Supplementary Information (SI) for Materials Advances.

Supporting Information

Solid-state and Aggregation-Induced Emission of Novel Bicyclic and Tricyclic Difluoroboron Heterocycles

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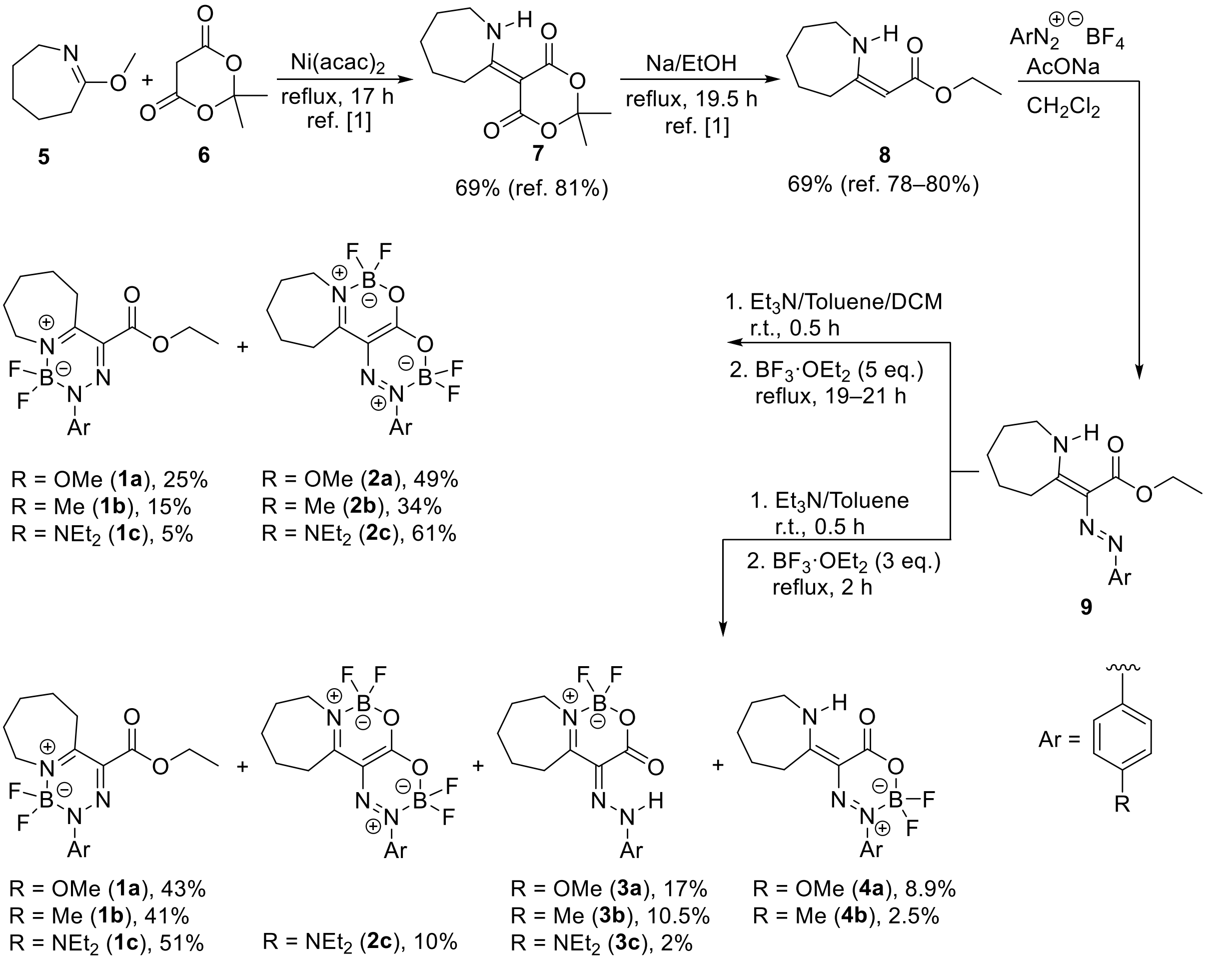
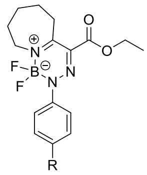
1. Results and Discussion



Scheme S1

The starting enaminoester **8** was prepared in two steps according to published methods (Scheme S1).[1] Meldrum's acid (**6**) reacted with lactimether **5** in the presence of a catalytic amount of Ni(acac)$_2$ to give the condensation product **7**. After refluxing with sodium ethanolate for 19.5 hours, enaminoester **8** was isolated. This enaminoester **8** was used for the reaction with diazonium tetrafluoroborates to give azo coupling products **9a**–**c**. The crude azo compounds **9a**–**c** were subjected to the reaction with triethylamine and boron-trifluoride etherate. Triazaborine **1a** was the main product if 3 equivalents of BF$_3$·OEt$_2$ and toluene were used, and the reaction proceeded at reflux for 2 hours (Table S1, Entry 1). When the toluene/dichloromethane mixture and 5 equivalents of BF$_3$·OEt$_2$ were used, triazaborine **1a**, oxazaborinone **3a**, and oxadiazaborinone **4a** were obtained as minor products together with bis-coordinated compound **2a** (Table S1, Entry 2). The extending of the reaction time led to the increasing of the yields of both **1a** and **2a** (Table S1, Entry 3). In the case of the methyl derivative **9b** and the diethylamino derivative **9c**, oxazaborinone **3b** and **3c** were also isolated in the yields of 10.5% and 2%, respectively (Table S1, Entry 4 and 6) when 3 equivalents of $BF_3 \cdot OEt_2$ was used. Another minor product **4b** was obtained for both 3 and 5 equivalents of $BF_3 \cdot OEt_2$ (Table S1, Entry 4 and 5).

Table S1. Yields of the prepared compounds **1–4**.



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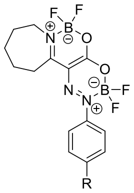

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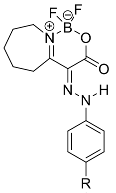

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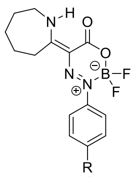
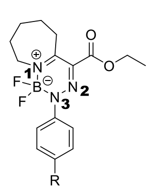


4

	R	$BF_3 \cdot OEt_2$ (eq.)	Solvent[a]	Reflux (h)	Yield (%)			
					1	**2**	**3**	**4**
1	OMe	3	Tol	2	43	–	–	–
2	OMe	5	Tol/DCM	2	13	27	17	8.9
3	OMe	5	Tol/DCM	19	25	49	–	–
4	Me	3	Tol	2	41	–	10.5	2.5
5	Me	5	Tol/DCM	21	15	34	5	6
6	NEt_2	3	Tol	2	51	10	2	–
7	NEt_2	5	Tol/DCM	21	5	61	–	–

[a] Tol = toluene, DCM = dichloromethane.

Table S2. ^{15}N, ^{11}B and ^{19}F NMR parameters for boron compounds **1**–**4**.



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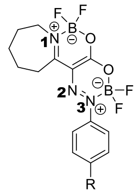

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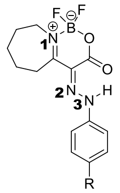

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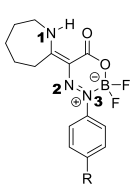
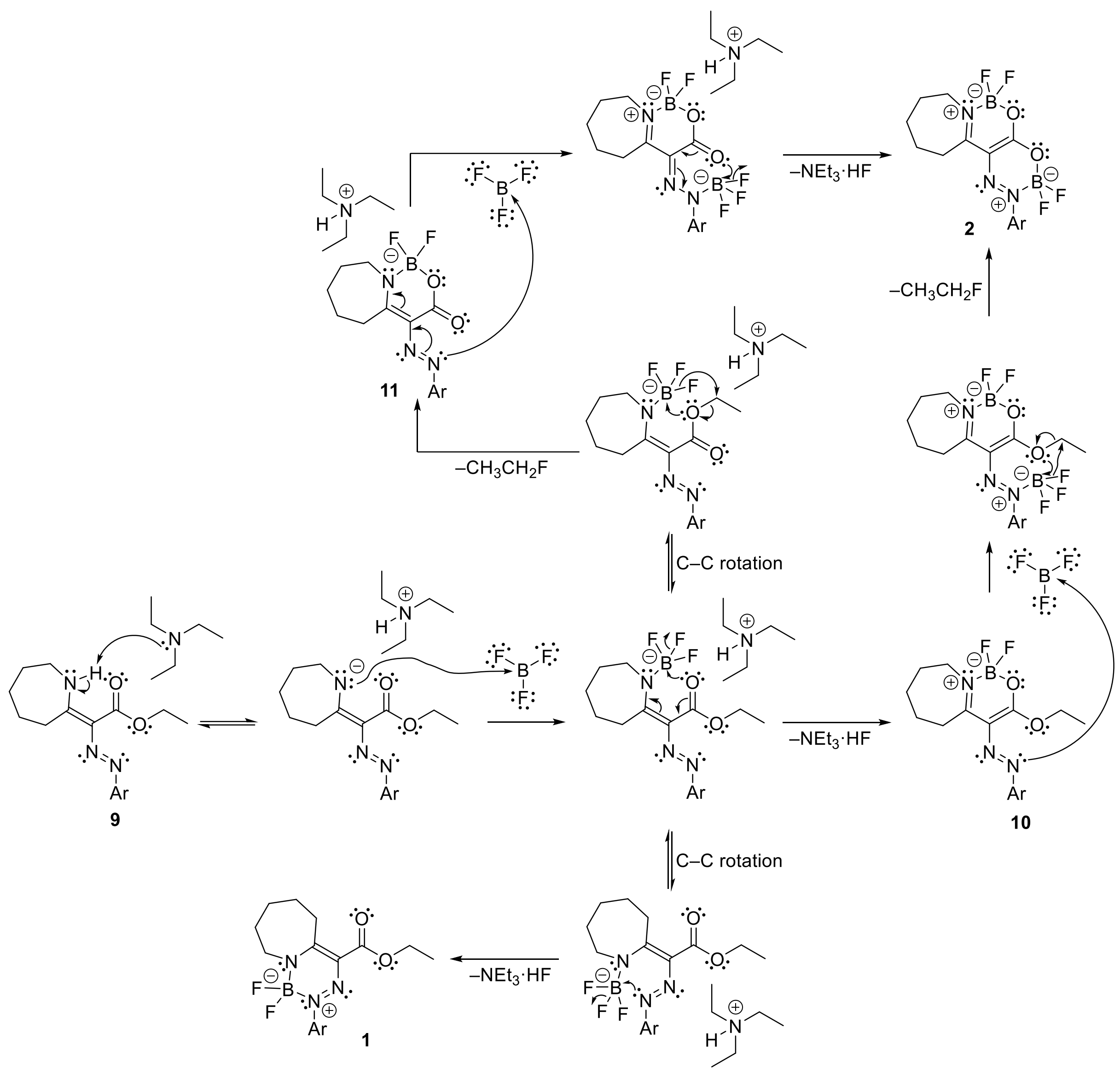


4

	R				δ (ppm)		
		$^{1}J_{N,H}$[a]	^{15}N1	^{15}N2	^{15}N3	^{11}B	^{19}F
1a	OMe	–	–186.0	12.2	–159.3	–0.44	–133.6
1b	Me	–	–184.2	12.8	–159.9	–0.44	–133.8
1c[b]	NEt$_2$	–	–191.8	10.1	–152.7	–0.45	–134.6
2a	OMe	–	–187.1	[e]	–127.1	0.06	–133.3
						–0.15	–142.2
2b	Me	–	–185.4	[e]	–127.2	0.01	–133.1
						–0.15	–142.3
2c[c]	NEt$_2$	–	–192.9	[e]	–119.9	0.11	–133.9
						–0.22	–141.7
3a	OMe	95.5	–180.2	–2.47	–187.9	–0.16	–146.2
3b	Me	97	–178.4	[e]	–189.6	–0.26	–146.4
3c[d]	NEt$_2$	94.5	–187.3	[e]	–181.1	–0.09	–145.8
4a	OMe	87.9	–220.9	[e]	–139.6	–0.20	[f]
4b	Me	89.5	–218.2	[e]	–139.5	–0.18	–137.3

[a] The coupling constants *J* are reported in Hertz. The coupling constants $^{1}J_{B,F}$ are reported in Experimental. [b] ^{15}N(NEt$_2$) = –304.8 ppm. [c] ^{15}N(NEt$_2$) = –293.4 ppm. [d] ^{15}N(NEt$_2$) = –302.8 ppm. [d] Not detected. [f] Not measured.



Scheme S2. Suggested mechanism for the formation of the boron compounds mentioned in the text.

The suggested mechanism for the formation of these heterocyclic compounds is shown in Scheme S2. After the deprotonation of azo-coupled enaminoester **9**, the coordination of BF_3 occurs, followed by the cyclization with elimination of the fluoride anion to give oxazaborine **10** and triazaborine **1**. Subsequently another BF_3 molecule is coordinated to the nitrogen of oxazaborine **10**. In the last step, intramolecular cyclization and nucleophilic substitution occur to give **2** and ethyl fluoride. Another route to the bis-coordinated product **2** is through oxazaborinone **11** (Analog **3** of this oxazaborinone has been isolated). After the deprotonation of azo-coupled enaminoester **9**, the coordination of BF_3 occurs, followed by intramolecular cyclization with nucleophilic substitution. Then another BF_3 molecule is coordinated to the nitrogen of oxazaborinone **11**. Product **2** is formed after the cyclization and cleavage of the fluoride anion.

2. Experimental Section

2.1 General Methods

All **chemicals** and dry dichloromethane, except those mentioned below, were purchased from commercial suppliers (Acros Organics (Part of Thermo Fisher Scientific, Geel, Belgium)), Sigma-Aldrich (Merck, Darmstadt, Germany), or Fluorochem (Hadfield, Derbyshire, UK). Toluene was dried over sodium.

NMR spectra were measured in $CDCl_3$, acetone-d_6 or in DMSO-d_6 using a Bruker AVANCE III 400 spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C), and 376 MHz (^{19}F) or using a Bruker Ascend 500 spectrometer equipped with Prodigy CryoProbe, operating at 500 MHz (^1H), 125 MHz (^{13}C), 160 MHz (^{11}B), 470 MHz (^{19}F) and 50 MHz (^{15}N). All the pulse sequences were taken from the Bruker software library. The ^{13}C NMR spectra were measured either in the standard way or by means of the APT pulse sequence. The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). The coupling constants *J* are reported in Hertz (Hz). TMS was used as an internal standard for ^1H NMR in $CDCl_3$ (δ 0.00). $CDCl_3$ was used as an internal standard for ^{13}C NMR (the middle signal of the solvent multiplet, δ 77.0). Nitromethane $CH_3{}^{15}NO_2$ was used as an external standard for ^{15}N NMR (δ 0.00). DMSO-d_6 was used as an internal standard for both ^1H NMR (the middle signal δ 2.55) and ^{13}C NMR (the middle signal δ 39.6). Fluorine-19 NMR spectra were measured without proton decoupling using α,α,α-trifluorotoluene as the secondary external standard (δ = –63.9 ppm against $CFCl_3$ as the primary standard).[2a] Boron-11 NMR were measured in 5 mm quartz NMR tubes (Norell) using B(OMe)3 as an external standard (δ = 18.1 ppm).[2b]

Elemental analyses were performed on a Flash 2000 CHNS Elemental Analyzer (Thermo Fisher Scientific, Milan, Italy).

Melting points were measured on a Kofler Boetius PHMK 80/2644 hot-stage microscope and were not corrected.

High-resolution mass spectra were recorded on a MALDI LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Italy) equipped with a nitrogen UV laser (337 nm, 60 Hz, 8–20 _J) in the positive ion mode. For the CID experiment using the linear trap quadrupole (LTQ) helium was used as the collision gas and 2,5-dihydroxybenzoic acid (DHB) as the MALDI matrix.

UV/Vis spectra were recorded on a UV/Vis spectrophotometer Hewlett-Packard 8453 (Waldbronn, Germany).

The X-ray data for colorless crystals of **1a** and **2a** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[3a] The absorption was corrected by integration methods.[3b] Structures were solved by direct methods (Sir92)[3c] and refined by full matrix least-square based on F^2 (SHELXL97 or SHELXL-2017/1).[3d] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C-H = 0.96, 0.97 and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic ring, respectively.

$R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2189206-2189207 for **2a** and **1a** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Photophysical Measurements. UV−Vis absorption spectra were recorded at 25 °C using a PerkinElmer Lambda 45 spectrophotometer. The fluorescence spectra were recorded with a PerkinElmer Lambda LS55 fluorimeter and with a modular UV−Vis−NIR spectrofluorimeter Edinburgh Instruments FLS920 equipped with a photomultiplier HamamatsuR928P. The latter instrument connected to a PCS900 PC card was used for the time-correlated single-photon counting (TCSPC) experiments (excitation laser λ = 405 nm). NPs suspension were diluted with milli-Q water. Emission quantum yields were measured by corrected emission spectra obtained with a barium sulfate coated integrating sphere (LabSphere, 4 inches diameter), following the procedure described by De Mello et al.[4]

DLS. The determination of the NP hydrodynamic diameter distributions was carried out through DLS measurements employing a Malvern Nano ZS instrument with a 633 nm laser diode. Samples were housed in disposable polystyrene cuvettes of 1 cm optical path length using water as solvent. The width of DLS hydrodynamic diameter distribution is indicated by PdI (polydispersion index). In the case of a monomodal distribution (Gaussian) calculated by means of cumulant analysis, PdI = $(\sigma/Z_{avg})^2$, where σ is the width of the distribution and Z_{avg} is average diameter of the particles population, respectively.

Laser Scanning Confocal Fluorescence and Fluorescence Lifetime Imaging (FLIM). The AIE aggregates were characterized with an inverted Nikon A1R laser scanning confocal microscope. Images were collected using a Nikon PLAN APO 100x oil immersion objective, NA 1.45. Pinhole was set to 1 Airy Unit. In Laser Scanning Confocal Fluorescence Imaging a 401 nm CW laser was used as excitation, which was reflected onto a dichroic mirror (405 nm), while emission photons were collected through a 450/50 or a 525/50 nm emission filter. In FLIM a time-correlated single photon counting (TCSPC) system of Picoquant GmbH Berlin was used with a 405 nm pulsed excitation laser at 80 MHz repetition frequency, the same dichroic mirror, a 470/40 nm bandpass emission filter, a Hybrid PMA detector and a Picoquant TimeHarp correlation board.

DFT Calculations The DFT calculations were performed using the density functional method B3LYP in conjunction with 6-311+G** basis set[5] as implemented in the Gaussian 16 suite.[6] The solvent effect was included using CPCM model.[7] For all optimized structures, frequency analyses at the same level of theory were used to assign them as genuine minima on the potential energy surface. The single point and TD-DFT calculations were performed on the optimized structures on the B3LYP/6-311+G** level of theory.

Electrochemistry. Electrochemical measurements were carried out in acetonitrile containing 0.1M Bu_4NPF_6. Cyclic voltammetry (CV), rotating disk voltammetry (RDV) were used in a three-electrode arrangement. The working electrode was glassy carbon (3 mm in diameter) for CV and RDV experiments. As the reference and auxiliary electrodes were used saturated calomel electrode (SCE) separated by a bridge filled with supporting. All potentials are given vs. SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 128 N (AUTOLAB, Metrohm Autolab B.V., Utrecht, The Netherlands) operated via NOVA 1.11 software.

2.2 Synthetic Procedures

7-Methoxy-3,4,5,6-tetrahydro-2*H*-azepine (5)

A modified method according to Wick was used. [1a] A screw-cup thick wall tube (Ace Pressure Tube®) equipped with a magnetic stirring bar was charged with dimethyl sulphate (18.9 mL, 0.2 Mol) and ε-caprolactame (23 g, 0.2 Mol) under cooling. The tube was sealed and heated to 75 °C for 24 h. The mixture was then cooled on ice and saturated aqueous potassium carbonate (60 mL) was subsequently added. The mixture was stirred for 30 min and then extracted with diethyl ether (4 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL) and dried over anhydrous sodium sulphate. After the evaporation of diethyl ether, the crude product was distilled under vacuum to give a colourless liquid (15.4 g, 61%). B.p. 36.5 °C/5 mbar; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.58 (s, 3H; OCH_3), 3.43–3.41 (m, 2H; CH_2), 2.41–2.39 (m, 2H; CH_2), 1.79–1.74 (m, 2H; CH_2), 1.60–1.55 (m, 2H; CH_2), 1.51–1.49 ppm (m, 2H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 52.0, 48.3, 31.7, 30.9, 27.6, 23.1 ppm.

5-(Azepan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (7)

A modified method according to Celerier was used. [1b] Anhydrous dichloromethane (150 mL), 7-methoxy-3,4,5,6-tetrahydro-2*H*-azepine (**1**) (15 g, 0.12 Mol), Meldrum's acid (**2**) (17.3 g, 0.12 Mol), and nickel(II) acetylacetonate (0.08 g, 0.31 mMol) were placed in a round-bottom flask fitted with a reflux condenser and equipped with a magnetic stirrer. The reaction mixture was refluxed for 17 hours. The solvent was removed, and the yellow precipitate was recrystallized from ethanol to give 19.9 g (69%) of pale-yellow crystals. M.p. 150–151 °C (ref. [1b] 147–149 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.49 (br s, 1H; NH), 3.62–3.59 (m, 2H; CH_2), 3.35–3.32 (m, 2H; CH_2), 1.89–1.74 (m, 2H; CH_2), 1.77–1.71 (m, 4H; CH_2), 1.69 ppm (s, 6H; 2× CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 179.9, 167.1, 163.0, 102.1, 83.6, 44.5, 29.9, 29.6, 27.3, 26.1, 23.2 ppm.

Ethyl 2-(azepane-2-ylidene)acetate (8)

A method according to Celerier was used. [1b] To a stirred solution of freshly distilled absolute ethanol (150 mL) and sodium (2.19 g, 0.095 Mol), 5-(azepan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3**) (19 g, 0.079 Mol) was added in one portion. The mixture was refluxed, and a white precipitate begins to appear. The reflux was continued for 19.5 hours. The solvent was removed with a rotary evaporator, and the white precipitate was placed in a beaker. Water (80 mL) was added, and a 1M aqueous hydrochloric acid was added dropwise to adjust pH 6. The reaction mixture was the extracted with chloroform (4 × 25 mL). The combined organic layers were dried over anhydrous sodium sulphate, and the solvent was removed with a rotary evaporator. The yellow solid residue was recrystallized from methanol to give 8.86 g (61%) of white powder. M.p. 51–52 °C (ref. [1a] 55–56 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.85 (br s, 1H; NH), 4.44 (s, 1H, =CH), 4.08 (q, $^3J_{C,H}$ = 7.1 Hz, 2H; OCH_2CH_3), 3.32–3.28 (m, 2H;

CH_2), 2.30–2.28 (m, 2H; CH_2), 1.71–1.63 (m, 2H; CH_2), 1.61–1.57 (m, 2H; CH_2), 1.25 ppm (t, $^3J_{C,H}$ = 7.1 Hz, 2H; OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 168.4, 80.6, 58.1, 44.1, 35.0, 30.3, 30.0, 26.3, 14.5 ppm.

General Procedure for the Synthesis of Heterocyclic Compounds 1–4.

Method A: To a cold (5 °C) solution of *β*-enaminoester **8** (5 mMol) in dry dichloromethane (10 mL), sodium acetate (0.41 g, 5 mMol) and diazonium tetrafluoroborate (5 mMol) was added. The reaction mixture was stirred 24 hours at room temperature. Sodium acetate was filtered off, and dichloromethane evaporated. The crude azo coupling product was dissolved in toluene (15 mL) and triethylamine (1.4 ml, 10 mMol) was added. After 20 minutes, boron trifluoride diethyl etherate (1.9 ml 48%, 15 mMol) was added at 0–10 °C. The reaction mixture was stirred for 30 minutes at room temperature and then refluxed for 2 h. The reaction mixture was cooled to room temperature and the solvents evaporated. Ethyl acetate (30 mL) was added to the crude residue and the organic phase was extracted with water (4 × 30 mL) and brine (1 × 30 mL). The organic phase was dried with sodium sulphate and ethyl acetate was evaporated. The crude residue was separated by Flash chromatography.

Method B: The procedure was the same as for Method A, except that the azo coupling product was dissolved in the toluene/dichloromethane mixture (15 mL/10 mL) and boron trifluoride diethyl etherate (3.16 ml 48%, 25 mMol) was used. After stirring the reaction mixture for 30 minutes at room temperature, the mixture was refluxed for 19–20 hours. In the case of *β*-enaminoester **8** and 4-*N*,*N*-diethylaminobenzenediazonium tetrafluoroborate, dichloromethane (100 mL) was added to the crude residue instead of ethyl acetate and the organic phase was extracted with water (4 × 40 mL).

The following compounds were prepared:

Ethyl 1,1-difluoro-2-(4-methoxyphenyl)-2,5,6,7,8,9-hexahydro-1*H*-1λ^4,10λ^4-[1,2,4,3]triazaborinino[4,5-*a*]azepine-4-carboxylate (1a)

After Flash chromatography ($CHCl_3$), the title compound was obtained as dark yellow crystals. Yield 0.79 g (43%, Method A), 0.24 g (13%, Method B, reflux 2 h), and 0.45 g (25%, Method B, reflux 19 h). R_f = 0.07 ($CHCl_3$); m.p. 90–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.71 (m, 2H; Ar-H), 6.93–6.91 (m, 2H; Ar-H), 4.34 (q, $^3J_{C,H}$ = 7.1 Hz, 2H; OCH_2CH_3), 3.92–3.91 (m, 2H; CH_2), 3.83 (s, 3H; OCH_3), 3.27–3.24 (m, 2H; CH_2), 1.91–1.86 (m, 2H; CH_2), 1.81–1.77 (m, 4H; 2× CH_2), 1.39 ppm (t, $^3J_{C,H}$ = 7.1 Hz, 2H; OCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9, 164.8, 158.7, 138.6, 124.0 (br), 122.4 (br), 114.1, 61.2, 55.5, 47.0, 29.7, 29.4 (br), 26.8, 22.7, 14.3 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.44 ppm (t, $^1J_{B,F}$ = 32 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –133.9 ppm (q, $^1J_{B,F}$ = 32 Hz); UV/VIS (acetonitrile): λ_{max} (ε) = 401 (9577 $mol^{-1}dm^3cm^{-1}$); elemental analysis calcd (%) for $C_{17}H_{22}BF_2N_3O_3$: C 55.91, H 6.07, N 11.51; found: C 56.04, H 6.06, N 11.25.

Ethyl 1,1-difluoro-2-(4-methylphenyl)-2,5,6,7,8,9-hexahydro-1*H*-1λ^4,10λ^4-[1,2,4,3]triazaborinino[4,5-*a*]azepine-4-carboxylate (1b)

After Flash chromatography ($CHCl_3$), the title compound was obtained as yellow crystals. Yield 0.72 g (41%, Method A), 0.26 g (15%, Method B, reflux 21 h). R_f = 0.14 ($CHCl_3$); m.p. 98–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.66 (m, 2H; Ar-H), 7.20–7.19 (m, 2H; Ar-H), 4.37 (q, $^3J_{C,H}$ = 7.1 Hz, 2H; OC*H*$_2$CH$_3$), 3.93–3.88 (m, 2H; CH$_2$), 3.26–3.24 (m, 2H; CH$_2$), 2.36 (s, 1H; CH$_3$), 1.90–1.85 (m, 2H; CH$_2$), 1.81–1.76 (m, 4H; 2× CH$_2$), 1.38 ppm (t, $^3J_{C,H}$ = 7.1 Hz, 2H; OCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.1, 164.8, 142.7 (br), 137.0, 129.4, 124.3 (br), 120.9 (br t, $J_{H,F}$ = 2.5 Hz), 61.2, 47.0, 29.7, 29.4 (br), 26.7, 22.6, 14.2 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.44 ppm (t, $^1J_{B,F}$ = 32 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –133.6 ppm (q, $^1J_{B,F}$ = 32 Hz); UV/VIS (acetonitrile): λ_{max} (*ε*) = 389 (10023 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{17}H_{22}BF_2N_3O_2$: C 58.47, H 6.35, N 12.03; found: C 58.44, H 6.29, N 12.31.

Ethyl 2-(4-(diethylamino)phenyl)-1,1-difluoro-2,5,6,7,8,9-hexahydro-1*H*-1λ^4,10λ^4-[1,2,4,3]triazaborinino[4,5-*a*]azepine-4-carboxylate (1c)

After Flash chromatography (EtOAc/n-hexane 1:3 (Method A) and CH_2Cl_2 (Method B)), the title compound was obtained as red crystals. Yield 1.03 g (51%, Method A), 0.10 g (5%, Method B, reflux 21 h). R_f = 0.32 (EtOAc/n-hexane 1:3); R_f = 0.14 (CH_2Cl_2); m.p. 76–78 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.65 (m, 2H; Ar-H), 6.66–6.64 (m, 2H; Ar-H), 4.32 (q, $^3J_{C,H}$ = 7.1 Hz, 2H; OC*H*$_2$CH$_3$), 3.89–3.87 (m, 2H; CH$_2$), 3.37 (q, $^3J_{C,H}$ = 7 Hz, 4H; 2 × NC*H*$_2$CH$_3$), 3.26–3.24 (m, 2H; CH$_2$), 1.87–1.83 (m, 2H; CH$_2$), 1.80–1.75 (m, 4H; 2× CH$_2$), 1.38 (t, $^3J_{C,H}$ = 7.1 Hz, 2H; OCH$_2$C*H*$_3$), 1.16 ppm (t, $^3J_{C,H}$ = 7 Hz, 2H; 2× NCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.1, 164.8, 147.0, 134.3 (br), 123.1 (br), 122.4 (br), 111.4, 60.9, 46.6, 44.5, 29.7, 29.1 (br), 27.0, 22.9, 14.3, 12.5 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.45 ppm (t, $^1J_{B,F}$ = 32 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –134.6 ppm (q, $^1J_{B,F}$ = 32 Hz); UV/VIS (acetonitrile): λ_{max} (*ε*) = 472 (9499 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{20}H_{29}BF_2N_4O_2$: C 59.13, H 7.19, N 13.79; found: C 59.22, H 7.07, N 14.01.

3,3,6,6-Tetrafluoro-2-(4-methoxyphenyl)-6,8,9,10,11,12-hexahydro-3*H*-2λ^4,3λ^4,6λ^4,7λ^4-[1,3,4,2]oxadiazaborinino[5',6':5,6][1,3,2]oxazaborinino[3,4-*a*]azepine (2a)

After Flash chromatography (EtOAc/n-hexane 1:3), the title compound was obtained as orange crystals. Yield 0.45 g (25%, Method B, reflux 2 h) and 0.95 g (49%, Method B, reflux 19 h). R_f = 0.03 (EtOAc/n-hexane 1:3); m.p. 192–194 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.71 (m, 2H; Ar-H), 6.99–6.96 (m, 2H; Ar-H), 3.92–3.90 (m, 2H; CH$_2$), 3.87 (s, 3H; OCH$_3$), 3.34–3.32 (m, 2H; CH$_2$), 1.98–1.93 (m, 2H; CH$_2$), 1.85–1.78 ppm (m, 4H; 2× CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.1, 162.0 (br), 160.8, 137.4, 122.9 (br t, $J_{C,F}$ = 2.2 Hz), 114.6 (2×C), 55.7, 48.7, 29.8, 27.3, 26.1, 22.6 ppm; ^{11}B NMR (128 MHz, Acetone-*d*$_6$): δ = 0.06 (br t, $^1J_{B,F}$ = 12.7 Hz) –0.15 ppm (br t, $^1J_{B,F}$ = 15.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ = –133.05 (br q, $^1J_{B,F}$ = 15.3 Hz), –142.98 ppm (br d, $^1J_{B,F}$ = 18 Hz); UV/VIS (acetonitrile): λ_{max} (*ε*) = 409

(24813 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{15}H_{17}B_2F_4N_3O_3$: C 46.80, H 4.45, N 10.92; found: C 47.04, H 4.31, N 11.02.

