

## Supporting Information

# Stability of a Series of BODIPYs in Acidic Conditions: An Experimental and Computational Study into the Role of the Substituents at Boron

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## $^{11}\text{B}$ NMR spectra

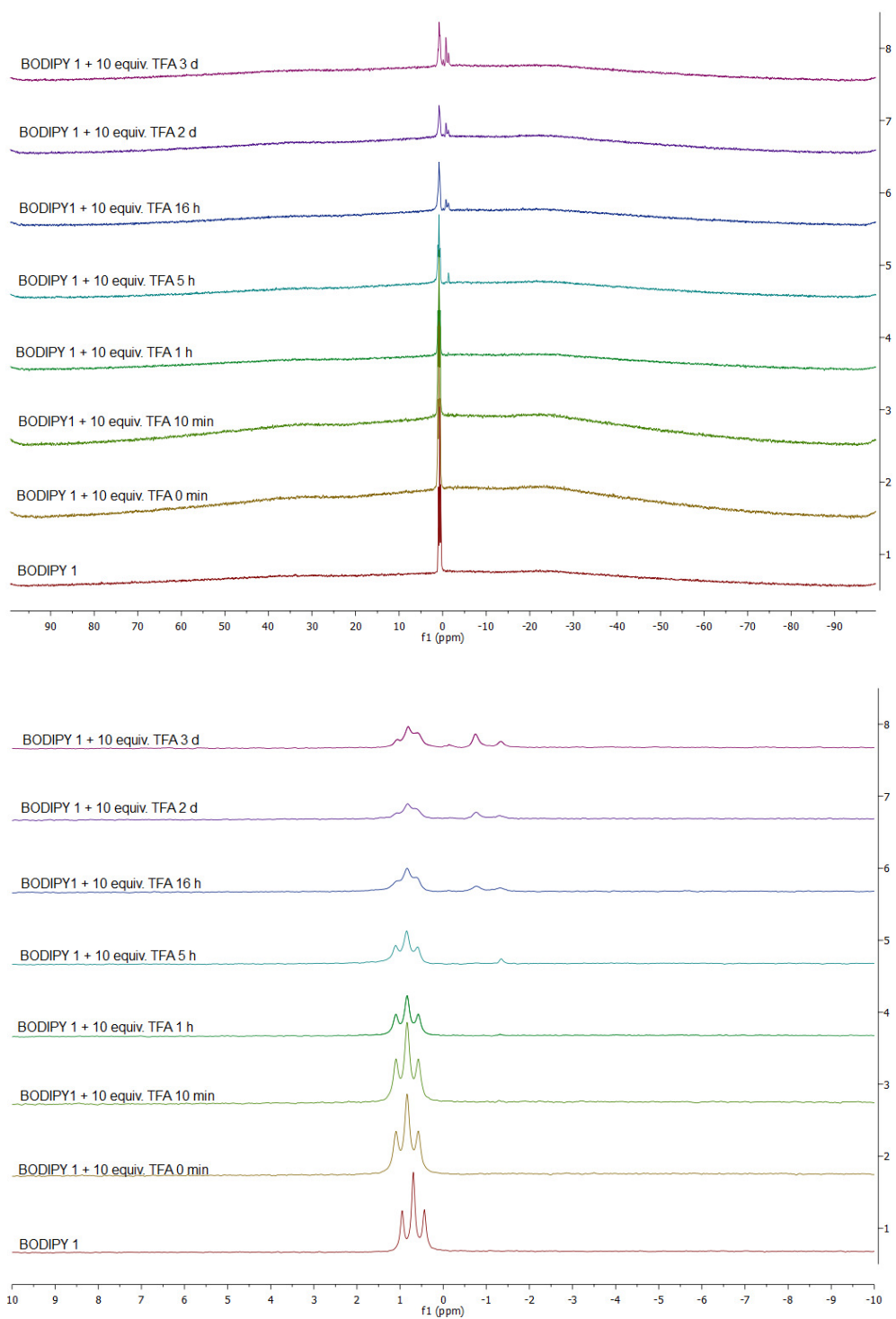


Figure S1.  $^{11}\text{B}$  NMR spectra of BODIPY 1 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

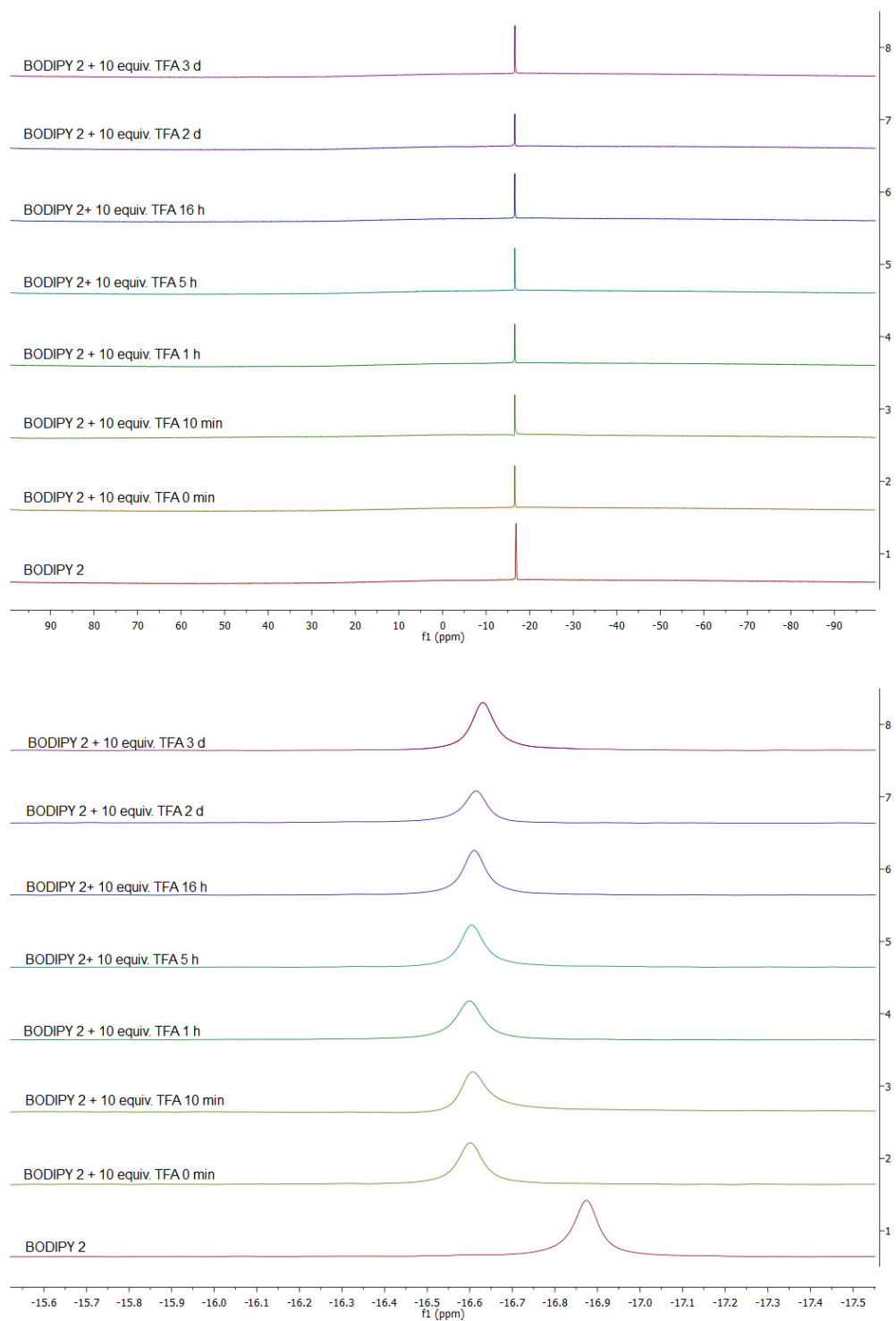


Figure S2.  $^{11}\text{B}$  NMR spectra of BODIPY 2 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

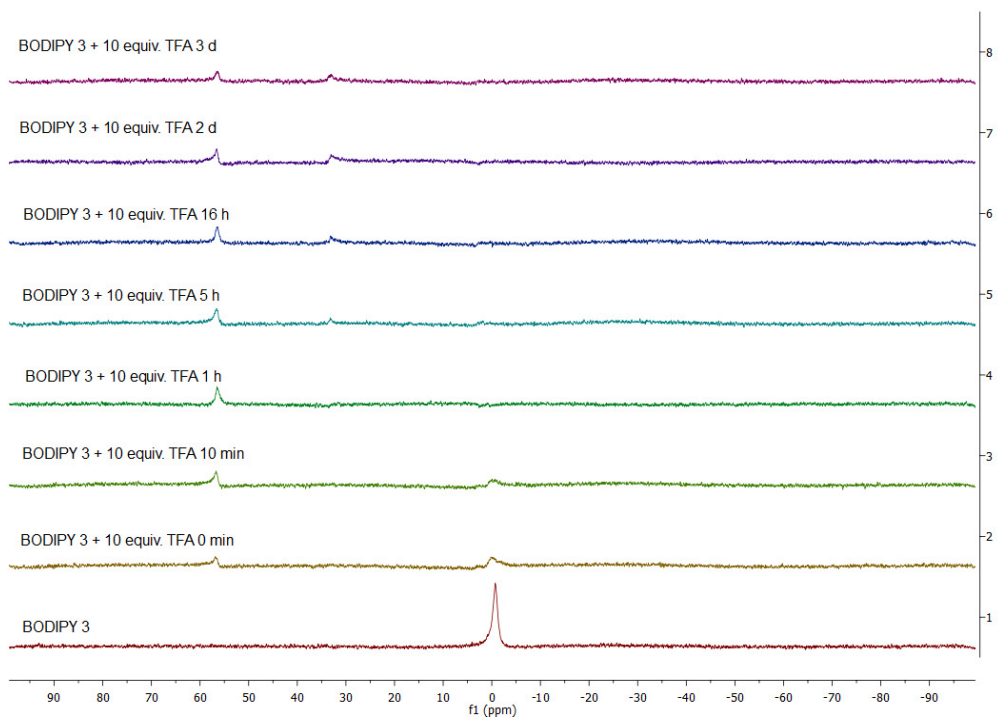


Figure S3.  $^{11}\text{B}$  NMR spectra of BODIPY 3 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

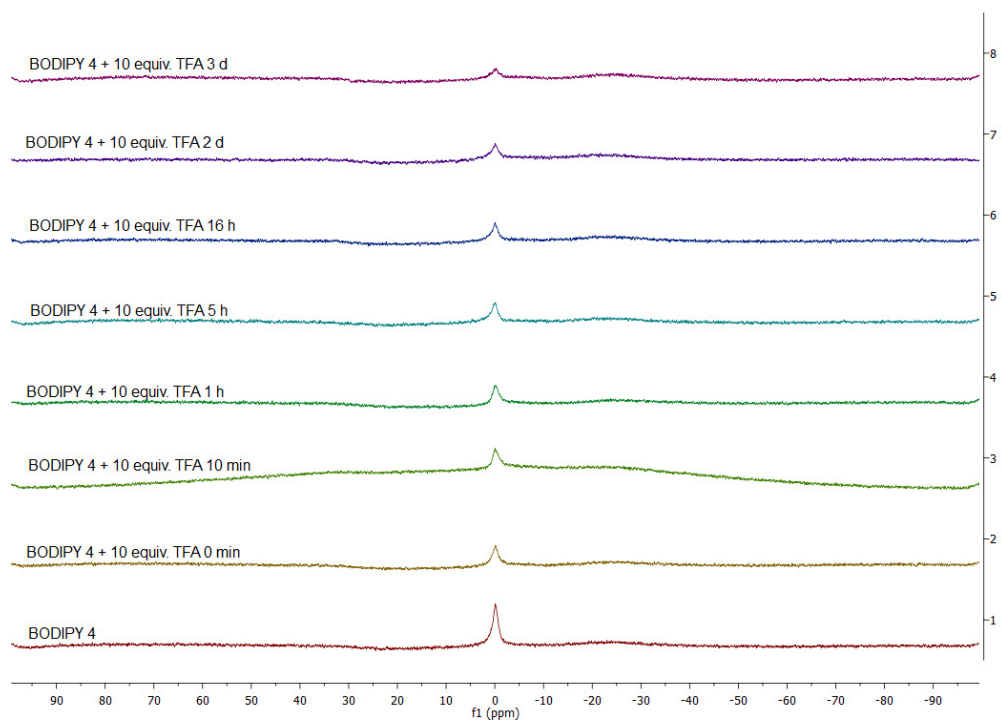


Figure S4.  $^{11}\text{B}$  NMR spectra of BODIPY 4 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

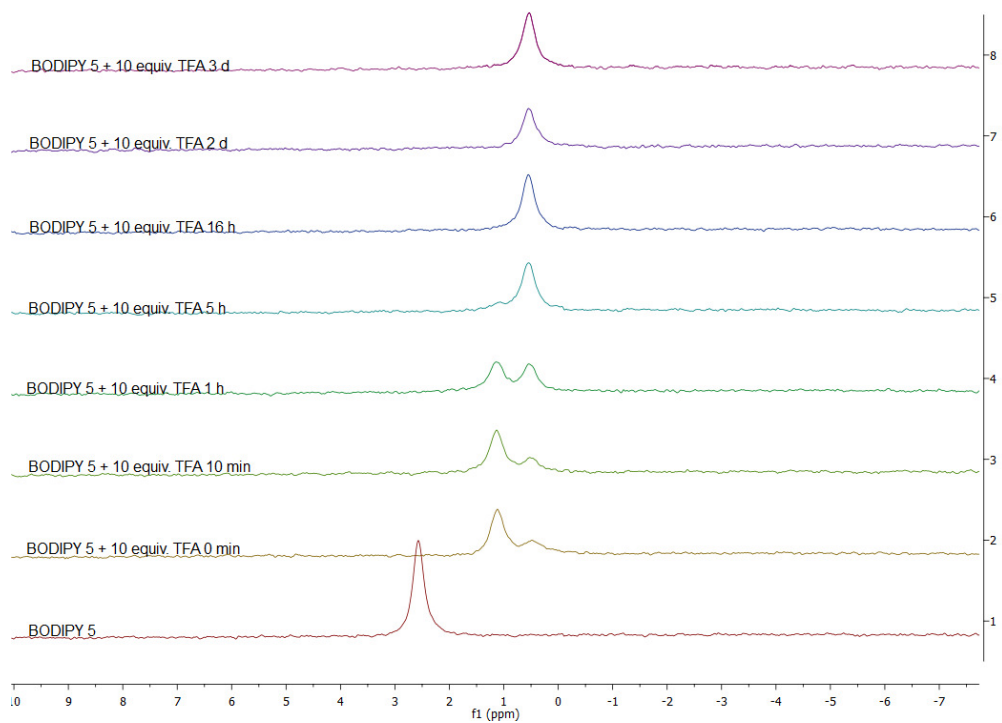
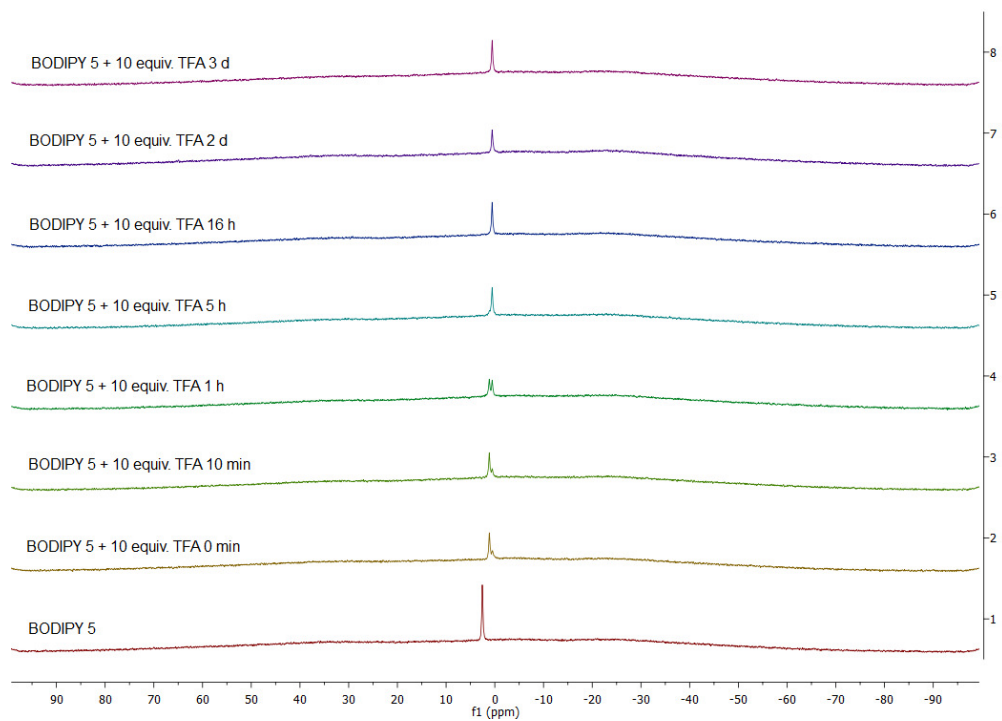


Figure S5.  $^{11}\text{B}$  NMR spectra of BODIPY 5 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

## Calculated Chemical Shifts

Table S1. B3LYP/6-31+G(d,p) calculated  $^{11}\text{B}$  chemical shift ( $\delta$ ) in  $\text{CDCl}_3$  for trivalent and tetravalent possible intermediates and products upon addition of TFA to BODIPYs 1-5.  $\text{BF}_3\text{OEt}_2$  is used as a reference.

