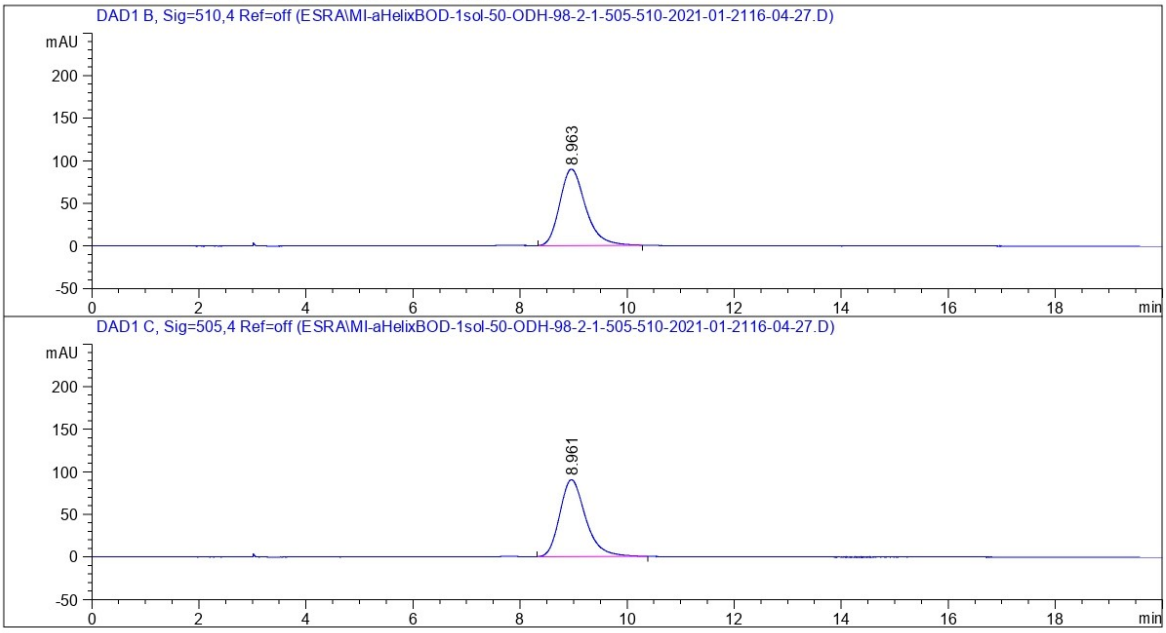


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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.961	BB	0.4640	3037.00146	90.27879	100.0000
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*** End of Report ***

II. Heating fast-eluting enantiomer for 1h at 75 °C.

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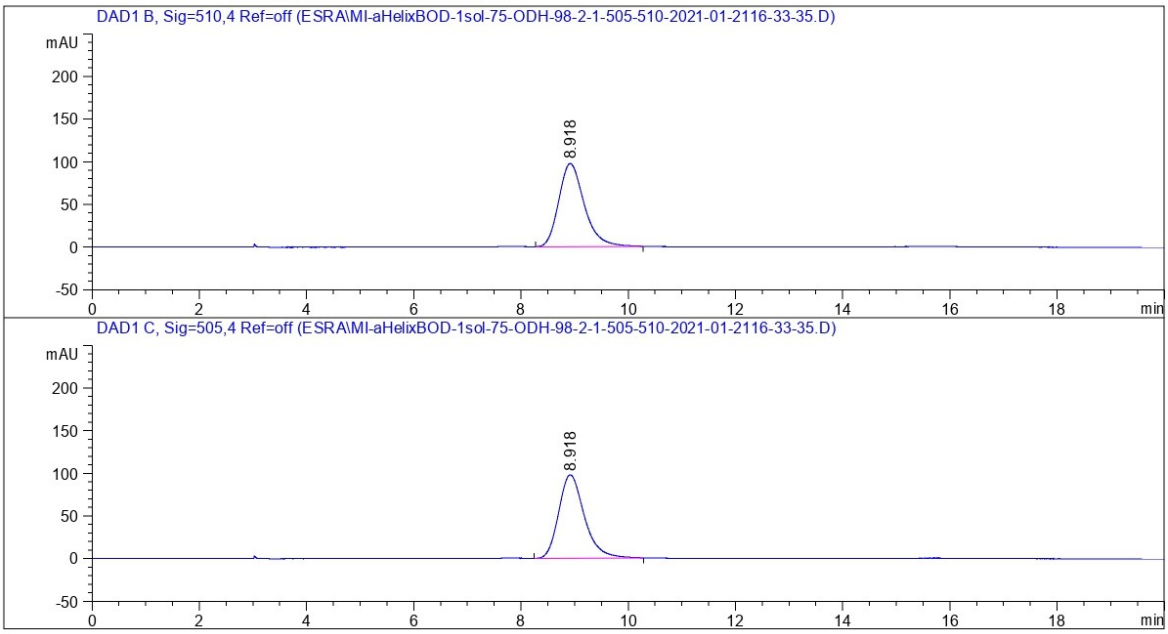


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Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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*** End of Report ***

III. Heating fast-eluting enantiomer for 1h at 100 °C.

Data File C:\Users\P...\ESRA\MI-aHelixBOD-1sol-100-ODH-98-2-1-505-510-2021-01-2116-57-13.D
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Sample Operator : SYSTEM
Acq. Instrument : HPLC                          Location :   P1-B-04
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                                                Inj Volume : 20.000 µl
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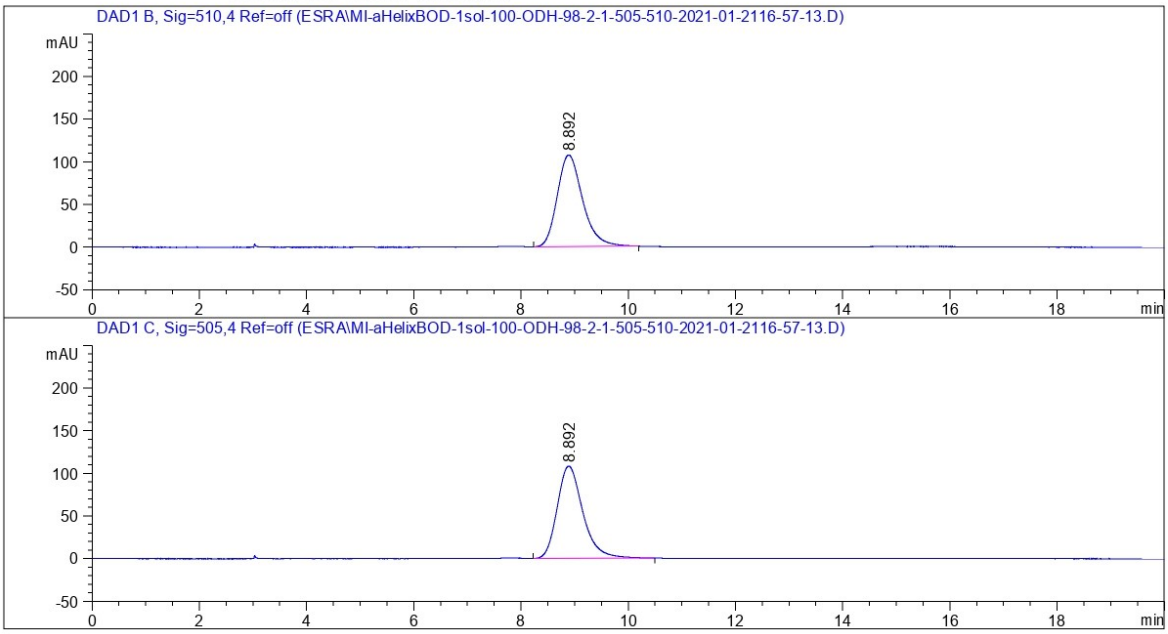


