Support Information

Regioselective 2,6-dihalogenation of BODIPYs in 1,1,1,3,3,3-hexafluoro-2-propanol and preparation of novel *meso*-alkyl polymeric BODIPY dyes

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Table of contents

Experimental Section

General remarks

All of the reagents and solvents are commercially available and were used without further purification. Melting points were determined with a WRS-1B apparatus and were uncorrected. IR spectra were recorded in KBr disks with a Bomem MB154S FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance III 500-MHz spectrometer. Mass spectra (EI and ESI) were measured with Jeol JMS-DX300 and Thermo Fisher LCQ instruments. Absorption spectra were performed by using a UV-1201 absorption spectrophotometer. Fluorescence measurements were conducted on a Varian Eclipse spectrofluorometer. The fluorescence quantum yields (Φ) were calculated using Rhodamine B in anhydrous ethanol (Φ = 0.73). Thermal analysis was measured with EXSTAR6000 instrument. Molecular weights of the polymers were determined by GPC analyses in THF (1 mL/min) using a Waters Breeze system equipped with a 717plus autosampler, a 1515 binary HPLC pump, a Wyatt miniDAWN TRISTAR detector, a Wyatt VicoStar viscometer detector and a 2414 refractive index detector. The substrates **1** were prepared according to the literature with slight modification.[1-4]

A general procedure for halogenation of BODIPYs 2

A mixture of the 1,3,5,7-tetramethyl-BODIPY **1** (0.2 mmol) and NBS (85.4 mg, 0.48 mmol; 0.96 mmol for **1m**) in HFIP (2 mL) was stirred at room temperature for a certain time (usually < 5 mins according to the TLC). After reaction, the solvent was removed and recovered by distillation. The residue was extracted with CH_2Cl_2, washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was further purified using column chromatography (EtOAc–petroleum ether or CH_2Cl_2-hexane) to afford the products **2**.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (2b)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 6 H, CH_3), 2.61 (s, 6 H, CH_3), 7.52–7.53 (m, 5 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 153.9, 142.1, 140.6, 134.4, 130.4, 129.5, 129.4, 127.8, 111.8, 13.6. EI-MS: *m*/*z* = 482 $[M]^+$.

2,6-Diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (2c)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H, CH_3), 2.65 (s, 6 H, CH_3), 7.52–7.53 (m, 5 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 156.8, 145.4, 141.4, 134.7, 131.3, 129.5, 129.4, 127.8, 85.7, 16.9. EI-MS: *m*/*z* = 576 $[M]^+$.

2,6-Dibromo-4,4-difluoro-8-phenyl-4-bora-3a,4a-diaza-*s*-indacene (2e)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.96 (s, 2H), 7.53-7.64 (m, 5H), 7.85 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.0, 144.2, 134.6, 132.8, 131.7, 131.5, 130.3, 128.8, 107.2. EI-MS: *m*/*z* = 426 $[M]^+$.

2,6-Dibromo-4,4-difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2f)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47 (s, 6 H, CH_3), 2.62 (s, 6 H, CH_3), 3.91(s, 3 H, OCH_3), 7.06 (d, *J* = 8.65 Hz, 2 H, ArH), 7.16 (d, *J* = 8.65 Hz, 2 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=160.6, 153.7, 142.3, 140.6, 130.9, 130.8, 129.1, 128.8, 126.3, 114.8, 111.7, 55.4, 13.9, 13.7. EI-MS: *m*/*z* = 512 $[M]^+$.

2,6-Diiodo-4,4-difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2g)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (s, 6 H, CH_3), 2.62 (s, 6 H, CH_3), 3.94(s, 3 H, OCH_3) 7.04-7.06 (d, *J* = 10 Hz, 2 H, ArH), 7.15-7.17 (d, *J* = 10 Hz, 2 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=160.6, 153.7, 142.3, 140.6, 130.9, 130.8, 129.1, 128.8, 126.3, 114.8, 111.7, 55.4, 13.8, 13.6. EI-MS: *m*/*z* = 606 $[M]^+$.

2,6-Dibromo-8-(4-chlorophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2h)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (s, 6 H, CH_3), 2.61 (s, 6 H, CH_3), 7.21-7.23 (d, *J* = 10 Hz, 2 H, ArH), 7.52-7.54 (d, *J* = 10 Hz, 2 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=154.4, 140.4, 140.3, 135.9, 132.8, 130.3, 129.8, 129.4, 128.6, 112.1, 13.9, 13.7. EI-MS: *m*/*z* = 517 $[M+H]^+$.

2,6-Diiodo-8-(4-chlorophenyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2i)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 7.20 (d, *J* = 10 Hz, 2 H, ArH), 7.52 (d, *J* = 10 Hz, 2 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 157.2, 145.1, 139.7, 135.8, 133.2, 131.2, 129.8, 129.4, 85.9, 17.2, 16.1. EI-MS: *m*/*z* = 611 $[M+H]^+$.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-nitrophenyl)-4-bora-3a,4a-diaza-*s*-indacene (2j)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 7.55 (d, 2 H, ArH), 8.44 (d, 2 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 155.3, 148.7, 141.2, 140.0, 138.6, 129.6, 124.6, 112.5, 14.0, 13.8. ESI-MS: *m*/*z* = 527 $[M]^+$.

2,6-Diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-(4-nitrophenyl)-4-bora-3a,4a-diaza-*s*-indacene (2k)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H, CH_3), 2.66 (s, 6 H, CH_3), 7.54 (d, 2 H, ArH), 8.42 (d, 2 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 158.1, 148.6, 141.7, 141.6, 138.1, 129.5, 124.7, 114.0, 14.9, 14.7. ESI-MS: *m*/*z* = 621 $[M]^+$.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-methyl-4-bora-3a,4a-diaza-*s*-indacene (2l)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 6 H, CH_3), 2.57 (s, 6 H, CH_3), 2.62 (s, 3 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 152.2, 141.9, 138.4, 29.7, 17.4, 16.4, 13.6. ESI-MS: *m*/*z* = 420 $[M]^+$.

2,6-Diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-methyl-4-bora-3a,4a-diaza-*s*-indacene (2m)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 6 H, CH_3), 2.61 (s, 6 H, CH_3), 2.62 (s, 3 H, CH_3). ^{13}C

NMR (125 MHz, $CDCl_3$): δ= 155.1, 143.0, 141.1, 132.2, 85.8, 19.8, 17.9, 16.0. ESI-MS: *m*/*z* = 467 $[M]^+$.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-pentyl-4-bora-3a,4a-diaza-*s*-indacene (2n)
^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, 3 H, CH_3), 1.36-1.66 (m, 8 H), 2.44 (s, 6 H, CH_3), 2.57 (s, 6 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 152.3, 147.3, 137.7, 130.5, 112.0, 32.5, 31.5, 29.0, 22.5, 15.5, 14.0, 13.7. ESI-MS: *m*/*z* = 476 $[M]^+$.

2,6-Diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-pentyl-4-bora-3a,4a-diaza-*s*-indacene (2o)
^1H NMR (500 MHz, $CDCl_3$): δ = 0.93-0.96 (t, 3 H, CH_3), 1.23-1.66 (m, 8 H, CH_2), 2.43 (s, 6 H, CH_3), 2.61 (s, 6 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 155.2, 142.2, 131.9, 128.7, 86.8, 32.5, 31.5, 29.3, 22.5, 18.5, 16.1, 14.0. ESI-MS: *m*/*z* = 570 $[M]^+$.

2,6-Dibromo-4,4-difluoro-1,3,5,7-tetramethyl-8-undecyl-4-bora-3a,4a-diaza-*s*-indacene (2p)
^1H NMR (500 MHz, $CDCl_3$): δ = 0.88-0.91 (t, 3 H, CH_3), 1.22-1.65 (m, 18 H, CH_2), 2.44 (s, 6 H, CH_3), 2.57 (s, 6 H, CH_3), 3.70-3.74 (m, 2 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 152.3, 147.3, 137.7, 130.5, 112.0, 31.8, 31.7, 30.3, 29.0, 22.6, 18.4, 15.5, 14.1, 13.7. ESI-MS: *m*/*z* = 560 $[M]^+$.

2,6-Diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-undecyl-4-bora-3a,4a-diaza-*s*-indacene (2q)
^1H NMR (500 MHz, $CDCl_3$): δ = 0.87-0.90 (t, 3 H, CH_3), 1.21-1.60 (m, 18 H, CH_2), 2.44 (s, 6 H, CH_3), 2.60 (s, 6 H, CH_3), 3.67-3.72 (m, 2 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 155.0, 146.5, 142.3, 131.3, 86.4, 31.9, 31.6, 30.3, 29.6, 29.4, 29.3, 22.7, 18.9, 18.3, 16.1, 14.1. ESI-MS: *m*/*z* = 654 $[M]^+$.

2,6-Dibromo-4,4-difluoro-8-(3,5-dinitrophenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2r)
^1H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 6 H, CH_3), 2.64 (s, 6 H, CH_3), 8.56 (s, 2 H, ArH), 9.23 (s, 1 H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ=158.0, 149.0, 141.8, 138.8, 134.5, 130.7, 129.2, 122.6, 119.4, 15.4, 14.8. EI-MS: *m*/*z* = 572 $[M]^+$.

2,6-Dibromo-4,4-difluoro-8-((bis(chloromethyl)amino)methyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2s)
^1H NMR (500 MHz, $CDCl_3$): δ = 2.43 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.51 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.00 (t, 2H, CH_2), 3.56 (t, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.0, 154.5, 142.4, 142.2, 140.4, 132.5, 131.9, 121.9, 119.9, 57.1, 51.9, 42.0, 17.5, 17.4, 16.5, 14.5. EI-MS: *m*/*z* = 532 $[M]^+$.

2,6-Dibromo-4,4-difluoro-8-(morpholinomethyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2t)
^1H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.74 (t, 4H, CH_2), 3.76 (t, 4H, CH_2), 3.85 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 154.0, 142.2, 142.0, 140.4, 132.4, 131.8, 121.7, 119.7, 67.1, 55.7, 54.1, 17.5, 17.4, 16.5, 14.5. EI-MS: *m*/*z* = 505 $[M]^+$.

2,6-Dibromo-4,4-difluoro-8-(4-((2-hydroxybenzylidene)amino)phenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (2u)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.23-1.55 (m, 6H, CH_3), 2.57 (s, 6H, CH_3), 6.96-6.99 (m, 2H, ArH), 7.05-7.44 (m, 6H, ArH), 8.72 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.5, 161.3, 155.7, 149.2, 143.0, 141.0, 133.7, 133.6, 132.5, 131.5, 129.3, 129.0, 122.0, 121.4, 119.2, 119.0, 117.6, 117.4, 115.4, 18.5, 14.6. EI-MS: *m*/*z* = 601 $[M]^+$.

Dibromo-BODIPY (2v)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.14 (s, 6H, CH_3), 2.58 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0, 138.6, 128.9, 128.5, 127.6, 13.8, 12.2. EI-MS: *m*/*z* = 810 $[M]^+$.

Typical procedure for the synthesis of polymer 3a-d

2,6-Dibromo-BODIPY (**2l**) (260.5 mg, 0.6 mmol), 1,4-Phenylenebisboronic acid (103 mg, 0.6 mmol) and K_2CO_3 (414 mg, 5 eq) were added to a 100 mL three-neck flask under a nitrogen atmosphere, followed by addition of $Pd(PPh_3)_4$ (12 mg), THF (30 mL) and water (10 mL). The mixture was stirred under reflux for 96 h. After reaction, the solvent was removed under reduced pressure. The solid was collected, washed with water (2 × 15 mL), methanol (2 × 15 mL), and dried under vacuum for 24 h at room temperature to give red solid (91.3 mg, 45%) .

Polymer 3a

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.56 (s, 6H, CH_3), 2.44 (s, 6H, CH_3)， 2.57 (s, 3H, CH_3)， 7.48 (m, 4H, ArH). M_n = 17110 g/mol, polydispersity: 1.17.

Polymer 3b

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92-0.95 (t, 3H, CH_3), 1.35-1.49 (m, 2H, CH_2), 1.60-1.67 (m, 2H, CH_2), 2.41 (s, 6H, CH_3), 2.51 (s, 6H, CH_3), 2.99 (t, 2H, CH_2), 7.24 (m, 4H, ArH). M_n = 19200 g/mol, polydispersity: 1.14.

Polymer 3c

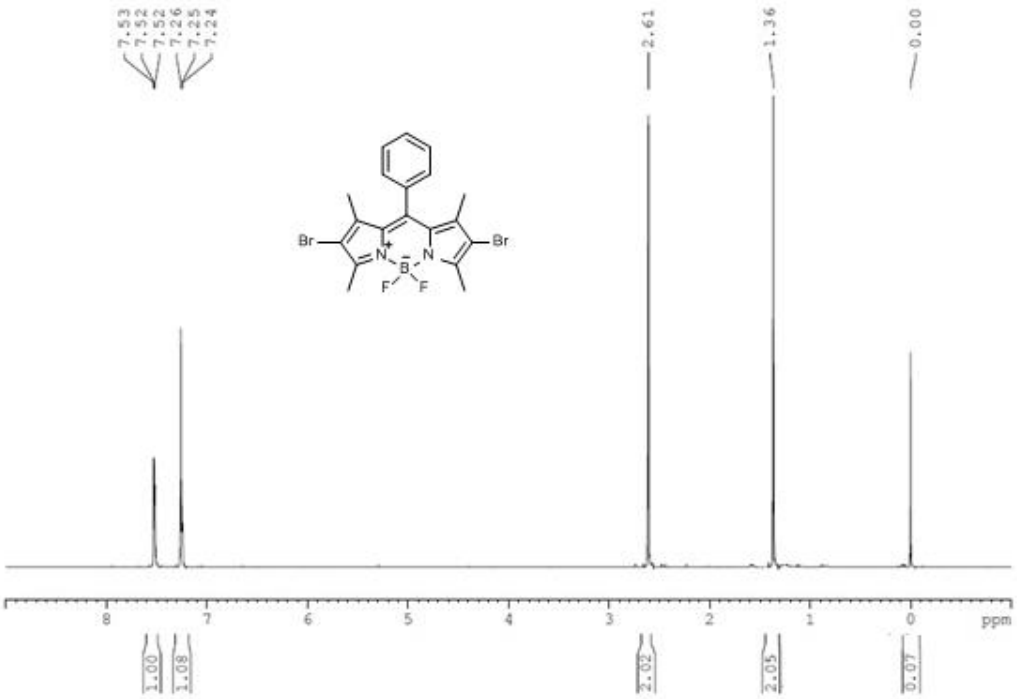
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88-0.91 (t, 3H, CH_3), 1.21-1.31 (m, 10H, CH_2), 1.34-1.38 (m, 2H, CH_2), 1.46-1.52 (m, 2H, CH_2), 1.54-1.66 (m, 4H, CH_2), 2.52 (s, 6H, CH_3), 2.61 (s, 6H, CH_3), 2.99-3.10 (t, 2H, CH_2), 7.22 (m, 4H, ArH). M_n = 22100 g/mol, polydispersity: 1.26.

