Supporting Information

Orthogonal Bodipy Trimers as Photosensitizers for Photodynamic Action

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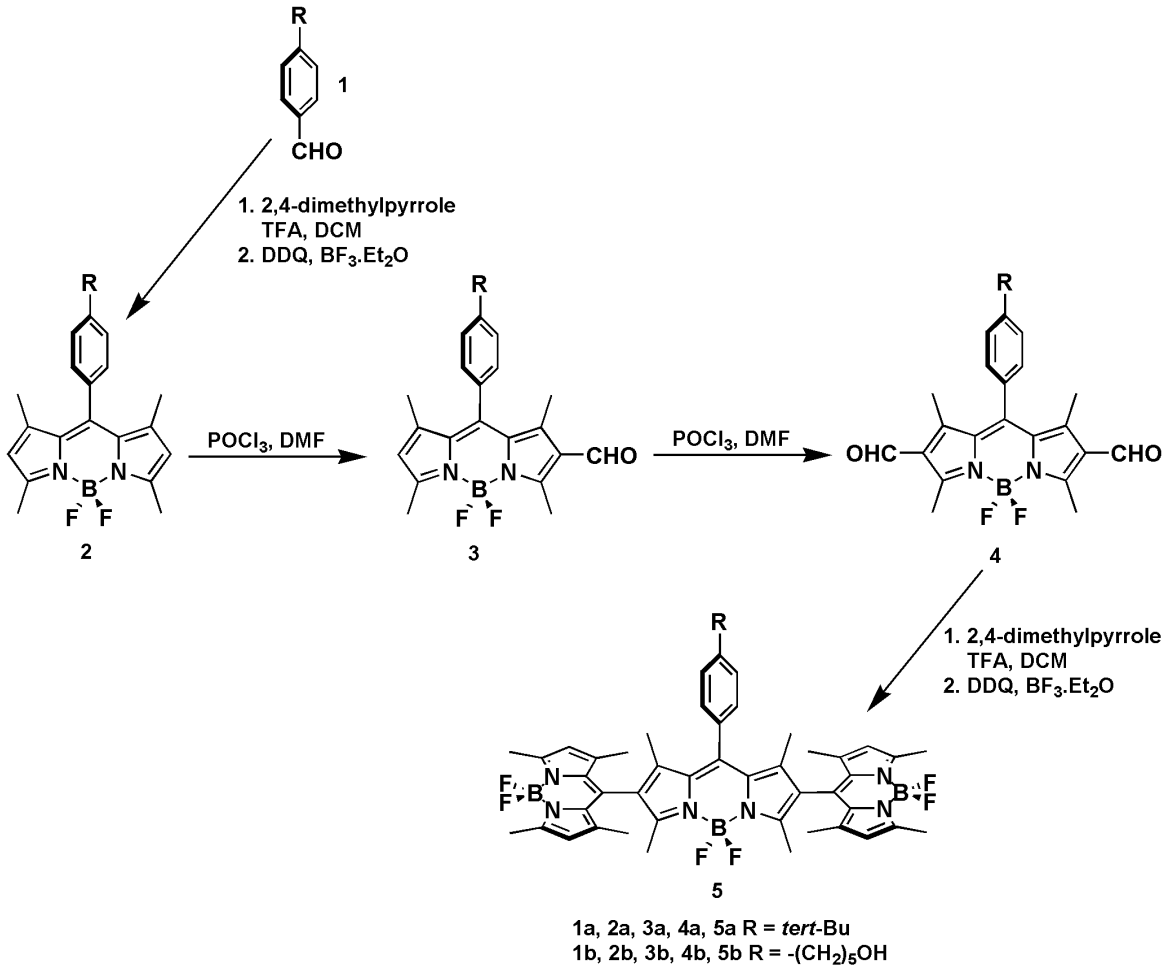
General:

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Spectrospin Avance DPX 400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts values are reported in ppm from tetramethylsilane as internal standard. Spin multiplicities are reported as the following: s (singlet), d (doublet), m (multiplet). HRMS data were acquired on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. UV-Vis Absorption spectra were taken on a Varian Cary-100 and Varian Cary 5000 UV-VIS-NIR absorption spectrophotometer. Fluorescence measurements were done on a Varian Eclipse spectrofluorometer. Spectrophotometric grade solvents were used for spectroscopy experiments. Flash column chromatography (FCC) was performed by using glass columns with a flash grade silica gel (Merck Silica Gel 60 (40–63 μm)). Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254), visualized by UV-Vis light and DNP stains as appropriate. All commercial chemicals were purchased from Merck, Sigma-Aldrich and ABCR and were used without any further purification. Compound **2a**[1] and **3a**[2] were synthesized according to literature.



Scheme 1. Schematic representation for the synthesis of compound **5**.

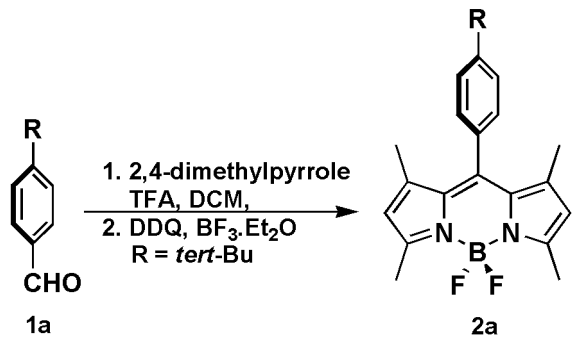


Figure 1. Synthesis of compound **2a**.

Synthesis of Compound 2a:[1]

To a 500 mL round-bottomed flask containing 250 mL argon-degassed dichloromethane, 2,4-dimethylpyrrole (1.05 mL, 10.26 mmol), 4-*tert*-butylbenzaldehyde (0.773 mL, 4.623 mmol) **(1a)** were added. Then, trifluoroacetic acid (400 µL) was added to the reaction mixture and left to stirr overnight. Then, p-chloranil (1.36 g, 5.5 mmol) was added and mixed for 1 additional hour. After that, TEA (3.5 mL) was added and mixed for 1 additional hour and $BF_3.OEt_2$ (3.5 mL) was added and the reaction mixture was left to stir at room temperature for 1h. When the starting material was consumed, water (100 mL) was added and the reaction mixture was extracted with DCM (3x100 mL), evaporated and dried over Na_2SO_4. The product was purified by silica gel column chromatography using DCM:Hexane (1:1) as the eluant and the compound was obtained as purple redish solid (1.49 g, 85 %). 1H NMR (CD2Cl2, 250 MHz): δ = 7.42 (d, 2H), 7.11 (d, 2H), 5.91 (s, 2H), 2.42 (s, 6H), 1.30 (s, 6H), 1.27 (s, 9H). 13C NMR (CD2Cl2, 62.5MHz): δ=155.7, 153.2, 144.2, 143.4, 132.2, 128.2, 126.5, 121.8, 35.5, 31.8, 15.0, 14.8. ESI-HRMS ($M-H^+$) calculated 380.2344, found 380.2297, Δ= 12.48 ppm

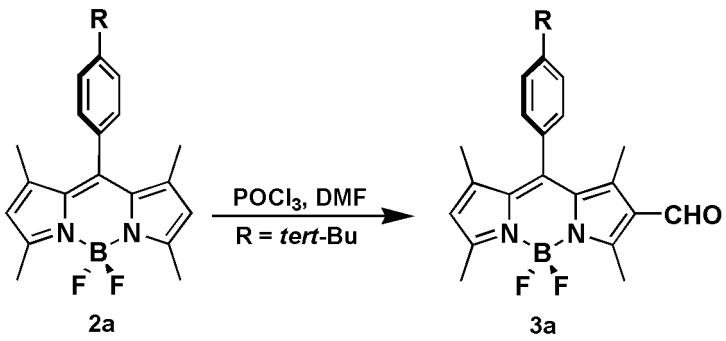


Figure 2. Synthesis of compound **3a**.

Synthesis of Compound 3a:[2]

1 mL of DMF and 1 mL of $POCl_3$ was stirred in an ice bath for 5 min under argon. Then it was warmed to room temperature and waited for 30 minutes. To this mixture compound **2a** (300 mg, 0.789 mmol) was added in dichloroethane (60 mL). The temperature was raised to 50^0C and stirred for 2 hours. The reaction was then cooled to room temperature and poured to an ice cold $NaHCO_3$ solution (150 mL). This mixture was extracted with DCM (3x100 mL) and dried over Na_2SO_4. Solvent was evaporated in *vacuo* and purified by silica gel column chromatography using DCM:MeOH (98:2) as the eluent. Product **3a** was obtained as an orange solid (289.9 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.55 (dd, *J* = 6.5, 1.8 Hz, 2H), 7.19 (dd, *J* = 6.4, 1.8 Hz, 2H), 6.16 (s, 1H), 2.83 (s, 3H), 2.62 (s, 3H), 1.66 (s, 3H), 1.44 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 161.3, 156.3, 153.2, 147.4, 144.1, 143.0, 134.2, 131.1, 127.3, 126.3, 123.9, 34.9, 31.3, 15.0, 14.7, 13.0, 11.4. MS (TOF-ESI): m/z: Calcd: 408.2293 $[M-H]^+$, Found: 408.2267 $[M-H]^+$, Δ= 6.51 ppm.

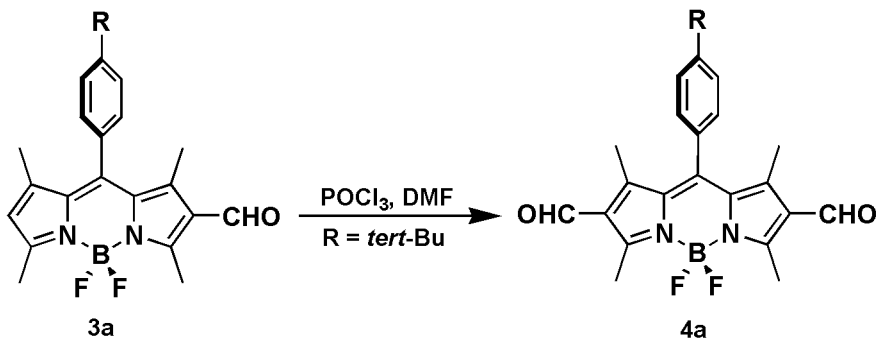


Figure 3. Synthesis of compound **4a**.

Synthesis of Compound 4a:

1 mL of DMF and 1 mL of $POCl_3$ was stirred in an ice bath for 5 min under argon. Then it was warmed to room temperature and waited for 30 minutes. To this mixture compound **3a** (200 mg, 0.490 mmol) was added in dichloroethane (60 mL). The temperature was raised to 50^0C and stirred for 2 hours. The reaction was then cooled to room temperature and poured to an ice cold $NaHCO_3$ solution (150 mL). This mixture was extracted with DCM (3x100 mL) and dried over Na_2SO_4. Solvent was evaporated in *vacuo* and purified by silica gel column chromatography using DCM:MeOH (98:2) as the eluent. Product **4a** was obtained as an orange solid (171 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.89 (s, 6H), 1.73 (s, 6H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 160.5, 154.0, 148.4, 147.9, 132.0, 130.5, 128.0, 127.0, 126.9, 35.0, 31.3, 13.7, 12.0. MS (TOF-ESI): m/z: Calcd: 481.21045 $[M-H]^+$, Found: 481.17248 $[M-H]^+$, Δ= 74.13 ppm.