3,3,6,6-Tetrafluoro-2-(4-methylphenyl)-6,8,9,10,11,12-hexahydro-3*H*-2λ^4,3λ^4,6λ^4,7λ^4-[1,3,4,2]oxadiazaborinino[5',6':5,6][1,3,2]oxazaborinino[3,4-*a*]azepine (2b)

After Flash chromatography (EtOAc/n-hexane 1:3), the title compound was obtained as orange crystals. Yield 0.63 g (34%, Method B, reflux 21 h). R_f = 0.15 (EtOAc/n-hexane 1:3); m.p. 237–240 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.64 (m, 2H; Ar-H), 7.29–7.27 (m, 2H; Ar-H), 3.94–3.92 (m, 2H; CH_2), 3.35–3.33 (m, 2H; CH_2), 1.99–1.94 (m, 2H; CH_2), 1.86–1.78 ppm (m, 4H; 2× CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3, 162.1 (br), 141.7, 140.3, 130.0, 121.2 (br t, $J_{C,F}$ = 2.2 Hz, 115.0, 48.8, 29.8, 27.3, 26.1, 22.5, 21.2 ppm; ^{11}B NMR (128 MHz, $CDCl_3$): δ = 0.01 (br t, $^1J_{B,F}$ = 14.6 Hz), –0.15 ppm (t, $^1J_{B,F}$ = 15.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ = –133.32 (br q, $^1J_{B,F}$ = 14.6 Hz), –142.31 ppm (br d, $^1J_{B,F}$ = 19.5 Hz); UV/VIS (acetonitrile): λ_{max} (ε) = 389 (24890 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{15}H_{17}B_2F_4N_3O_2$: C 48.83, H 4.64, N 11.39; found: C 49.05, H 6.65, N 11.07.

***N*,*N*-diethyl-4-(3,3,6,6-tetrafluoro-6,8,9,10,11,12-hexahydro-3*H*-2λ^4,3λ^4,6λ^4,7λ^4-[1,3,4,2]oxadiazaborinino[5',6':5,6][1,3,2]oxazaborinino[3,4-*a*]azepin-2-yl)aniline (2c)**

After Flash chromatography (EtOAc/n-hexane 1:3 (Method A) and CH_2Cl_2 (Method B)), the title compound was obtained as orange crystals. Yield 0.22 g (10%, Method A), 1.30 g (61%, Method B, reflux 21 h). R_f = 0.12 (EtOAc/n-hexane 1:3); R_f = 0.48 (CH_2Cl_2); m.p. 195–198 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69–6.67 (m, 2H; Ar-H), 6.68–6.66 (m, 2H; Ar-H), 3.89–3.87 (m, 2H; CH_2), 3.43 (q, $^3J_{C,H}$ = 7 Hz, 4H; 2× NCH_2CH_3), 3.33–3.31 (m, 2H; CH_2), 1.95–1.91 (m, 2H; CH_2), 1.84–1.76 (m, 4H; 2× CH_2), 1.21 ppm (t, $^3J_{C,H}$ = 7 Hz, 2H; 2× NCH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.7, 161.8, 148.8, 133.0, 123.1 (br), 113.3, 111.2, 48.3, 44.7, 29.9, 27.2, 26.4, 22.7, 12.6 ppm; ^{11}B NMR (128 MHz, Acetone-d_6): δ = 0.07 (br t, $^1J_{B,F}$ = 12.8 Hz), –0.25 ppm (br t, $^1J_{B,F}$ = 15.3 Hz); ^{19}F NMR (470 MHz, Acetone-d_6): δ = –133.93 (br q, $^1J_{B,F}$ = 15.3 Hz), –142.14 ppm (br d, $^1J_{B,F}$ = 22 Hz); UV/VIS (acetonitrile): λ_{max} (ε) = 517 (13449 mol^{-1}dm^{3}cm^{-1}); elemental analysis calcd (%) for $C_{18}H_{24}B_2F_4N_4O_2$: C 50.75, H 5.68, N 13.15; found: C 50.59, H 5.81, N 13.20.

1,1-Difluoro-4-(2-(4-methoxyphenyl)hydrazineylidene)-4,5,6,7,8,9-hexahydro-1λ^4,10λ^4-[1,3,2]oxazaborinino[3,4-*a*]azepin-3(1*H*)-one (3a)

After Flash chromatography (EtOAc/n-hexane 1:3), the title compound was obtained as dark yellow crystals. Yield 0.29 g (17%, Method B, reflux 2 h). R_f = 0 (EtOAc/n-hexane 1:3); R_f = 0.44 (EtOAc); m.p. 219–222 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 14.79 (s, 1H; NH), 7.40–7.39 (m, 2H; Ar-H), 6.99–6.97 (m, 2H; Ar-H), 3.91–3.90 (m, 2H; CH_2), 3.85 (s, 3H; OCH_3), 3.27–3.25 (m, 2H; CH_2), 1.94–1.89 (m, 2H; CH_2), 1.83–1.79 (m, 2H; CH_2), 1.77–1.73 ppm (m, 2H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.7, 161.4 (br), 158.9, 134.2, 118.34, 118.26, 115.1, 55.6, 48.6, 29.8, 27.0 (br), 26.1, 22.8 ppm; ^{11}B NMR (160 MHz, DMSO-d_6): δ = –0.16 ppm (t, $^1J_{B,F}$ = 15 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ =–146.2 (q, $^1J_{B,F}$ = 14 Hz) ppm; HRMS (MALDI): *m/z* cald for $C_{15}H_{19}BF_2N_3O_3$: 338.1488 [*M*+H]$^+$; found: 338.1489; cald for $C_{15}H_{18}BF_2N_3O_3$+K$^+$: 376.1046 [*M*+K]$^+$; found: 376.1050; cald for $C_{15}H_{18}BF_2N_3O_3$+Na$^+$: 360.1307 [*M*+Na]$^+$; found: 360.1311; cald for $C_{15}H_{18}BF_2N_3O_3$–F: 318.1425 [*M*–F]$^+$; found: 318.1427; elemental analysis calcd (%) for $C_{15}H_{18}BF_2N_3O_3$: C 53.44, H 5.38, N 12.46; found: C 53.14, H 5.30, N 12.29.

1,1-Difluoro-4-(2-(4-methylphenyl)hydrazineylidene)-4,5,6,7,8,9-hexahydro-1λ^4,10λ^4-[1,3,2]oxazaborinino[3,4-*a*]azepin-3(1*H*)-one (3b)

After Flash chromatography ($CHCl_3$), the title compound was obtained as dark yellow crystals. Yield 0.17 g (10.5%, Method A), yield 0.10 g (6%, Method B, reflux 21 h). R_f = 0.07 ($CHCl_3$); m.p. 230–233 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 14.69 (s, 1H; NH), 7.34–7.32 (m, 2H; Ar-H), 7.25–7.24 (m, 2H; Ar-H), 3.92–3.91 (m, 2H; CH_2), 3.28–3.26 (m, 2H; CH_2), 2.38 (s, 3H; CH_3), 1.93–1.89 (m, 2H; CH_2), 1.84–1.79 (m, 2H; CH_2), 1.78–1.72 ppm (m, 2H; CH_2); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ = 14.22 (s, 1H; NH), 7.59–7.58 (m, 2H; Ar-H), 7.34–7.32 (m, 2H; Ar-H), 3.91–3.89 (m, 2H; CH_2), 3.35–3.34 (m, 2H; CH_2), 2.36 (s, 3H; CH_3), 1.88–1.83 (m, 2H; CH_2), 1.72–1.68 ppm (m, 2H; 2 × CH_2); ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ = 179.0, 161.4, 138.9, 136.7, 130.4, 118.5, 117.3, 48.0, 29.1, 26.6 (br), 25.8, 22.4, 20.8 ppm; ^{11}B NMR (160 MHz, DMSO-*d*$_6$): δ = –0.26 ppm (t, $^1J_{B,F}$ = 15.5 Hz); ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ = –146.4 (q, $^1J_{B,F}$ = 14.5 Hz) ppm; HRMS (MALDI): *m/z* cald for $C_{15}H_{19}BF_2N_3O_2$: 322.1538 [*M*+H]$^+$; found: 322.1537; cald for $C_{15}H_{18}BF_2N_3O_2$+K$^+$: 360.1097 [*M*+K]$^+$; found: 360.1097; cald for $C_{15}H_{18}BF_2N_3O_2$+Na$^+$: 344.1358 [*M*+Na]$^+$; found: 344.1357; cald for $C_{15}H_{18}BF_2N_3O_2$–F: 302.1476 [*M*–F]$^+$; found: 302.1473; elemental analysis calcd (%) for $C_{15}H_{18}BF_2N_3O_2$: C 56.10, H 5.65, N 13.09; found: C 56.34, H 5.61, N 13.13.

4-(2-(4-(Diethylamino)phenyl)hydrazineylidene)-1,1-difluoro-4,5,6,7,8,9-hexahydro-1λ^4,10λ^4-[1,3,2]oxazaborinino[3,4-*a*]azepin-3(1*H*)-one (3c)

After Flash chromatography (EtOAc/n-hexane 1:3), the title compound was obtained as dark red crystals. Yield 0.03 g (1.6%, Method A). R_f = 0 (EtOAc/n-hexane 1:3); R_f = 0.69 (EtOAc); m.p. 203–207 °C; ^{1}H NMR(500 MHz, $CDCl_3$): δ = 14.97 (s, 1H; NH), 7.34–7.32 (m, 2H; Ar-H), 6.70–7.68 (m, 2H; Ar-H), 3.87–3.86 (m, 2H; CH_2), 3.41 (q, $^3J_{H,H}$ = 7 Hz, C*H*$_2$CH$_3$), 3.25–3.23 (m, 2H; CH_2), 1.90–1.87 (m, 2H; CH_2), 1.82–1.78 (m, 2H; CH_2), 1.75–1.70 ppm (m, 2H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.0, 161.9, 147.4, 129.6, 118.9, 117.0, 111.9, 48.2, 44.7, 29.9, 26.9 (br), 26.4, 23.1, 12.5 ppm; ^{11}B (160 MHz, $CDCl_3$): δ = –0.09 ppm (t, $^1J_{B,F}$ = 15.6 Hz); ^{19}F (376 MHz, $CDCl_3$): δ = –145.8 ppm (q, $^1J_{B,F}$ = 15.1 Hz); HRMS (MALDI): *m/z* cald for $C_{18}H_{26}BF_2N_4O_2$: 379.2117 [*M*+H]$^+$; found: 379.2119; cald for $C_{18}H_{25}BF_2N_4O_2$+K$^+$: 417.1676 [*M*+K]$^+$; found: 417.1679; cald for $C_{18}H_{25}BF_2N_4O_2$+Na$^+$: 401.1936 [*M*+Na]$^+$; found: 401.1939; cald for $C_{18}H_{25}BF_2N_4O_2$–F: 359.2055 [*M*–F]$^+$; found: 359.2057;

5-(Azepan-2-ylidene)-2,2-difluoro-3-(4-methoxyphenyl)-2,5-dihydro-6*H*-1,3λ^4,4,2λ^4-oxadiazaborinin-6-one (4a)

After Flash chromatography (EtOAc/n-hexane 1:3), the title compound was obtained as dark yellow crystals. Yield 0.15 g (8.9%, Method B, reflux 2 h). R_f = 0.14 (EtOAc/n-hexane 1:3); m.p. 233–236 °C; ^{1}H

NMR (500 MHz, $CDCl_3$): δ = 12.59 (s, 1H; NH), 7.70–7.68 (m, 2H; Ar-H), 7.94–7.92 (m, 2H; Ar-H), 3.84 (s, 3H; OCH_3), 3.79–3.77 (m, 2H; CH_2), 3.33–3.30 (m, 2H; CH_2), 1.98–1.93 (m, 2H; CH_2), 1.82–1.76 (m, 4H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.3, 160.5, 159.4, 138.3, 122.2 (br t, $J_{C,F}$ = 2.2 Hz), 118.4, 114.2, 55.6, 46.6, 30.1, 27.3, 26.6, 23.1 ppm; ^{11}B NMR (160 MHz, $CDCl_3$): δ = –0.20 ppm (t, $^1J_{B,F}$ = 18.1 Hz); HRMS (MALDI): *m/z* cald for $C_{15}H_{19}BF_2N_3O_3$: 338.1488 $[M+H]^+$; found: 338.1489; cald for $C_{15}H_{18}BF_2N_3O_3+K^+$: 376.1046 $[M+K]^+$; found: 376.1051; cald for $C_{15}H_{18}BF_2N_3O_3+Na^+$: 360.1307 $[M+Na]^+$; found: 360.1311; cald for $C_{15}H_{18}BF_2N_3O_3$–F: 318.1425 $[M–F]^+$; found: 318.1426; elemental analysis calcd (%) for $C_{15}H_{18}BF_2N_3O_3$: C 53.44, H 5.38, N 12.46; found: C 53.69, H 5.45, N 12.37.

5-(Azepan-2-ylidene)-2,2-difluoro-3-(4-methylphenyl)-2,5-dihydro-6*H*-1, 3λ^4,4,2λ^4-oxadiazaborinin-6-one (4b)

After Flash chromatography ($CHCl_3$ → EtOAc), the title compound was obtained as dark yellow crystals. Yield 0.04 g (2.5%, Method A), yield 0.08 g (5%, Method B, reflux 21 h). R_f = 0 ($CHCl_3$); R_f = 0.45 (EtOAc); m.p. 234–238 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 12.64 (s, 1H; NH), 7.63–7.61 (m, 2H; Ar-H), 7.22–7.21 (m, 2H; Ar-H), 3.81–3.78 (m, 2H; CH_2), 3.33–3.31 (m, 2H; CH_2), 2.37 (s, 3H; CH_3), 1.97–1.93 (m, 2H; CH_2), 1.82–1.76 ppm (m, 2H; 2 × CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.7, 160.4, 142.4, 138.0, 129.6, 120.7 (br t, $J_{C,F}$ = 2.2 Hz), 118.8, 46.7, 30.1, 27.3, 26.5, 23.0, 21.1 ppm; ^{11}B NMR (160 MHz, $CDCl_3$): δ = –0.18 ppm (t, $^1J_{B,F}$ = 18 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –137.3 (q, $^1J_{B,F}$ = 18 Hz) ppm; HRMS (MALDI): *m/z* cald for $C_{15}H_{19}BF_2N_3O_2$: 322.1538 $[M+H]^+$; found: 322.1539; cald for $C_{15}H_{18}BF_2N_3O_2+K^+$: 360.1097 $[M+K]^+$; found: 360.1099; cald for $C_{15}H_{18}BF_2N_3O_2+Na^+$: 344.1358 $[M+Na]^+$; found: 344.1359; cald for $C_{15}H_{18}BF_2N_3O_2$–F: 302.1476 $[M–F]^+$; found: 302.1476; elemental analysis calcd (%) for $C_{15}H_{18}BF_2N_3O_2$: C 56.10, H 5.65, N 13.09; found: C 56.31, H 5.67, N 13.17.

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3. NMR Spectra

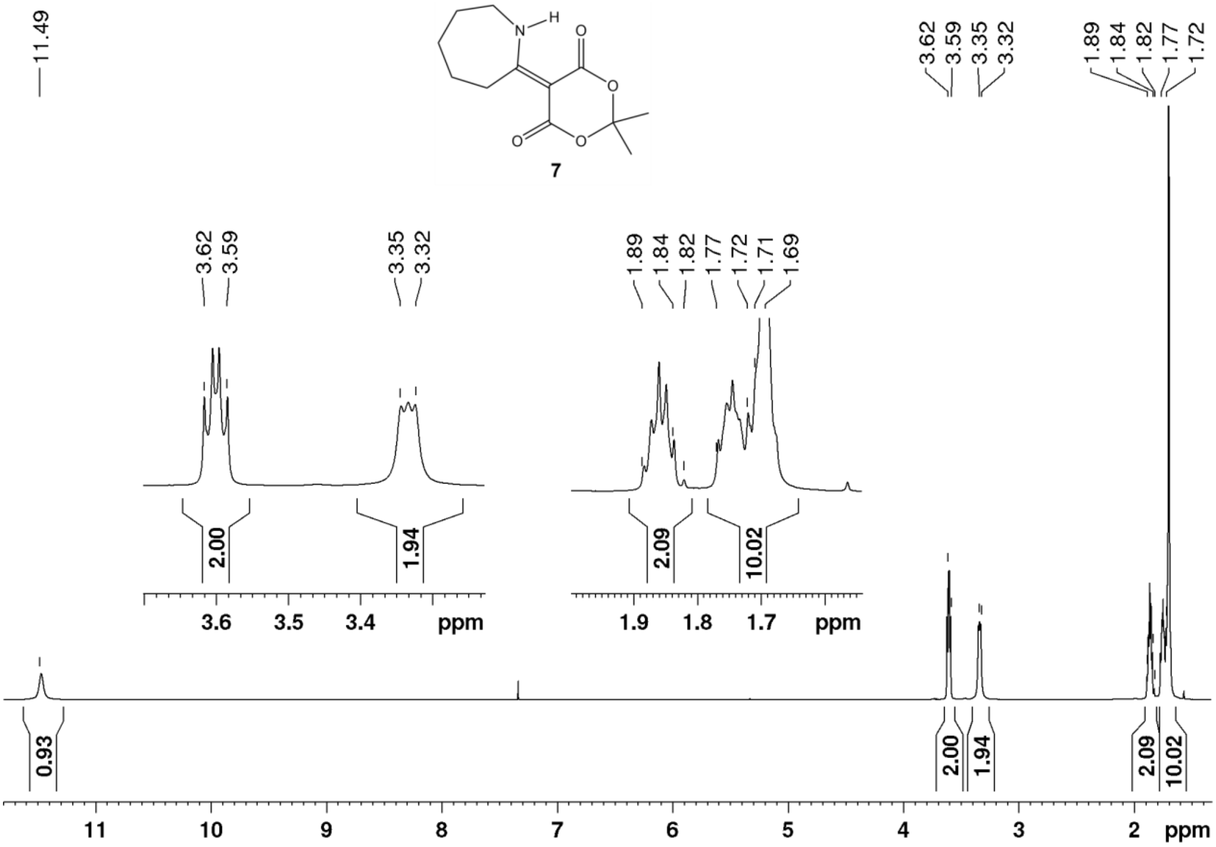


Figure S1. 500 MHz ^{1}H-NMR spectrum of compound **7** in $CDCl_3$.

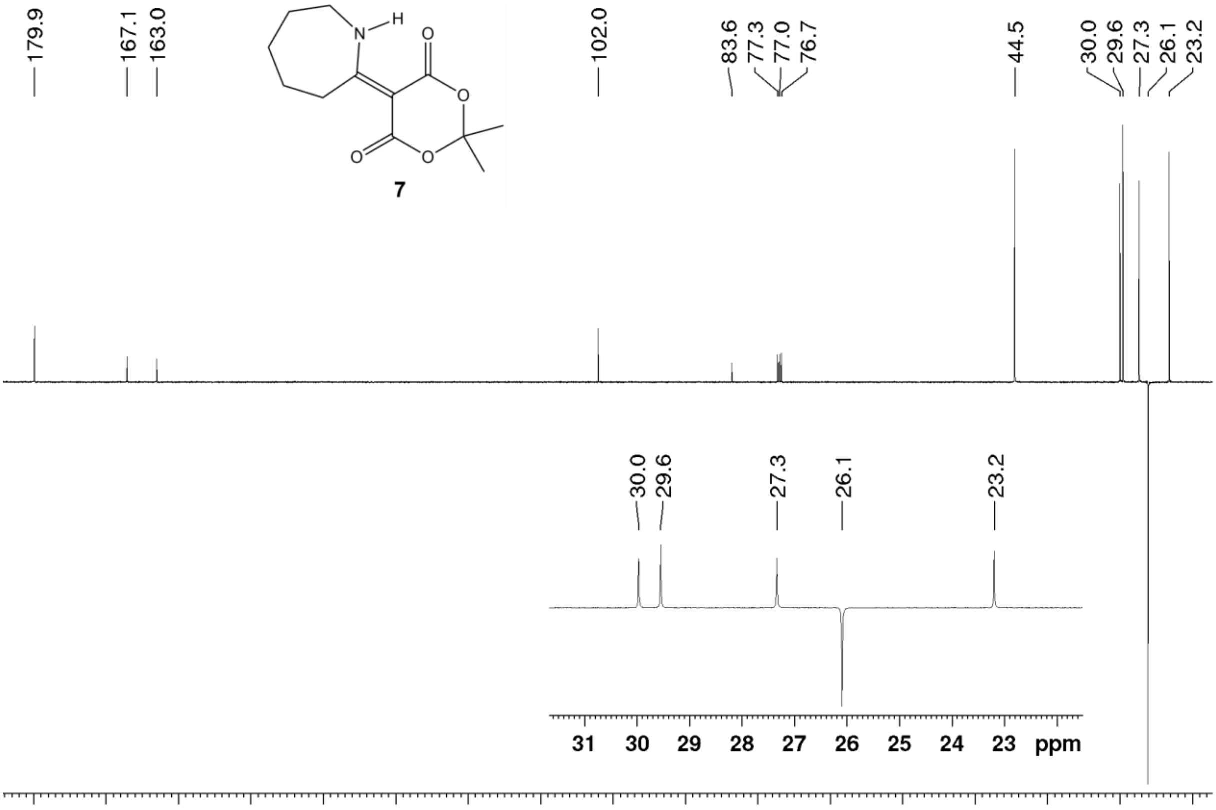


Figure S2. 125 MHz ^{13}C-NMR spectrum of compound **7** in $CDCl_3$.

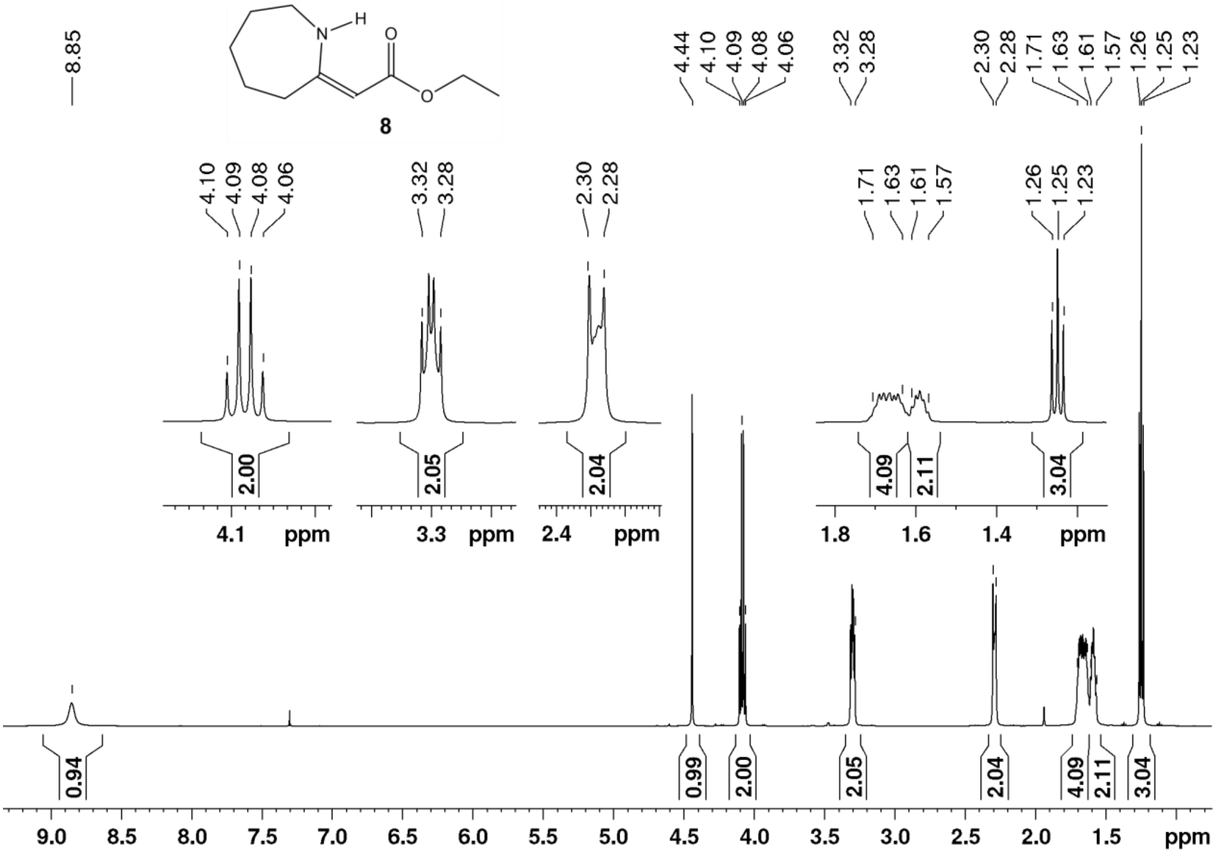


Figure S3. 500 MHz ^{1}H-NMR spectrum of compound **8** in CDCl$_3$.

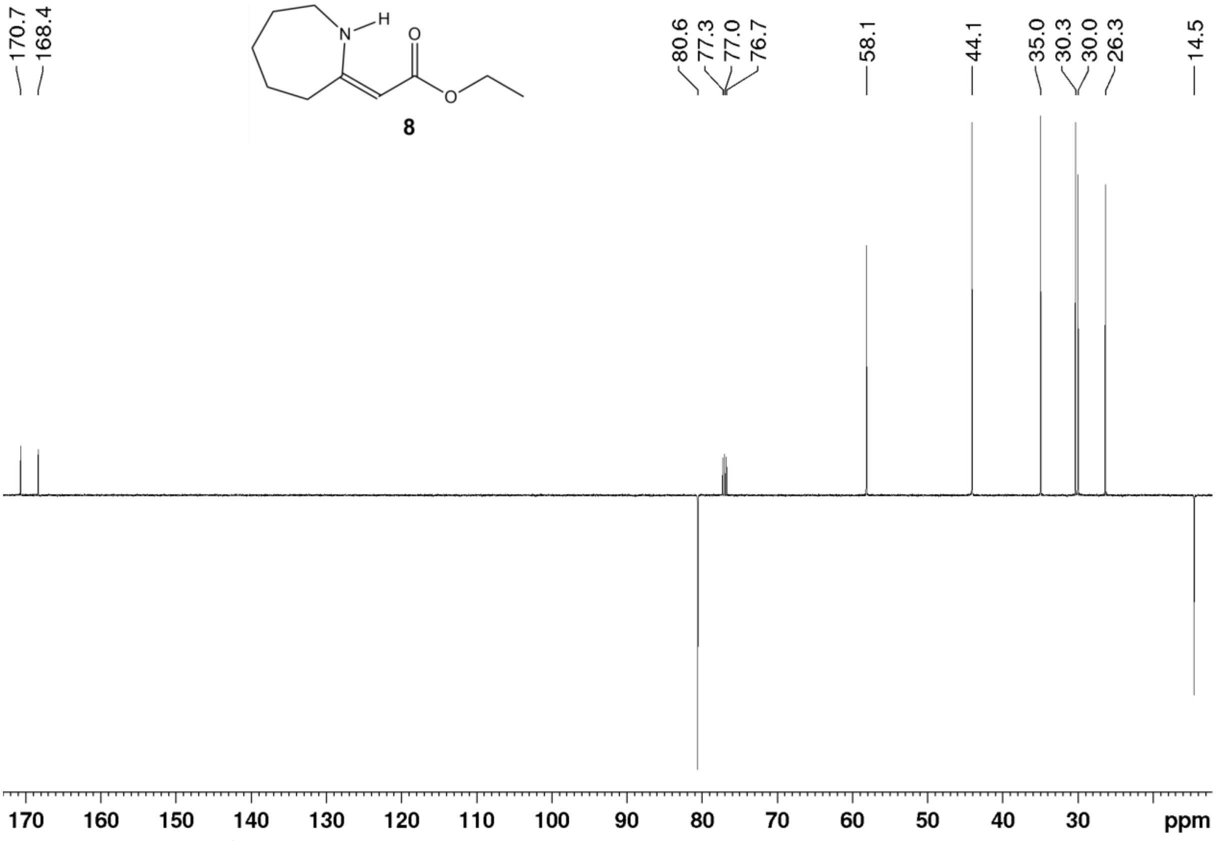


Figure S4. 125 MHz ^{13}C-APT NMR spectrum of compound **8** in CDCl$_3$.

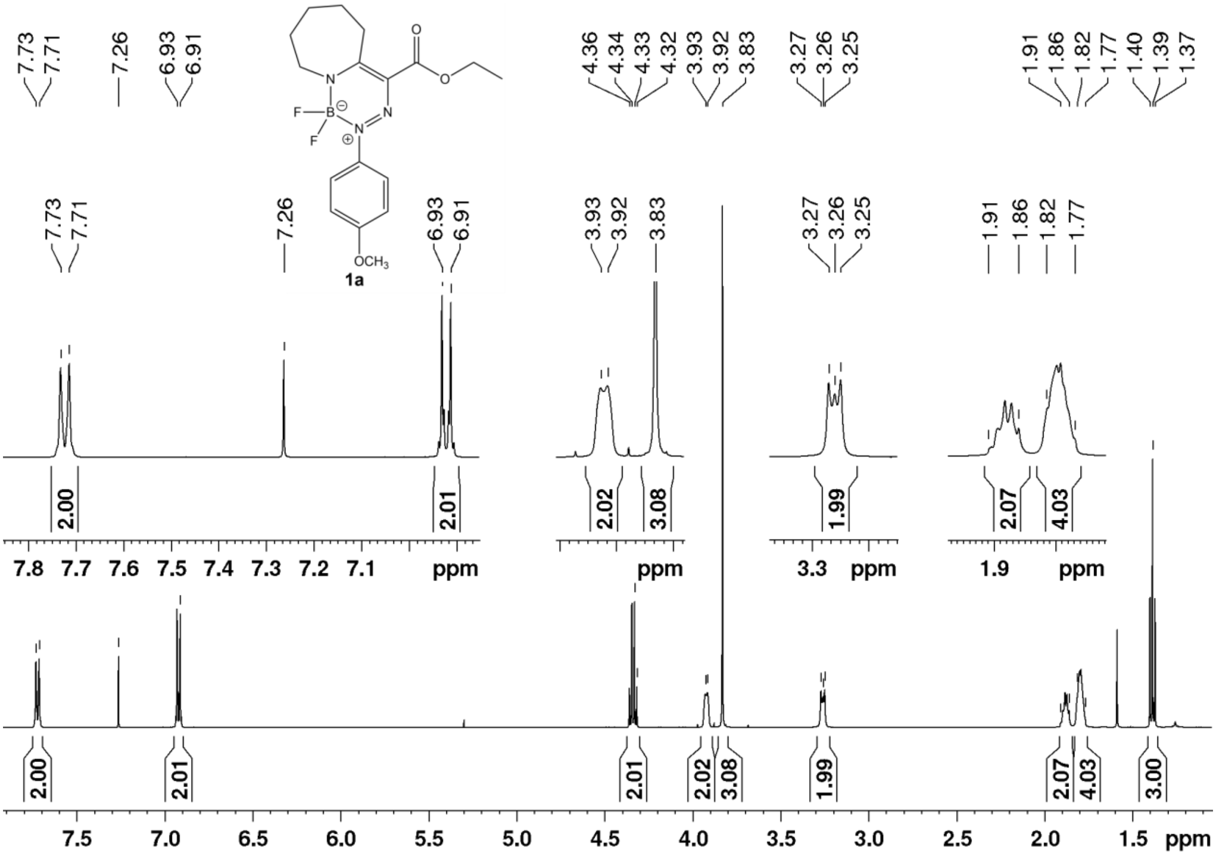


Figure S5. 500 MHz ^{1}H-NMR spectrum of compound **1a** in $CDCl_3$.