Possible products and intermediates	$^{11}\text{B}$ $\delta$ (ppm)	Possible products and intermediates	$^{11}\text{B}$ $\delta$ (ppm)
BX <sub>3</sub> (trivalent)		BX <sub>4</sub> (tetravalent)	
Simple B-containing compounds			
BF <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> )	10.47	[BF <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	1.04
BF(O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub>	12.38	[BF(O <sub>2</sub> CCF <sub>3</sub> ) <sub>3</sub> ] <sup>-</sup>	1.23
BCN <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> )	14.39	[BCN <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	-12.12
BMe <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> )	56.29	[BMe <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	9.81
BPh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub>	45.98	[BPh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	8.28
B(OMe) <sub>2</sub> (OCOCF <sub>3</sub> )	14.82	[B(OMe) <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	2.75
B(O <sub>2</sub> CCF <sub>3</sub> ) <sub>3</sub>	11.34	[B(O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub> ] <sup>-</sup>	-0.75
BODIPYs			
[BODIPY-O <sub>2</sub> CCF <sub>3</sub> ] <sup>+</sup>	20.29	BODIPY-(O <sub>2</sub> CCF <sub>3</sub> ) <sub>2</sub>	-0.77
[BODIPY-F] <sup>+</sup>	18.12	BODIPY-F-O <sub>2</sub> CCF <sub>3</sub>	0.34
[BODIPY-CN] <sup>+</sup>	13.10	BODIPY-CN-O <sub>2</sub> CCF <sub>3</sub>	-8.04
[BODIPY-Me] <sup>+</sup>	31.88	BODIPY-Me-O <sub>2</sub> CCF <sub>3</sub>	2.23
[BODIPY-Ph] <sup>+</sup>	28.51	BODIPY-Ph-O <sub>2</sub> CCF <sub>3</sub>	-0.29
[BODIPY-OMe] <sup>+</sup>	17.86	BODIPY-OMe-O <sub>2</sub> CCF <sub>3</sub>	0.72

Table S2. B3LYP/6-31+G(d,p) calculated  $^{11}\text{B}$  and  $^1\text{H}$  chemical shift ( $\delta$ ) in  $\text{CDCl}_3$  for hydrogen-bonded complexes between TFA and BODIPYs **1-5**.  $\text{BF}_3\text{OEt}_2$  is used as a reference for  $^{11}\text{B}$  and TMS if used as a reference for  $^1\text{H}$ .

Hydrogen bonded complex	$^{11}\text{B}$ $\delta$ (ppm)	$^1\text{H}$ $\delta$ (ppm)
BODIPY <b>1</b> ...THF	1.67	11.31
BODIPY <b>2</b> ...THF	-17.95	12.13
BODIPY <b>2</b> ...(THF) <sub>2</sub>	-17.14	11.92/11.85
BODIPY <b>4</b> ...THF	-2.85	6.69
BODIPY <b>5</b> ...THF	0.64	16.69



## $^1\text{H}$ NMR Spectra

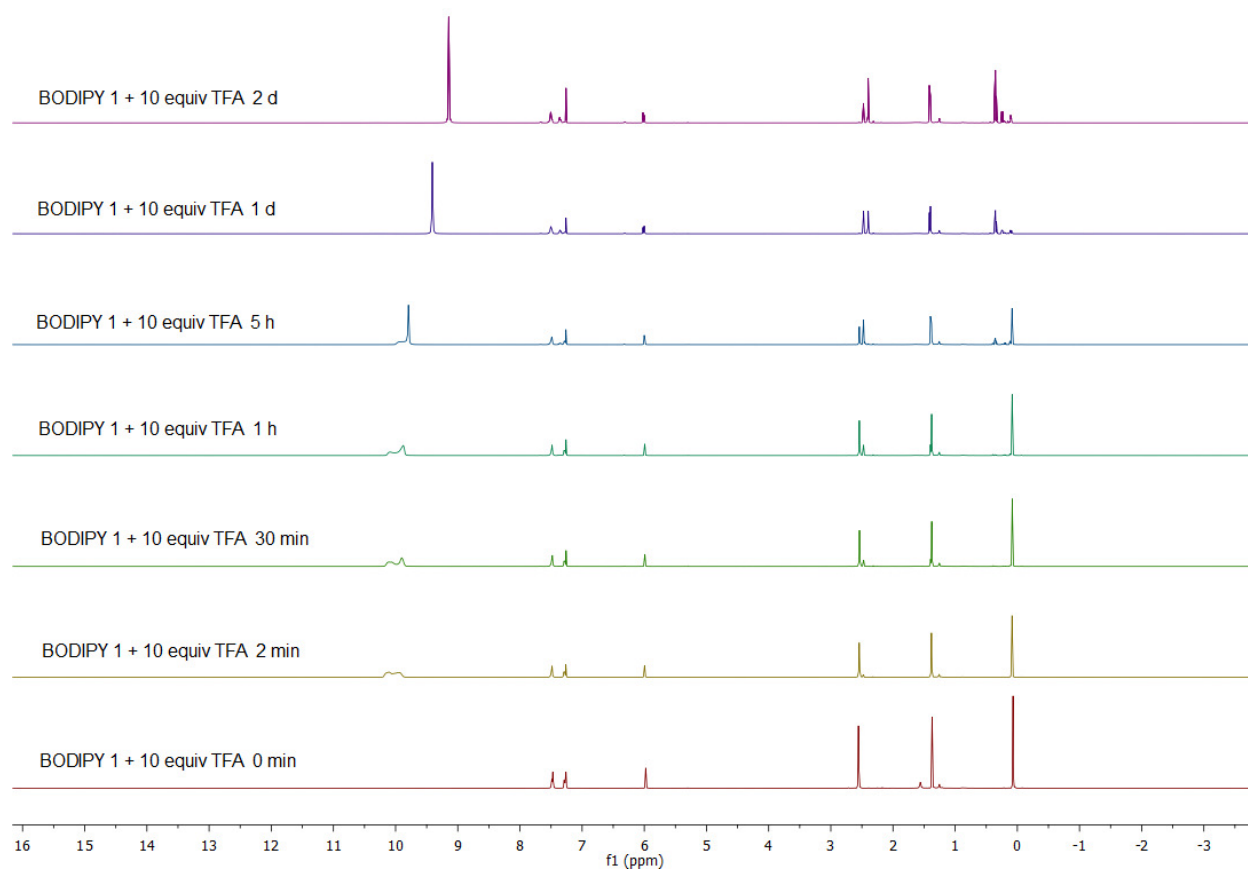


Figure S6.  $^1\text{H}$  NMR spectra of BODIPY 1 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

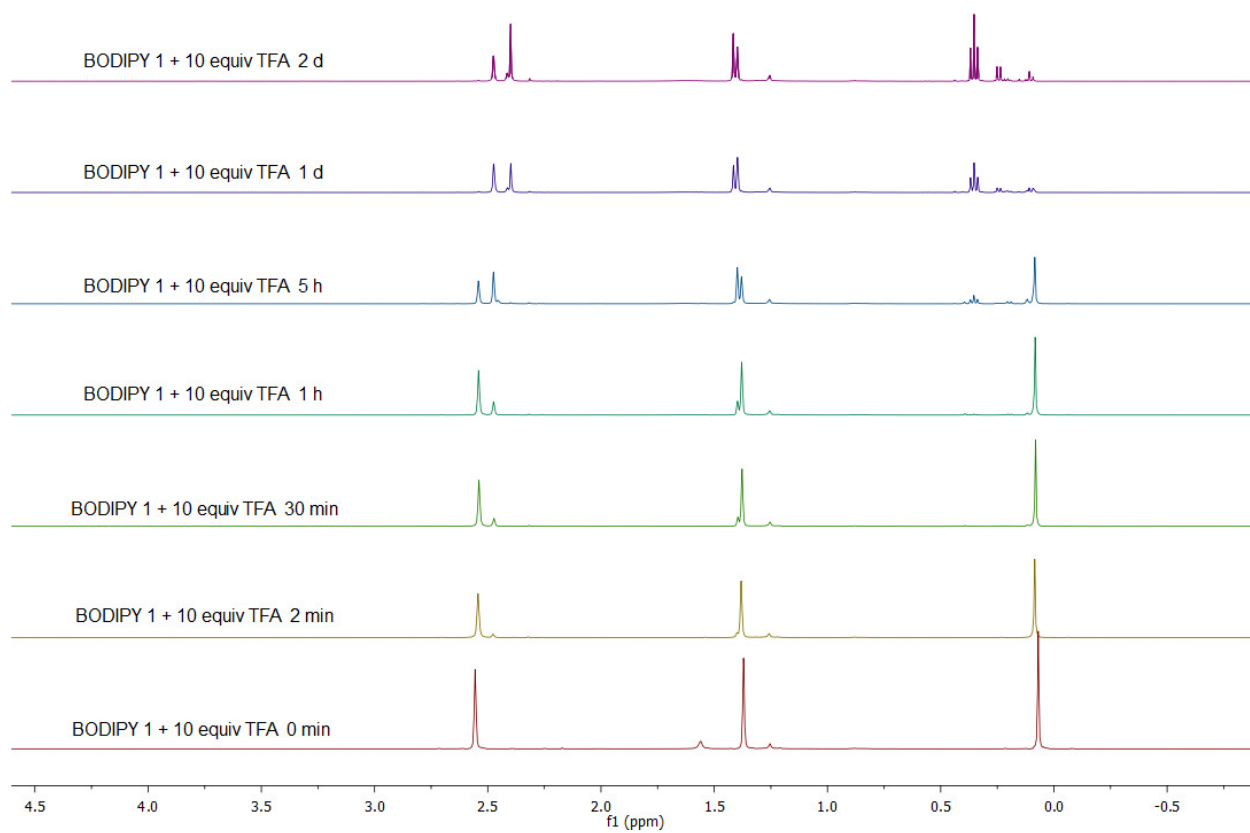


Figure S7. <sup>1</sup>H NMR spectra of BODIPY **1** with 10 equivalents of trifluoroacetic acid in CDCl<sub>3</sub>.

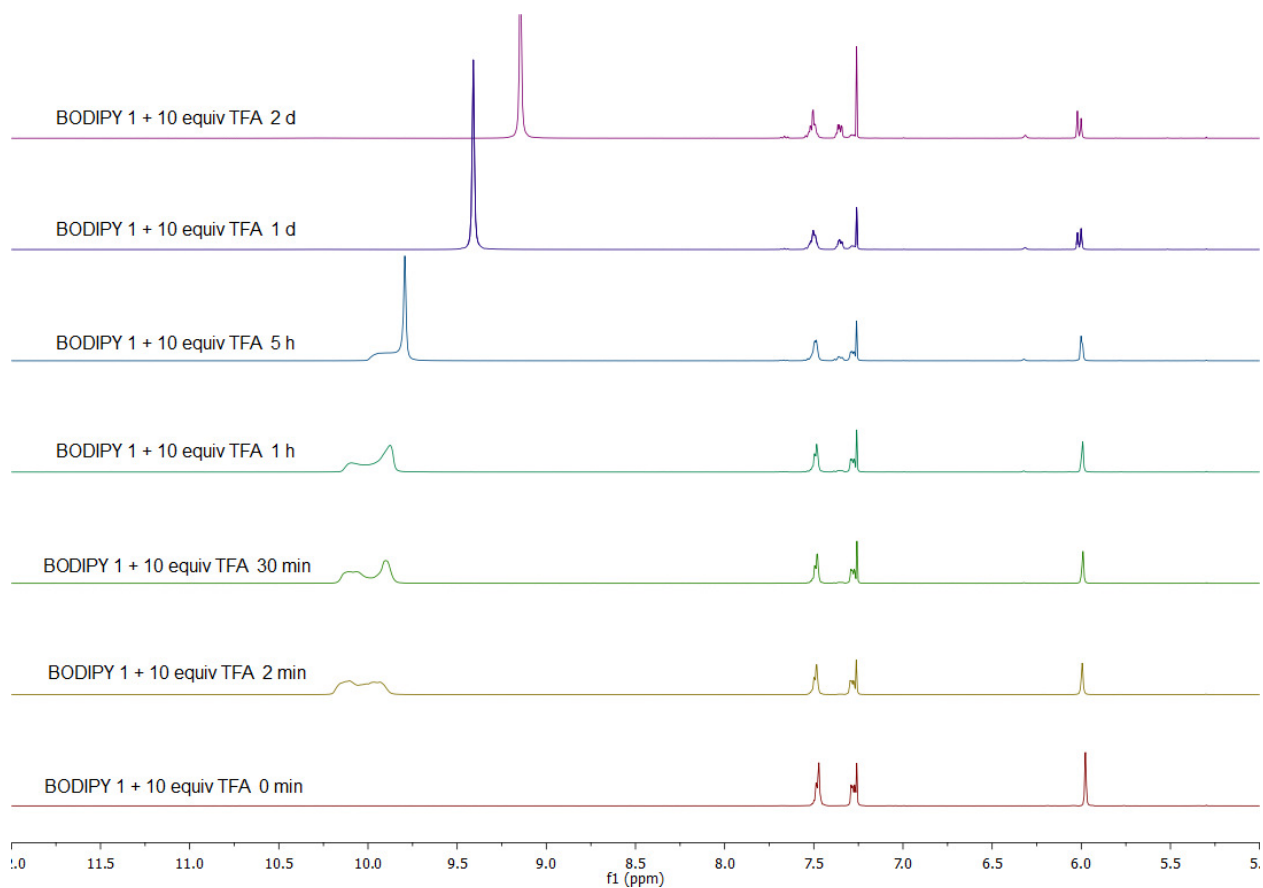


Figure S8.  $^1\text{H}$  NMR spectra of BODIPY 1 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

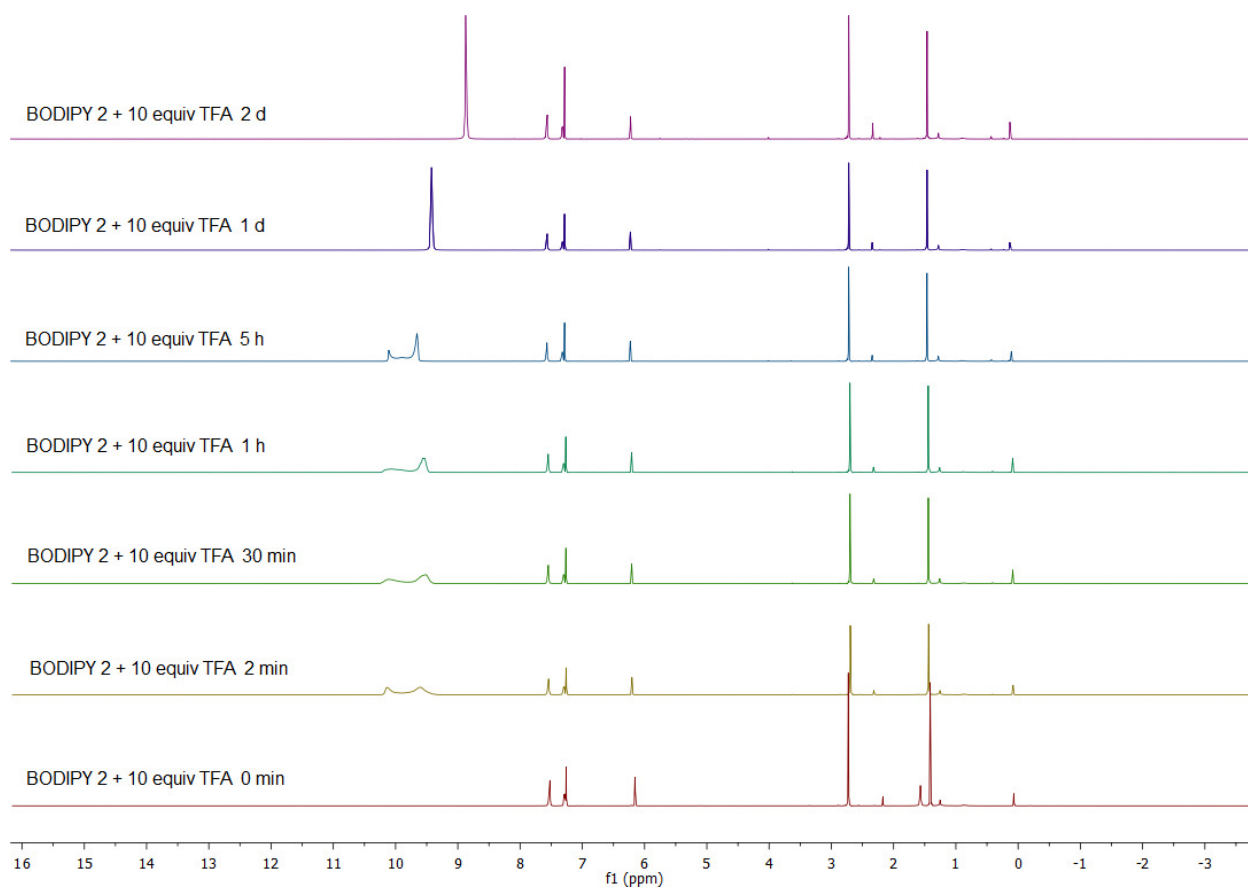
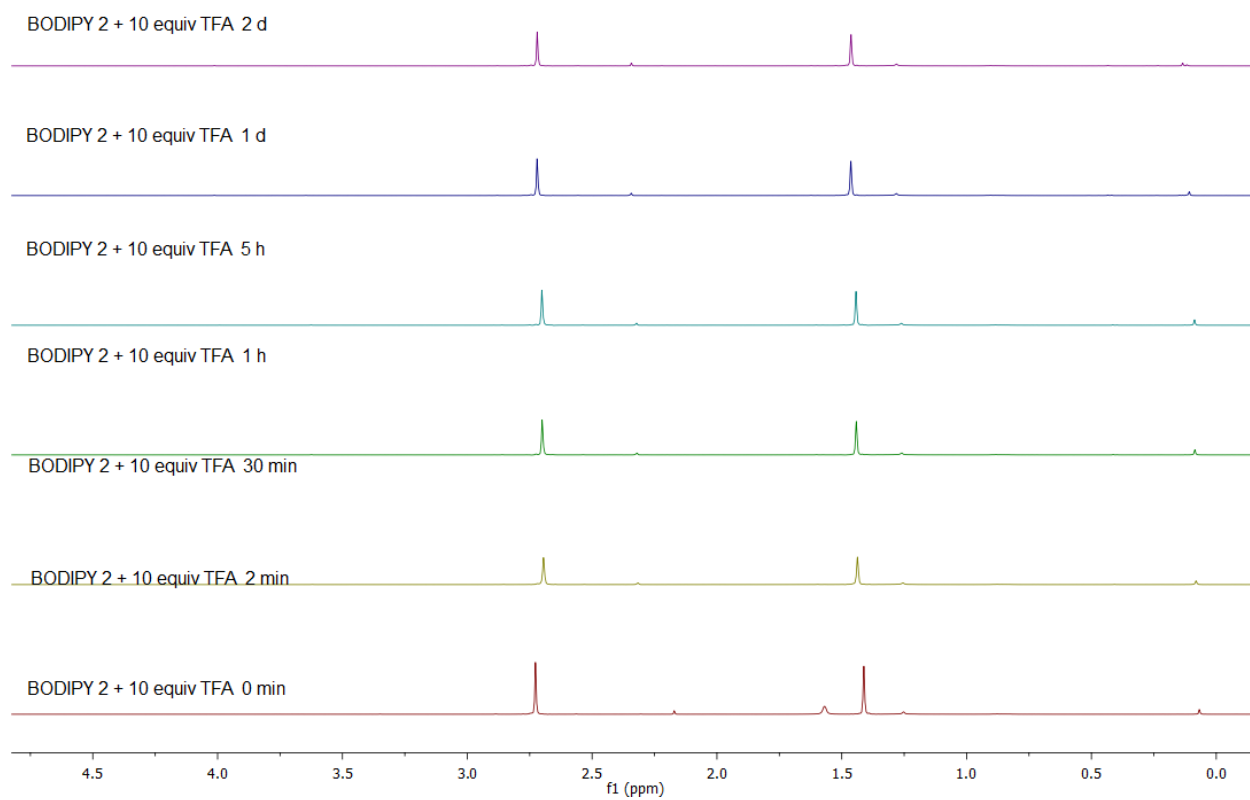


Figure S9.  $^1\text{H}$  NMR spectra of BODIPY 2 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .