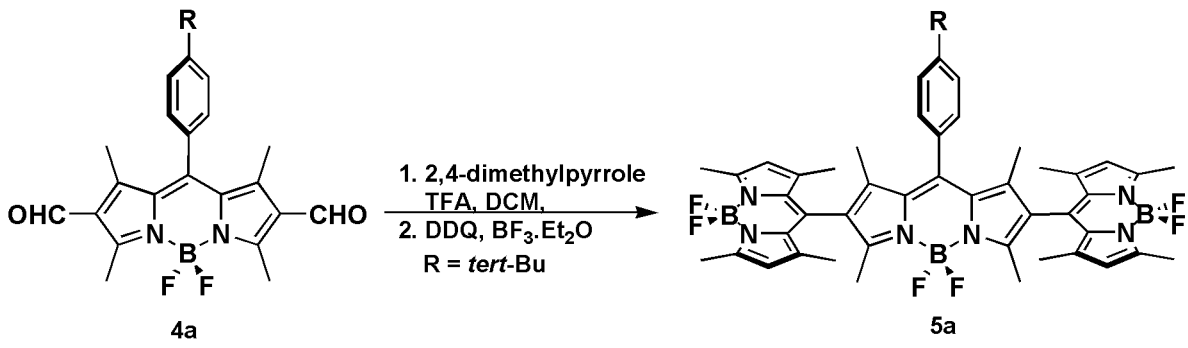


Figure 4. Synthesis of compound **5a**.

Synthesis of Compound 5a:

To a 500 mL round-bottomed flask containing 250 mL argon-degassed dichloromethane, 2,4-dimethylpyrrole (2.10 mL, 20.5 mmol), compound **4a** (200 mg, 0.458 mmol) were added. Then, trifluoroacetic acid (500 µL) was added to the reaction mixture and left to stirr overnight. Then, p-chloranil (2.72 g, 11 mmol) was added and mixed for 1 additional hour. After that, TEA (5 mL) was added and mixed for 1 additional hour and $BF_3.OEt_2$ (5 mL) was added and the reaction mixture was left to stir at room temperature for 1h. When the starting material was consumed, water (100 mL) was added and the reaction mixture was extracted with DCM (3x100 mL), evaporated and dried over Na_2SO_4. The product was purified by silica gel column chromatography using DCM:Hexane (1:1) as the eluant and the compound was obtained as purple redish solid (160 mg, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.03 (s, 4H), 2.56 (s, 12H), 2.48 (s, 6H), 1.79 (s, 12H), 1.34 (s, 9H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.6, 153.5, 144.0, 142.3, 140.8, 132.9, 131.7, 131.0, 127.2, 126.9, 126.4, 121.3, 53.4, 34.8, 31.6, 31.3, 22.6, 14.6, 14.3, 14.1, 13.0, 12.4. ESI-HRMS ($M-H^+$) calculated 869.46295, found 869.44414, Δ= 21.63 ppm.

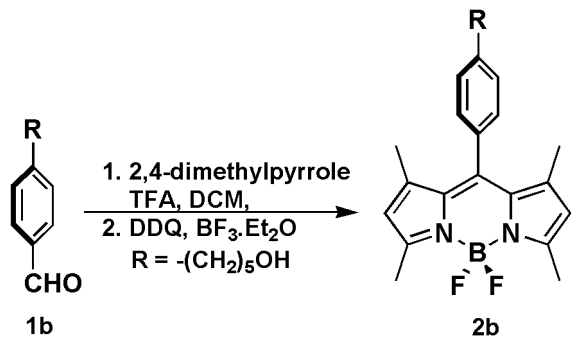


Figure 5. Synthesis of compound **2b**.

Synthesis of Compound 2b:

To a 500 mL round-bottomed flask containing 250 mL argon-degassed dichloromethane, 2,4-dimethylpyrrole (1.05 mL, 10.26 mmol), 4-((5-hydroxypentyl)oxy)benzaldehyde (300 mg, 1.44 mmol) **(1b)** were added. Then, trifluoroacetic acid (400 µL) was added to the reaction mixture and left to stirr overnight. Then, p-chloranil (1.36 g, 5.5 mmol) was added and mixed for 1 additional hour. After that, TEA (3.5 mL) was added and mixed for 1 additional hour and $BF_3.OEt_2$ (3.5 mL) was added and the reaction mixture was left to stir at room temperature for 1h. When the starting material was consumed, water (100 mL) was added and the reaction mixture was extracted with DCM (3x100 mL), evaporated and dried over Na_2SO_4. The product was purified by silica gel column chromatography using DCM:Hexane (1:1) as the eluant and the compound was obtained as purple redish solid (0.380 g, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 2H), 7.04 – 7.00 (m, 2H), 5.99 (s, 2H), 4.19 (t, *J* = 6.0 Hz, 2H), 3.91 (t, *J* = 5.9 Hz, 2H), 2.56 (s, 6H), 2.10 (dq, *J* = 12.1, 6.0 Hz, 2H), 1.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 155.3, 143.2, 141.8, 131.8, 130.4, 129.2, 127.2, 121.1, 115.1, 65.6, 60.2, 32.0, 14.6. ESI-HRMS ($M-H^+$) calculated 438.24102, found 438.241662, Δ= 6.0 ppm.

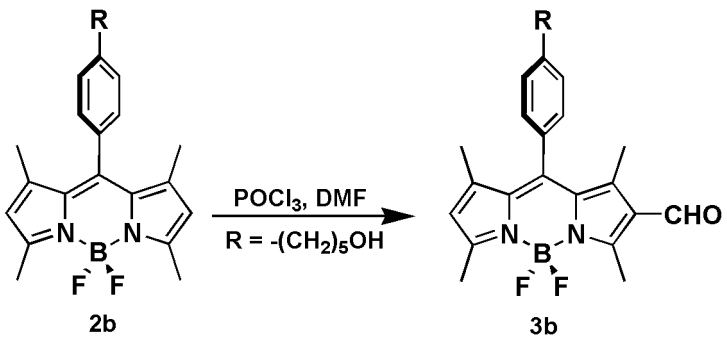


Figure 6. Synthesis of compound **3b**.

Synthesis of Compound 3b:[2]

1 mL of DMF and 1 mL of $POCl_3$ was stirred in an ice bath for 5 min under argon. Then it was warmed to room temperature and waited for 30 minutes. To this mixture compound **2b** (200 mg, 0.469 mmol) was added in dichloroethane (60 mL). The temperature was raised to 50^0C and stirred for 2 hours. The reaction was then cooled to room temperature and poured to an ice cold $NaHCO_3$ solution (150 mL). This mixture was extracted with DCM (3x100 mL) and dried over Na_2SO_4. Solvent was evaporated in *vacuo* and purified by silica gel column chromatography using DCM:MeOH (98:2) as the eluent. Product **3b** was obtained as (385 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.17 (s, 1H), 4.21 (t, *J* = 5.9 Hz, 2H), 3.81 (t, *J* = 6.3 Hz, 2H), 2.83 (s, 3H), 2.63 (s, 3H), 2.31 (dd, *J* = 12.0, 5.9 Hz, 2H), 1.73 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 161.5, 159.7, 156.4, 147.3, 143.7, 142.9, 134.5, 129.1, 126.4, 123.9, 115.4, 64.5, 41.4, 32.2, 15.1, 13.0, 11.8. MS (TOF-ESI): m/z: Calcd: 546.1621 $[M-Br]^-$, Found: 546.16003 $[M-Br]^-$, Δ= 3.79 ppm.

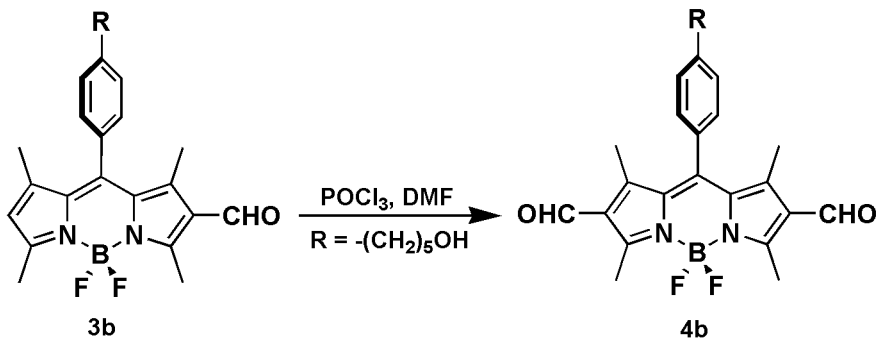


Figure 7. Synthesis of compound **4b**.

Synthesis of Compound 4b:

1 mL of DMF and 1 mL of $POCl_3$ was stirred in an ice bath for 5 min under argon. Then it was warmed to room temperature and waited for 30 minutes. To this mixture compound **3b** (200 mg, 0.440 mmol) was added in dichloroethane (60 mL). The temperature was raised to 50^0C and stirred for 2 hours. The reaction was then cooled to room temperature and poured to an ice cold $NaHCO_3$ solution (150 mL). This mixture was extracted with DCM (3x100 mL) and dried over Na_2SO_4. Solvent was evaporated in *vacuo* and purified by silica gel column chromatography using DCM:MeOH (98:2) as the eluent. Product **4b** was obtained as (174.6 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 2H), 7.23 – 7.19 (m, 2H), 7.14 – 7.10 (m, 2H), 4.24 (t, *J* = 5.9 Hz, 2H), 3.82 (t, *J* = 6.2 Hz, 2H), 2.90 (s, 6H), 2.33 (dd, *J* = 12.1, 6.1 Hz, 2H), 1.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 160.6, 160.2, 148.3, 147.5, 132.3, 128.9, 128.1, 125.7, 115.8, 64.6, 41.3, 32.2, 13.7, 12.3.

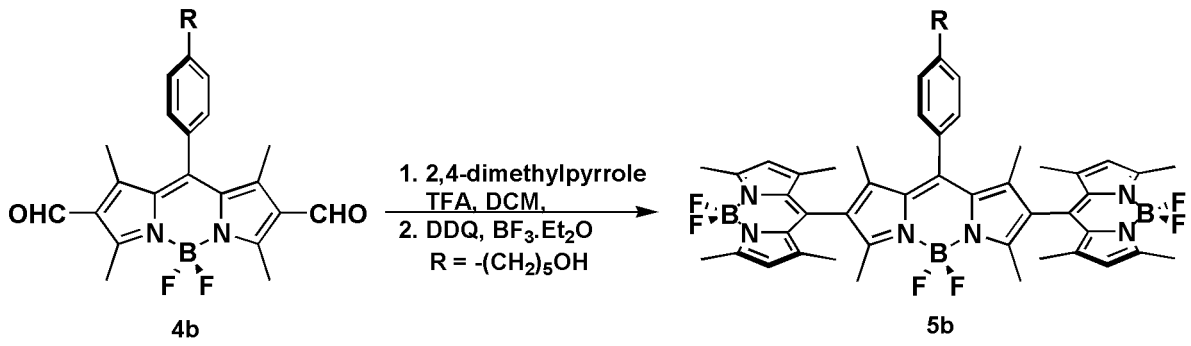


Figure 8. Synthesis of compound **5b**.