Polymer 3d

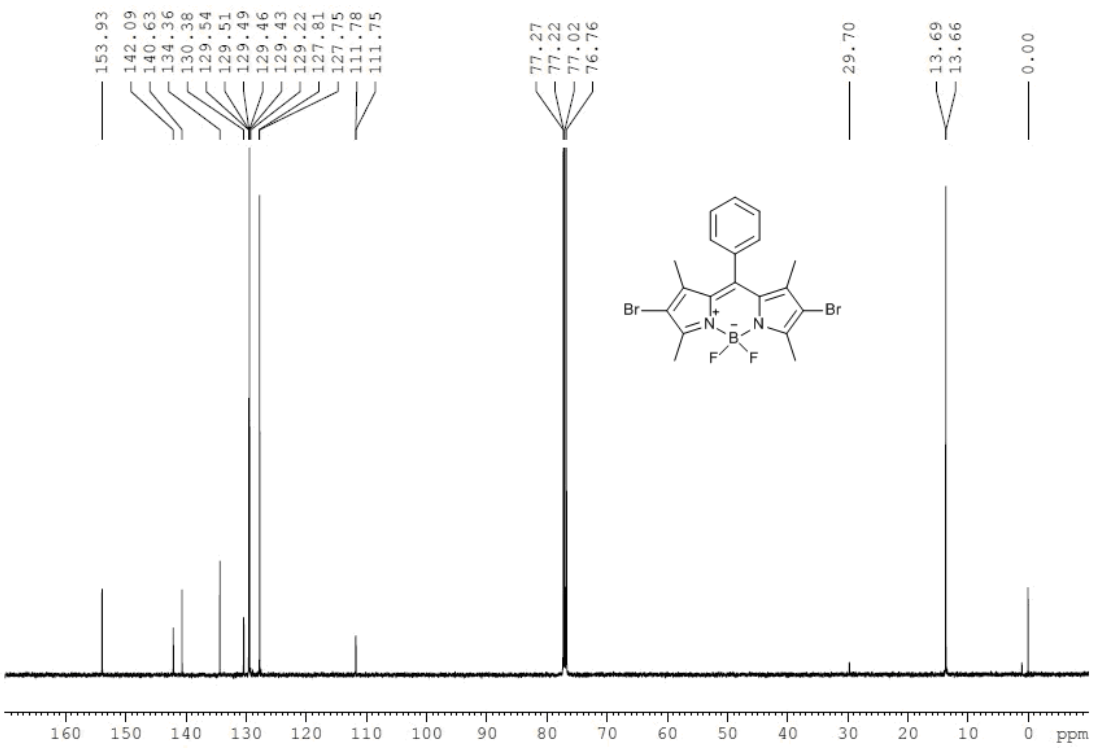
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87-0.88 (t, 3H, CH_3), 1.22-1.30 (m, 8H, CH_2), 1.42-1.83 (m, 30H, CH_2), 2.55 (s, 6H, CH_3), 2.62 (s, 6H, CH_3), 2.99-3.10 (t, 2H, CH_2), 7.02-7.64 (m, 4H, ArH). M_n = 20100 g/mol, polydispersity: 1.27.

Selected spectroscopic data of compounds

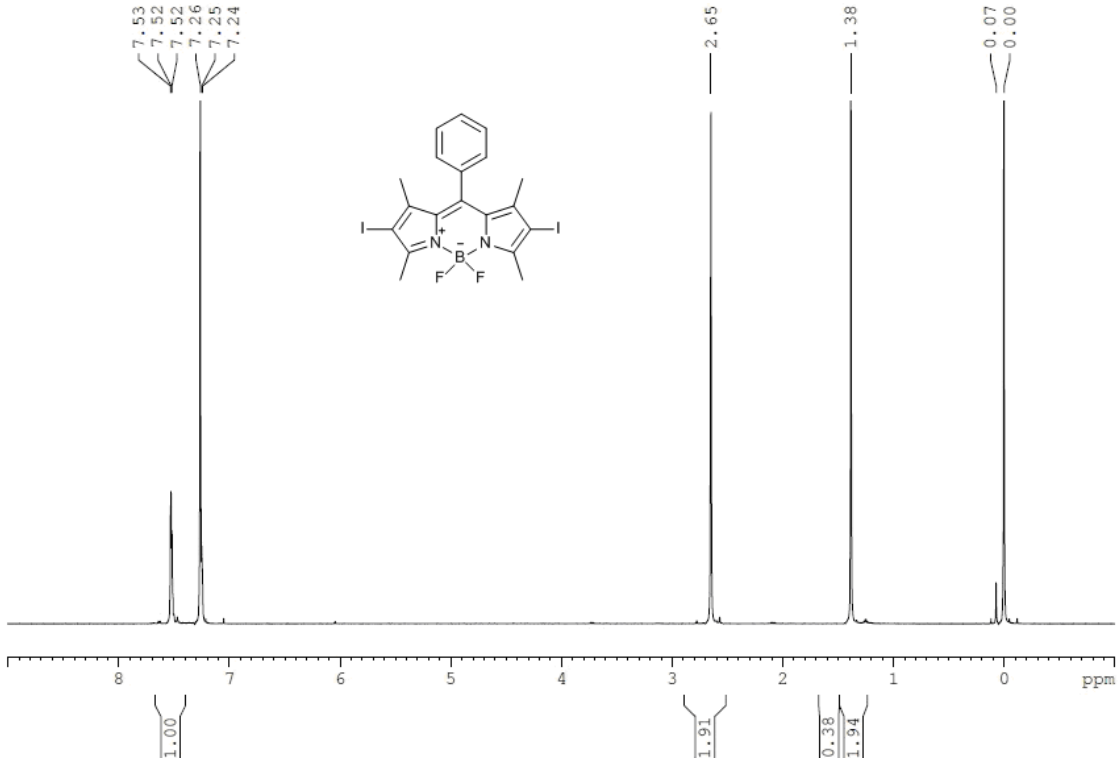
^{1}H NMR of **2b**



^{13}C NMR of **2b**



^{1}H NMR of **2c**



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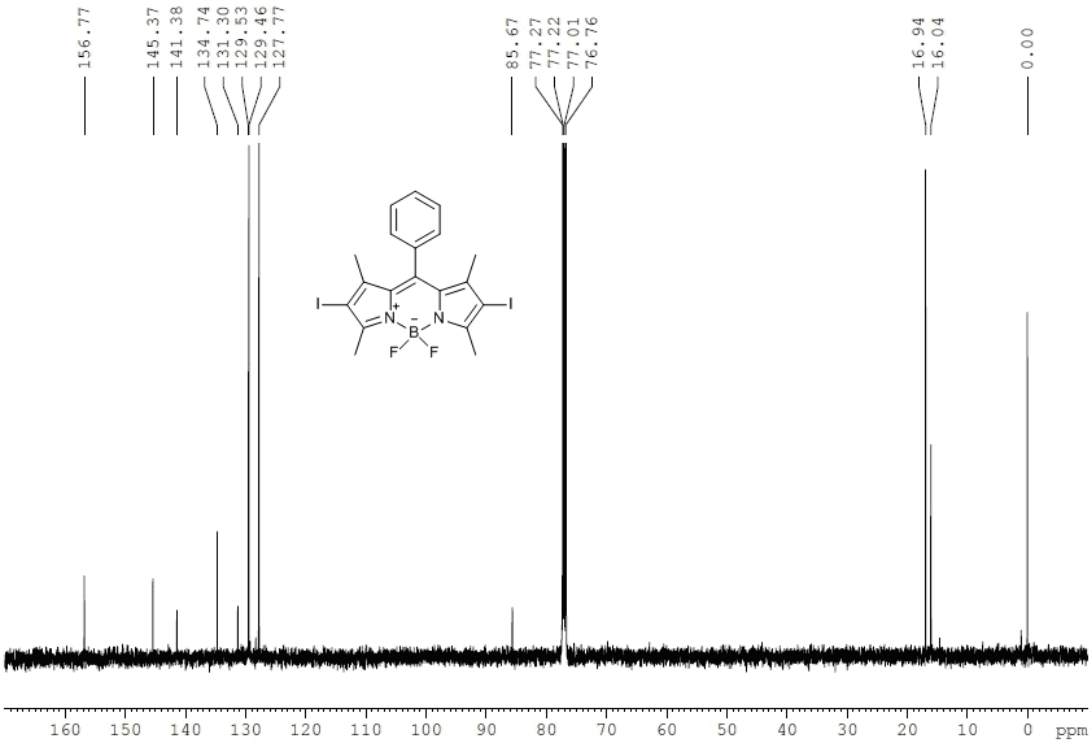
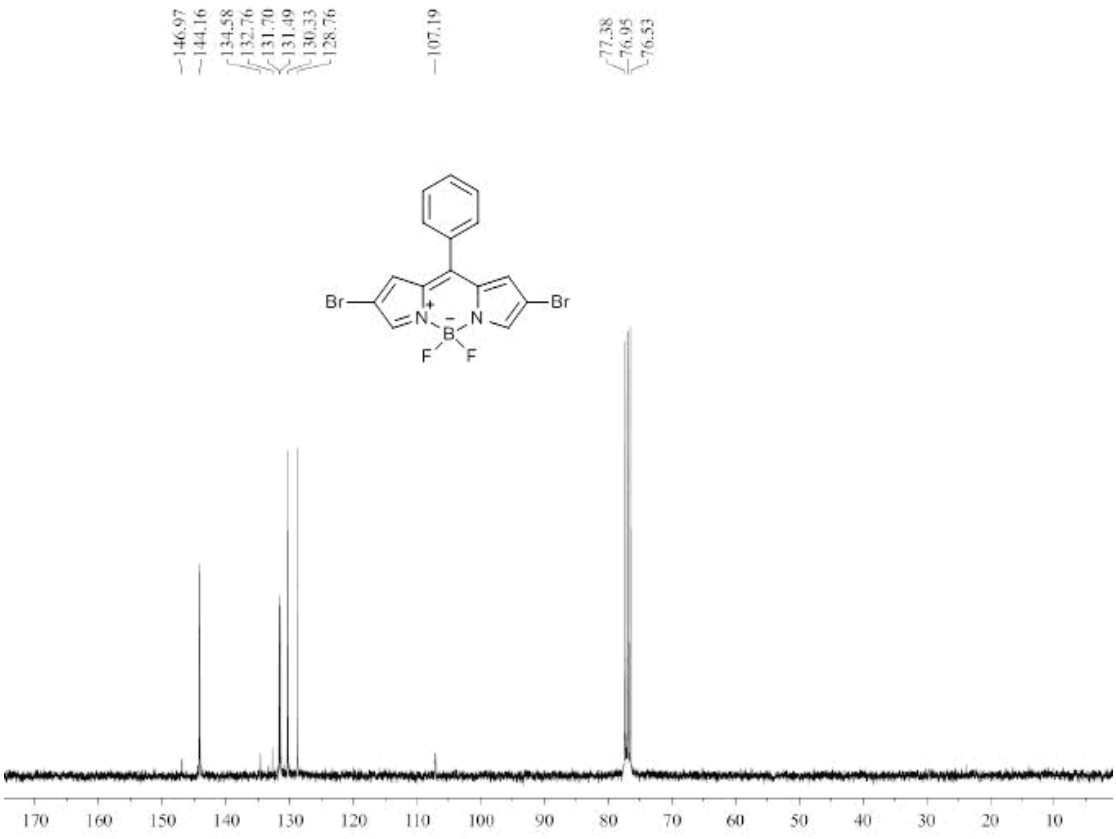
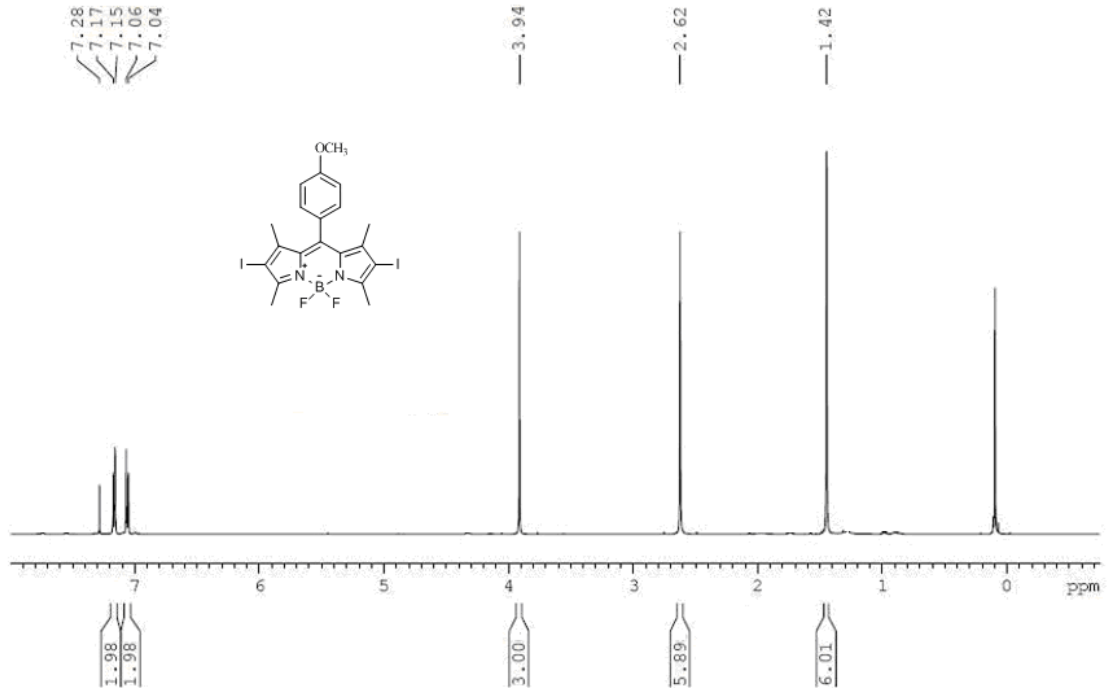


