Bridged Bis-BODIPYs: Synthesis, Structures and Properties

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Synthesis of bis aldehydes

Synthesis of triphenylamine bis-aldehyde

Phosphoryl chloride (9.5 mL, 101.9 mmol) was added slowly to dry DMF (7.3 mL, 94.3 mmol) at 0°C and the mixture was stirred for 1 hr at RT and then a solution of triphenylamine (1 g, 4.1 mmol) in dichloroethane was added and stirred for 1 h. After this, the reaction mixture was refluxed for 15h. Finally the solution was cooled and poured into water. The organic layer was extracted with dichloromethane, dried with sodium sulphate and the solvent was removed under reduced pressure. The desired compound was isolated via silica gel column chromatography using a mixture of ethyl acetate/hexane (10:90). Yield: 45 % (550mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.89 (s, 2H), 7.77 (d, J = 9 Hz, 4H, Ar-H), 7.40 (t, J = 8 Hz, 2H, Ar-H), 7.18 (m, 6H, Ar-H).

Synthesis of bis-formyl thiophene[S1]

In an oven dried 250 mL 2 neck RB, Thiophene (1 mL, 12.479 mmol) was added and is dissolved in 40 mL dry hexane. After 5 min. TMEDA (2 mL) was added and stirred for 5 min at room temperature. After 5 min. n-BuLi (75 mL) was added and the reaction mixture is refluxed for 3h after stirring at room temperature for 10 min. After 3h, the reaction mixture is cooled to room temperature and then cooled to -40^{0}C and added dry THF (60 ML) and DMF (2.5 mL) and allowed the reaction mixture to come into room temperature naturally. Then the reaction is quenched by adding water and extracted the organic layer with ethyl acetate. Organic layer was separated and dried over Na_2SO_4 and concentrated over rotary evaporator. The crude residue was purified in wet column chromatography and eluted the desired compound using ethyl acetate: Hexane (95: 5) mixture to yield 30% (524.08 mg) of bis-formyl thiophene.. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 10.043 (s, 2H), 7.843(s, 2H).

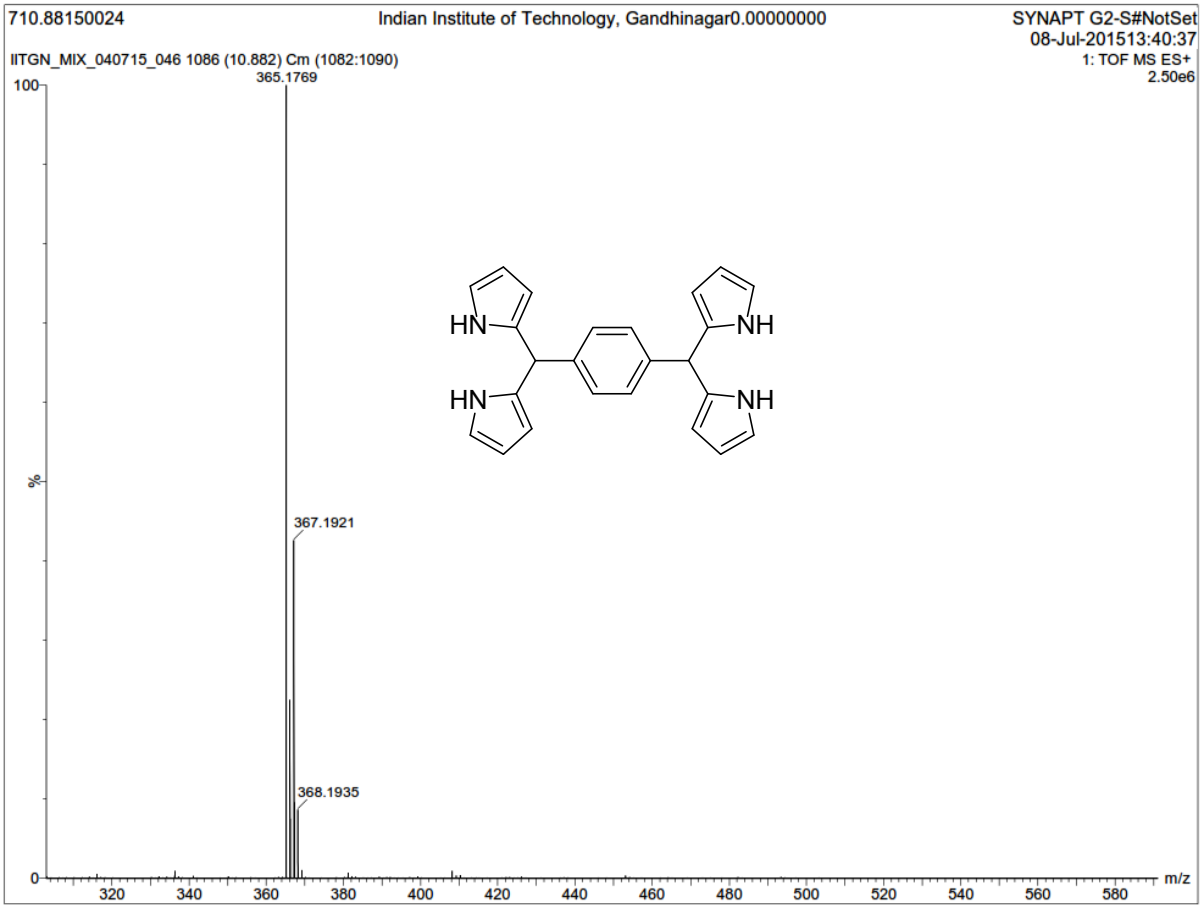
Synthesis of bis-formyl furan

Taken an oven dried 250 mL two neck RB and added l mL of furan in 40 mL dry hexane under nitrogen atmosphere. After 5 min, added 6mL TMEDA and stirred for 5 min at room temperature. After 5 min. n-BuLi (24 mL) was added and allowed to stir in RT for another 10 min. After 10 minutes, allowed the reaction mixture to reflux. After reflexing for 3 h, reaction mixture is cooled to RT. After 10 min the reaction mixture is cooled to -10^{0}C and added THF (20 mL) followed by DMF (2.7 mL) and allowed the reaction mixture to come in room temperature. The reaction is quenched by adding water and separated the organic layer and

washed with water. Collected the organic layer by adding ethyl acetate dried over Na_2SO_4 and concentrated over rotary evaporator. The crude residue was dissolved in small amount of dichloromethane and purified by column chromatography on silica gel (ethyl acetate/hexane = 5: 95) to yield 25 % (425 mg) of bis formyl furan. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.868 (s, 2H), 7.341 (s, 2H).

Reference

S1) G. M. Xia, P. Lu and S. Q. Liu, *Acta Chim. Slov*. 2005, **52**, 336.



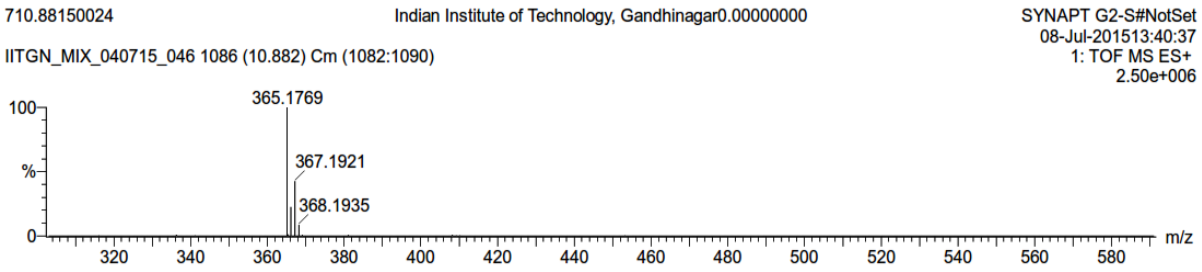


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Figure 1: HRMS spectrum of Bis-dipyrrane **7.**

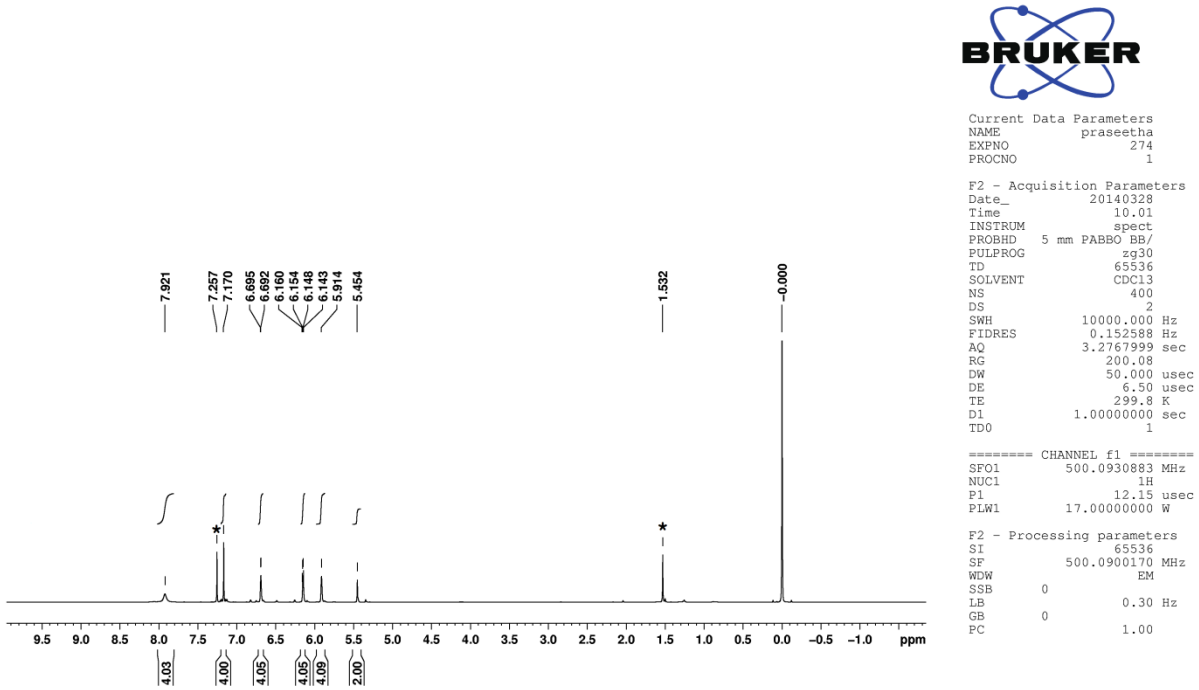
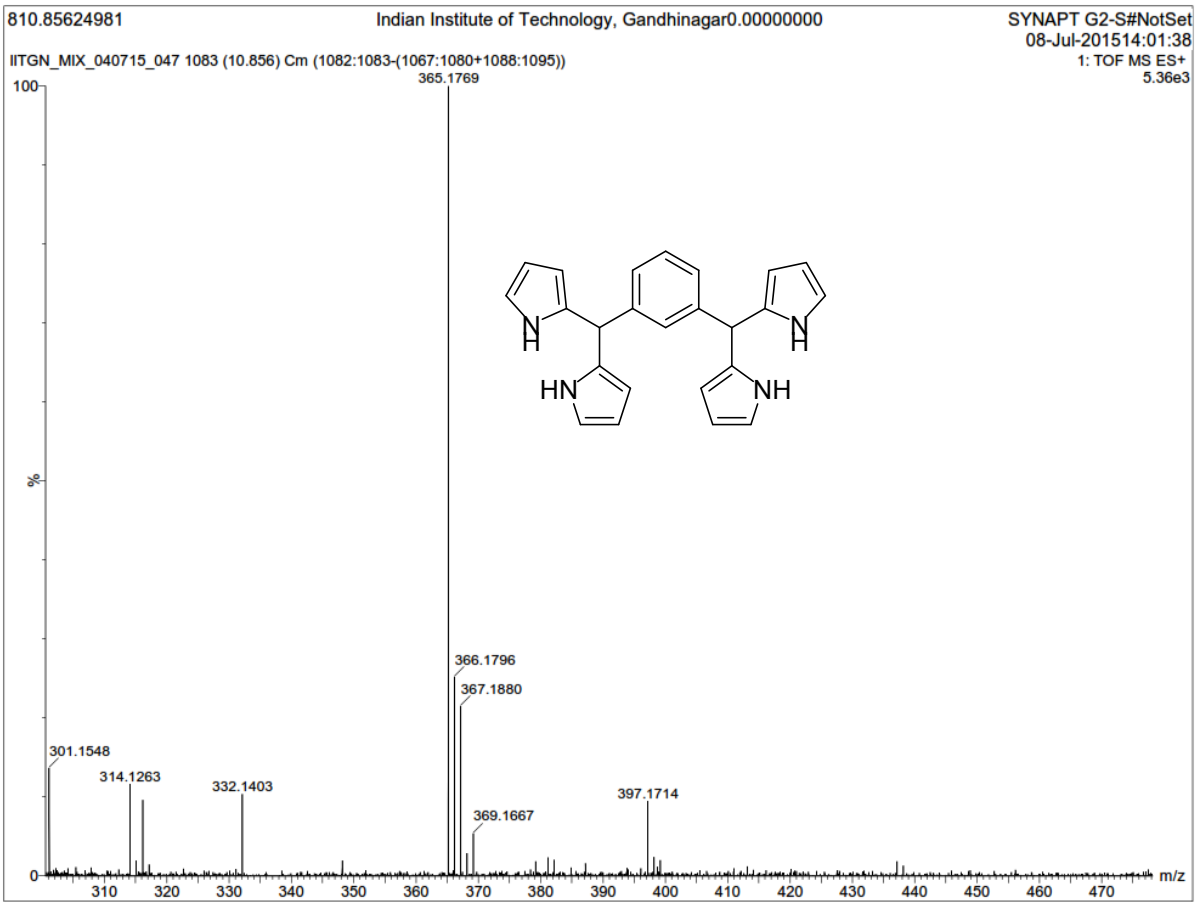


Figure 2: ^{1}H NMR spectrum of Bis-dipyrrane **7** in $CDCl_3$.



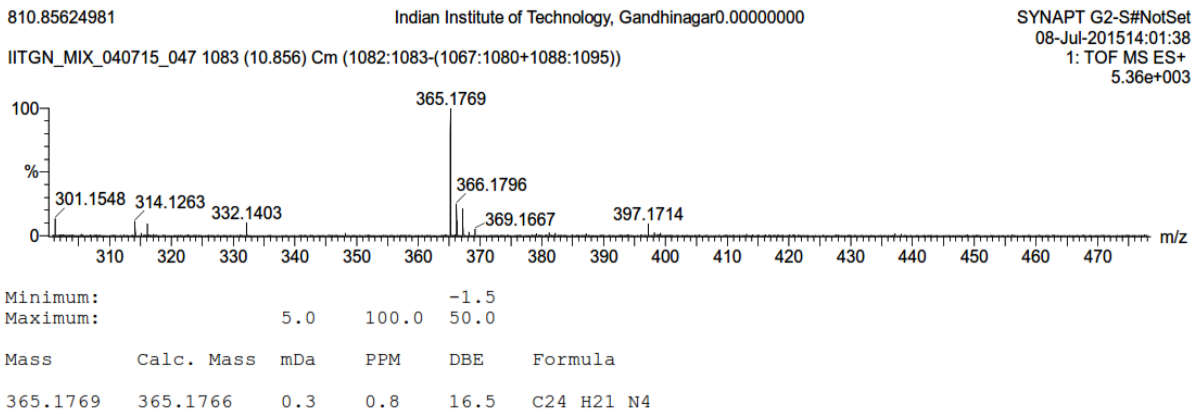


Figure 3: HRMS spectrum of Bis-dipyrrane **8.**

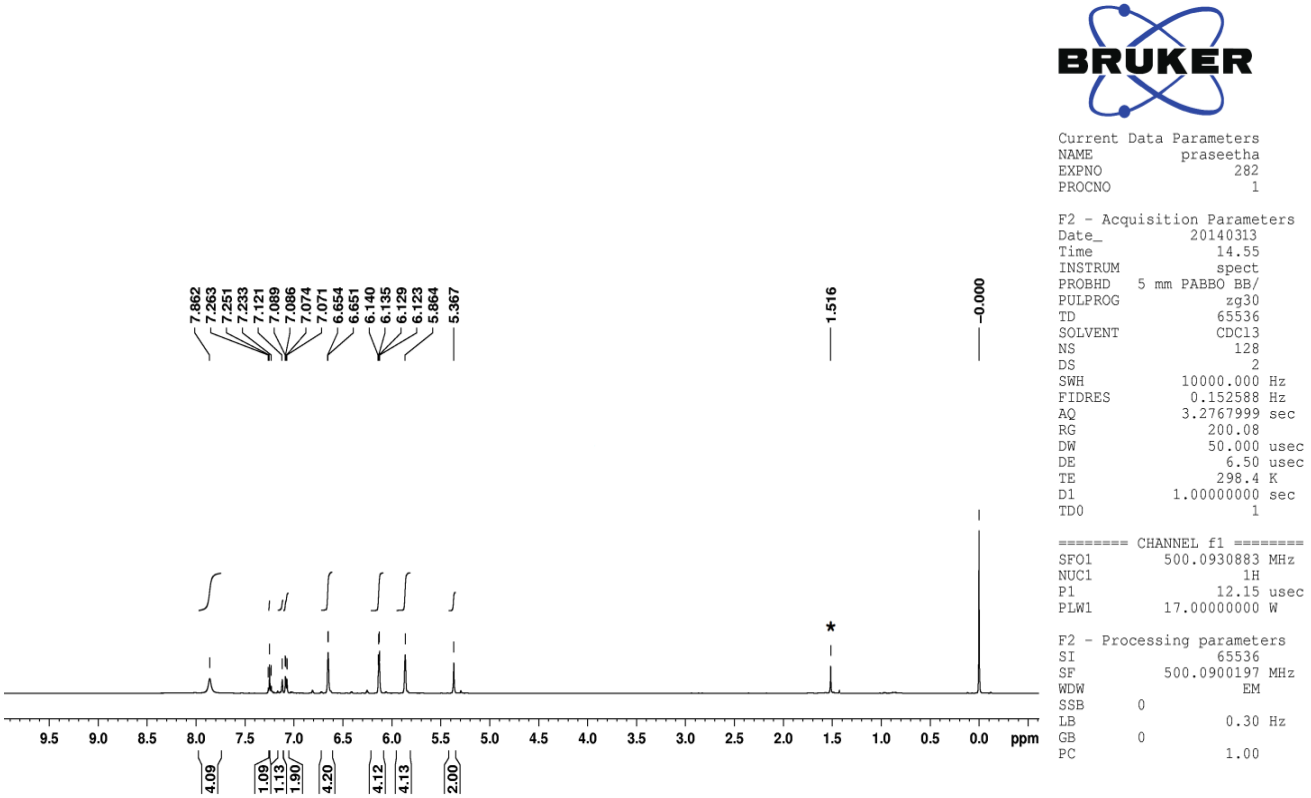
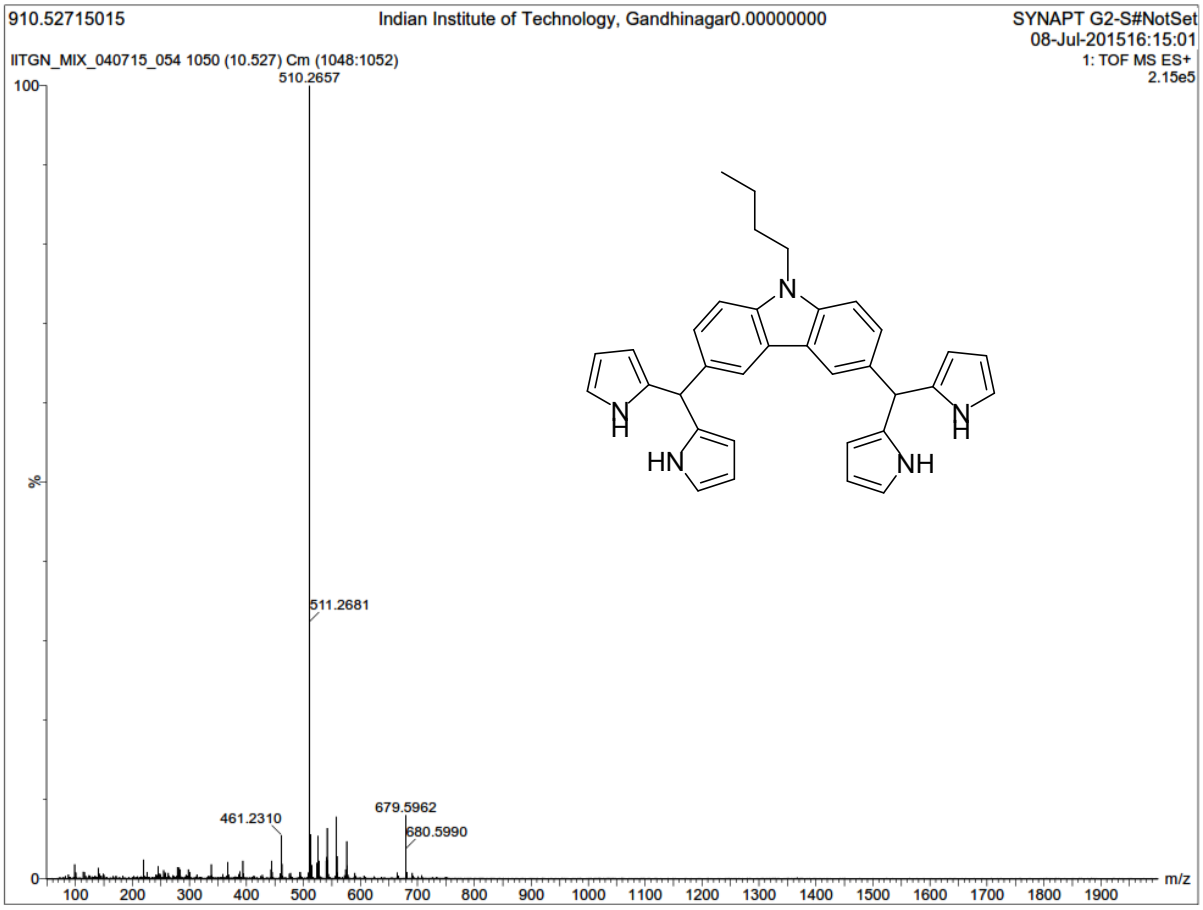


Figure 4: ^{1}H NMR spectrum of Bis-dipyrrane **8** in $CDCl_3$.