Synthesis of Compound 5b:

To a 500 mL round-bottomed flask containing 250 mL argon-degassed dichloromethane, 2,4-dimethylpyrrole (2.10 mL, 20.5 mmol), compound **4b** (200 mg, 0.415 mmol) were added. Then, trifluoroacetic acid (500 μL) was added to the reaction mixture and left to stirr overnight. Then, p-chloranil (2.72 g, 11 mmol) was added and mixed for 1 additional hour. After that, TEA (5 mL) was added and mixed for 1 additional hour and $BF_3.OEt_2$ (5 mL) was added and the reaction mixture was left to stir at room temperature for 1h. When the starting material was consumed, water (100 mL) was added and the reaction mixture was extracted with DCM (3x100 mL), evaporated and dried over Na_2SO_4. The product **5b** was purified by silica gel column chromatography using DCM:Hexane (1:1) as the eluent (218 g, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.03 (s, 4H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.56 (s, 12H), 2.47 (s, 6H), 1.84 (d, *J* = 6.8 Hz, 2H), 1.78 (s, 12H), 1.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 156.0, 153.7, 143.8, 142.3, 140.7, 132.9, 132.2, 131.7, 128.9, 126.9, 125.8, 121.4, 115.6, 32.4, 31.6, 29.0, 26.6, 25.4, 14.7, 14.3, 13.0, 12.7. ESI-HRMS ($M-H^+$) calculated 929.48358, found 929.4435, Δ= 43.06 ppm.

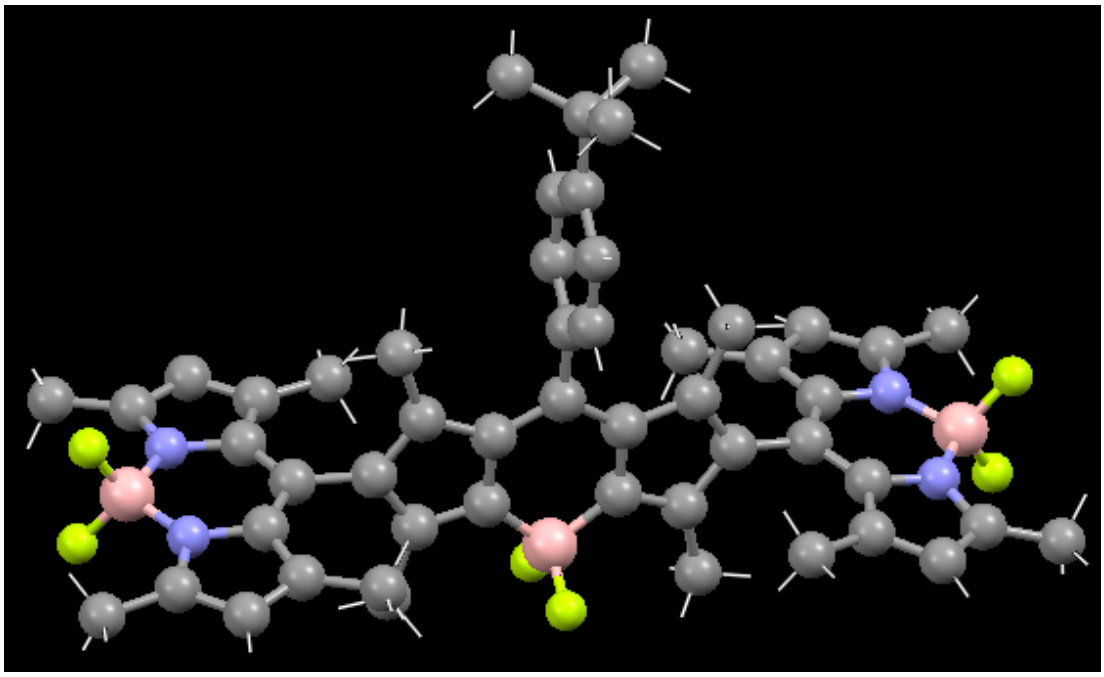


Figure 9. ORTEP drawing of compound **5a**.

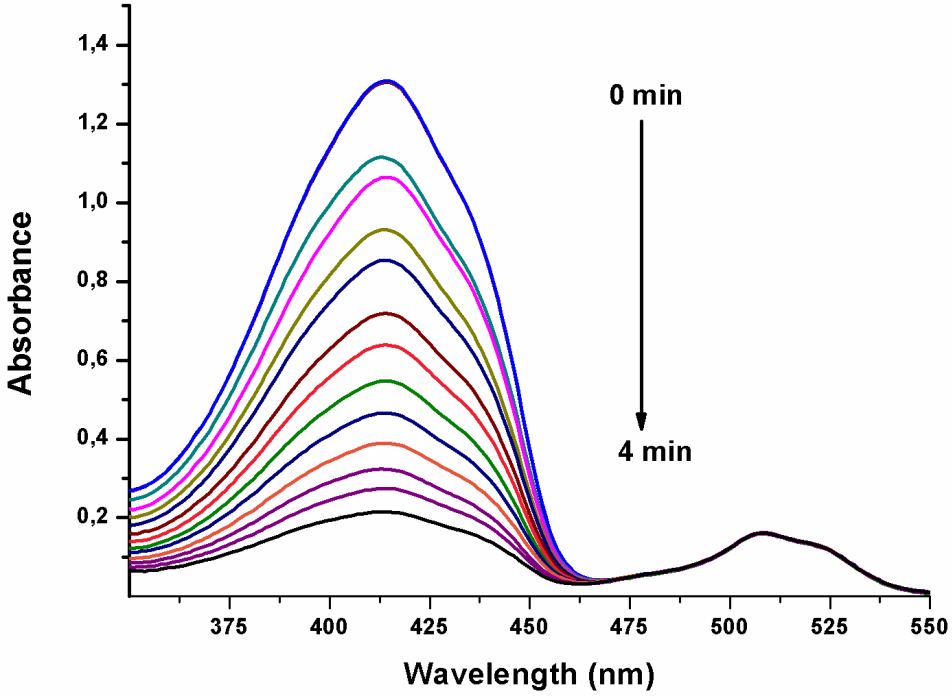


Figure 10. Singlet oxygen generation experiment in DCM solution. Decrease in Absorbance spectrum of trap molecule (DPBF) in the presence of 5.0 μM compound **5b**.

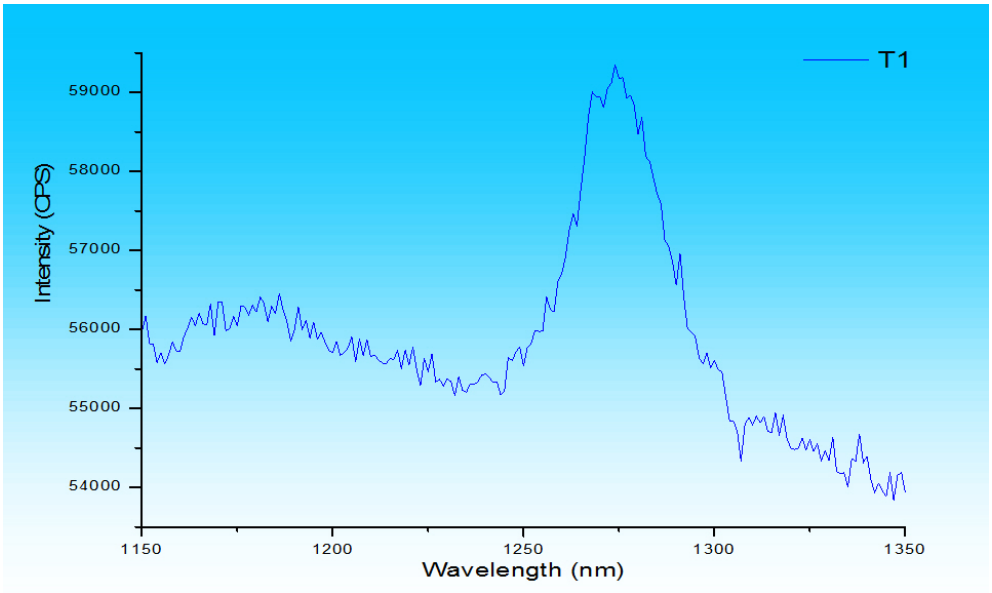


Figure 11. Singlet oxygen phosphorescence with sensitization from compound **5a**.

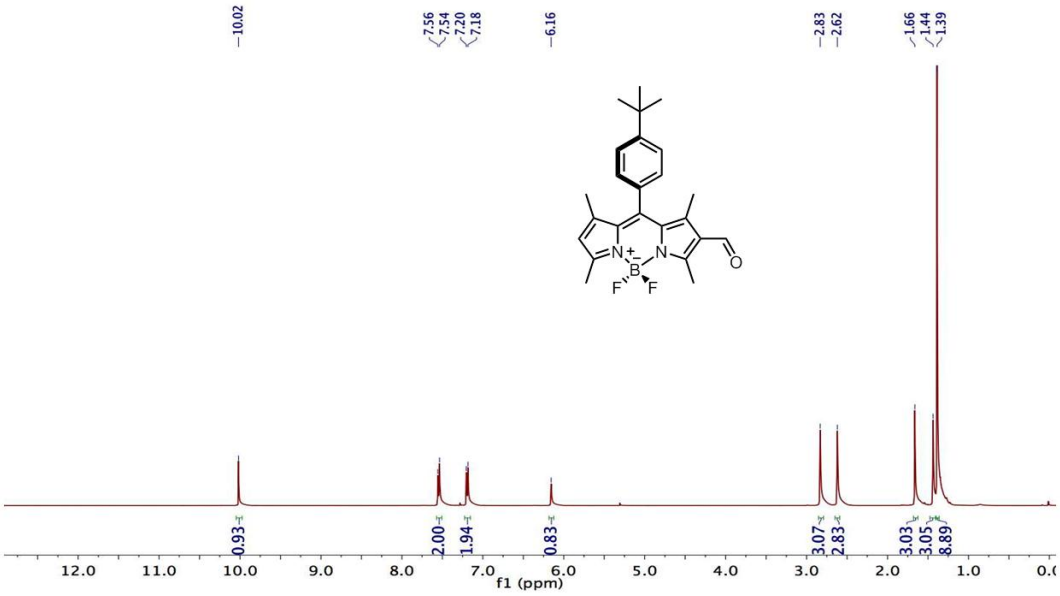


Figure 12. ^{1}H-NMR of compound **3a**.

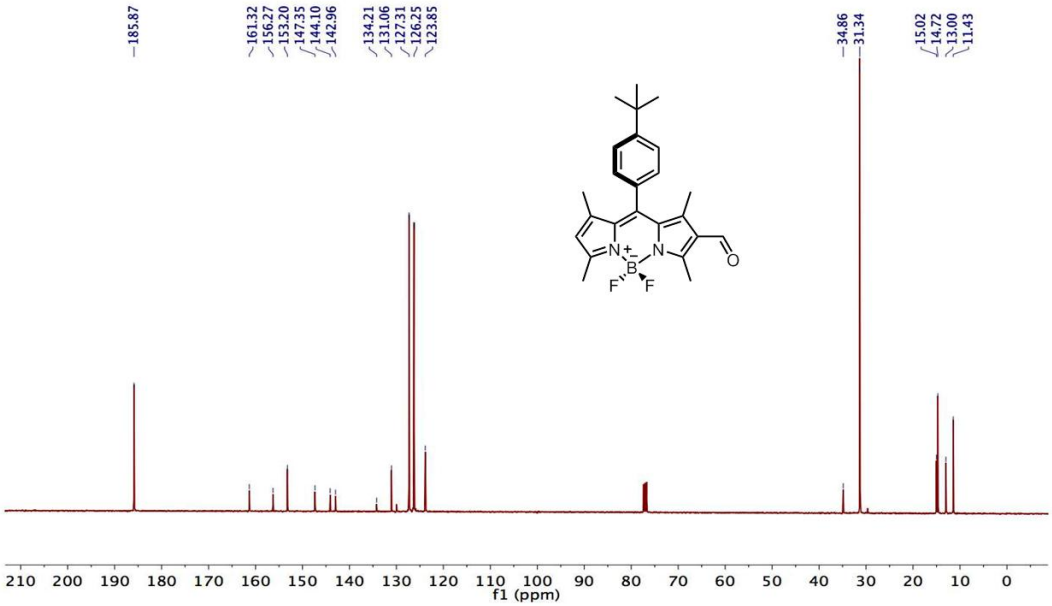


Figure 13. ^{13}C-NMR of compound **3a**.