^{1}H NMR of **2e**

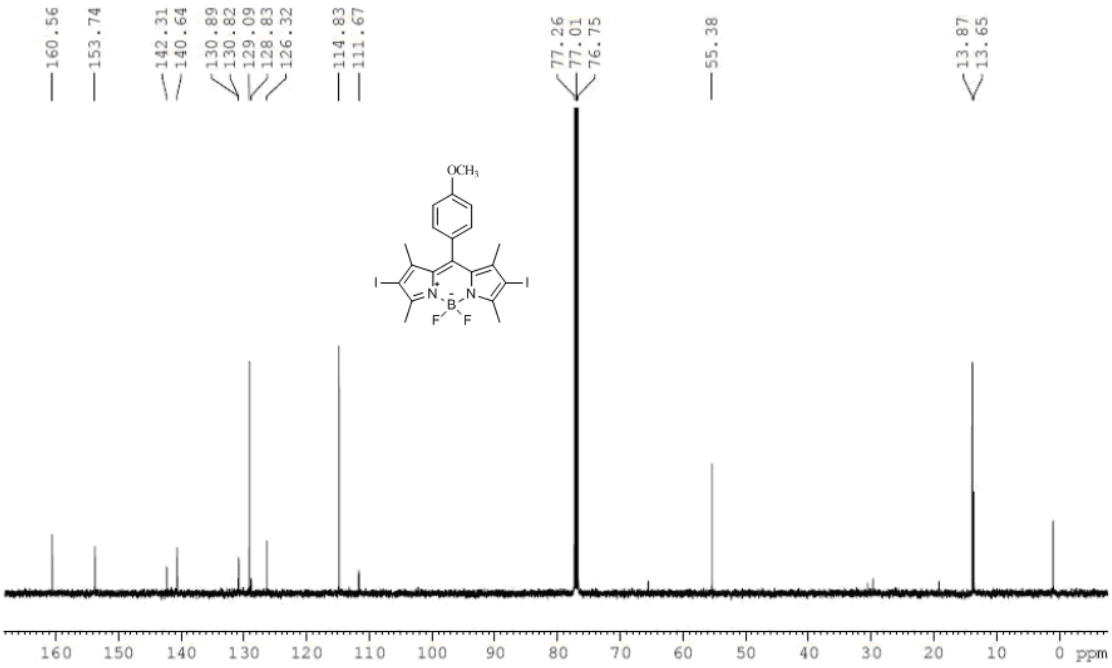
^{13}C NMR of **2e**



^{1}H NMR of **2g**



^{13}C NMR of **2g**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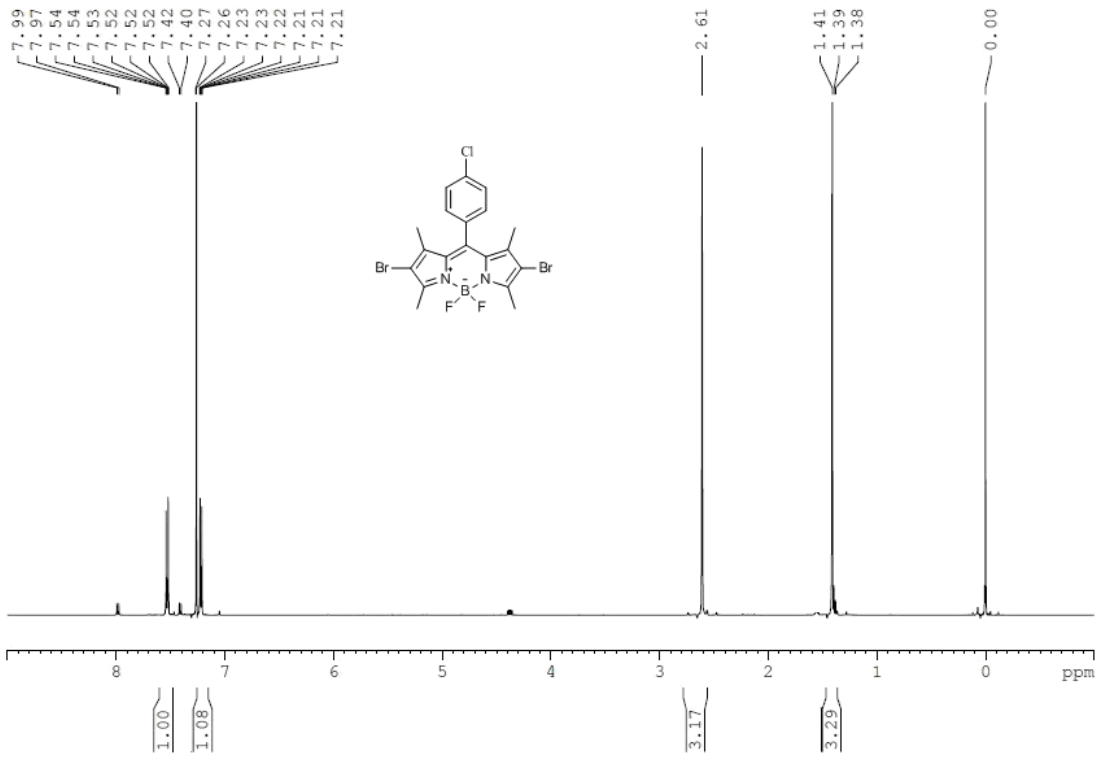
^{1}H NMR of **2h**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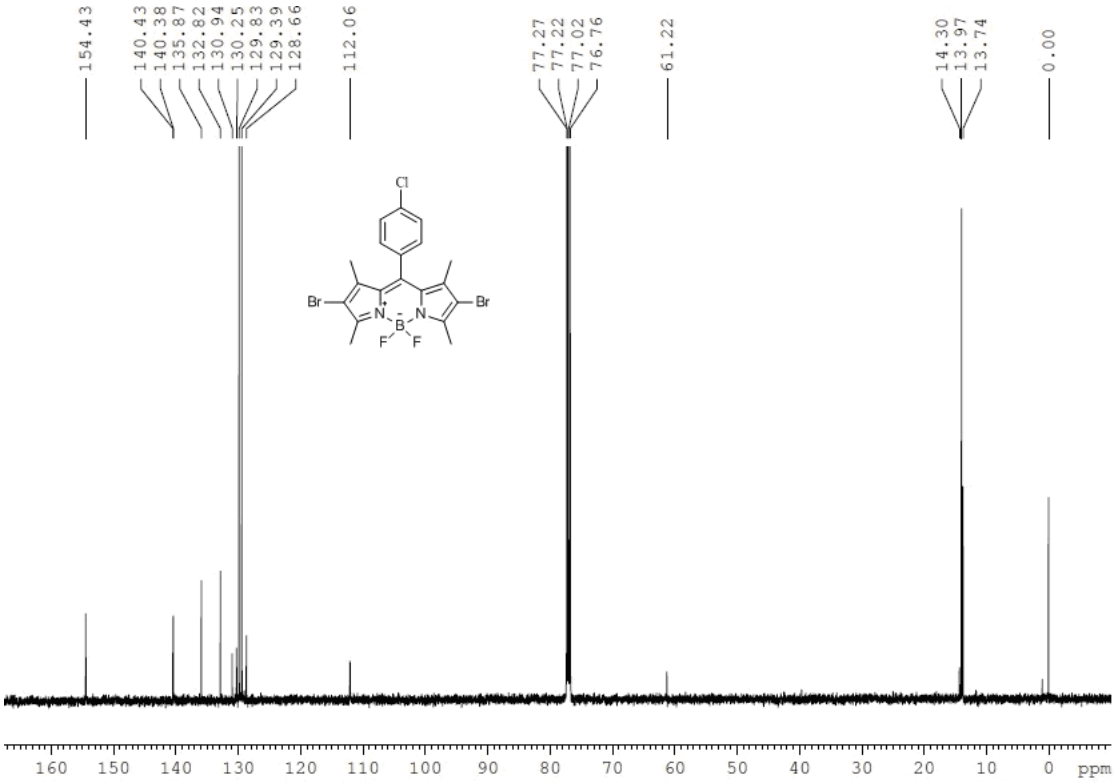
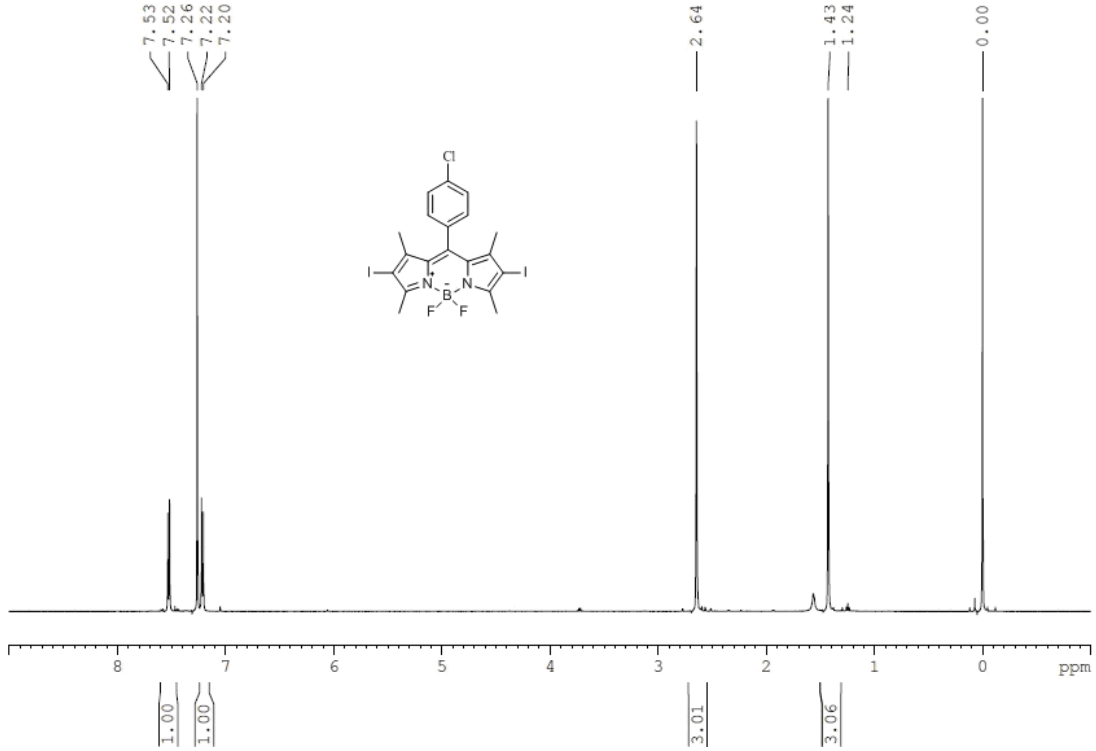
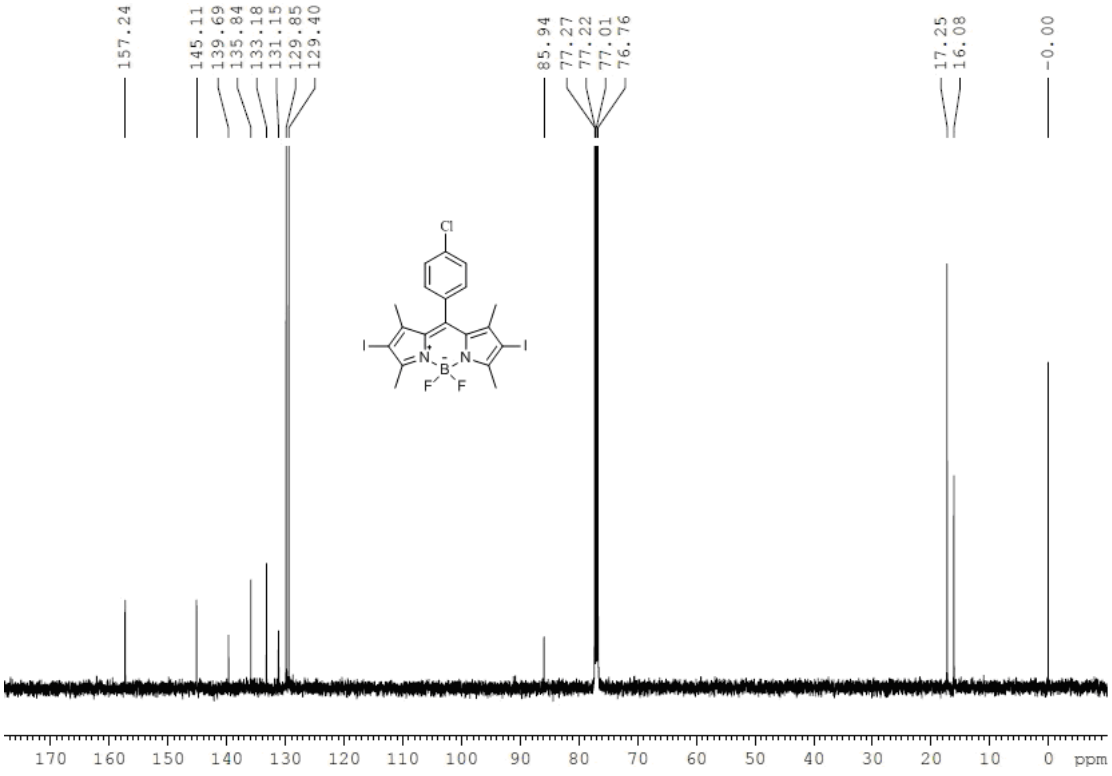
^{13}C NMR of **2h**