*Figure S10.  $^1\text{H}$  NMR spectra of BODIPY 2 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .*

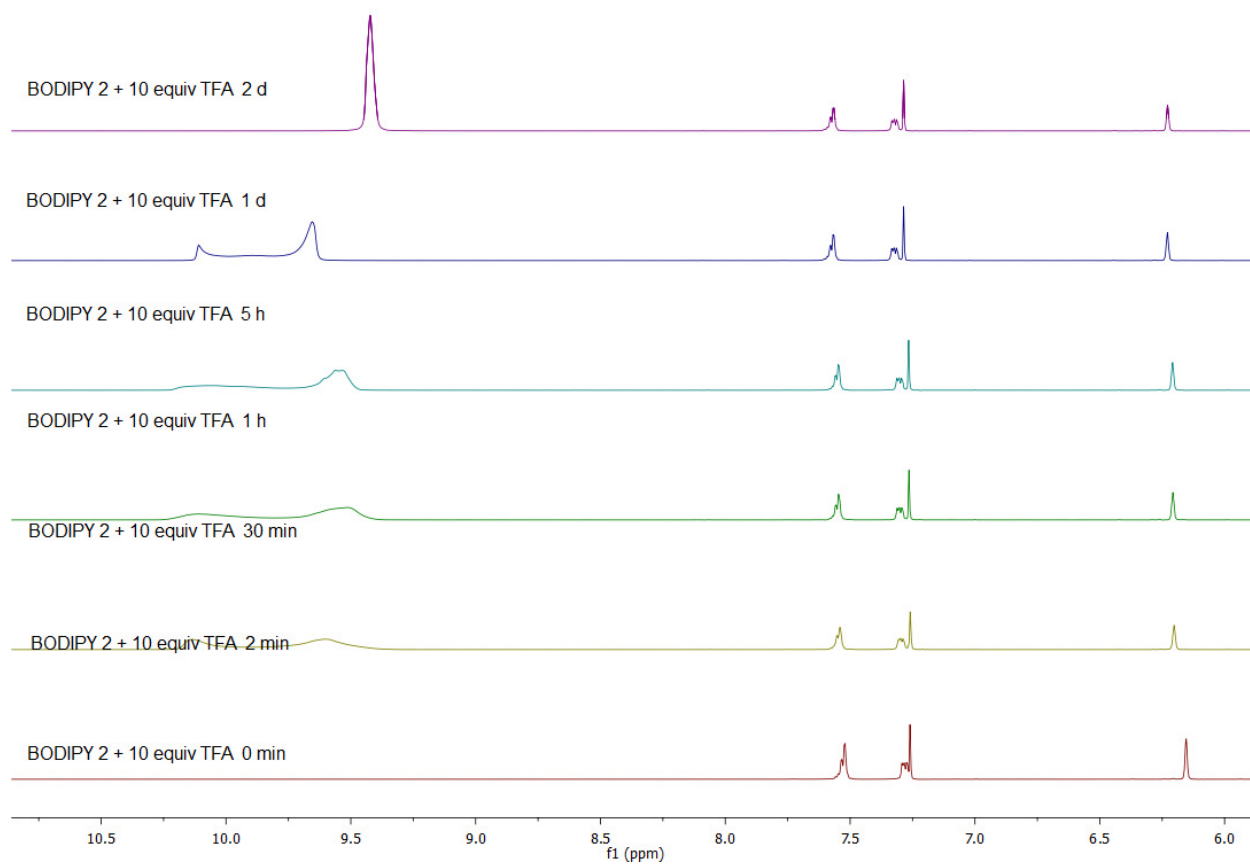


Figure S11.  $^1\text{H}$  NMR spectra of BODIPY 2 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

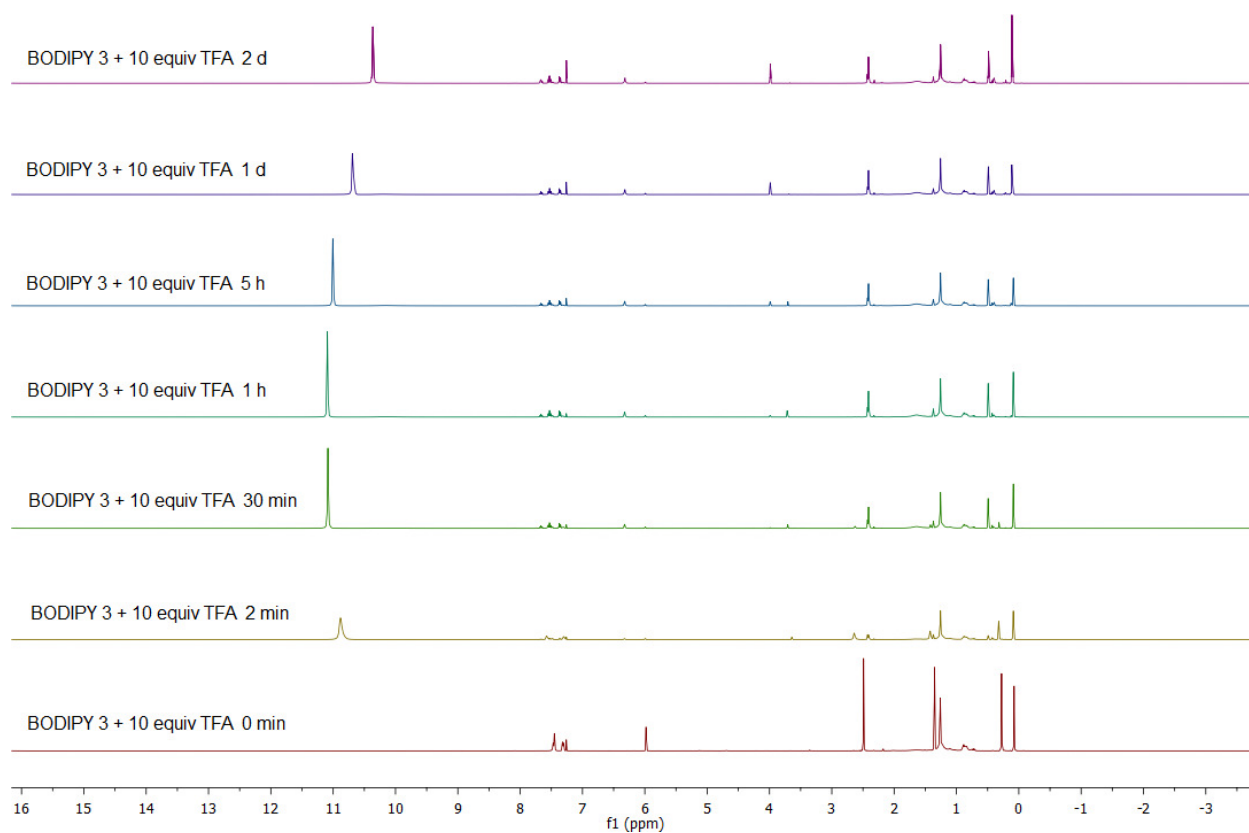


Figure S12.  $^1\text{H}$  NMR spectra of BODIPY **3** with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

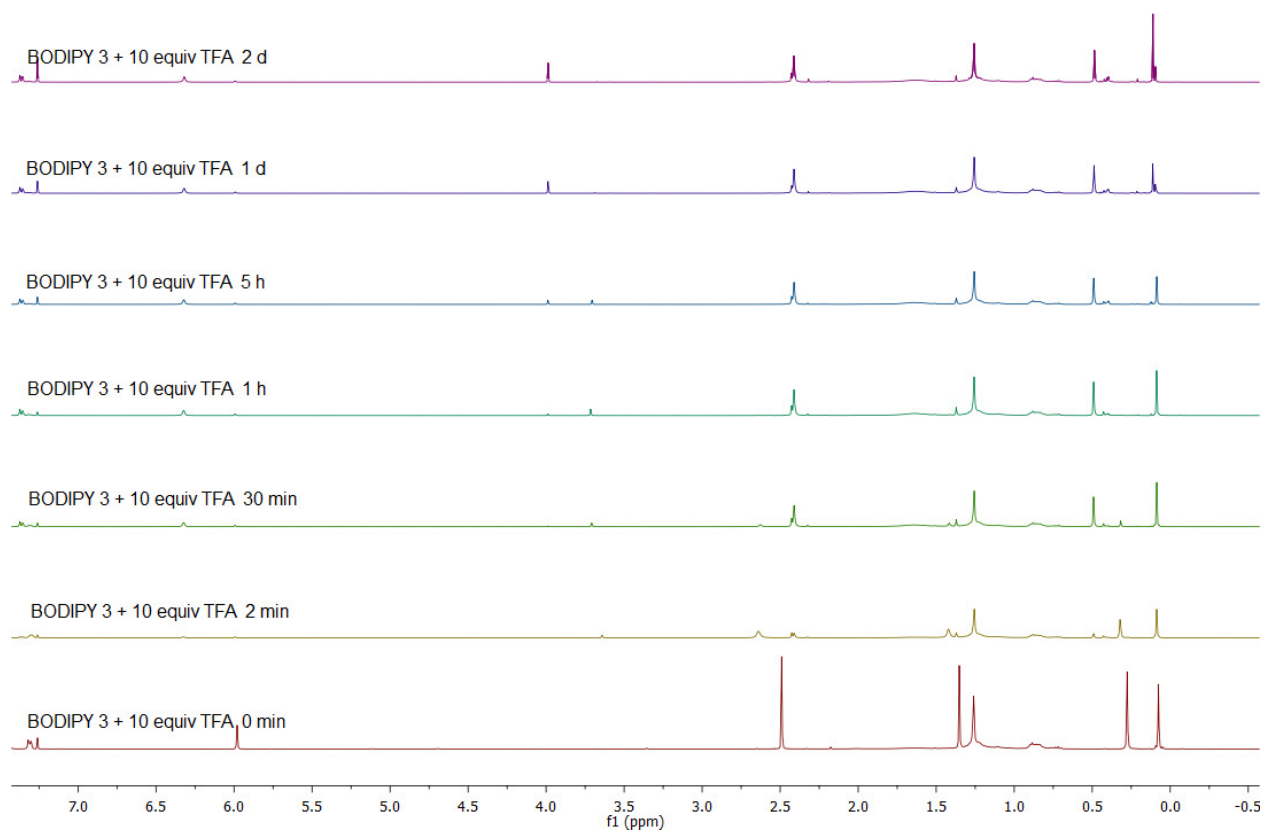


Figure S13.  $^1\text{H}$  NMR spectra of BODIPY 3 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .



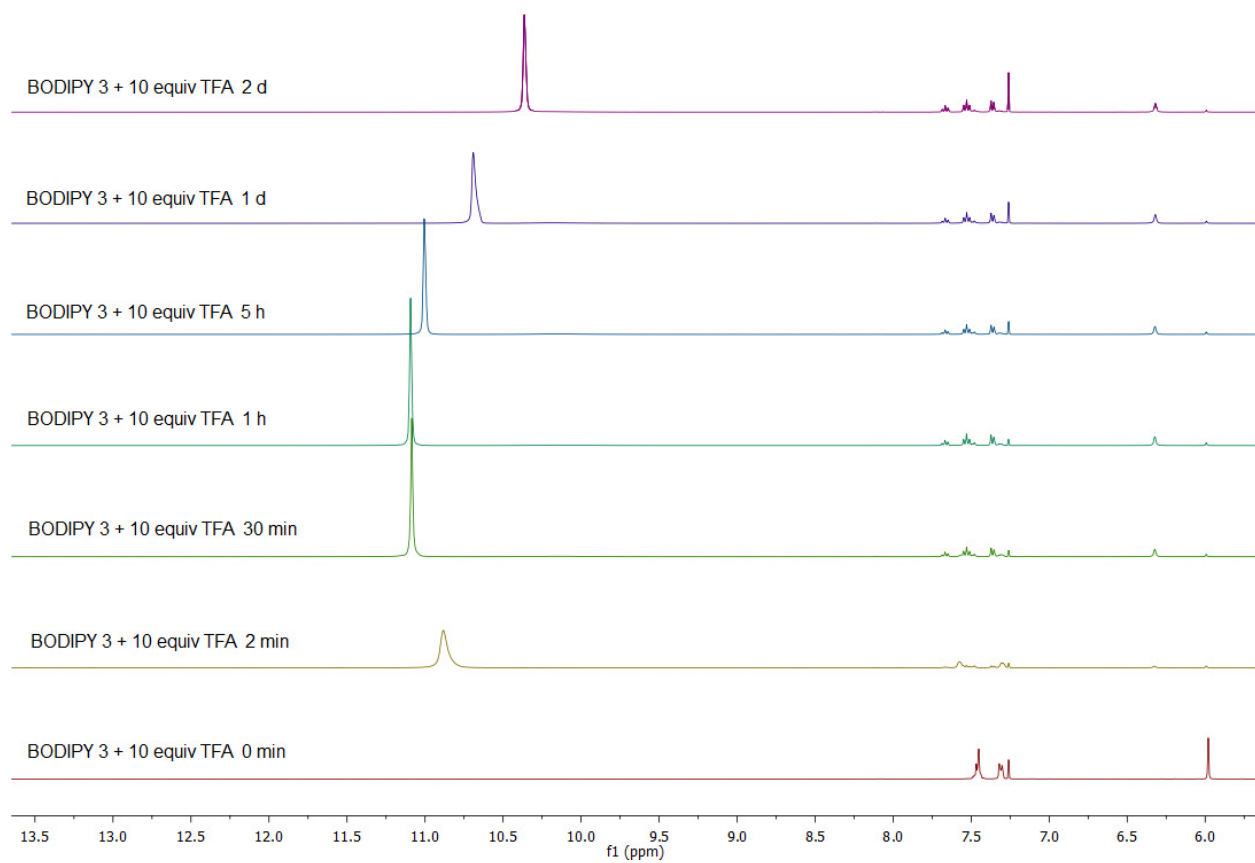


Figure S14.  $^1\text{H}$  NMR spectra of BODIPY 3 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