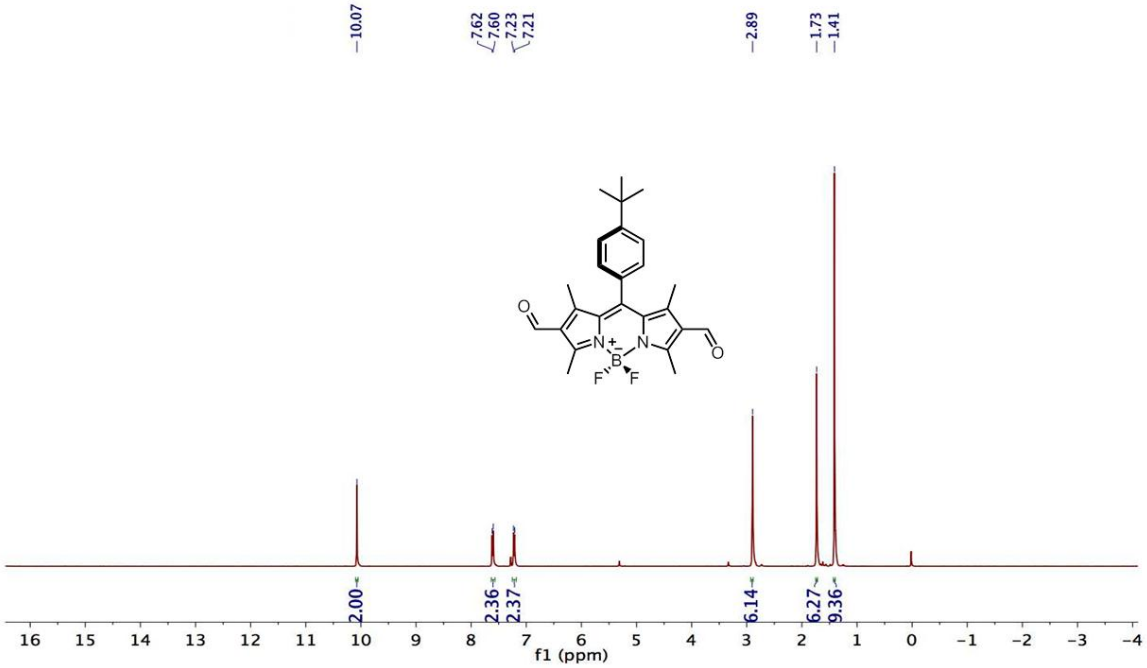


Figure 14. ^{1}H-NMR of compound **4a**.

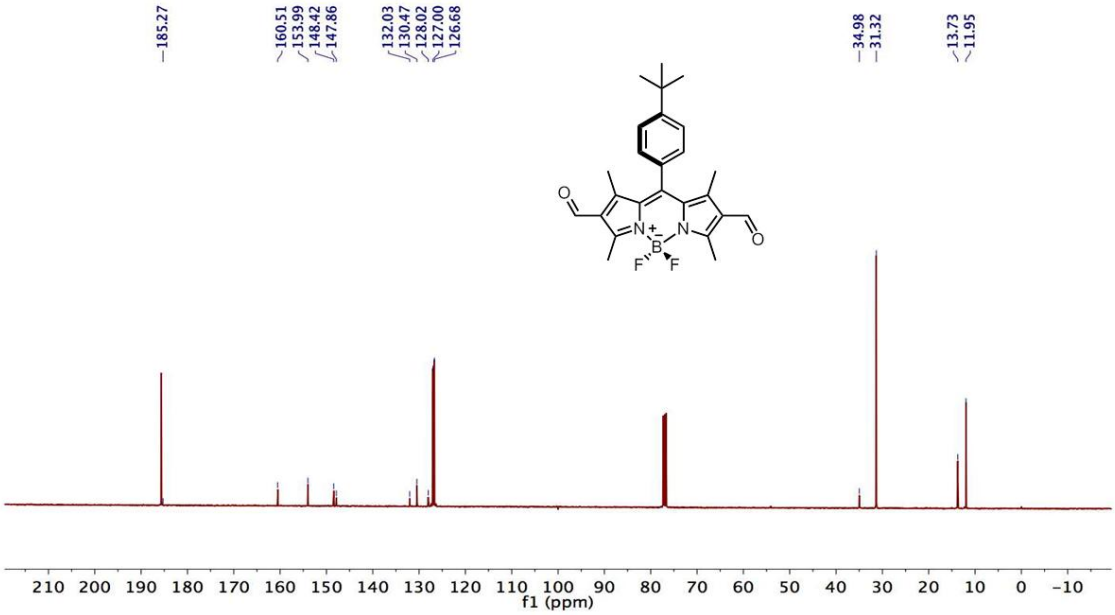


Figure **15**. ^{13}C-NMR of compound **4a**.

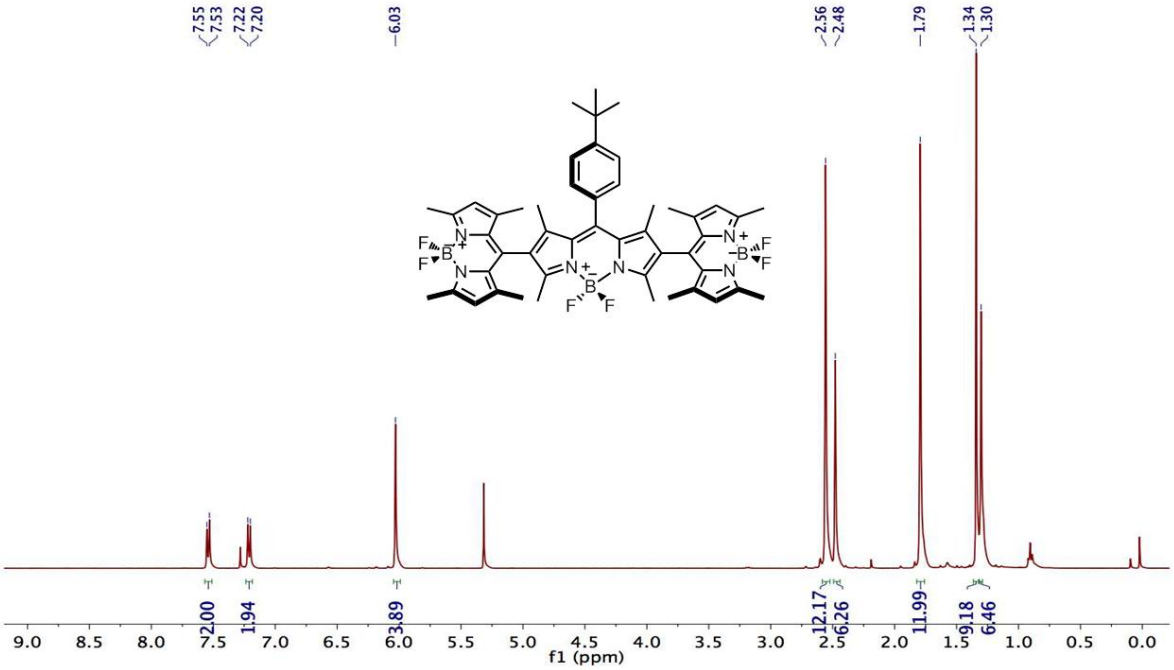


Figure 16. ^{1}H-NMR of compound **5a**.

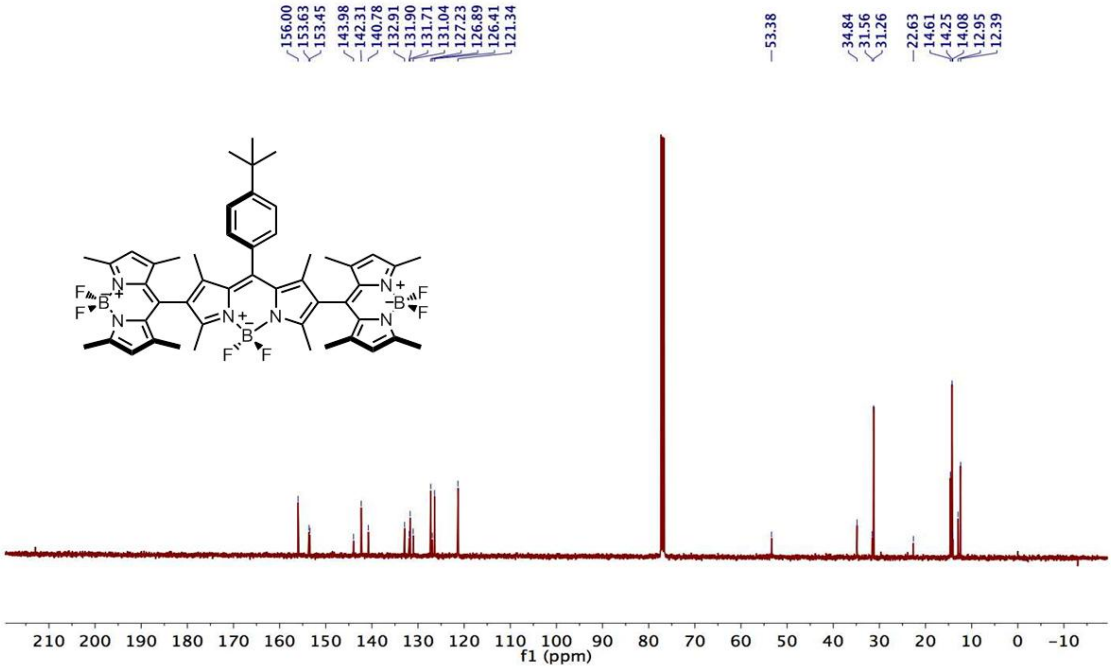


Figure 17. ^{13}C-NMR of compound **5a**.