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=====================================================================
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      0.1000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=510,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.892 BB    0.4313 3534.71582  107.46067 100.0000

Totals :                  3534.71582  107.46067
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Data File C:\Users\P...\ESRA\MI-aHelixBOD-1sol-100-ODH-98-2-1-505-510-2021-01-2116-57-13.D
Sample Name: MI-aHelixBOD-1sol-100-ODH-98-2-1-505-510

Signal 2: DAD1 C, Sig=505,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.892	BB	0.4581	3590.99292	108.21491	100.0000
Totals :				3590.99292	108.21491	

*** End of Report ***

IV. Heating fast-eluting enantiomer for 1h at 125 °C.

Data File C:\Users\P...\ESRA\MI-aHelixBOD-1sol-125-ODH-98-2-1-505-510-2021-01-2216-16-30.D
Sample Name: MI-aHelixBOD-1sol-125-ODH-98-2-1-505-510

```
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Sample Operator : SYSTEM
Acq. Instrument : HPLC                          Location :   P1-C-01
Injection Date  : 1/22/2021 4:17:10 PM               Inj :   1
                                                Inj Volume : 20.000 µl
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Last changed    : 1/21/2021 2:54:07 PM by SYSTEM
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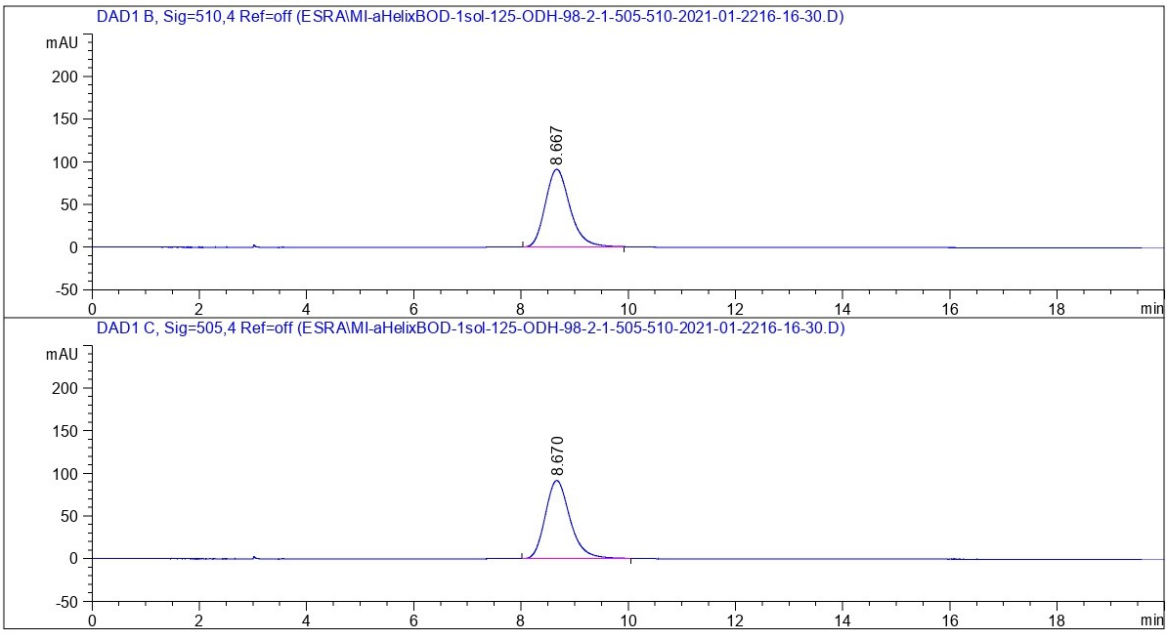


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======================================================================
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      0.1000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=510,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.667 BB    0.4343 2898.66748   91.06919 100.0000

Totals :                  2898.66748   91.06919
```

Data File C:\Users\P...\ESRA\MI-aHelixBOD-1sol-125-ODH-98-2-1-505-510-2021-01-2216-16-30.D
Sample Name: MI-aHelixBOD-1sol-125-ODH-98-2-1-505-510

Signal 2: DAD1 C, Sig=505,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.670	BB	0.4387	2928.68408	91.55736	100.0000
Totals :				2928.68408	91.55736	

*** End of Report ***

V. Heating fast-eluting enantiomer for 1h at 150 °C (open atm).

Data File C:\Users\P...\ESRA\MI-aHelixBOD-1sol-150-ODH-98-2-1-505-510-2021-01-2216-43-13.D
Sample Name: MI-aHelixBOD-1sol-150-ODH-98-2-1-505-510

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======================================================================
Acq. Operator   : SYSTEM
Sample Operator : SYSTEM
Acq. Instrument : HPLC                          Location :   P1-C-02
Injection Date  : 1/22/2021 4:43:57 PM               Inj :   1
                                                Inj Volume : 20.000 µl
Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Methods\ESRA\98-2-1-210-254-100 min
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Last changed    : 1/21/2021 2:54:07 PM by SYSTEM
Analysis Method : C:\Users\Public\Documents\ChemStation\1\Methods\1_CIHAZ YIKAMA.M
Last changed    : 4/27/2021 2:23:31 PM by SYSTEM
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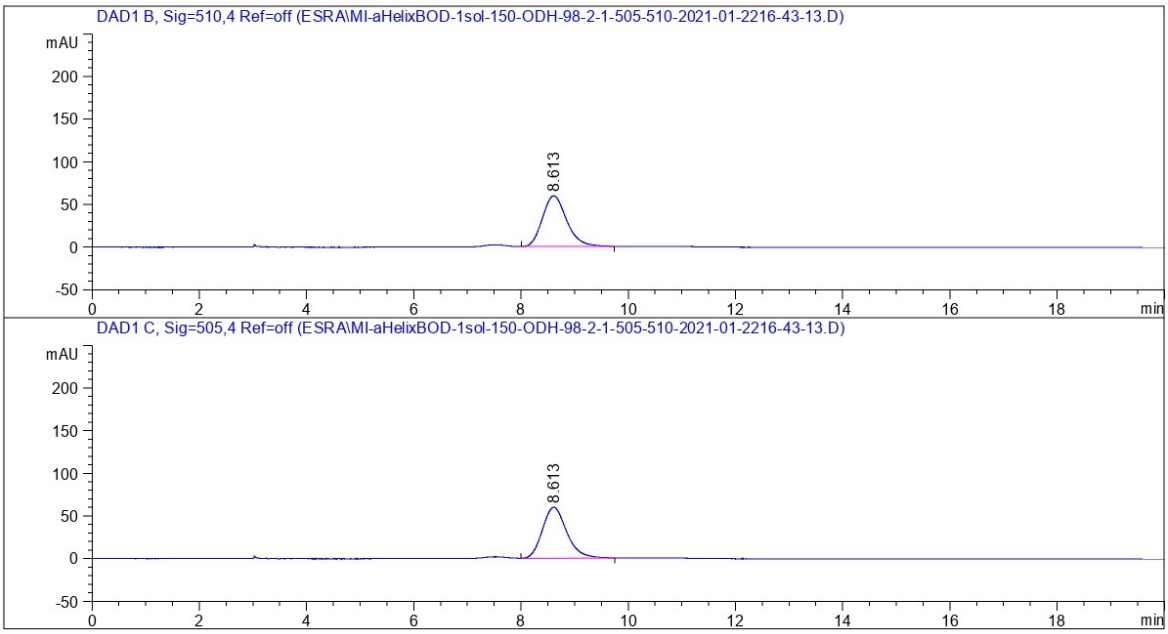