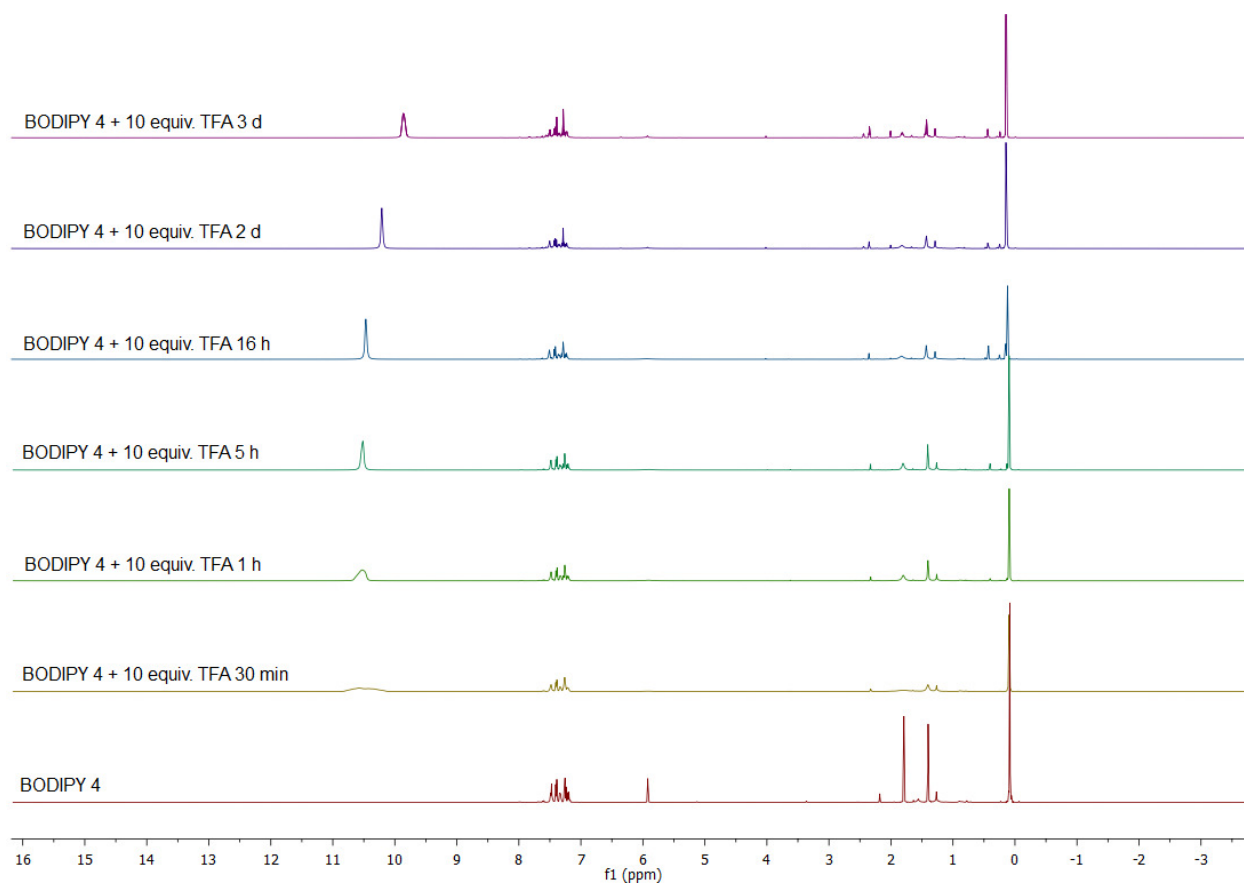
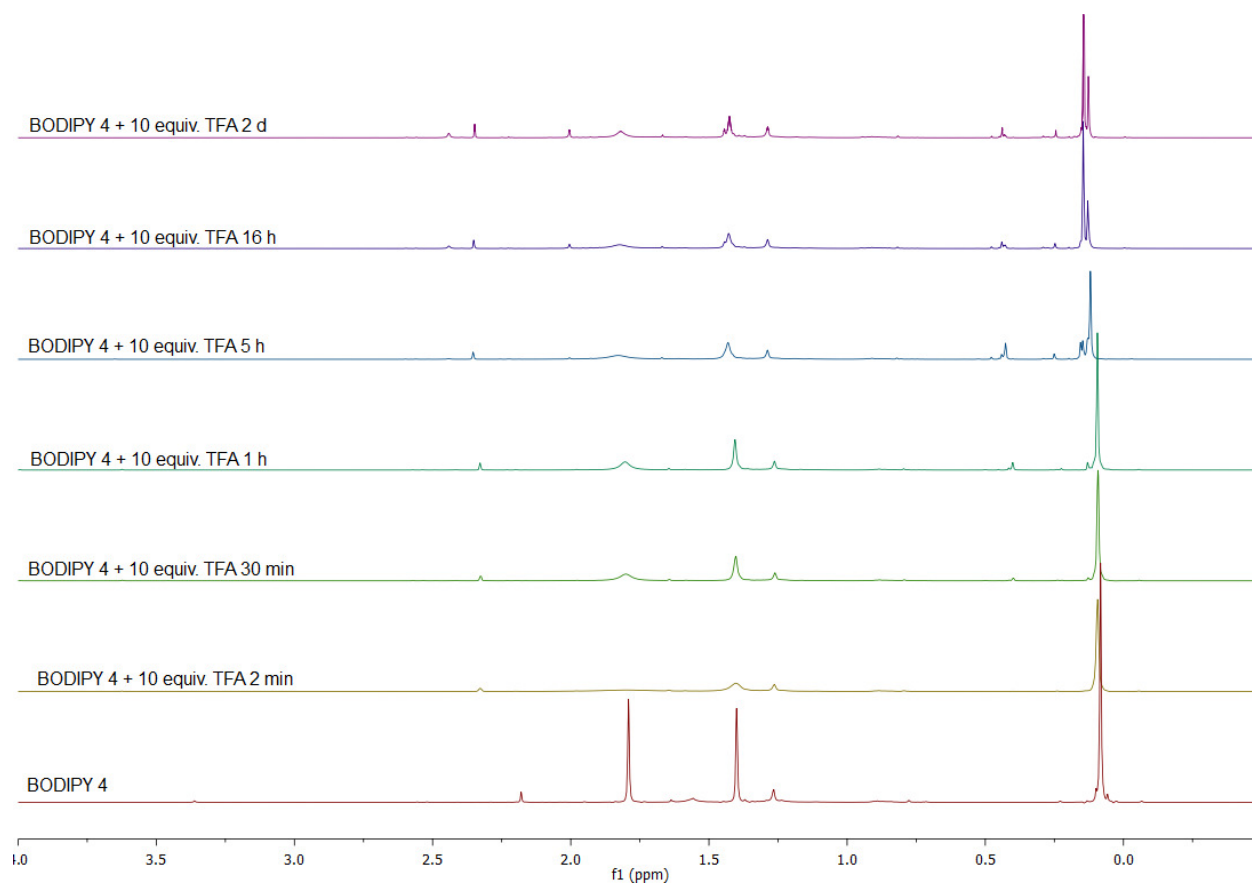
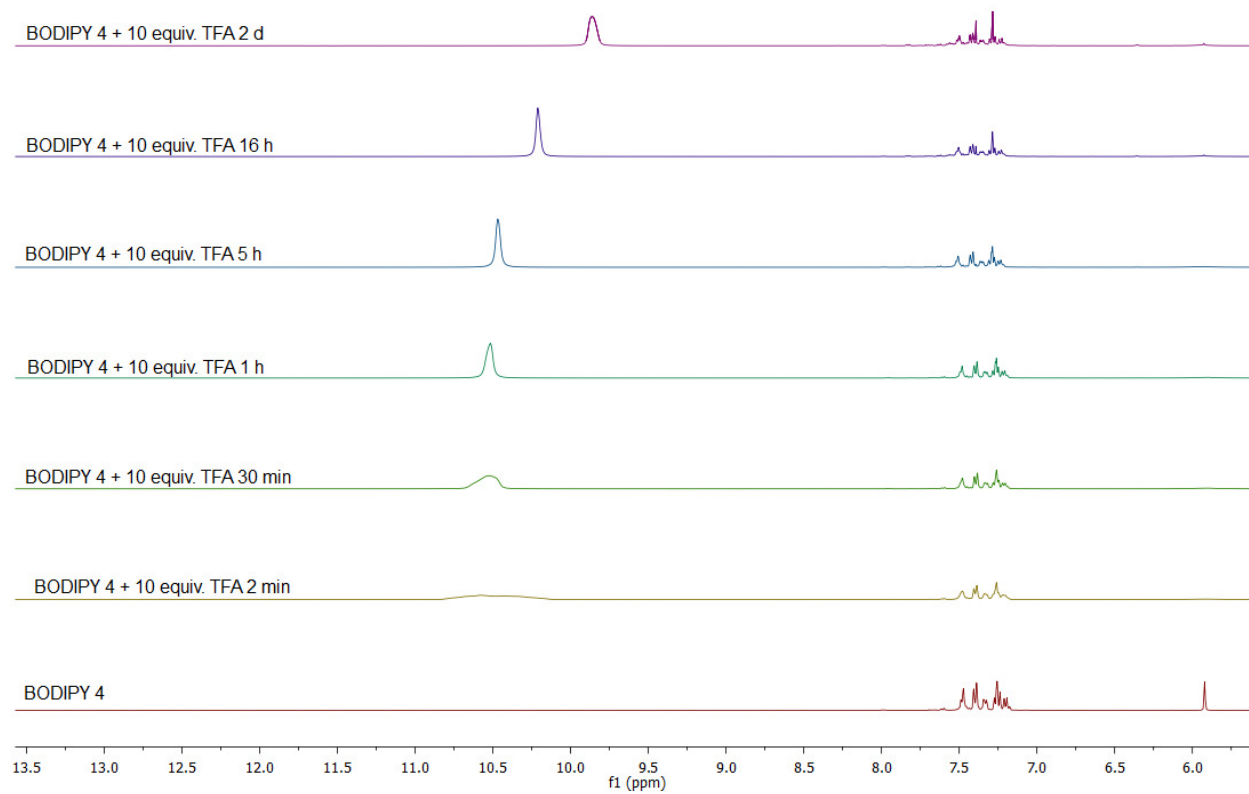


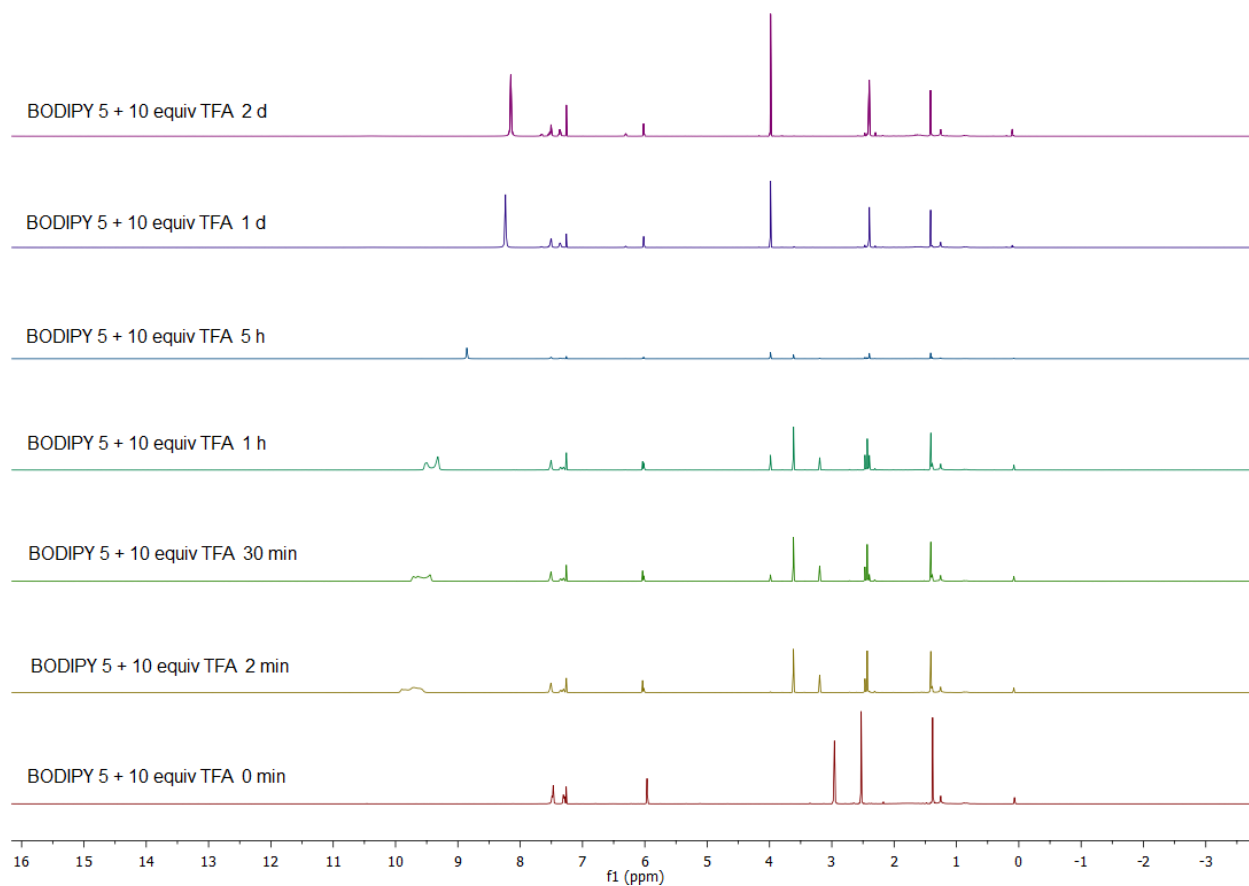
Figure S15. <sup>1</sup>H NMR spectra of BODIPY 4 with 10 equivalents of trifluoroacetic acid in CDCl<sub>3</sub>.



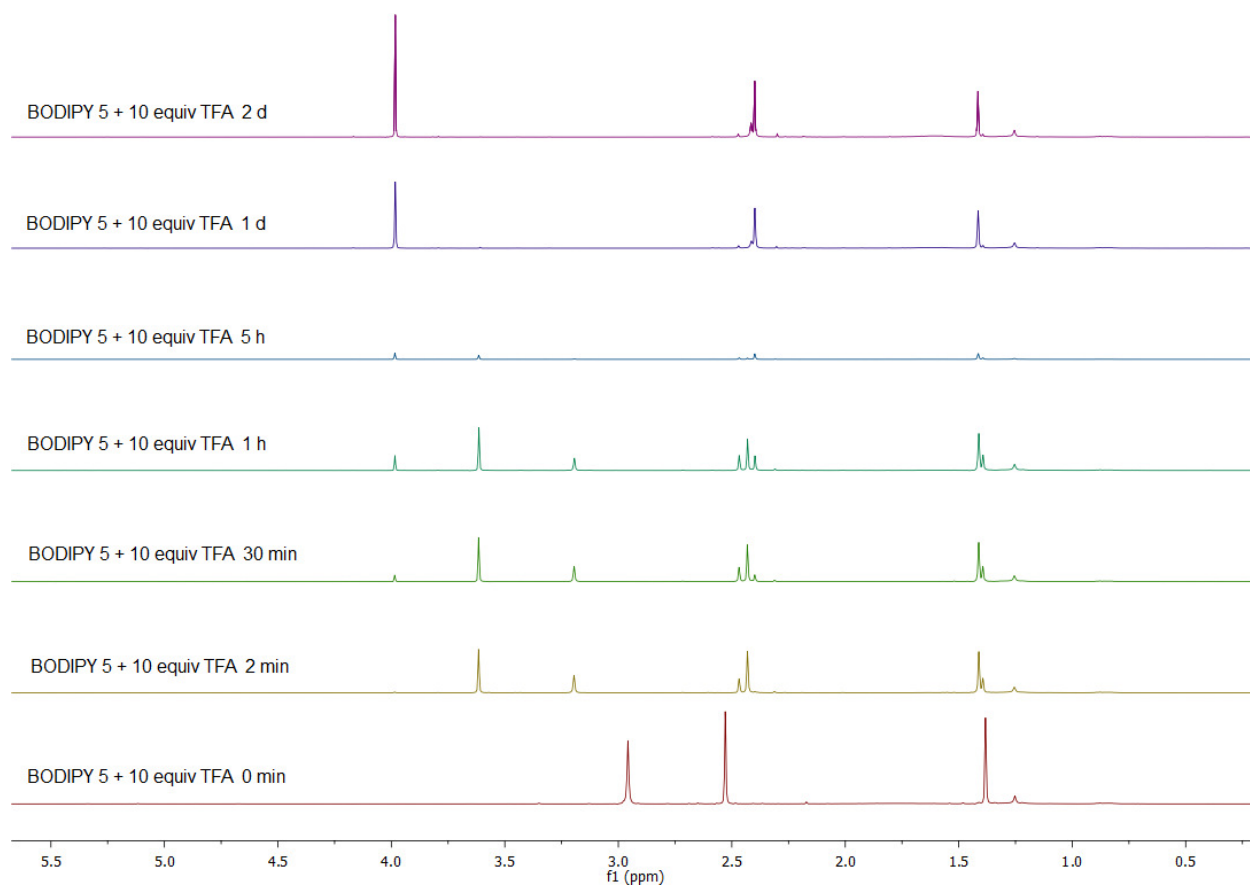
*Figure S16. <sup>1</sup>H NMR spectra of BODIPY 4 with 10 equivalents of trifluoroacetic acid in CDCl<sub>3</sub>.*



*Figure S17. <sup>1</sup>H NMR spectra of BODIPY 4 with 10 equivalents of trifluoroacetic acid in CDCl<sub>3</sub>.*



*Figure S18.  $^1\text{H}$  NMR spectra of BODIPY 5 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .*



*Figure S19.  $^1\text{H}$  NMR spectra of BODIPY 5 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .*

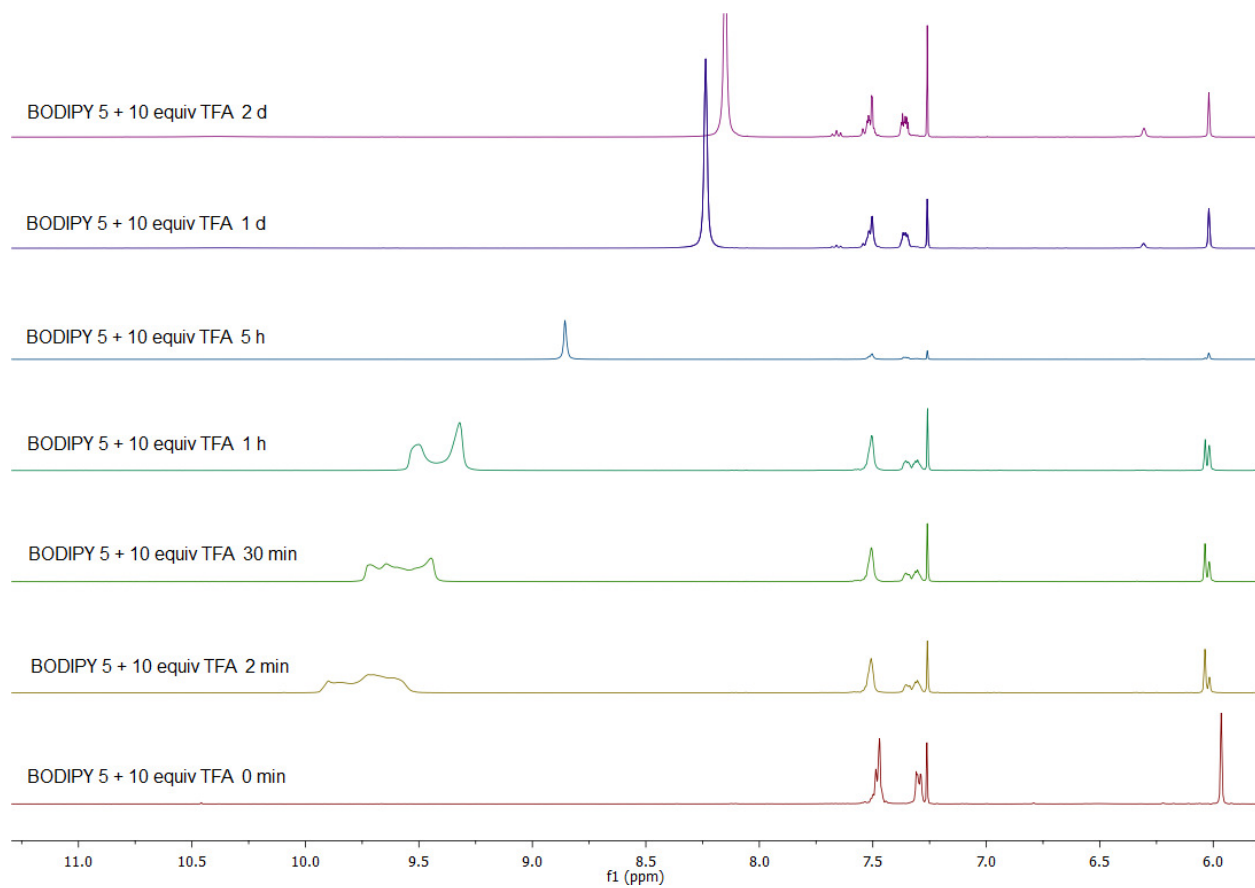


Figure S20.  $^1\text{H}$  NMR spectra of BODIPY 5 with 10 equivalents of trifluoroacetic acid in  $\text{CDCl}_3$ .