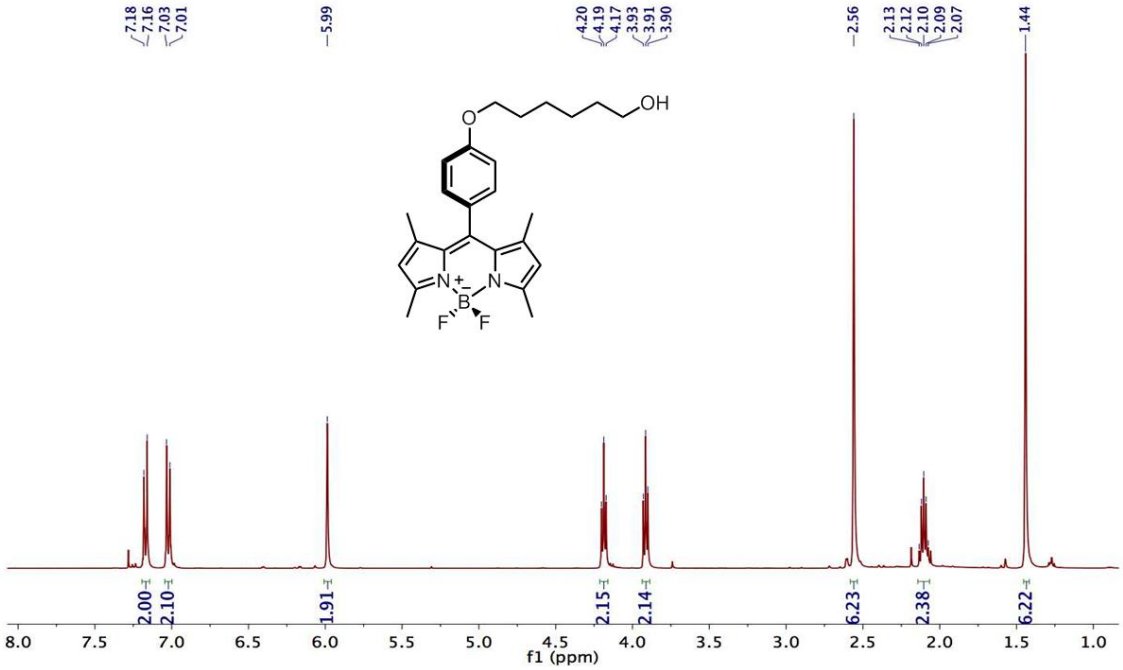


Figure 18. ^{1}H-NMR of compound **2b**.

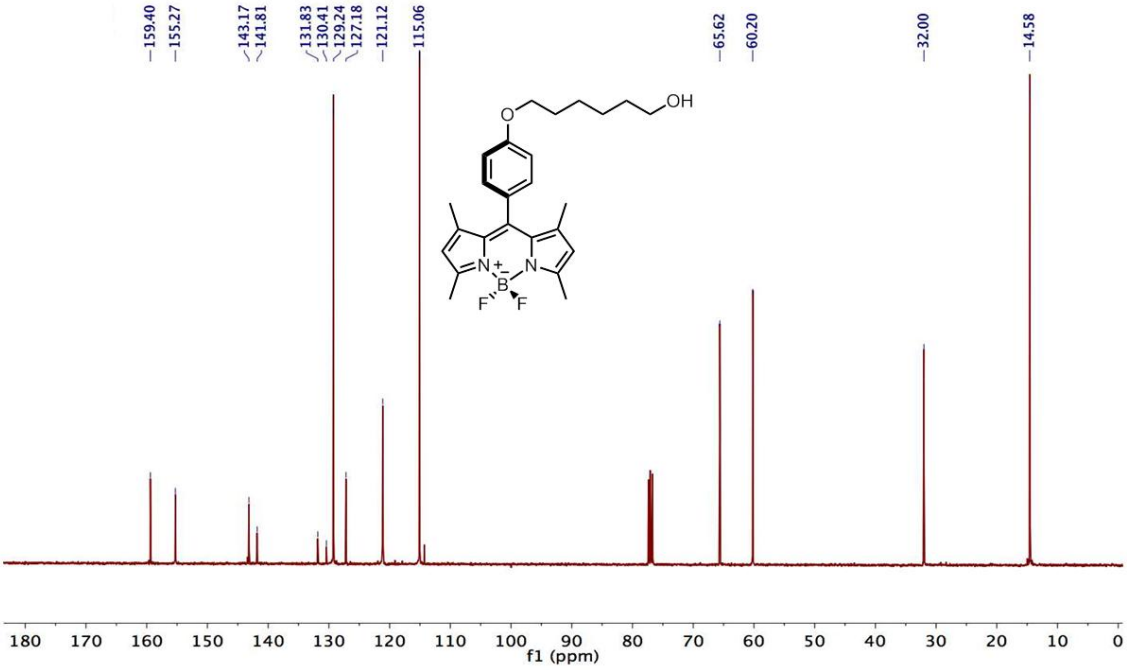


Figure 19. ^{13}C-NMR of compound **2b**.

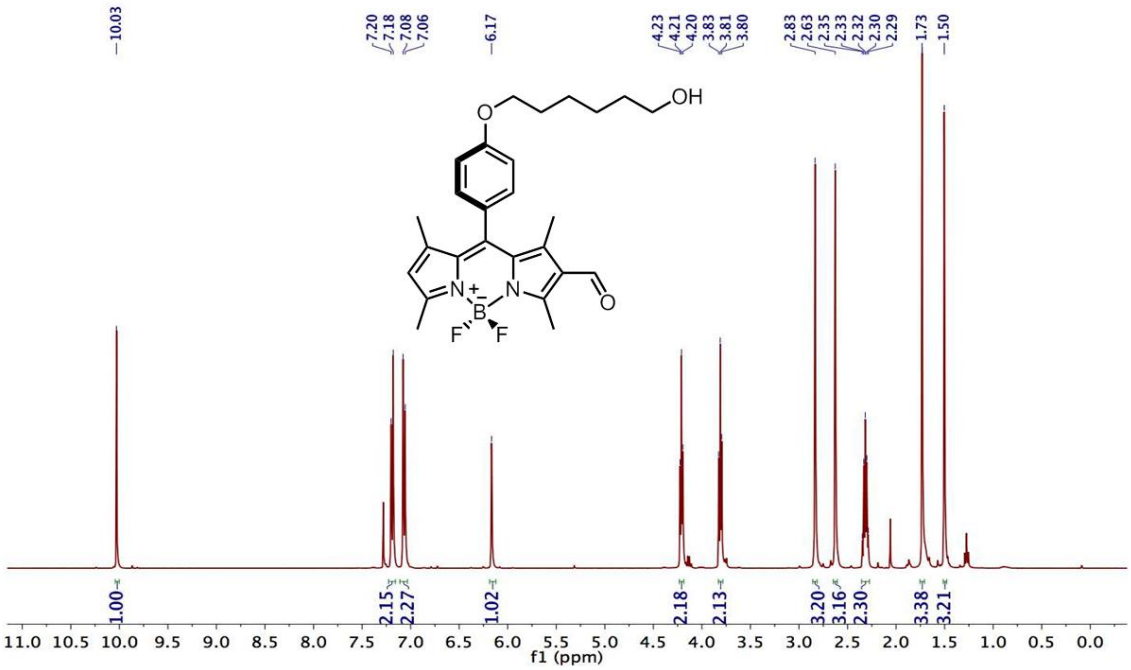


Figure 20. ^{1}H-NMR of compound **3b**.

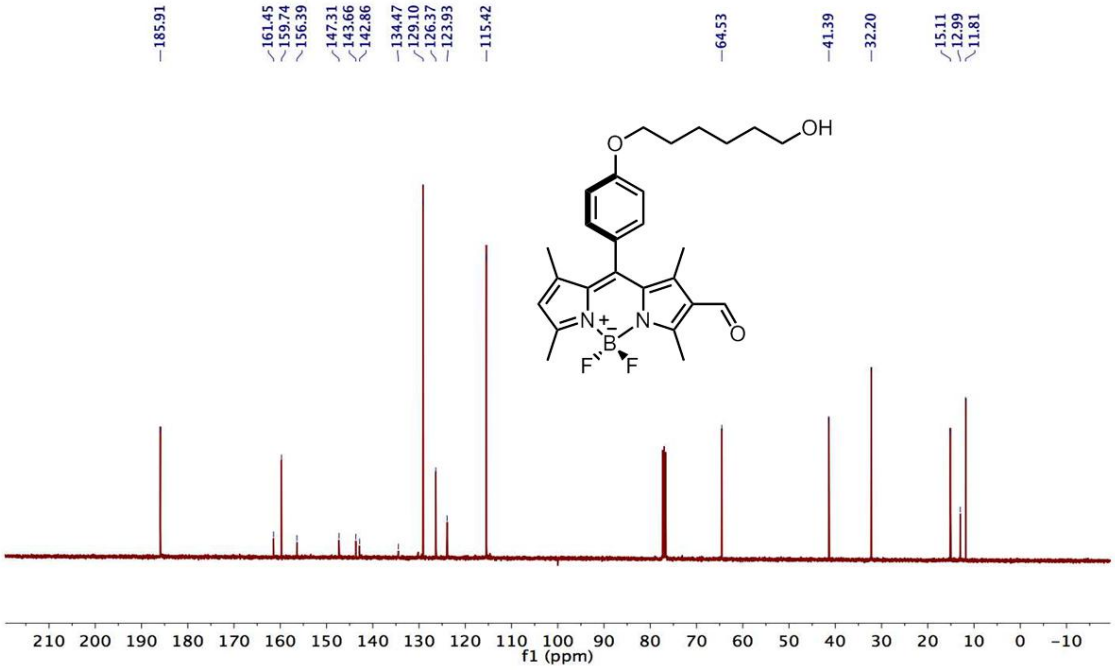


Figure 21. ^{13}C-NMR of compound **3b**.

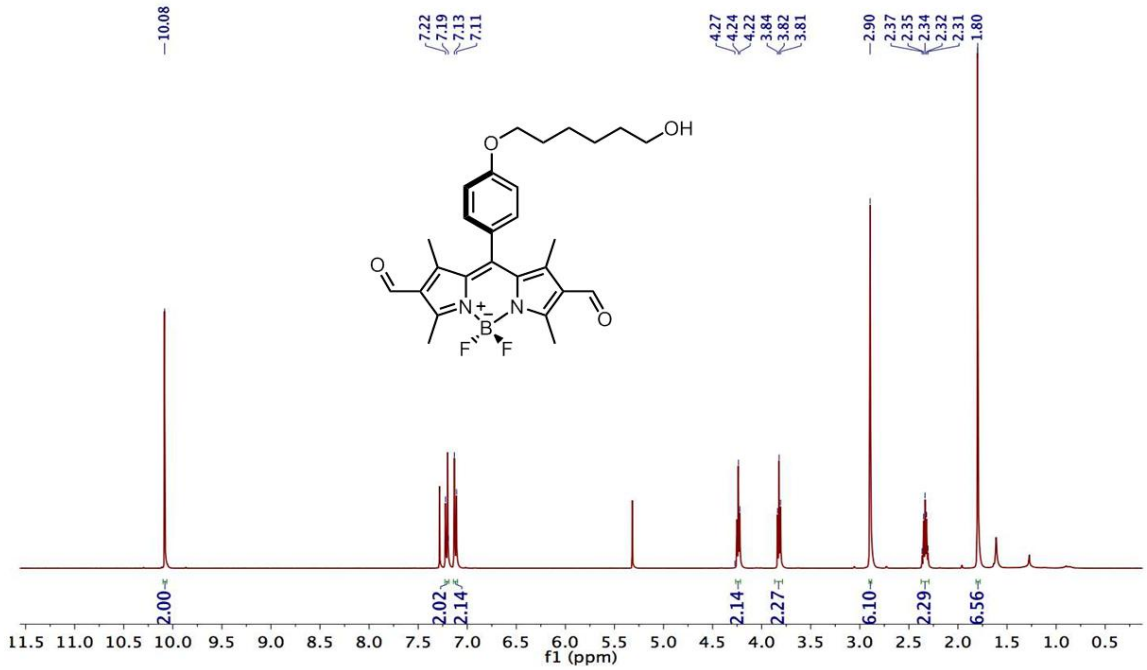


Figure 22. ^{1}H-NMR of compound **4b**.