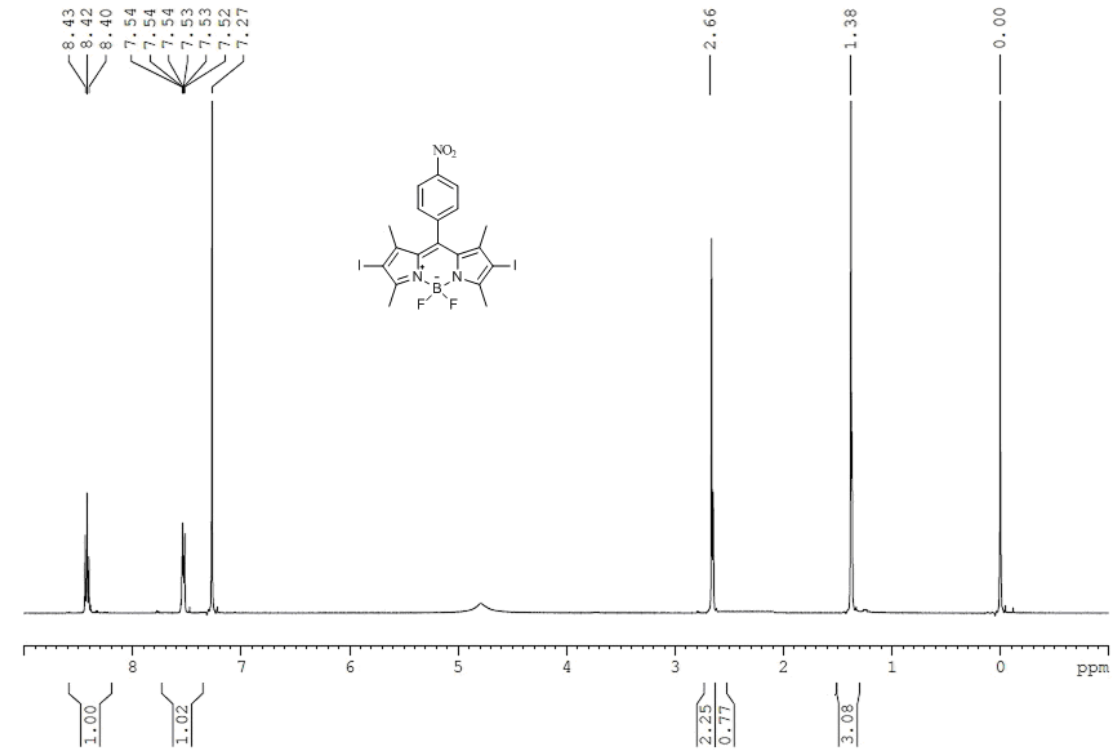
^{1}H NMR of **2i**



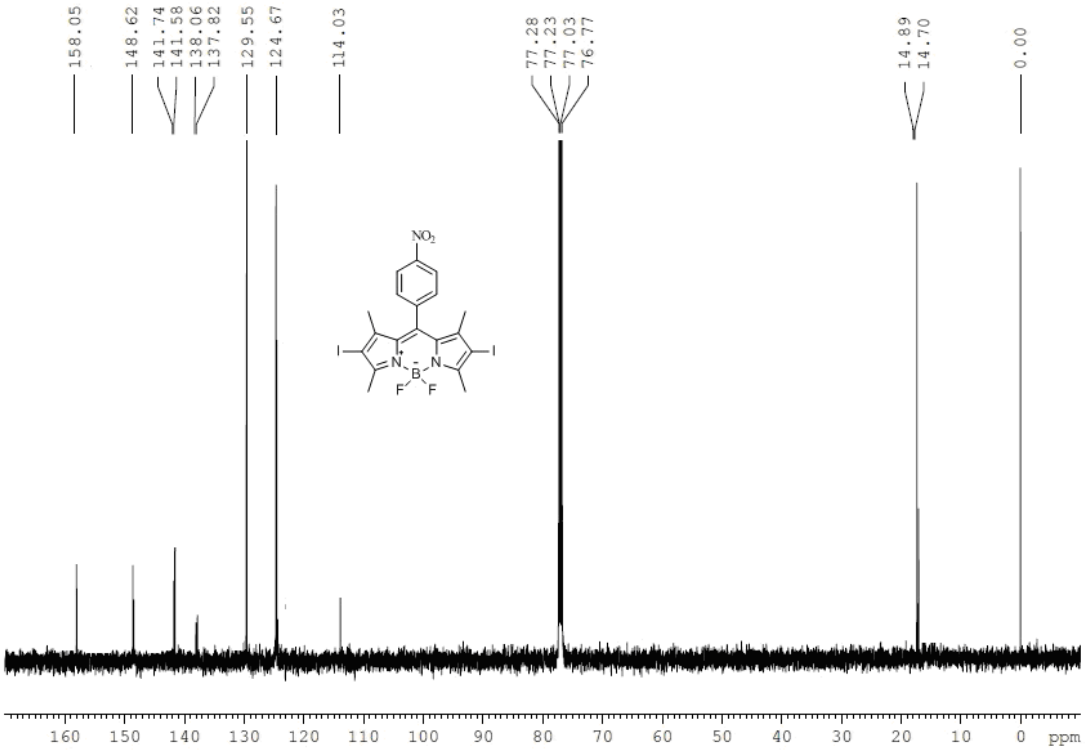
^{13}C NMR of **2i**



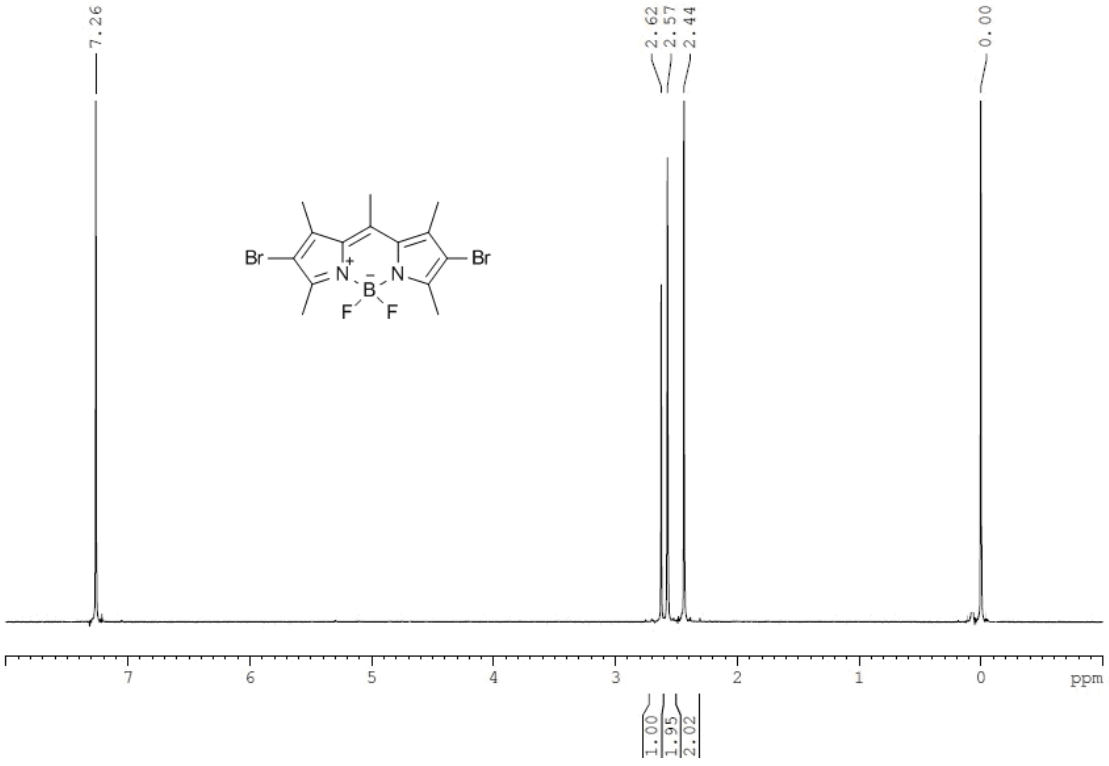
^{1}H NMR of **2k**



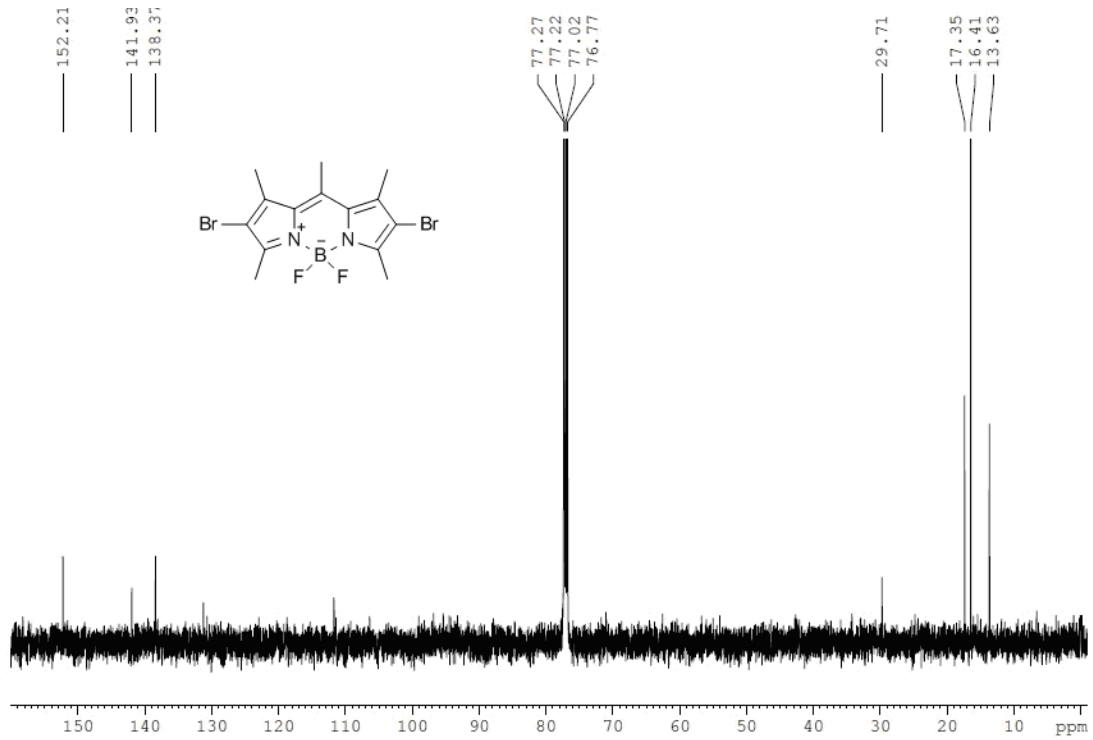
^{13}C NMR of **2k**



^{1}H NMR of **2l**



^{13}C NMR of **2l**



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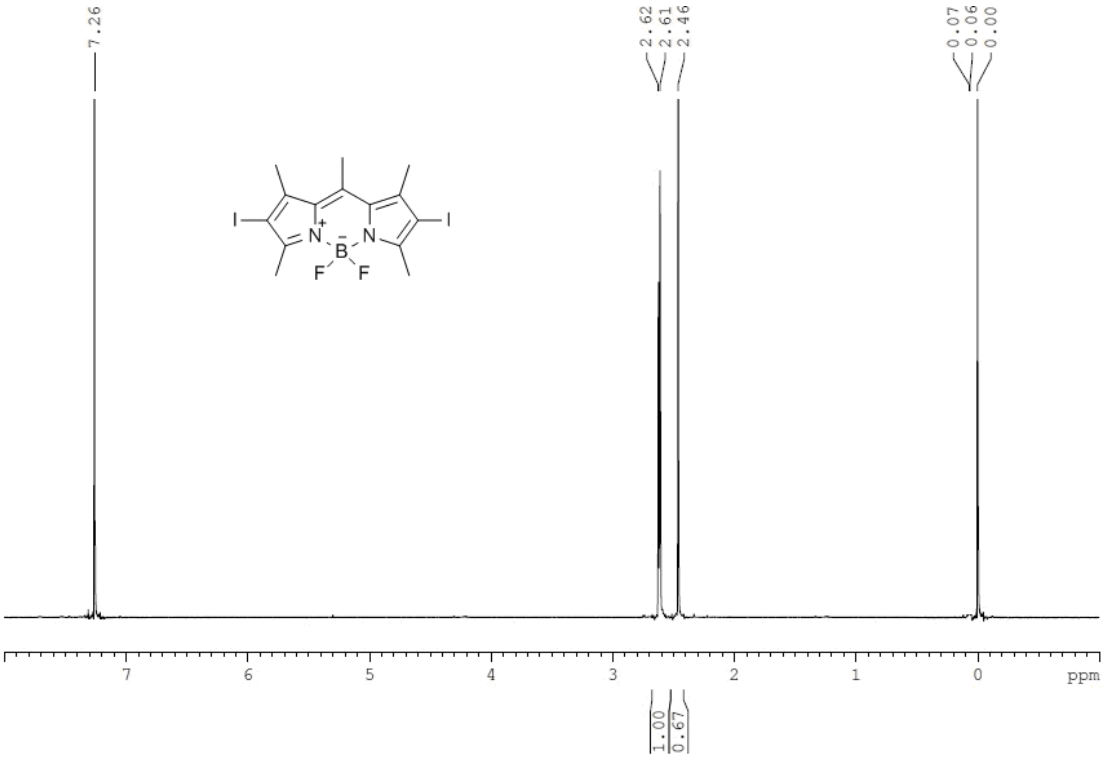
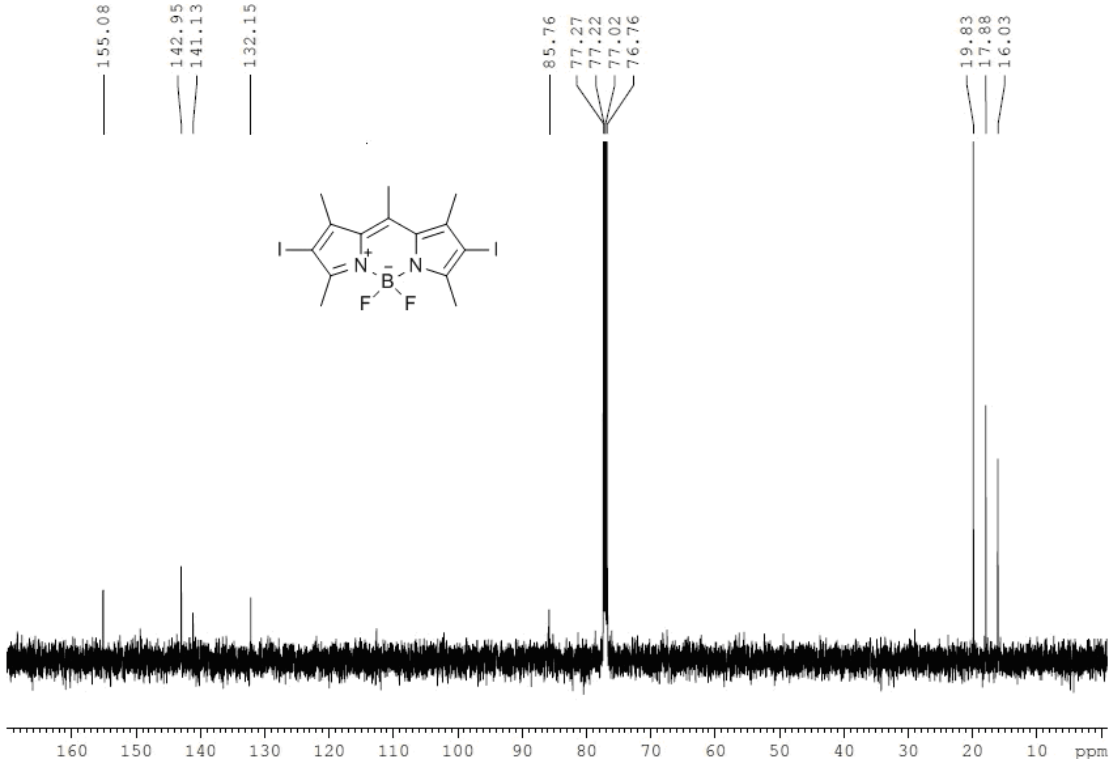


^{13}C NMR of **2m**



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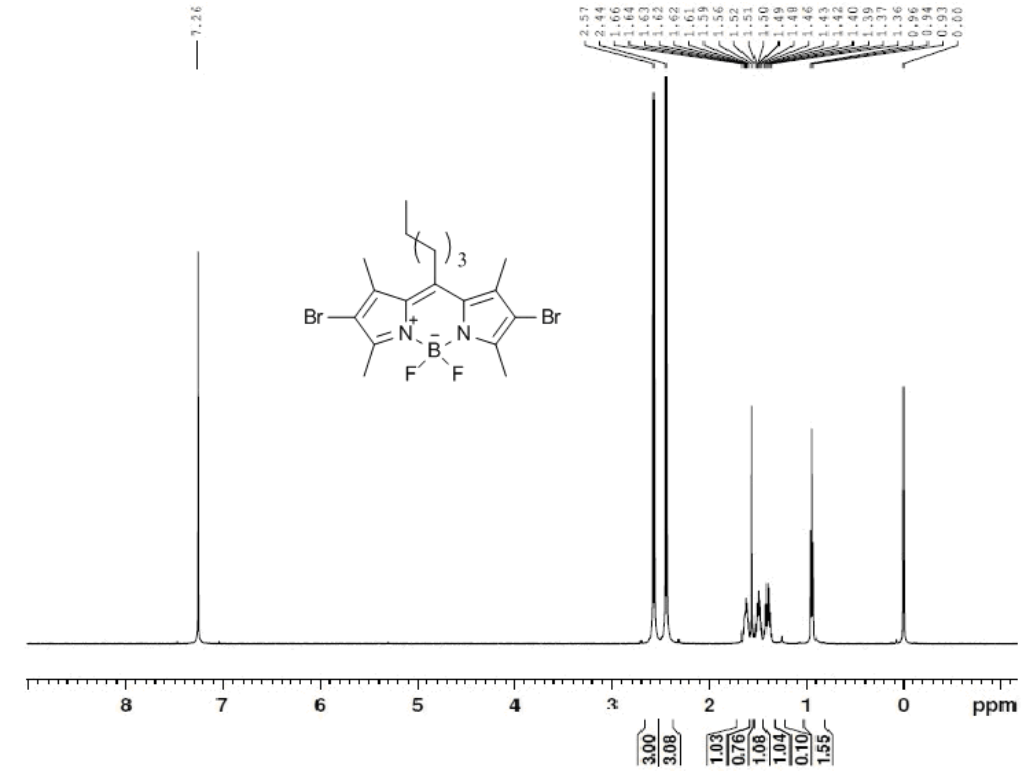
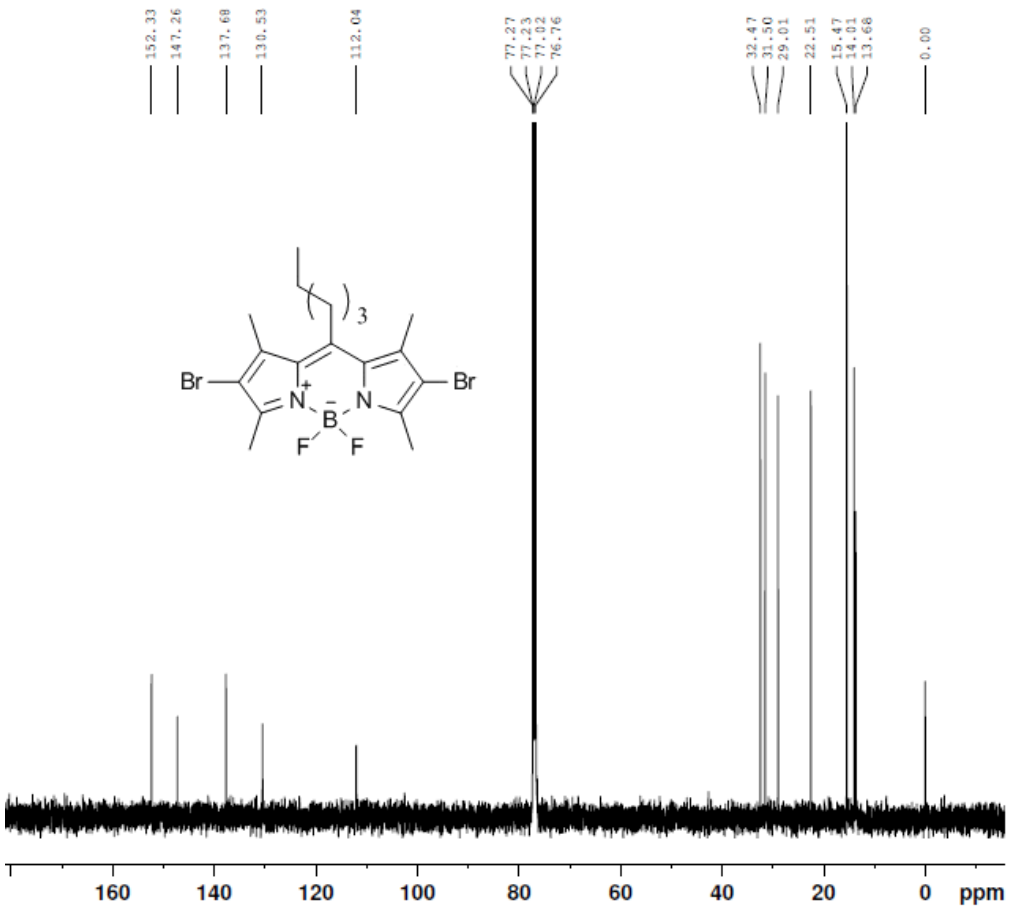
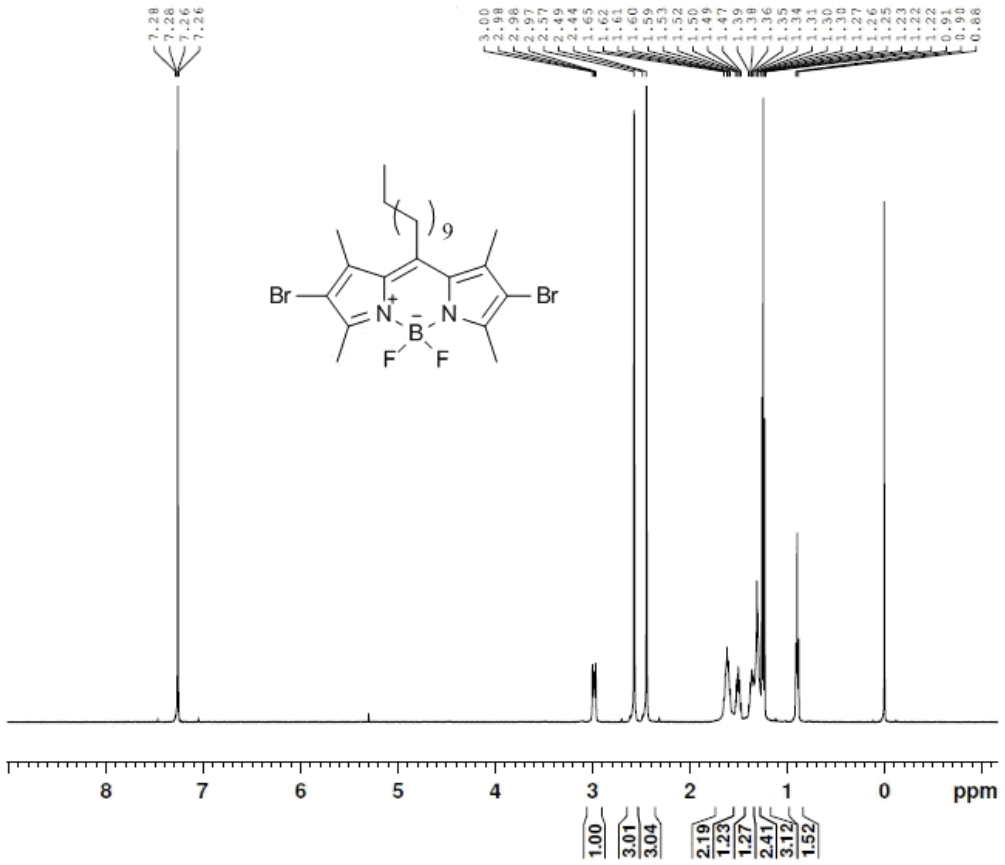