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======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      0.1000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=510,4 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.613 BB    0.3761 1868.30725   59.45347 100.0000

Totals :                  1868.30725   59.45347
```

Data File C:\Users\P...\ESRA\MI-aHelixBOD-1sol-150-ODH-98-2-1-505-510-2021-01-2216-43-13.D
Sample Name: MI-aHelixBOD-1sol-150-ODH-98-2-1-505-510

Signal 2: DAD1 C, Sig=505,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.613	BB	0.3900	1873.17346	59.62061	100.0000
Totals :				1873.17346	59.62061	

*** End of Report ***

Normalized Absorbance and Photochemical stability

We were aware of the recent work by the group of Nagano and Urano, in which 4-aryloxy boron dipyrromethenes were shown to uncage photolytically in polar protic solvents such as methanol.[2] Consequently, we wanted to test the photostability of the dye in methanol by irradiating it with a light pulse (λ_{ex} 490 nm) for one hour at 10 second intervals and recording its fluorescence. Fig. S1 (Right) shows that the racemic dye is considerably photostable; the fluorescence of the dye remained almost constant (<1% decomposition) over that period.

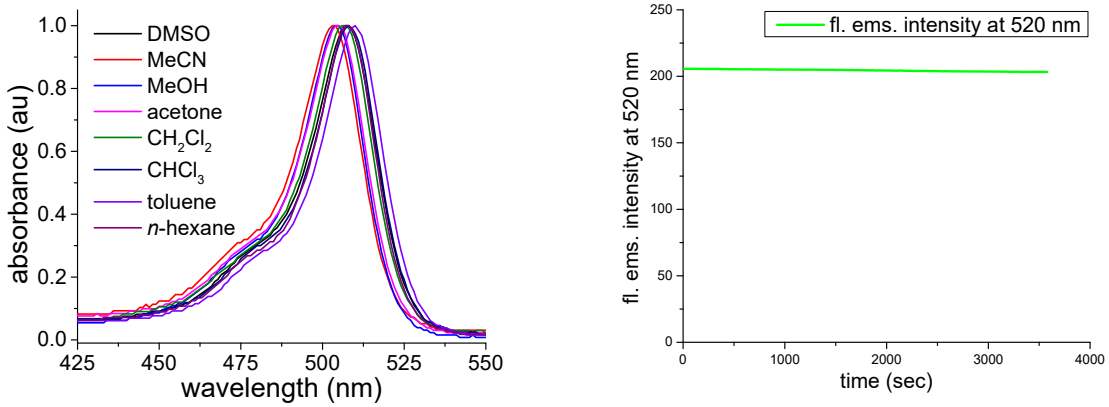

Fig. S1 (Left) Normalized absorption spectra of (±)-*B*C**-BODIPY (2 μM) in solvents of varying polarity. **(Right)** Time-dependent fluorescence intensity profile of (±)-*B*C**-BODIPY (2 μM) in methanol at 520 nm. A laser pulse of 490 nm is given for 3600 sec with 10-sec intervals.

Electrochemical properties

The electrochemical properties of B*C*-BODIPY were also studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The analysis was performed *vs.* Ag/AgCl in degassed, anhydrous acetonitrile solution containing [Bu_4N^+][PF_6^-] (0.1 M) as a supporting electrolyte. Reversibility of oxidation and reduction processes can be seen from the looping CV (Fig. S2) and symmetric DPV spectra (Fig. S3 and Table S1).

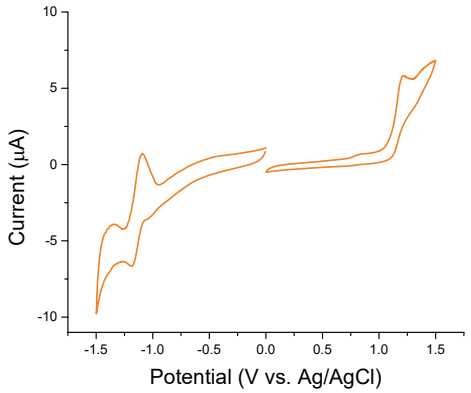

Fig. S2 Cyclic voltammetry of (±)-*B*C**-BODIPY in MeCN.

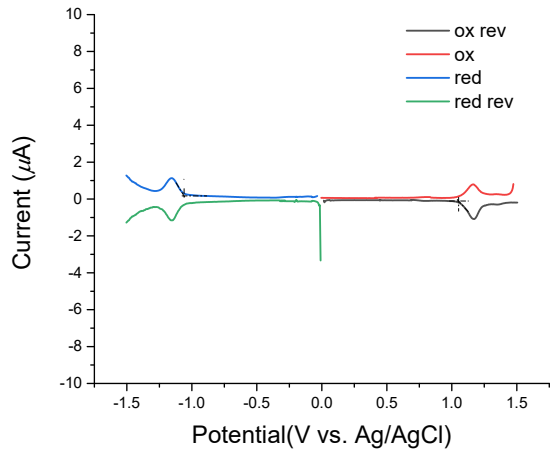