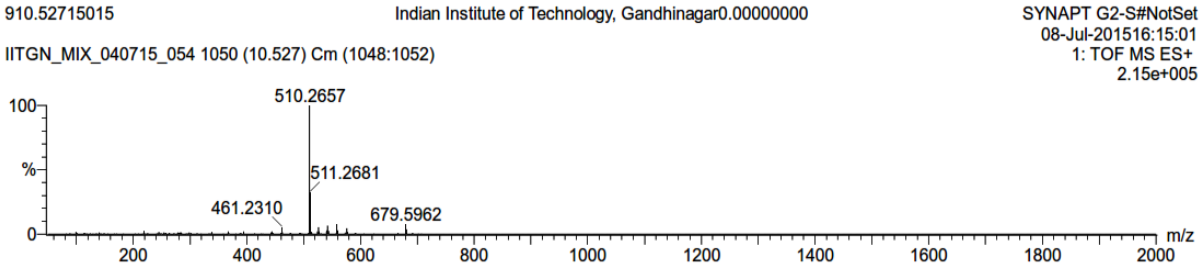


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Figure 5: HRMS spectrum of Bis-dipyrrane **9.**

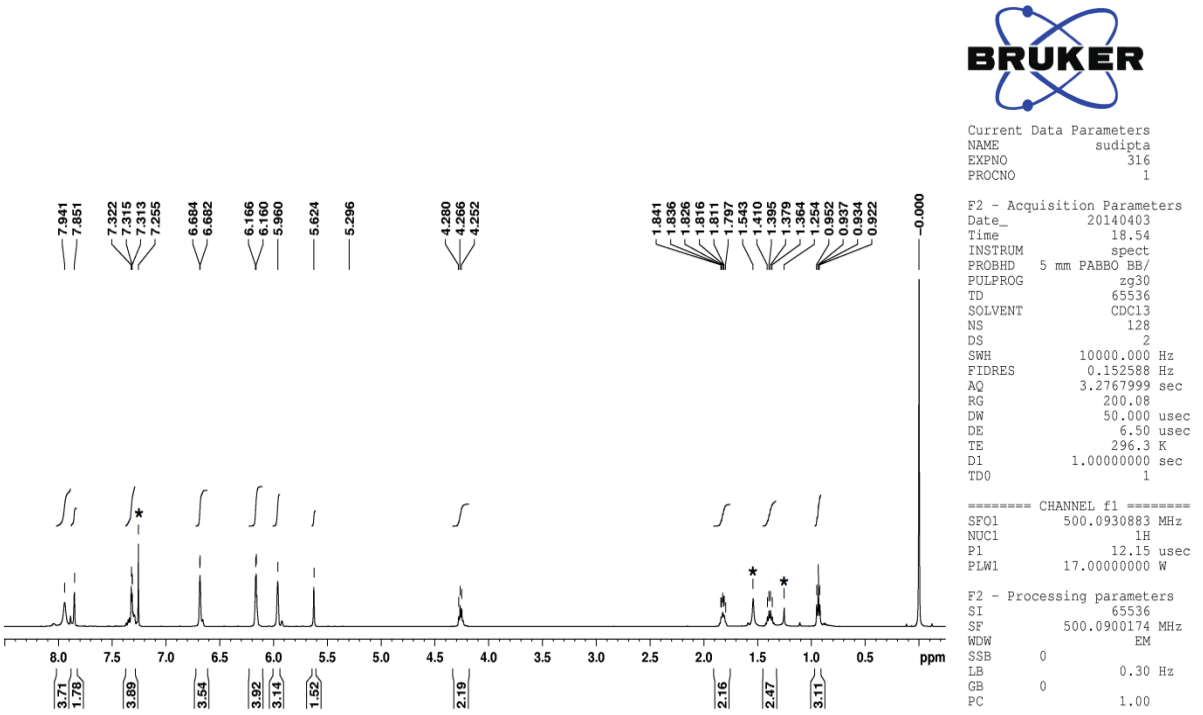
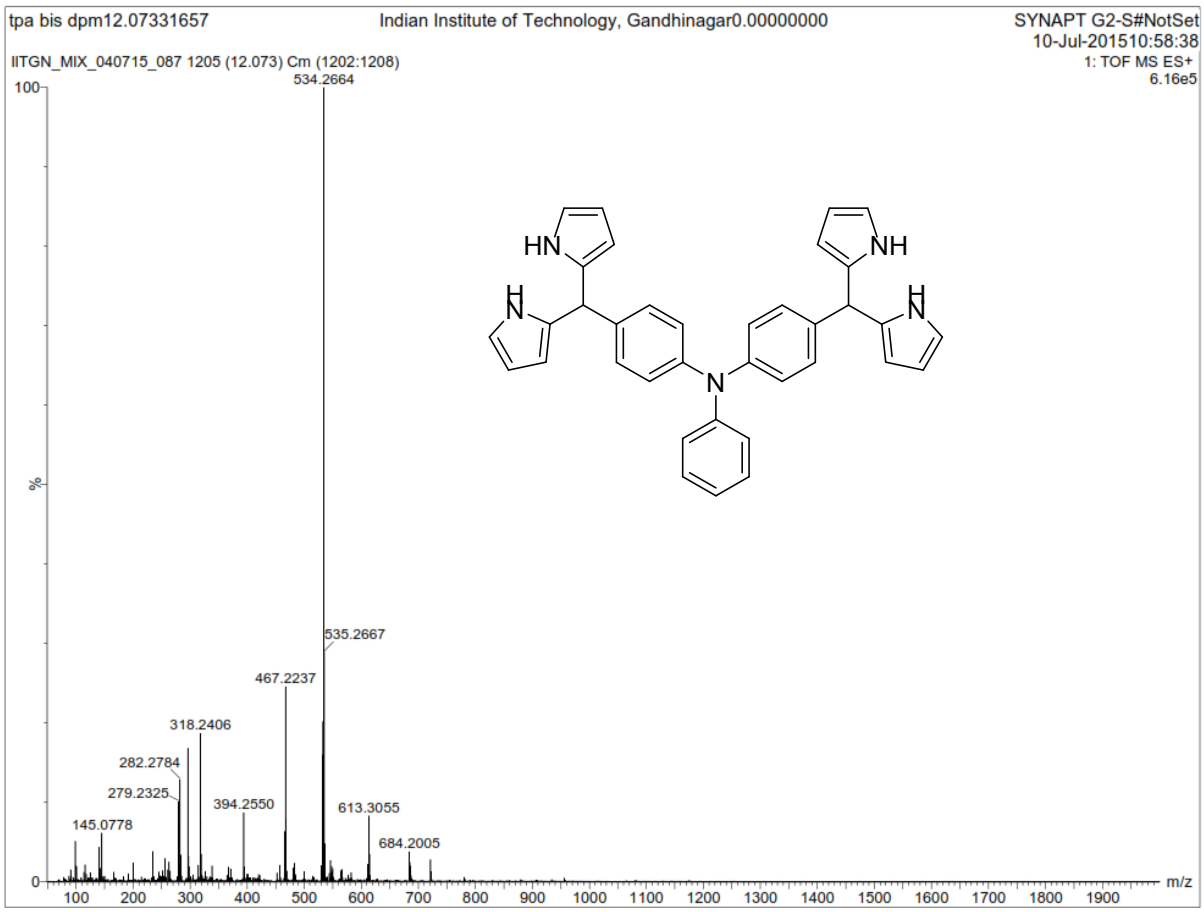


Figure 6: ^{1}H NMR spectrum of Bis-dipyrrane **9** in $CDCl_3$.



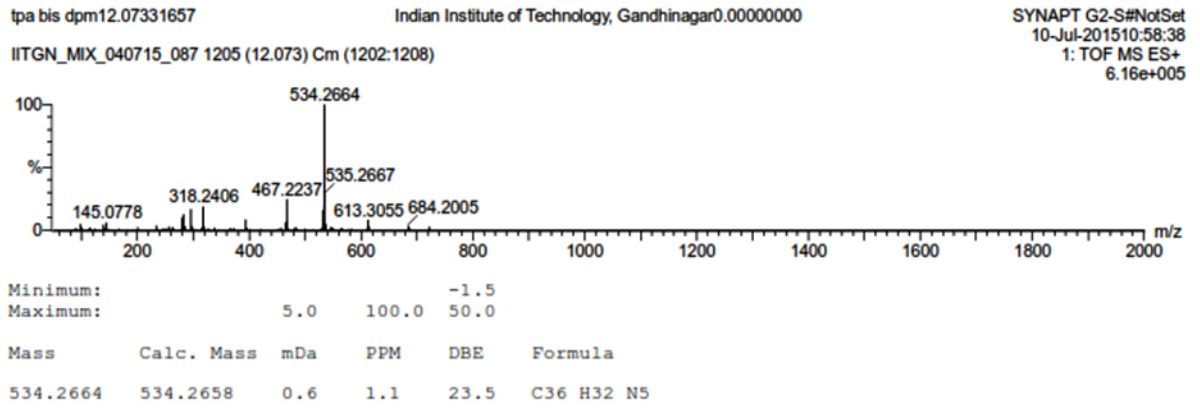


Figure 7: HRMS spectrum of Bis-dipyrrane **10**.

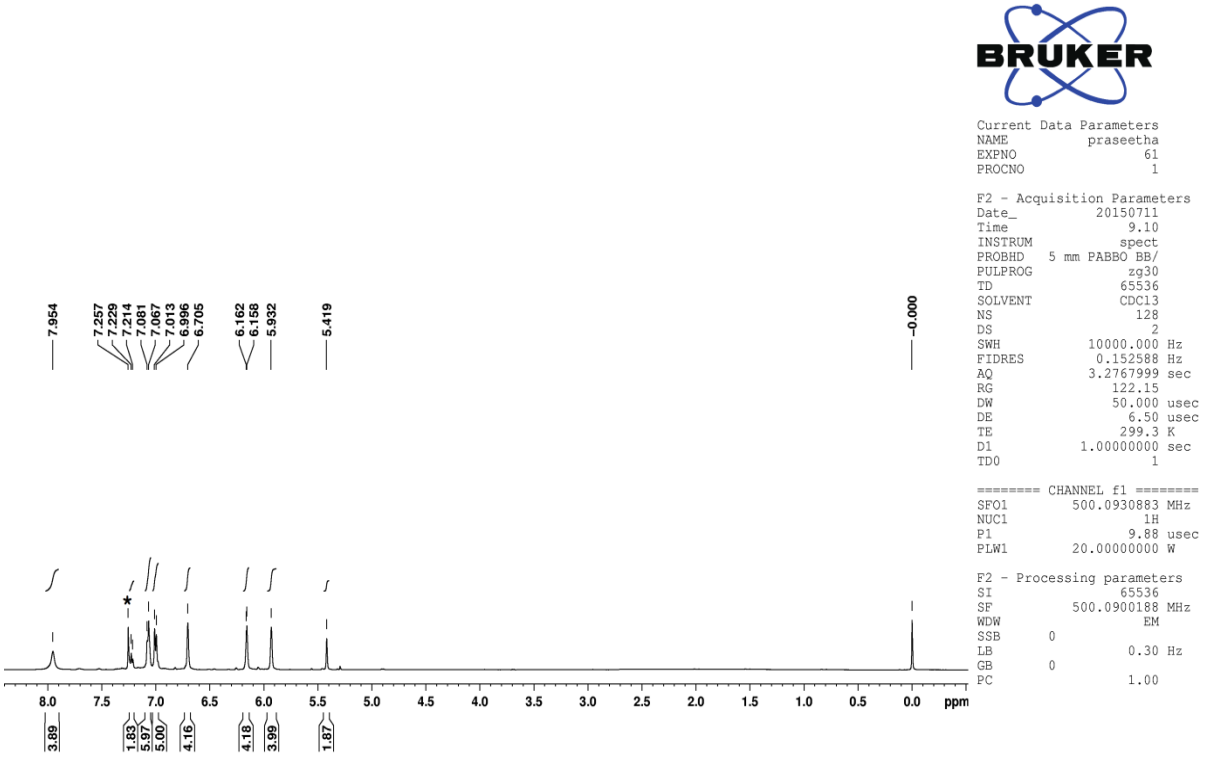
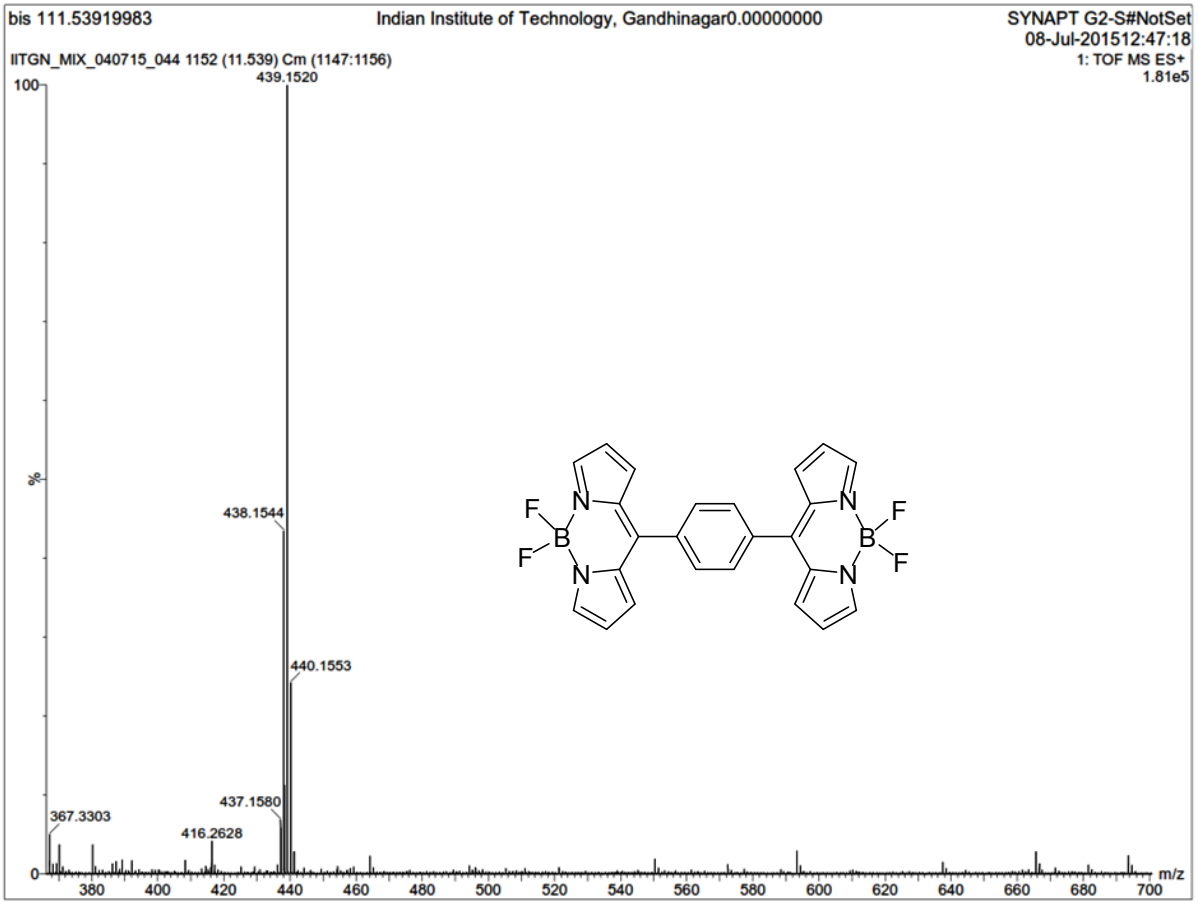
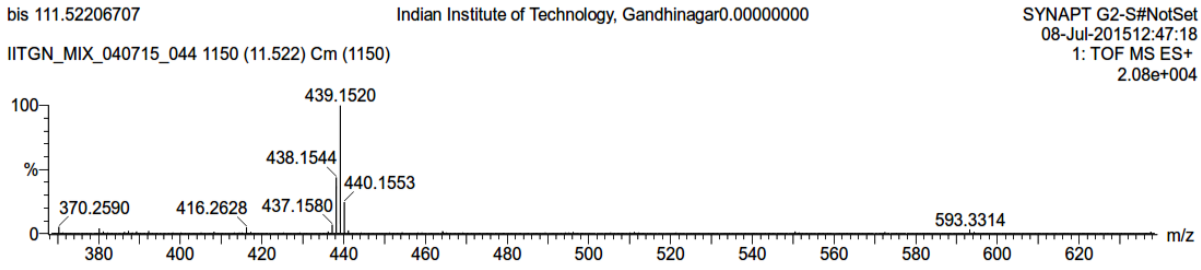


Figure 8: ^{1}H NMR spectrum of Bis-dipyrrane **10** in $CDCl_3$.





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Maximum:		5.0	100.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
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Figure 9: HRMS spectrum of Bis-BODIPY **1.**

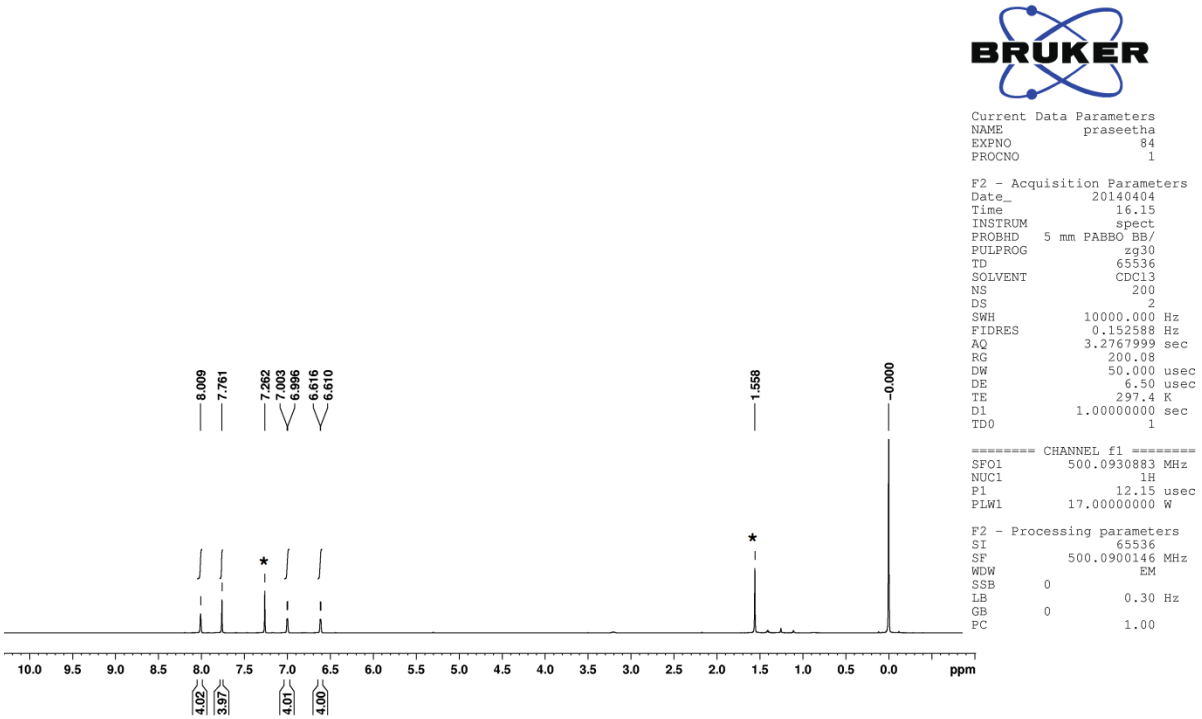

Figure 10: ^{1}H NMR spectrum of Bis-BODIPY **1** in $CDCl_3$.