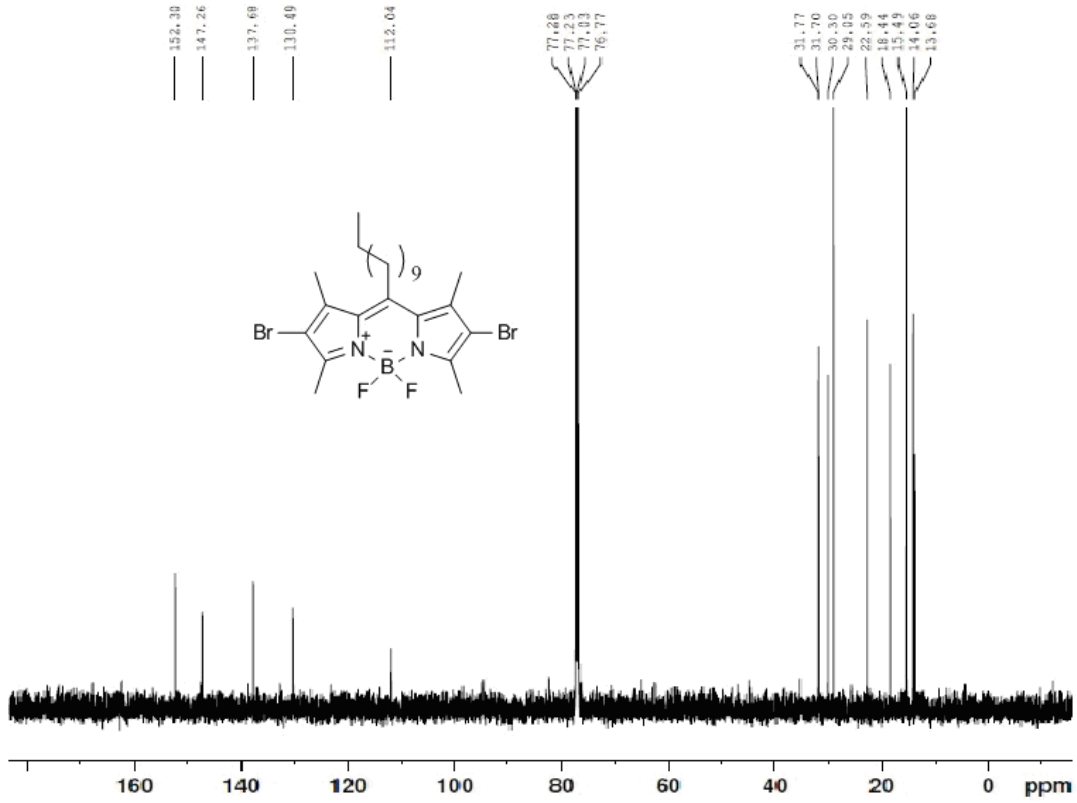
^{13}C NMR of **2n**


152.33
147.26
137.68
130.53
112.04
77.27
77.23
77.02
76.76
32.47
31.50
29.01
22.51
15.47
14.01
13.68
0.00
Br
Br
N
B
N
F
F
3
160
140
120
100
80
60
40
20
0
ppm

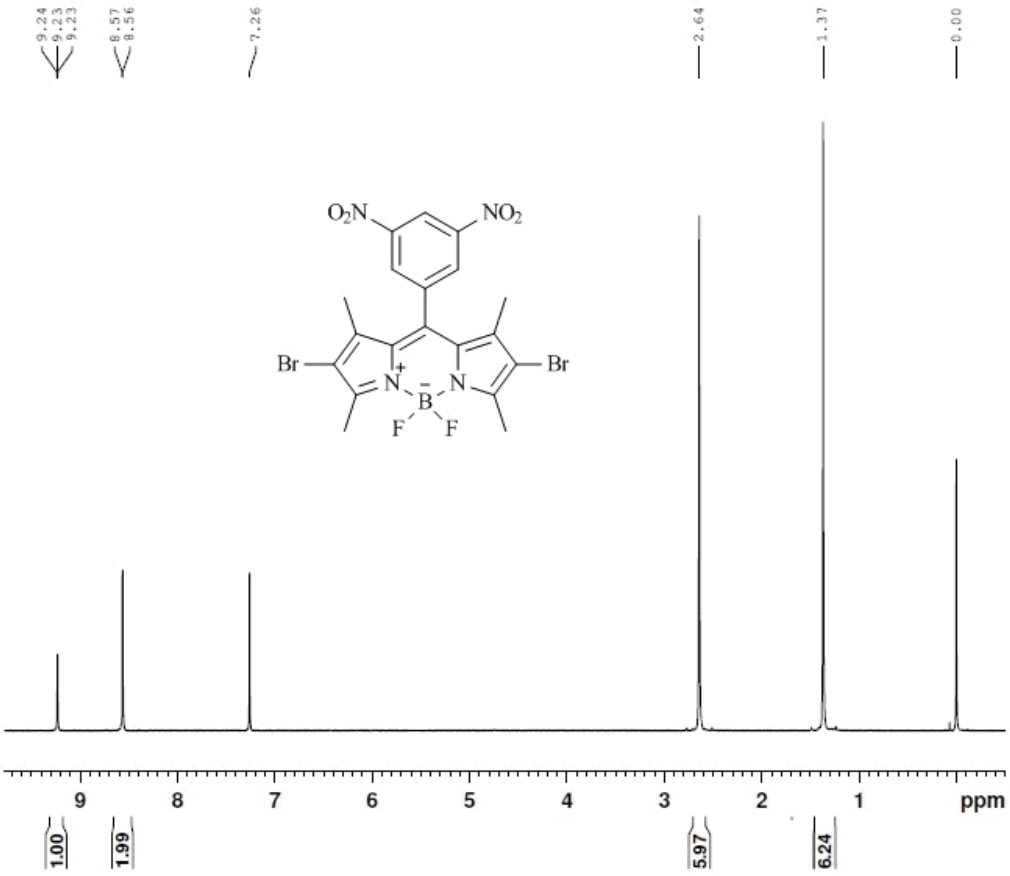
^{1}H NMR of **2p**


7.28
7.28
7.26
7.26
7.26
3.00
2.98
2.98
2.97
2.57
2.49
2.44
1.65
1.62
1.61
1.60
1.59
1.53
1.52
1.50
1.49
1.47
1.39
1.38
1.36
1.35
1.34
1.31
1.30
1.30
1.27
1.26
1.25
1.23
1.22
1.22
0.91
0.90
0.88
Br
Br
N
B
N
F
F
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.01
3.04
2.19
1.23
1.27
2.41
3.12
1.52