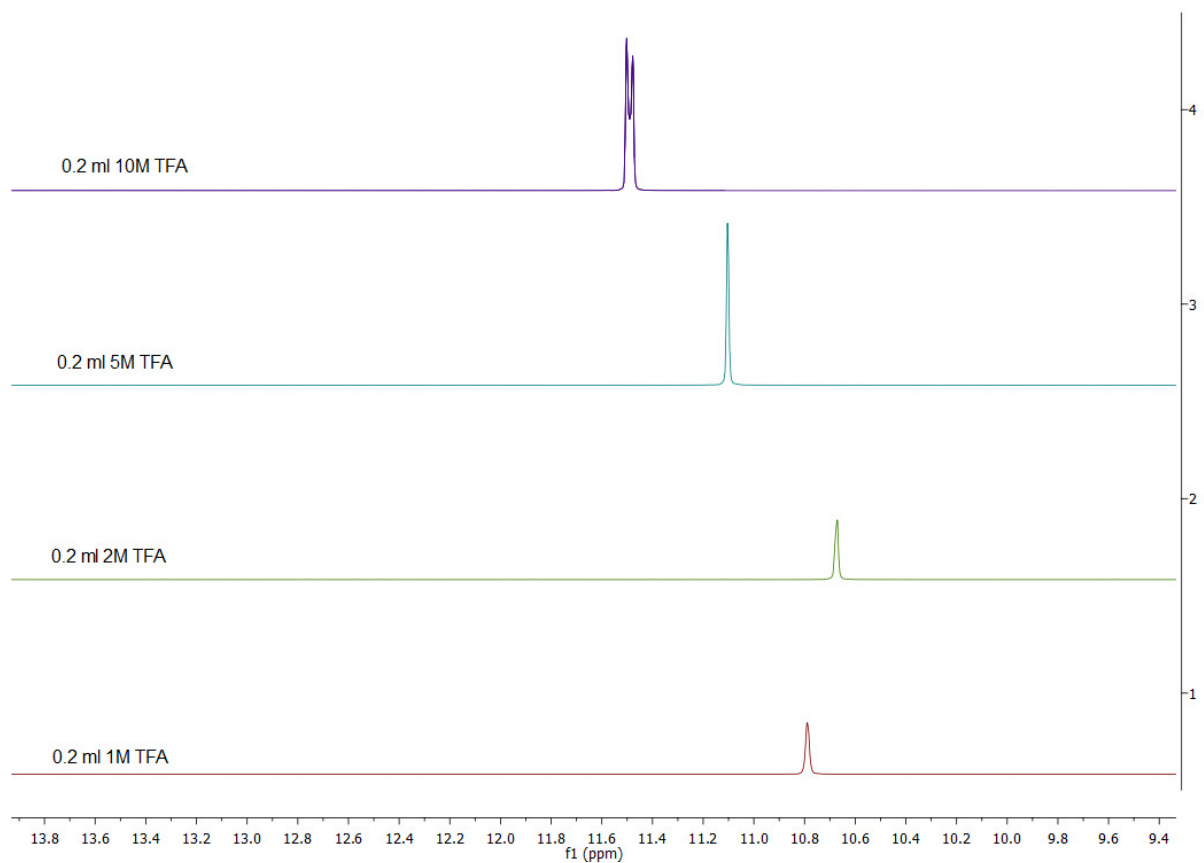


Figure S21.  $^1\text{H}$  NMR spectra of 0.3 M, 0.7 M, 1.7 M, and 3.3 M trifluoroacetic acid in  $\text{CDCl}_3$ .



## TLC Studies

Developing solvent: DCM:hexane=1:1

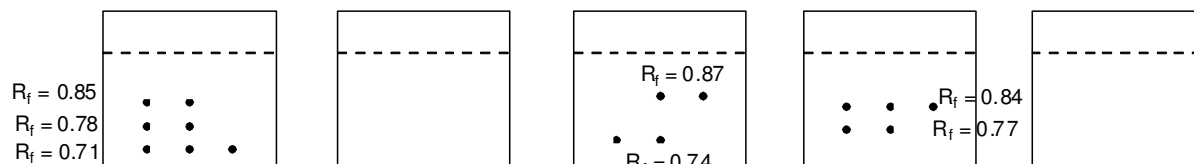


Figure S22. TLC analysis of BODIPY **1-5** and three days after the addition of TFA BODIPY **1'-5'**

## Fluorescence Spectra

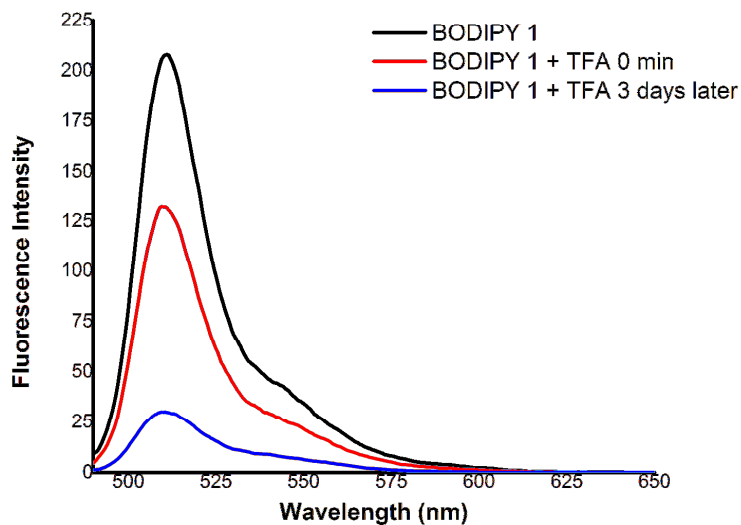


Figure S23. Fluorescence spectra of BODIPY 1 (black) in THF; BODIPY 1 upon addition (red) with addition of 10 equivalents of TFA and after three days (blue) in THF.

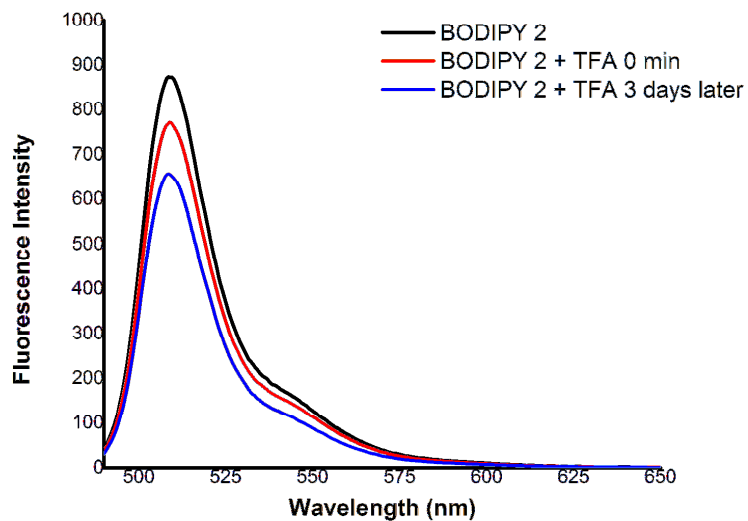


Figure S24. Fluorescence spectra of BODIPY 2 (black) in THF; BODIPY 2 upon addition (red) with addition of 10 equivalents of TFA and after three days (blue) in THF.

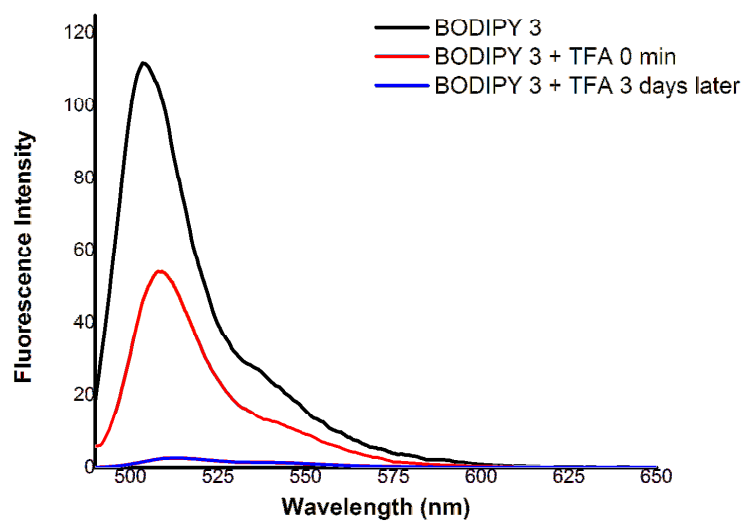


Figure S25. Fluorescence spectra of BODIPY 3 (black) in THF; BODIPY 3 upon addition (red) with addition of 10 equivalents of TFA and after three days (blue) in THF.

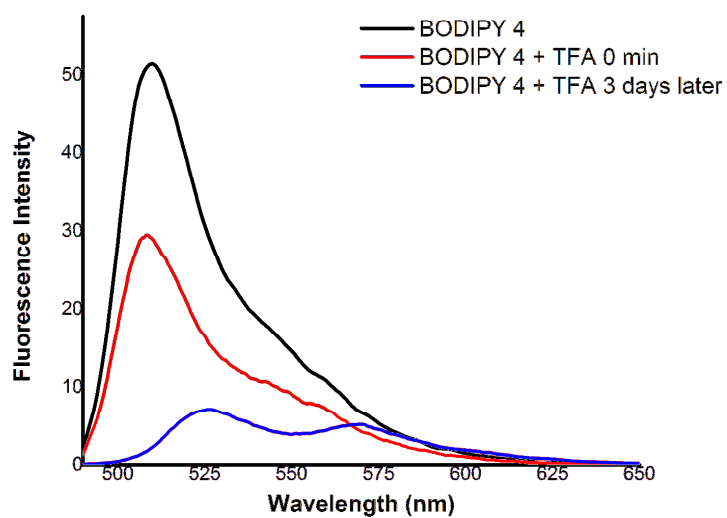


Figure S26. Fluorescence spectra of BODIPY 4 (black) in THF; BODIPY 4 upon addition (red) with addition of 10 equivalents of TFA and after three days (blue) in THF.

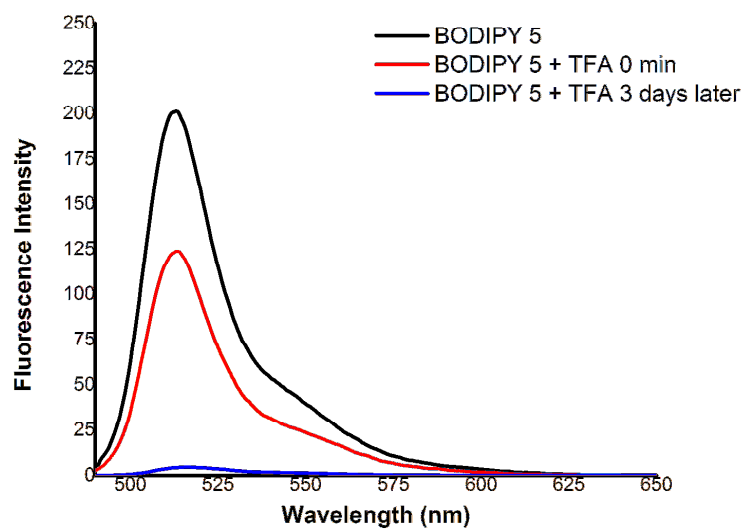
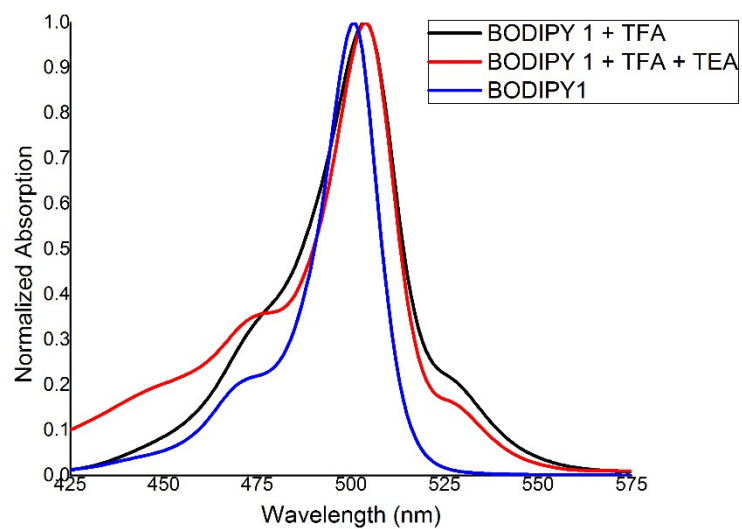


Figure S27. Fluorescence spectra of BODIPY 5 (black) in THF; BODIPY 5 upon addition (red) with addition of 10 equivalents of TFA and after three days (blue) in THF.

## UV-Vis Spectra



*Figure S28. Normalized UV-vis spectra of BODIPY 1 (blue) in THF; BODIPY 1 with addition of 10 equivalents of TFA after three days (black) in THF; neutralized sample with excess amount of triethylamine (red).*

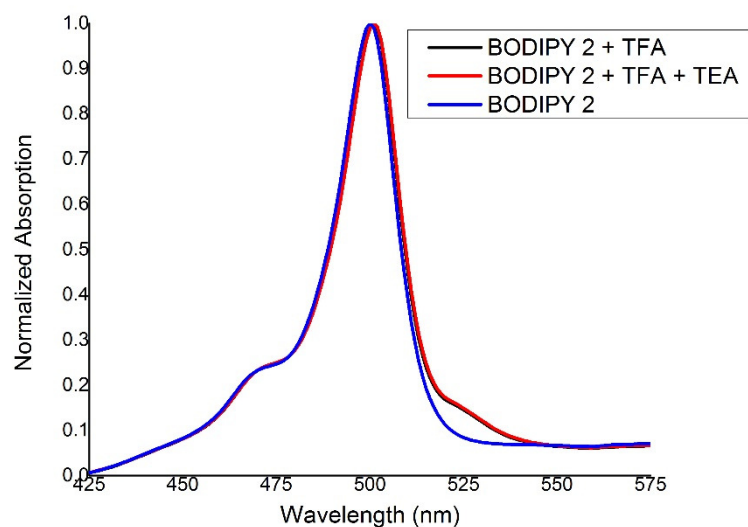


Figure S29. Normalized UV-vis spectra of BODIPY **2** (blue) in THF; BODIPY **2** with addition of 10 equivalents of TFA after three days (black) in THF; neutralized sample with excess amount of triethylamine (red).

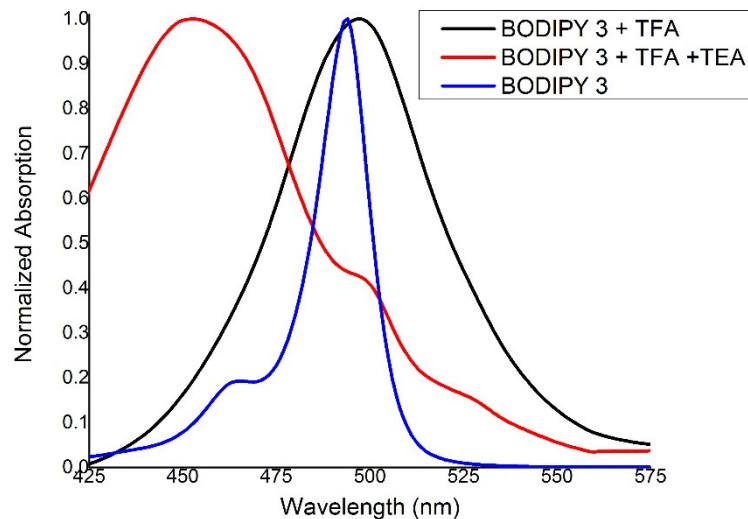


Figure S30. Normalized UV-vis spectra of BODIPY **3** (blue) in THF; BODIPY **3** with addition of 10 equivalents of TFA after three days (black) in THF; neutralized sample with excess amount of triethylamine (red).

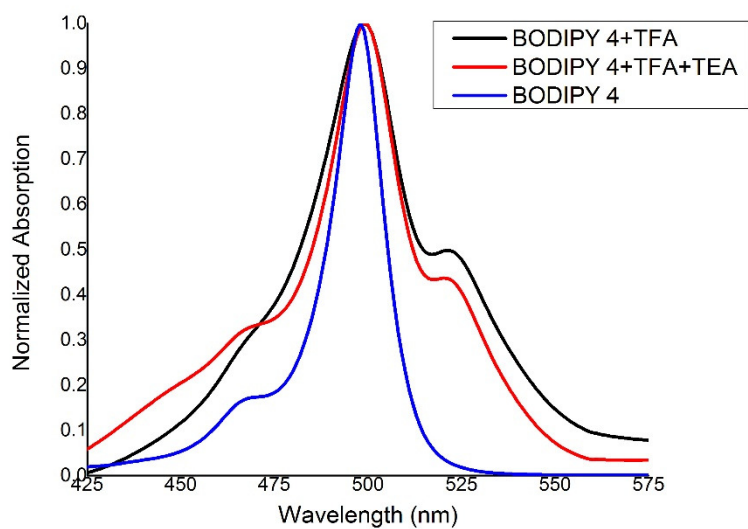


Figure S31. Normalized UV-vis spectra of BODIPY 4 (blue) in THF; BODIPY 4 with addition of 10 equivalents of TFA after three days (black) in THF; neutralized sample with excess amount of triethylamine (red).

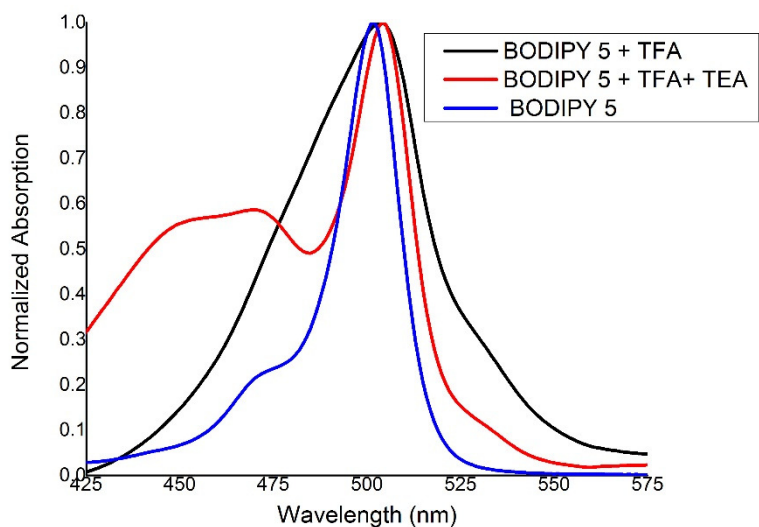


Figure S32. Normalized UV-vis spectra of BODIPY 5 (blue) in THF; BODIPY 5 with addition of 10 equivalents of TFA after three days (black) in THF; neutralized sample with excess amount of triethylamine (red).