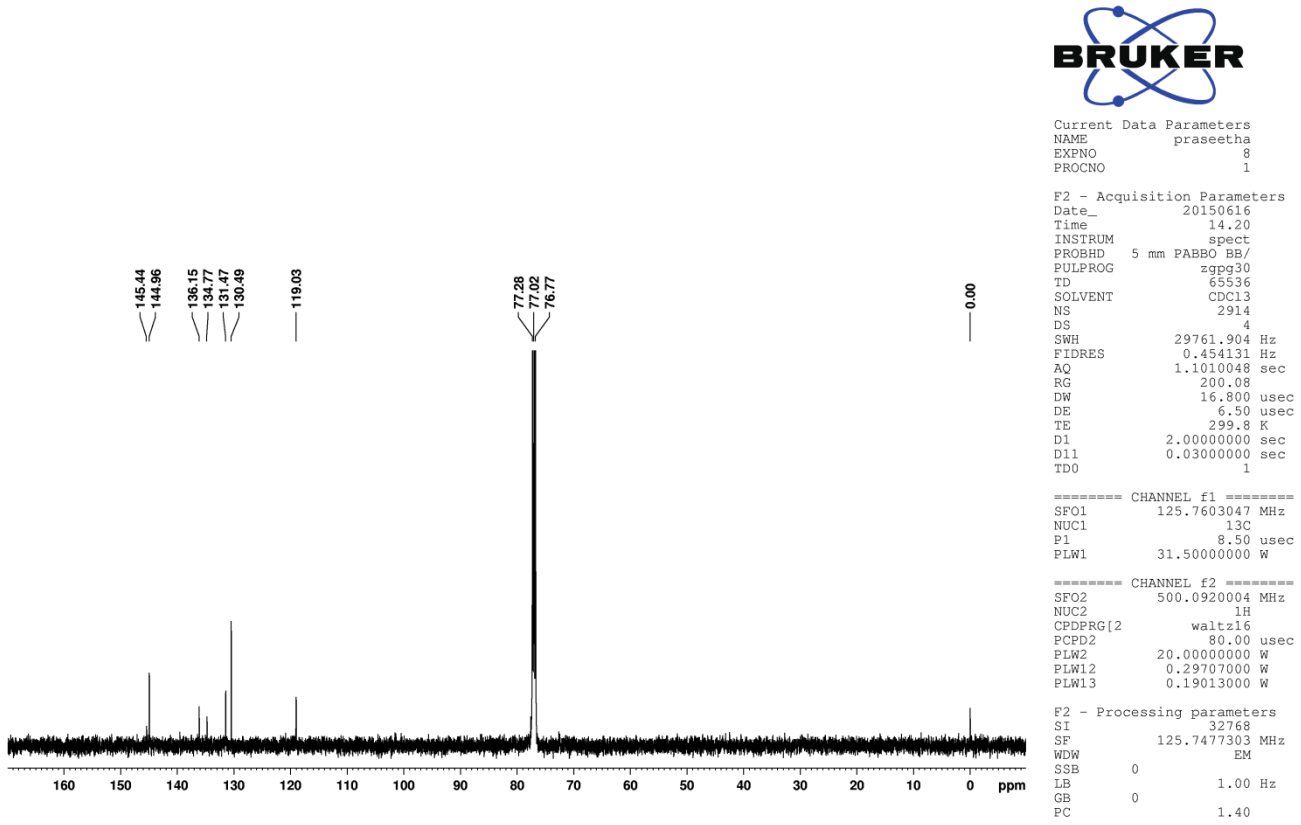

Figure 11: ^{13}C NMR spectrum of Bis-BODIPY **1** in $CDCl_3$.

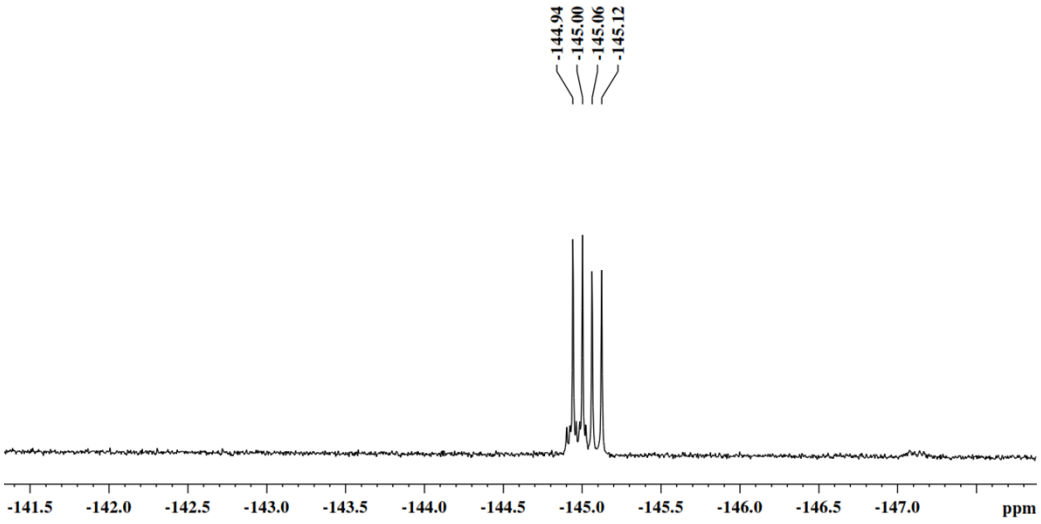

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Figure 12: ^{19}F NMR spectrum of Bis-BODIPY **1** in $CDCl_3$.

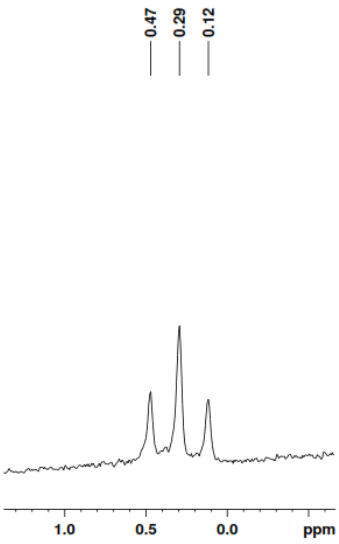

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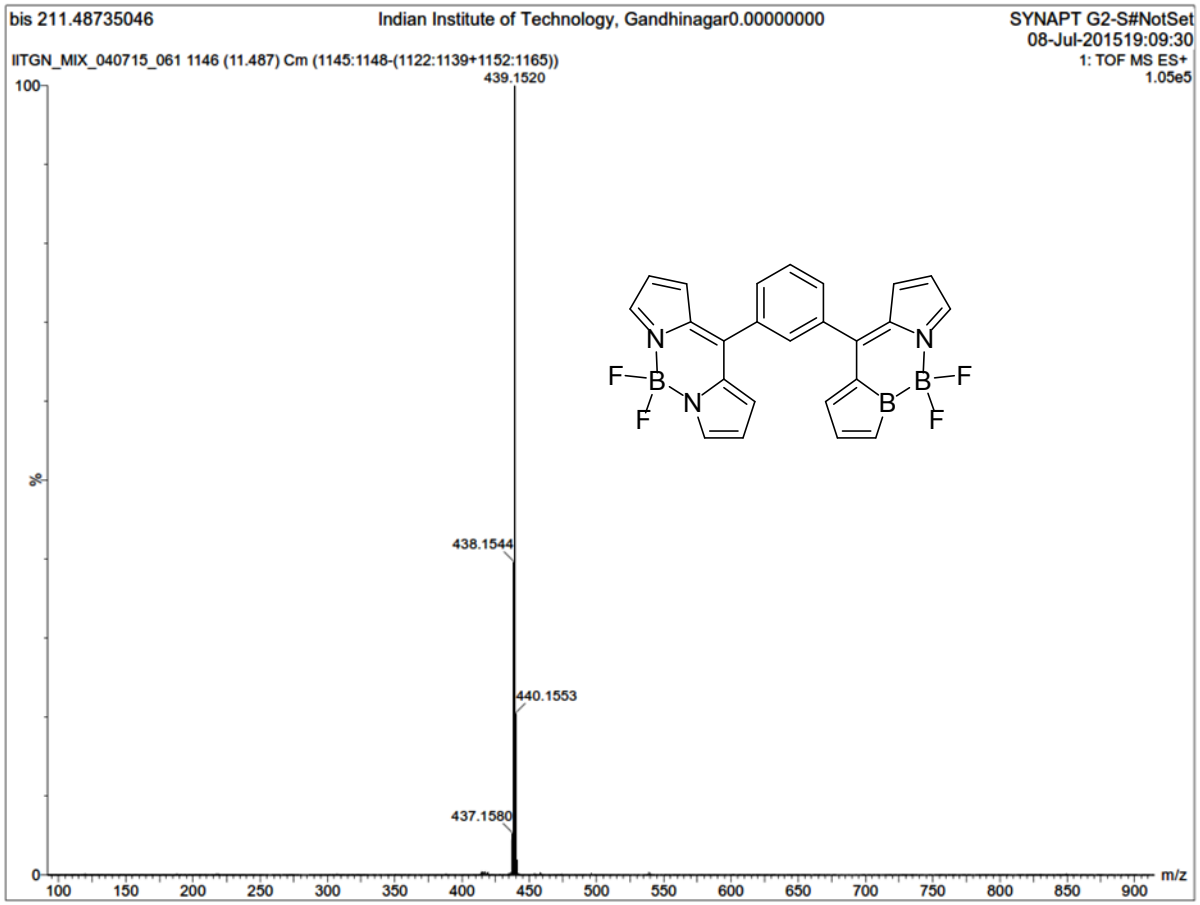
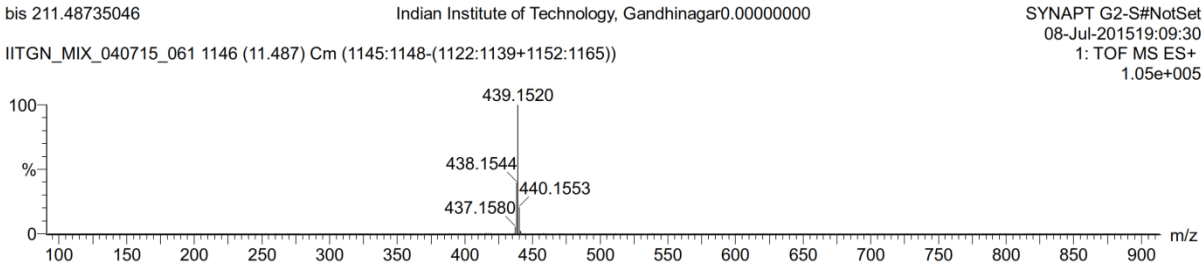
Figure 13: ^{11}B NMR spectrum of Bis-BODIPY **1** in $CDCl_3$.





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Maximum:		5.0	100.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
439.1520	439.1513	0.7	1.6	18.5	C24 H16 B2 N4 F3

Figure 14: HRMS spectrum of Bis-BODIPY **2**.

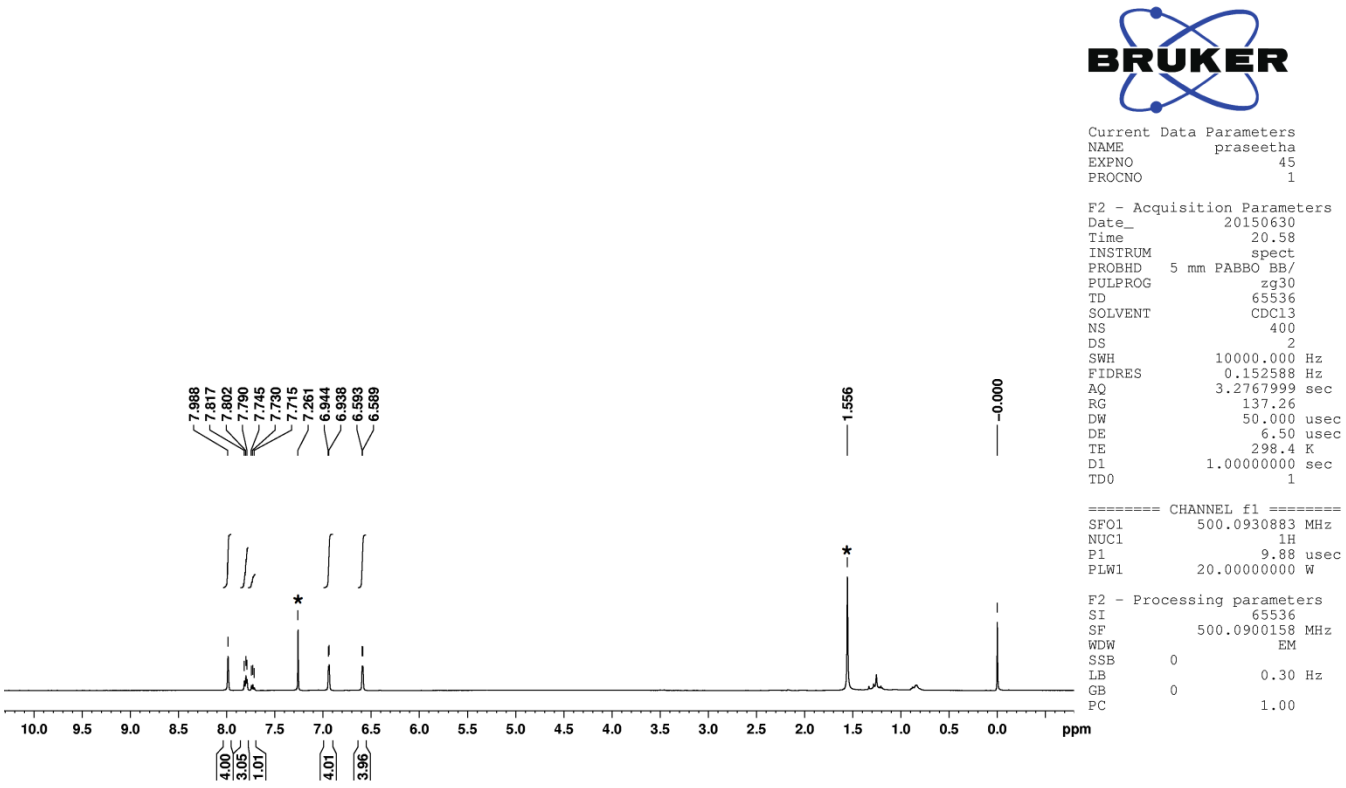


Figure 15: ^{1}H NMR spectrum of Bis-BODIPY **2** in $CDCl_3$.

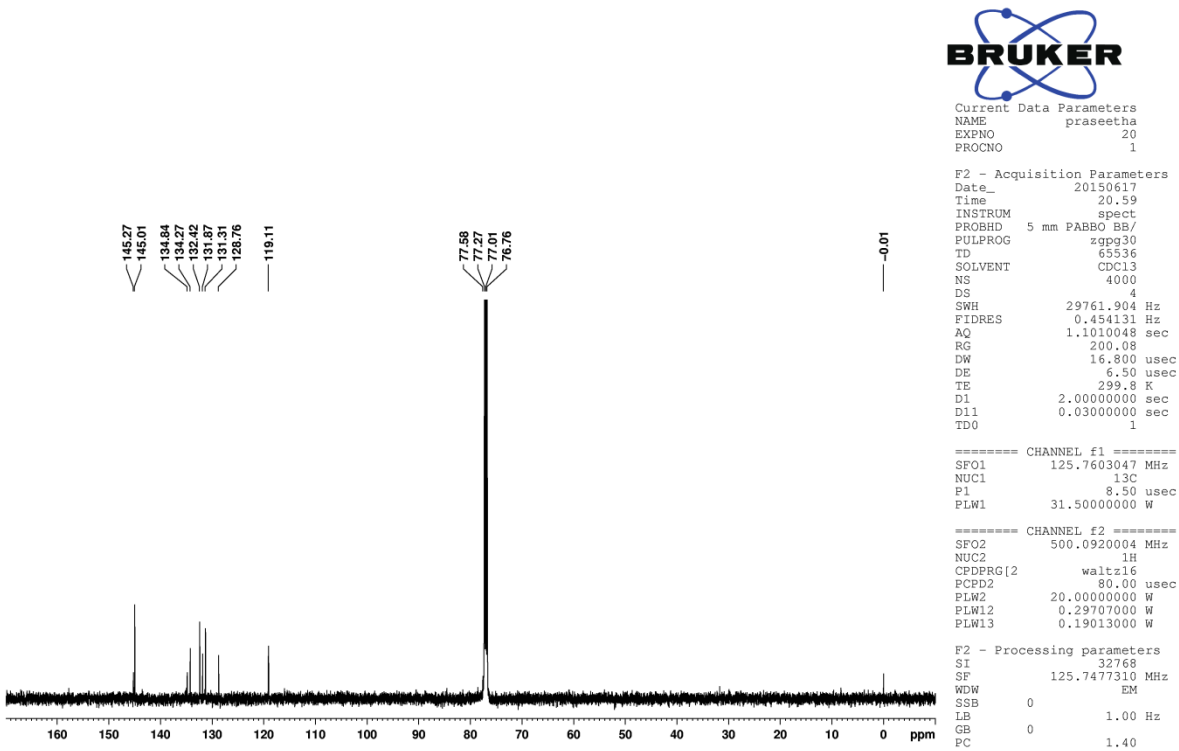


Figure 16: ^{13}C NMR spectrum of Bis-BODIPY **2** in $CDCl_3$.

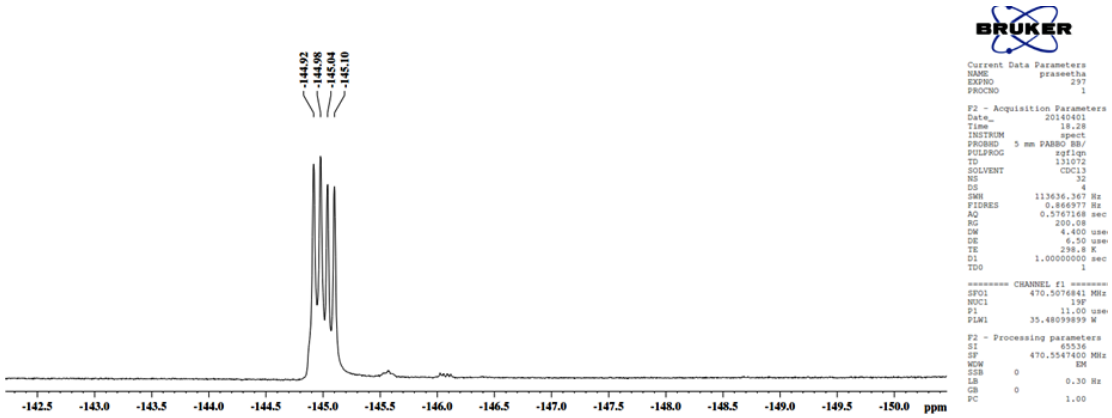
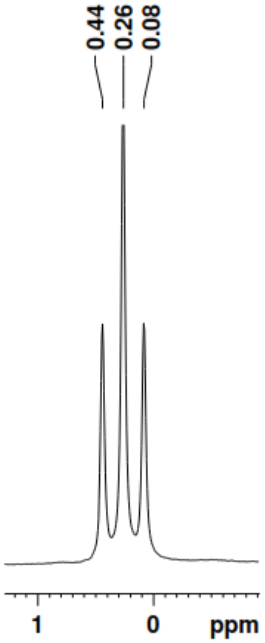


Figure 17: ^{19}F NMR spectrum of Bis-BODIPY **2** in $CDCl_3$.



BRUKER

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D1           1.00000000 sec
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P1                   9.00 usec
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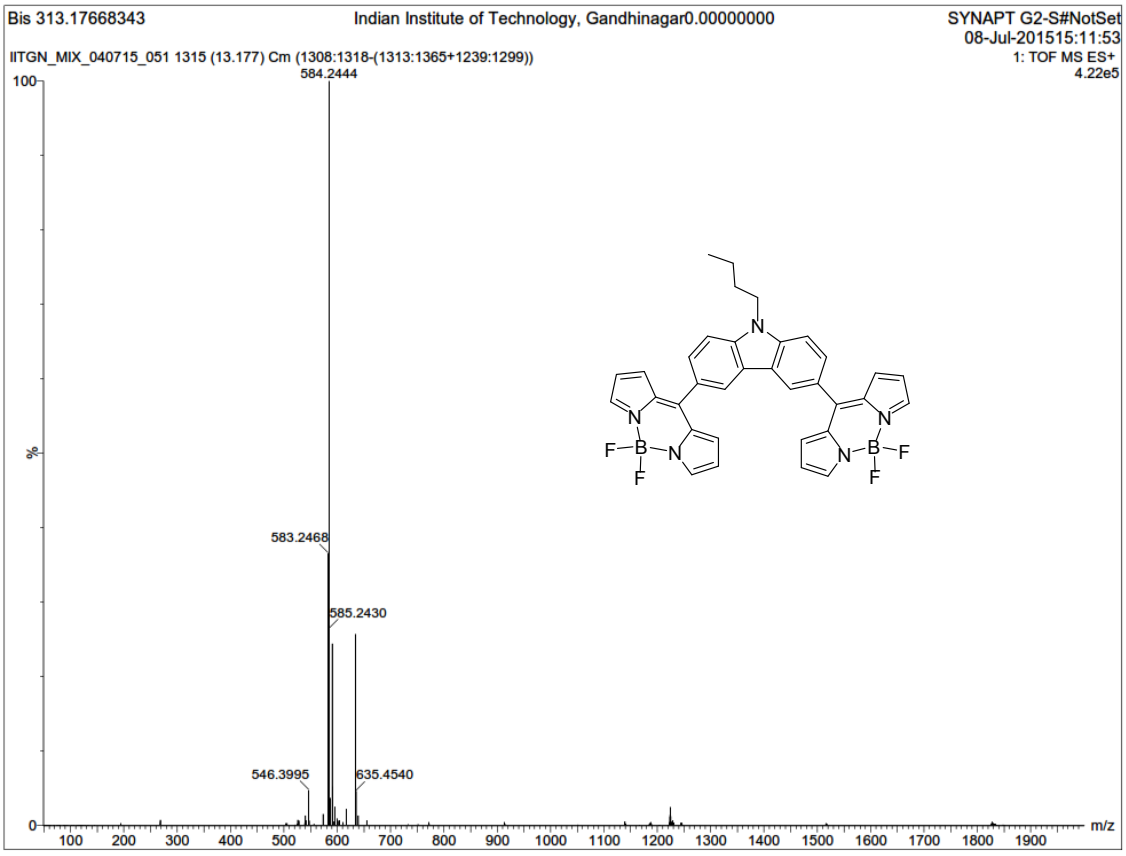