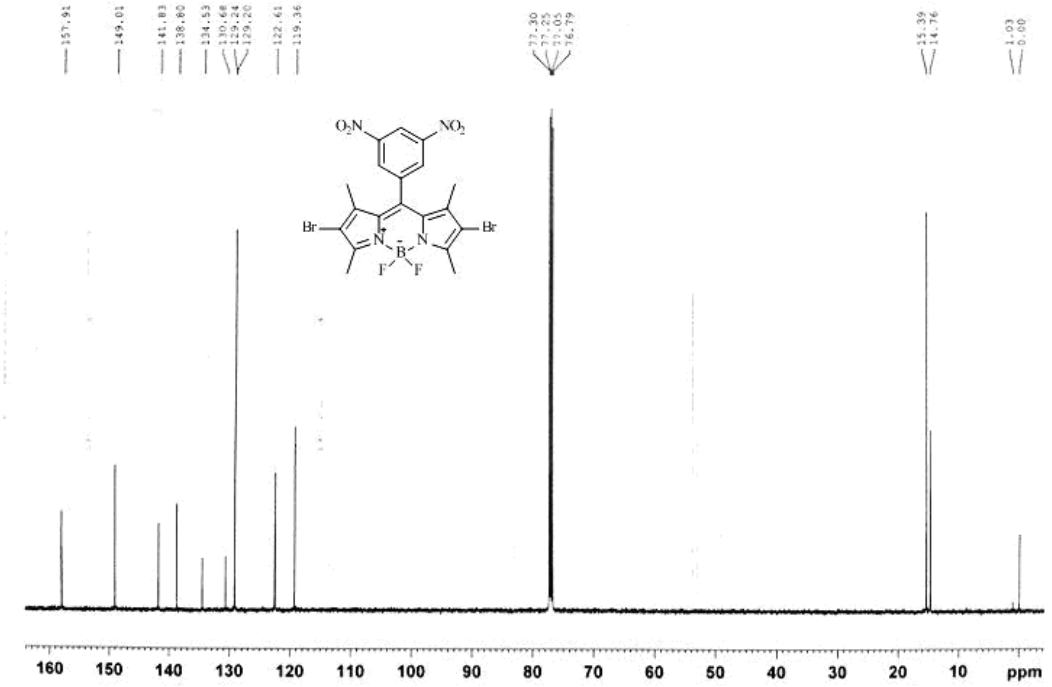
^{13}C NMR of **2p**



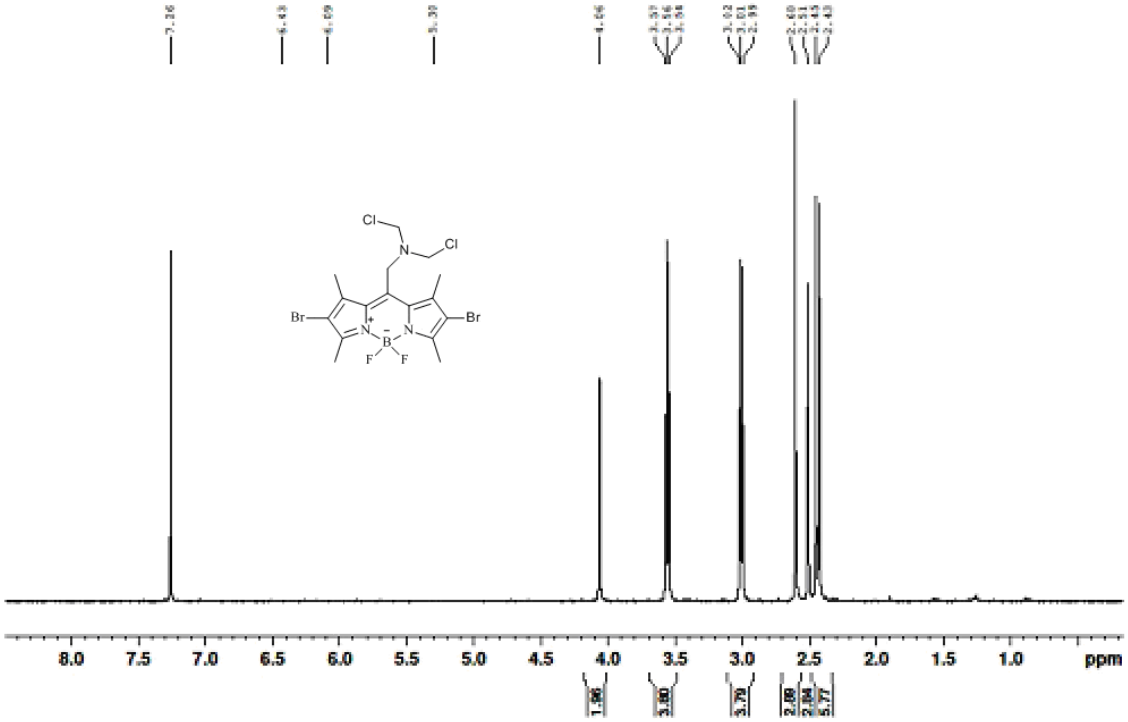
^{1}H NMR of **2r**



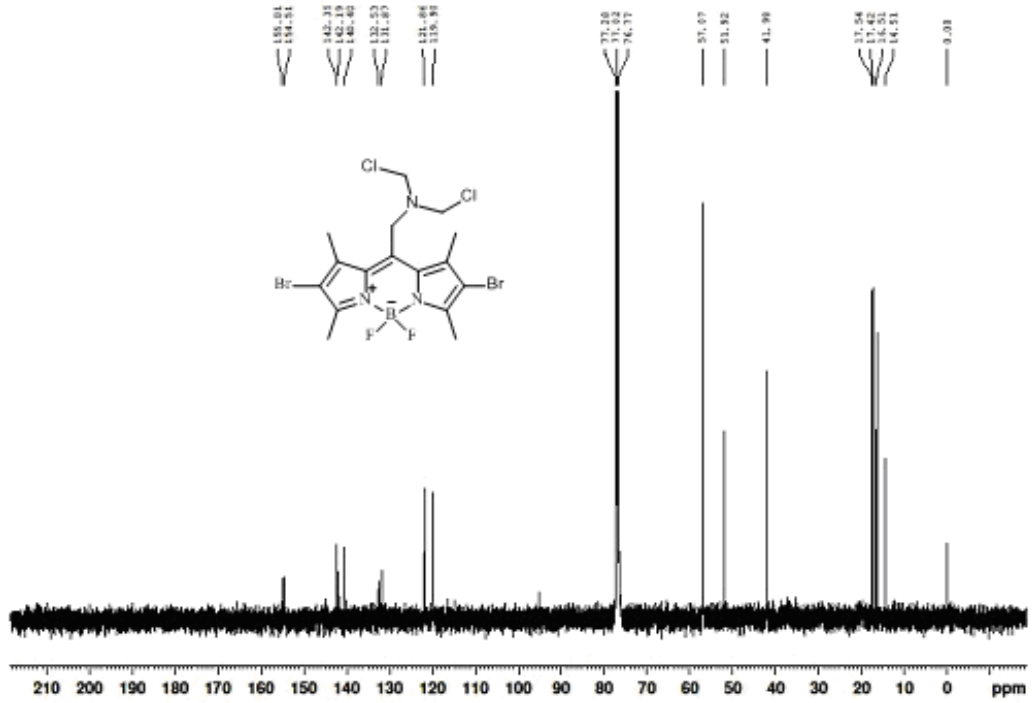
^{13}C NMR of **2r**



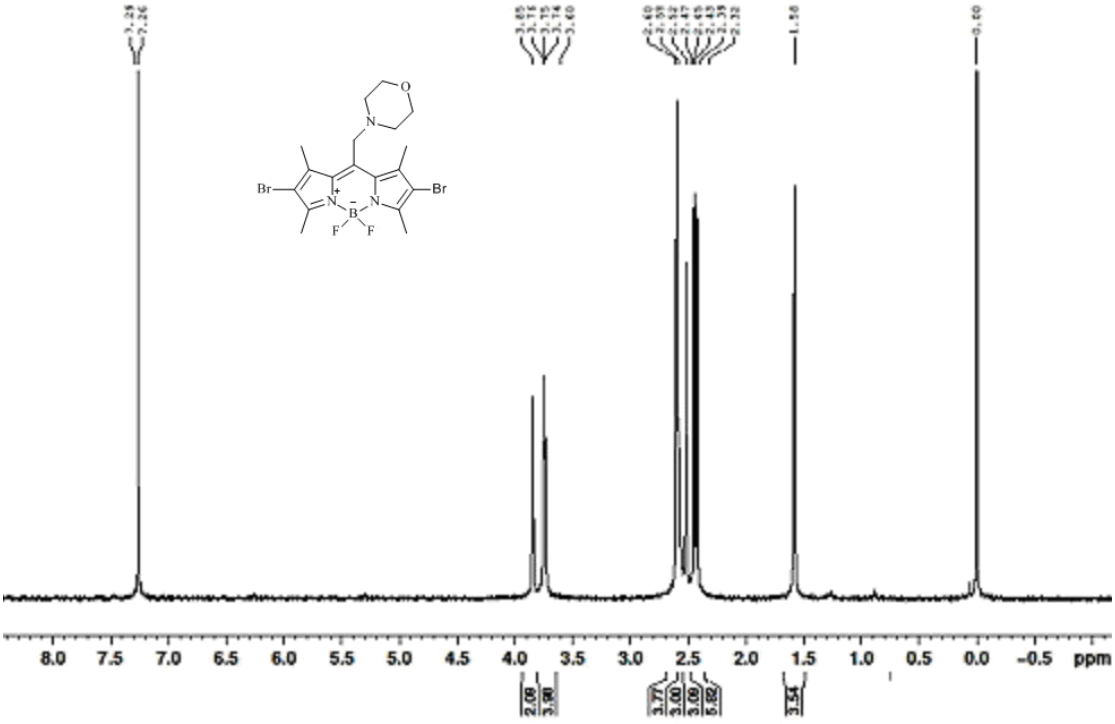
^{1}H NMR of **2s**



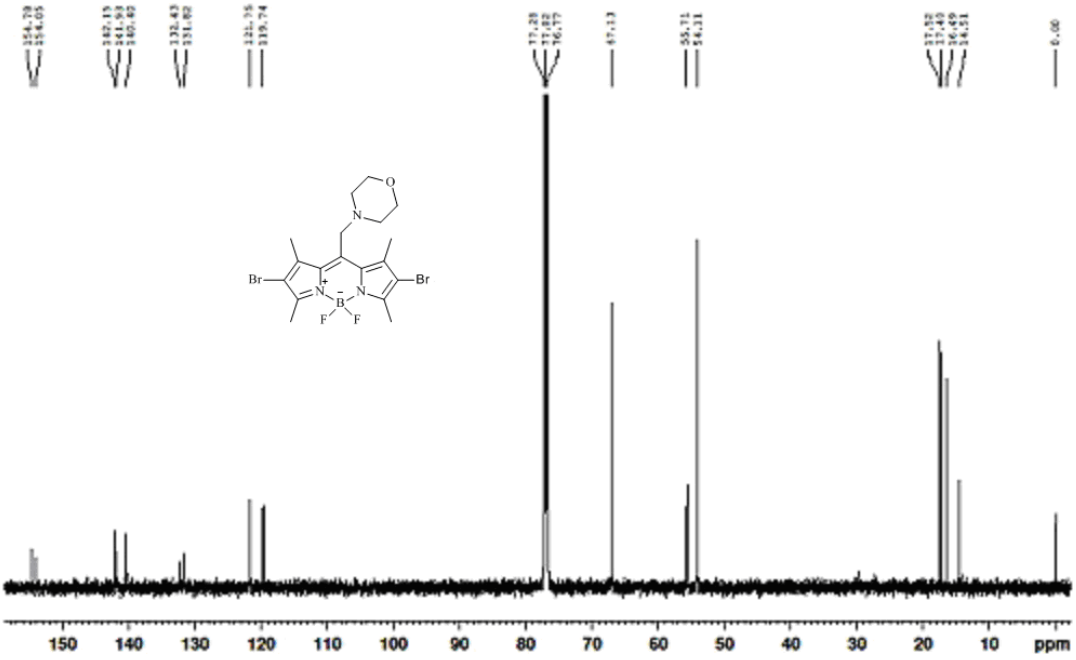
^{13}C NMR of **2s**



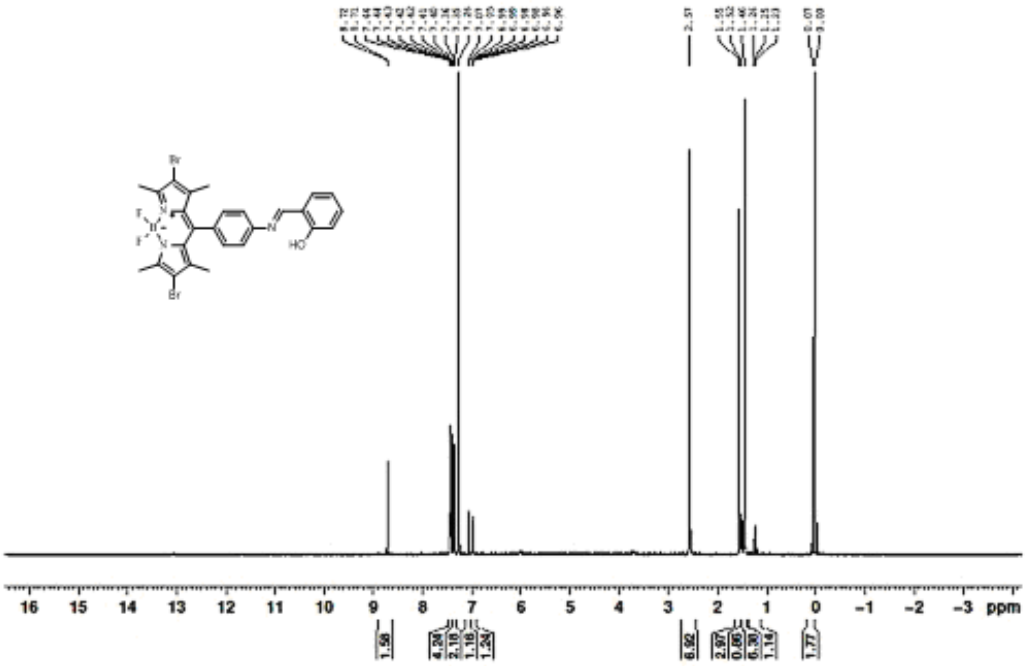
^{1}H NMR of **2t**



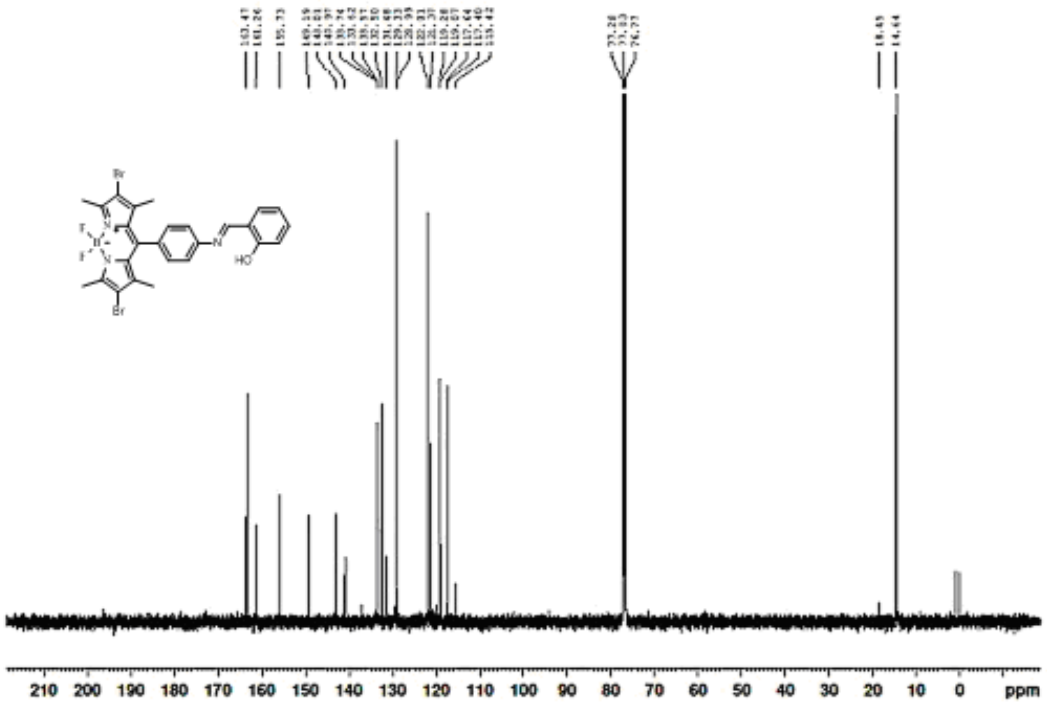
^{13}C NMR of **2t**



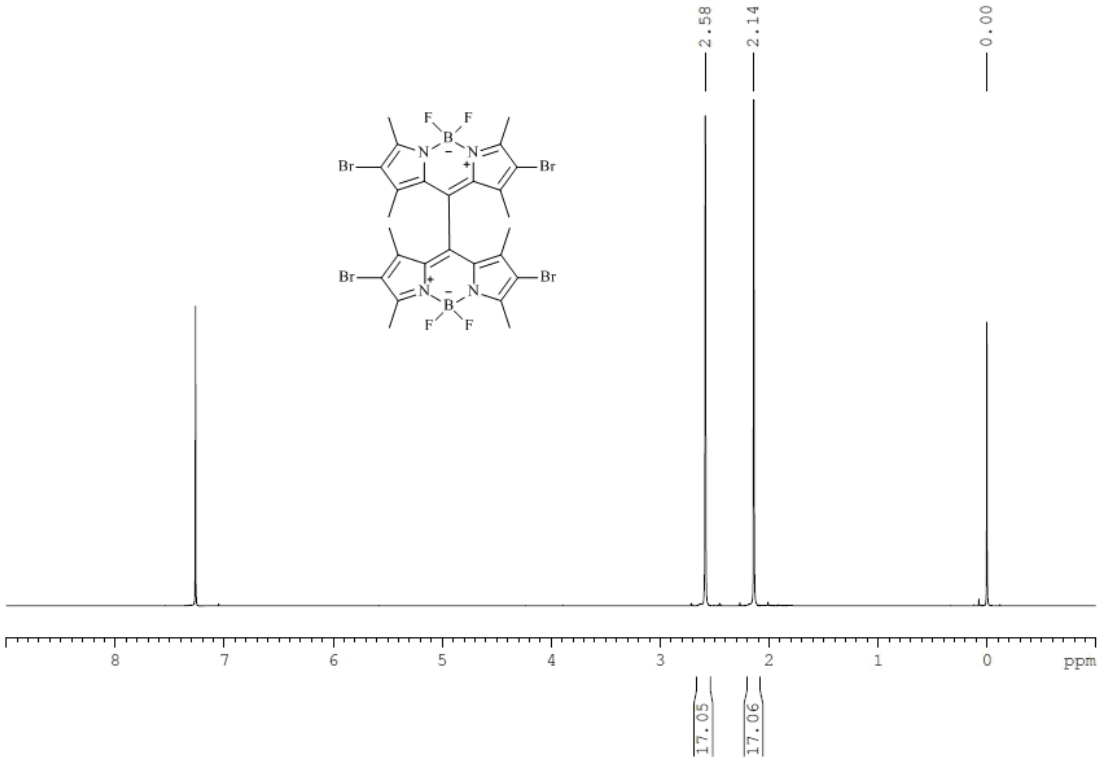
^{1}H NMR of **2u**



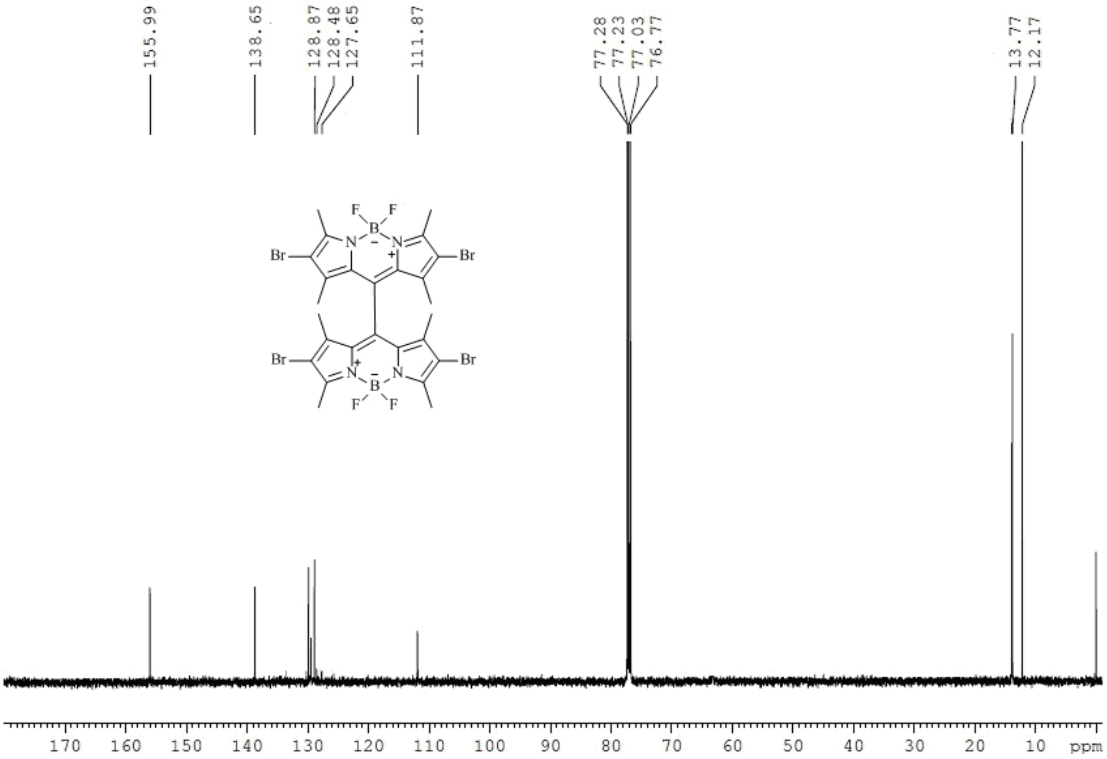
^{13}C NMR of **2u**



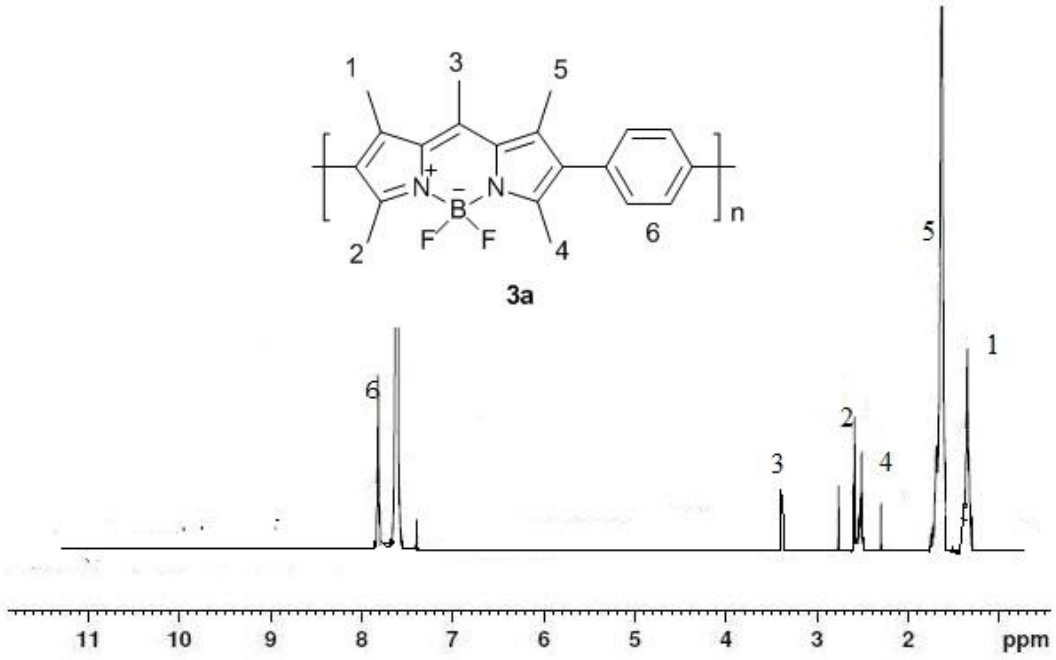
^{1}H NMR of **2v**



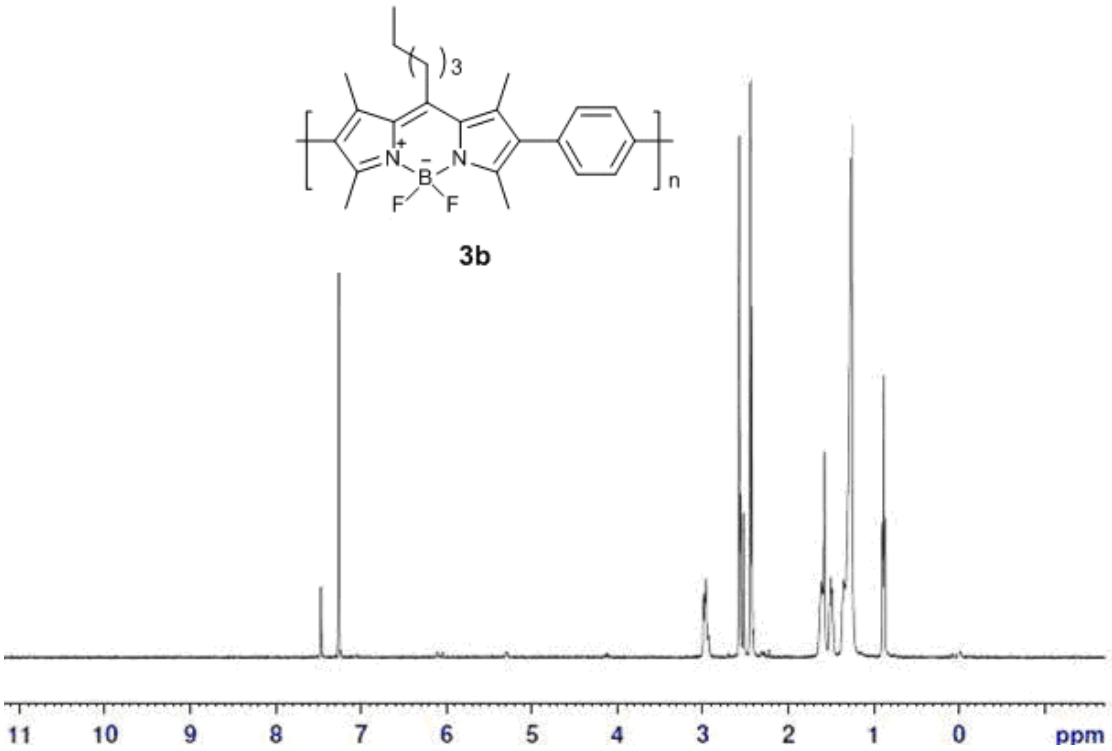
^{13}C NMR of **2v**



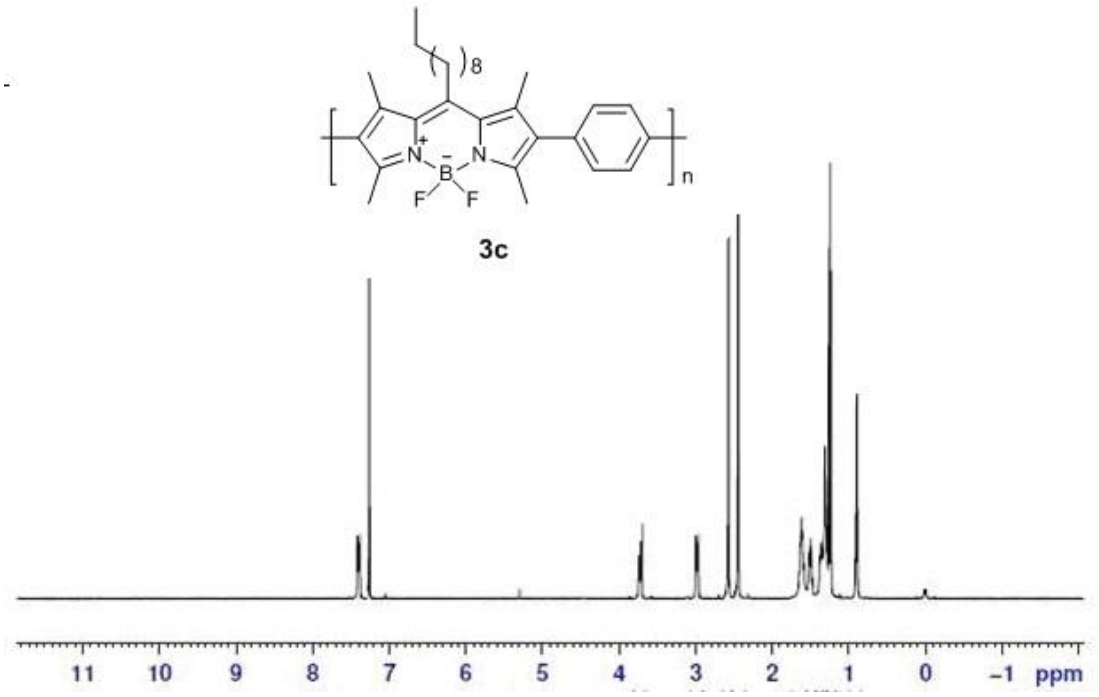
^{1}H NMR of **3a**



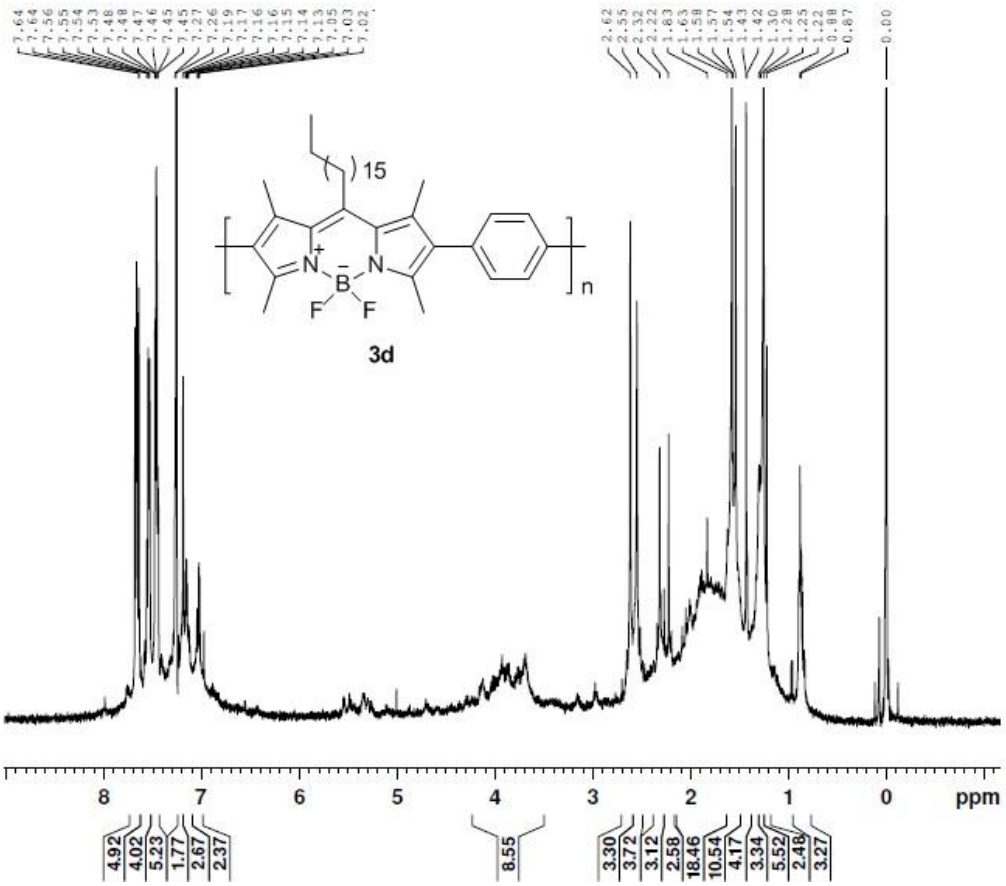
^{1}H NMR of **3b**



^{1}H NMR of **3c**



^{1}H NMR of **3d**

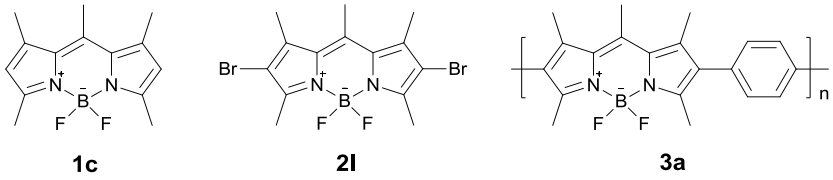


Photophysical properties of *meso*-alkyl BODIPY polymeric dyes

	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Stocks (nm)	Φ_f	M_n (g/mol)	D (M_n/M_w)
3a	hexane	546	573	27	0.615	17110	1.17
	CH_2Cl_2	545	574	29	0.601		
	THF	545	577	32	0.593		
	ethanol	543	578	35	0.566		
3b	hexane	548	578	30	0.515	19200	1.14