Fig. S3 DPV of *B*C**-BODIPY in MeCN.

Table S1 Electrochemical properties of *B*C**-BODIPY in MeCN

	E_{ox}^{onset} (eV)[a]	E_{red}^{onset} (eV)[a]	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[c]	E_{gap} (eV)[d]
*B*C**-BODIPY	1.05	-1.06	-5.76	-3.65	2.1

[a]Calculated from the DPV, [b]Calculated with E_{HOMO}: - (4.71 + E_{ox}^{onset}), [c]Calculated with E_{LUMO}: - (4.71 + E_{red}^{onset})
[d]Calculated with E_{gap} : E_{LUMO} - E_{HOMO}

Table S2 Electrochemical properties of *F*-BODIPY (**2**)[a]

	$E_{1/2}^{red}$ (mV)	$E_{1/2}^{ox}$ (mV)	E_{00} (eV)
F-BODIPY (**2**)	-1570	760	2.48

[a]Electrochemical data of this compound in acetonitrile (potentials in mV vs Fe^{+}/Fe). The data are taken from the lit.[3]

Copies of NMR (1D and 2D), HRMS and IR spectra of *B*C**-BODIPY

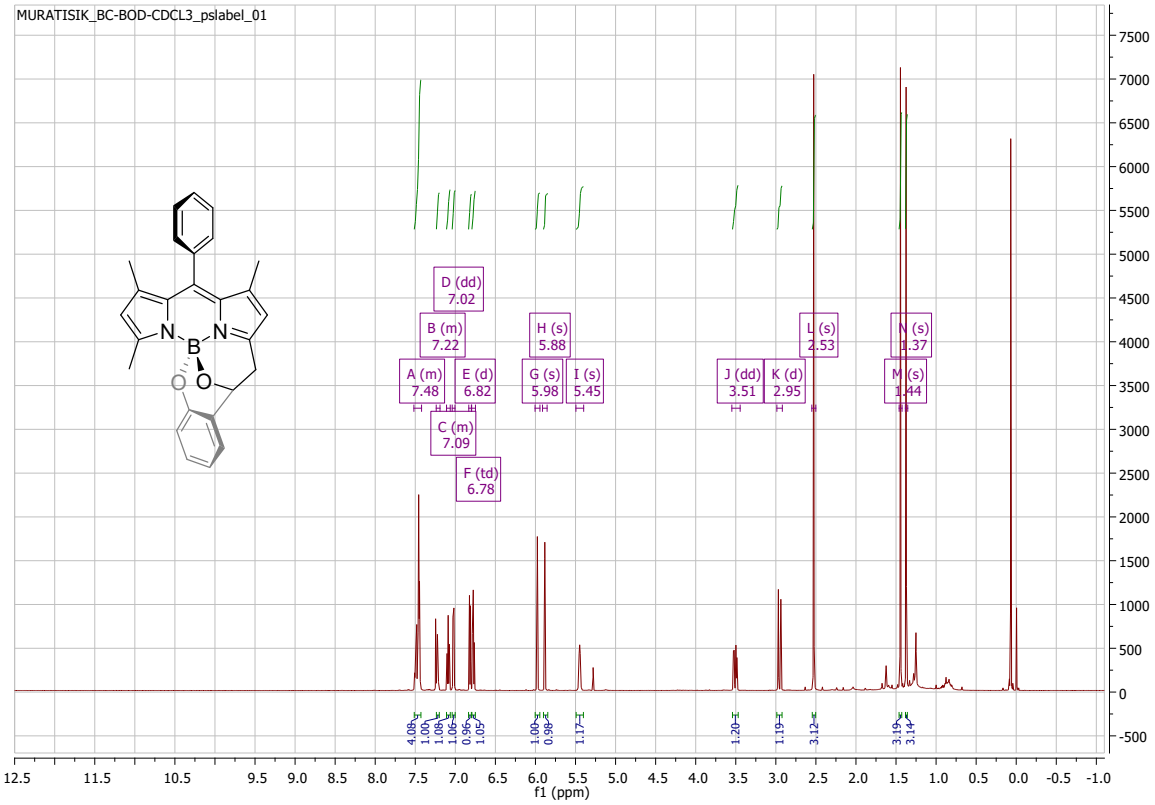

Fig. S4 ^{1}H NMR spectrum (600 MHz) of *B*C**-BODIPY in $CDCl_3$.

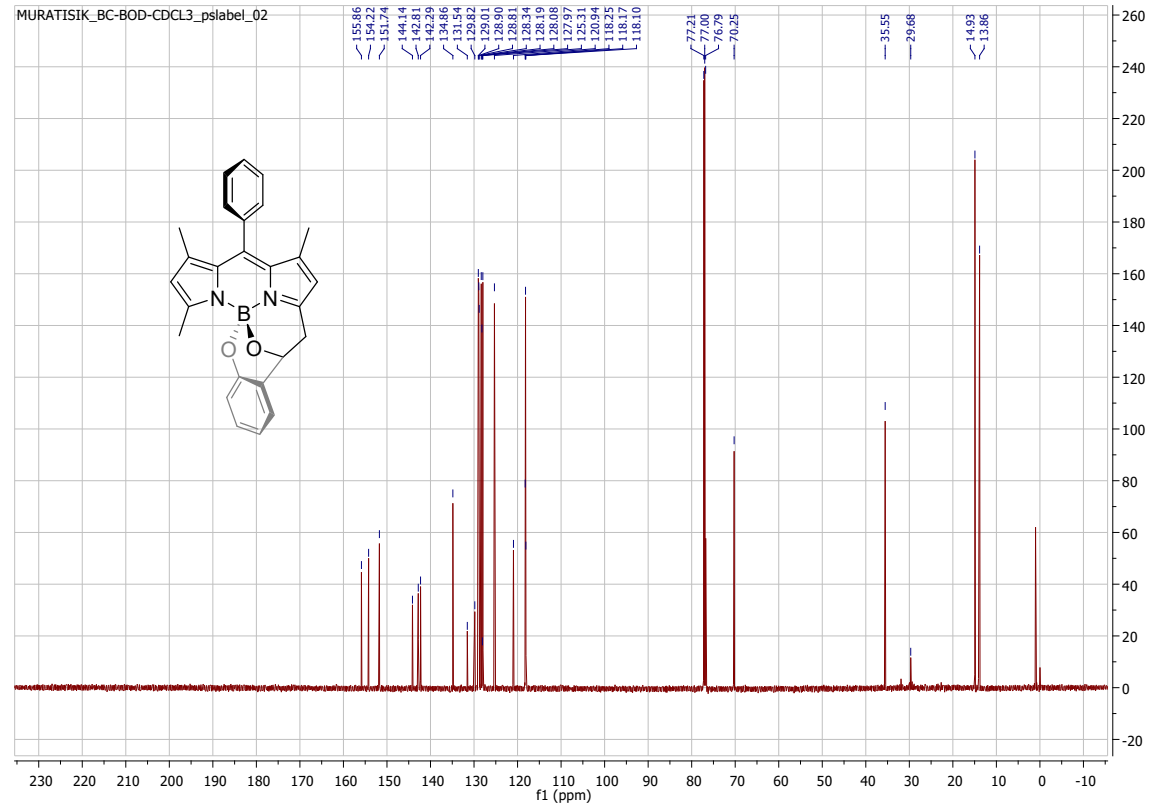

Fig. S5 ^{13}C NMR spectrum (151 MHz) of *B*C**-BODIPY in $CDCl_3$.

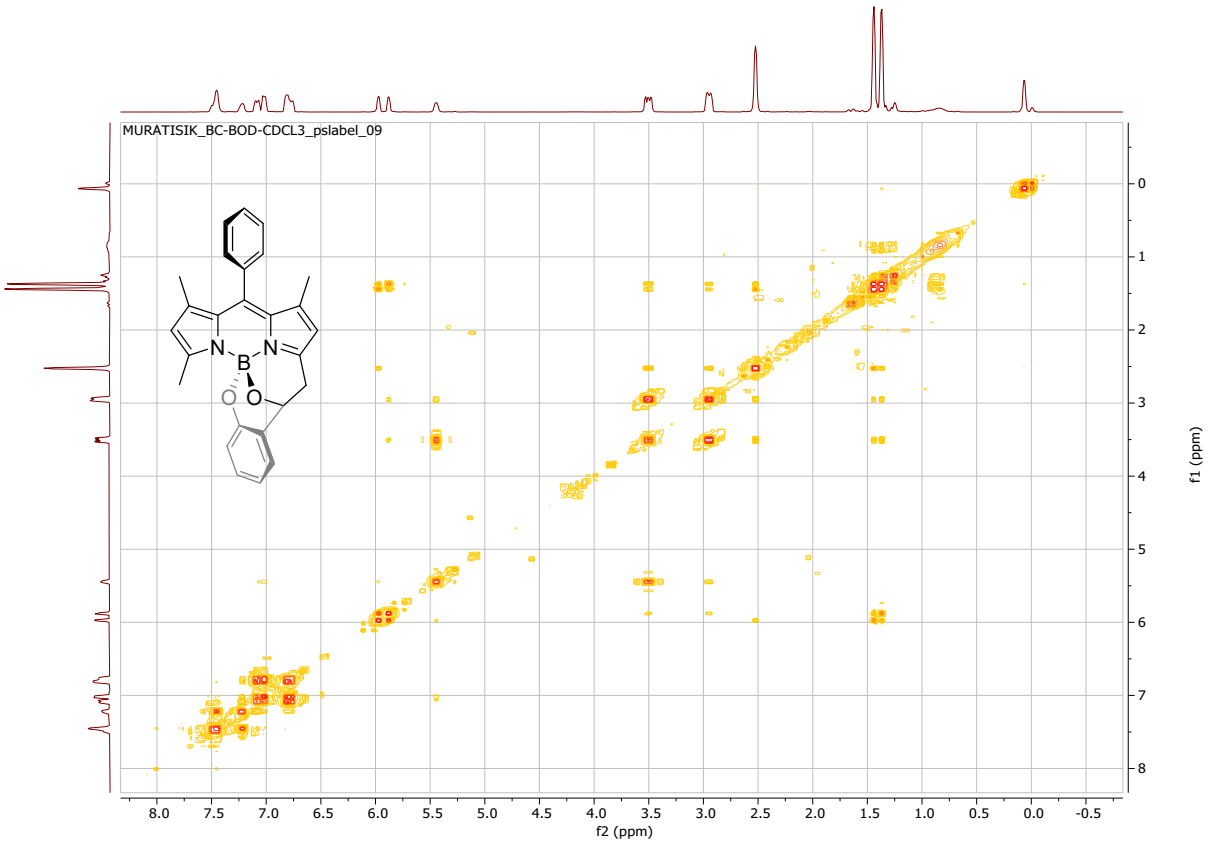