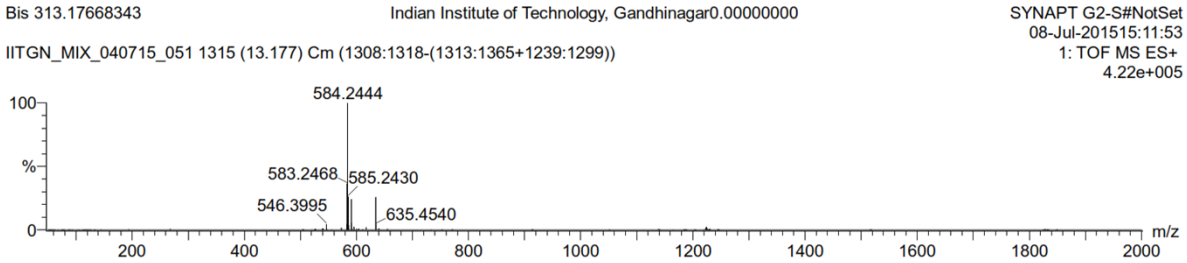

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Figure 19: HRMS spectrum Bis-BODIPY **3.**

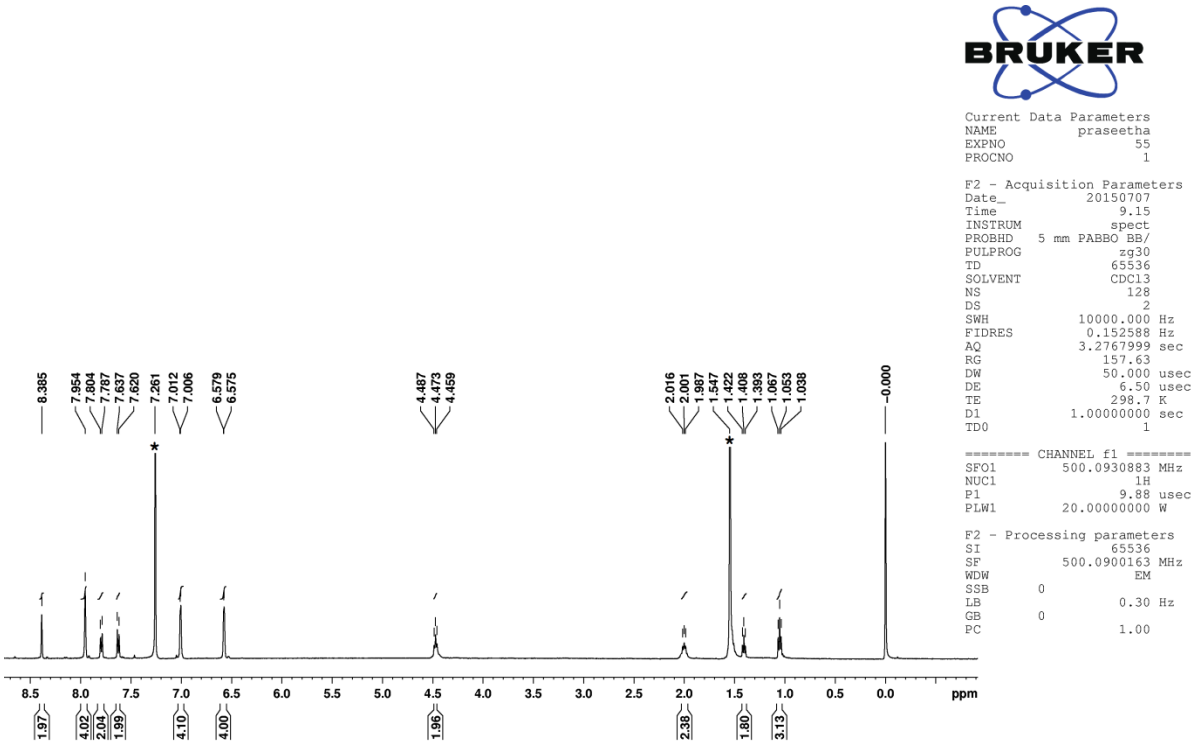


Figure 20: ^{1}H NMR spectrum of Bis-BODIPY **3** in $CDCl_3$.

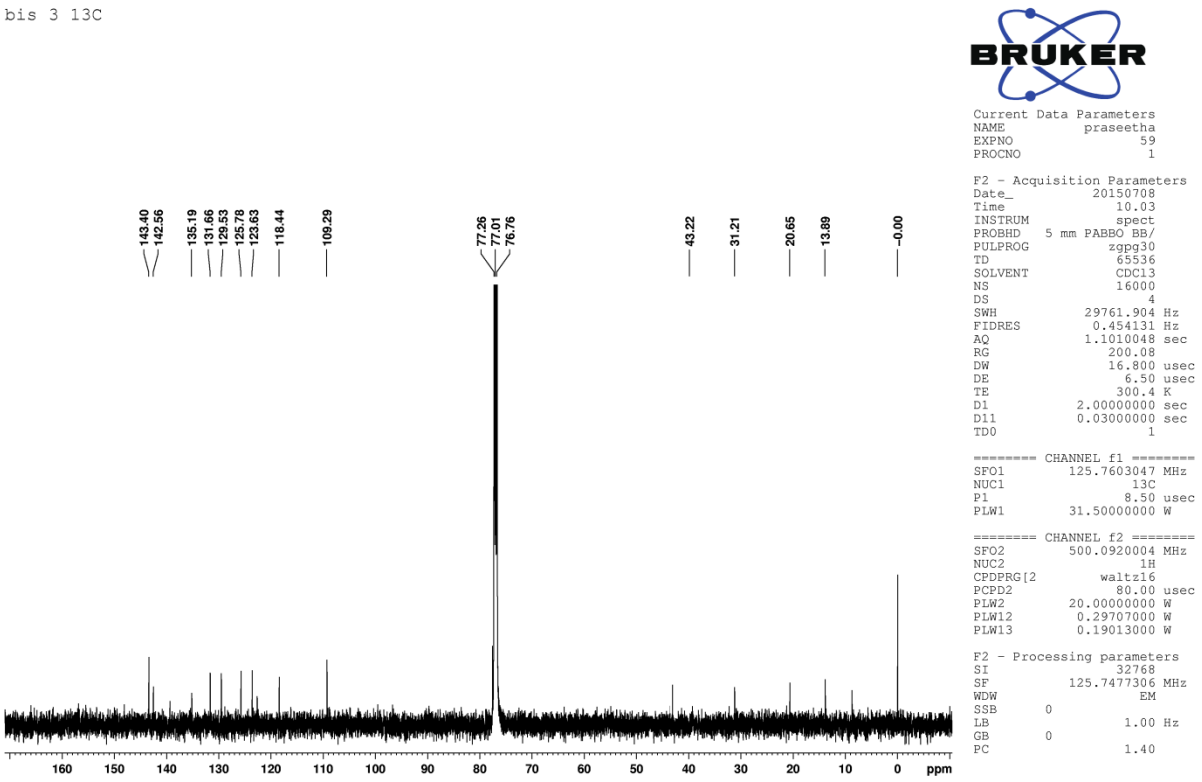


Figure 21: ^{13}C NMR spectrum of Bis-BODIPY **3** in $CDCl_3$.

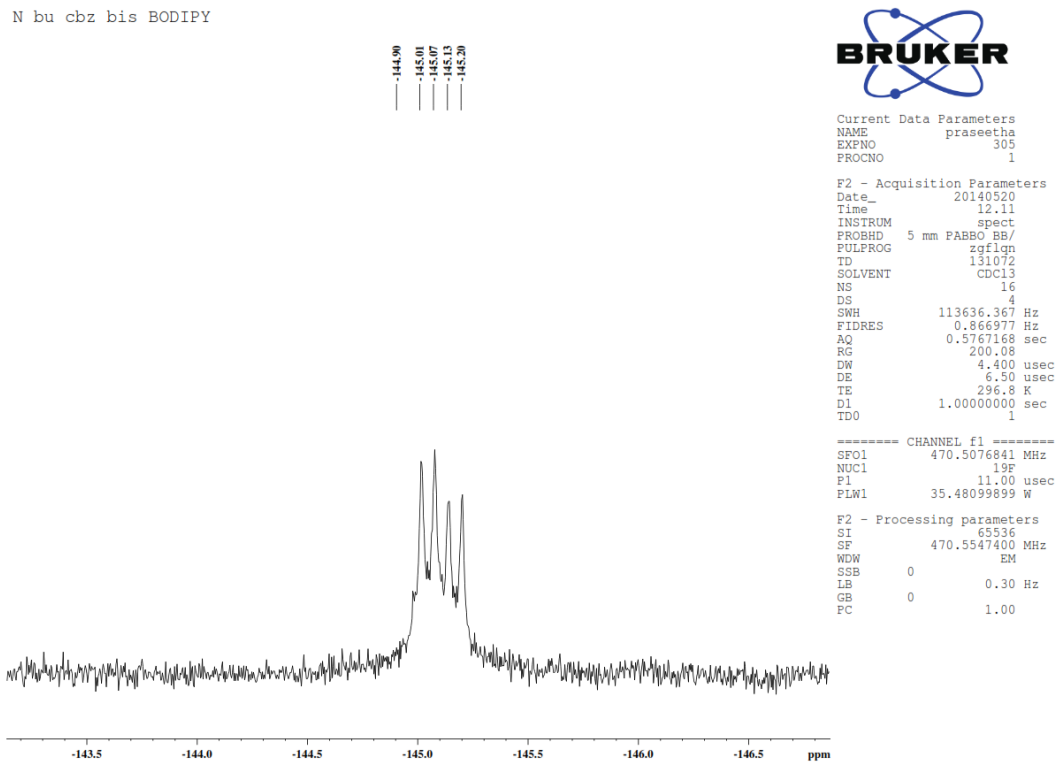


Figure 22: ^{19}F NMR spectrum of Bis-BODIPY **3** in $CDCl_3$.

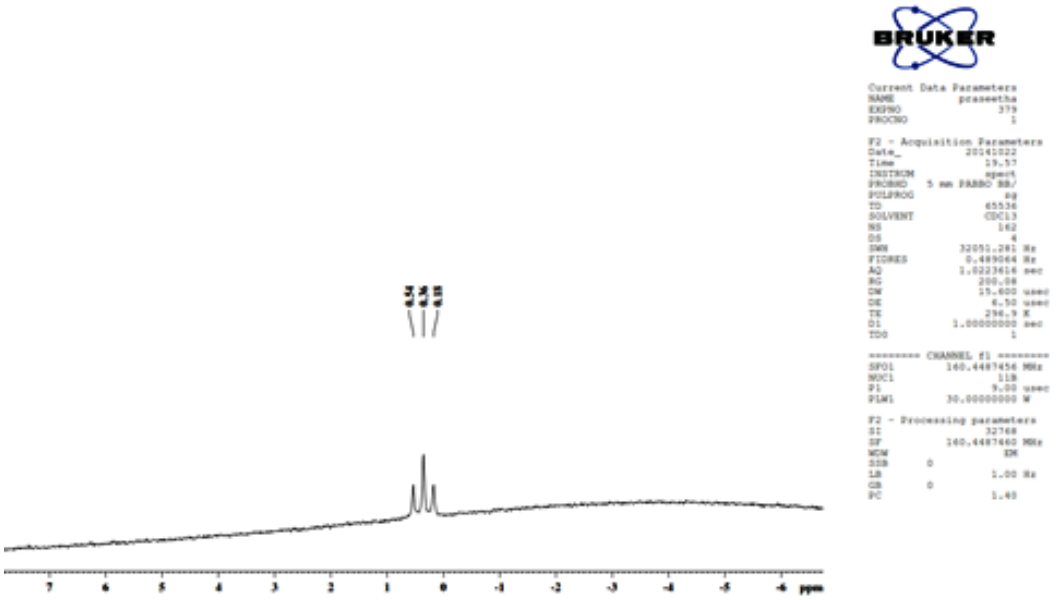
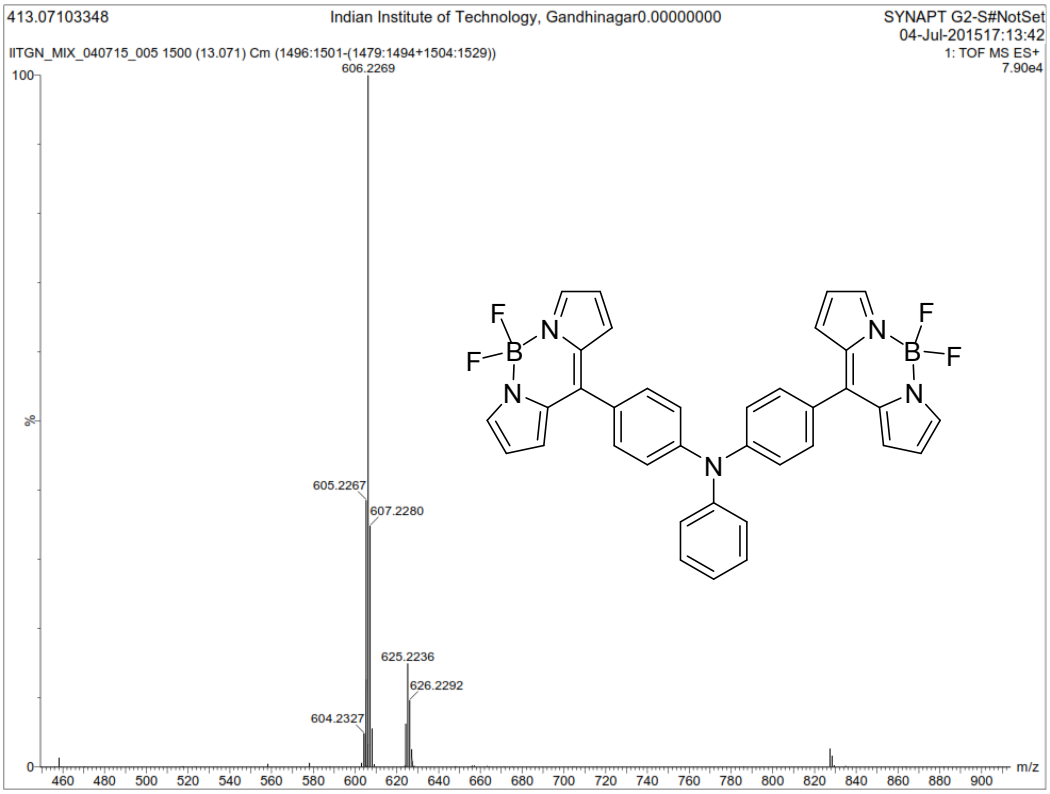


Figure 23: ^{11}B NMR spectrum of Bis-BODIPY **3** in $CDCl_3$.



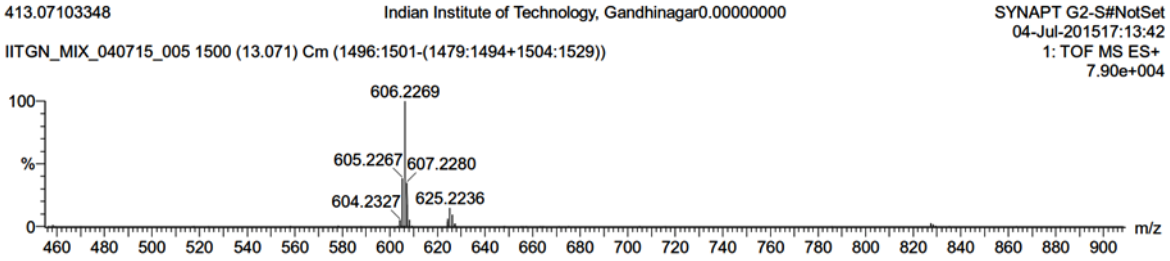



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Figure 24: HRMS spectrum of Bis-BODIPY **4**.

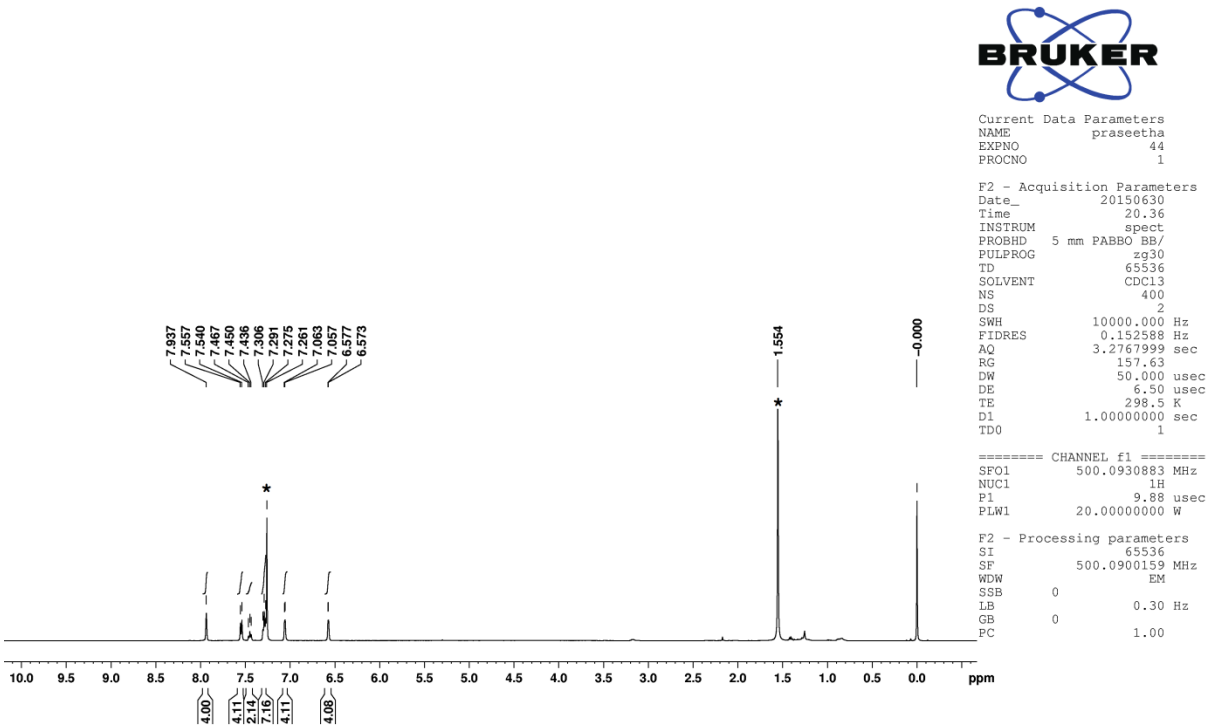


Figure 25: ^{1}H NMR spectrum of Bis-BODIPY **4** in $CDCl_3$.

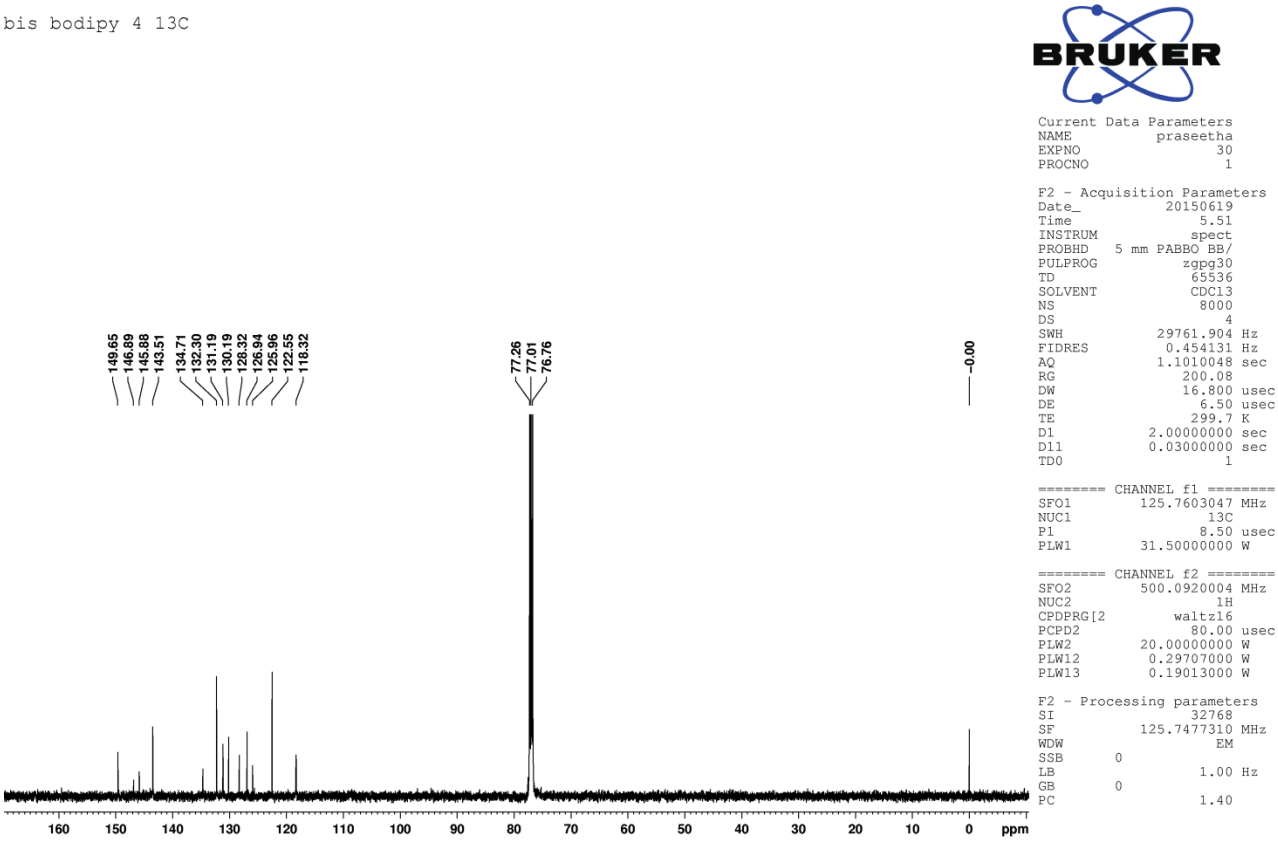


Figure 26: ^{13}C NMR spectrum of Bis-BODIPY **4** in $CDCl_3$.