	CH_2Cl_2	547	580	33	0.501		
	THF	547	581	34	0.493		
	ethanol	545	581	36	0.466		
3c	hexane	548	577	29	0.485	22100	1.26
	CH_2Cl_2	546	578	32	0.471		
	THF	546	580	34	0.453		

	ethanol	546	581	35	0.426		
3d	hexane	548	577	29	0.485	20100	1.27
	CH_2Cl_2	546	578	32	0.471		
	THF	546	580	34	0.453		
	ethanol	544	579	35	0.426		

[a] The fluorescence quantum yields (Φ) were calculated using Rhodamine B in anhydrous ethanol (Φ = 0.73)



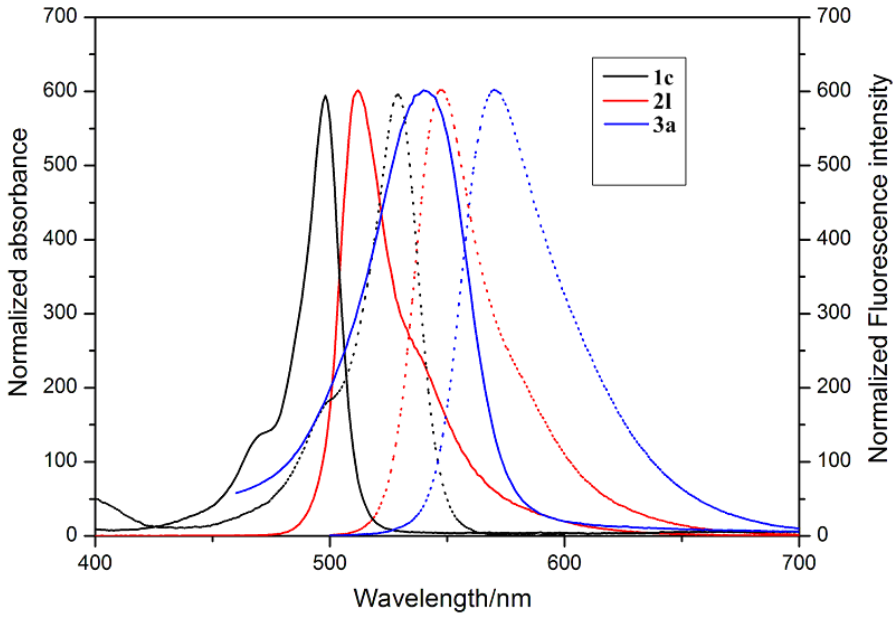


Fig. 1 Normalized absorption (solid lines) and emission (dashed lines) spectra of BODIPYs **1c** (black), **2l** (red) and **3a** (blue) in dichloromethane.

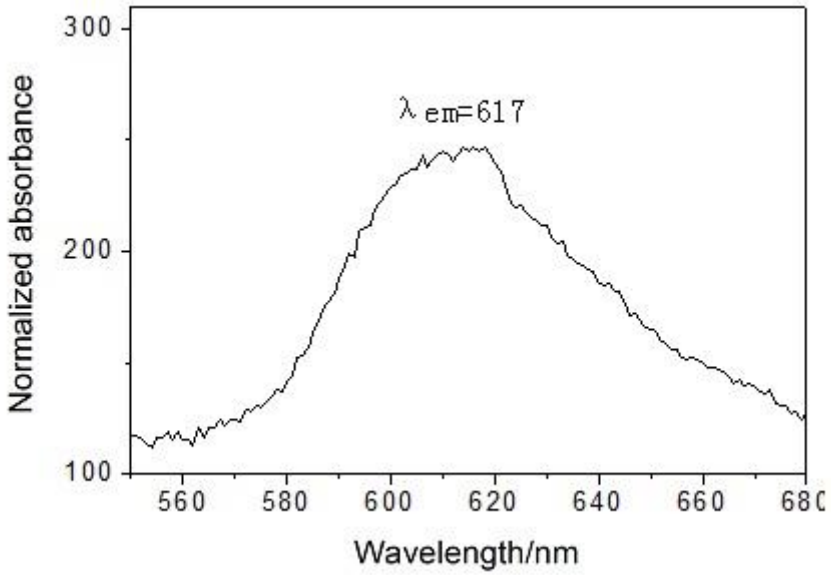
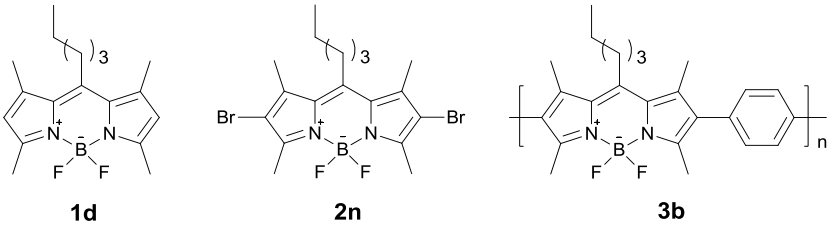


Fig. 2 Solid-state of fluorescence of **3a**



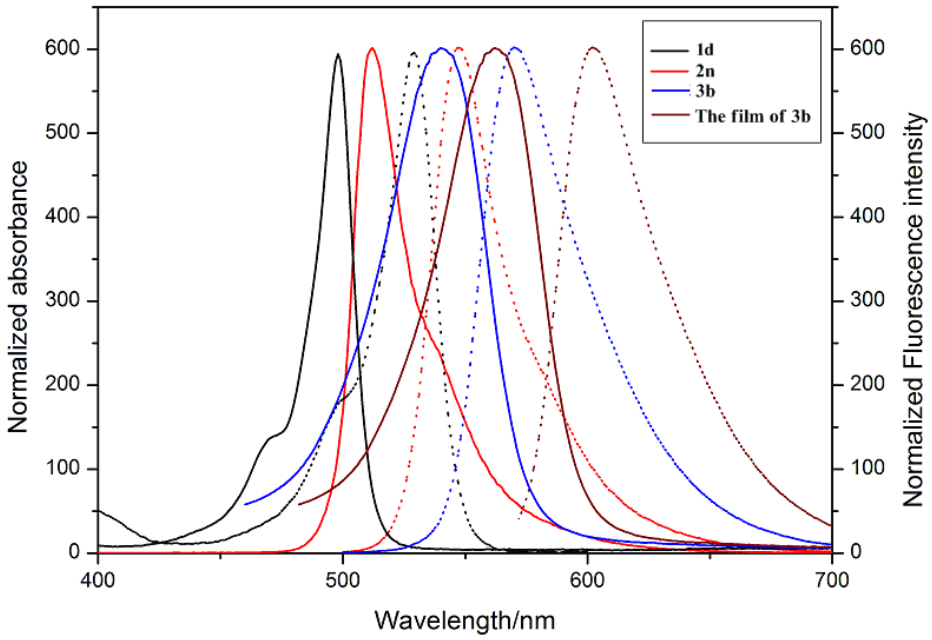


Fig. 3 Normalized absorption (solid lines) and emission (dashed lines) spectra of BODIPYs **1d** (black), **2n** (red), **3b** (blue) and thin film of **3b** (wine) in dichloromethane.

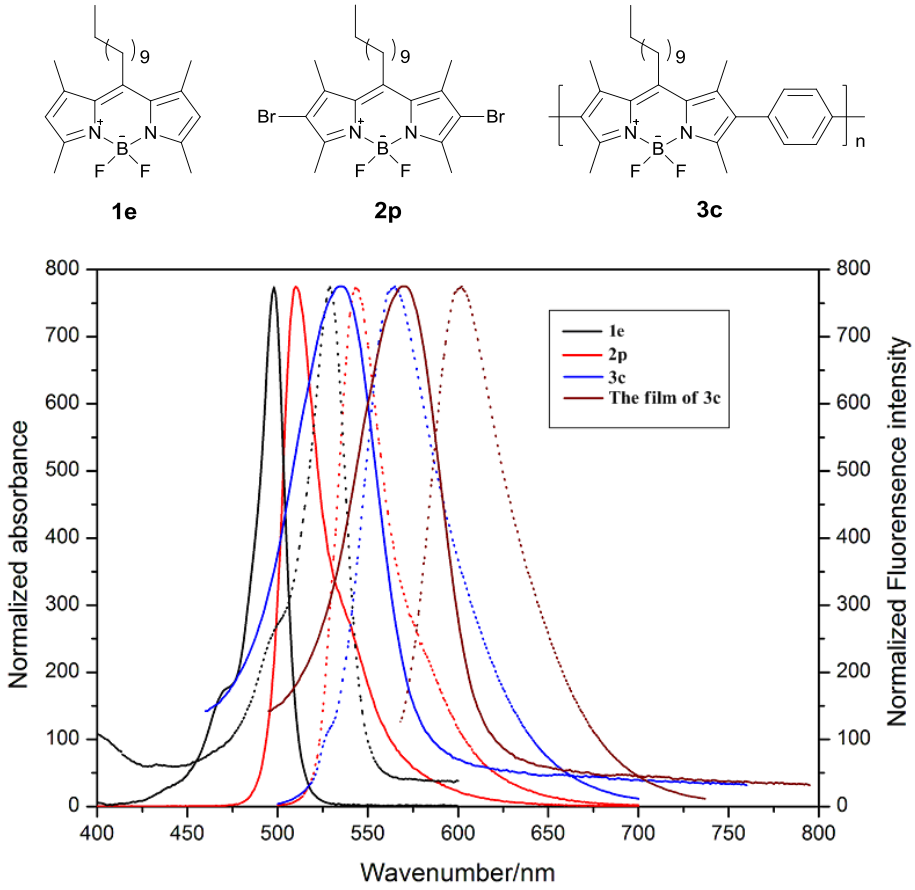


Fig. 4 Normalized absorption (solid lines) and emission (dashed lines) spectra of BODIPYs **1e** (black), **2p** (red), **3c** (blue) and thin film of **3c** (wine) in dichloromethane.