Fig. S6 ^{1}H-^{1}H COSY NMR spectrum (600 MHz) of *B*C**-BODIPY in $CDCl_3$.

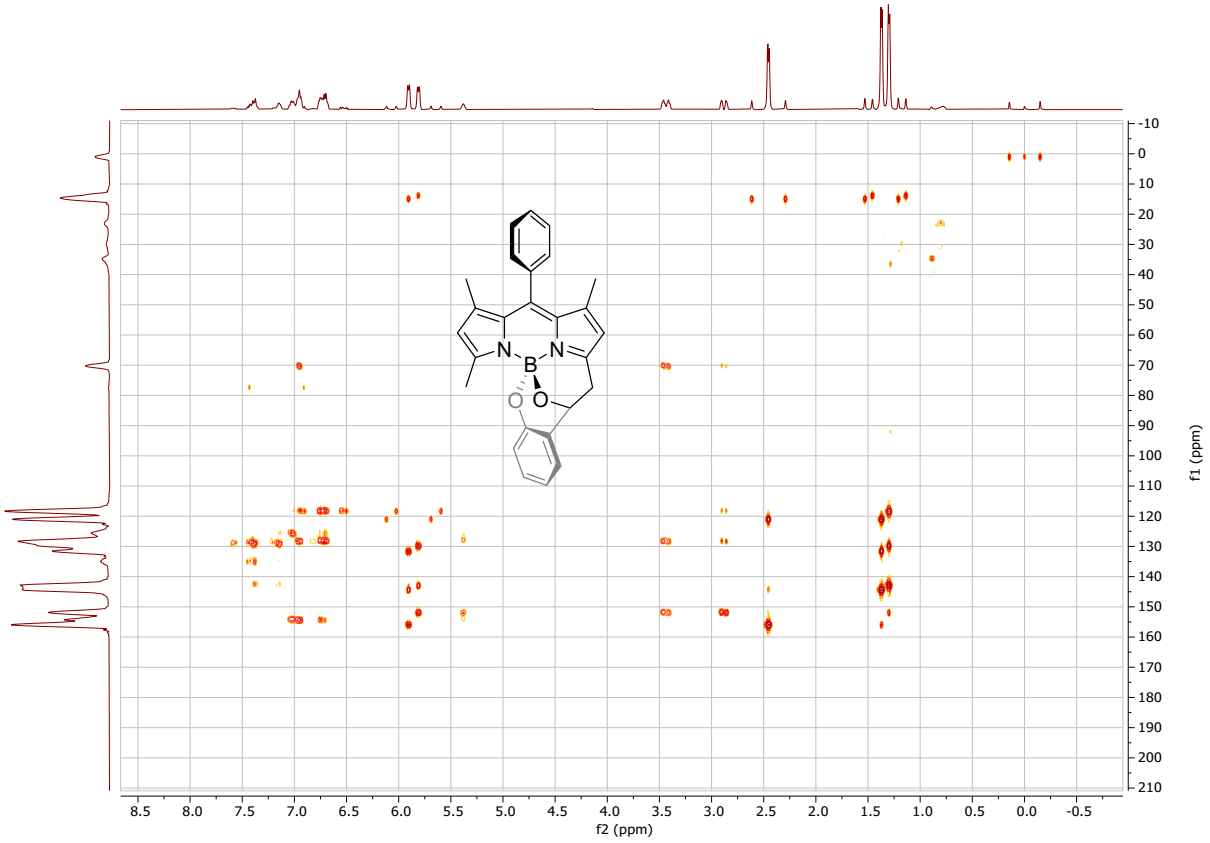

Fig. S7 HMBC NMR spectrum (400 MHz) of *B*C**-BODIPY in $CDCl_3$.

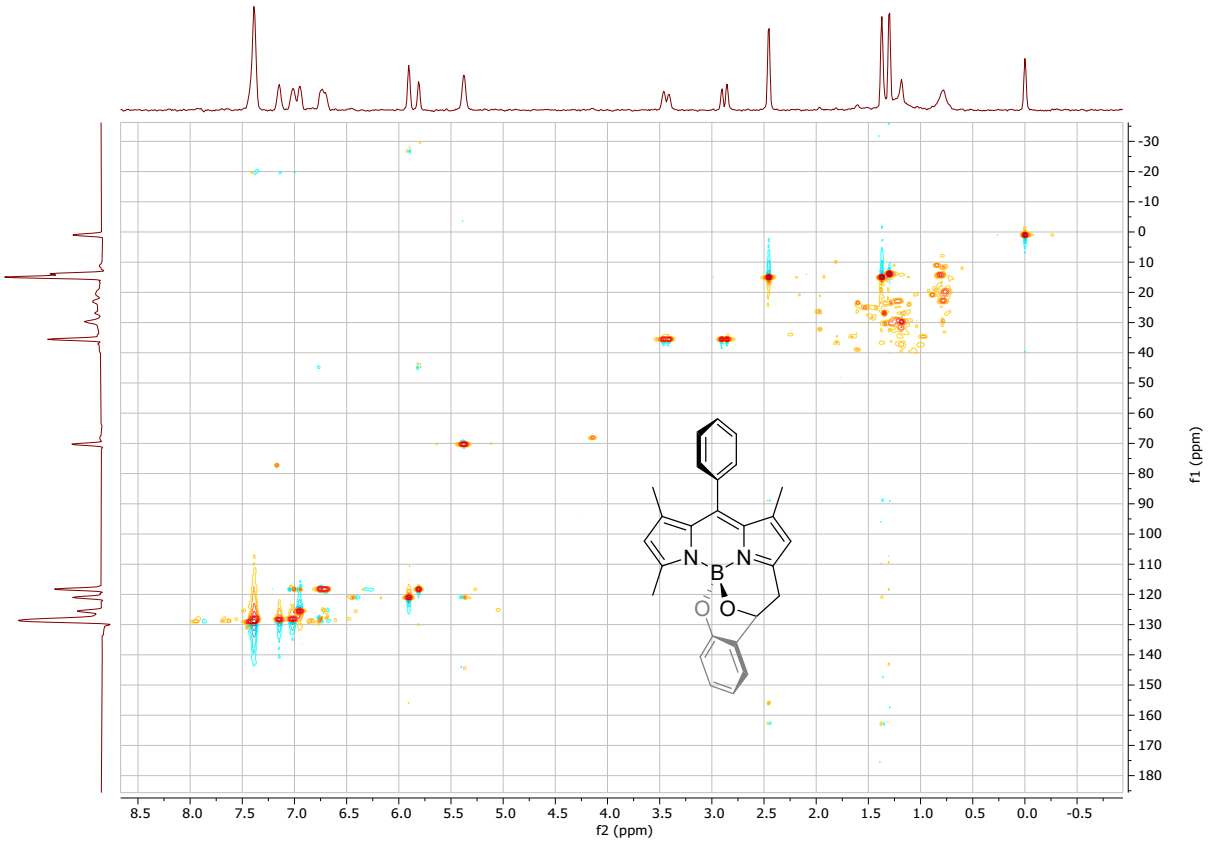

Fig. S8 HSQC NMR spectrum (400 MHz) of *B*C**-BODIPY in $CDCl_3$.

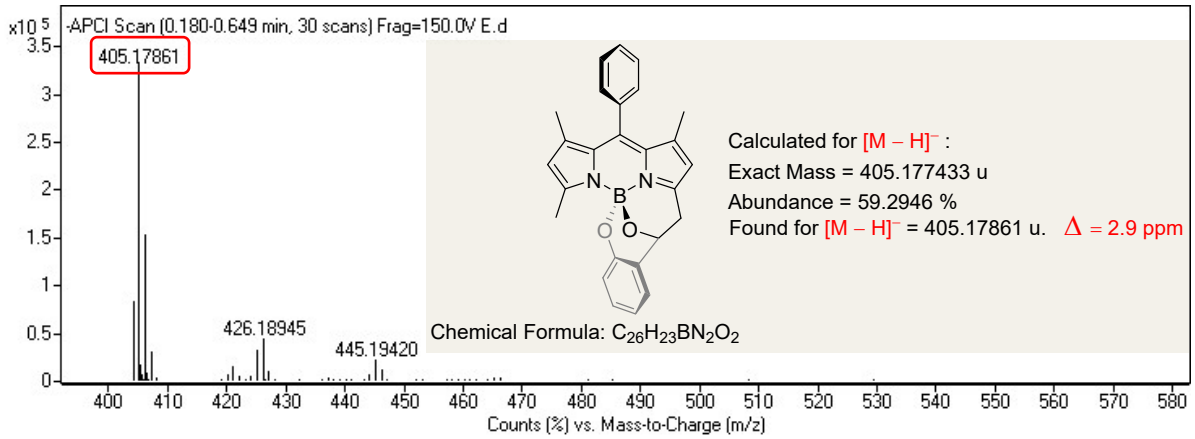

Fig. S9 HRMS (APCI negative) chromatogram of *B*C**-BODIPY.

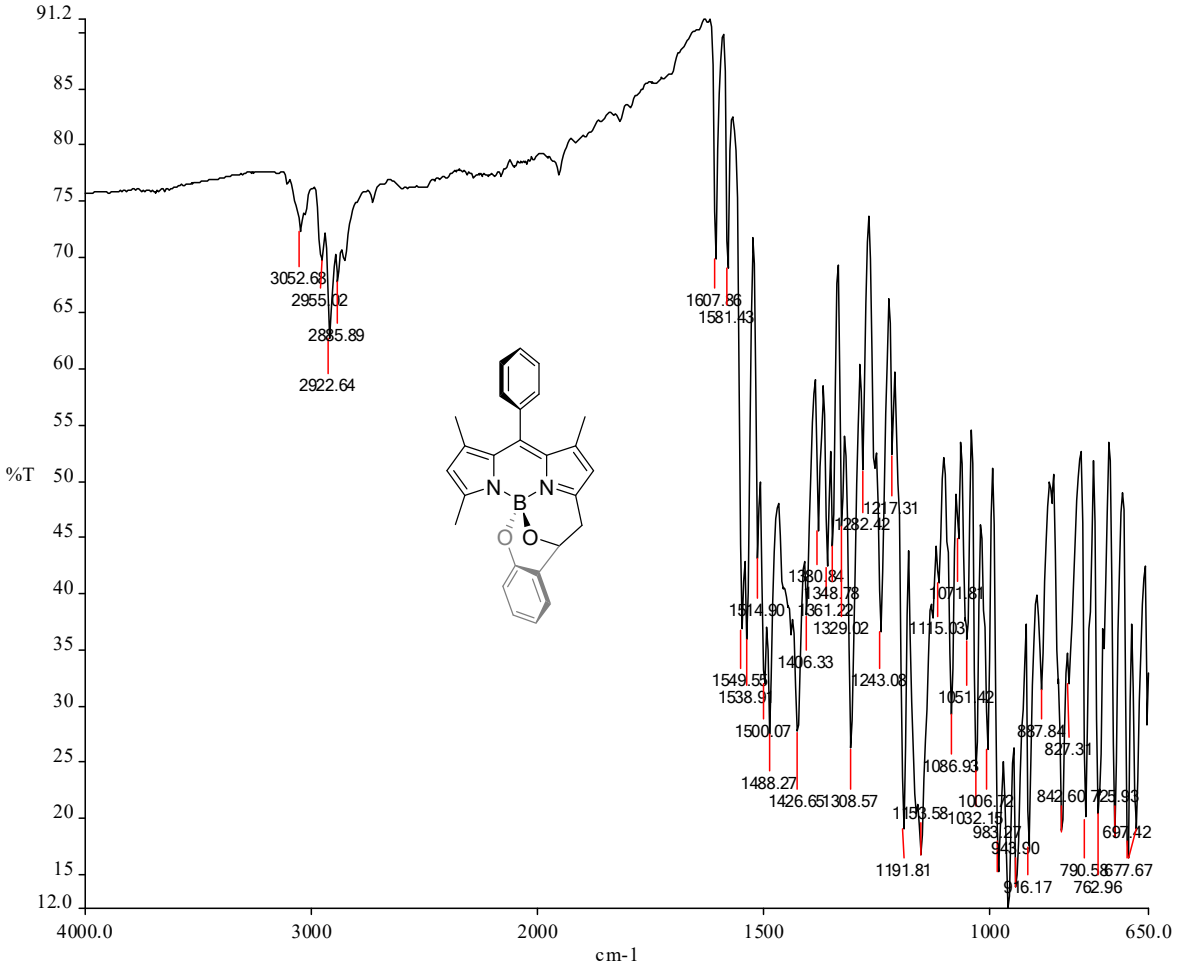

Fig. S10 IR (neat) spectrum of *B*C**-BODIPY.

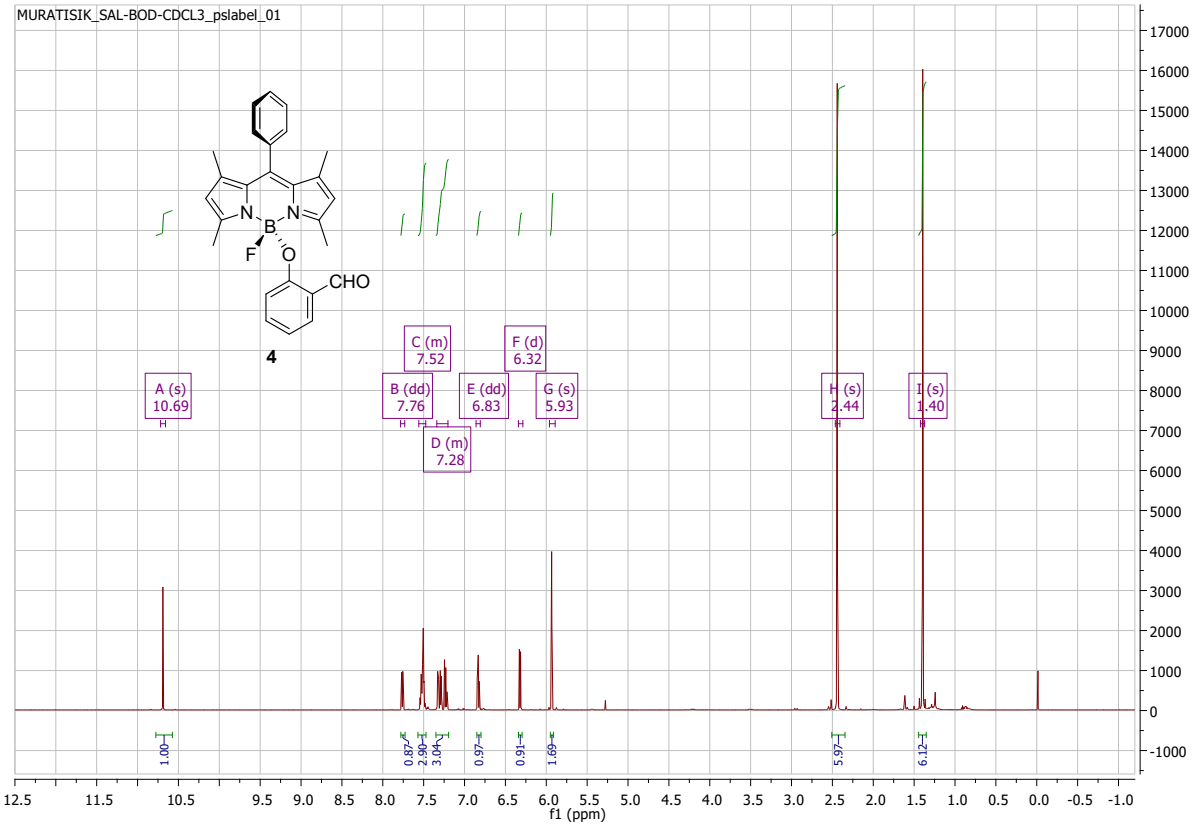

Fig. S11 ^{1}H NMR spectrum (600 MHz) of compound **4** in $CDCl_3$.

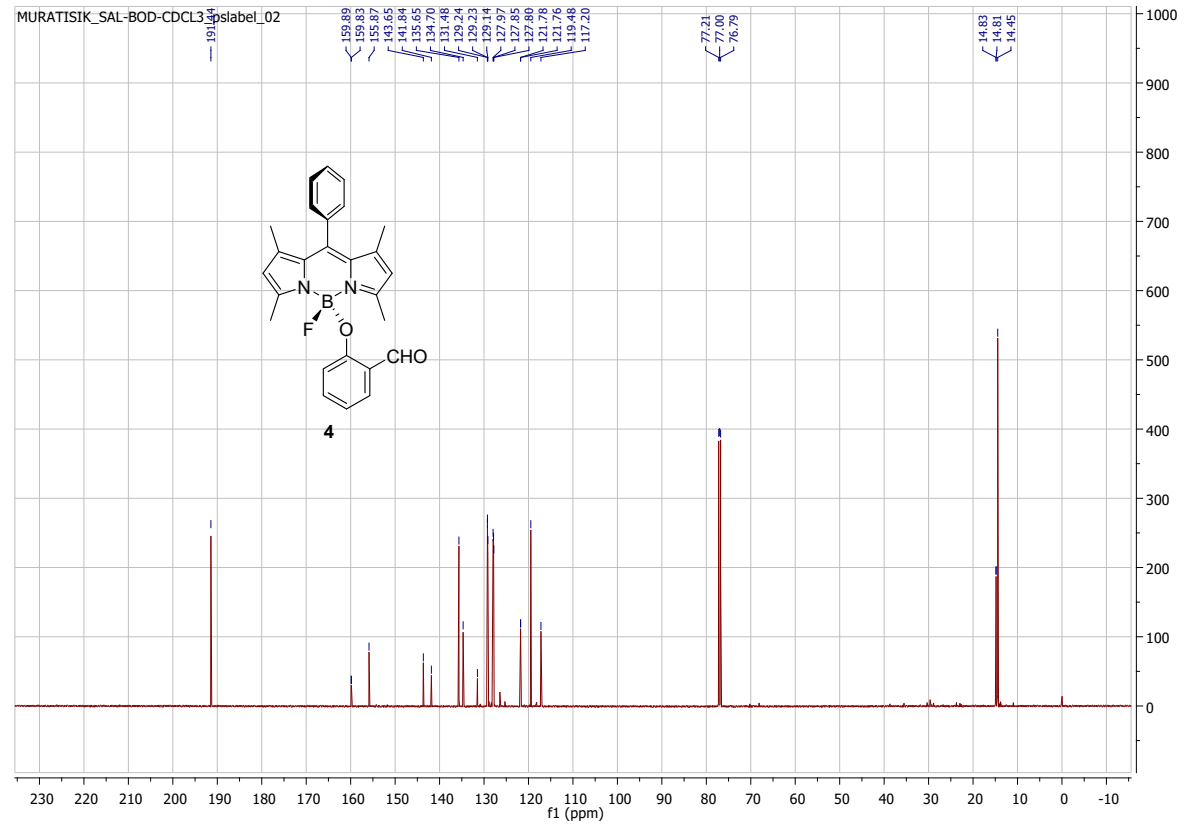

Fig. S12 ^{13}C NMR spectrum (151 MHz) of compound **4** in $CDCl_3$.

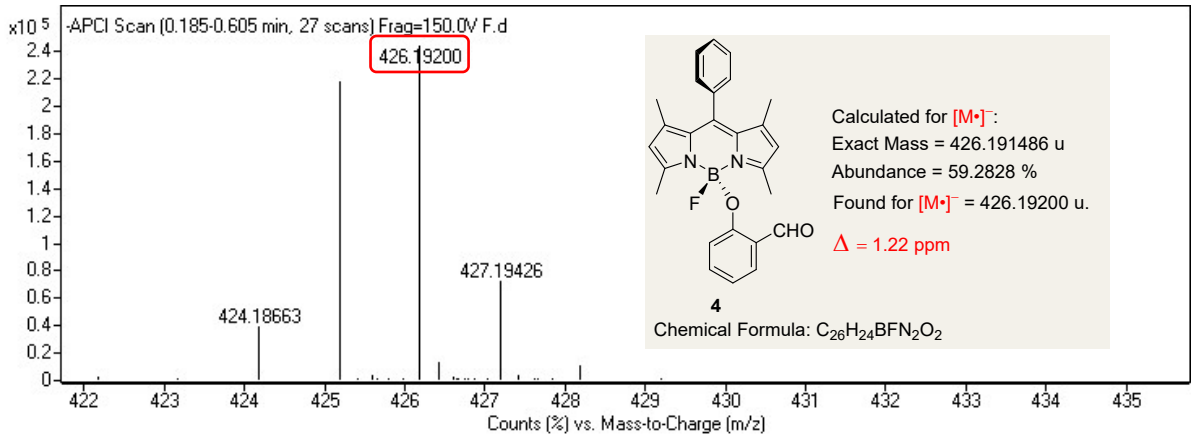

Fig. S13 HRMS (APCI negative) chromatogram of compound **4**.

X-ray diffraction data

For the crystal structure determination, single-crystal of the compound *B*C**-BODIPY was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and oscillation scans technique with Δw = 5º for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement were performed using CrystalClear (Rigaku/MSC Inc.,2005) software.