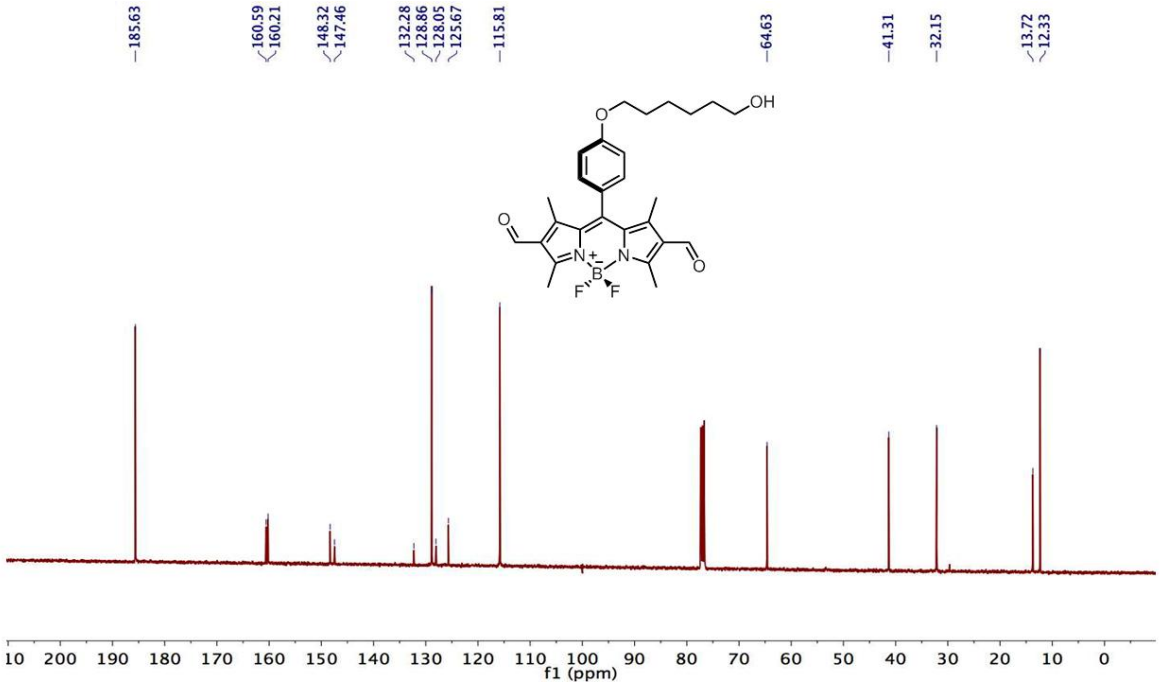


Figure 23. ^{13}C-NMR of compound **4b**.

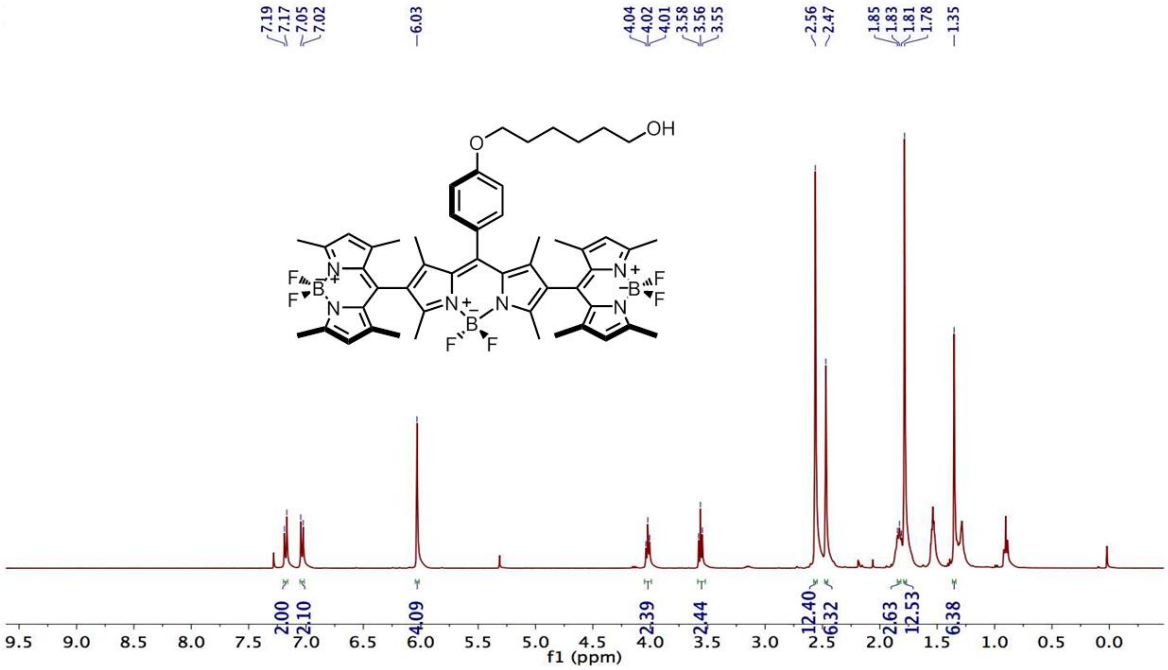


Figure 24. ^{1}H-NMR of compound **5b**.

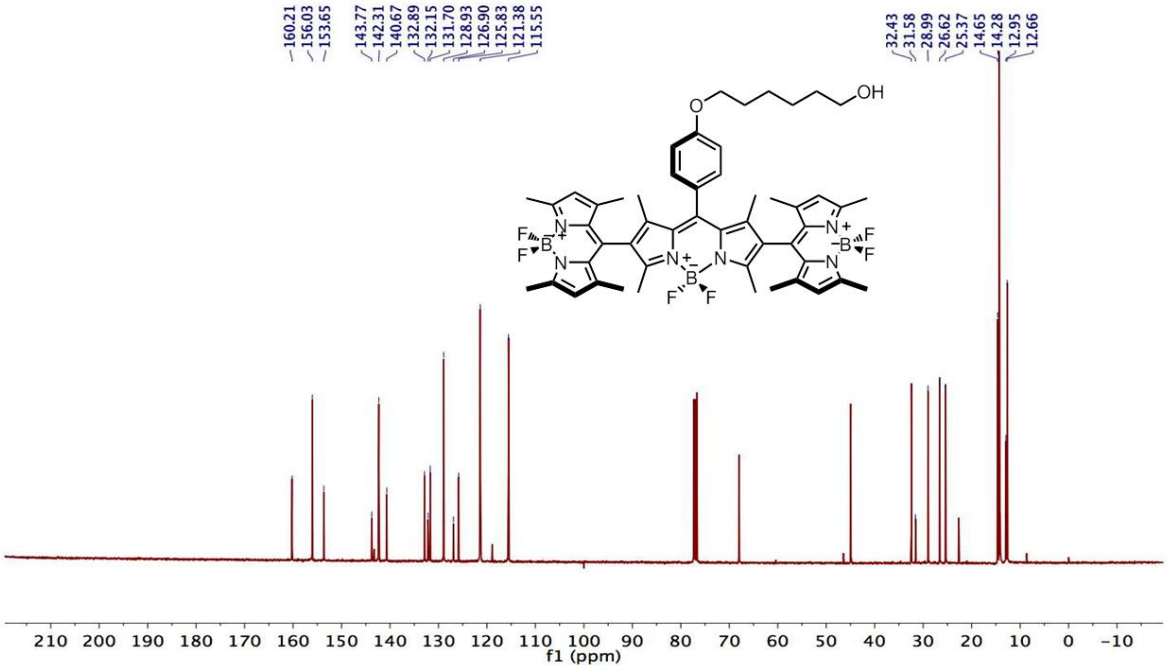


Figure 25. ^{13}C-NMR of compound **5b**.

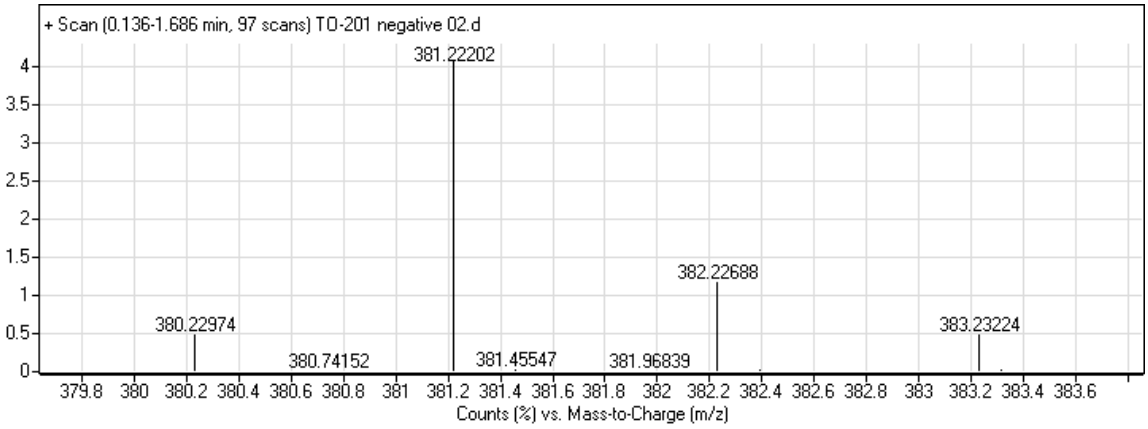


Figure 26. Mass spectrum of compound **2a**.

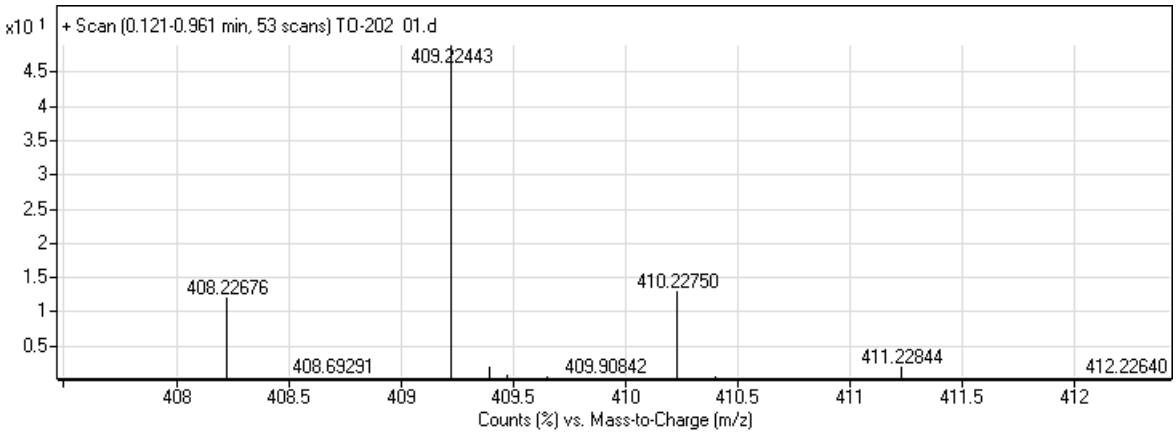


Figure 27. Mass spectrum of compound **3a**.