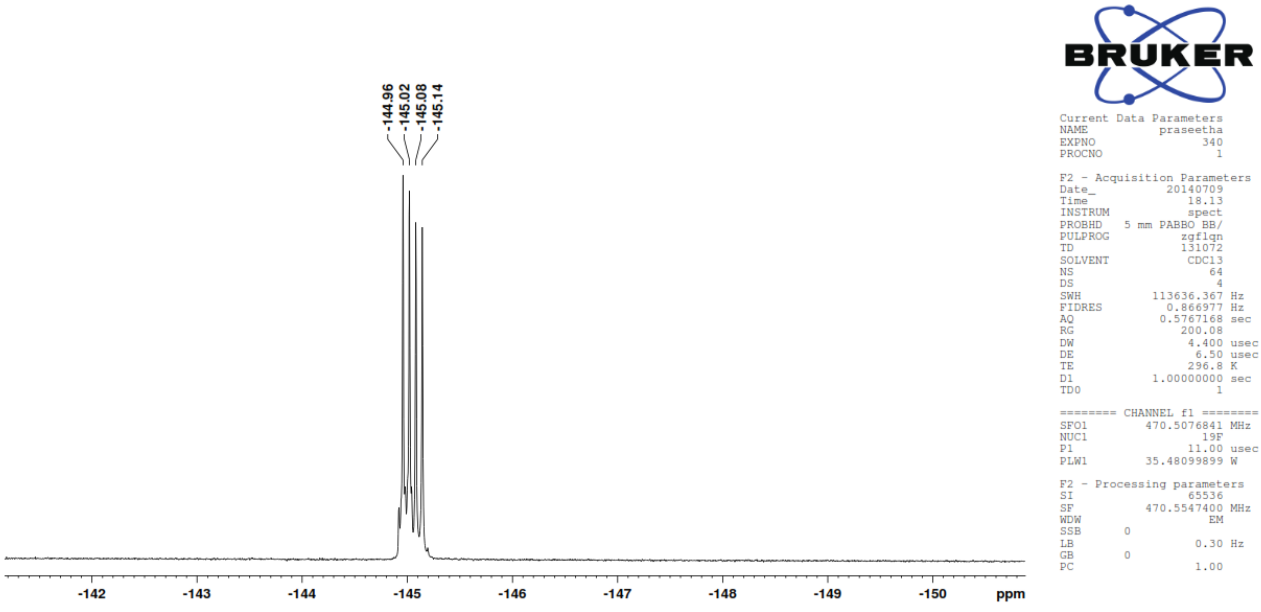


Figure 27: ^{19}F NMR spectrum of Bis-BODIPY **4** in $CDCl_3$.

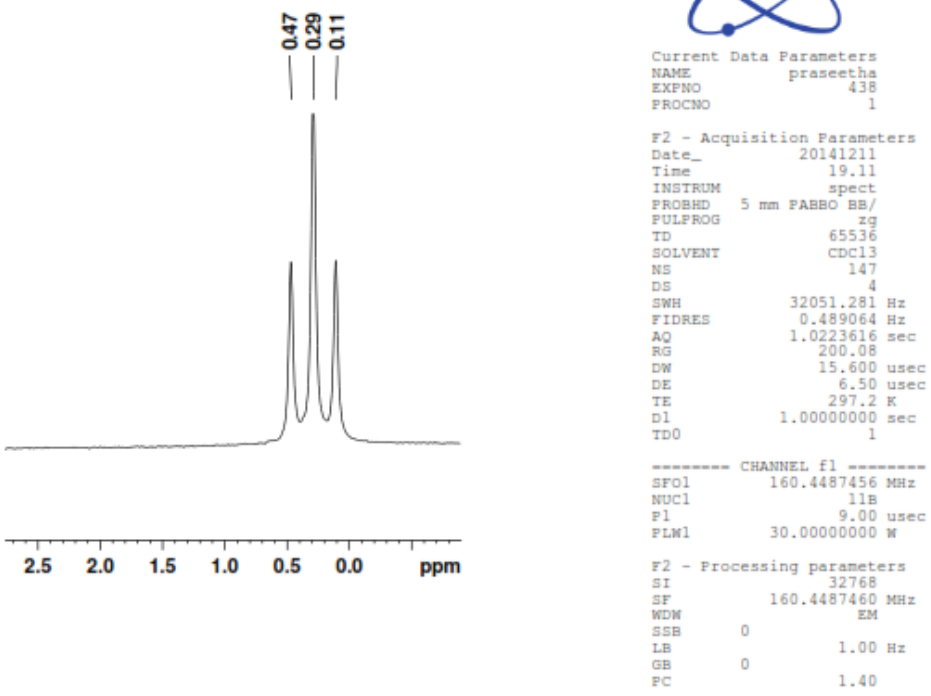
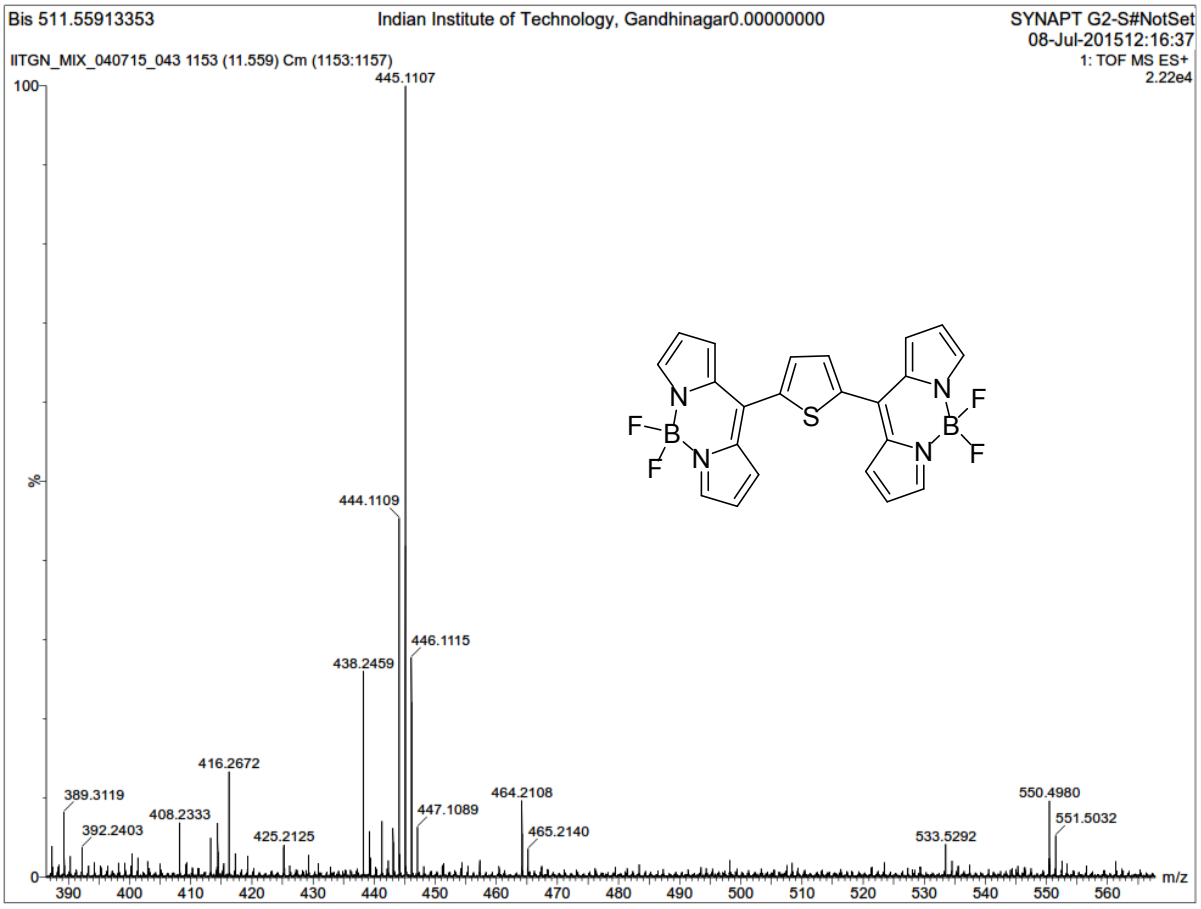
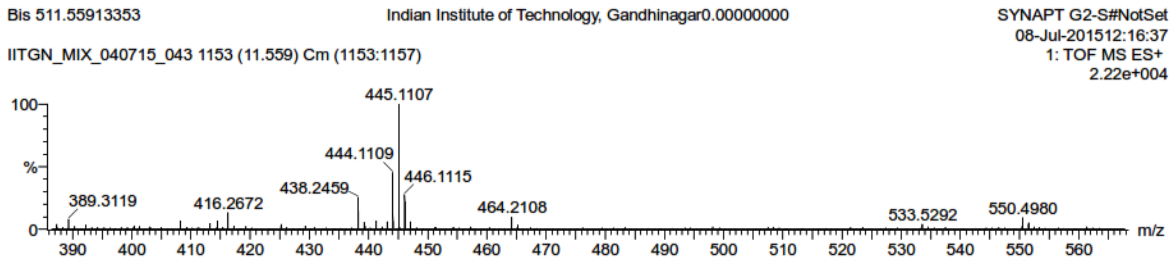


Figure 28: ^{11}B NMR spectrum of Bis-BODIPY **4** in $CDCl_3$.





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Mass	**Calc. Mass**	**mDa**	**PPM**	**DBE**	**Formula**
445.1107	445.1077	3.0	6.7	17.5	C22 H14 B2 N4 F3 S

Figure 29: HRMS spectrum Bis-BODIPY **5**.

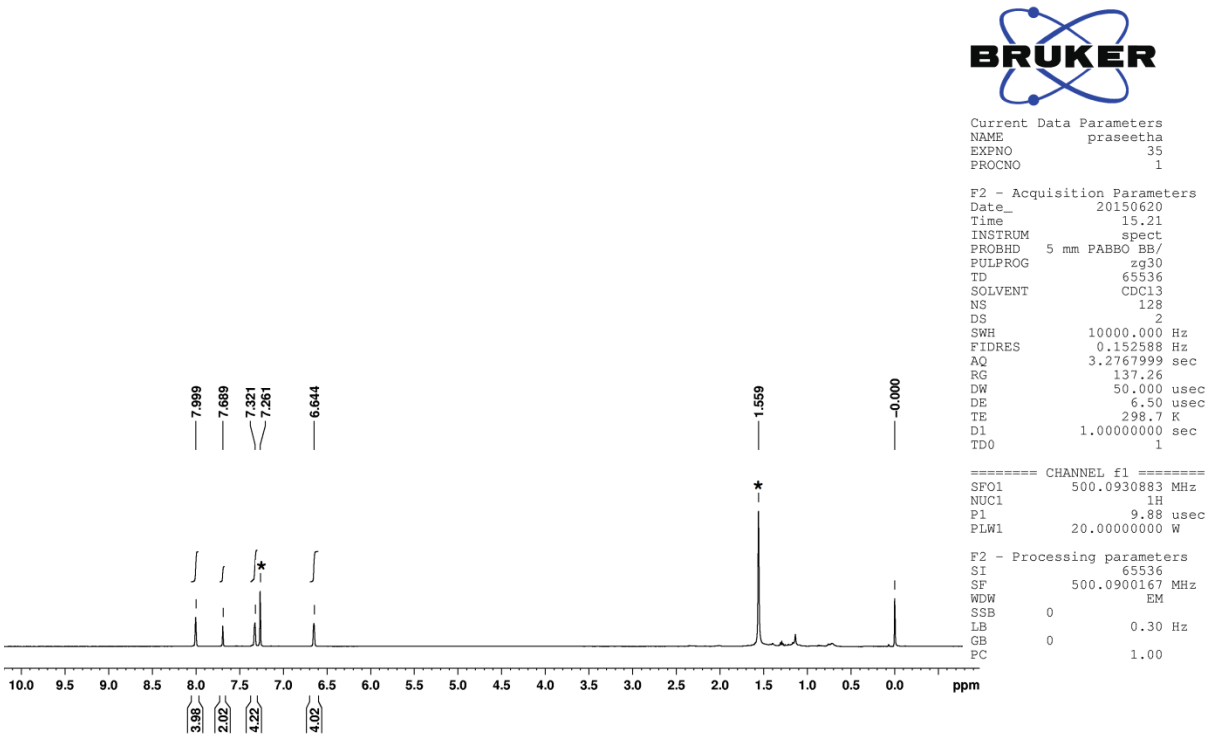


Figure 30: ^{1}H NMR spectrum Bis-BODIPY **5** in $CDCl_3$.

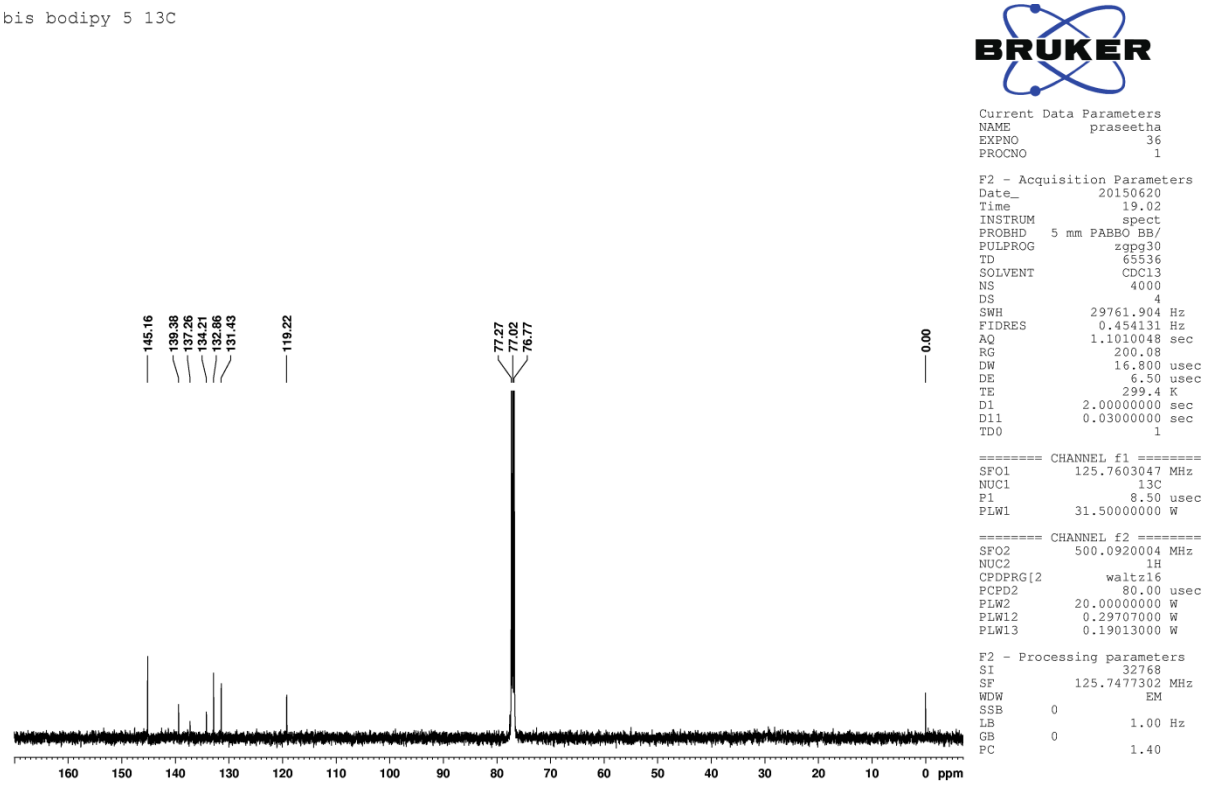
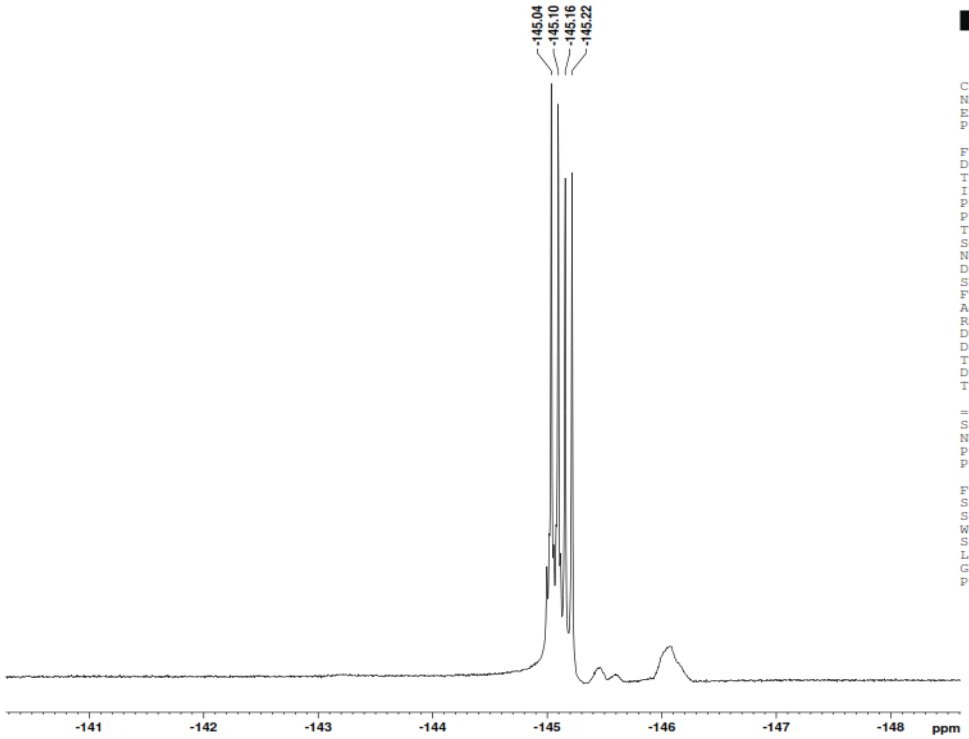
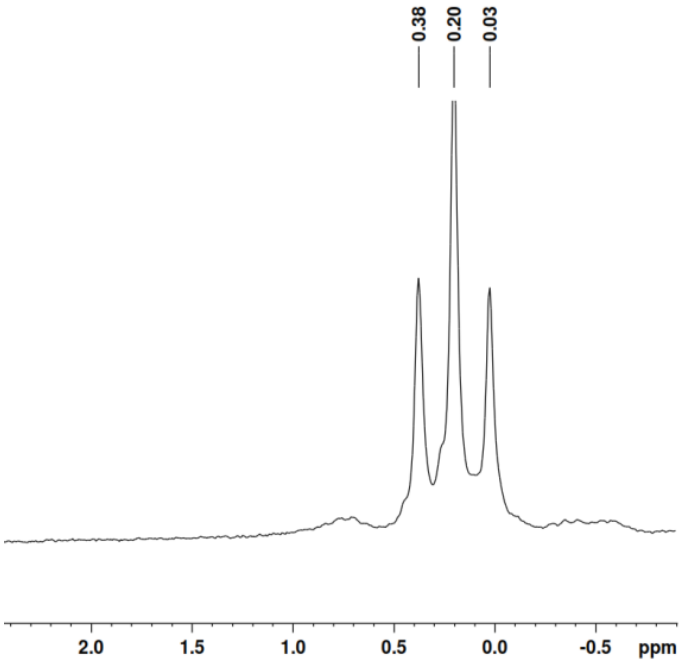


Figure 31: ^{13}C NMR spectrum of Bis-BODIPY **5** in $CDCl_3$.