## Frontier Orbitals

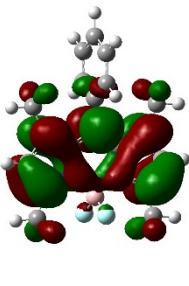
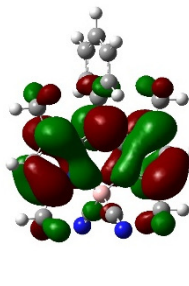
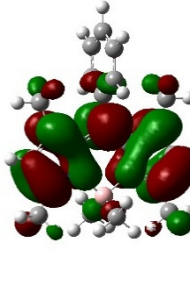
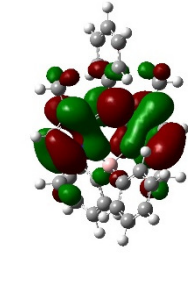
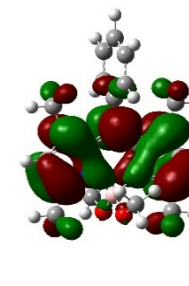
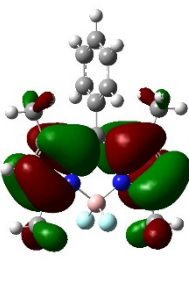
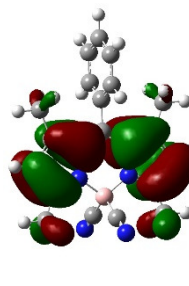
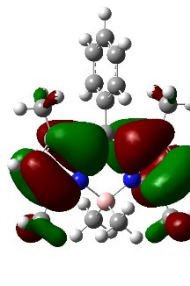
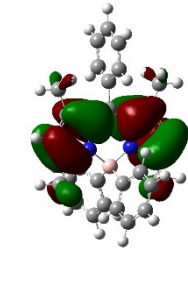
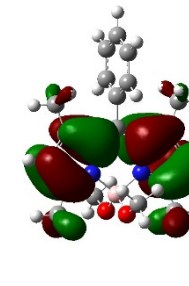
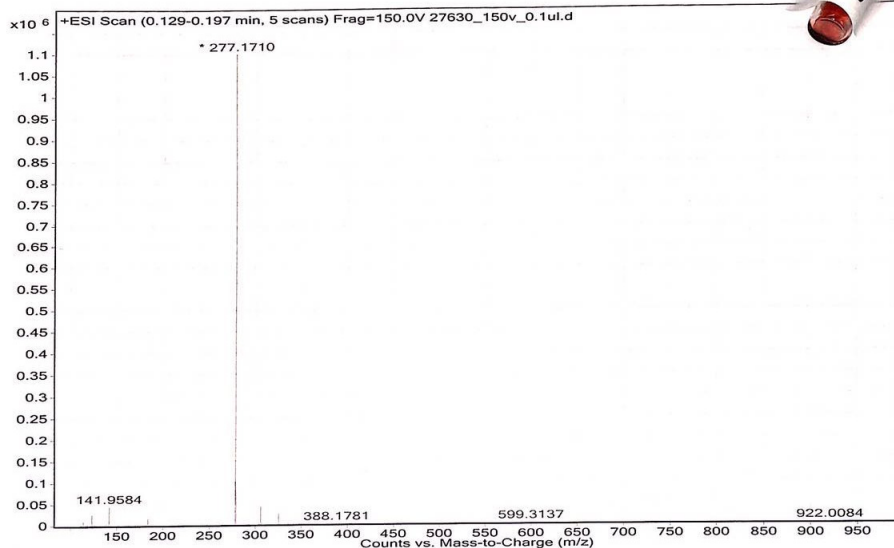
				
-0.0976	-0.1113	-0.0849	-0.0899	-0.0922
				
-0.2072	-0.2227	-0.1981	-0.2020	-0.2022
<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>

Figure S33. Frontier orbitals of BODIPYs **1-5**. Energies in a.u.

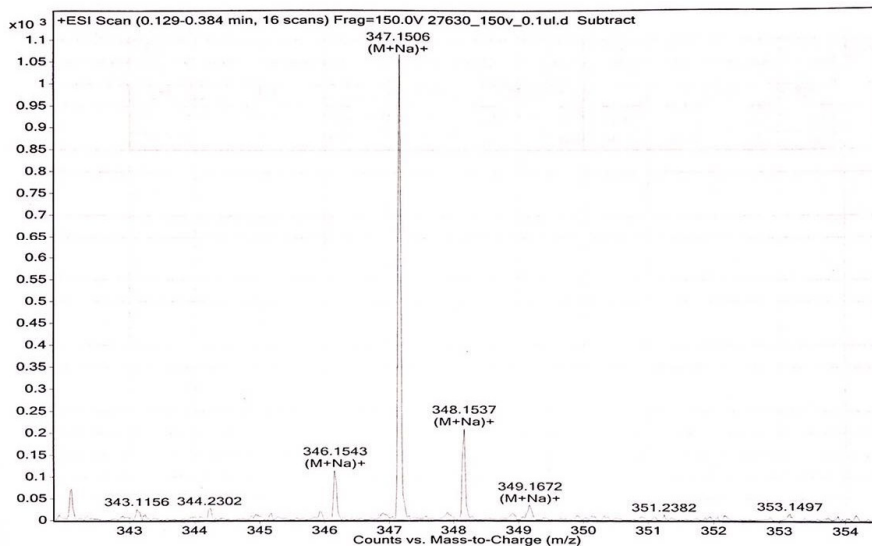


# Mass Spectrometry Studies

**Sample Name** Position PI-C1 **Instrument Name** Instrument 1 **User Name**  
**Inj Vol** -1 **InjPosition** Sample **IRM Calibration Status**  
**Data Filename** 27630\_150v\_0.1ul.d **ACQ Method** **Comment** **Acquired Time**



**Sample Name** Position PI-C1 **Instrument Name** Instrument 1 **User Name**  
**Inj Vol** -1 **InjPosition** Sample **IRM Calibration Status** Some Ions Missed  
**Data Filename** 27630\_150v\_0.1ul.d **ACQ Method** **Comment** **Acquired Time** 3/13/2017 2:31:47 PM



## MS Formula Results: + Scan (0.129-0.197 min) (27630\_150v\_0.1ul.d)

m/z	Ion	Formula	Abundance
346.1554	(M+Na)+	C19 H19 B F2 N2 Na	311.1

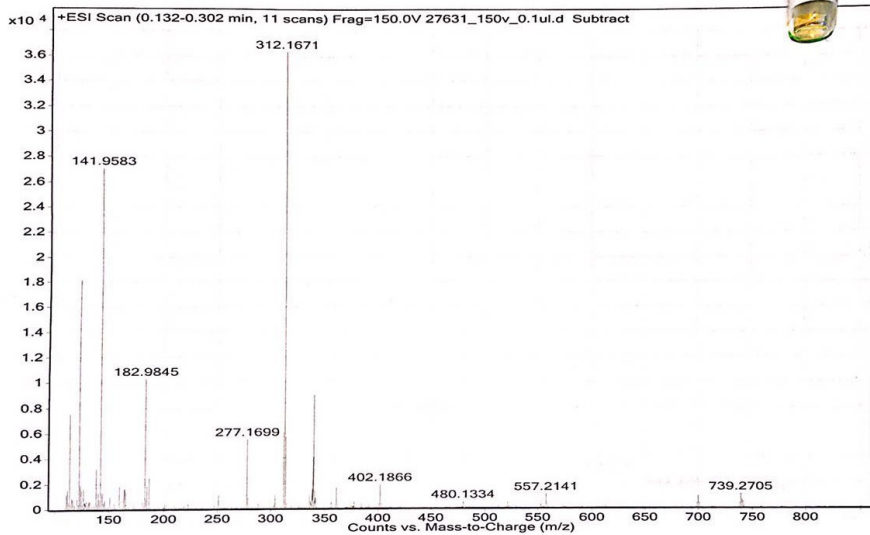
Best	Formula (M)	Ion Formula	Calc m/z	Score	Mass	Calc Mass	Abs Diff (ppm)	Mass Match
✓	C19 H19 B F2 N2	C19 H19 B F2 N2 Na	346.1538	78.92	323.1647	323.1646	0.28	99.95

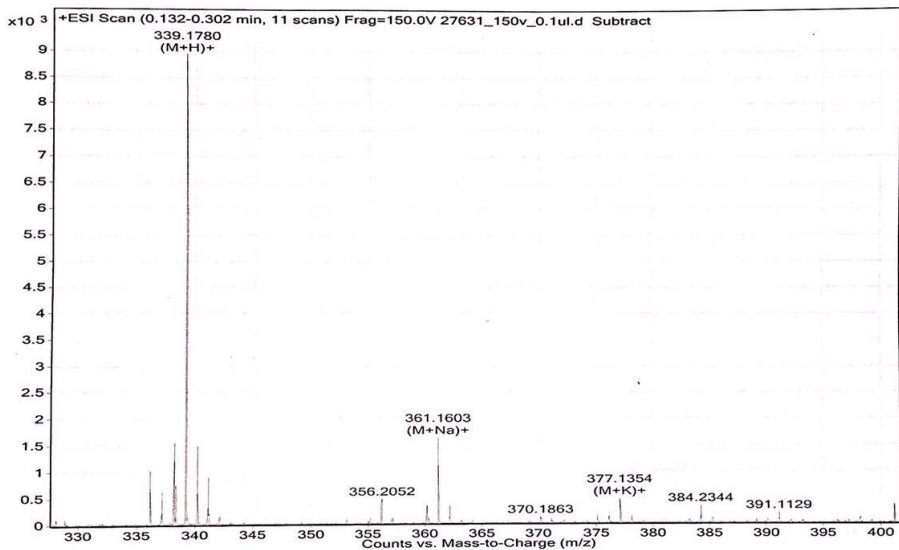
Isotope	Abund%	Calc Abund%	Calc Abund Sum%	m/z	Calc m/z	Diff (ppm)	Abund Sum%
1	11.55	23.58	16.32	346.1554	346.1538	-4.63	8.8
2	100	100	69.2	347.1506	347.1505	-0.24	76.17
3	19.73	20.93	14.48	348.154	348.1535	-1.59	15.03

Figure S34. Mass spectra of BODIPY 1 with 10 equivalents of TFA (after three days)

Sample Name Position P1-C2 Instrument Name Instrument 1 User Name  
 Inj Vol -1 InjPosition Sample SampleType Sample IRM Calibration Status Missed  
 Data Filename 27631\_150v\_0.1ul.d ACQ Method Comment Acquired Time 2:44:17 PM



Sample Name Position P1-C2 Instrument Name Instrument 1 User Name  
 Inj Vol -1 InjPosition Sample SampleType Sample IRM Calibration Status Some Ions Missed  
 Data Filename 27631\_150v\_0.1ul.d ACQ Method Comment Acquired Time 3/13/2017 2:44:17 PM



MS Formula Results: + Scan (0.132-0.302 min) Sub (27631\_150v\_0.1ul.d)

m/z	Ion	Formula	Abundance
338.1793	(M+H)+	C21 H20 B N4	1588.9

Best	Formula (M)	Ion Formula	Calc m/z	Score	Mass	Calc Mass	Abs Diff (ppm)	Mass Match
<input checked="" type="checkbox"/>	C21 H19 B N4	C21 H20 B N4	338.1812	85.54	337.174	337.1739	0.31	99.93

Isotope	Abund%	Calc Abund%	Calc Abund Sum%	m/z	Calc m/z	Diff (ppm)	Abund Sum%
1	17.68	23.42	15.92	338.1793	338.1812	5.5	13.11
2	100	100	67.98	339.1778	339.1779	-0.34	74.16
3	17.17	23.68	16.1	340.181	340.1807	-0.85	12.73

Figure S35. Mass spectra of BODIPY 2 with 10 equivalents of TFA (after three days)

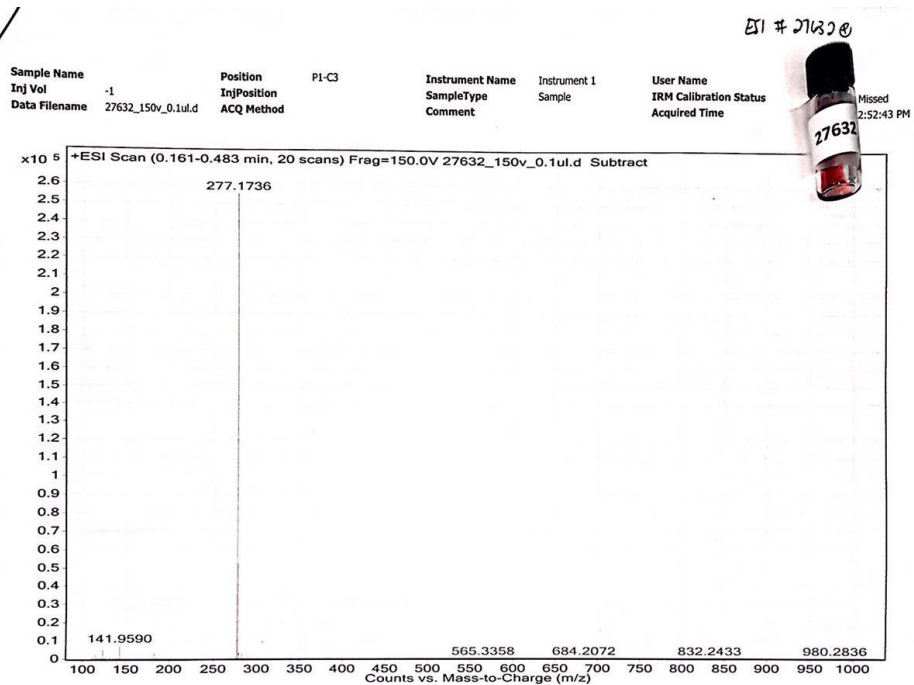


Figure S36. Mass spectra of BODIPY 3 with 10 equivalents of TFA (after three days)

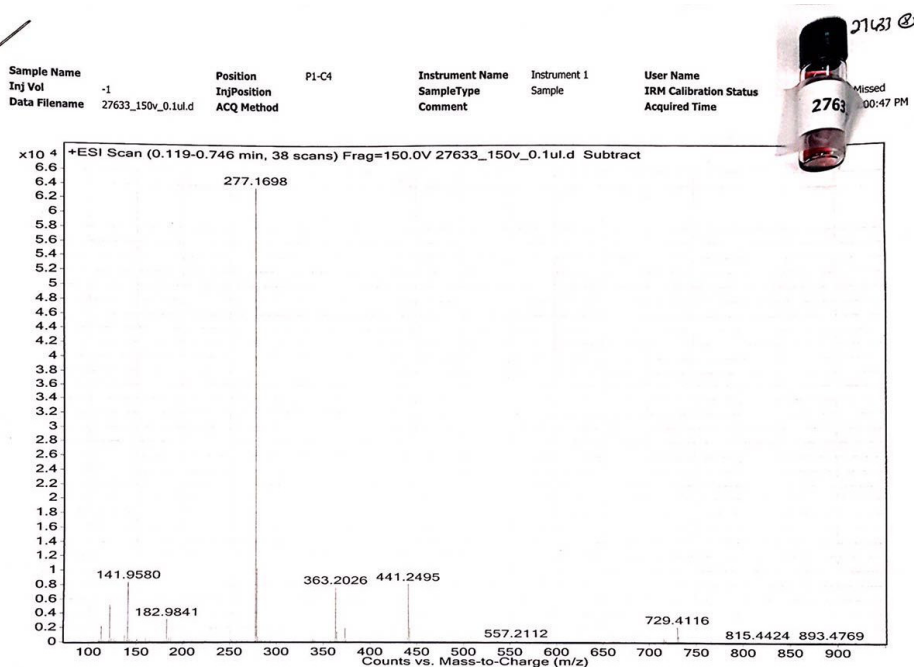


Figure S37. Mass spectra of BODIPY 4 with 10 equivalents of TFA (after three days)

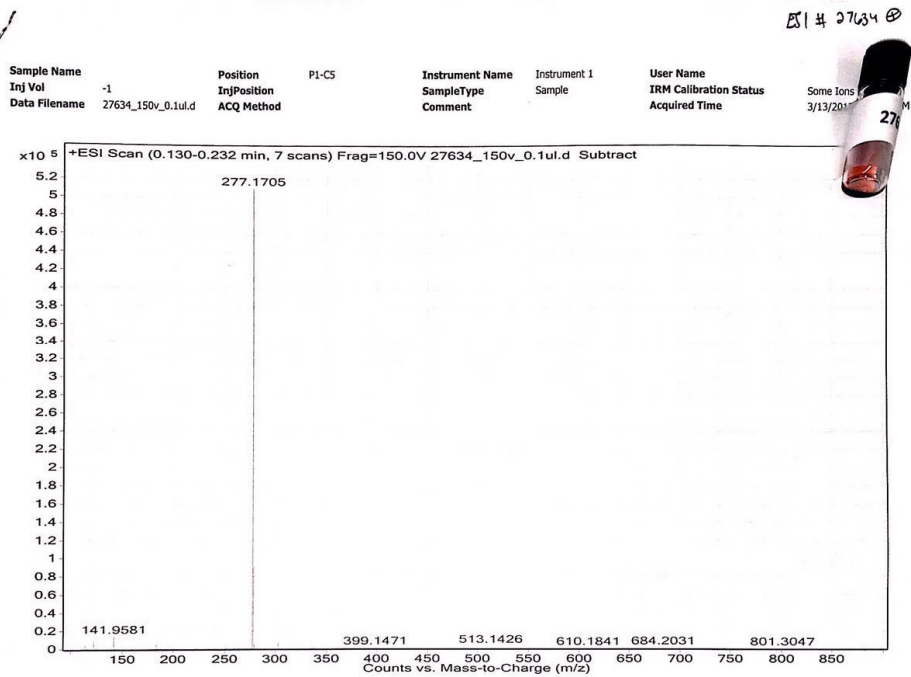
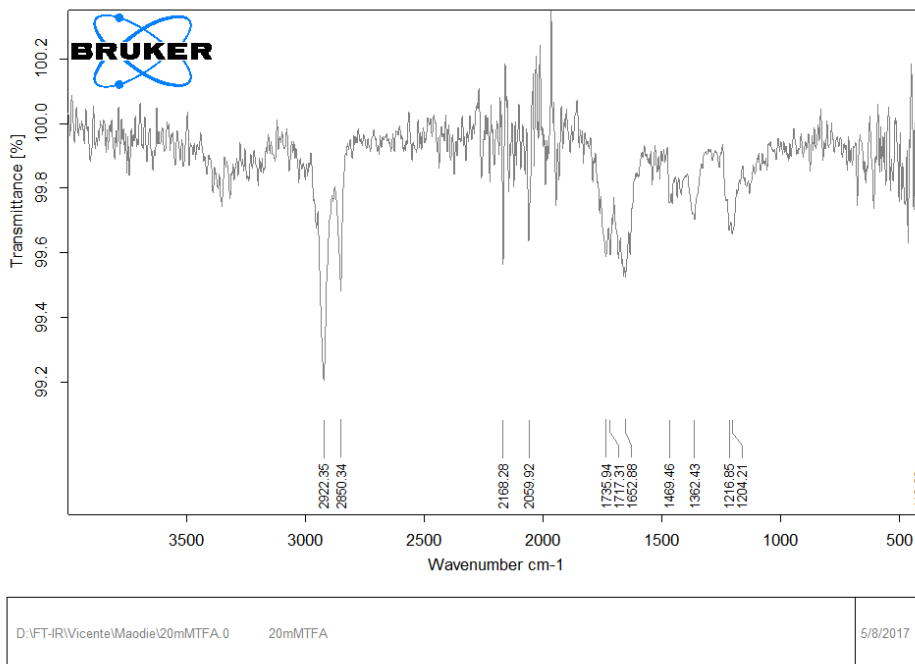