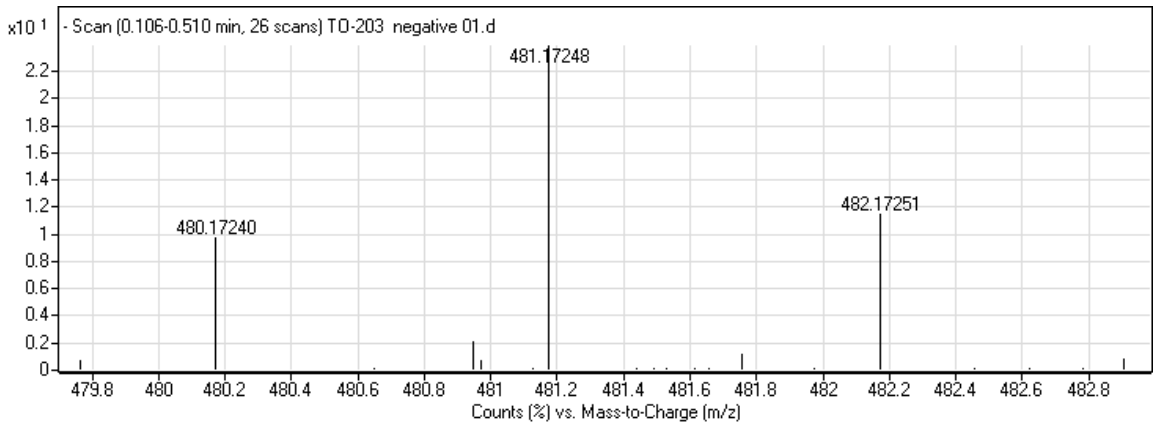


Figure28. Mass spectrum of compound **4a**.

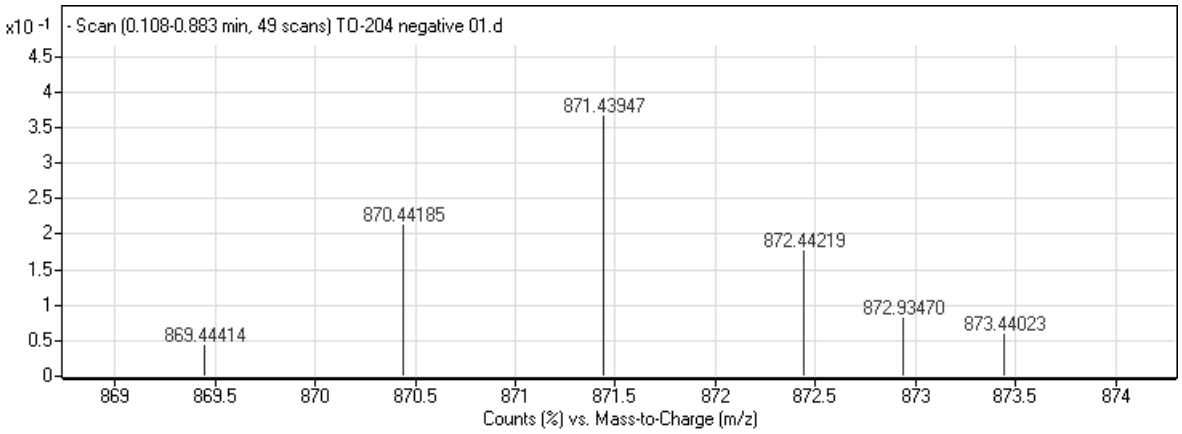


Figure 29. Mass spectrum of compound **5a**.

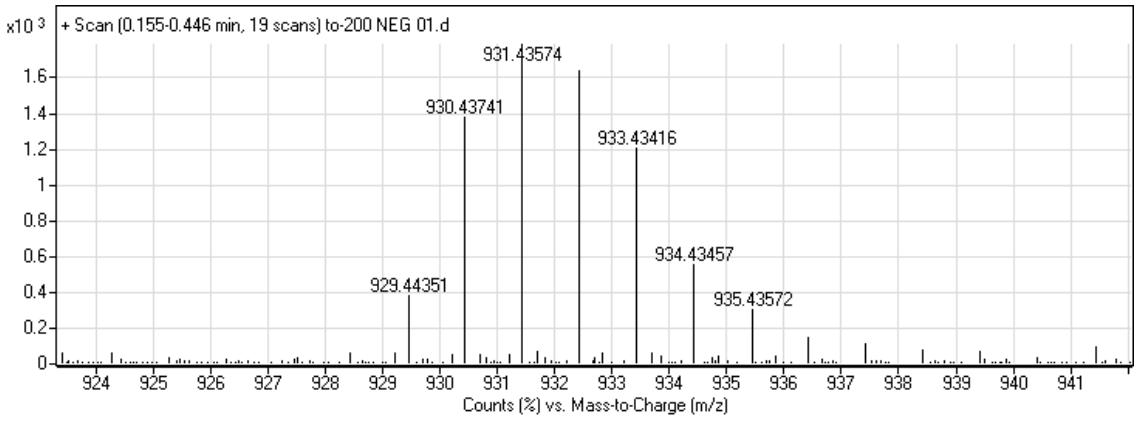


Figure 30. Mass spectrum of compound **5b**.

X-ray Diffraction Structure Analysis:

The C_{49} H_{53} B_3 F_6 N_6 crystallizes in the orthorhombic structure, space group P b n m with a = 8.6510(2) Å, b = 18.3861(5) Å, c = 29.434(5) Å, V = 4681.7(8) $Å^3$, and Z = 4.

Single crsyatal data were collected with RIGAKU R-Axis Rapid II DW with Dual Wavelenght Micro Max 007DW XG and VariMax DW optics Single Crystal X-Ray Diffractometer System with Curved Imaging Plate Detector. Program used to data collection, cell refinement and data reduction: CrystalClear-SM Expert 2.0 r16 (Rigaku, 2014). The crystal structure of the title compound was solved by direct methods and refined by the full-matrix least-squares refinement on F^2 using the programs SHELXS-2014/7[3] and SHELXL-2014/7[4] (Sheldrick, 2014), respectively, in the WinGX package[5]. All non-hydrogen atoms were successfully refined using anisotropic displacement parameters. Hydrogen atoms bound to methyl and phenyl carbons were placed at their idealised positions with bond lengths and isotropic thermal displacement parameters for aromatic groups are C–H = 0.93 Å and U_{iso} (H) = 1.2U_{eq} (C), for methyl groups are C–H = 0.96 Å and U_{iso} (H) = 1.5U_{eq} (C). Hydrogen atoms on the C12 and C27 atoms taken from a difference Fourier map and fixed all parameters.

Information concerning crystallographic data collection and structure refinement details is summarised in Table S1. Tables S2 and S3 summarise the most relevant geometrical parameters of molecule. Table S4 lists the most structurally relevant molecular contacts present in the crystal structure of the title crystal. Structural drawings have been created using the ORTEP III[6] and MERCURY[7] in WinGX software package.

Table S1. Crystal data and experimental details of the title compound. **5a**.

Structural formula	C_{49} H_{53} B_3 F_6 N_6
Formula weight	872.43
Crystal system	orthorhombic
Space group	Pbnm
Crystal shape /color	platelet /orange
Lattice parameters	
a (Å)	8.6510(2)
b (Å)	18.3861(5)
c (Å)	29.434(5)
Volume (Å^3)	4681.7(8)
Z	4
D_{calc} (Mg/m^3)	1.238
Absorbtion coefficient (mm^{-1})	0.089
F(000)	1832
h, k, l ranges	-11→ 11, -23 → 23, -38 → 38
Reflections collected/unique	107891 /5443 [R_{int} = 0.063]
Parameters	323
Goodness of fit on F^2	1.107
R [all]	0.085
wR [I>2σ(I)]	0.2036
Extinction coefficient	0.0053(11)
Largest difference peak and hole (e/Å^3)	0.219 and -0.261

Crystallographic data (including structure factors) for the crystal structure of C_{49} H_{53} B_3 F_6 N_6 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-**5a**.

Table S2: Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms of $C_{49}H_{53}B_3F_6N_6$ compound.

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	Y	z	U_{eq} (Å^2)
B1	-0.8942(4)	0.9914(2)	0.25	0.0618(9)
B2	-0.8394(3)	0.91473(13)	0.51525(7)	0.0525(5)
F1	-0.8571(3)	1.06524(11)	0.25	0.0906(7)
F2	-1.0519(2)	0.98385(14)	0.25	0.0935(7)
F3	-0.73685(15)	0.87937(8)	0.54404(4)	0.0771(4)
F4	-0.95786(14)	0.94361(8)	0.54131(4)	0.0726(4)
N1	-0.8231(2)	0.95484(9)	0.29204(5)	0.0581(5)
N2	-0.90440(19)	0.86124(9)	0.48007(5)	0.0562(4)
N3	-0.75605(17)	0.97496(9)	0.48864(5)	0.0495(4)
C1	-0.6997(2)	0.90534(11)	0.29151(6)	0.0543(5)
C2	-0.6385(3)	0.88171(15)	0.25	0.0507(6)
C3	-0.5072(3)	0.82885(15)	0.25	0.0495(6)
C4	-0.3549(3)	0.85093(16)	0.25	0.0572(7)
C5	-0.2352(3)	0.80015(16)	0.25	0.0578(7)
C6	-0.2643(3)	0.72624(15)	0.25	0.0512(6)
C7	-0.4182(3)	0.70489(16)	0.25	0.0604(7)
C8	-0.5373(3)	0.75421(16)	0.25	0.0600(7)
C9	-0.1376(3)	0.66735(16)	0.25	0.0587(7)
C10	-0.1550(3)	0.61933(14)	0.29203(9)	0.0839(8)
C11	0.0252(3)	0.6995(2)	0.25	0.0760(9)
C12	-0.6675(2)	0.88600(11)	0.33760(6)	0.0558(5)
C13	-0.5476(3)	0.83462(13)	0.35561(7)	0.0733(7)
C14	-0.7713(2)	0.92452(11)	0.36419(6)	0.0552(5)
C15	-0.8655(2)	0.96659(12)	0.33545(6)	0.0599(5)

C16	-0.9921(3)	1.01678(15)	0.34883(7)	0.0836(8)
C17	-0.7924(2)	0.92156(11)	0.41440(6)	0.0517(5)
C18	-0.8823(2)	0.86549(11)	0.43302(6)	0.0551(5)
C19	-0.9689(3)	0.80912(13)	0.41255(8)	0.0732(6)
C20	-0.9901(4)	0.79149(18)	0.36363(10)	0.1119(11)
C21	-1.0398(4)	0.77157(14)	0.44719(10)	0.0836(8)
C22	-0.9998(3)	0.80354(13)	0.48852(9)	0.0725(6)
C23	-1.0464(4)	0.78224(17)	0.53510(10)	0.0979(9)
C24	-0.7303(2)	0.97564(11)	0.44163(6)	0.0501(5)
C25	-0.6472(2)	1.04125(12)	0.43120(7)	0.0623(5)
C26	-0.5887(3)	1.06700(16)	0.38619(9)	0.0906(8)
C27	-0.6290(3)	1.07727(14)	0.47162(9)	0.0690(6)
C28	-0.6962(2)	1.03635(11)	0.50627(7)	0.0583(5)
C29	-0.7072(3)	1.05534(15)	0.55524(8)	0.0802(7)

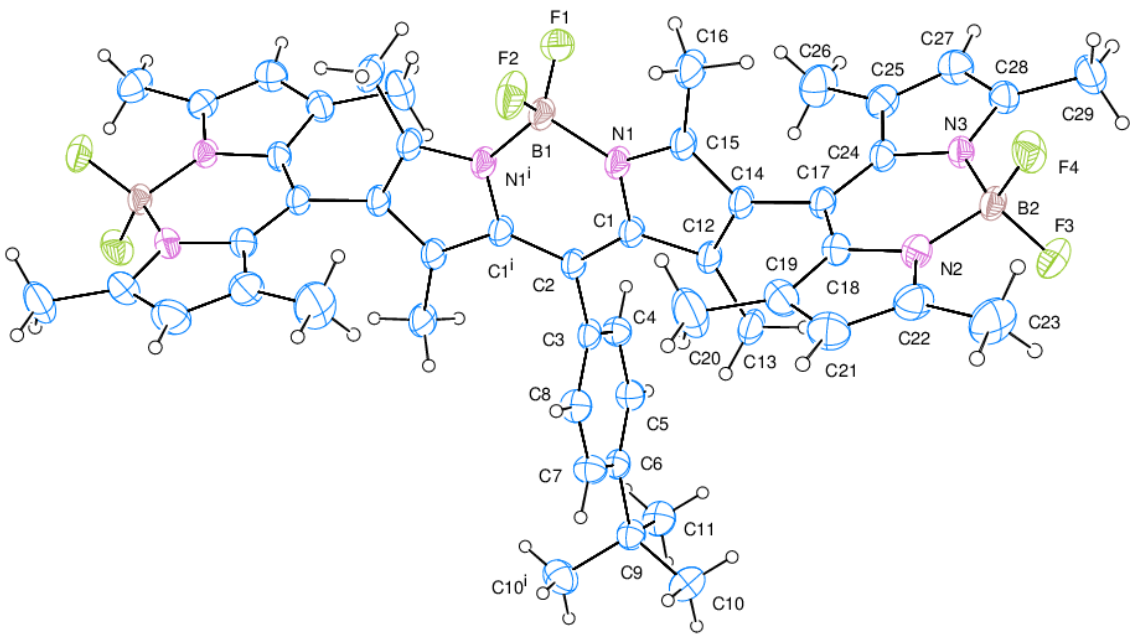


Figure 31. The molecular figure of the title compound with the atomic numbering scheme. (Symmetry code i: x, y, 1/2-z)

Table S3. Selected bond lengths (Å) and bond angles (°).