[3] The structures were solved by direct methods using SHELXS-97 which allowed for the location of most of the heaviest atoms, with the remaining non-hydrogen atoms being located from different Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-97.[4] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogens attached to carbons were located at their geometric positions using appropriate HFIX instructions in SHELXL. The final difference Fourier maps showed no peaks of chemical significance.

*Crystal data for B*C**-BODIPY*:* $C_{26}H_{23}N_2O_2B$, crystal system, space group: orthorhombic, $Pca2_1$; (no:29); unit cell dimensions: a =9.8114(5), b = 21.6884(8), c = 9.7138(6) Å, α= 90, β = 90, γ = 90º; volume; 2067.0(3) Å^3, Z=4; calculated density: 1.306 g/cm^3; absorption coefficient: 0.082 mm^{-1}; F(000): 856; θ-range for data collection 2.4-26.0º; refinement method: full matrix least-square on F^2; data/parameters: 4026/285; goodness-of-fit on F^2: 1.060; final R-indices [$I > 2\sigma(I)$]: R_1 = 0.043, wR_2 = 0.103; largest diff. peak and hole: 0.177 and -0.164 e Å^{-3}.

CCDC-2095290 number contains the supplementary crystallographic data for this structure. These data are provided free of charge via the joint CCDC/FIZ Karlsruhe deposition service www.ccdc.cam.ac.uk/structures

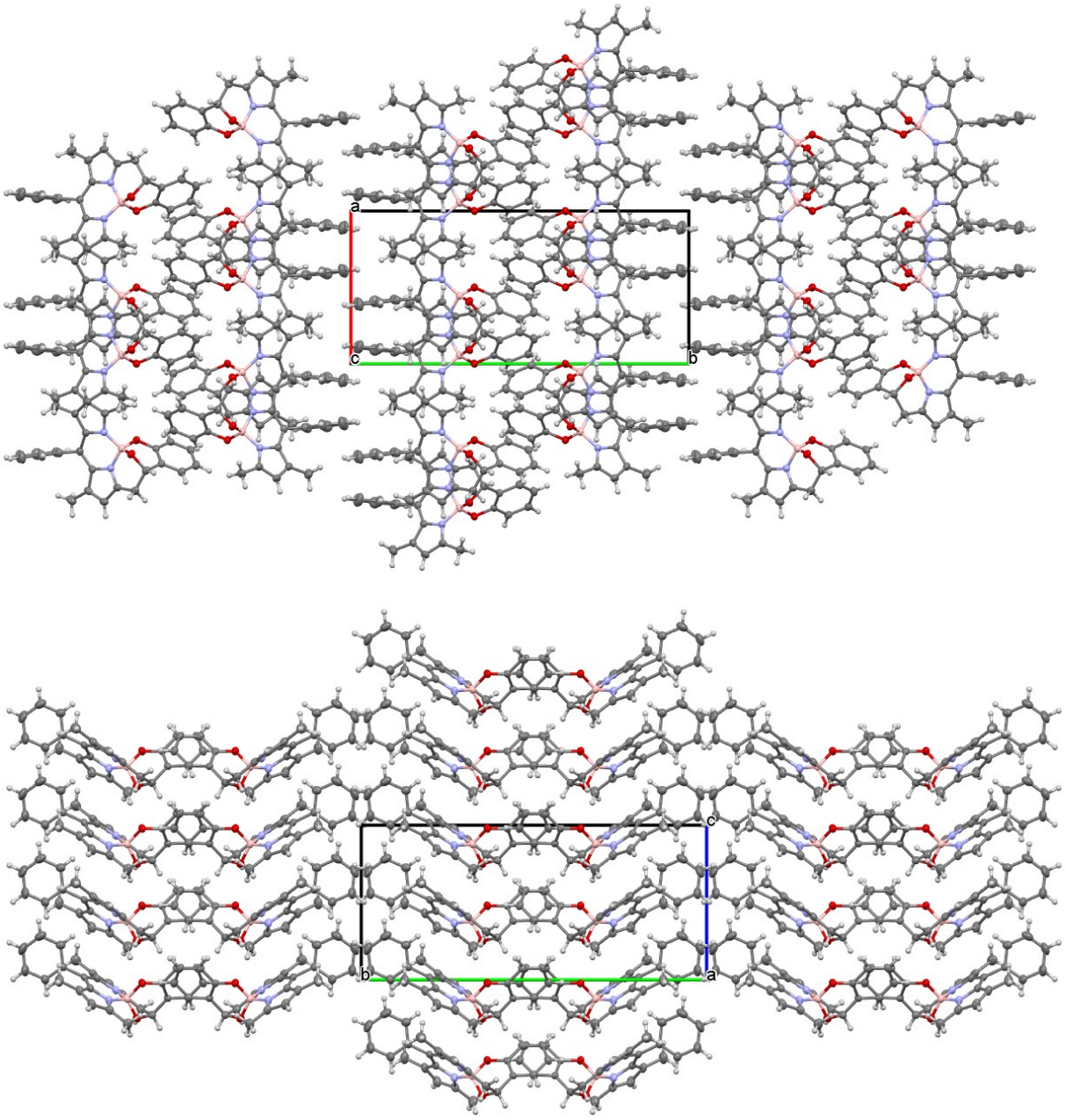

Fig. S12 Stacking of the molecules with the unit cell viewed down along the (top) *c*-axis and the (bottom) *a*-axis. Note: The strongest intermolecular interaction is the X-H···Cg (Pi-Ring) interaction [C26-H···C20/C25(ring centroid) 3.585(4) Å]. The π-π stacking interactions are relatively weak, for which the ring centroids are found to be in the range of 4.90–5.95 Å.

References

(1) H. Sunahara, Y. Urano, H. Kojima and T. Nagano, *J. Am. Chem. Soc*., 2007, **129**, 5597.
(2) N. Umeda and H. Takahashi, *et al.*, *ACS Chem. Biol.*, 2014, **9**, 2242.
(3) M.; Kollmannsberger, T. Gareis, S. Heinl, J. Daub and J. Breu, *Angew. Chem., Int. Ed.,* 1997, **36**, 1333.
(4) *Rigaku/MSC, Inc., 9009 New Trails Drive, TheWoodlands, TX 77381.*
(5) G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112.