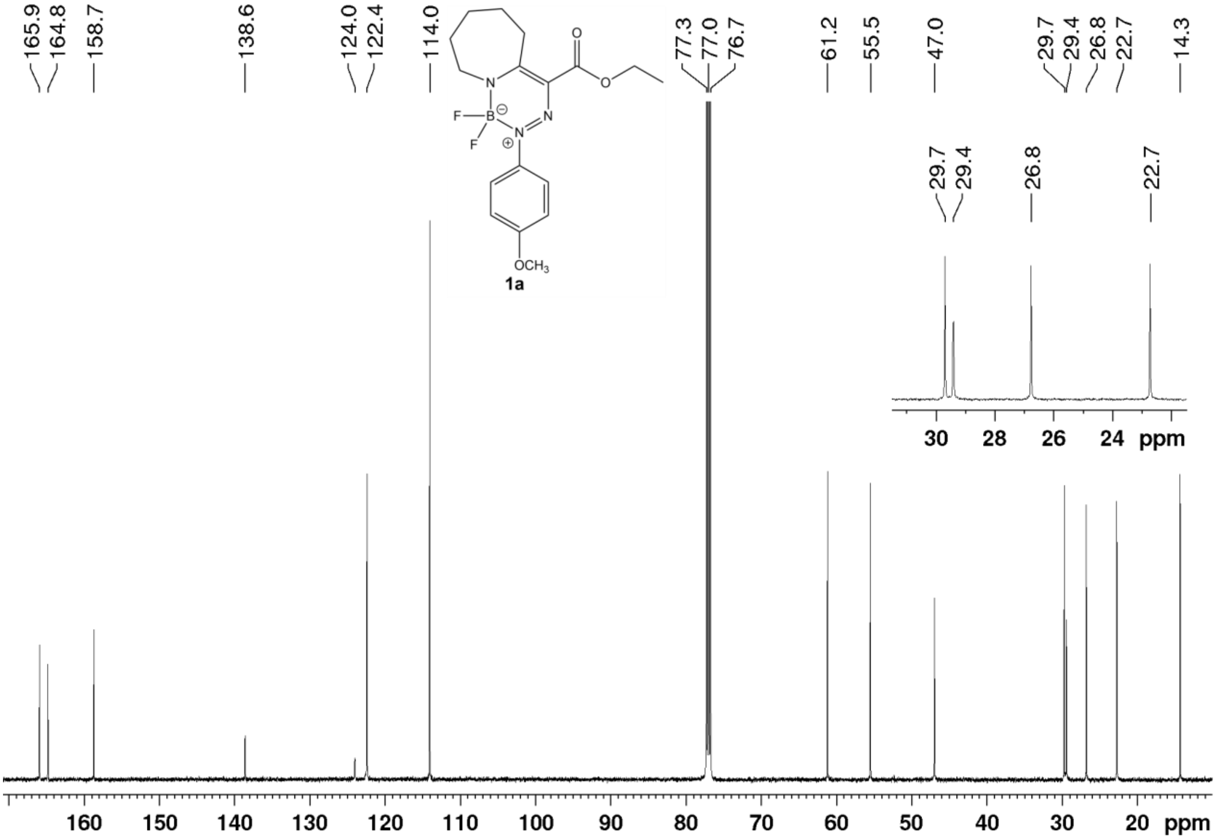
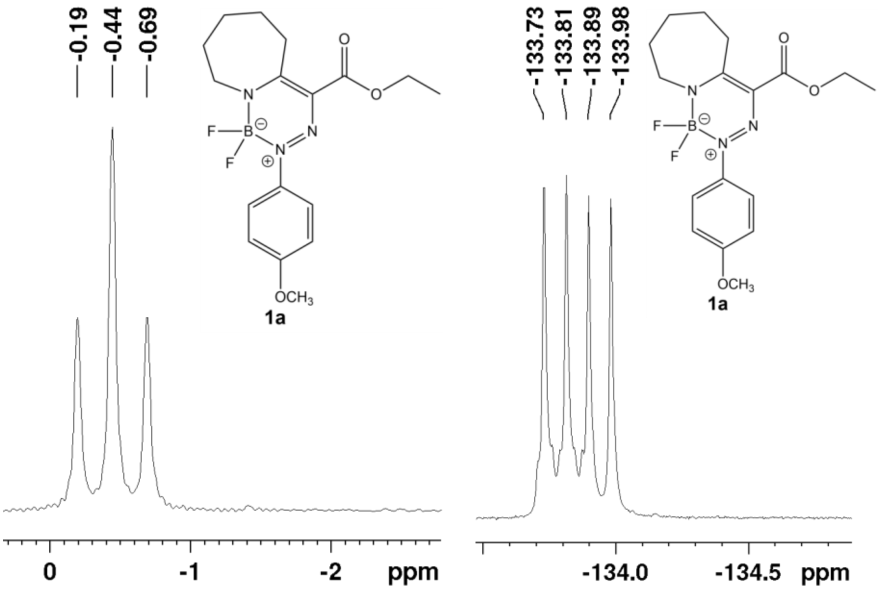


Figure S6. 125 MHz ^{13}C -MR spectrum of compound **1a** in $CDCl_3$.



a) b)

Figure S7. a) 128 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **1a** in CDCl$_3$.

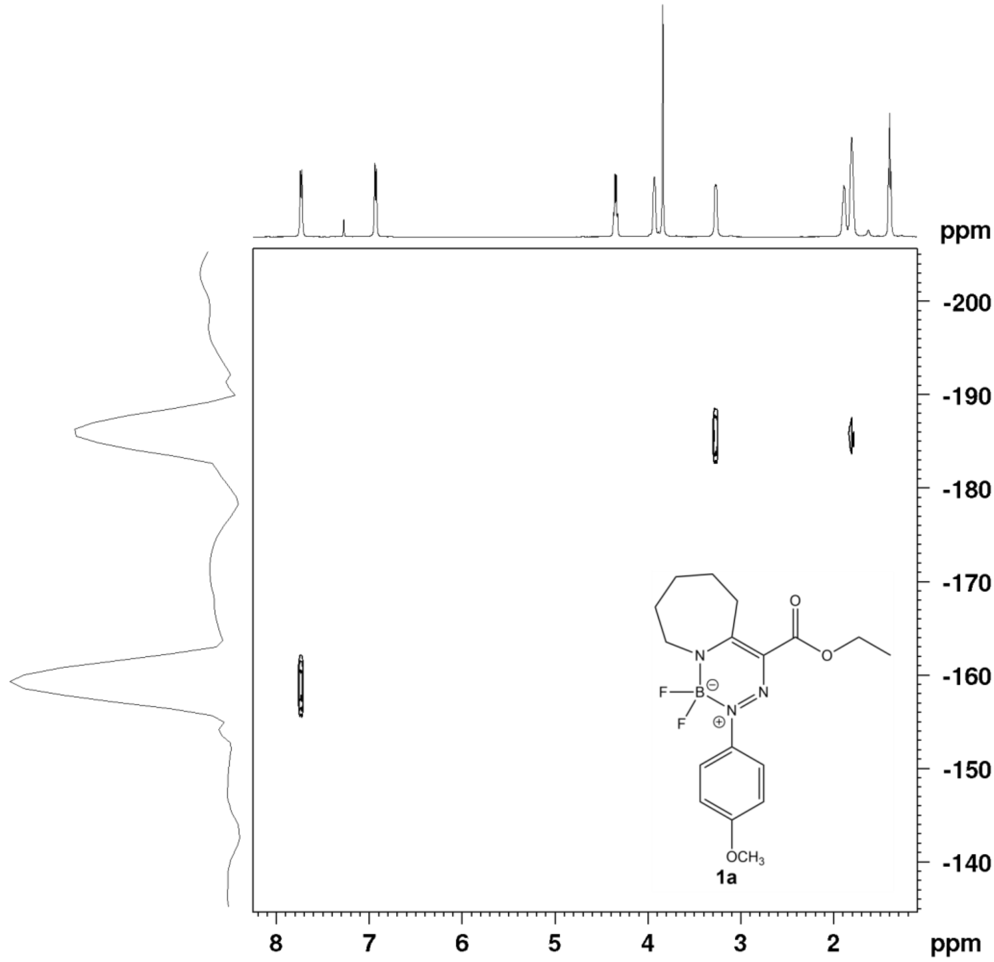


Figure S8. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **1a** in CDCl$_3$.

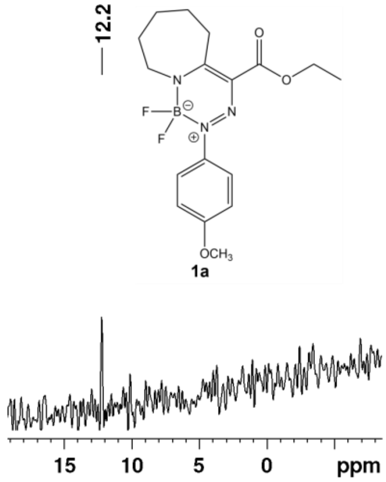


Figure S9. 50 MHz ^{15}N-NMR spectrum of compound **1a** in CDCl$_3$.

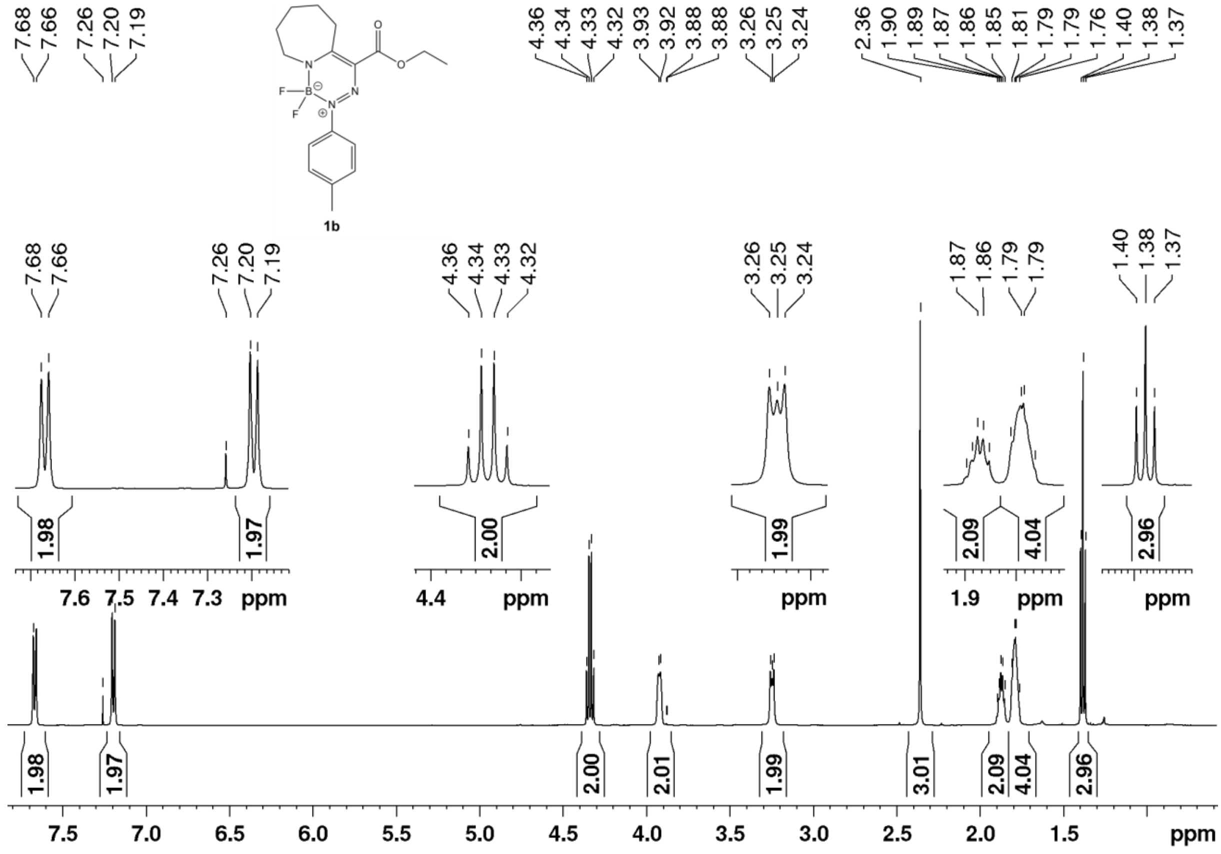


Figure S10. 500 MHz ^{1}H-NMR spectrum of compound **1b** in CDCl$_3$.

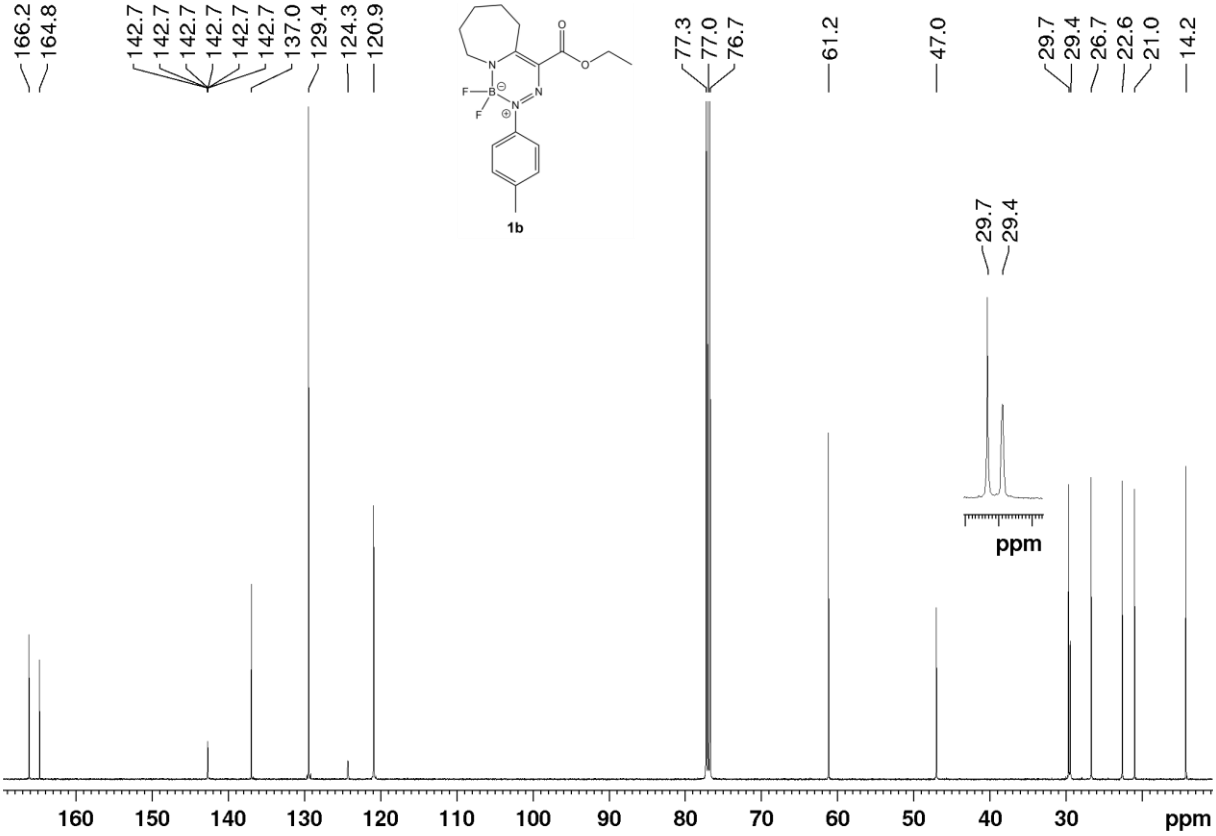


Figure S11. 125 MHz ^{13}C-NMR spectrum of compound **1b** in CDCl$_3$.

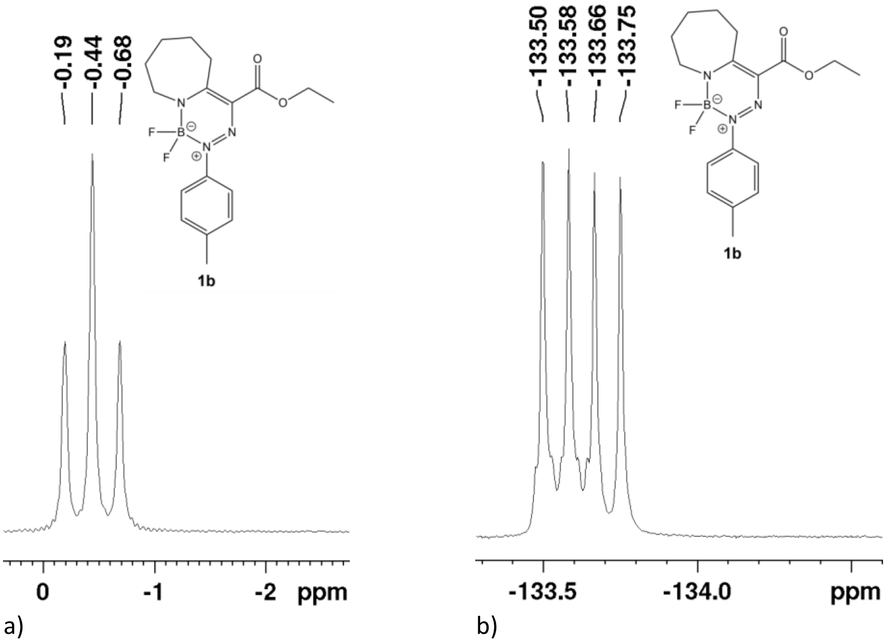


Figure S12. a) 128 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **1b** in CDCl$_3$.

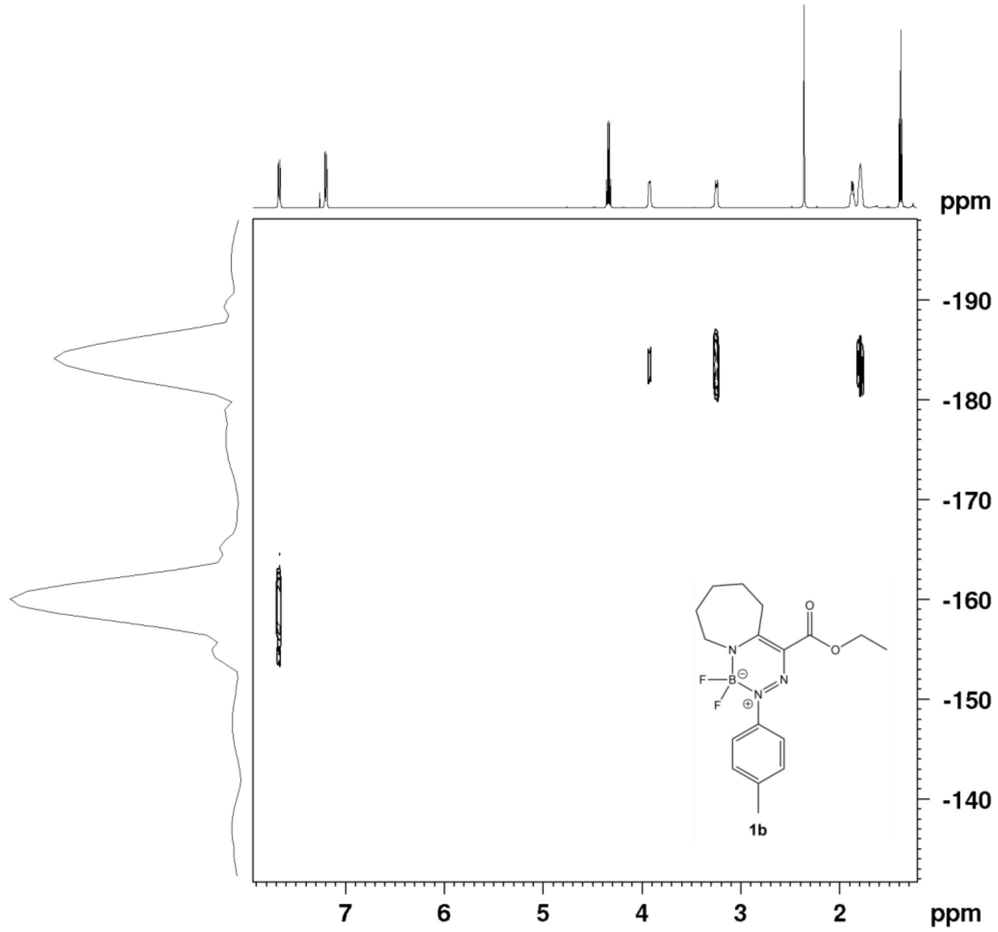


Figure S13. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **1b** in CDCl$_3$.

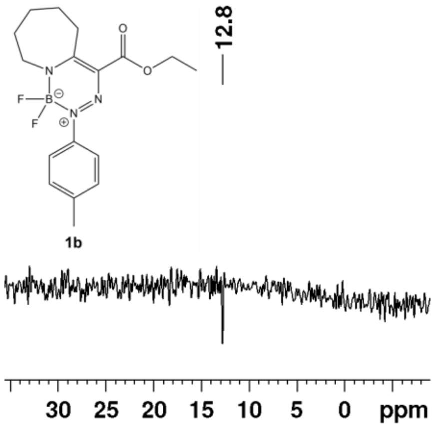


Figure S14. 50 MHz ^{15}N-NMR spectrum of compound **1b** in CDCl$_3$.

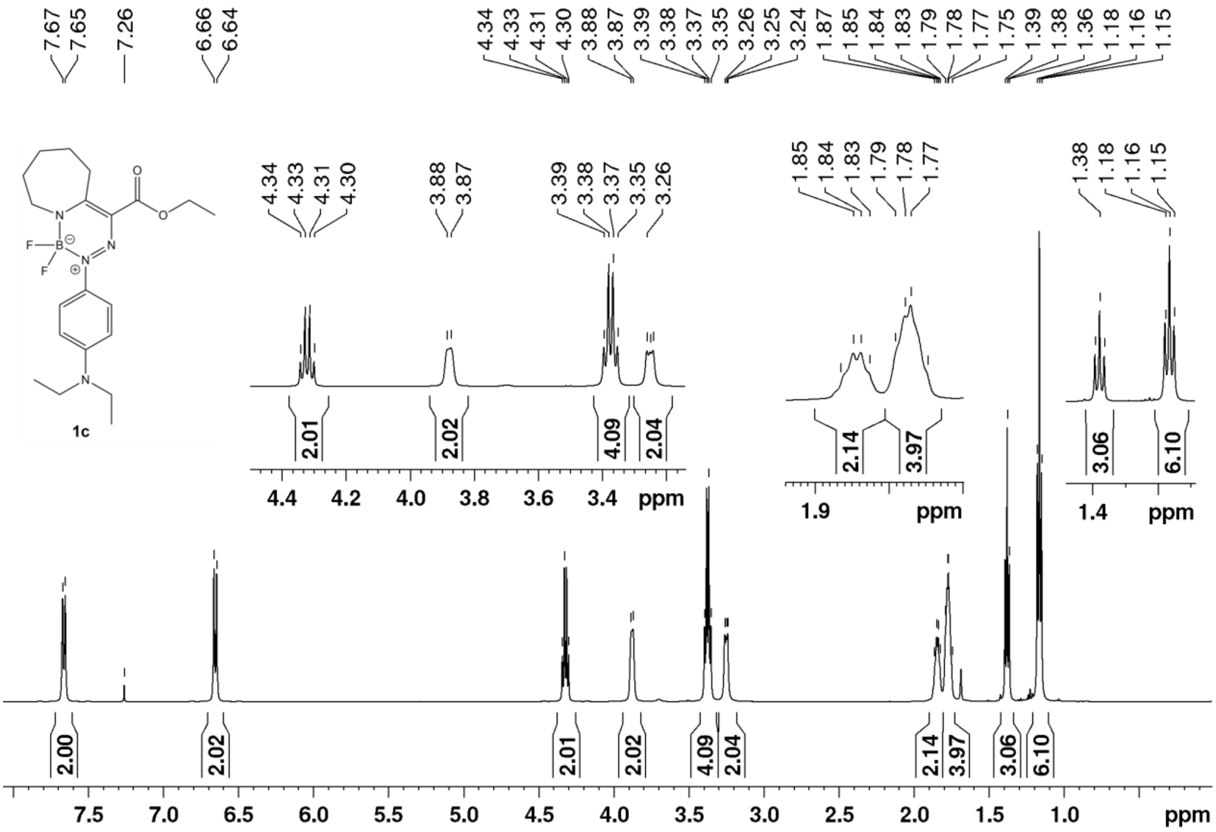


Figure S15. 500 MHz ^{1}H-NMR spectrum of compound **1c** in CDCl$_3$.

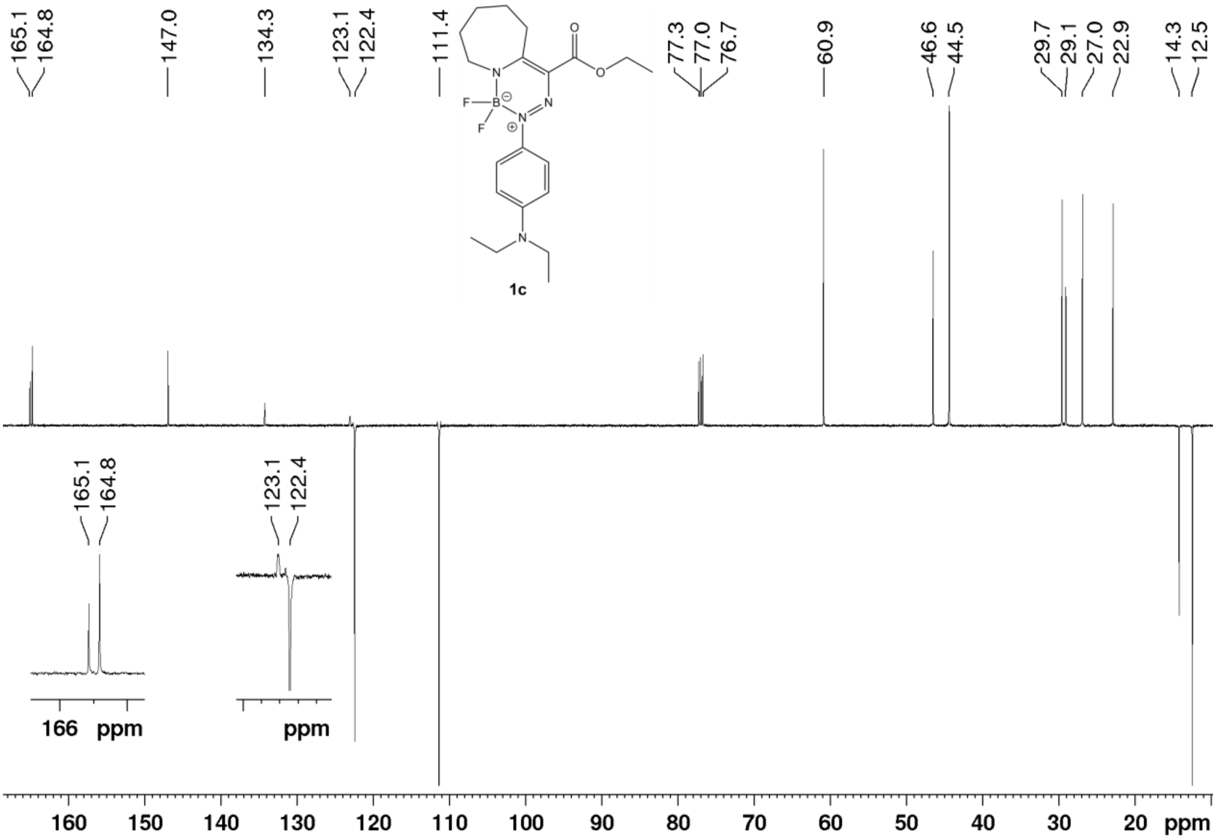
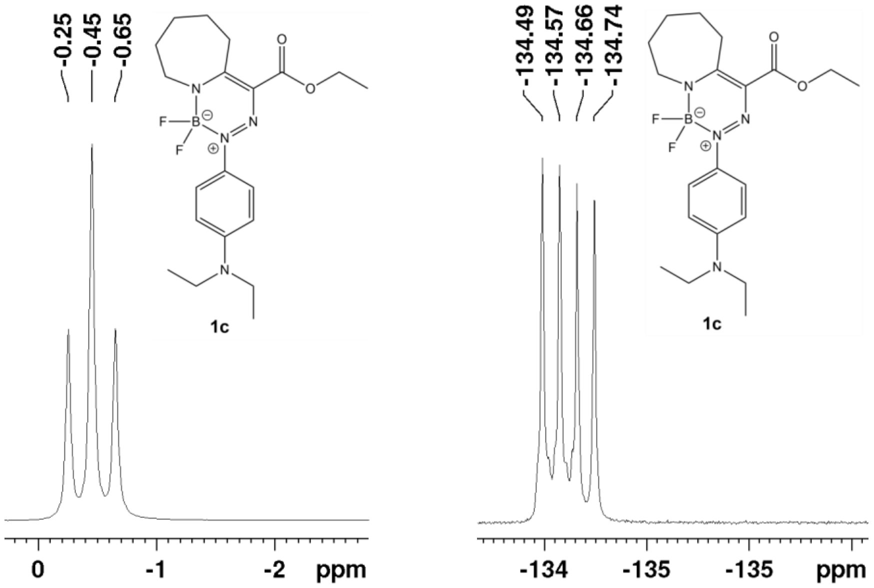


Figure S16. 125 MHz ^{13}C-APT NMR spectrum of compound **1c** in CDCl$_3$.



a)   b)

Figure S17. a) 160 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **1c** in $CDCl_3$.