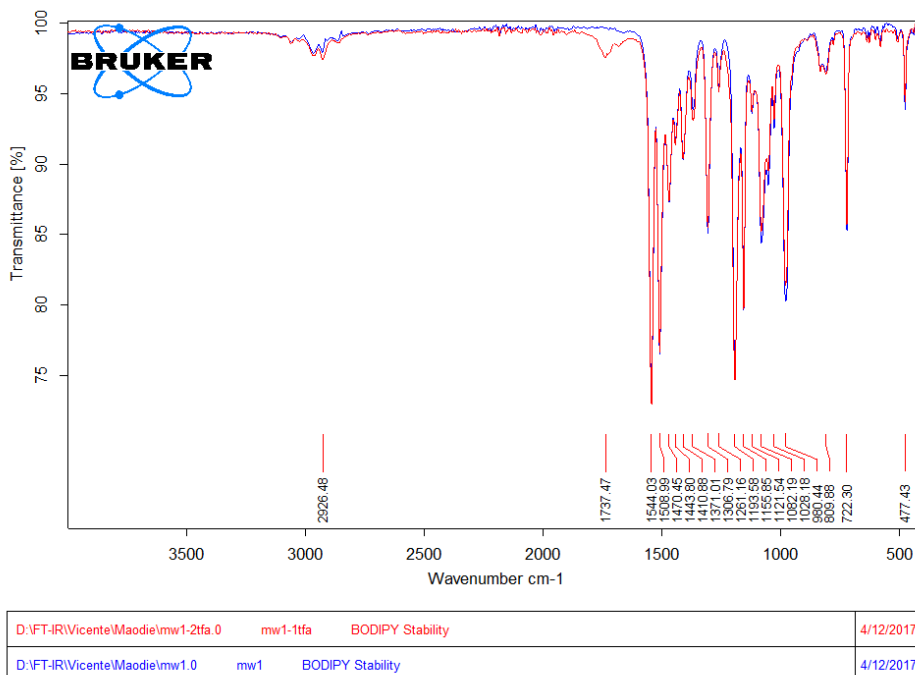
Figure S38. Mass spectra of BODIPY 5 with 10 equivalents of TFA (after three days)

# Infrared Spectra



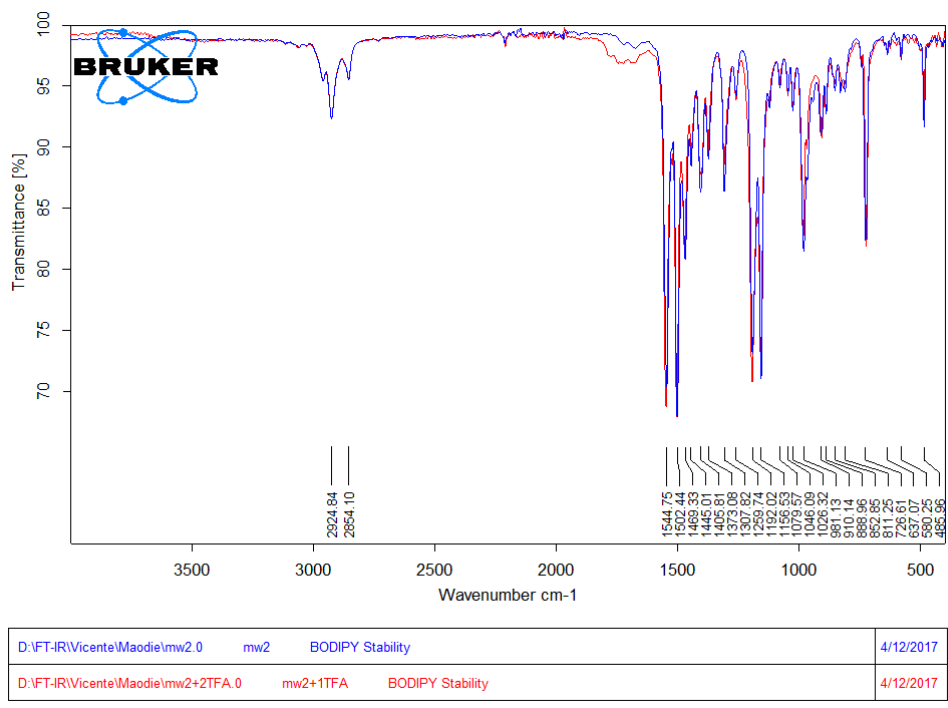
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Figure S39 The infrared spectra of 20 mM TFA in dichloromethane.



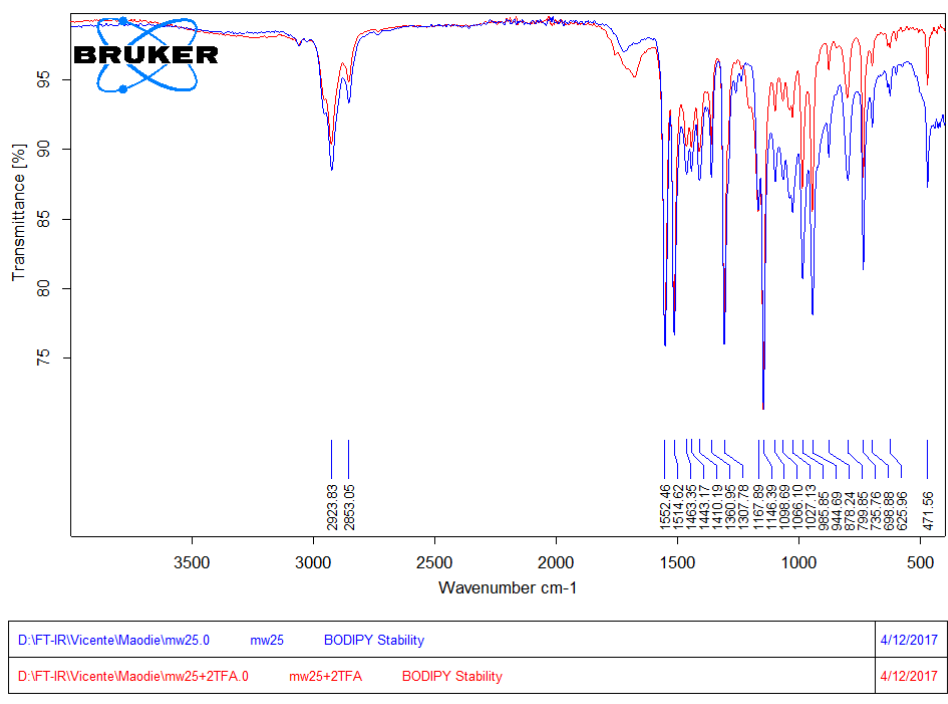
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Figure S40. Infrared spectra of 10 mM BODIPY 1 before (blue) and after (red) addition of 2 equivalents of TFA in dichloromethane.



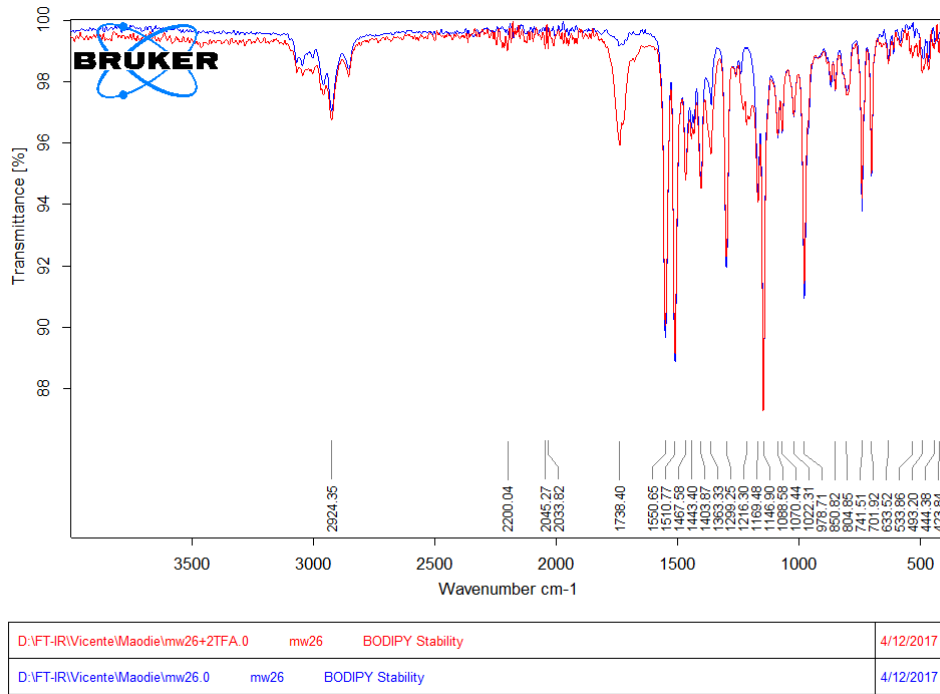
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Figure S41. Infrared spectra of 10 mM BODIPY 2 before (blue) and after (red) addition of 2 equivalents of TFA in dichloromethane.



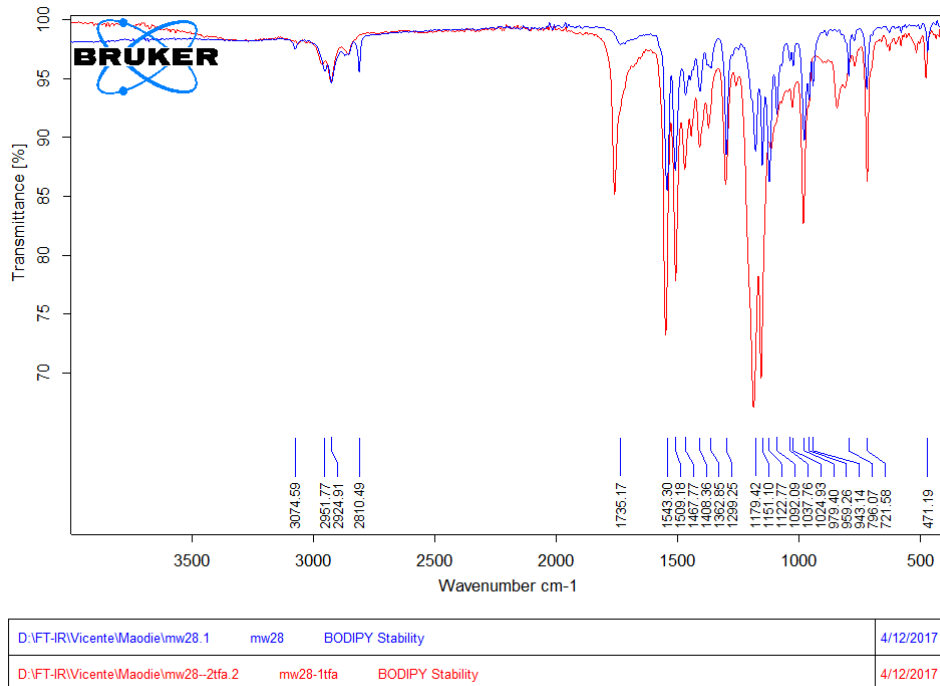
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Figure S42. Infrared spectra of 10 mM BODIPY 3 before (blue) and after (red) addition of 2 equivalents of TFA in dichloromethane.



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Figure S43. Infrared spectra of 10 mM BODIPY 4 before (blue) and after (red) addition of 2 equivalents of TFA in dichloromethane.

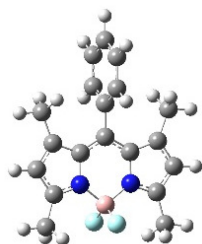


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Figure S44. Infrared spectra of 10 mM BODIPY 5 before (blue) and after (red) addition of 2 equivalents of TFA in dichloromethane.

# Optimized Cartesian Coordinates of ground and excited states of BODIPYs and Hydrogen-bonded Complex

Table S3 B3LYP/6-31+G(d,p) optimized Cartesian coordinates of BODIPY 1.

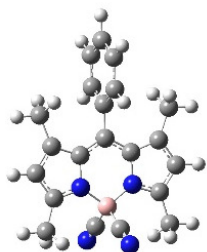


C	-0.37142000	-2.58259800	0.00001300
C	0.77351200	-3.37599000	0.00002400
C	0.08925200	-1.22366900	0.00001500
C	1.90431700	-2.53555200	0.00003000
N	1.49361900	-1.24717800	0.00001400
C	0.08925100	1.22366900	-0.00001700
C	-0.37142300	2.58259700	-0.00001200
C	0.77350800	3.37599000	-0.00002400
C	1.90431400	2.53555400	-0.00003200
N	1.49361800	1.24717900	-0.00001200
B	2.40901900	0.00000100	0.00000200
F	3.23354300	0.00001300	1.14788900
F	3.23354500	-0.00001000	-1.14788500
C	-0.60231700	-0.00000100	-0.00000200
C	-2.09840400	-0.00000100	-0.00000100
C	-2.80681600	0.00009300	1.21000600
C	-2.80681800	-0.00009400	-1.21000800
C	-4.20419300	0.00009700	1.20925000
H	-2.26343000	0.00016700	2.15062200
C	-4.20419500	-0.00009900	-1.20925100
H	-2.26343200	-0.00016900	-2.15062500
C	-4.90612900	-0.00000100	0.00000000
H	-4.74229400	0.00017300	2.15265000
H	-4.74229600	-0.00017400	-2.15265000
H	-5.99210200	-0.00000100	0.00000100
C	3.34098100	2.94500700	-0.00004200
H	3.86158400	2.55509700	0.88043300
H	3.86157400	2.55508300	-0.88051800
H	3.41682900	4.03424900	-0.00005100
C	3.34098400	-2.94500300	0.00003800
H	3.86158600	-2.55509200	-0.88043800
H	3.86157800	-2.55508100	0.88051300
H	3.41683400	-4.03424600	0.00004500
C	-1.77245900	3.12004500	0.00001300
H	-2.33755300	2.79403200	-0.87837100
H	-2.33752800	2.79401600	0.87840800



H	-1.74468200	4.21299800	0.00002200
H	0.80329800	4.45770500	-0.00002500
H	0.80330300	-4.45770400	0.00002500
C	-1.77245500	-3.12004900	-0.00000800
H	-2.33754800	-2.79403500	0.87837600
H	-2.33752600	-2.79402100	-0.87840300
H	-1.74467700	-4.21300200	-0.00001600

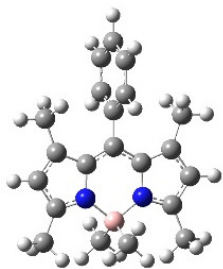
Table S4. B3LYP/6-31+G(d,p) optimized Cartesian coordinates of BODIPY 2.



C	-0.58528700	2.57747600	0.00000500
C	0.55398700	3.37809800	0.00000900
C	-0.11922800	1.22276600	0.00000600
C	1.69093000	2.55126200	0.00001100
N	1.28933600	1.25443700	0.00000600
C	-0.11914100	-1.22282400	-0.00000600
C	-0.58507300	-2.57758500	-0.00000500
C	0.55428000	-3.37809500	-0.00001200
C	1.69114000	-2.55114700	-0.00001300
N	1.28942600	-1.25436500	-0.00000500
B	2.18922900	0.00007000	0.00000200
C	-0.80878400	-0.00005000	0.00000000
C	-2.30467100	-0.00007100	0.00000000
C	-3.01173600	-0.00002000	-1.21062900
C	-3.01173600	-0.00008600	1.21062800
C	-4.40900600	-0.00001200	-1.20942800
H	-2.46852700	0.00001200	-2.15129500
C	-4.40900600	-0.00008100	1.20942800
H	-2.46852700	-0.00010600	2.15129500
C	-5.11055800	-0.00004900	0.00000000
H	-4.94713700	0.00002200	-2.15269900
H	-4.94713700	-0.00009900	2.15269900
H	-6.19645500	-0.00004200	0.00000000
C	3.11804900	-2.98967800	-0.00001900
H	3.65296100	-2.62215700	-0.88207000
H	3.65296500	-2.62216500	0.88203300
H	3.16422300	-4.08029000	-0.00002400
C	3.11779100	2.98995200	0.00001300
H	3.65274200	2.62249400	0.88206300
H	3.65274400	2.62249600	-0.88203800
H	3.16384600	4.08056900	0.00001400
C	-1.98788500	-3.10923300	0.00000400
H	-2.55072200	-2.78082100	0.87859200
H	-2.55072800	-2.78083300	-0.87858500
H	-1.96290500	-4.20200100	0.00001100
H	0.57761900	-4.45966300	-0.00001400
H	0.57721900	4.45966800	0.00000900
C	-1.98815900	3.10896000	-0.00000300
H	-2.55095800	2.78047800	-0.87859100
H	-2.55096200	2.78049200	0.87858700
H	-1.96330900	4.20173200	-0.00001100
C	3.12509800	0.00009900	1.31435000
C	3.12510100	0.00011000	-1.31434400

N	3.77920700	0.00003300	2.27691500
N	3.77921200	0.00005200	-2.27690800

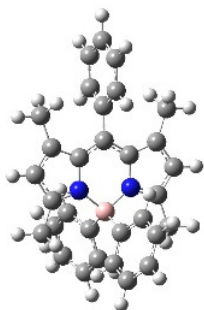
Table S5. B3LYP/6-31+G(d,p) optimized Cartesian coordinates of BODIPY 3.