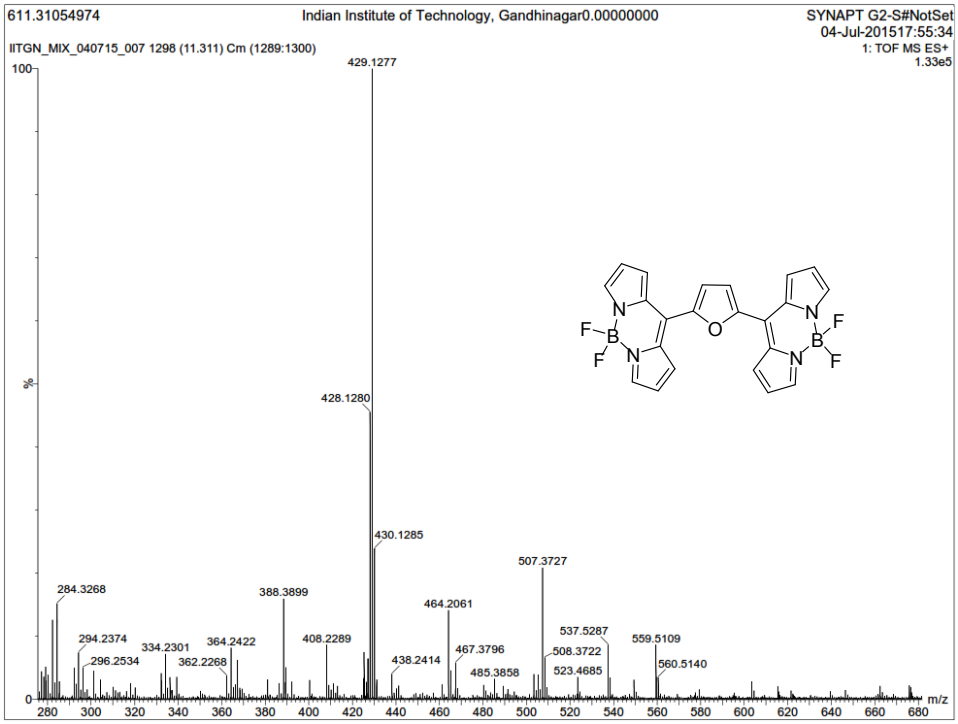

```
Current Data Parameters
NAME                praseetha
EXPNO                     424
PROCNO                      1

F2 - Acquisition Parameters
Date_              20141119
Time                  21.58
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG             zgflqn
TD                  131072
SOLVENT               CDCl3
NS                      128
DS                        4
SWH              113636.367 Hz
FIDRES             0.866977 Hz
AQ                 0.5767168 sec
RG                    200.08
DW                   4.400 usec
DE                   6.50 usec
TE                   299.7 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            470.5076841 MHz
NUC1                     19F
P1                     11.00 usec
PLW1           35.48099899 W

F2 - Processing parameters
SI                      65536
SF              470.5547400 MHz
WDW                        EM
SSB         0
LB                      0.30 Hz
GB          0
PC                      1.00
```

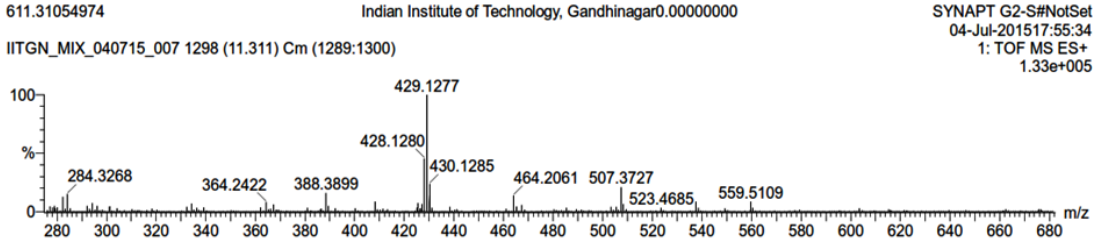
Figure 32: ^{19}F NMR spectrum of Bis-BODIPY **5** in $CDCl_3$.




```
Current Data Parameters
NAME                praseetha
EXPNO                     425
PROCNO                      1

F2 - Acquisition Parameters
Date_              20141119
Time                  22.01
INSTRUM               spect
PROBHD     5 mm PABBO BB/
PULPROG                 zg
TD                   65536
SOLVENT               CDCl3
NS                      128
DS                        4
SWH              32051.281 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                    200.08
DW                  15.600 usec
DE                   6.50 usec
TE                   299.7 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            160.4487456 MHz
NUC1                     11B
P1                      9.00 usec
PLW1           30.00000000 W

F2 - Processing parameters
SI                      32768
SF              160.4487460 MHz
WDW                        EM
SSB         0
LB                      1.00 Hz
GB          0
PC                      1.40
```

Figure 33: ^{11}B NMR spectrum of Bis-BODIPY **5** in $CDCl_3$.





Minimum:				-1.5	
Maximum:		5.0	100.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
429.1277	429.1306	-2.9	-6.8	17.5	C22 H14 B2 N4 O F3

Figure 34: HRMS spectrum Bis-BODIPY **6.**

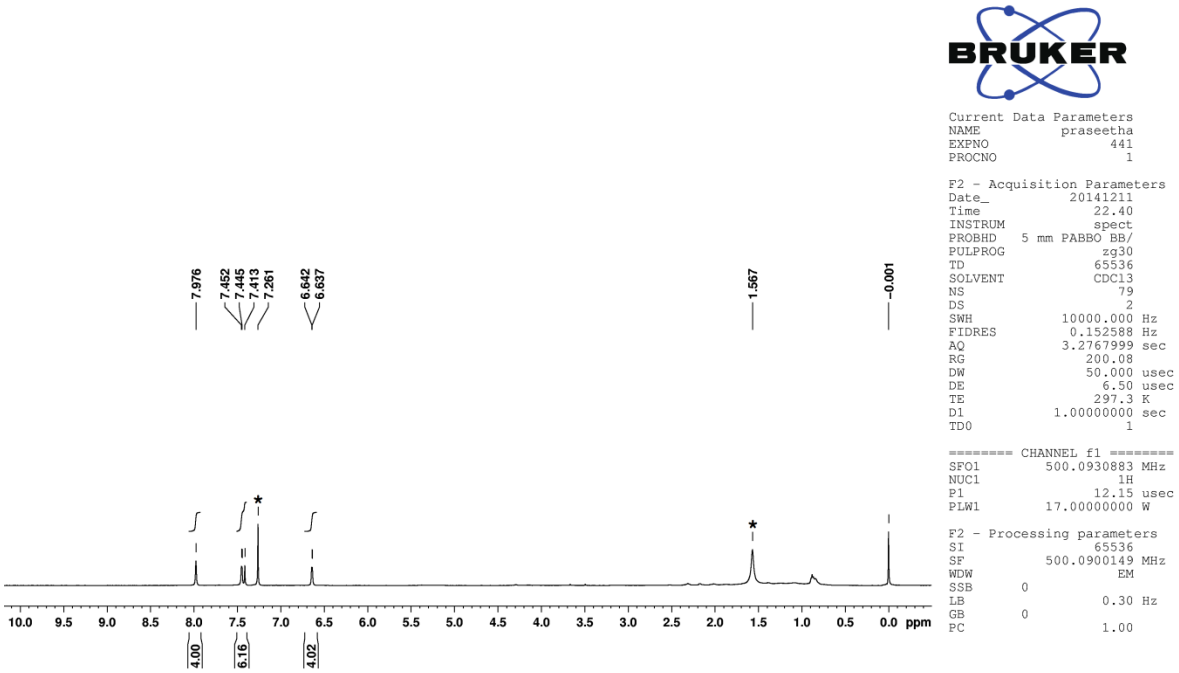


Figure 35: ^{1}H NMR spectrum of Bis-BODIPY **6** in $CDCl_3$.

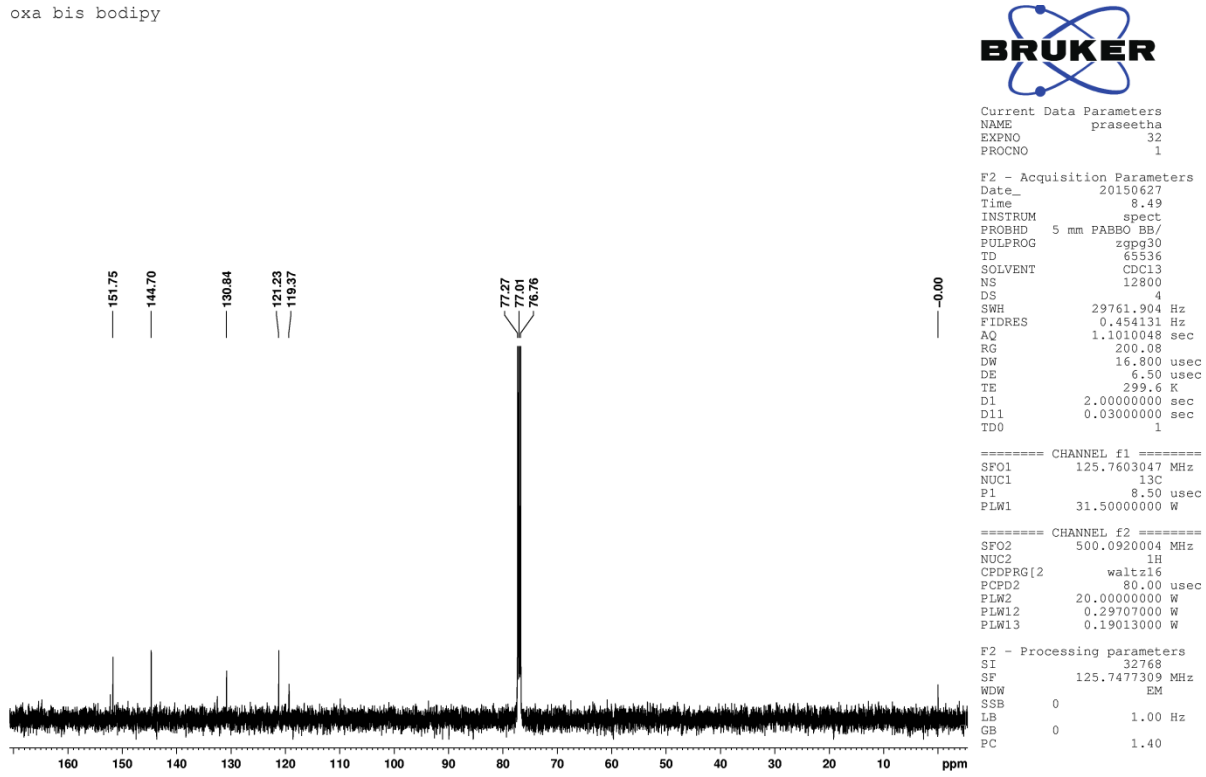


Figure 36: ^{13}C NMR spectrum of Bis-BODIPY **6** in $CDCl_3$.

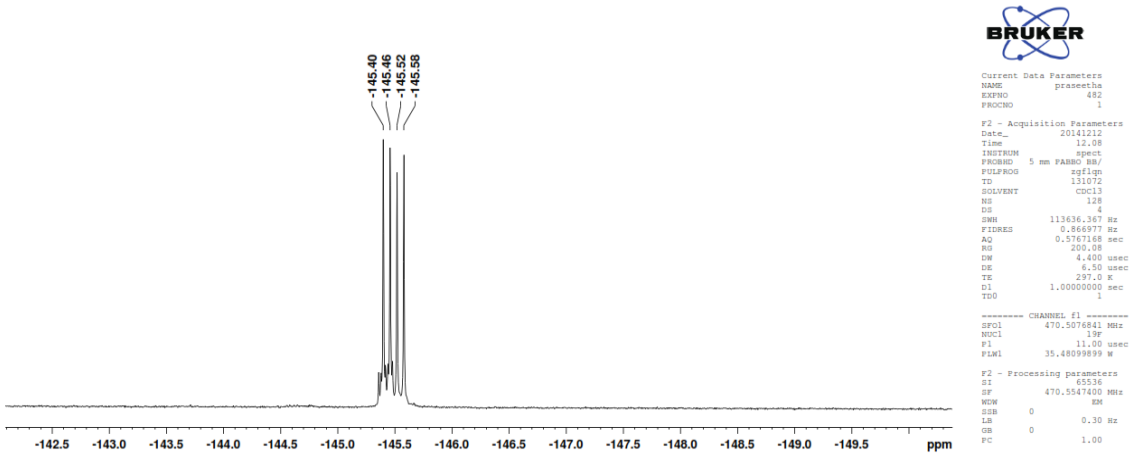


Figure 37: ^{19}FNMR spectrum of Bis-BODIPY **6** in $CDCl_3$.

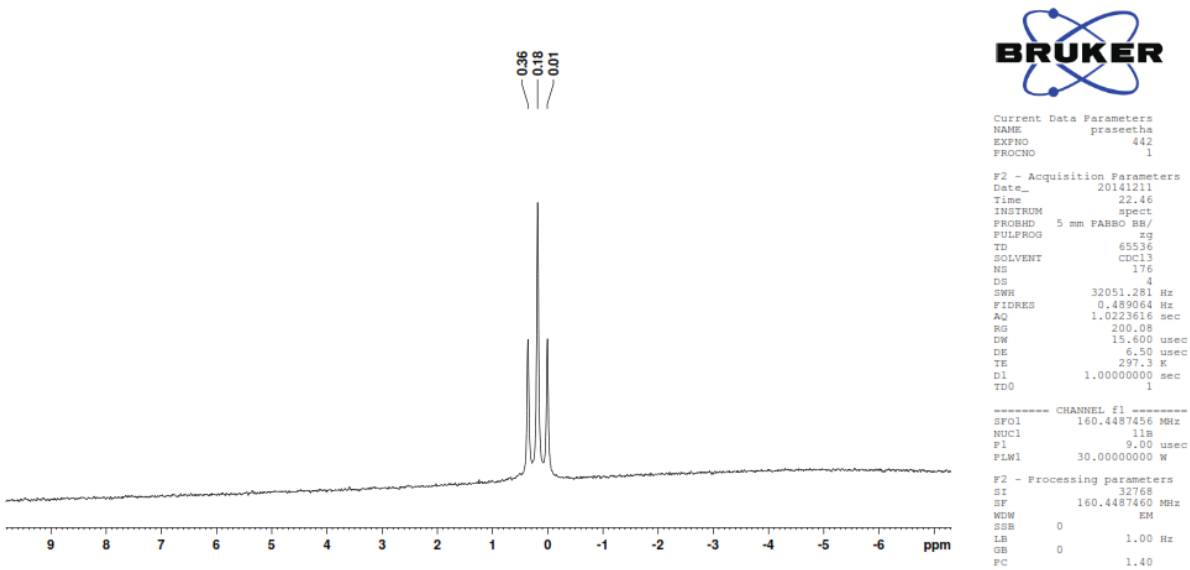


Figure 38: ^{11}B NMR spectrum of Bis-BODIPY **6** in $CDCl_3$.

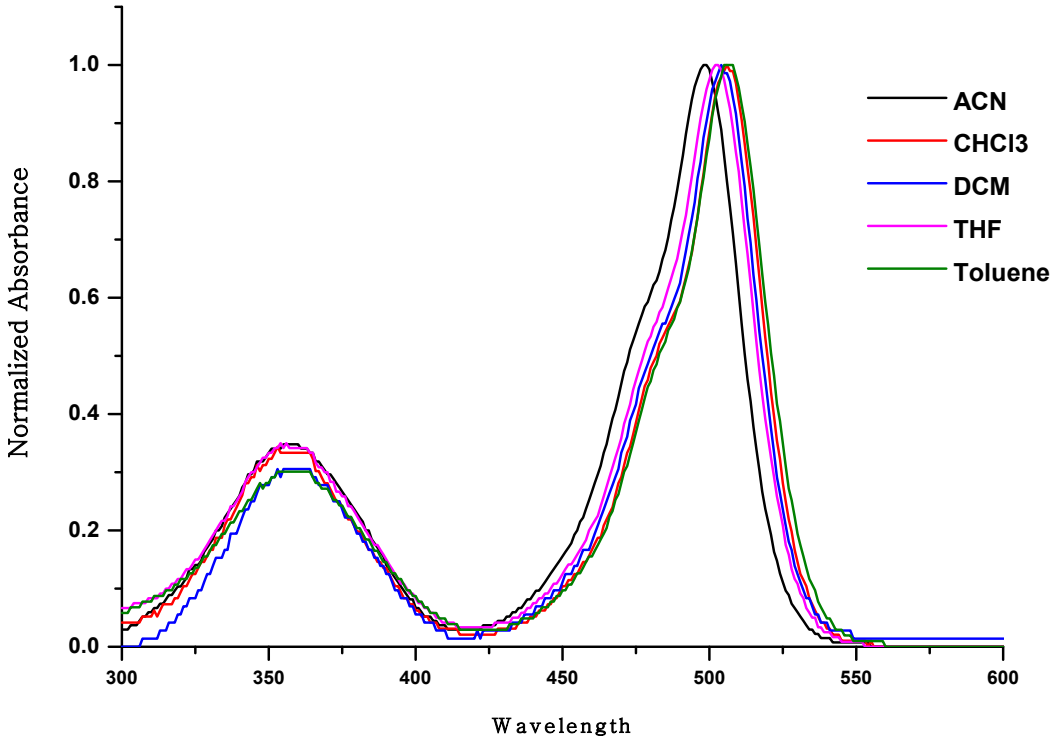


Figure 39: UV-Vis spectra of Bis- BODIPY **1** in different solvents.

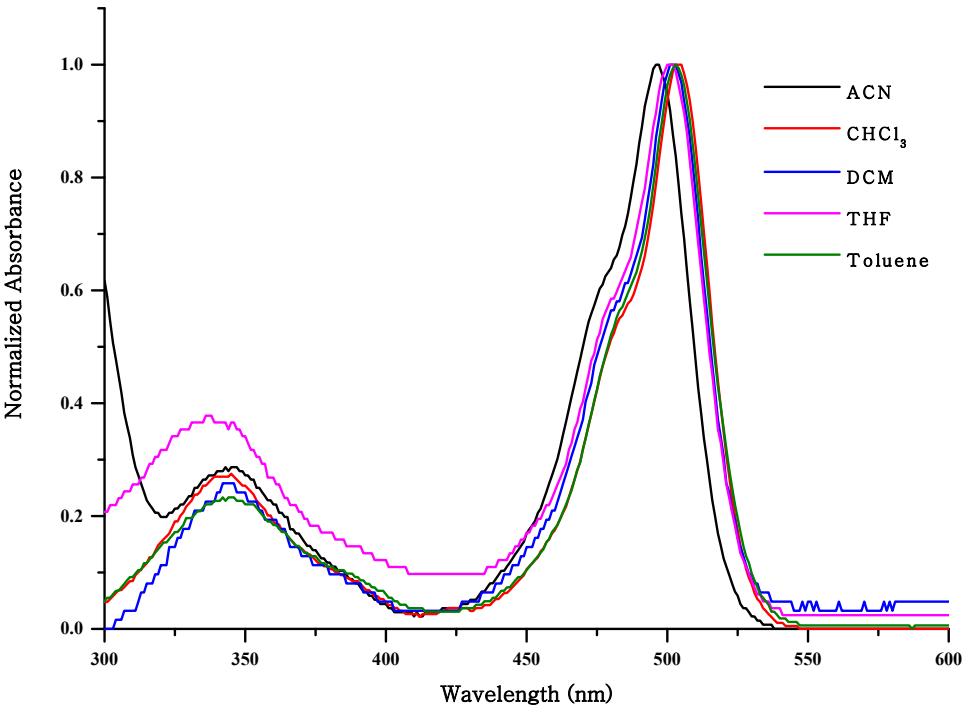


Figure 40: UV-Vis spectra of Bis- BODIPY **2** in different solvents.

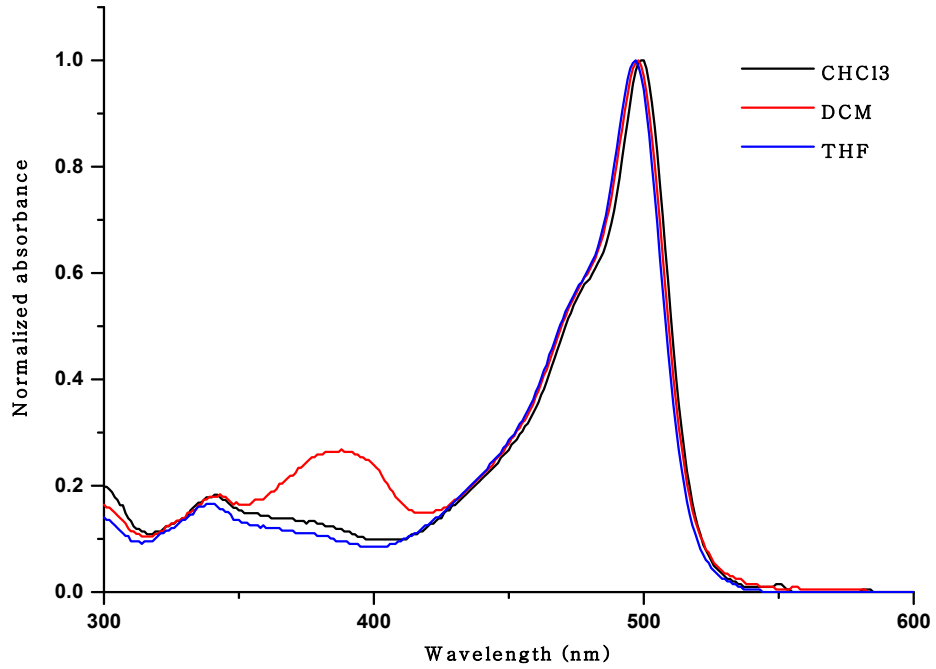


Figure 41: UV-Vis spectra of Bis- BODIPY **3** in different solvents.

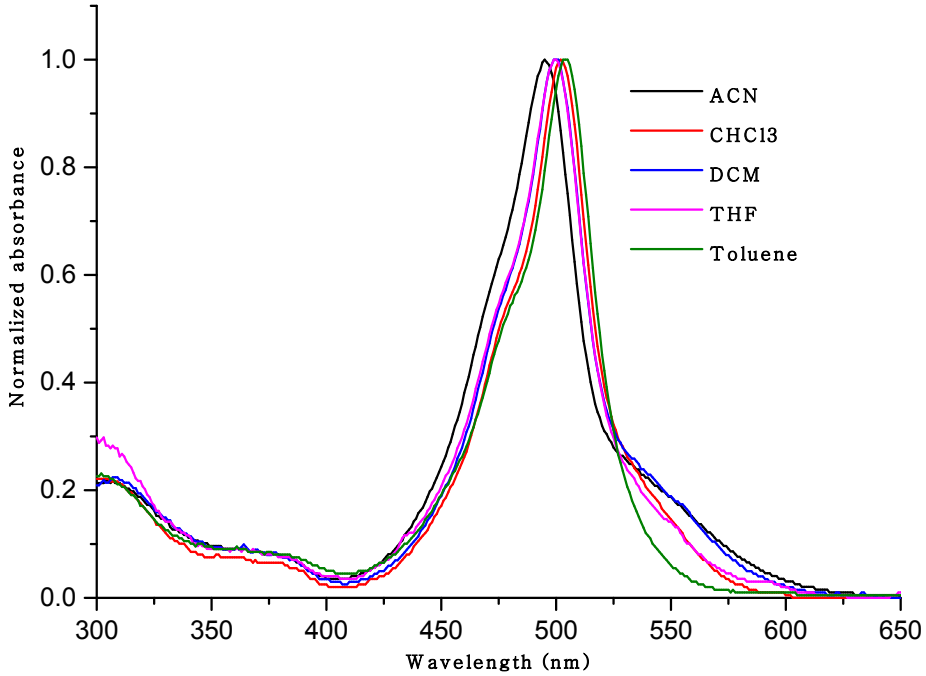


Figure 42: UV-Vis spectra of Bis- BODIPY **4** in different solvents.