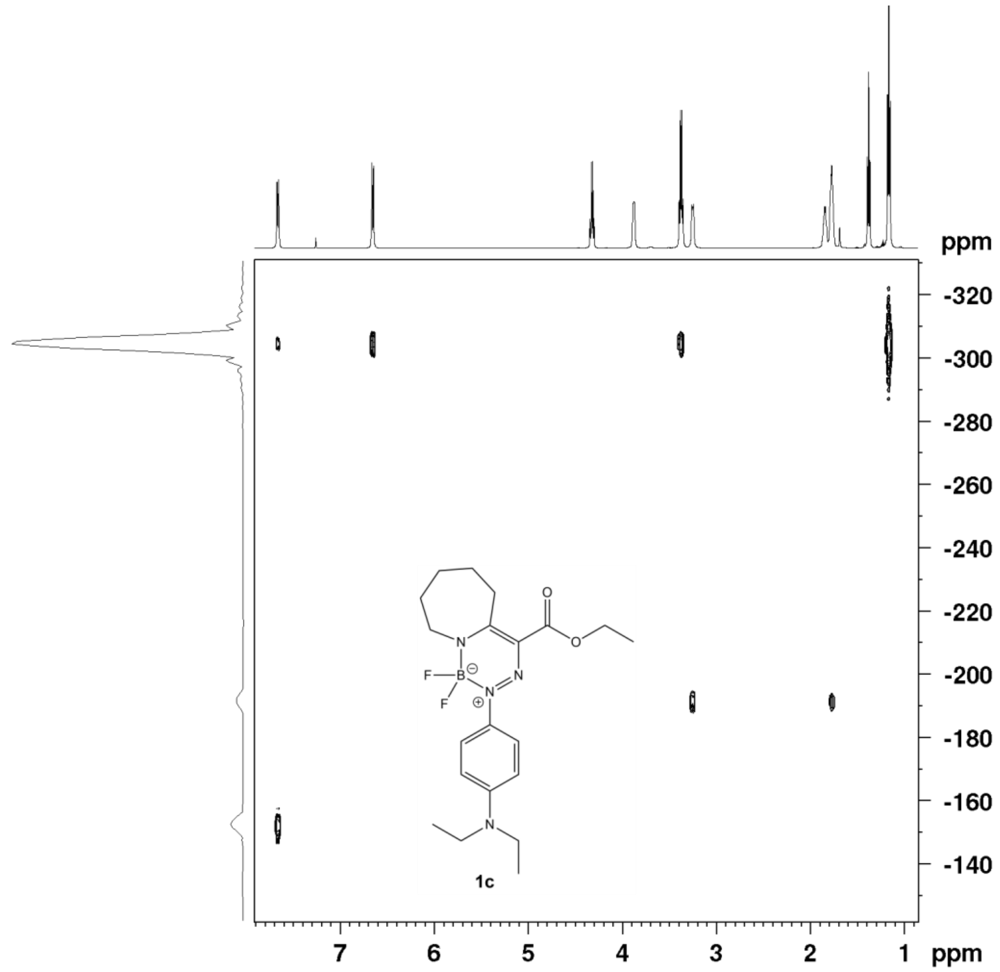


Figure S18. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **1c** in $CDCl_3$.

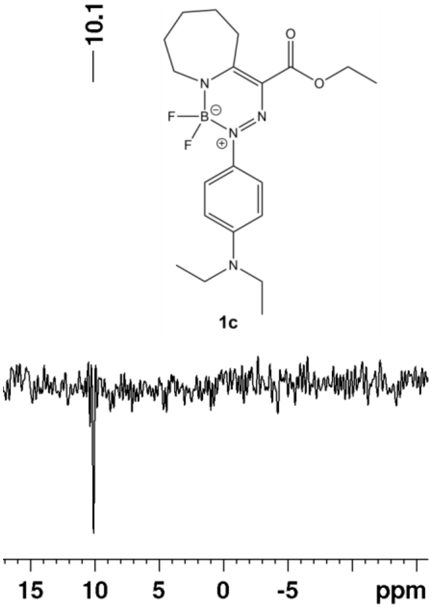


Figure S19. 50 MHz ^{15}N-NMR spectrum of compound **1c** in CDCl$_3$.

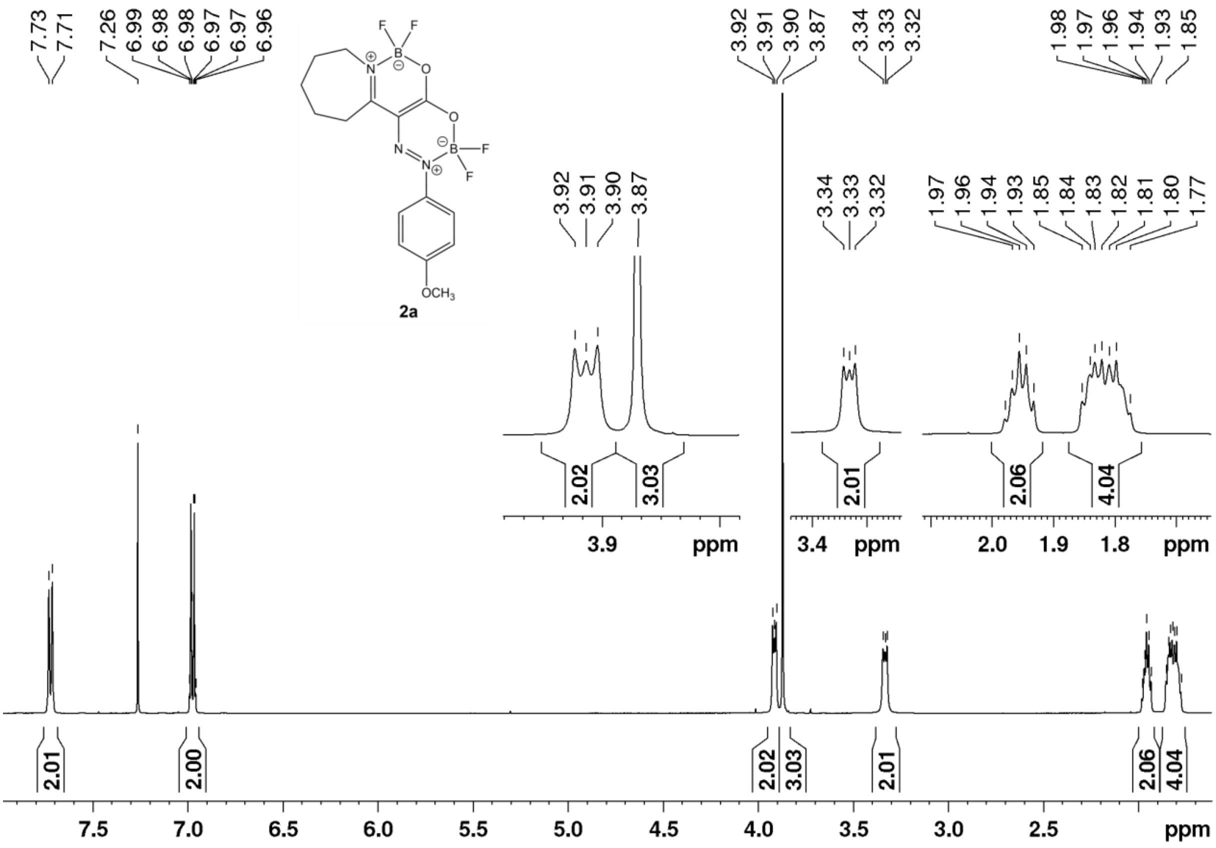


Figure S20. 500 MHz ^{1}H-NMR spectrum of compound **2a** in CDCl$_3$.

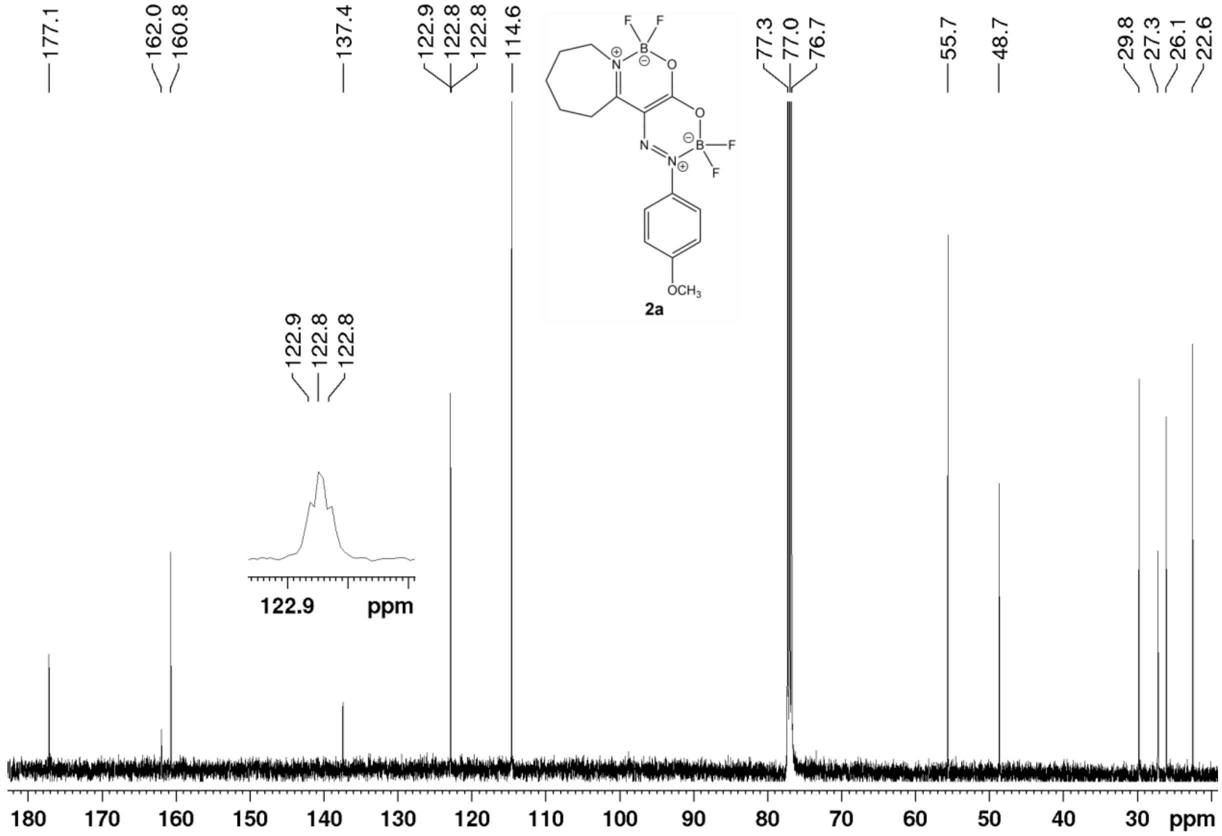


Figure S21. 125 MHz ^{13}C-NMR spectrum of compound **2a** in CDCl$_3$.

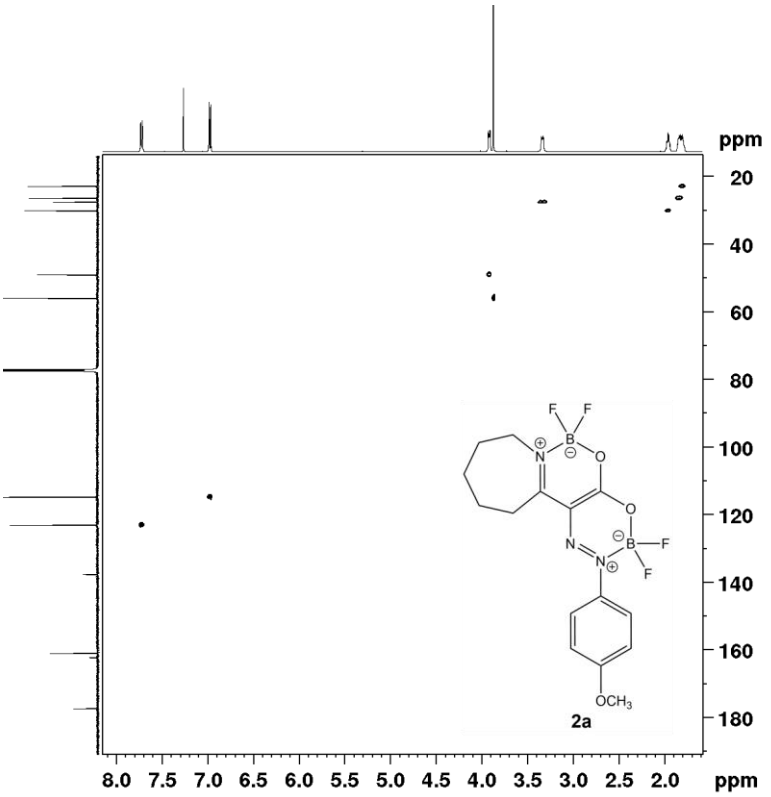


Figure S22. 500 MHz ^{1}H–^{13}C NMR HSQC spectrum of compound **2a** in CDCl$_3$.

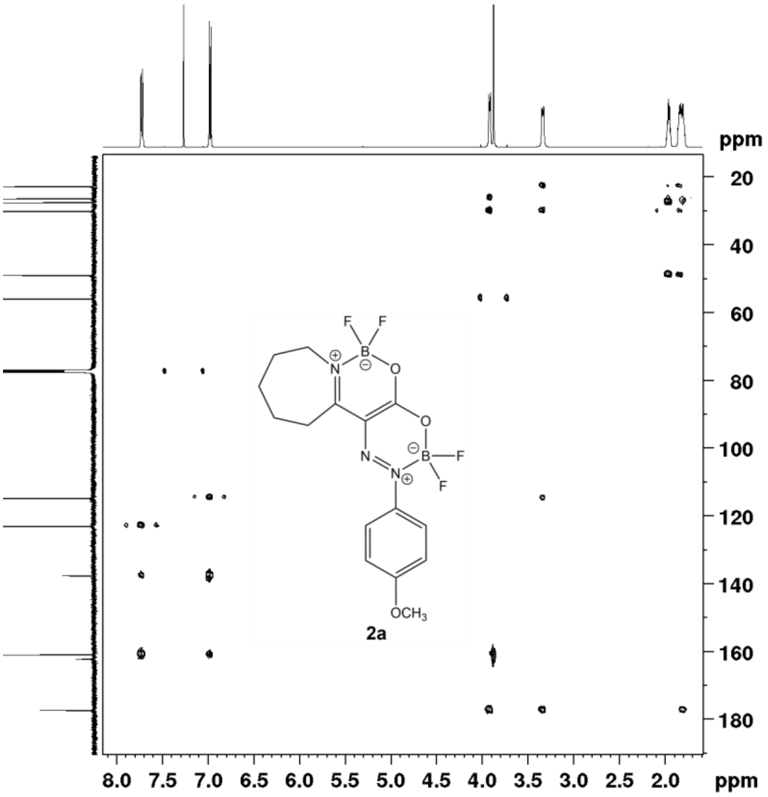
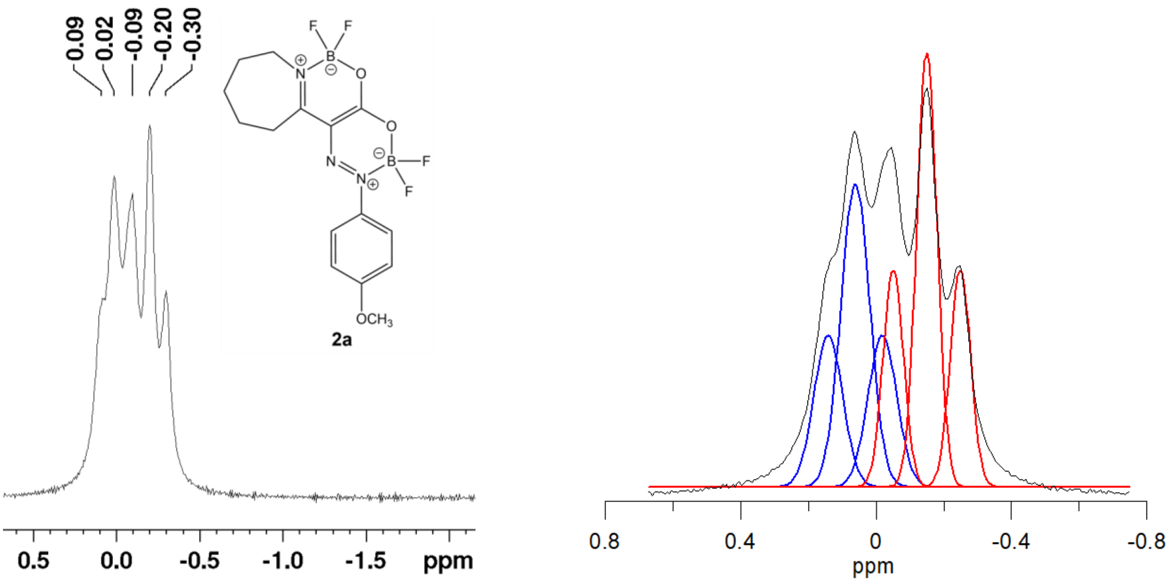


Figure S23. 500 MHz ^{1}H–^{13}C NMR HMBC spectrum of compound **2a** in CDCl$_3$.



a) b)

Figure S24. a) 160 MHz ^{11}B-NMR spectrum of compound **2a** in Acetone-*d*$_6$. b) Deconvolution of ^{11}B-NMR spectrum of compound **2a**.

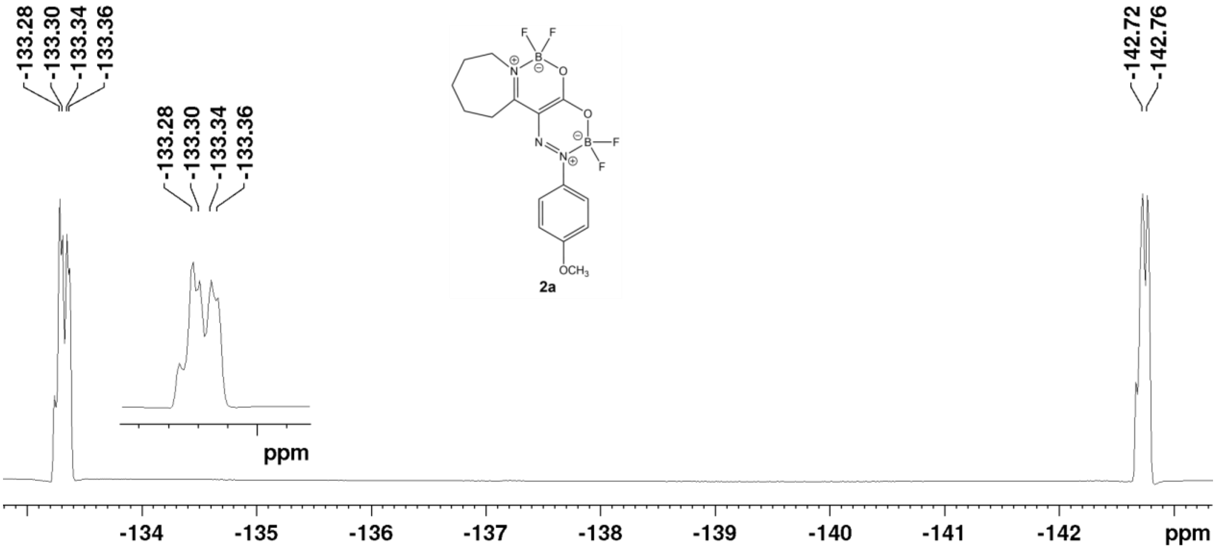


Figure S25. 376 MHz ^{19}F-NMR of compound **2a** in Acetone-d_6.

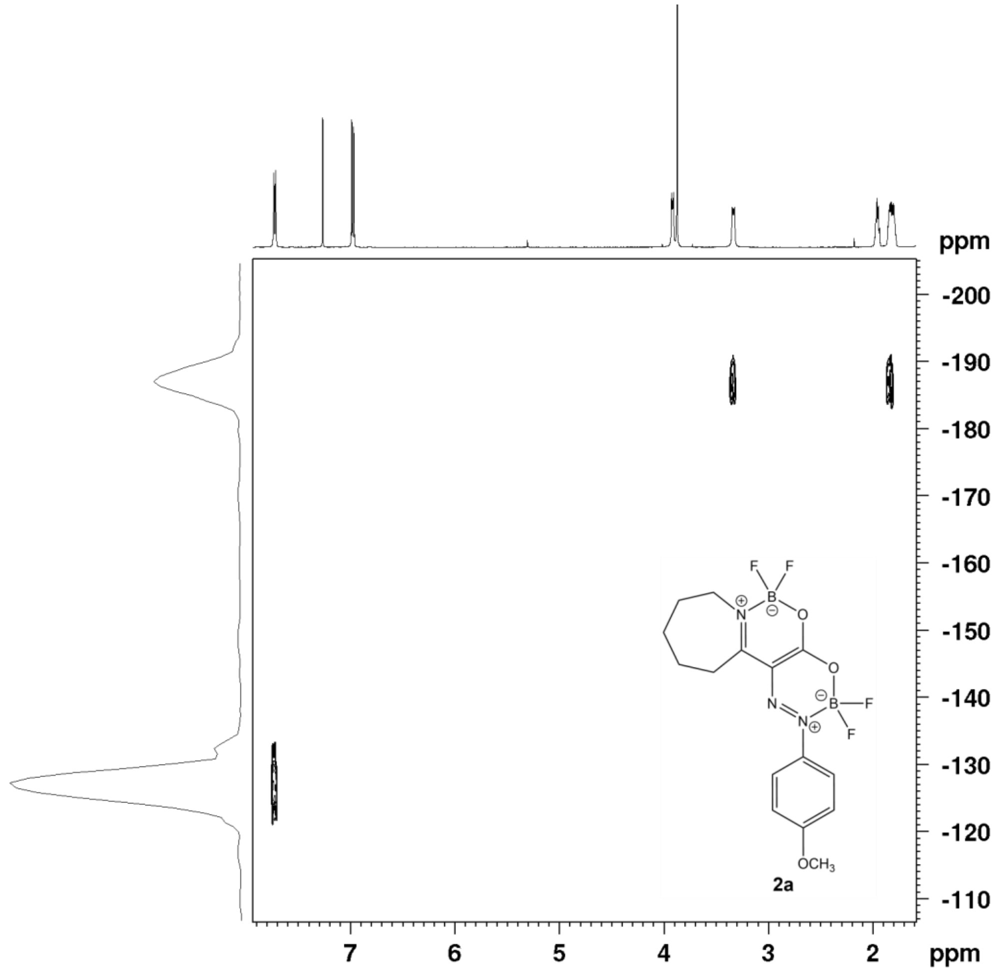


Figure S26. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **2a** in CDCl$_3$.

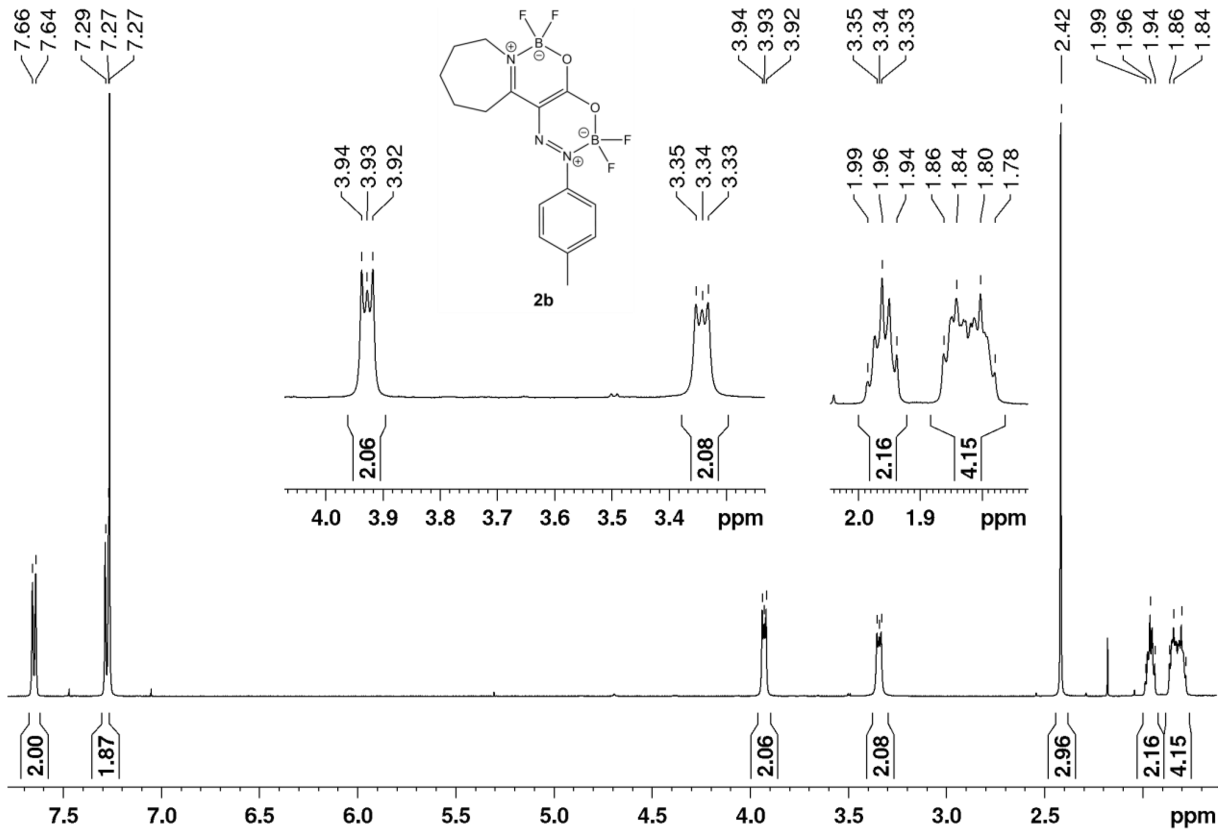


Figure S27. 500 MHz ^{1}H-NMR spectrum of compound **2b** in CDCl$_3$.

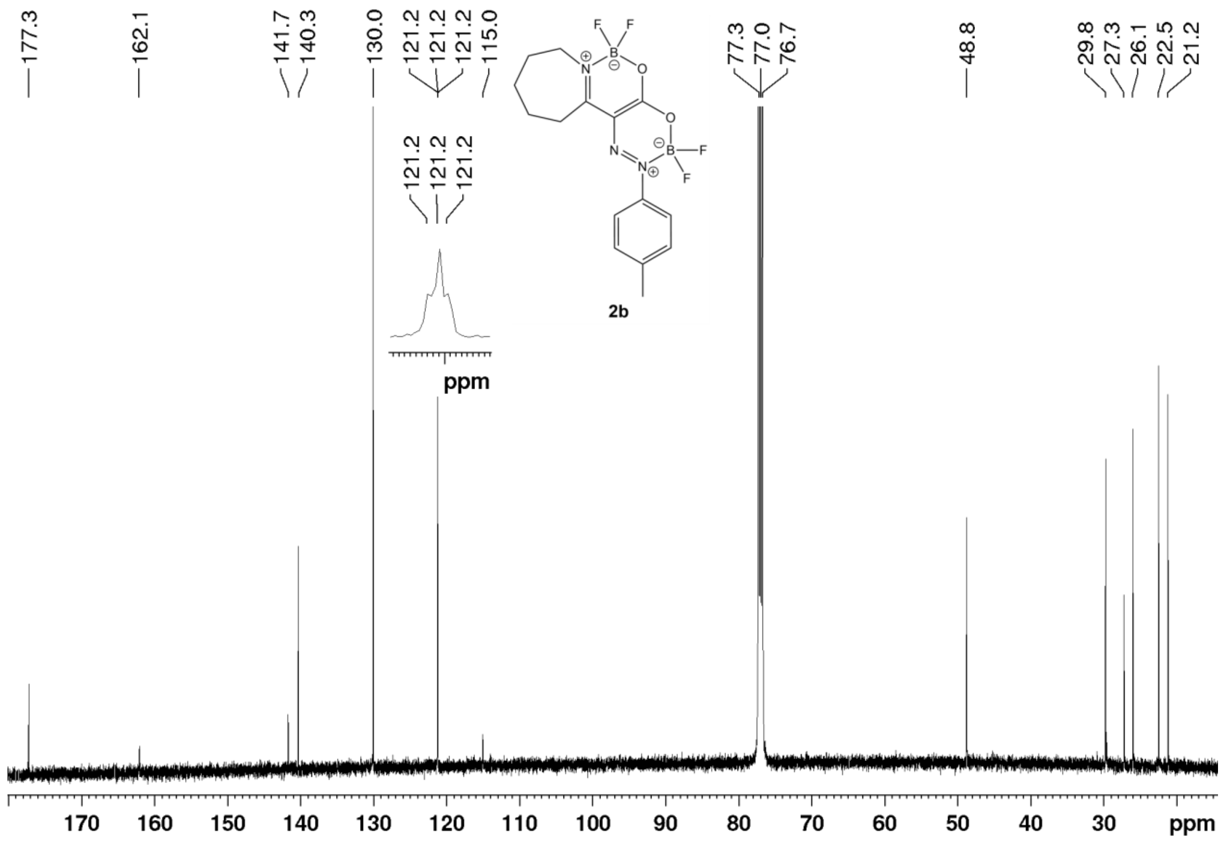
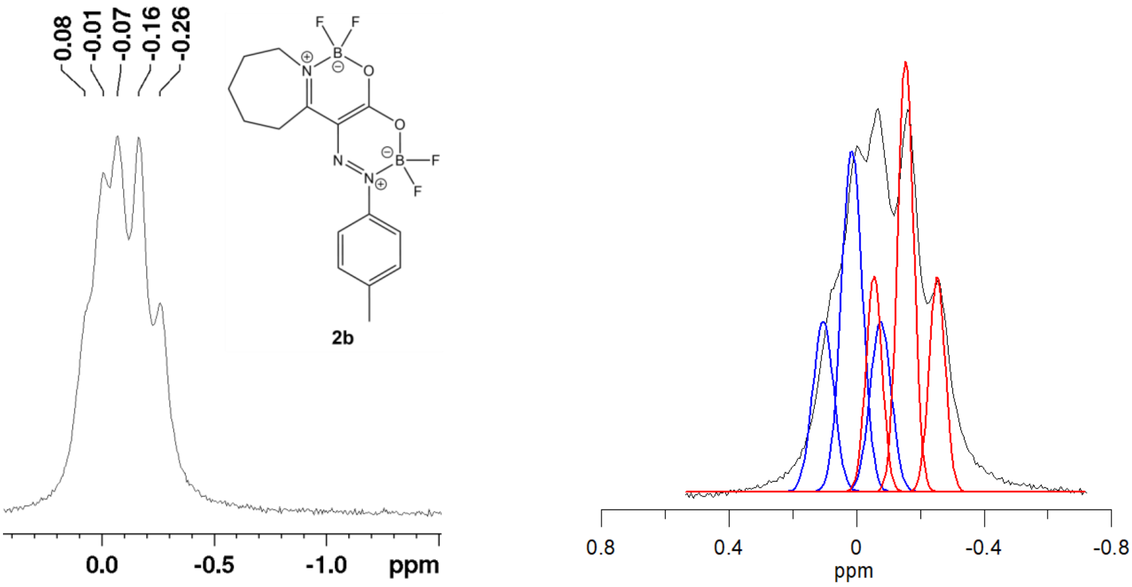


Figure S28. 125 MHz ^{13}C-NMR spectrum of compound **2b** in CDCl$_3$.



a)

b)

Figure S29. a) 160 MHz ^{11}B-NMR spectrum of compound **2b** in Acetone-*d*$_6$. b) Deconvolution of ^{11}B-NMR spectrum of compound **2b**.

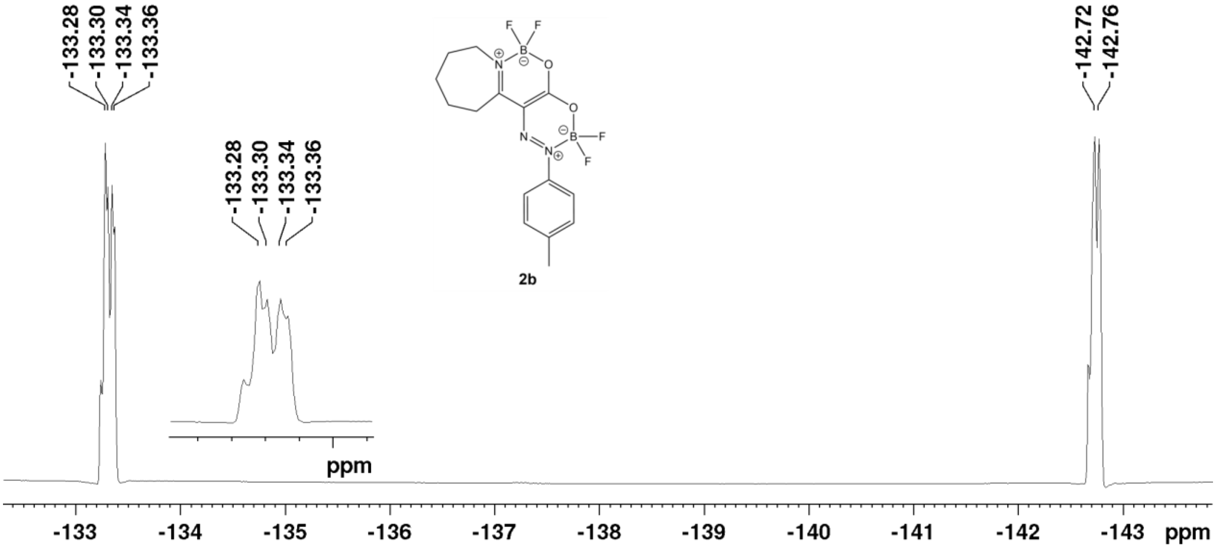


Figure S30. 376 MHz ^{19}F-NMR of compound **2b** in Acetone-*d*$_6$.