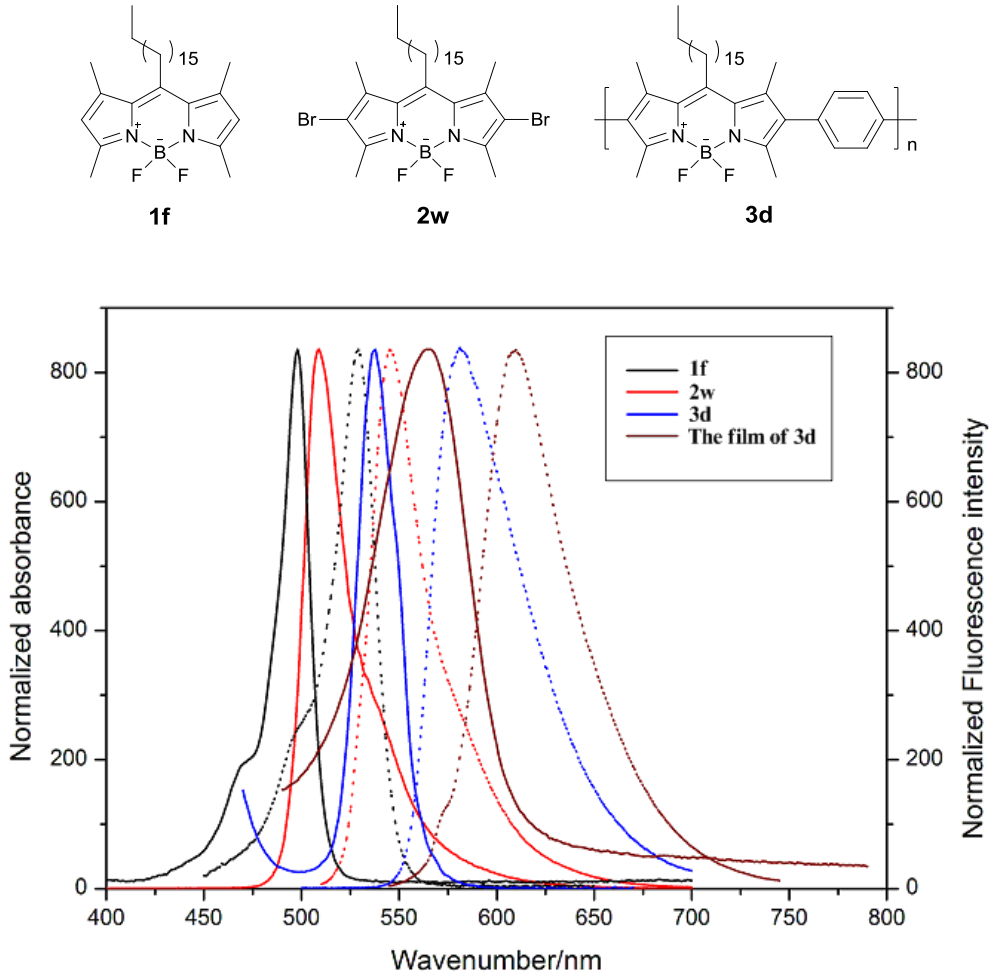
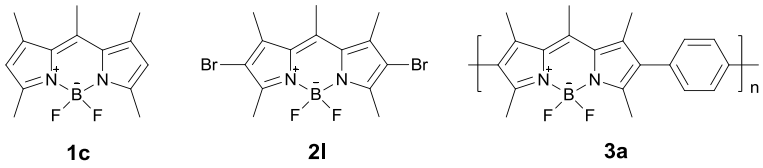


Fig. 5 Normalized absorption (solid lines) and emission (dashed lines) spectra of BODIPYs **1f** (black), **2w** (red), **3d** (blue) and thin film of **3d** (wine) in dichloromethane.

Thermal stabilities



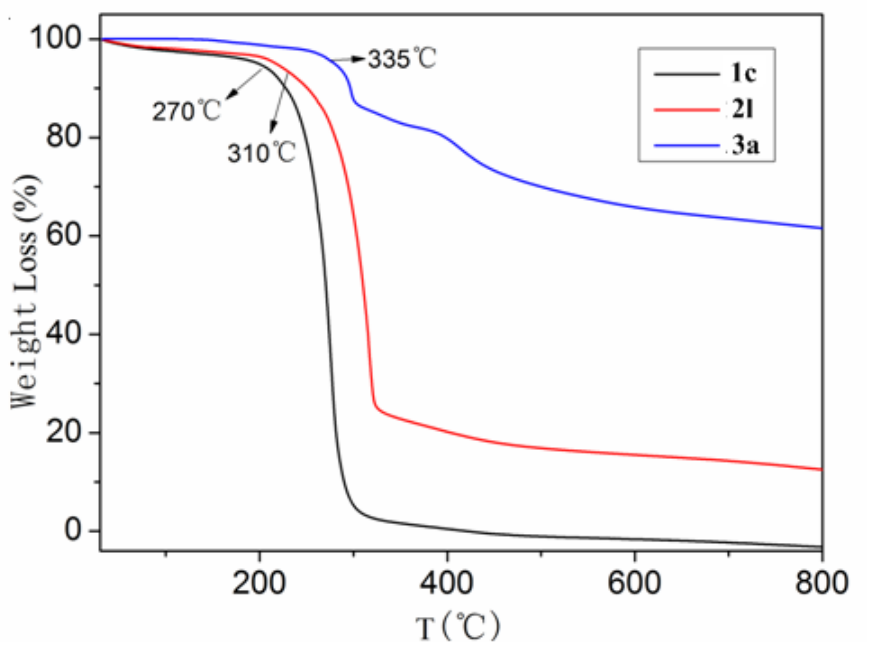


Fig. 6 Thermogravimetric analysis of BODIPYs **1c** (black), **2l** (red) and **3a** (blue) in dichloromethane.

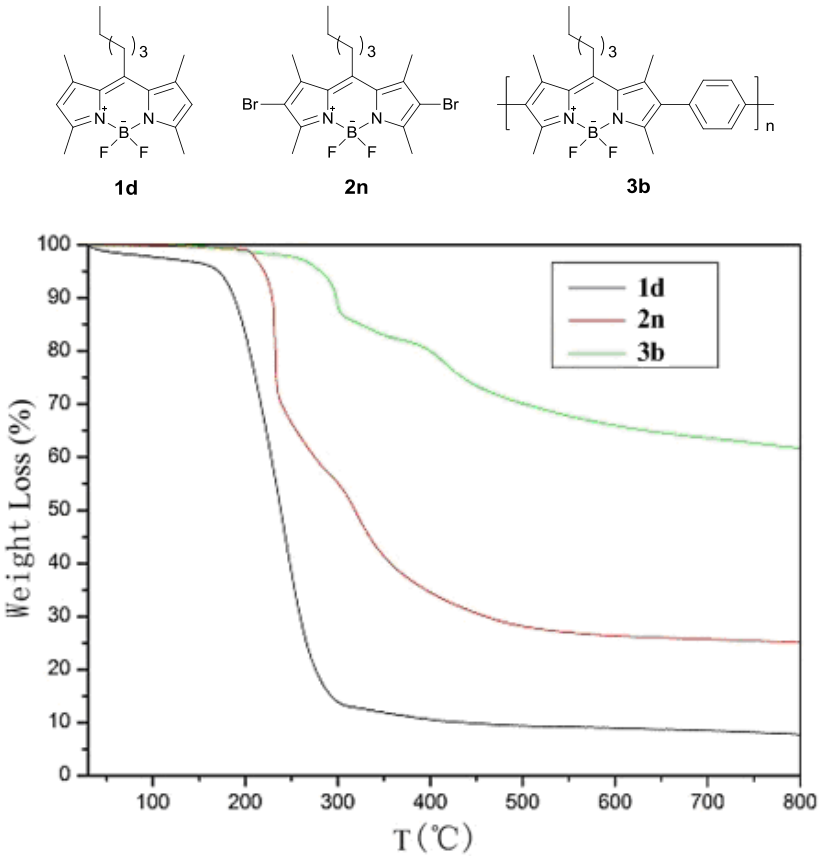
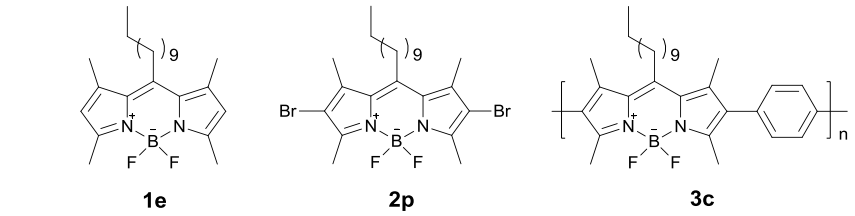


Fig. 7 Thermogravimetric analysis of BODIPYs **1d** (black), **2n** (red) and **3b** (green) in dichloromethane.



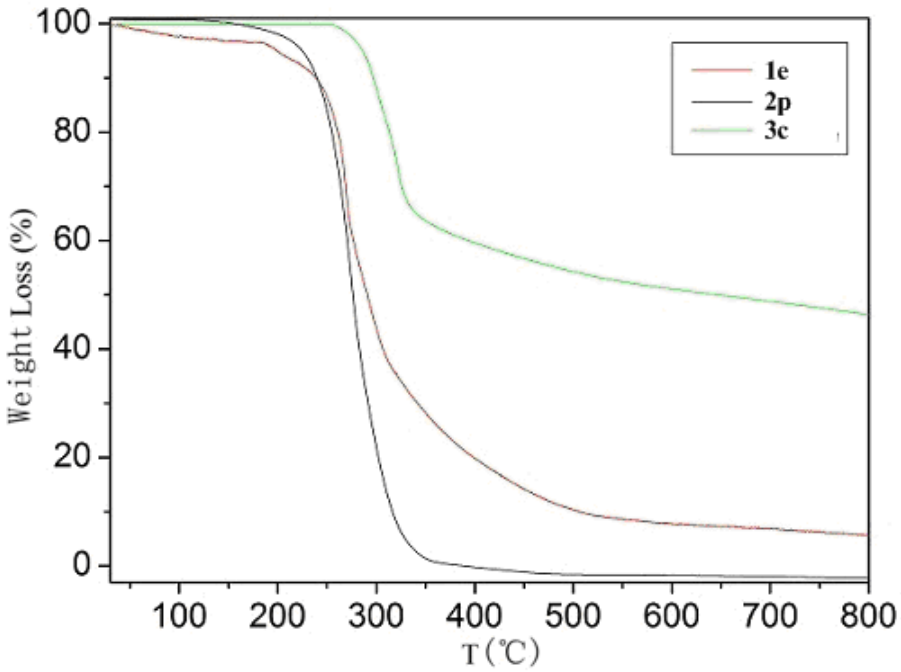


Fig. 8 Thermogravimetric analysis of BODIPYs **1e**(red), **2p** (black) and **3c** (green) in dichloromethane.

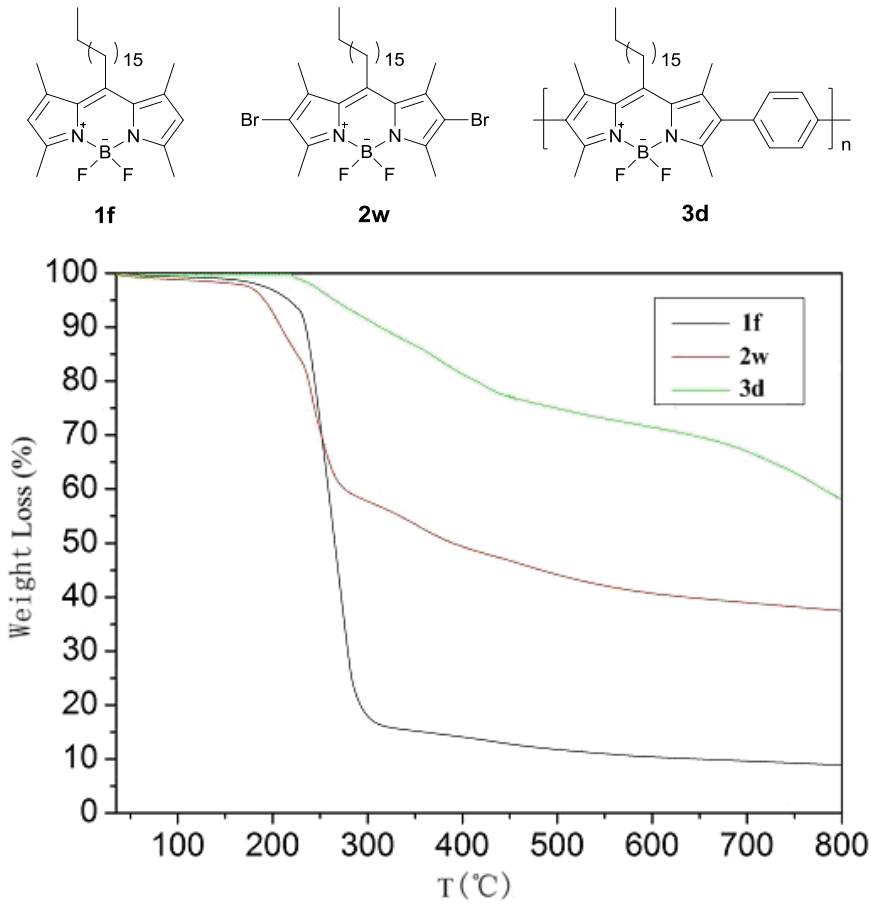


Fig. 9 Thermogravimetric analysis of BODIPYs **1f** (black), **2w** (red) and **3d** (green) in dichloromethane.

Recycling of HFIP

The recycling experiment was carried out on a 1 mmol scale of substrate **1a** in 10 mL HFIP. After reaction, the solvent HFIP was distilled and used directly for next run. The yields of four successive runs were shown Fig. 10.

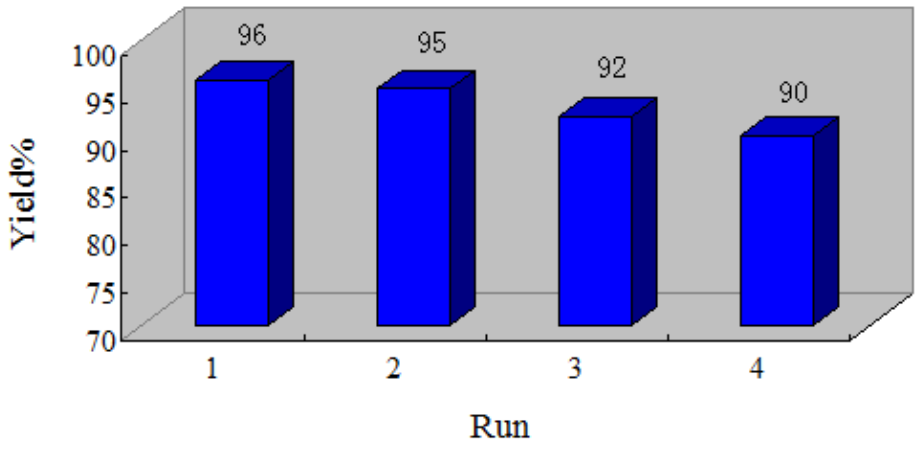


Fig. 10 The recycling experiment.

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2. J.-H. Ye, G. Wang, C. Huang, Z. Hu, W. Zhang and Y. Zhang, *Synlett* **2012**, 104.
3. L.-J. Jiao, W.-D. Pang, L.-Y. Zhou, Y. Wei, X.-L. Mu, G.-F. Bai and E.-H. Hao, *J. Org. Chem.*, **2011**, *76*, 9988.

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