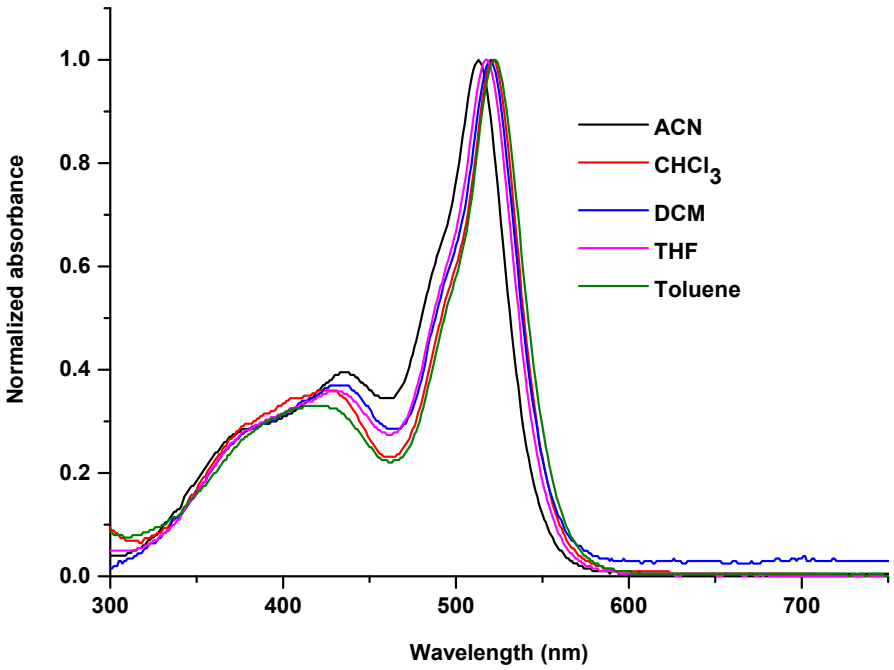


Figure 43: UV-Vis spectra of Bis- BODIPY **5** in different solvents.

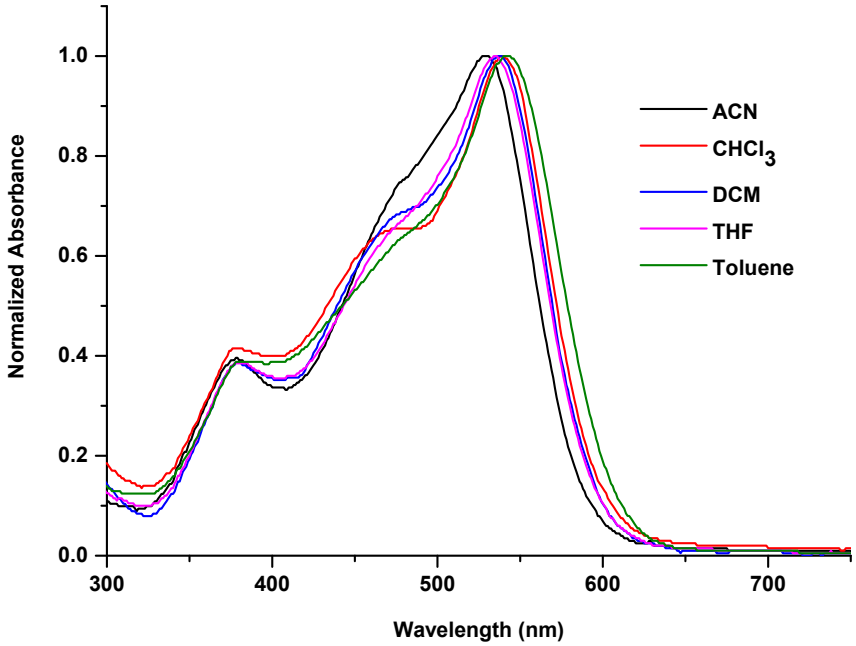


Figure 44: UV-Vis spectra of Bis- BODIPY **6** in different solvents.

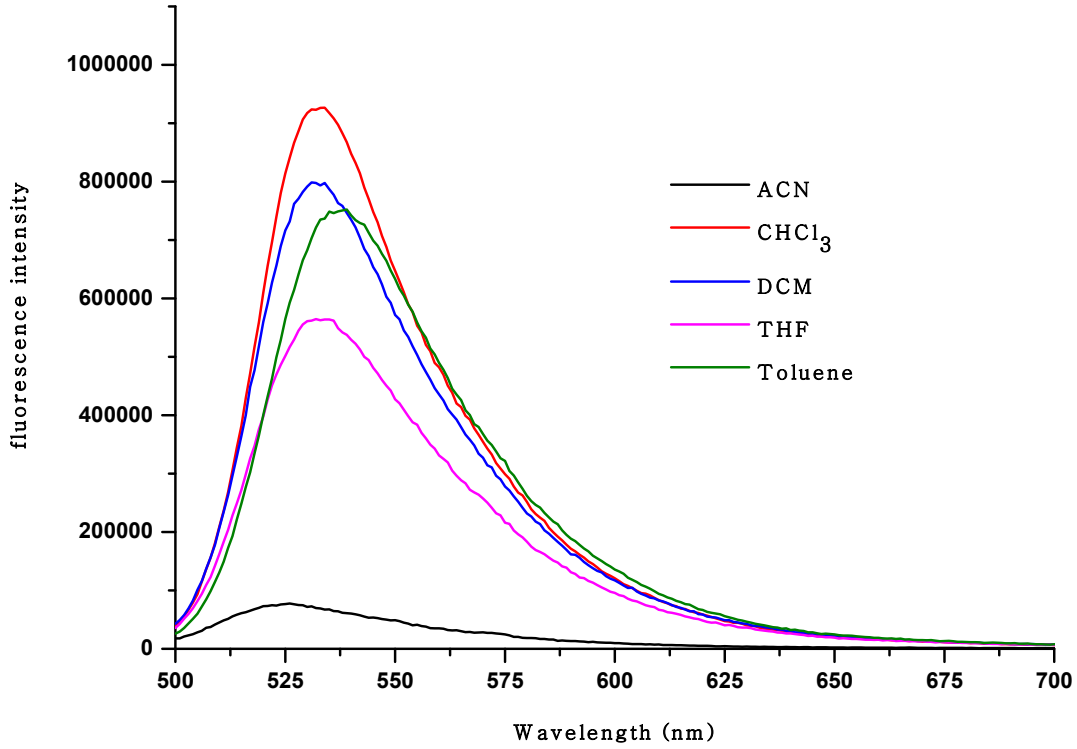


Figure 45: Steady state fluorescence spectra of Bis- BODIPY **1** in different solvents.

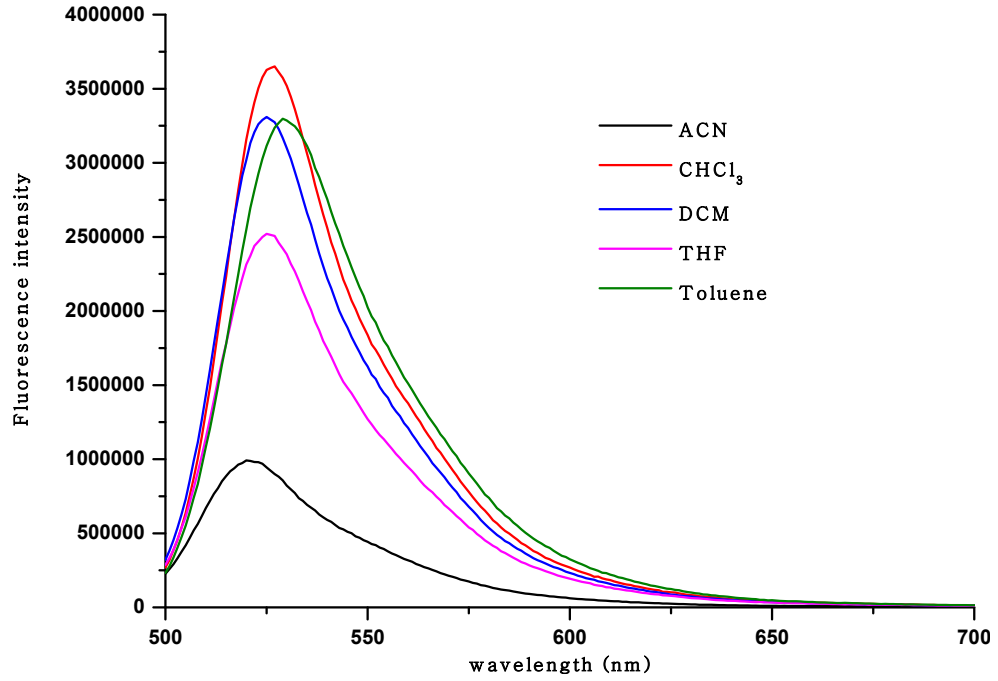


Figure 46: Steady state fluorescence spectra of Bis- BODIPY **2** in different solvents.

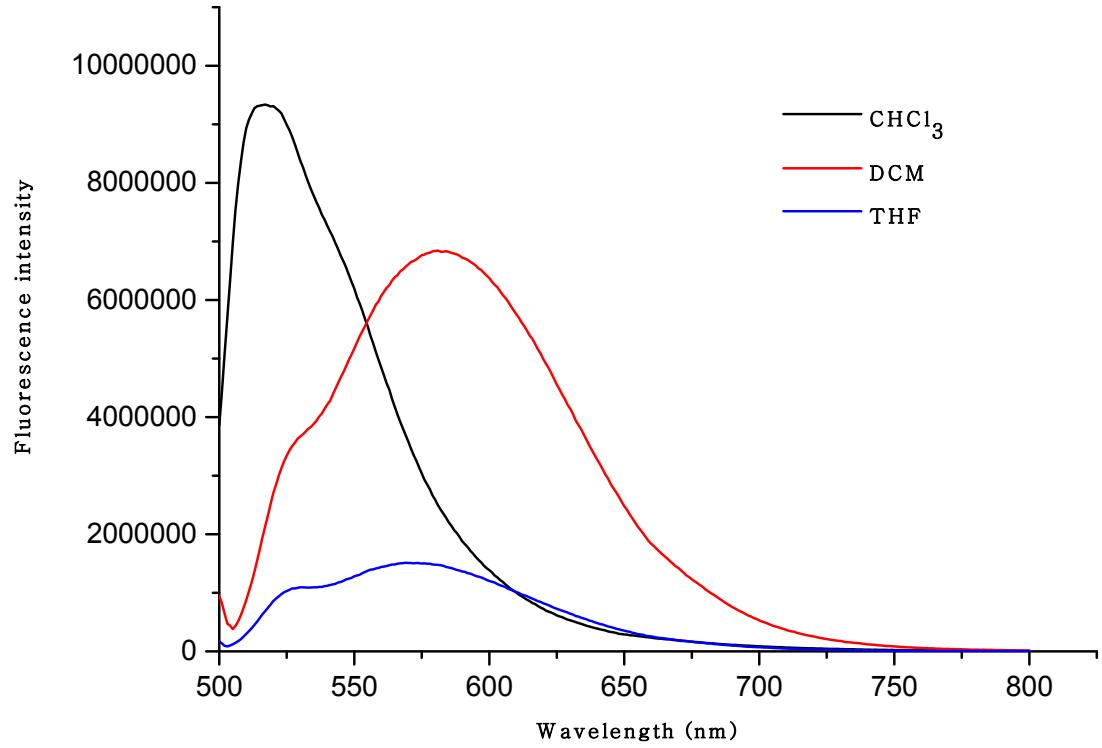


Figure 47: Steady state fluorescence spectra of Bis- BODIPY **3** in different solvents.

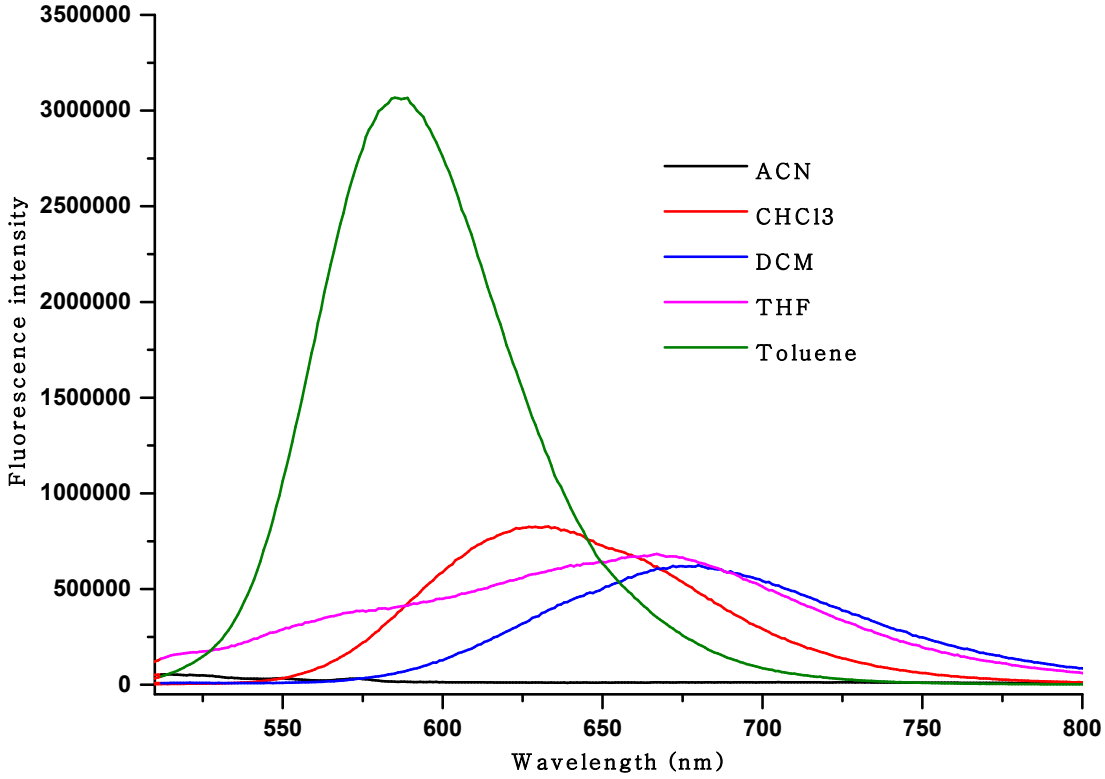


Figure 48: Steady state fluorescence spectra of Bis- BODIPY **4** in different solvents.

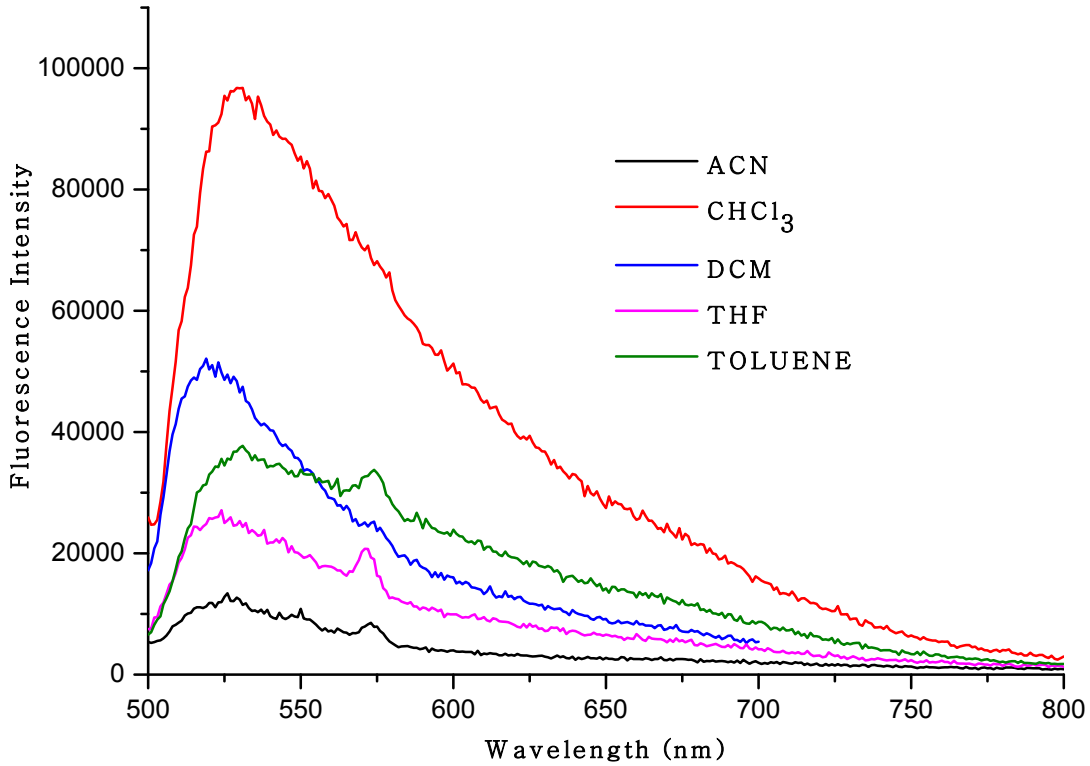


Figure 49: Steady state fluorescence spectra of Bis- BODIPY **5** in different solvents.

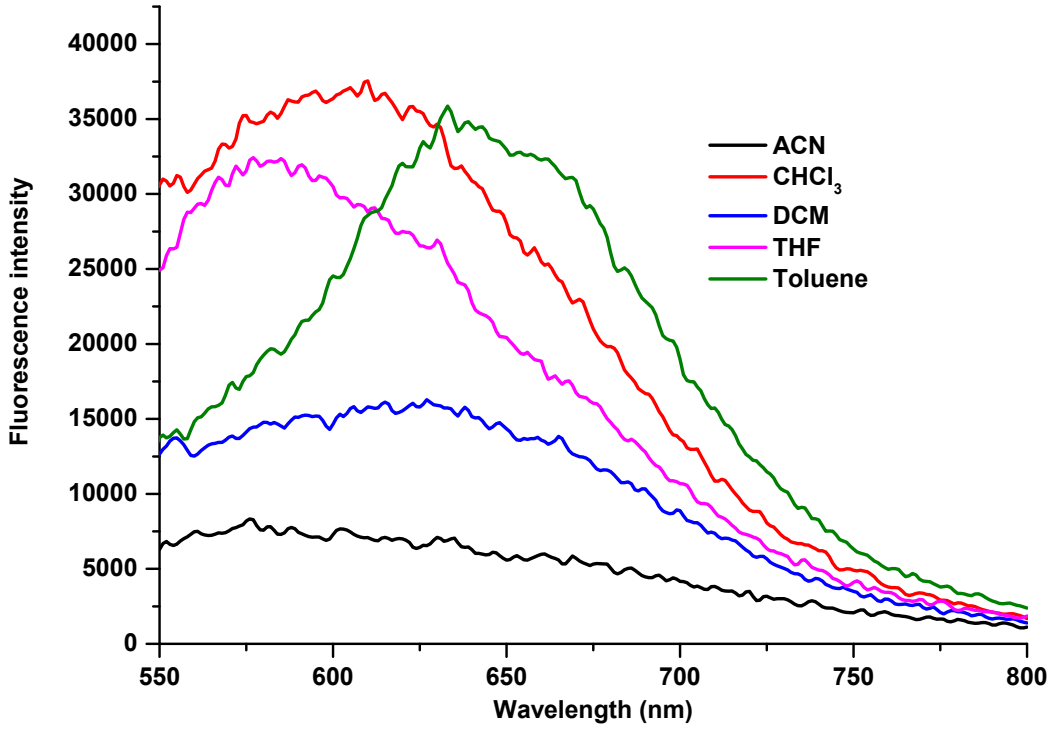


Figure 50: Steady state fluorescence spectra of Bis- BODIPY **6** in different solvents.

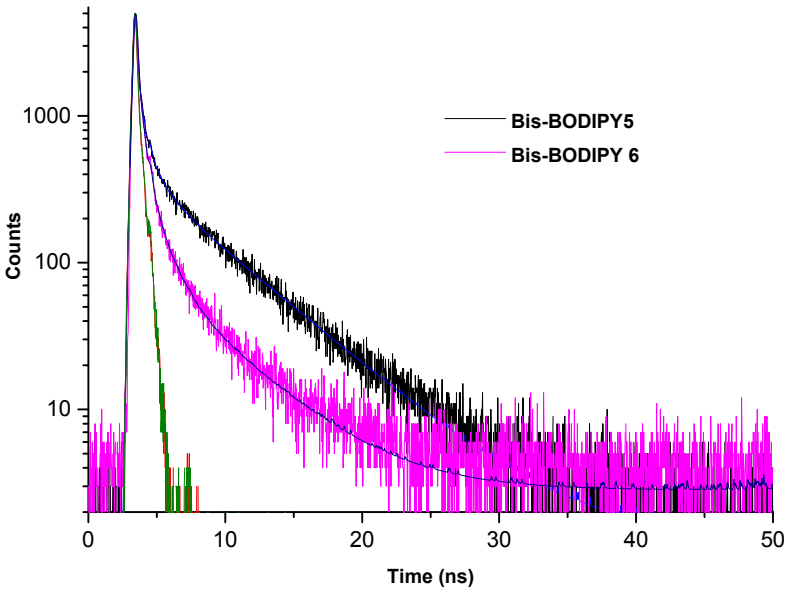


Figure 51: TCSPC of Bis- BODIPY **5** and **6** in Dichloromethane.