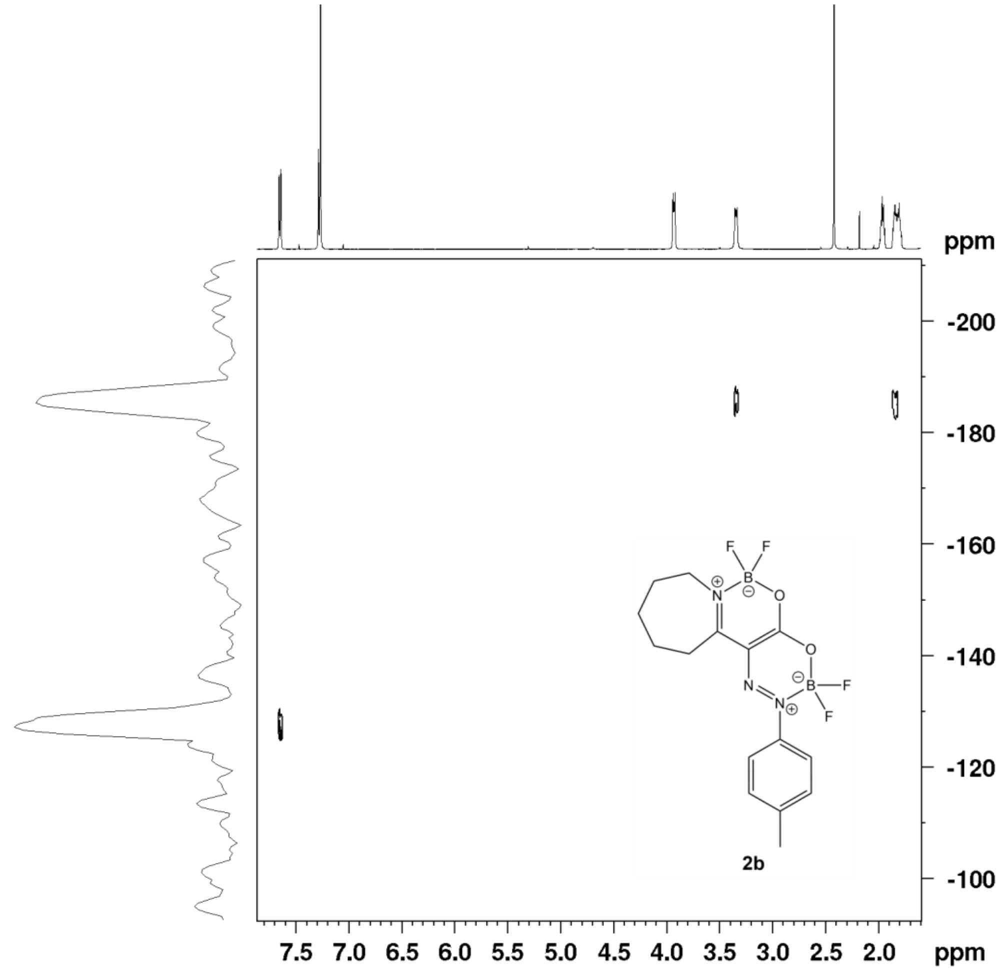


Figure S31. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **2b** in $CDCl_3$.

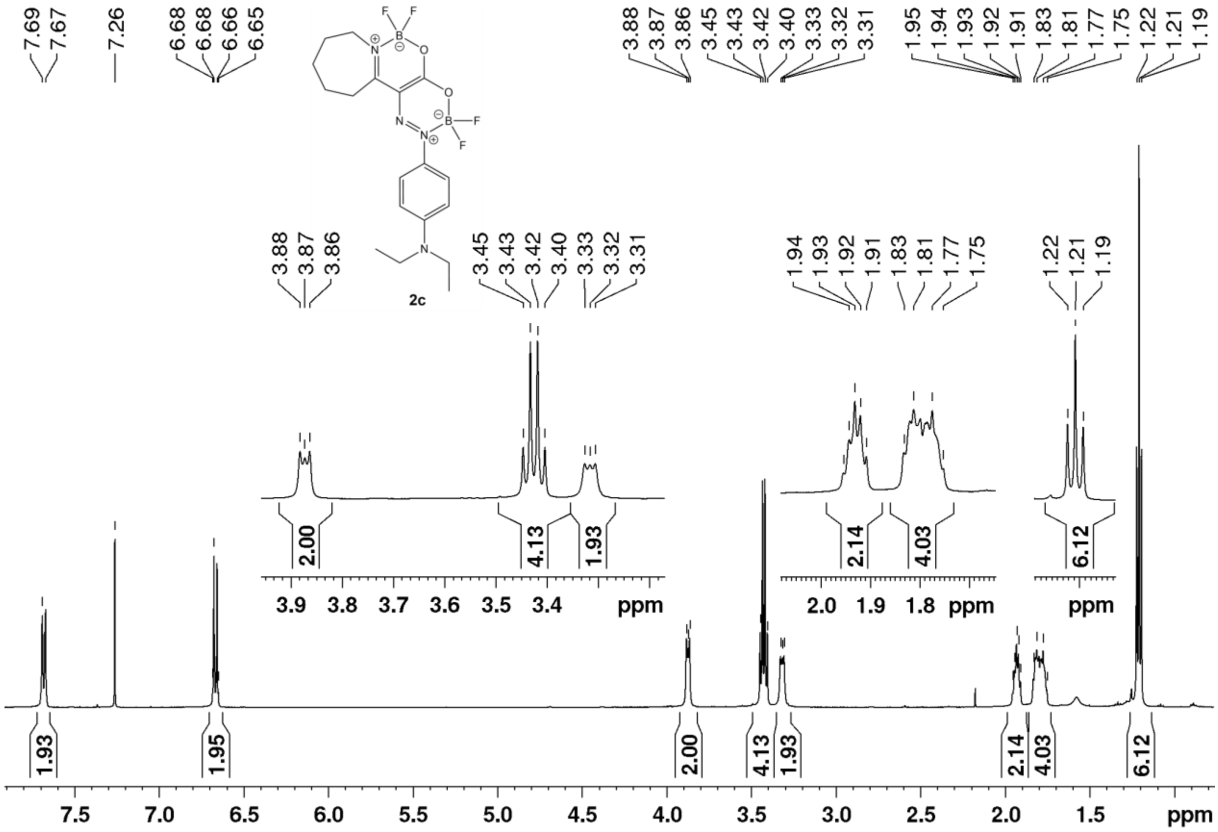


Figure S32. 500 MHz ^{1}H-NMR spectrum of compound **2c** in CDCl$_3$.

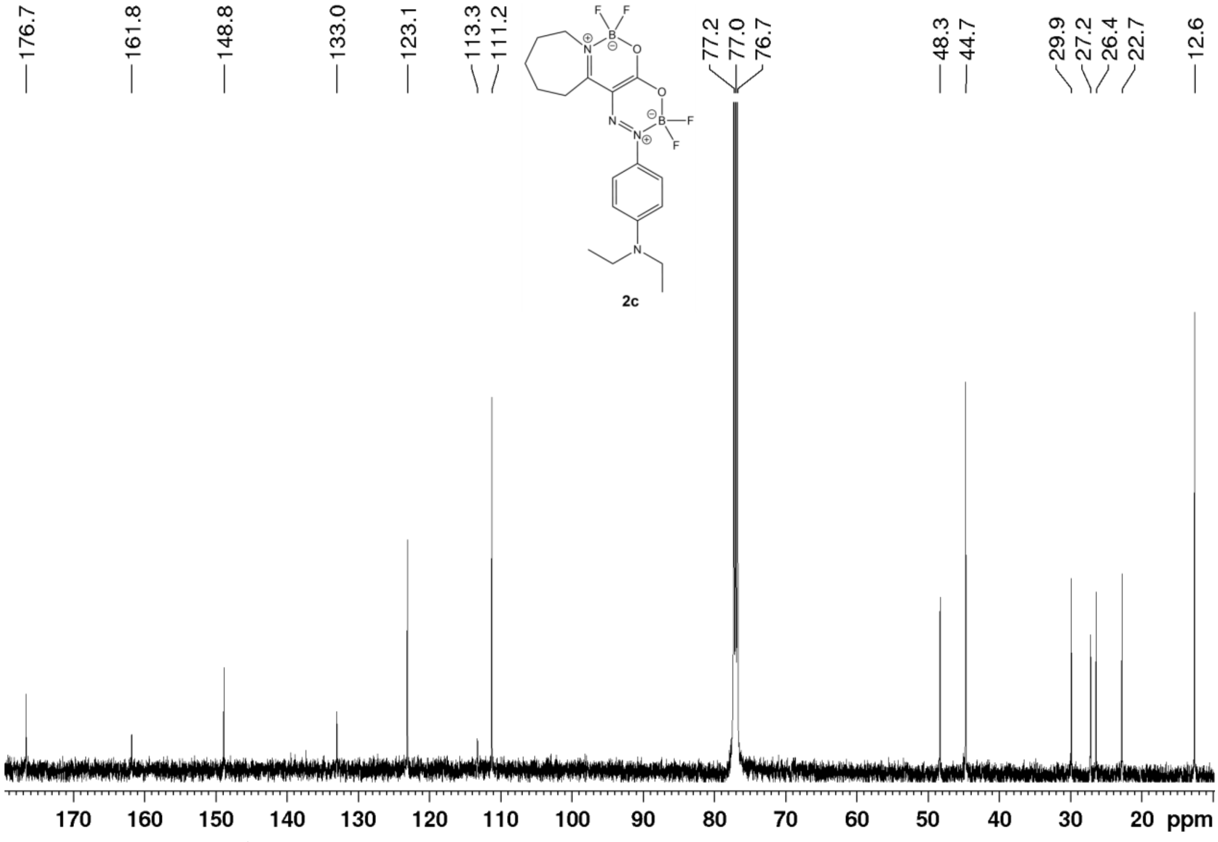


Figure S33. 125 MHz ^{13}C-NMR spectrum of compound **2c** in CDCl$_3$.

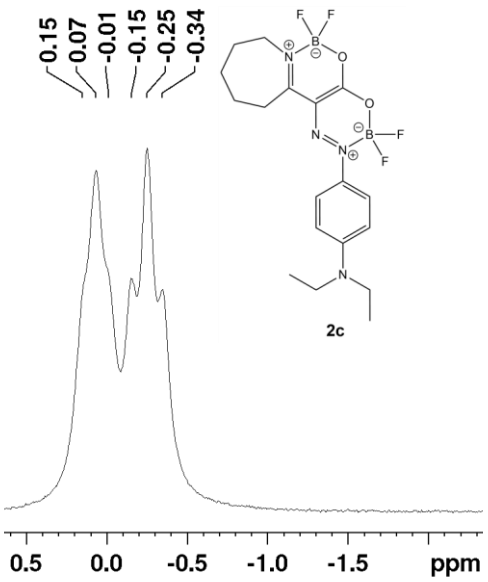


Figure S34. a) 160 MHz ^{11}B-NMR spectrum of compound **2c** in Acetone-*d*$_6$.

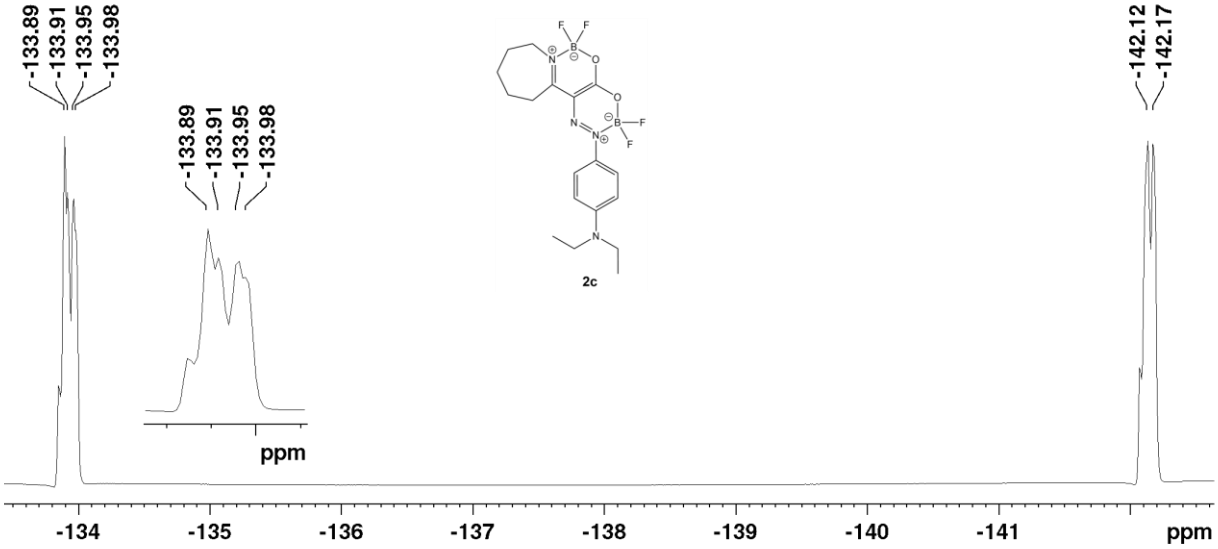


Figure S35. 376 MHz ^{19}F-NMR of compound **2c** in Acetone-*d*$_6$.

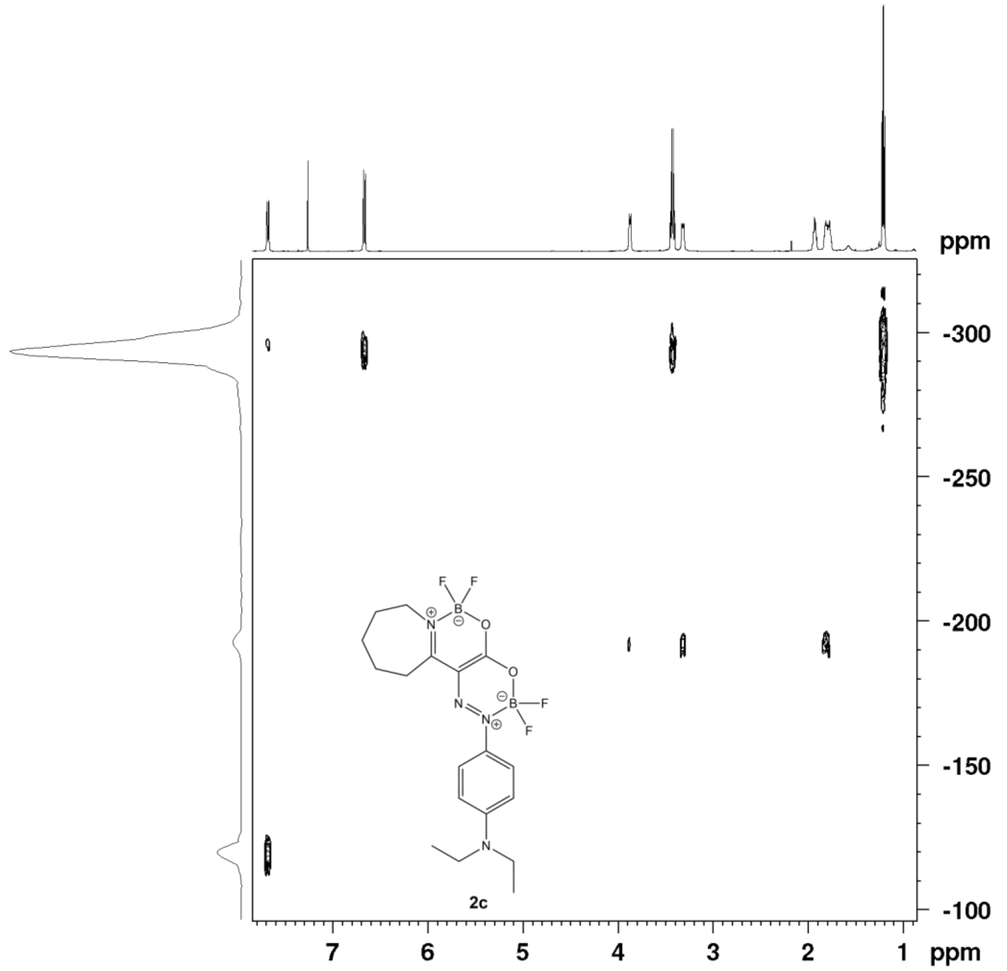


Figure S36. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **2c** in $CDCl_3$.

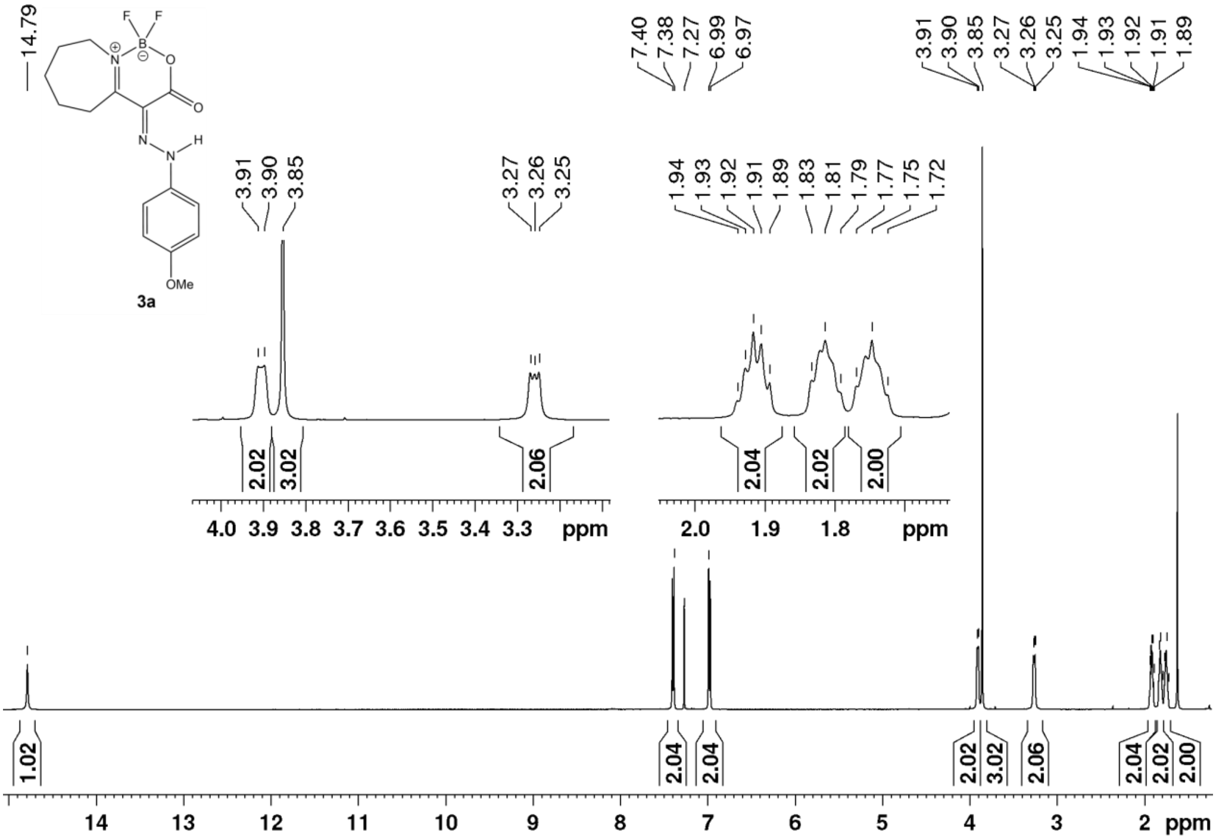


Figure S37. 500 MHz ^{1}H-NMR spectrum of compound **3a** in CDCl$_3$.

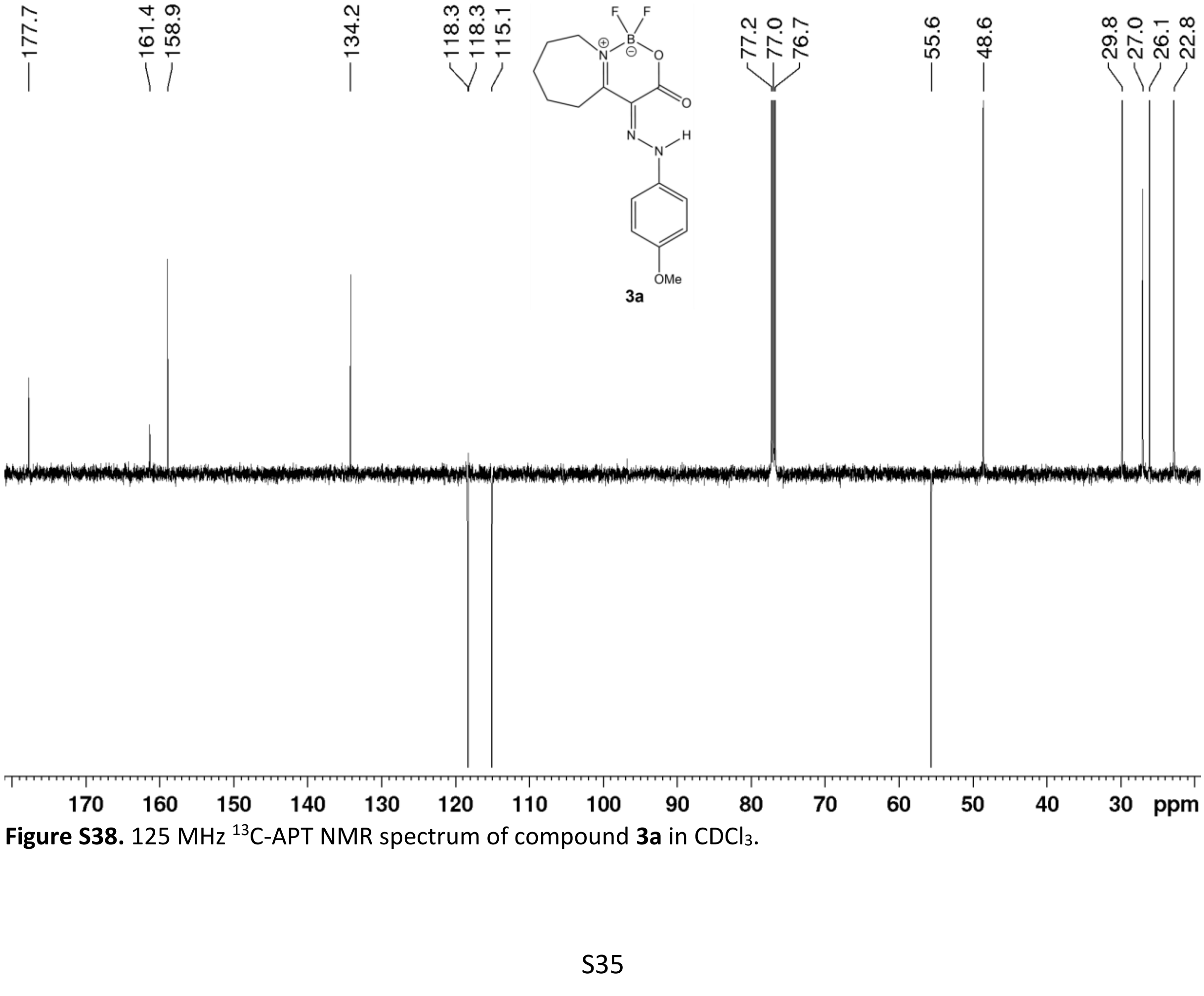
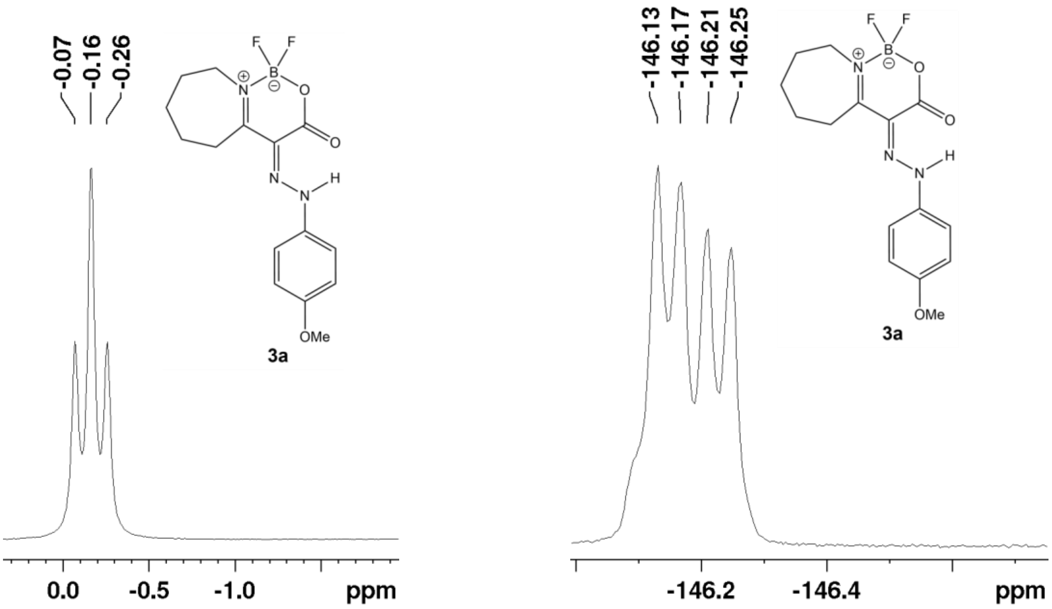


Figure S38. 125 MHz ^{13}C-APT NMR spectrum of compound **3a** in CDCl$_3$.



a) b)

Figure S39. a) 160 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **3a** in CDCl$_3$.

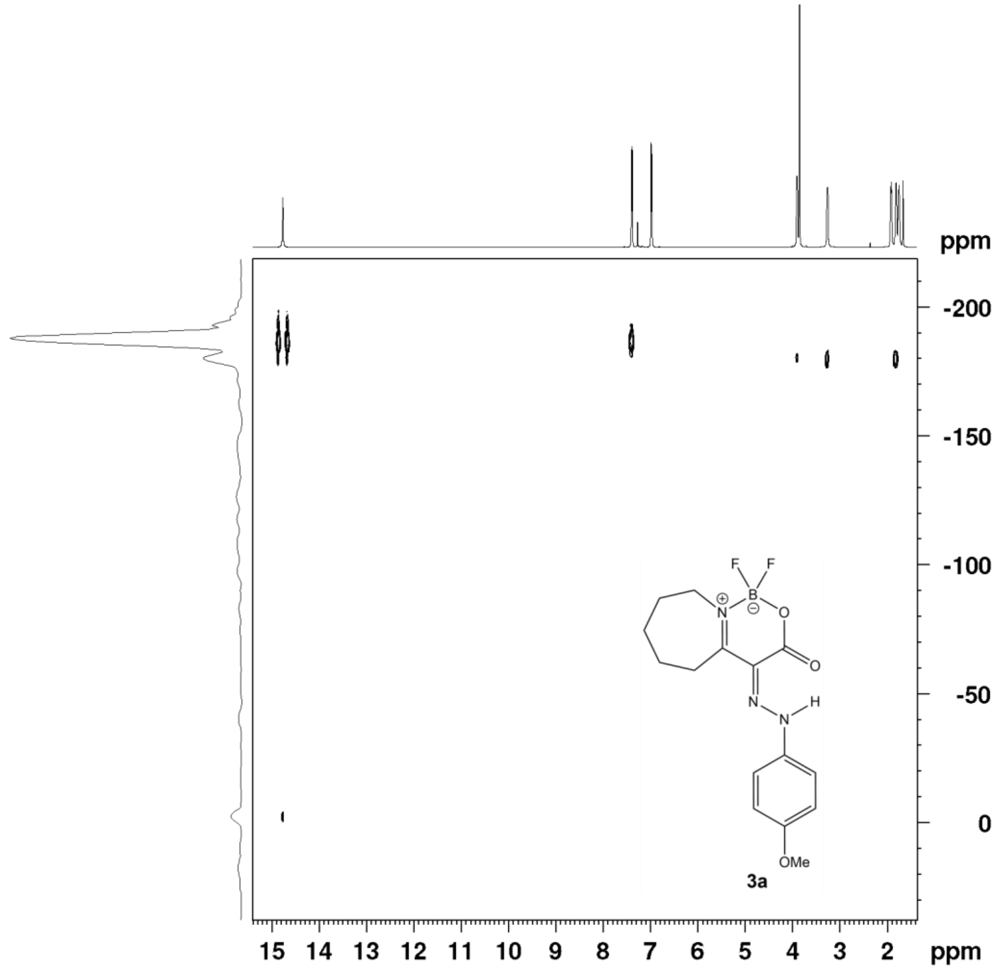


Figure S40. 500 MHz ^{1}H–^{15}N NMR spectrum of compound 3**a** in CDCl$_3$.

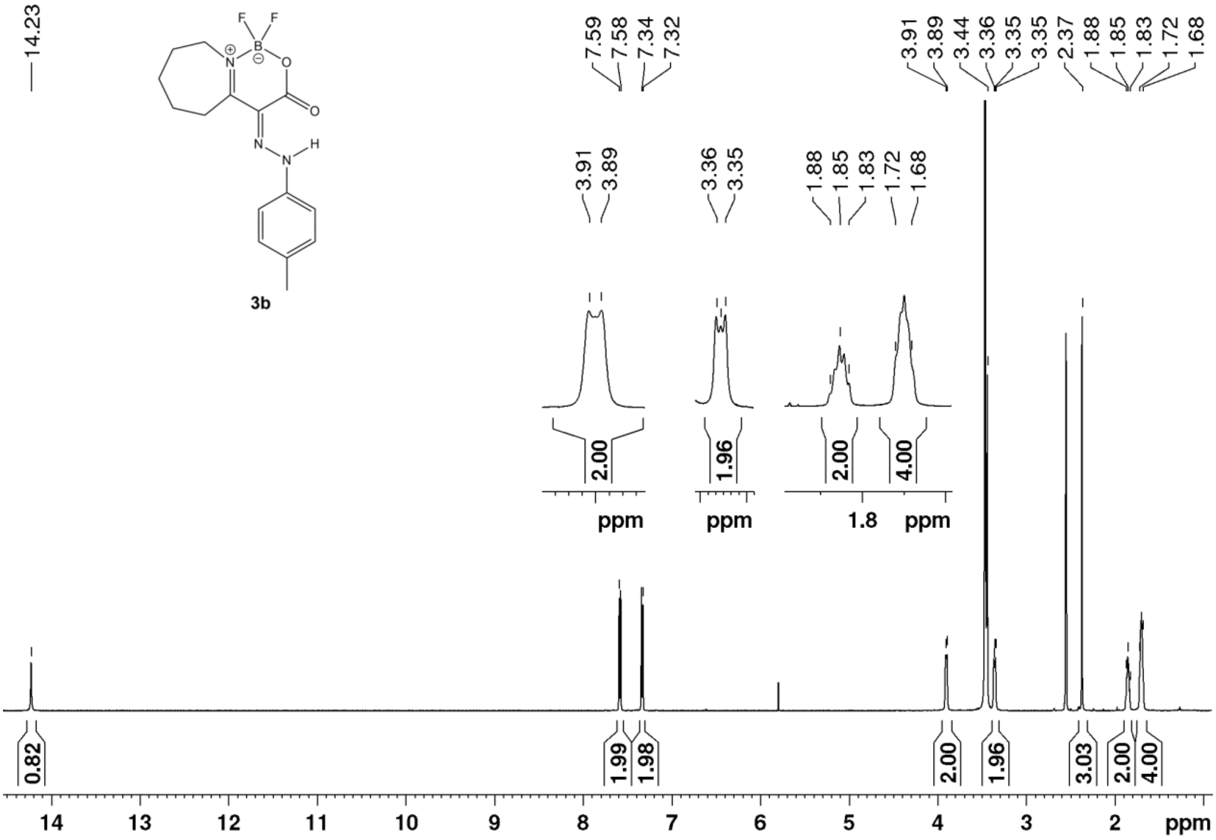


Figure S41. 500 MHz ^{1}H-NMR spectrum of compound **3b** in DMSO-d_6.