C	0.40420400	-2.57414000	-0.03736100
C	-0.71572000	-3.39019100	-0.00317800
C	-0.09906300	-1.22742600	-0.02391700
C	-1.87036600	-2.57425300	0.03306300
N	-1.50621200	-1.27463800	0.00635600
C	-0.09906500	1.22749400	0.02383000
C	0.40420800	2.57420400	0.03730300
C	-0.71571600	3.39025700	0.00301000
C	-1.87036300	2.57433200	-0.03320400
N	-1.50621500	1.27470700	-0.00644900
B	-2.47327800	0.00002300	0.00001400
C	0.58078000	0.00002700	-0.00004700
C	2.07822400	-0.00000400	0.00000500
C	2.78780500	0.02473600	-1.20886800
C	2.78771000	-0.02482400	1.20893200
C	4.18520500	0.02460300	-1.20872800
H	2.24447200	0.04431900	-2.14939500
C	4.18511100	-0.02480200	1.20889900
H	2.24430200	-0.04437900	2.14941600
C	4.88753500	-0.00012300	0.00011200
H	4.72326700	0.04393300	-2.15207300
H	4.72309900	-0.04418300	2.15228500
H	5.97358200	-0.00016700	0.00015400
C	-3.26672600	3.10474800	-0.14677300
H	-3.58110300	3.14901700	-1.19653400
H	-3.99948400	2.50292600	0.38908400
H	-3.29819400	4.12437400	0.24680900
C	-3.26672400	-3.10468800	0.14666700
H	-3.58019600	-3.15098800	1.19662200
H	-3.99983900	-2.50173100	-0.38738100
H	-3.29867100	-4.12355900	-0.24884600
C	1.81568700	3.08663400	0.08199500
H	2.35107600	2.74883800	0.97434400
H	2.40406000	2.76168600	-0.78118800
H	1.80263200	4.18035900	0.08937300
H	-0.72273800	4.47291500	0.00043300
H	-0.72274400	-4.47284900	-0.00064400
C	1.81569200	-3.08655000	-0.08198000
H	2.35109700	-2.74878400	-0.97433200
H	2.40403500	-2.76154300	0.78120200
H	1.80265900	-4.18027500	-0.08930600
C	-3.33612300	-0.01413600	1.38832300
H	-3.94918200	0.88333700	1.52617700

H	-4.02826800	-0.86253700	1.43818000
H	-2.67606900	-0.08426700	2.26462000
C	-3.33632500	0.01414100	-1.38818300
H	-4.02940200	0.86181300	-1.43741900
H	-2.67644000	0.08552500	-2.26450900
H	-3.94840300	-0.88391800	-1.52658000

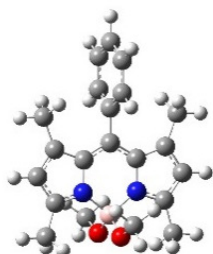
Table S6. B3LYP/6-31+G(d,p) optimized Cartesian coordinates of BODIPY 4.



C	1.53896100	0.66053900	2.48767500
C	0.41374600	0.89128700	3.26586200
C	1.04502800	0.30569000	1.18606100
C	-0.73577800	0.68297500	2.47287600
N	-0.36269200	0.32722900	1.22348000
C	1.04505800	-0.30439500	-1.18634400
C	1.53902300	-0.65872200	-2.48808600
C	0.41384300	-0.89032200	-3.26607400
C	-0.73569200	-0.68306600	-2.47282600
N	-0.36264700	-0.32711800	-1.22347800
B	-1.33109900	-0.00060200	0.00015000
C	1.72933600	0.00092000	-0.00020300
C	3.22644600	0.00151000	-0.00034100
C	3.93598300	-1.15883700	0.33937300
C	3.93500500	1.16241000	-0.34019300
C	5.33326500	-1.15838200	0.33822700
H	3.39263500	-2.06149800	0.60396400
C	5.33228700	1.16305700	-0.33930800
H	3.39089400	2.06464400	-0.60467700
C	6.03505500	0.00261400	-0.00060900
H	5.87164700	-2.06396800	0.60237700
H	5.86990700	2.06906700	-0.60355900
H	7.12106600	0.00304000	-0.00071200
C	-2.14401500	-0.82921000	-2.94879300
H	-2.76220900	-1.37538300	-2.23244200
H	-2.61128500	0.14840200	-3.10748900
H	-2.15018200	-1.36664600	-3.90032400
C	-2.14411700	0.82790300	2.94916100
H	-2.76288000	1.37377900	2.23307200
H	-2.61057500	-0.15012000	3.10768800
H	-2.15051100	1.36508300	3.90083400
C	2.94876100	-0.78208100	-2.99107700
H	3.49308800	0.16511500	-2.92962300
H	3.52890000	-1.51783900	-2.42641500
H	2.93232000	-1.09514300	-4.03884100
H	0.40141200	-1.18629800	-4.30722700
H	0.40127600	1.18736400	4.30698600
C	2.94869500	0.78519300	2.99035600
H	3.49403000	-0.16138300	2.92839300

H	3.52788900	1.52180200	2.42582400
H	2.93218900	1.09785200	4.03823900
C	-2.16787500	-1.36663600	0.36983900
C	-3.48610300	-1.39807400	0.86387100
C	-1.52161300	-2.61653900	0.25701600
C	-4.12733500	-2.59432100	1.21107400
H	-4.03593100	-0.47116000	0.99087300
C	-2.14486800	-3.81865100	0.60318500
H	-0.50134000	-2.65459000	-0.11777300
C	-3.45952800	-3.81398600	1.08113800
H	-5.14846900	-2.56931400	1.58390200
H	-1.60646800	-4.75754400	0.49839600
H	-3.95301200	-4.74458400	1.34835500
C	-2.16986100	1.36427900	-0.36929400
C	-3.48842000	1.39394400	-0.86254200
C	-1.52511800	2.61501900	-0.25704800
C	-4.13139600	2.58932100	-1.20951000
H	-4.03709900	0.46629400	-0.98914000
C	-2.15012100	3.81628300	-0.60300500
H	-0.50466700	2.65441200	0.11711900
C	-3.46507300	3.80985800	-1.08014500
H	-5.15271700	2.56296100	-1.58173100
H	-1.61286300	4.75588200	-0.49869000
H	-3.95991200	4.73978500	-1.34719200

Table S7. B3LYP/6-31+G(d,p) optimized Cartesian coordinates of BODIPY 5.

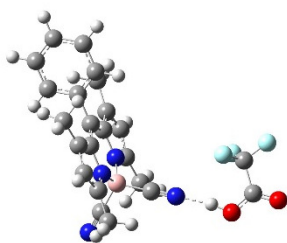


C	0.00000000	2.58217300	0.61416600
C	0.00000000	3.38120300	-0.52448200
C	0.00000000	1.22545600	0.14046000
C	0.00000000	2.54445900	-1.66203400
N	0.00000000	1.25423900	-1.26347500
C	0.00000000	-1.22545600	0.14046000
C	0.00000000	-2.58217300	0.61416600
C	0.00000000	-3.38120300	-0.52448200
C	0.00000000	-2.54445900	-1.66203400
N	0.00000000	-1.25423900	-1.26347500
B	0.00000000	0.00000000	-2.23869400
C	0.00000000	0.00000000	0.82898700
C	0.00000000	0.00000000	2.32570500
C	-1.20935100	0.00000000	3.03526800
C	1.20935100	0.00000000	3.03526800
C	-1.20905000	0.00000000	4.43265900
H	-2.15020100	0.00000000	2.49223200
C	1.20905000	0.00000000	4.43265900
H	2.15020100	0.00000000	2.49223200
C	0.00000000	0.00000000	5.13494300
H	-2.15258500	0.00000000	4.97065600
H	2.15258500	0.00000000	4.97065600
H	0.00000000	0.00000000	6.22094600
C	0.00000000	-2.97705500	-3.09287500
H	-0.87662300	-2.58973400	-3.62070400
H	0.87662300	-2.58973400	-3.62070400
H	0.00000000	-4.06798800	-3.14982200
C	0.00000000	2.97705500	-3.09287500
H	0.87662300	2.58973400	-3.62070400
H	-0.87662300	2.58973400	-3.62070400
H	0.00000000	4.06798800	-3.14982200
C	0.00000000	-3.11314600	2.01855700
H	0.87814000	-2.78600200	2.58352400
H	-0.87814000	-2.78600200	2.58352400
H	0.00000000	-4.20646600	1.99506100
H	0.00000000	-4.46339600	-0.54884800
H	0.00000000	4.46339600	-0.54884800
C	0.00000000	3.11314600	2.01855700
H	-0.87814000	2.78600200	2.58352400
H	0.87814000	2.78600200	2.58352400
H	0.00000000	4.20646600	1.99506100
C	2.44414300	0.00000000	-2.51577800
H	2.61663700	0.88999600	-1.89129300



H	2.61663700	-0.88999600	-1.89129300
H	3.18364800	0.00000000	-3.32313600
O	1.15719100	0.00000000	-3.09645800
C	-2.44414300	0.00000000	-2.51577800
H	-2.61663700	-0.88999600	-1.89129300
H	-2.61663700	0.88999600	-1.89129300
H	-3.18364800	0.00000000	-3.32313600
O	-1.15719100	0.00000000	-3.09645800

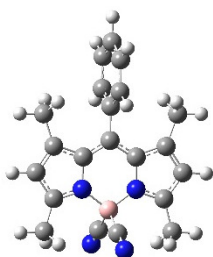
Table S2. B3LYP/6-31+G(d,p) optimized Cartesian coordinates of the unusually stable hydrogen-bonded complex between BODIPY **2** and TFA.



C	-1.82784600	-0.55468500	2.53596800
C	-0.90290400	-0.04468400	3.44414000
C	-1.55434600	0.08771000	1.28582500
C	-0.08074700	0.88344300	2.78409600
N	-0.47072800	0.96690100	1.48464100
C	-1.71354100	0.73015100	-1.06773800
C	-2.16386500	0.80048200	-2.42522800
C	-1.34528400	1.73376100	-3.05729900
C	-0.41675200	2.22899400	-2.12685800
N	-0.63530800	1.62719700	-0.92792700
B	0.15039900	1.83859300	0.37867300
C	-2.16319500	-0.02663100	0.02602800
C	-3.31475100	-0.96444600	-0.15185700
C	-4.62755400	-0.51532700	0.04887900
C	-3.09130300	-2.29808100	-0.52157900
C	-5.70369900	-1.39042500	-0.11865600
H	-4.80563200	0.51728100	0.33513900
C	-4.16914900	-3.17125100	-0.68886800
H	-2.07591500	-2.65094100	-0.67806400
C	-5.47706700	-2.71982100	-0.48791900
H	-6.71674900	-1.03262400	0.03940900
H	-3.98557900	-4.20244100	-0.97561000
H	-6.31395000	-3.39932700	-0.61835800
C	0.64330500	3.25024100	-2.37598400
H	0.47332000	4.15772800	-1.78691600
H	1.64011500	2.87641100	-2.11982500
H	0.64372000	3.52339500	-3.43269900
C	1.04224100	1.66720600	3.37881300
H	0.84854600	2.74420000	3.33782400
H	1.17134500	1.38199500	4.42445000
H	1.98764000	1.48513900	2.85684000
C	-3.27596600	0.05872200	-3.10533300
H	-3.12480800	-1.02423600	-3.07334100
H	-4.24555700	0.25839600	-2.64010800
H	-3.33082700	0.36479300	-4.15311300
H	-1.40291900	2.03804600	-4.09379300
H	-0.81904700	-0.30969800	4.48953100
C	-2.87187300	-1.57473600	2.88142700
H	-3.88411000	-1.20494800	2.69457700
H	-2.75578900	-2.49263200	2.29765600
H	-2.79249500	-1.83254300	3.94058200
O	6.98026600	-1.09024600	-0.65787800

C	4.74580300	-1.91412900	-0.32361500
F	4.11895800	-1.81148900	0.87209700
F	5.29239800	-3.13236200	-0.40316600
F	3.80318900	-1.81153100	-1.29013500
C	5.82097500	-0.79662500	-0.48160300
O	5.37258900	0.44010000	-0.40974500
H	4.38515700	0.56355800	-0.26057000
C	1.69388000	1.38941200	0.15135900
N	2.78661900	1.03839500	-0.01833500
C	0.11971900	3.39028100	0.80469900
N	0.06710300	4.51056600	1.11393800

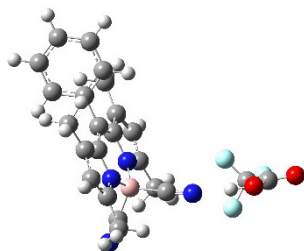
Table S9. M06-2X/6-31+G(d,p) optimized Cartesian coordinates for the first excited state of BODIPY 2.



C	0.57946100	-2.58395300	0.00000300
C	-0.55983600	-3.37234000	0.00000400
C	0.11616200	-1.21816700	0.00000700
C	-1.69839200	-2.53336700	0.00000900
N	-1.28580300	-1.24023000	0.00000700
C	0.11614400	1.21818200	0.00000000
C	0.57941600	2.58397900	-0.00001100
C	-0.55989700	3.37234300	-0.00003600
C	-1.69843700	2.53334800	-0.00003300
N	-1.28582300	1.24021900	0.00000400
B	-2.18327200	-0.00001200	0.00001700
C	0.83256800	0.00001200	0.00000700
C	2.32019200	0.00001300	0.00000300
C	3.02504400	0.00001300	-1.20758100
C	3.02505000	0.00000300	1.20758400
C	4.41898500	0.00001200	-1.20776100
H	2.47606300	0.00001600	-2.14569500
C	4.41899100	0.00000100	1.20775600
H	2.47607400	-0.00000200	2.14570000
C	5.11718600	0.00000700	-0.00000400
H	4.95898400	0.00001400	-2.14942000
H	4.95899500	-0.00000500	2.14941200
H	6.20264600	0.00000600	-0.00000700
C	-3.12620400	2.94010900	-0.00007100
H	-3.65170700	2.55448200	-0.88212700
H	-3.65173900	2.55454800	0.88199300
H	-3.19583200	4.02818800	-0.00011200
C	-3.12615200	-2.94015800	0.00001500
H	-3.65167600	-2.55457500	0.88207700
H	-3.65168200	-2.55457700	-0.88204400
H	-3.19575600	-4.02823800	0.00001600
C	1.99096100	3.07923300	-0.00001200
H	2.54443900	2.73368900	0.87896600
H	2.54444700	2.73366200	-0.87897600
H	1.99062000	4.17139300	-0.00002900
H	-0.59722300	4.45419700	-0.00006100
H	-0.59714000	-4.45419400	0.00000300
C	1.99101900	-3.07917000	-0.00000100

H	2.54449100	-2.73359300	-0.87897200
H	2.54449300	-2.73359900	0.87897100
H	1.99070900	-4.17132900	-0.00000400
C	-3.13113000	-0.00002000	1.31040600
C	-3.13116300	-0.00001000	-1.31034900
N	-3.79434500	-0.00003900	2.26073900
N	-3.79440900	-0.00001400	-2.26066100

Table S10. M06-2X/6-31+G(d,p) optimized Cartesian coordinates for the first excited state of the hydrogen-bonded complex between BODIPY 2 and TFA.



C	-1.17340000	-2.12469800	1.36945600
C	0.03111700	-2.20809600	2.04993800
C	-1.24446200	-0.78082600	0.85239200
C	0.68910200	-0.95952500	1.97525700
N	-0.08623200	-0.10289400	1.26215400
C	-2.07968800	1.23231700	-0.23782900
C	-2.91638500	2.13121500	-0.99317200
C	-2.25359700	3.34843900	-1.00723200
C	-1.04110800	3.22005900	-0.29306600
N	-0.94333000	1.94783600	0.17102100
B	0.25717000	1.33484100	0.88422400
C	-2.24290800	-0.13368400	0.08789100
C	-3.45015700	-0.87768200	-0.35413400
C	-4.66181600	-0.72918600	0.32866900
C	-3.38173700	-1.73802700	-1.45477300
C	-5.79136600	-1.43276800	-0.08448400
H	-4.71306200	-0.06333400	1.18624500
C	-4.51231400	-2.43929300	-1.86973300
H	-2.43947800	-1.85253100	-1.98433100
C	-5.71801500	-2.28843200	-1.18422200
H	-6.72755700	-1.31479700	0.45213500
H	-4.45220400	-3.10259600	-2.72685000
H	-6.59822300	-2.83650600	-1.50533600
C	-0.01476400	4.26506100	-0.04783100
H	-0.01925200	4.58073400	1.00307500
H	0.99666800	3.90728800	-0.27173800
H	-0.22360300	5.13560700	-0.67050900
C	1.98798600	-0.57935700	2.58658500
H	1.83171100	0.03003100	3.48648900
H	2.53449000	-1.47928700	2.87246800
H	2.61047400	0.00679300	1.90261800
C	-4.23073700	1.84437500	-1.64725500
H	-4.19378900	0.93995800	-2.26162800
H	-5.02720500	1.69655300	-0.91010800
H	-4.50791100	2.68781900	-2.28329800
H	-2.58756100	4.25890400	-1.48838700
H	0.41995200	-3.07430200	2.56987800
C	-2.17462600	-3.22686700	1.22612900

H	-3.18364800	-2.90133600	1.49602900
H	-2.22480500	-3.59797300	0.19691500
H	-1.89067600	-4.05825100	1.87497800
O	6.12374900	-1.10344900	-2.43008900
C	4.79835200	-1.06342700	-0.43944400
F	4.87765300	-0.05452700	0.44169100
F	5.58429400	-2.04750500	-0.02113400
F	3.53123600	-1.50512500	-0.43842000
C	5.20712000	-0.57986200	-1.85442700
O	4.49037300	0.40831600	-2.33142300
H	3.74372300	0.73052600	-1.74023200
C	1.54643700	1.31474900	-0.11479500
N	2.45533500	1.24096100	-0.82503300
C	0.65083700	2.19621100	2.18568600
N	0.91297700	2.81606900	3.12838700