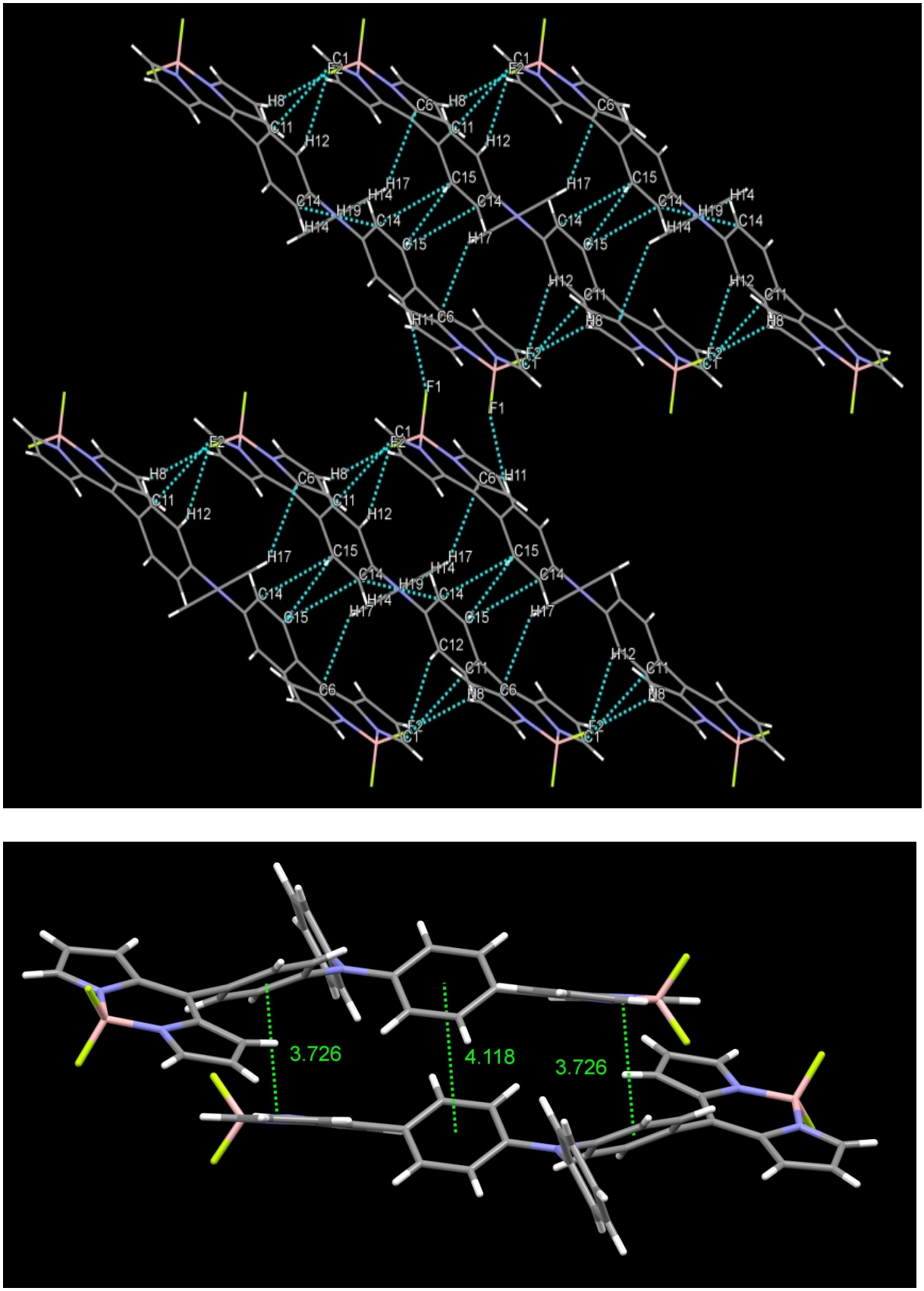


Figure 52: Packing diagram (above) and π–π stacking diagram (below) of bis -BODIPY **4**.

PARAMETERS	Bis-BODIPY 1	Bis- BODIPY 2	Bis- BODIPY 4
Empirical Formula	$C_{24}H_{16}B_2F_4N_4$	$C_{24}H_{16}B_2F_4N_4$	$C_{36}H_{25}B_2F_4N_5$
Formula Weight	458.03	458.03	625.24
Crystal Color, Habit	red, prism	orange, block	orange, needle
Crystal System	monoclinic	monoclinic	monoclinic
Lattice Type	Primitive	I-centered	C-centered
Lattice Parameters	a = 6.0628(2) Å	13.0203(3) Å	25.107(13) Å
	b = 11.7071(4) Å	10.3330(3) Å	9.399(4) Å
	c = 14.5542(5) Å	15.098(3) Å	13.496(7) Å
	b = 96.260(7) o	90.00(1) o	110.599(6) o
	V = 1026.86(6) Å3	2031.3(3) Å3	2981(3) Å3
Space Group	P21/n (#14)	I2/a (#15)	C2/c (#15)

Table 1: Crystal data refinement parameters of Bis-BODIPYs **1**, **2** and **4**.

DFT calculation data

Table 2

Bis-BODIPY 1

Bond lengths (Å)

Atom 1	Atom 2	Bond length (Å) X-RAY	DFT	Atom1	Atom 2	Bond length (Å) X-RAY	DFT
F1	B1	1.396	1.381	F2	B1	1.379	1.381
N1	C1	1.344	1.340	N1	C4	1.392	1.393
N1	B1	1.552	1.569	N2	C6	1.393	1.393
N2	C9	1.3417	1.340	N2	B1	1.554	1.569
C1	C2	1.403	1.410	C2	C3	1.380	1.388
C3	C4	1.410	1.422	C4	C5	1.398	1.405
C5	C6	1.399	1.405	C5	C11	1.484	1.483
C6	C7	1.414	1.422	C7	C8	1.379	1.387
C8	C9	1.400	1.410	C10	C11	1.398	1.404
C10	$C12^1$	1.384	1.391	C11	C12	1.3991	1.404

Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

Atoms				Bond angle		Atoms				Bond angle	
A1	A2	A3	A4	DFT	X-RAY	A1	A2	A3	A4	DFT	X-RAY
C1	N1	C4	C3	-0.35	-1.96	C1	N1	C4	C5	178.23	178.28
C4	N1	C1	C2	0.01	1.69	C1	N1	B1	F1	58.46	58.7
C1	N1	B1	F2	-64.98	- 62.3	C1	N1	B1	N2	176.89	176.80
B1	N1	C1	C2	-176.68	-174.09	C4	N1	B1	F1	-117.63	-116.33
C4	N1	B1	F2	118.92	122.69	C4	N1	B1	N2	0.80	1.75
B1	N1	C4	C3	176.29	173.90	B1	N1	C4	C5	-1.57	-5.9
C6	N2	C9	C8	0.01	0.34	C9	N2	C6	C5	178.22	178.82
C9	N2	C6	C7	-0.35	-0.80	C6	N2	B1	F1	118.87	121.36
C6	N2	B1	F2	-117.68	-118.13	C6	N2	B1	N1	0.75	3.10

B1	N2	C6	C5	-1.54	-3.9	B1	N2	C6	C7	176.31	176.50
C9	N2	B1	F1	-65.02	-61.85	C9	N2	B1	F2	58.43	58.66
C9	N2	B1	N1	178.86	179.89	B1	N2	C9	C8	-176.705	-176.95
N1	C1	C2	C3	-0.34	-0.75	C1	C2	C3	C4	-0.55	-0.48
C2	C3	C4	N1	0.57	1.51	C2	C3	C4	C5	-178.14	-178.77
N1	C4	C5	C6	0.74	5.1	N1	C4	C5	C11	-179.25	-173.11
C3	C4	C5	C6	-176.56	-174.56	C3	C4	C5	C11	3.43	7.2
C4	C5	C6	N2	-0.74	-0.5	C4	C5	C6	C7	76.55	179.06
C4	C5	C11	C10	-125.81	-127.45	C4	C5	C11	C12	54.18	54.00
C6	C5	C11	C10	54.18	54.31	C6	C5	C11	C12	-125.81	-124.25
C11	C5	C6	N2	179.25	177.77	C11	C5	C6	C7	-3.4	-2.7
N2	C6	C7	C8	0.57	0.96	C5	C6	C7	C8	-178.14	-178.60
C6	C7	C8	C9	-0.55	-0.74	C7	C8	C9	N2	0.34	0.26
C11	C10	$C12^1$	$C11^1$	-0.00027	-0.4	$C12^1$	C10	C11	C5	-180.00	-178.16
$C12^1$	C10	C11	C12	0.00053	0.4	C5	C11	C12	$C10^1$	180.00	178.18
C10	C11	C12	$C10^1$	-0.00050	-0.4						

Bis-BODIPY 2

Atom1	Atom2	Bond length (Å)		Atom1	Atom 2	Bond length(Å)	
		DFT	X-RAY			DFT	X-RAY
F1	B1	1.381	1.3809	F2	B1	1.381	1.3901
N1	C1	1.34	1.337	N1	C4	1.393	1.3947
N1	B1	1.569	1.547	N2	C6	1.394	1.3941
N2	C9	1.340	1.3497	N2	B1	1.569	1.553
C1	C2	1.41	1.402	C2	C3	1.38	1.371
C3	C4	1.421	1.416	C4	C5	1.404	1.395
C5	C6	1.405	1.404	C5	C1	1.486	1.483
C6	C7	1.422	1.408	C7	C8	1.387	1.385
C8	C9	1.410	1.385	C10	C11	1.403	1.3941
C10	$C11^1$	1.403	1.3941	C11	C12	1.404	1.396
C12	C13	1.393	1.3847				

Bond angles (^{o})

	Atoms	Bond Angle			Atoms	Bond Angle	
A1	A2	A3DFT	X-RAY	A1	A2	A3DFT	X-RAY
C1	N1	C4 107.94	107.74	C1	N1	B1 125.58	126.39
C4	N1	B1 126.42	125.52	C6	N2	C9 107.93	107.39
C6	N2	B1 126.38	125.72	C9	N2	B1 125.52	126.88
N1	C1	C2 110.40	110.22	C1	C2	C3 106.59	107.06
C2	C3	C4 107.23	107.40	N1	C4	C3 107.81	107.54
N1	C4	C5 121.04	120.98	C3	C4	C5 131.07	131.43
C4	C5	C6 120.13	120.03	C4	C5	C11 120.27	119.86
C6	C5	C11 119.59	120.07	N2	C6	C5 121.02	120.74
N2	C6	C7 107.83	107.74	C5	C6	C7 131.11	131.36
C6	C7	C8 107.17	107.39	C7	C8	C9 106.63	107.00
N2	C9	C8 110.41	110.48	C11	C10	$C11^1$ 120.89	121.09
C5	C11	C10 120.48	119.63	C5	C11	C12 120.42	121.22
C10	C11	C12 119.07	119.15	C11	C12	C13 120.26	119.68
C12	C13	$C12^1$ 120.37	121.23	F1	B1	F2 111.71	109.42
F1	B1	N1 110.23	110.89	F1	B1	N2 109.77	110.87
F2	B1	N1 109.78	110.17	F2	B1	N2 110.22	109.89
N1	B1	N2 104.88	105.54				

Torsion Angles(^{o})

(Those having bond angles > 160 or < 20 degrees are excluded.)

Atoms				Bond angle		Atoms				Bond angle	
A1	A2	A3	A4	DFT	X-RAY	A1	A2	A3	A4	DFT	X-RAY
C1	N1	C4	C3	-0.01	-1.51	C1	N1	C4	C5	177.78	176.08
C4	N1	C1	C2	0.05	0.55	C1	N1	B1	F1	-56.78	-53.31
C1	N1	B1	F2	66.69	67.98	C1	N1	B1	N2	-175.20	-173.45
B1	N1	C1	C2	-175.79	-172.98	C4	N1	B1	F1	121.73	134.27
C4	N1	B1	F2	-114.79	-104.44	C4	N1	B1	N2	3.62	14.14
B1	N1	C4	C3	177.25	172.08	B1	N1	C4	C5	-0.185	-10.3
C6	N2	C9	C8	0.05	0.69	C9	N2	C6	C5	-177.79	-176.73
C9	N2	C6	C7	-0.380	-0.85	C6	N2	B1	F1	-121.78	-131.29
C6	N2	B1	F2	114.74	107.62	C6	N2	B1	N1	-3.670	-11.14
B1	N2	C6	C5	3.14	4.3	B1	N2	C6	C7	-177.26	-179.86
C9	N2	B1	F1	56.81	49.89	C9	N2	B1	F2	-66.66	-71.20
C9	N2	B1	N1	175.22	170.03	B1	N2	C9	C8	177.59	179.69
N1	C1	C2	C3	0.356	0.67	C1	C2	C3	C4	-0.575	-1.58
C2	C3	C4	N1	0.597	1.92	C2	C3	C4	C5	-177.60	-175.32
N1	C4	C5	C6	1.26	0.8	N1	C4	C5	C11	-178.82	-176.94
C3	C4	C5	C6	177.82	177.75	C3	C4	C5	C11	2.20	0.0
C4	C5	C6	N2	1.26	2.08	C4	C5	C6	C7	-175.49	-172.68
C4	C5	C11	C10	56.22	2.01	C4	C5	C11	C12	-123.68	-128.14
C6	C5	C11	C10	-123.68	- 125.74	C6	C5	C11	C12	56.22	54.11
C11	C5	C6	N2	179.59	179.83	C11	C5	C6	C7	4.40	5.1
N2	C6	C7	C8	0.59	0.69	C5	C6	C7	C8	177.61	175.97
C6	C7	C8	C9	-0.48	-0.28	C7	C8	C9	N2	-0.27	-0.26
C11	C10	$C11^1$	$C5^1$	-176. 91	-179.73	C11	C10	$C11^1$	$C12^1$	1.76	0.42
$C11^1$	C10	C11	C5	-176.91	-179.73	$C11^1$	C10	C11	C12	1.76	0.42
C5	C11	C12	C13	178.45	179.31	C10	C11	C12	C13	-0.23	-0.84
C11	C12	C13	$C12^1$	1.29	0.42						

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Bond lengths (Å)

Atom	Atom	Distance		Atom	Atom	Distance	
		DFT	X-RAY			DFT	X-RAY
F1	B1	1.381	1.386	F2	B1	1.383	1.389
N1	C1	1.341	1.342	N1	C4	1.394	1.396
N1	B1	1.566	1.545	N2	C6	1.394	1.398
N2	C9	1.341	1.343	N2	B1	1.566	1.550
N3	C13	1.414	1.408	N3	$C13^1$	1.415	1.408
N3	C16	1.430	1.433	C1	C2	1.408	1.400
C2	C3	1.388	1.378	C3	C4	1.421	1.421
C4	C5	1.408	1.406	C5	C6	1.408	1.412
C5	C10	1.477	1.474	C6	C7	1.421	1.416
C7	C8	1.388	1.382	C8	C9	1.408	1.391
C10	C11	1.407	1.404	C10	C15	1.406	1.402
C11	C12	1.389	1.383	C12	C13	1.405	1.395
C13	C14	1.406	1.399	C14	C15	1.389	1.381
C16	C17	1.401	1.392	C16	$C17^1$	1.401	1.392
C17	C18	1.394	1.384	C18	C19	1.396	1.385

Bond angles (^{o})

Atom	Atom	Atom	Bond Angle		Atom	Atom	Atom	Bond Angle	
			DFT	X-RAY				DFT	X-RAY
C1	N1	C4	108.01	107.83	C1	N1	B1	125.72	125.86
C4	N1	B1	126.21	126.27	C6	N2	C9	108.01	107.78
C6	N2	B1	126.06	125.83	C9	N2	B1	125.72	125.88
C13	N3	$C13^1$	121.17	122.60	C13	N3	C16	119.49	118.70
$C13^1$	N3	C16	119.32	118.70	N1	C1	C2	110.36	110.42
C1	C2	C3	106.62	106.87	C2	C3	C4	107.24	107.56
N1	C4	C3	107.73	107.30	N1	C4	C5	120.98	120.73
C3	C4	C5	131.25	131.96	C4	C5	C6	119.80	119.92

C4	C5	C10	120.34	120.54	C6	C5	C10	119.86	119.52
N2	C6	C5	120.98	120.70	N2	C6	C7	107.73	107.26
C5	C6	C7	131.26	132.02	C6	C7	C8	107.24	107.44
C7	C8	C9	106.62	107.1	N2	C9	C8	110.36	110.42
C5	C10	C11	120.87	120.69	C5	C10	C15	121.34	121.40
C11	C10	C15	117.82	117.91	C10	C11	C12	121.25	121.27
C11	C12	C13	120.61	120.22	N3	C13	C12	120.49	119.89
N3	C13	C14	121.02	121.09	C12	C13	C14	118.47	119.01
C13	C14	C15	120.60	120.60	C10	C15	C14	121.26	120.93
N3	C16	C17	120.20	120.06	N3	C16	$C17^1$	120.20	120.06
C17	C16	$C17^1$	119.48	119.9	C16	C17	C18	120.07	120.0
C17	C18	C19	120.41	119.8	C18	C19	$C18^1$	119.52	120.5
F1	B1	F2	111.60	109.53	F1	B1	N1	110.19	110.12
F1	B1	N2	109.57	109.7	F2	B1	N1	110.43	111.3
F2	B1	N2	109.94	109.87	N1	B1	N2	104.81	106.21

Torsion Angles(°)

(Those having bond angles > 160 or < 20 degrees are excluded.)

Atoms				Bond angle		Atoms				Bond angle	
A1	A2	A3	A4	DFT	X-RAY	A1	A2	A3	A4	DFT	X-RAY
C1	N1	C4	C3	-0.59	-0.5	C1	N1	C4	C5	176.40	179.49
C4	N1	C1	C2	-0.03	-0.0	C1	N1	B1	F1	-59.49	-65.1
C1	N1	B1	F2	63.88	56.6	C1	N1	B1	N2	178.66	176.2
B1	N1	C1	C2	-179.92	-178.11	C4	N1	B1	F1	108.33	117.2
C4	N1	B1	F2	-128.18	-121.2	C4	N1	B1	N2	-9.46	-1.6
B1	N1	C4	C3	179.33	177.60	B1	N1	C4	C5	-2.88	-2.4
C6	N2	C9	C8	-0.10	-0.5	C9	N2	C6	C5	179.97	-178.73
C9	N2	C6	C7	- 0.2	-0.1	C6	N2	B1	F1	- 109.58	-112.9
C6	N2	B1	F2	126.9	126.6	C6	N2	B1	N1	8.27	6.1
B1	N2	C6	C5	-8.24	-6.6	B1	N2	C6	C7	171.12	172.08
C9	N2	B1	F1	60.88	57.9	C9	N2	B1	F2	-59.49	-62.6
C9	N2	B1	N1	178.66	176.9	B1	N2	C9	C8	-171.70	-172.67
C13	N3	$C13^1$	$C12^1$	142.9	148.31	C13	N3	$C13^1$	$C14^1$	-37.07	-32.8
$C13^1$	N3	C13	C12	143.83	148.31	$C13^1$	N3	C13	C14	-37.07	-32.8
C13	N3	C16	C17	130.32	118.32	C13	N3	C16	$C17^1$	- 49.64	-61.68
C16	N3	C13	C12	-36.86	-31.7	C16	N3	C13	C14	142.72	147.24
$C13^1$	N3	C16	C17	-49.64	-61.68	$C13^1$	N3	C16	$C17^1$	130.32	118.32
C16	N3	$C13^1$	$C12^1$	-36.86	-31.7	C16	N3	$C13^1$	$C14^1$	142.72	147.24
N1	C1	C2	C3	0.44	0.5	C1	C2	C3	C4	-0.79	-0.8
C2	C3	C4	N1	0.87	0.8	C2	C3	C4	C5	-179.8	-179.2
N1	C4	C5	C6	2.02	2.6	N1	C4	C5	C10	-178.83	-175.98
C3	C4	C5	C6	-179.05	-177.4	C3	C4	C5	C10	6.34	4.0
C4	C5	C6	N2	2.02	1.7	C4	C5	C6	C7	-179.05	-176.6
C4	C5	C10	C11	50.97	44.6	C4	C5	C10	C15	-129.39	-135.9
C6	C5	C10	C11	-129.39	-134.0	C6	C5	C10	C15	50.47	45.5
C10	C5	C6	N2	- 178.97	-179.71	C10	C5	C6	C7	1.81	2.0
N2	C6	C7	C8	0.87	0.7	C5	C6	C7	C8	175.86	179.1
C6	C7	C8	C9	-0.79	-0.9	C7	C8	C9	N2	0.44	0.9
C5	C10	C11	C12	179.78	177.32	C5	C10	C15	C14	-179.25	-178.51
C11	C10	C15	C14	0.77	0.9	C15	C10	C11	C12	-0.17	-2.1
C10	C11	C12	C13	0.066	1.2	C11	C12	C13	N3	179.92	179.95
C11	C12	C13	C14	0.45	1.0	N3	C13	C14	C15	179.32	178.87
C12	C13	C14	C15	-0.23	-2.2	C13	C14	C15	C10	0.06	1.2
N3	C16	C17	C18	-179.51	-179.96	N3	C16	$C17^1$	$C18^1$	-179.63	-179.96
C17	C16	$C17^1$	$C18^1$	0.39	0.0	$C17^1$	C16	C17	C18	0.45	0.0
C16	C17	C18	C19	-0.84	-0.1	C17	C18	C19	$C18^1$	0.41	0.0