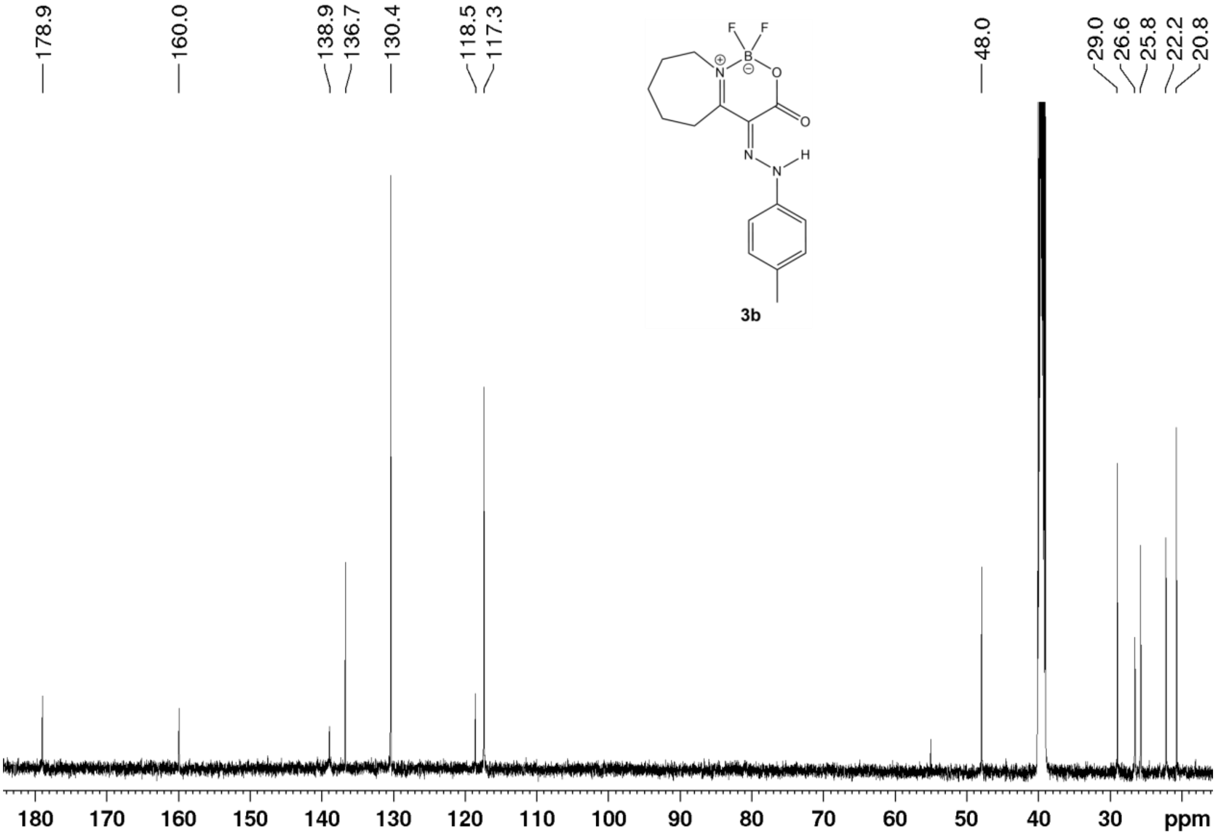
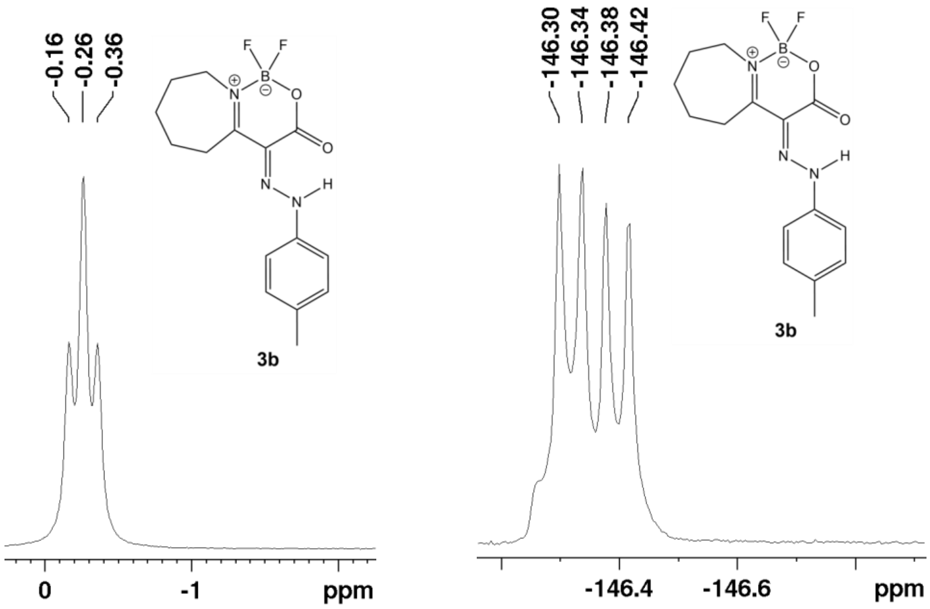


Figure S42. 125 MHz ^{13}C-NMR spectrum of compound **3b** in DMSO-d_6.



a) b)

Figure S43. a) 160 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **3b** in DMSO-d_6.

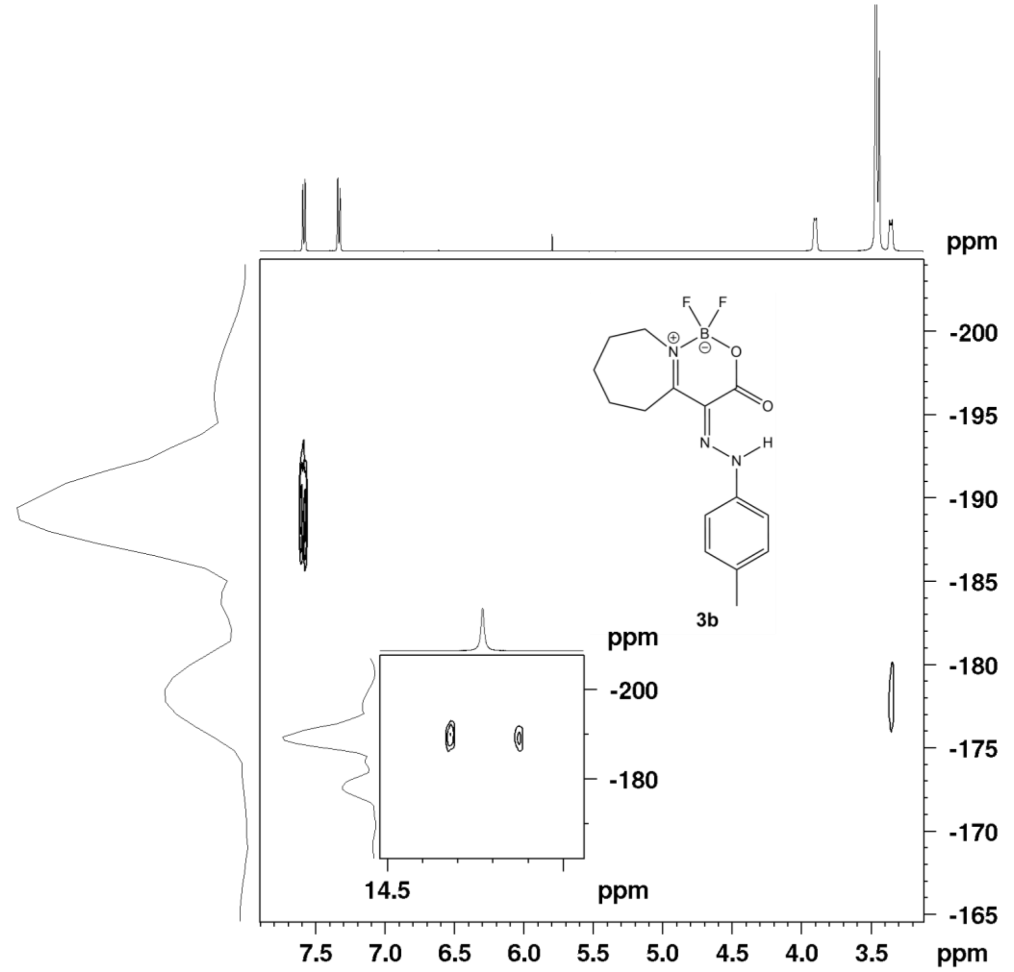


Figure S44. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **3b** in DMSO-d_6.

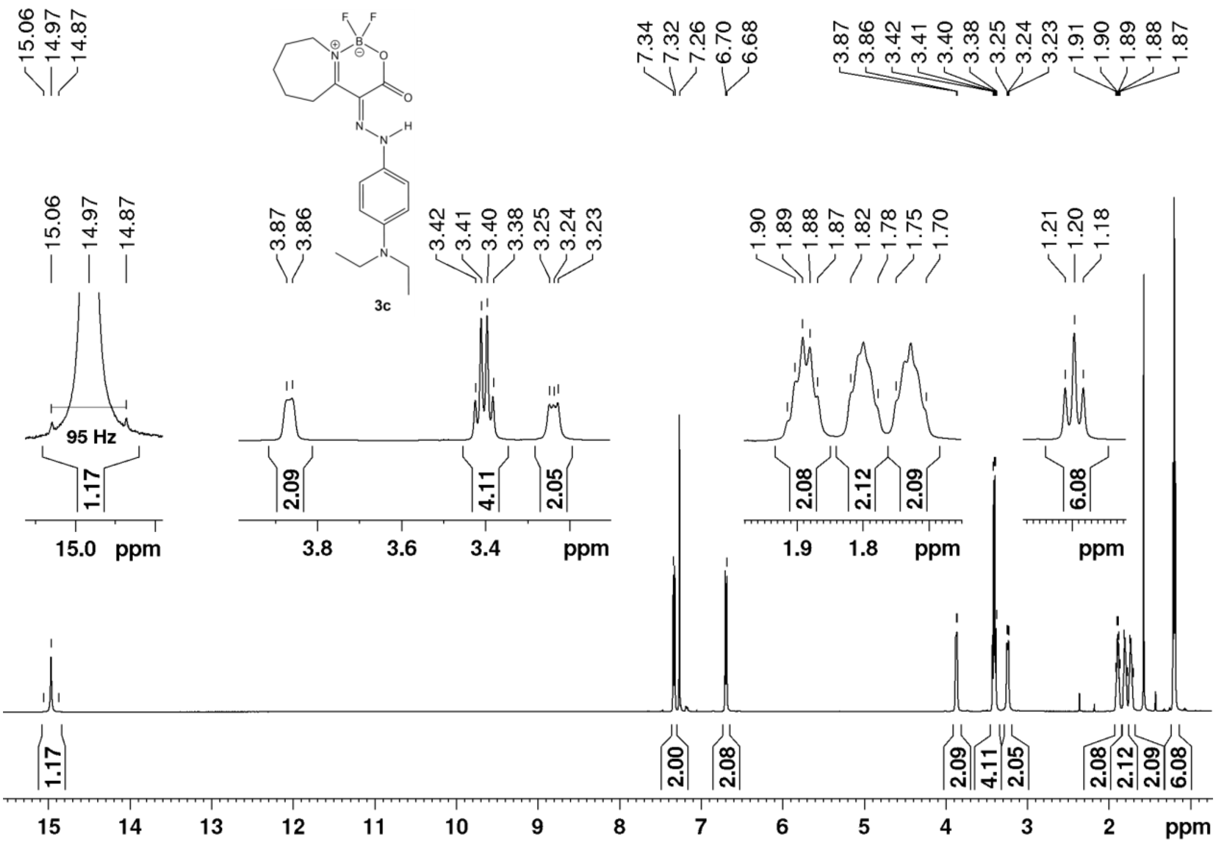


Figure S45. 500 MHz ^{1}H-NMR spectrum of compound **3c** in CDCl$_3$.

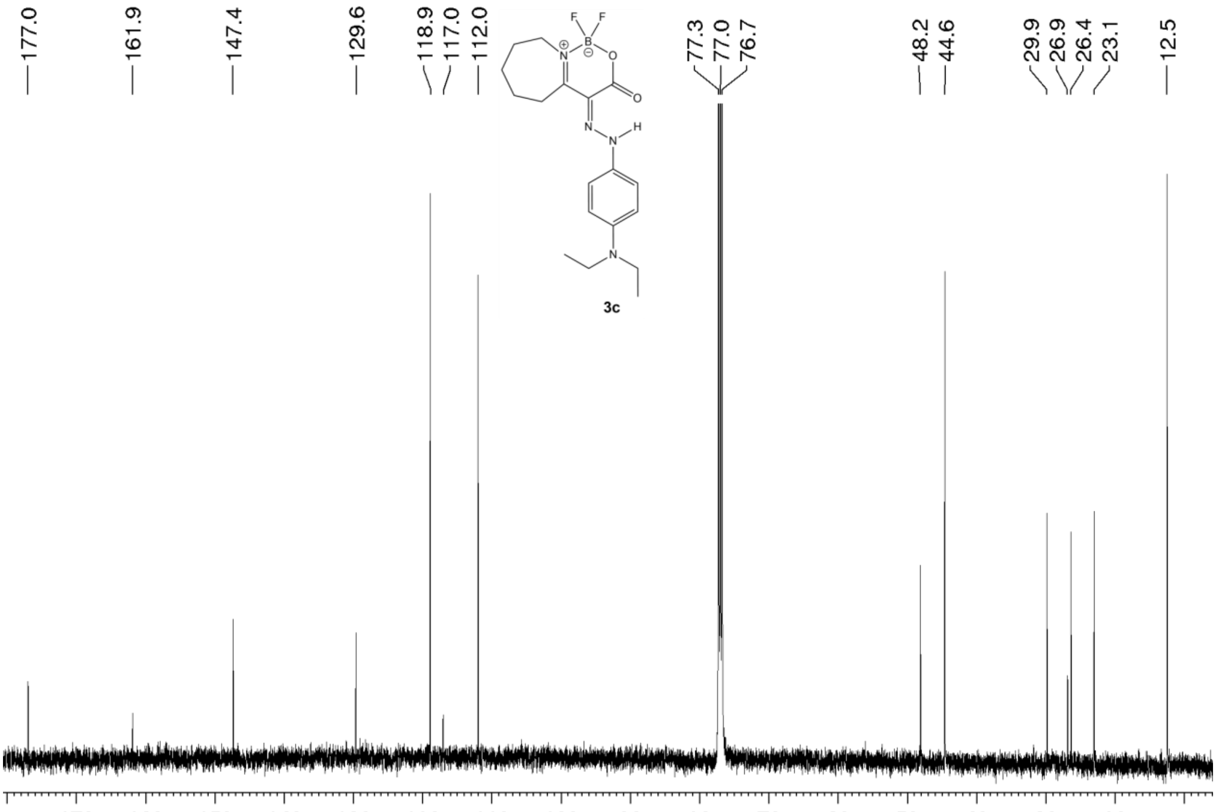
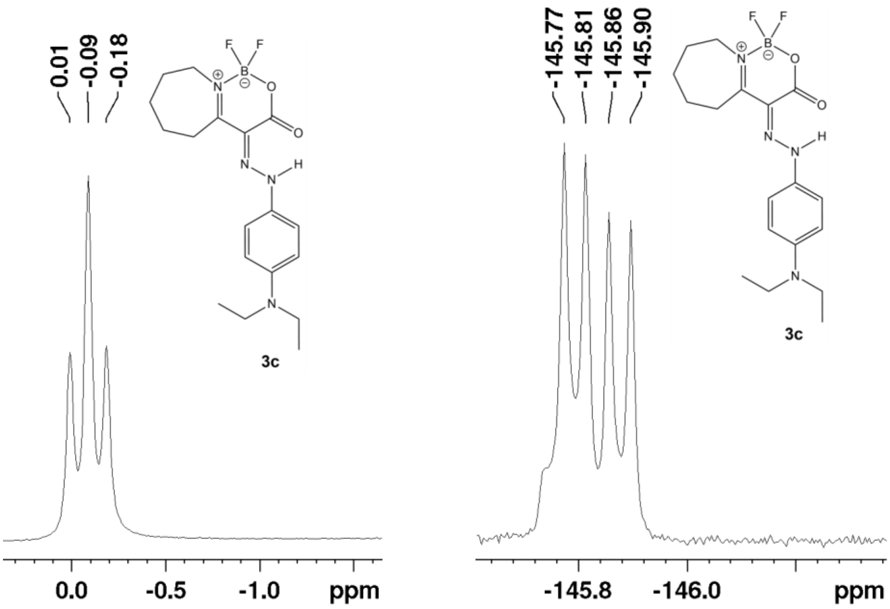


Figure S46. 125 MHz ^{13}C-NMR spectrum of compound **3c** in CDCl$_3$.



a) b)

Figure S47. a) 160 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **3c** in CDCl$_3$.

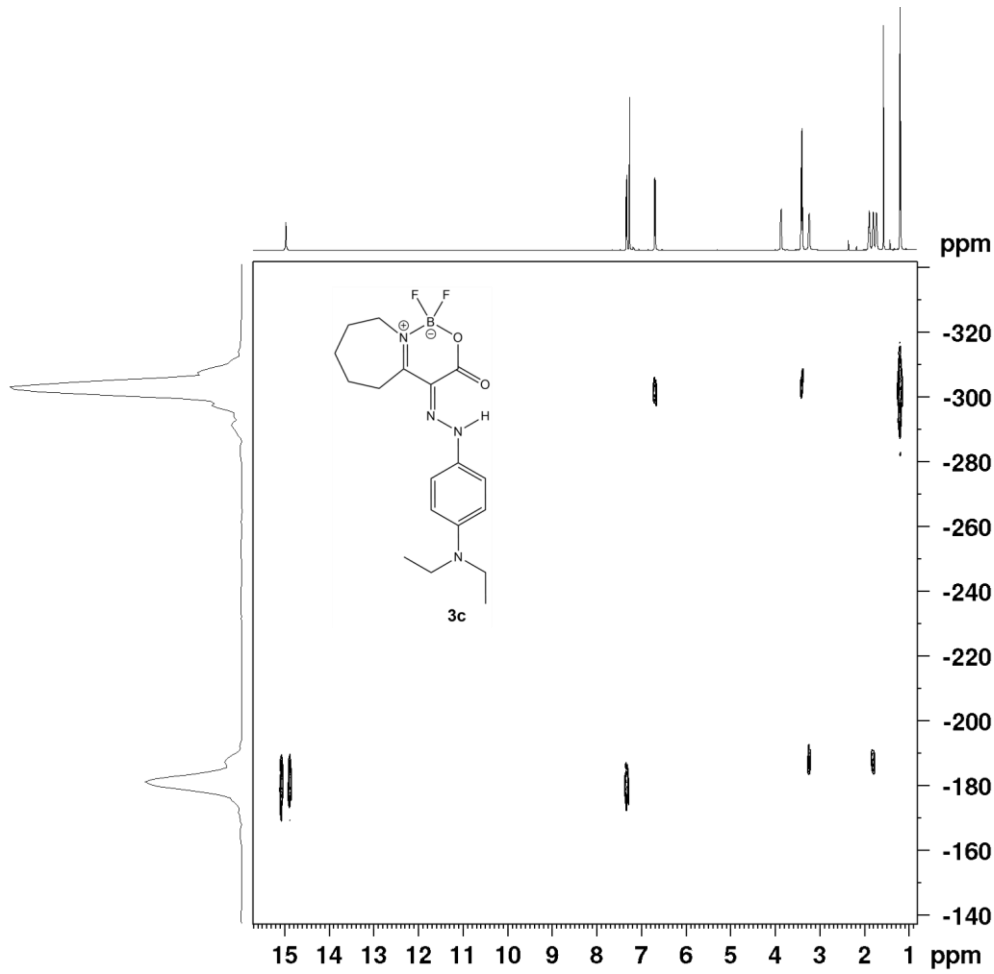


Figure S48. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **3c** in CDCl$_3$.

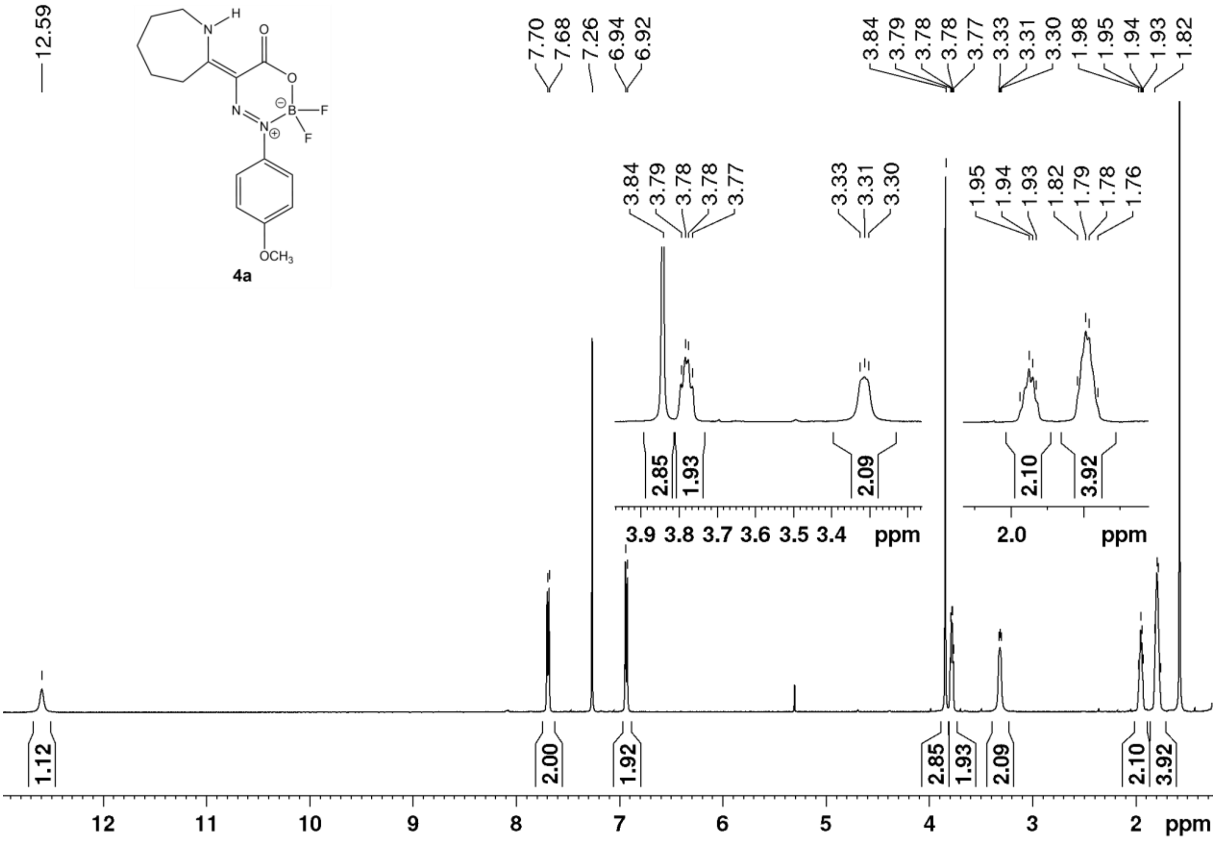


Figure S49. 500 MHz ^{1}H-NMR spectrum of compound **4a** in $CDCl_3$.

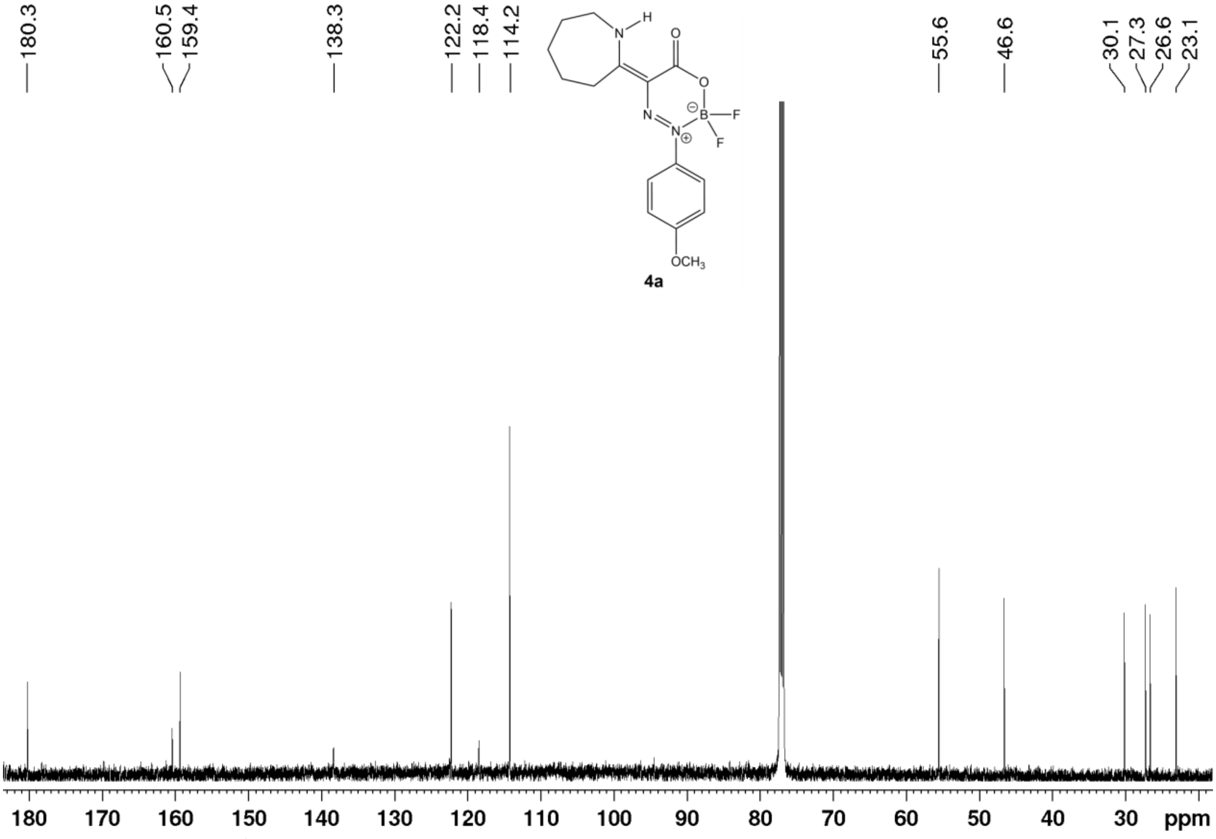


Figure S50. 125 MHz ^{13}C-NMR spectrum of compound **4a** in $CDCl_3$.

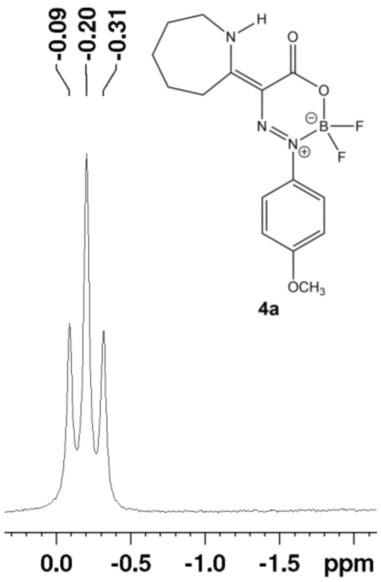


Figure S51. 160 MHz ^{11}B-NMR spectrum of compound **4a** in CDCl$_3$.

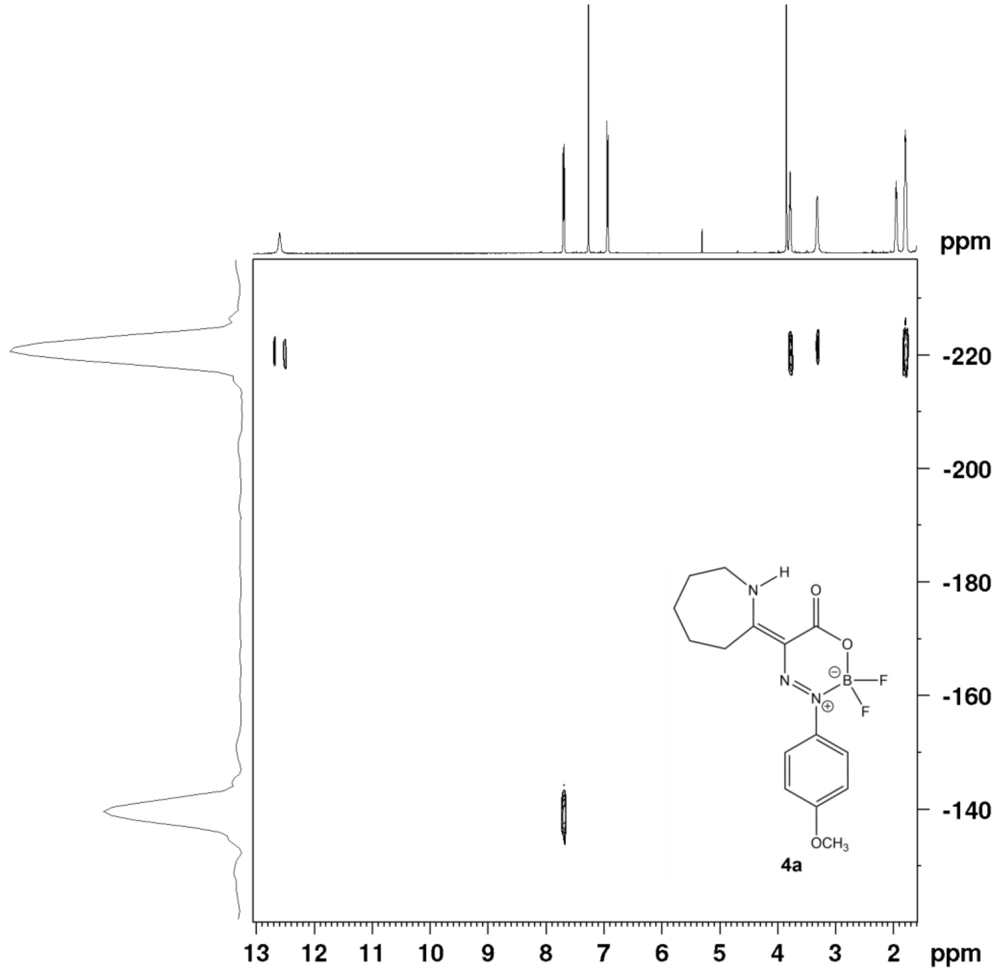


Figure S52. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **4a** in CDCl$_3$.

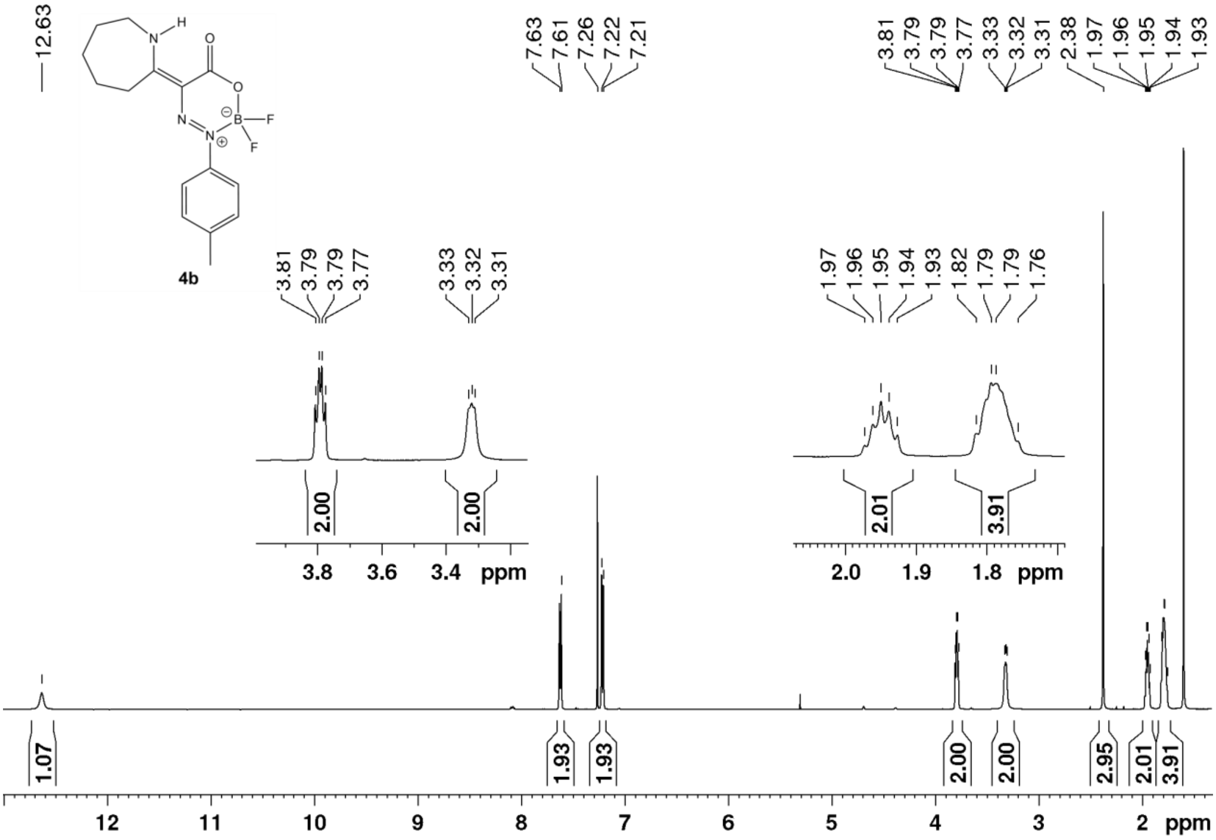


Figure S53. 500 MHz ^{1}H-NMR spectrum of compound **4b** in CDCl$_3$.

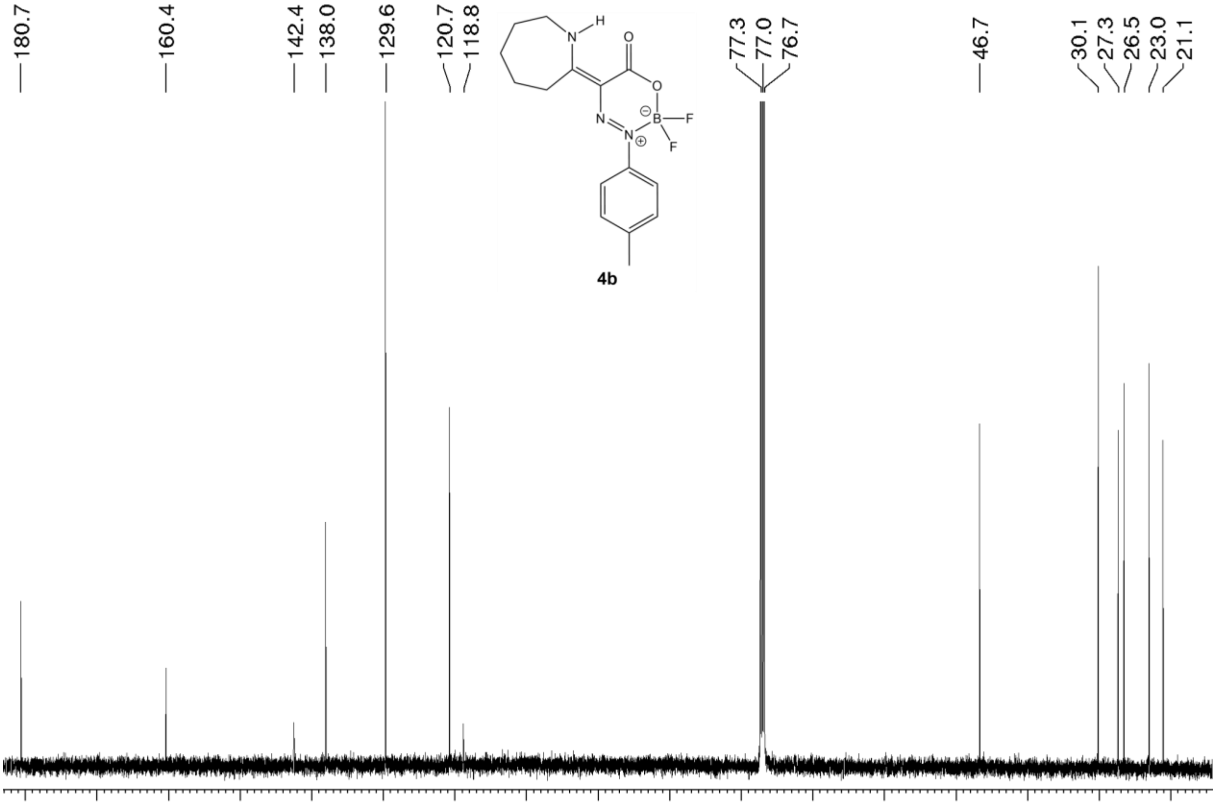
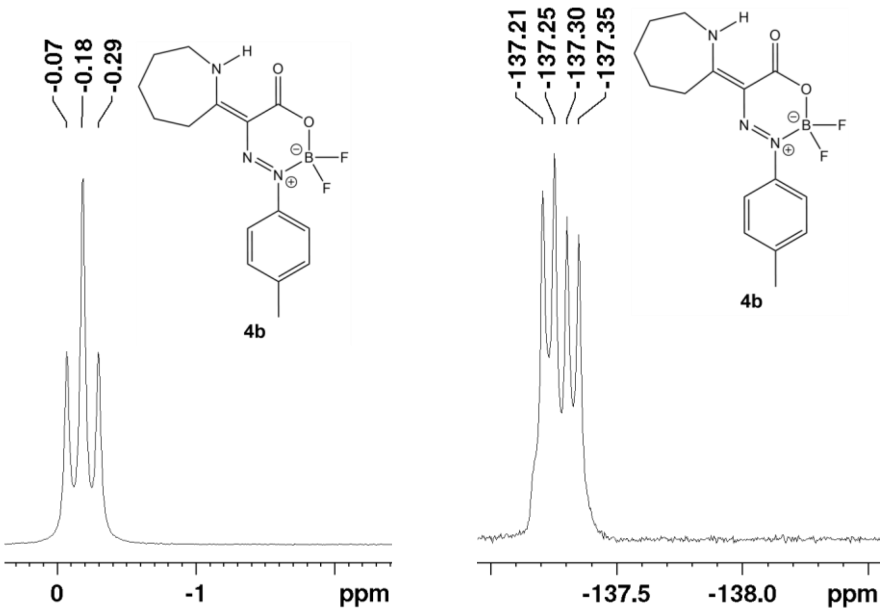


Figure S54. 125 MHz ^{13}C-NMR spectrum of compound **4b** in CDCl$_3$.



a)

b)

Figure S55. a) 160 MHz ^{11}B-NMR spectrum and b) 376 MHz ^{19}F-NMR of compound **4b** in CDCl₃.

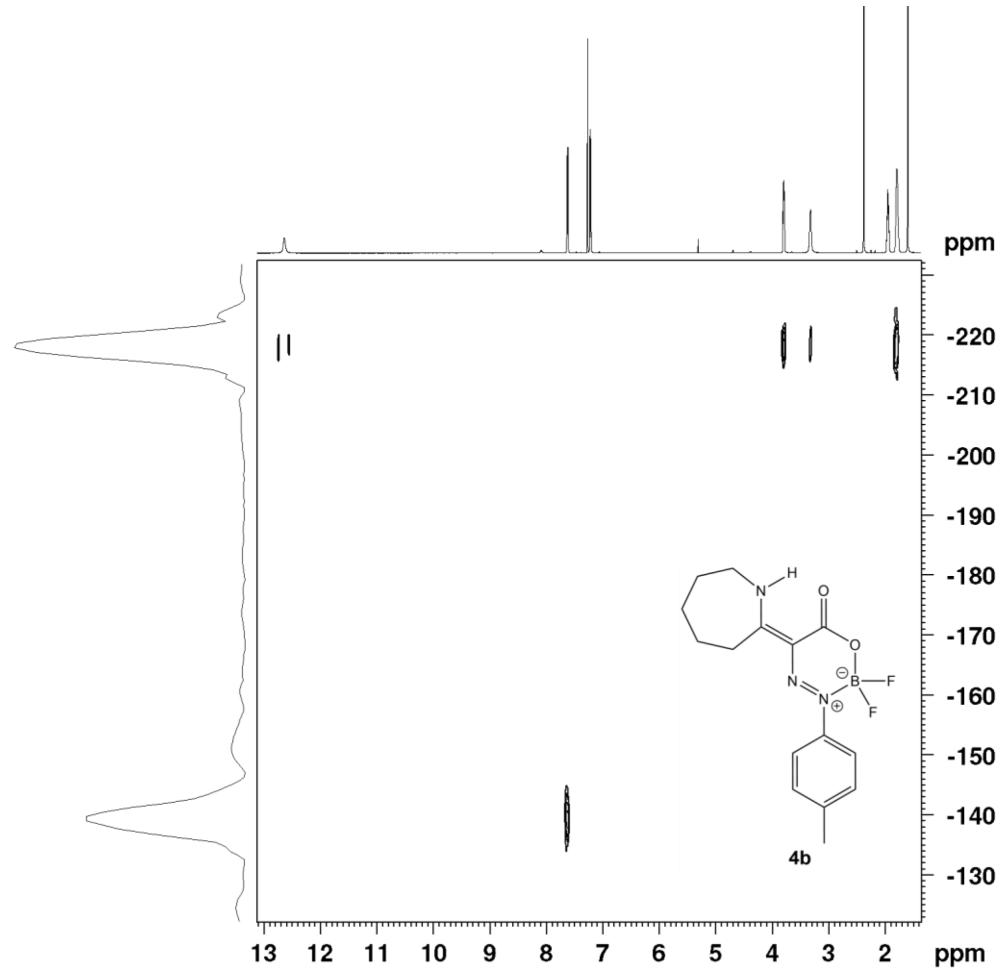


Figure S56. 500 MHz ^{1}H–^{15}N NMR spectrum of compound **4b** in CDCl₃.

Table S3: Experimental details for **1a**

Crystal data	
Chemical formula	$C_{17}H_{22}BF_2N_3O_3$
M_r	365.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	10.8390 (7), 10.572 (1), 15.3710 (7)
β (°)	98.905 (5)
V (Å^3)	1740.1 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.11
Crystal size (mm)	0.44 × 0.32 × 0.11

Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.639, 0.765
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13196, 3927, 2865
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650

Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.100, 1.08
No. of reflections	3927
No. of parameters	237
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.20, −0.25

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL2017*/1 (Sheldrick, 2017), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008).

Table S4: Experimental details for **2a**

Crystal data	
Chemical formula	$C_{15}H_{17}B_2F_4N_3O_3$
M_r	384.93
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	8.3810 (3), 18.3330 (8), 12.3330 (11)
β (°)	120.667 (5)
V (Å^3)	1629.93 (19)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.14
Crystal size (mm)	0.39 × 0.29 × 0.23

Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.669, 0.765
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12342, 3589, 3029
R_{int}	0.020
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650

Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.087, 1.08
No. of reflections	3589
No. of parameters	245
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.23

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL2017*/1 (Sheldrick, 2017), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008).

Table S5: Selected interatomic distances [Å] and bond angles [°] for compound **1a**			
Interatomic distances			
F1—B1	1.3882(19)	C1—N2	1.3231(19)
C1—C3	1.425(2)	C1—C2	1.493(2)
O1—C2	1.2065(19)	N1—N2	1.3128(16)
N1—B1	1.542(2)	B1—F2	1.3894(19)
B1—N3	1.541(2)	C2—O2	1.330(2)
N3—C3	1.3096(19)		
Bond angles			
N2—N1—B1	124.31(12)	C11—N1—B1	121.62(11)
F1—B1—F2	108.75(13)	F1—B1—N3	109.72(13)
F2—B1—N3	108.94(13)	F1—B1—N1	111.46(13)
F2—B1—N1	110.43(13)	N3—B1—N1	107.51(12)
N1—N2—C1	120.23(13)	O1—C2—O2	123.92(14)
O1—C2—C1	124.04(15)	O2—C2—C1	112.04(13)
C3—N3—B1	124.92(13)	N3—C3—C1	117.50(14)
C13—C12—C11	120.88(15)		

Table S6: Selected interatomic distances [Å] and bond angles [°] for compound **2a**			
Interatomic distances			
F1—B1	1.3677(18)	C1—O2	1.2767(15)
C1—O1	1.2800(15)	C1—C2	1.4170(17)
N1—N2	1.2882(15)	N1—C9	1.4335(16)
N1—B1	1.5778 (17)	O1—B1	1.4895(17)
B1—F2	1.3603(18)	C2—N2	1.3407(16)
C2—C3	1.4397(17)	O2—B2	1.5021(17)
B2—F4	1.3641(18)	B2—N3	1.5595(17)
C3—N3	1.2992(16)	O3—C12	1.3577(15)
O3—C15	1.4341(17)		
Bond angles			
C2—C1—O1	116.65 (11)	N2—N1—C9	114.36 (10)
N2—N1—B1	123.94 (10)	C9—N1—B1	121.69 (10)
C1—O1—B1	123.76 (10)	F2—B1—F1	112.27(12)
F2—B1—O1	108.38(12)	F1—B1—O1	108.53(11)
F2—B1—N1	110.02(11)	F1—B1—N1	109.74(11)
O1—B1—N1	107.78(10)	N1—N2—C2	120.05(11)
F4—B2—F3	111.90(12)	F4—B2—O2	107.58(11)
F3—B2—O2	108.13(11)	F4—B2—N3	109.85(11)
F3—B2—N3	109.68(11)		

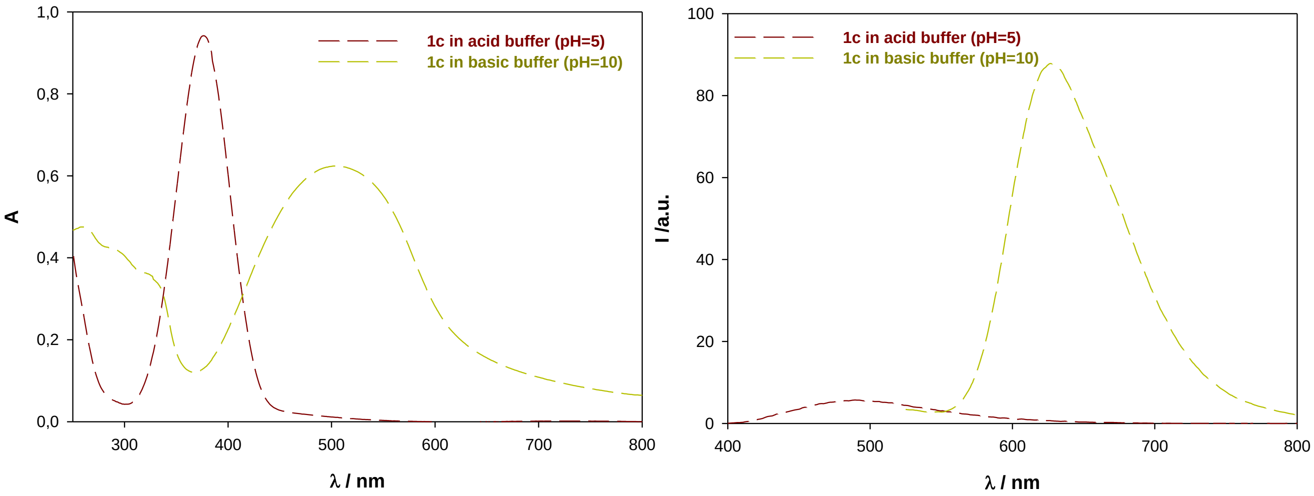


Figure S57. Absorption (left) and emission spectra (right) of compound **1c** in acidic (pH=5) and basic aqueous buffers (pH=10).

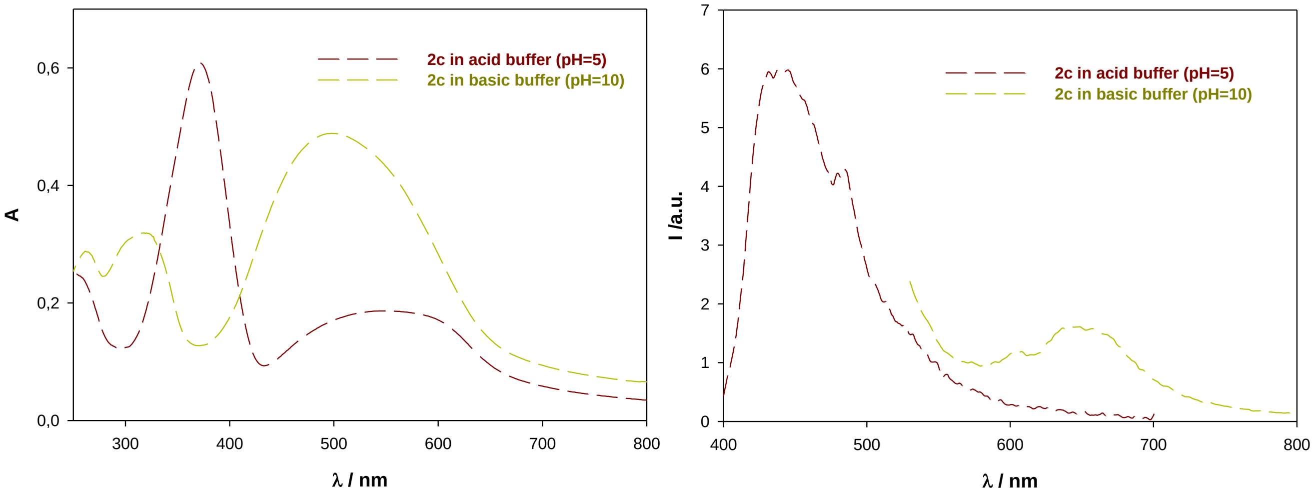


Figure S58. Absorption (left) and emission spectra (right) of compound **2c** in acidic (pH=5) and basic aqueous buffers (pH=10).

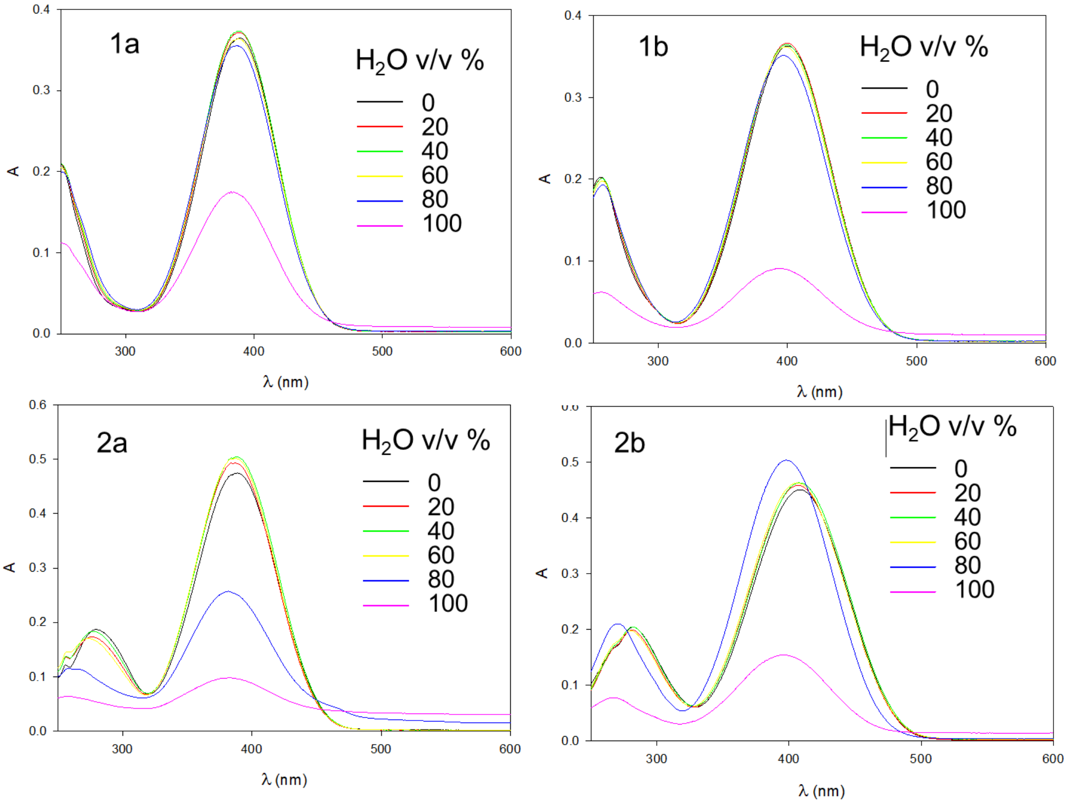


Figure S59 - Absorbance spectra of compounds **1a**, **1b**, **2a** and **2b** (20 μM) acetonitrile:water mixtures at increasing water content.

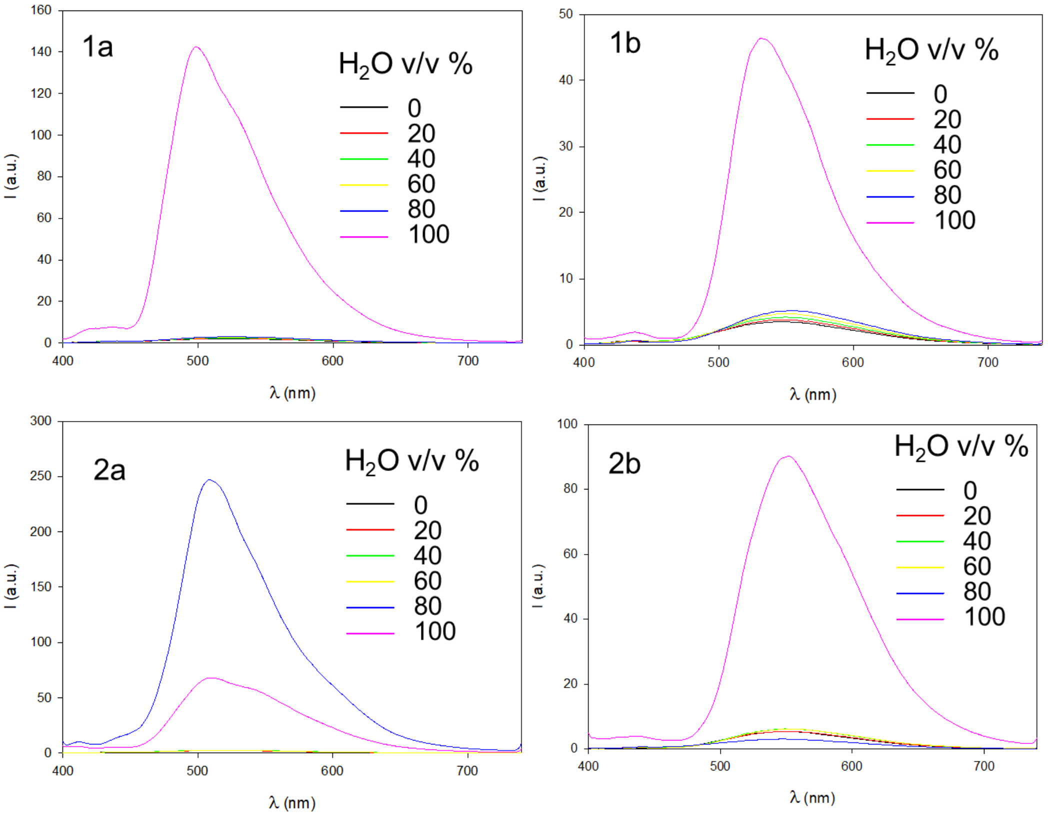


Figure S60 - Emission spectra of compounds **1a**, **1b**, **2a** and **2b** (20 μM, λ_{exc} = 360 nm) in acetonitrile:water mixtures at increasing water content.

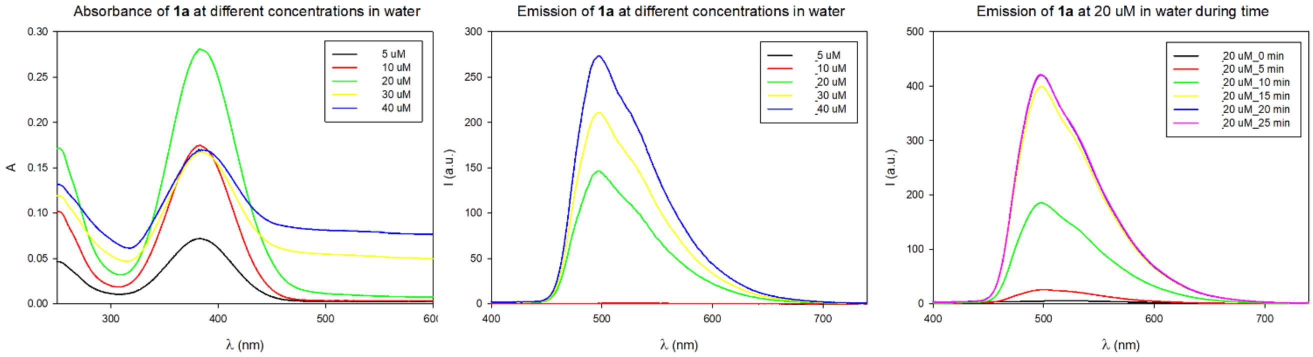


Figure S61 – Absorbance (left) and emission (center) spectra of compound **1a** at different concentration in water (5-40 µM, λ_{exc} = 360 nm), and emission spectra during time at fixed concentration of 20 µM (right), showing that aggregation (and consequently AIE) takes place at a minimum concentration of 20 µM for this compound.

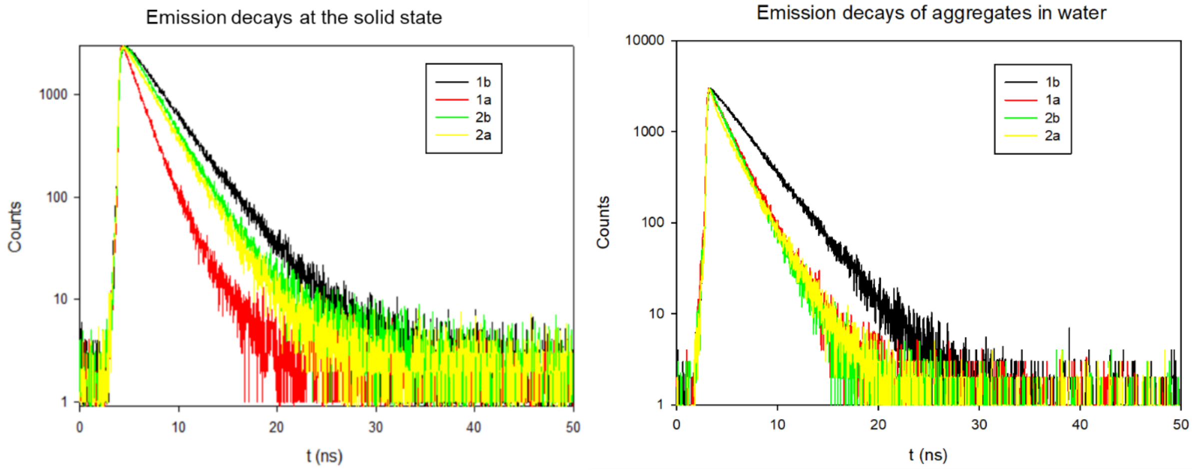


Figure S62 – Emission decays at the solid state (left) and in the aggregated state in water (right, 20 µM, λ_{exc} = 365 nm).

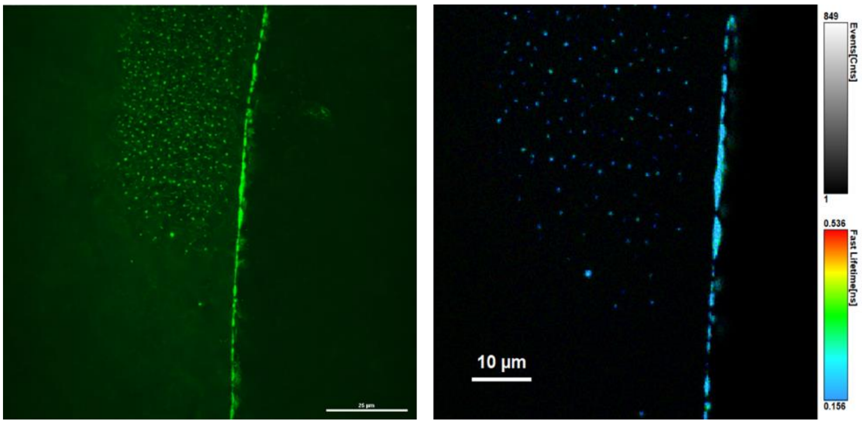


Figure S63 – Confocal (left) and FLIM (right) images of aggregates formed in water by compound **1b**.

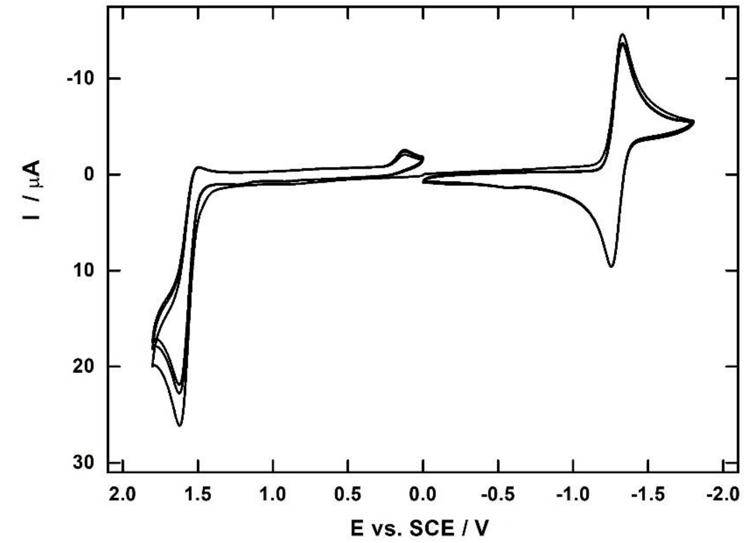


Figure S64. Representative cyclic voltammograms of the oxidation and reduction of **1b** at glassy carbon electrode in acetonitrile containing 0.1M $Bu_4N^+PF_6^-$; v = 100 mV.s^{-1}.

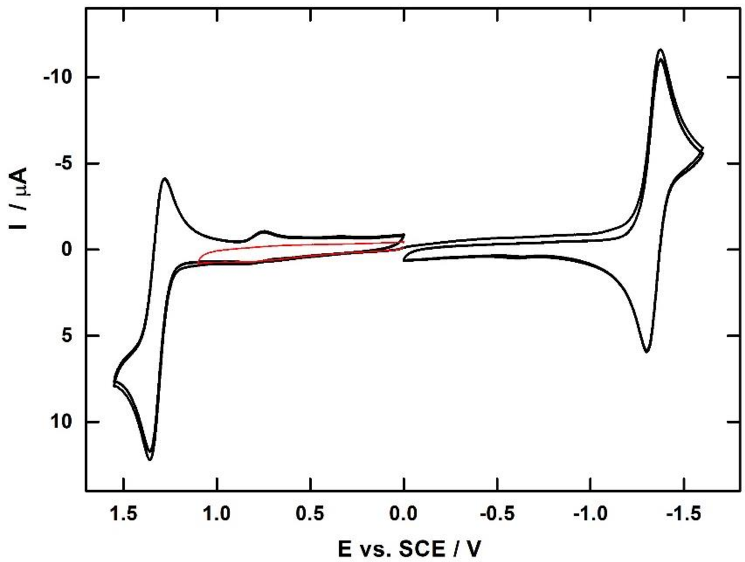


Figure S65. Representative CV curves of the oxidation and reduction of **1a** at glassy carbon electrode in acetonitrile containing 0.1M $Bu_4N^+PF_6^-$; v = 100 mV.s^{-1}.

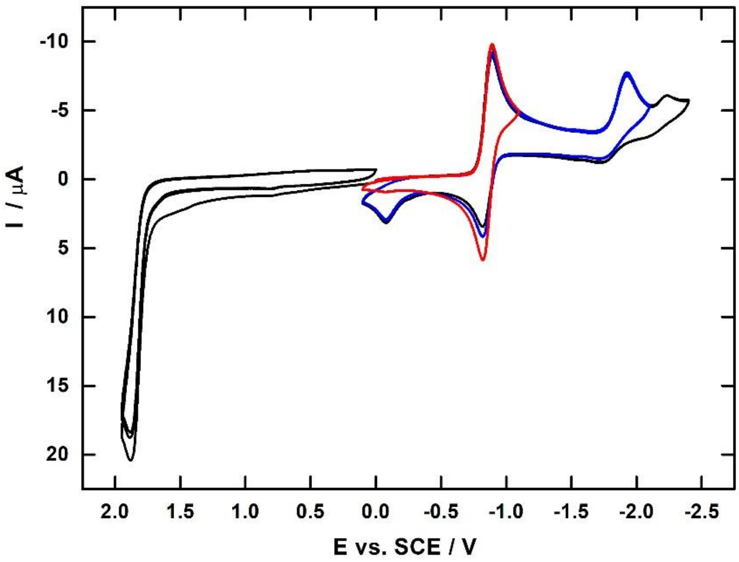


Figure S66. Representative cyclic voltammograms of the oxidation and reduction of **2b** at glassy carbon electrode in acetonitrile containing 0.1M $Bu_4N^+PF_6^-$; v = 100 mV.s^{-1}.

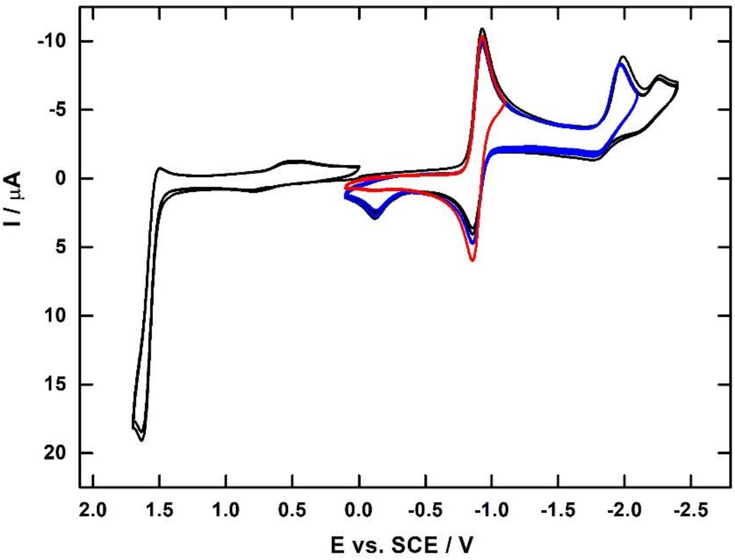


Figure S67. Representative cyclic voltammograms of the oxidation and reduction of **2a** at glassy carbon electrode in acetonitrile containing 0.1M $Bu_4N^+PF_6^-$; v = 100 mV.s^{-1}.

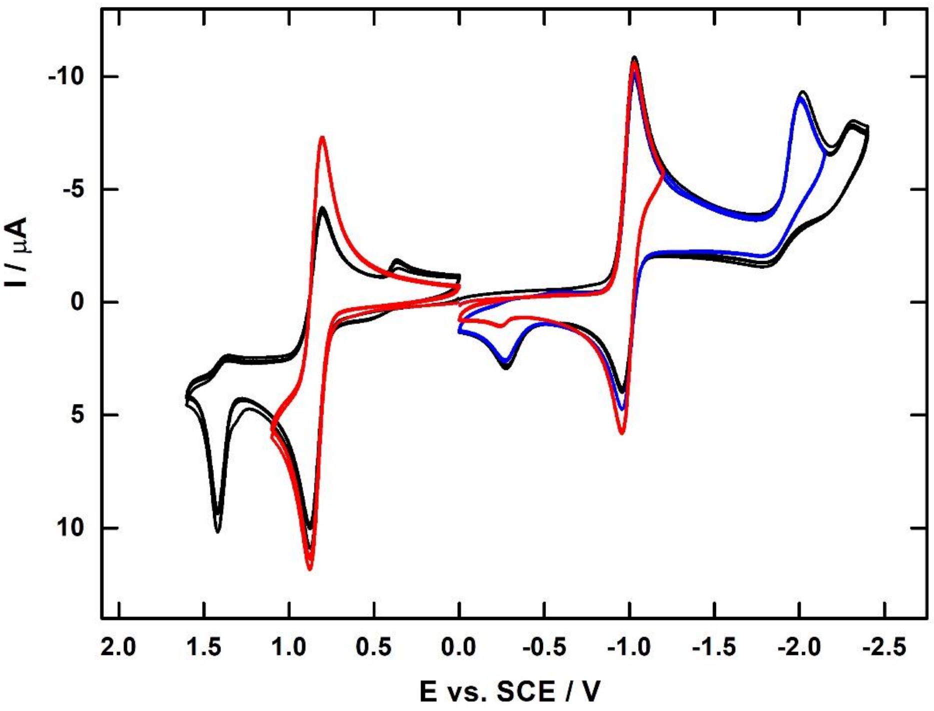


Figure S68. Representative cyclic voltammograms of the oxidation and reduction of **2c** at glassy carbon electrode in acetonitrile containing 0.1M $Bu_4N^+PF_6^-$; v = 100 mV.s^{-1}.

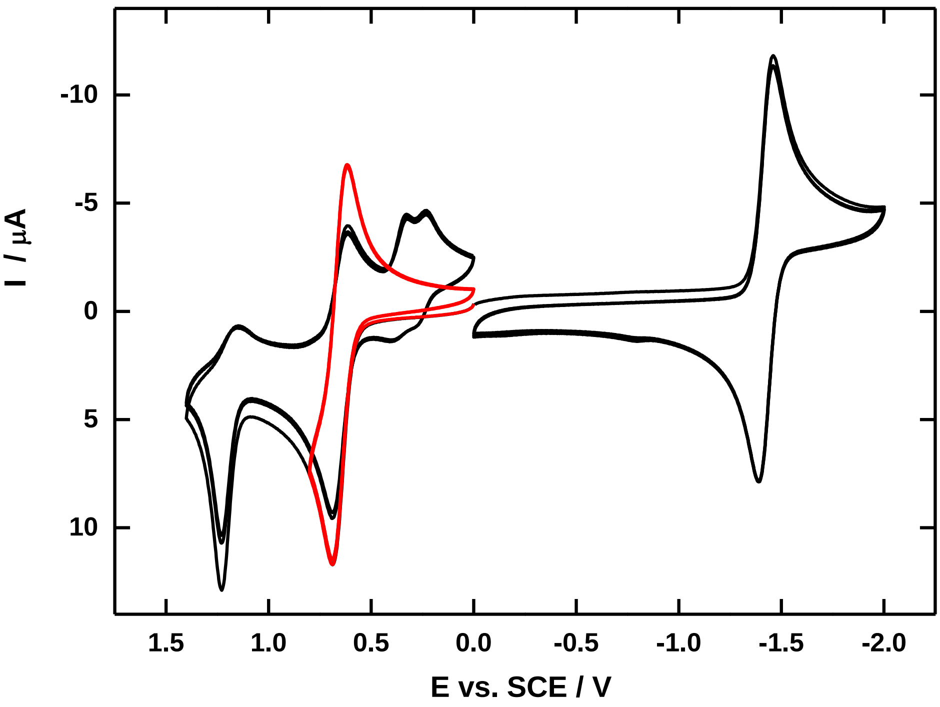
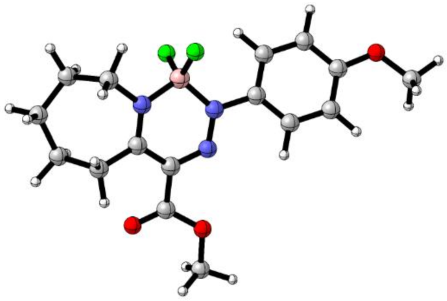


Figure S69. Representative cyclic voltammograms of the oxidation and reduction of **1c** at glassy carbon electrode in acetonitrile containing 0.1M $Bu_4N^+PF_6^-$; v = 100 mV.s^{-1}.

4. Coordinates

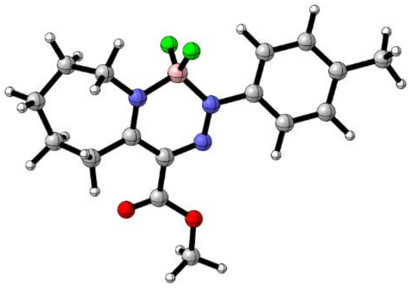


45

1a 0 1 scf done:-1236.821337 Sum of electronic and thermal Free Energies -1236.516457 imag. freq.: 0

C	-2.1141840	-0.0584240	-0.2834740
C	2.0566400	0.0244290	0.2162560
C	2.6979800	1.1160820	-0.3664390
C	2.8191680	-0.9781390	0.8282620
C	4.0852250	1.2255020	-0.3316000
H	2.1092340	1.8805700	-0.8550770
C	4.1996940	-0.8761010	0.8606380
H	2.3326080	-1.8247070	1.2913900
C	4.8451140	0.2259820	0.2845640
H	4.5561210	2.0799090	-0.7962510
H	4.7974300	-1.6418330	1.3392230
C	-1.9302530	2.4348200	0.2400330
O	-3.0817040	2.6207060	0.5884110
C	-1.3221880	1.0933800	0.0420650
B	-0.0706050	-1.4559290	0.1723530
F	0.5793400	-2.3182860	-0.7254250
F	-0.0468470	-2.0338470	1.4629500
N	0.6330130	-0.0760180	0.1841290
N	-0.0029770	1.0518860	0.1863050
C	-1.5535950	4.7654630	0.2884740
H	-1.8645290	4.8550830	1.3293710
H	-0.7147080	5.4248100	0.0822710
H	-2.3927010	4.9972210	-0.3673950
O	-1.0635440	3.4340700	0.0250720
N	-1.5292580	-1.2360990	-0.2664090
C	-3.5501680	0.0593520	-0.7077730
H	-3.7834350	1.1009880	-0.8913140
C	-2.2738480	-2.4749910	-0.5916040
H	-2.6922440	-2.3891880	-1.5976570
H	-1.5339830	-3.2700380	-0.6212410
C	-3.3636880	-2.8134810	0.4329240
H	-3.5699820	-3.8835940	0.3414940
H	-2.9576790	-2.6555620	1.4368630
C	-4.6735230	-2.0419260	0.2513500
H	-5.1012160	-2.3030960	-0.7240640
C	-4.5347810	-0.5204190	0.3317840
H	-4.2216130	-0.2141060	1.3343810

H	-5.5113110	-0.0627920	0.1563390
H	-5.3920630	-2.3782440	1.0045500
H	-3.6663660	-0.4750790	-1.6562260
C	6.9105340	1.3416070	-0.1943820
H	7.9638210	1.1443620	-0.0087270
H	6.7352530	1.4132340	-1.2712820
H	6.6216350	2.2783170	0.2900630
O	6.2027040	0.2341550	0.3681930

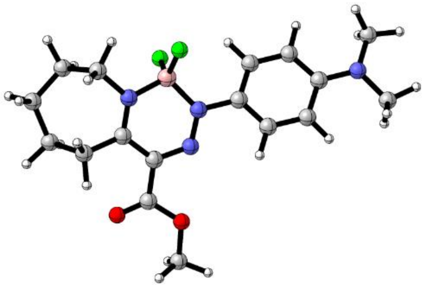


44

1b 0 1 scf done:-1161.589293 Sum of electronic and thermal Free Energies -1161.289212 imag. freq.: 0

C	-2.1237960	-0.0730340	-0.2917760
C	2.0664610	-0.0279570	0.0376230
C	2.6928340	1.0580010	-0.5788930
C	2.8400700	-1.0302830	0.6269040
C	4.0798130	1.1406080	-0.5915230
H	2.0902380	1.8257370	-1.0452240
C	4.2275780	-0.9344340	0.6006880
H	2.3635610	-1.8666230	1.1184240
C	4.8742240	0.1470050	-0.0066500
H	4.5538170	1.9885920	-1.0737150
H	4.8172660	-1.7134390	1.0712060
C	6.3778710	0.2252170	-0.0584370
H	6.7578980	-0.2246770	-0.9818660
H	6.7223240	1.2611680	-0.0342190
H	6.8315210	-0.3101880	0.7778800
C	-1.8920550	2.4247010	0.1930880
O	-3.0226890	2.6231180	0.5973720
C	-1.3048660	1.0747980	-0.0154600
B	-0.0776190	-1.4871690	0.0995410
F	0.5211430	-2.3687170	-0.8145890
F	-0.0078140	-2.0488940	1.3949320
N	0.6405630	-0.1155600	0.0613780
N	0.0168520	1.0203730	0.0728160
C	-1.4945920	4.7524790	0.1891410
H	-1.7491680	4.8588380	1.2436570
H	-0.6620840	5.4009870	-0.0702170
H	-2.3650440	4.9828660	-0.4249810
O	-1.0305550	3.4128900	-0.0808830
N	-1.5527950	-1.2562070	-0.2796720
C	-3.5732420	0.0585840	-0.6627730

H	-3.7994100	1.1006990	-0.8528670
C	-2.3244970	-2.4911490	-0.5540320
H	-2.7790300	-2.4170250	-1.5452610
H	-1.5960360	-3.2959960	-0.5970260
C	-3.3792160	-2.7973920	0.5163330
H	-3.6010980	-3.8663180	0.4518870
H	-2.9341310	-2.6269050	1.5014790
C	-4.6857600	-2.0130560	0.3695220
H	-5.1514620	-2.2841700	-0.5855520
C	-4.5261290	-0.4925400	0.4208540
H	-4.1732040	-0.1746260	1.4064150
H	-5.5026990	-0.0253090	0.2732670
H	-5.3803890	-2.3287360	1.1534230
H	-3.7319870	-0.4874010	-1.5984620

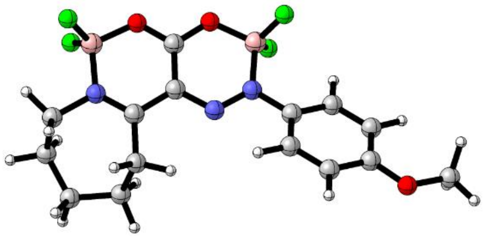


49

1c 0 1 scf done: 0 1 -1256.278443 Sum of electronic and thermal Free Energies -1255.935922 imag. freq.: 0

C	-2.1271570	-0.0603930	-0.2772100
C	2.0542500	-0.0473600	0.1087650
C	2.7057330	1.0539240	-0.4546800
C	2.8244530	-1.0731760	0.6645830
C	4.0875990	1.1361940	-0.4591520
H	2.1188120	1.8486440	-0.8957230
C	4.2079830	-0.9994900	0.6632420
H	2.3425750	-1.9256720	1.1224110
C	4.8860470	0.1042090	0.0923430
H	4.5492930	2.0034030	-0.9081190
H	4.7636100	-1.8056220	1.1192040
C	-1.8972190	2.4223960	0.2517580
O	-3.0430450	2.6279970	0.6104340
C	-1.3141570	1.0753100	0.0343030
B	-0.0976340	-1.4892650	0.1348960
F	0.5195120	-2.3733190	-0.7661060
F	-0.0540860	-2.0536770	1.4323810
N	0.6319850	-0.1203120	0.1217170
N	0.0128460	1.0152600	0.1446520
C	-1.4812560	4.7465770	0.3242840
H	-1.7867280	4.8292610	1.3674700
H	-0.6322830	5.3946090	0.1229600
H	-2.3189250	5.0016420	-0.3249060
O	-1.0149310	3.4113060	0.0423900
N	-1.5580910	-1.2491490	-0.2783580

C	-3.5699780	0.0770100	-0.6737040
H	-3.7933390	1.1224310	-0.8475200
C	-2.3272980	-2.4740130	-0.5961760
H	-2.7638670	-2.3774540	-1.5936850
H	-1.6005930	-3.2802290	-0.6444190
C	-3.4030850	-2.8041430	0.4461590
H	-3.6256640	-3.8709560	0.3531290
H	-2.9769330	-2.6569470	1.4434110
C	-4.7054500	-2.0141950	0.2926710
H	-5.1537530	-2.2636660	-0.6766390
C	-4.5441630	-0.4953390	0.3791650
H	-4.2090000	-0.1997450	1.3779480
H	-5.5176570	-0.0236470	0.2244280
H	-5.4152800	-2.3454470	1.0564290
H	-3.7101010	-0.4505030	-1.6229390
N	6.2591340	0.1659930	0.0615250
C	7.0419360	-0.8220290	0.7904370
H	8.0986920	-0.6367300	0.6108880
H	6.8606370	-0.7797630	1.8725560
H	6.8163360	-1.8335230	0.4436200
C	6.9170960	1.4001560	-0.3445480
H	7.9937460	1.2453430	-0.3335170
H	6.6309750	1.6817590	-1.3610480
H	6.6791870	2.2368530	0.3253020



44

2a 0 1 scf done: 0 1 -1421.712997 Sum of electronic and thermal Free Energies -1421.435892 imag. freq.: 0

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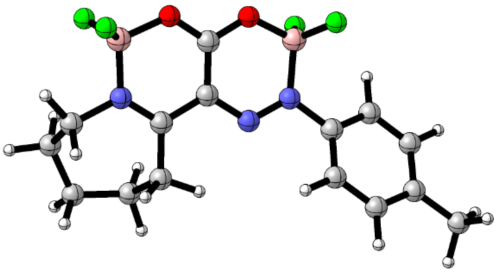
C	-1.0559630	-0.2498870	-0.1691700
C	-2.1046630	0.7265770	-0.3287800
C	-4.4711820	1.2705970	-0.5163220
H	-5.3559220	0.6691580	-0.7101220
C	-1.7575270	2.1836720	-0.3662400
H	-0.6802750	2.2744540	-0.4652120
C	2.4949790	-0.0997070	-0.0834360
C	2.7195340	1.0536040	-0.8479050
C	3.5615910	-0.7164990	0.5698070
C	3.9913770	1.5839080	-0.9405970
H	1.8961740	1.5168640	-1.3735690
C	4.8439720	-0.1844150	0.4784880
H	3.3995360	-1.6003450	1.1698930
C	5.0661100	0.9719280	-0.2762850
H	4.1799290	2.4678900	-1.5366820

H	5.6514610	-0.6748600	1.0023670
H	-4.3110430	1.9011430	-1.3944530
H	-2.2101810	2.6281560	-1.2579980
F	1.7766100	-2.9556020	-0.4695440
F	1.2019430	-2.4120510	1.6890940
F	-4.6123210	-1.3928050	0.7315610
B	0.9688310	-2.1790020	0.3379730
B	-3.7726650	-1.1757750	-0.3578490
O	-0.4536030	-2.5170180	0.0384630
O	-2.5768520	-2.0678400	-0.1969060
N	-3.3433340	0.3155960	-0.4025190
N	1.1824770	-0.6457190	0.0239070
N	0.2157090	0.1773630	-0.1486280
C	-2.2369210	2.9394570	0.8949220
H	-1.6445790	3.8541400	0.9711570
H	-2.0065990	2.3422860	1.7829650
C	-4.6769120	2.1178200	0.7429630
H	-4.6004380	1.4663870	1.6189170
H	-5.7042540	2.4913240	0.7165360
C	-3.7217450	3.3078330	0.8665220
H	-3.8975600	3.9881020	0.0247440
H	-3.9667310	3.8676130	1.7736280
F	-4.4028640	-1.5226060	-1.5497650
C	7.4115870	0.9797210	0.2101170
H	7.5836230	-0.0366120	-0.1533880
H	8.2563250	1.6111240	-0.0543040
H	7.2849810	0.9701250	1.2957000
O	6.2741470	1.5659710	-0.4315620



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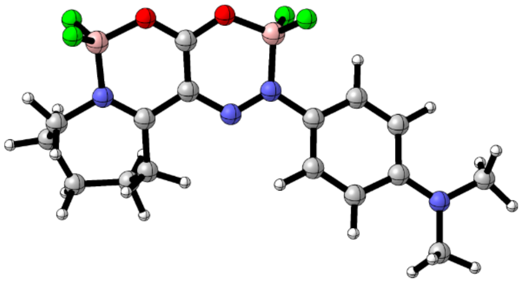
2b 0 1 scf done: 0 1 -1346.480312 Sum of electronic and thermal Free Energies -1346.207742 imag. freq.: 0

C	-1.0173630	-1.6361740	-0.0977440
C	-0.7378660	-0.2379770	-0.1596110
C	-1.8144120	0.7082530	-0.3262150
C	-4.1934130	1.1803820	-0.5388180
H	-5.0568120	0.5536350	-0.7479000
C	-1.5110410	2.1751910	-0.3491150
H	-0.4359490	2.2993310	-0.4348840
C	2.8051800	0.0235620	-0.0334100
C	3.0033720	1.1632670	-0.8177500
C	3.8763880	-0.5438530	0.6594680
C	4.2661020	1.7336780	-0.8920590

H	2.1740560	1.5861220	-1.3680750
C	5.1346440	0.0414480	0.5721350
H	3.7282350	-1.4169080	1.2789430
C	5.3553870	1.1852340	-0.2018830
H	4.4117490	2.6153650	-1.5060510
H	5.9579680	-0.3980810	1.1235410
H	-4.0417330	1.8224210	-1.4100200
H	-1.9670840	2.6121710	-1.2428780
C	6.7282480	1.7916900	-0.3196800
H	7.2404310	1.4138810	-1.2109030
H	6.6746540	2.8785200	-0.4105990
H	7.3464470	1.5446440	0.5451100
F	2.1811070	-2.8541360	-0.4328800
F	1.5598020	-2.3377910	1.7196590
F	-4.2751130	-1.4971400	0.6756100
B	1.3398010	-2.1061460	0.3665760
B	-3.4217230	-1.2453320	-0.3943640
O	-0.0694520	-2.4871360	0.0471420
O	-2.2016610	-2.1017520	-0.2154020
N	-3.0377870	0.2596910	-0.4184790
N	1.5074700	-0.5672900	0.0587700
N	0.5176740	0.2262760	-0.1231610
C	-2.0279670	2.9064270	0.9118180
H	-1.4655460	3.8386320	1.0008230
H	-1.7886870	2.3105080	1.7983030
C	-4.4392920	2.0101260	0.7249310
H	-4.3522050	1.3539450	1.5963350
H	-5.4774250	2.3515530	0.6898960
C	-3.5232540	3.2282870	0.8689350
H	-3.7107610	3.9096000	0.0305830
H	-3.7960030	3.7725750	1.7775050
F	-4.0149280	-1.6002510	-1.6020760



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2c 0 1 scf done: 0 1 -1441.171973 Sum of electronic and thermal Free Energies -1440.857623 imag. freq.: 0

C	-1.7430280	-1.6351480	-0.1361860
C	-1.3416060	-0.2737070	-0.1569300
C	-2.3291550	0.7622260	-0.2990400
C	-4.6586260	1.4496380	-0.5031340
H	-5.5745460	0.9067910	-0.7237450
C	-1.8999510	2.1984750	-0.2925780
H	-0.8178300	2.2289750	-0.3739320

C	2.2130830	-0.3466330	-0.0110390
C	2.5290300	0.8573060	-0.6558620
C	3.2452320	-1.0939910	0.5713580
C	3.8309130	1.3115030	-0.7057800
H	1.7438040	1.4271250	-1.1334770
C	4.5513820	-0.6443700	0.5293400
H	3.0281490	-2.0221090	1.0802780
C	4.8889220	0.5780970	-0.1052320
H	4.0358700	2.2336320	-1.2293670
H	5.3163140	-1.2443350	0.9994990
H	-4.4512390	2.0929950	-1.3620890
H	-2.3121830	2.6908150	-1.1790150
F	1.3286960	-3.1343990	-0.5057920
F	0.7548530	-2.6197460	1.6611300
F	-4.9747020	-1.2395430	0.6611940
B	0.5561180	-2.3316570	0.3135300
B	-4.1040130	-1.0350880	-0.4093970
O	-0.8742810	-2.5760230	-0.0186360
O	-2.9660190	-1.9971730	-0.2634790
N	-3.5915010	0.4275230	-0.4013070
N	0.8730560	-0.8030680	0.0549080
N	-0.0414790	0.0824040	-0.1010360
C	-2.3536130	2.9501300	0.9800140
H	-1.7108880	3.8269620	1.0879840
H	-2.1718900	2.3190550	1.8559030
C	-4.8341950	2.2759600	0.7745910
H	-4.8076630	1.5996300	1.6345790
H	-5.8378810	2.7091080	0.7448050
C	-3.8139730	3.4050530	0.9410730
H	-3.9373320	4.1142850	0.1138850
H	-4.0397370	3.9565410	1.8582950
F	-4.7411300	-1.3089320	-1.6196940
N	6.1763940	1.0274900	-0.1457650
C	7.2527710	0.2220350	0.4163210
H	7.3273020	-0.7520510	-0.0792210
H	8.1947360	0.7472450	0.2807790
H	7.1067170	0.0541800	1.4879950
C	6.5005130	2.2734880	-0.8284040
H	5.9460070	3.1148930	-0.4022240
H	7.5623630	2.4741490	-0.7109500
H	6.2770770	2.2183700	-1.8996970

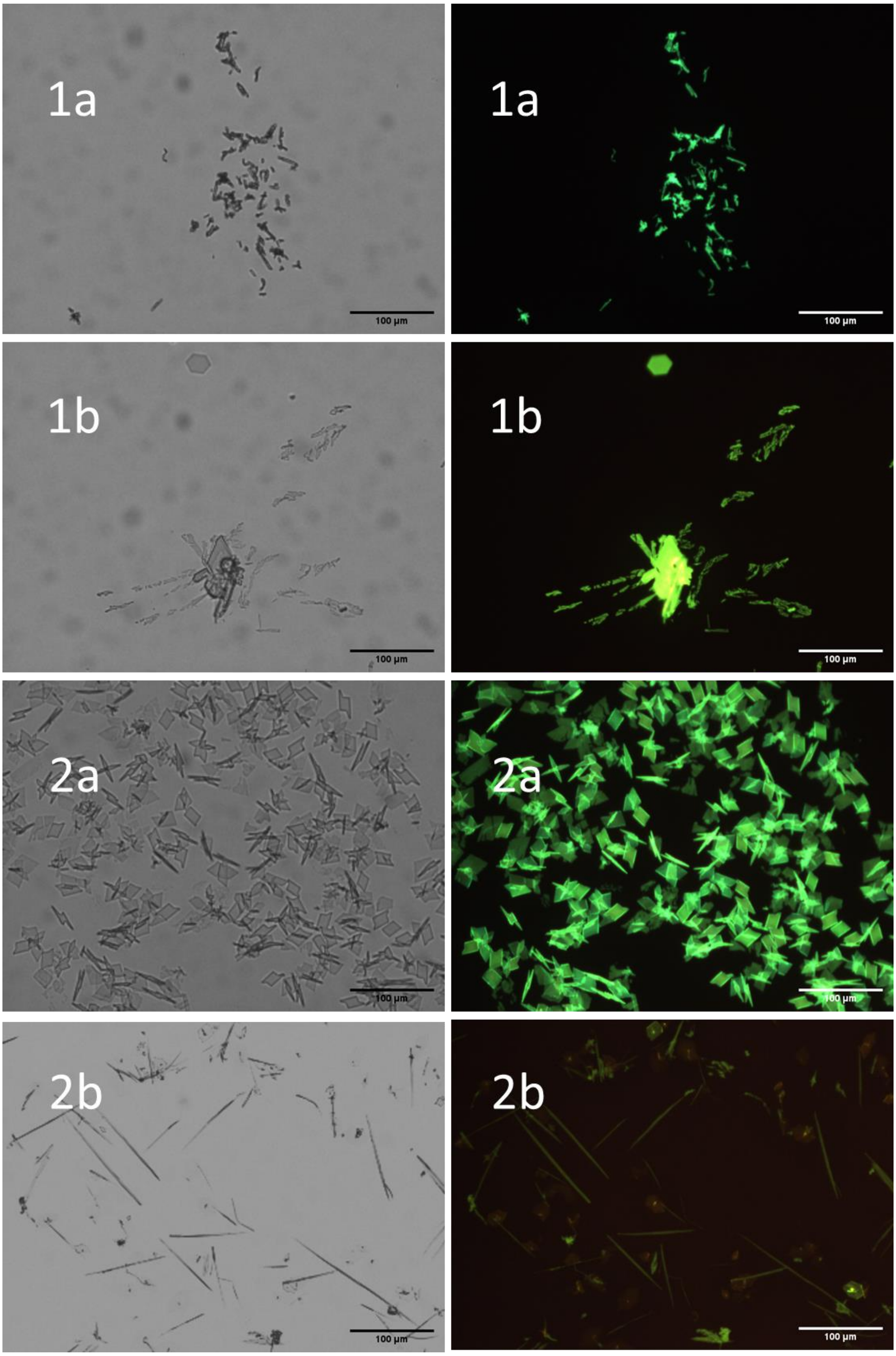

Figure S70 – Bright field (left) and fluorescence images of aggregates in water of samples 1a, 2a, 1b, and 2b.