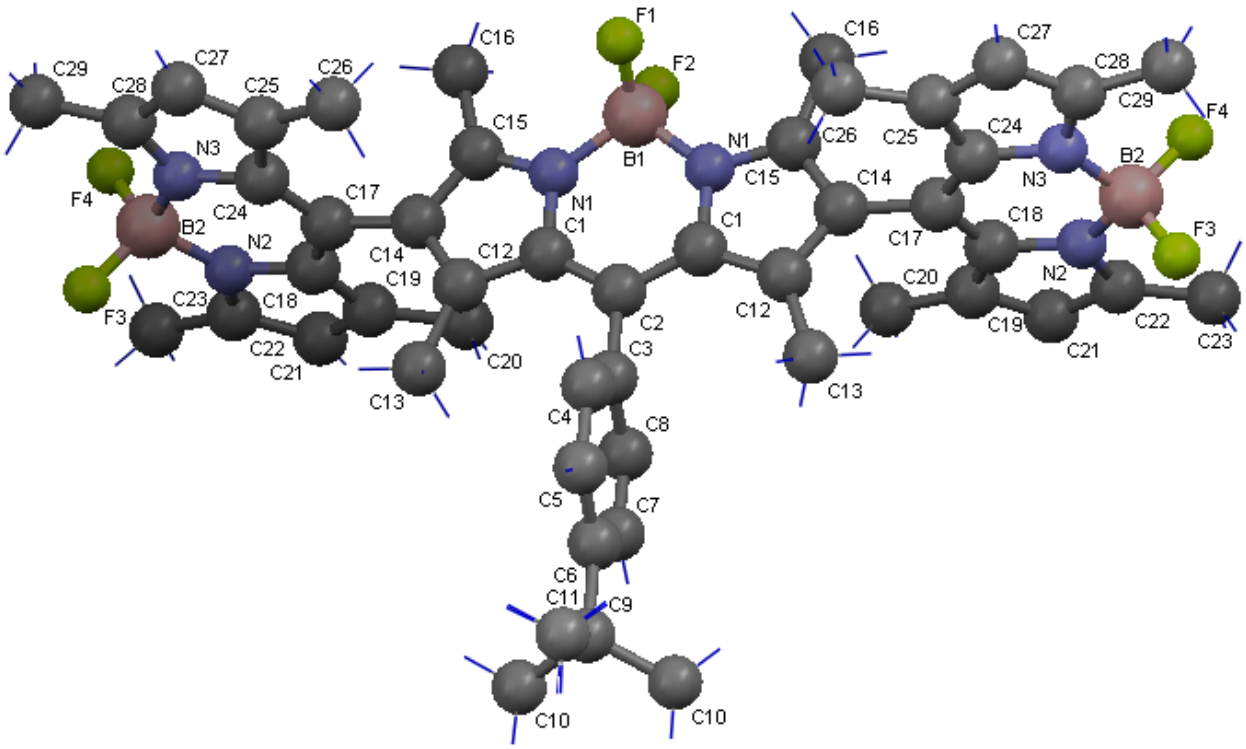
B1 –	F1	1.395(4)	B2 –	F4 – F3	108.29(16)
B1 –	F2	1.371(4)	B2 –	F4 – N2	110.35(17)
B2 –	F3	1.388(2)	B2 –	F3 – N2	110.24(17)
B2 –	F4	1.386(2)	B2 –	F4 – N3	110.68(17)
B1 –	N1	1.537(2)	B2 –	F3 – N3	110.44(16)
B2 –	N2	1.535(3)	B2 –	N2 –N3	106.85(15)
B2 –	N3	1.536(3)	B1 –	F2 – F1	109.1(3)
N1 –	C1	1.402(2)	B1 –	F2 – N1^{i}	110.7(2)
N1 –	C15	1.347(2)	B1 –	F1 – N1	109.5(2)
N2 –	C18	1.400(2)	B1 –	N1 – N1^{i}	107.2(2)
N2 –	C22	1.367(3)	N2 –	C22 – B2	126.57(17)
N3 –	C24	1.401(2)	N2 –	C18 – B2	125.55(16)
N3 –	C28	1.346(3)	N1 –	C15 – B1	125.77(18)
			N1 –	C1 – B1	125.43(16)
			N3 –	C28 – B2	126.06(17)
			N3 –	C24 – B2	125.75(16)

Symmetry code i: 1, y, 1/2-z

Table S4. Structural parameters of hydrogen bonds between donor (D), acceptor (A) and hydrogen (H).

Compound	D – H ··· A	D–H (Å)	A···H (Å)	D···A (Å)	D–H···H (°)
1	C7 – H7···F1^{a}	0.93	2.41	3.221(4)	146
2	C16 – H16B···F4^{b}	0.96	2.40	3.343(2)	166
3	C21 – H21···F3^{c}	0.98(3)	2.35(3)	3.267(3)	154(3)
4	C23 – H23C···F4	0.96	2.54	3.070(4)	115

Symmetry codes [a: 1/2-x,-1/2+y,1/2-z ; b : 1-x,1-y,-z ; c : 1/2+x,1/2-y,-z]


F1
F2
B1
N1
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
C21
C22
C23
C24
C25
C26
C27
C28
C29
N2
N3
B2
F3
F4

Plane-A: B1, C2, C3, C4, C5, C6, C7, C8, C9

Plane-B: B1, N1, C1, C2, C12, C13, C14, C15, C16, $C1^{i}$, $C2^{i}$, $C12^{i}$, $C13^{i}$, $C14^{i}$, $C15^{i}$, $C16^{i}$

Plane-C: B2, N2, N3, C17, C18, C19, C20, C21, C22, C23, C24, C25, C26, C27, C28, C29

Plane-D: $B2^{i}$, $N2^{i}$, $N3^{i}$, $C17^{i}$, $C18^{i}$, $C19^{i}$, $C20^{i}$, $C21^{i}$, $C22^{i}$, $C23^{i}$, $C24^{i}$, $C25^{i}$, $C26^{i}$, $C27^{i}$, $C28^{i}$, $C29^{i}$

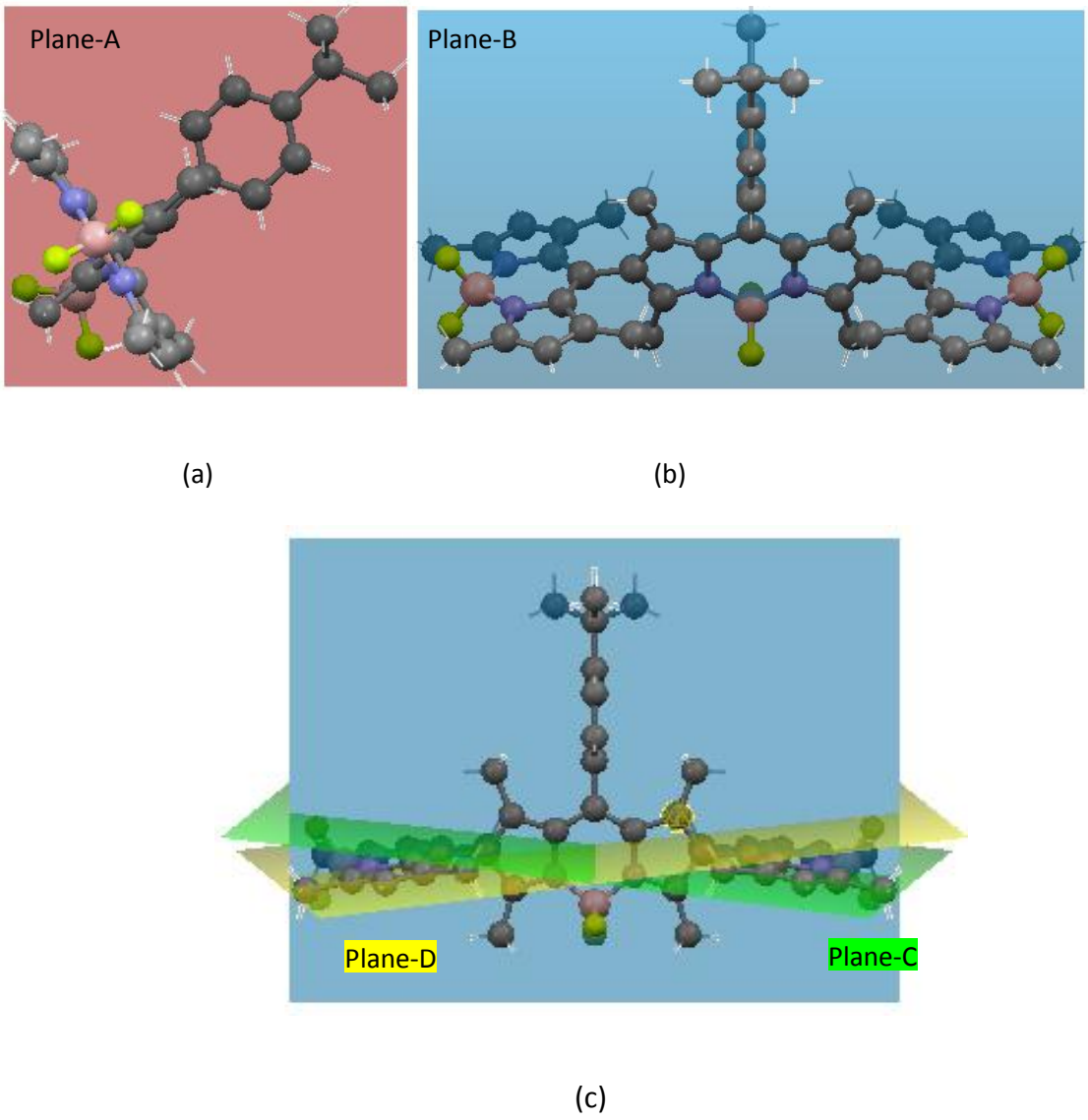
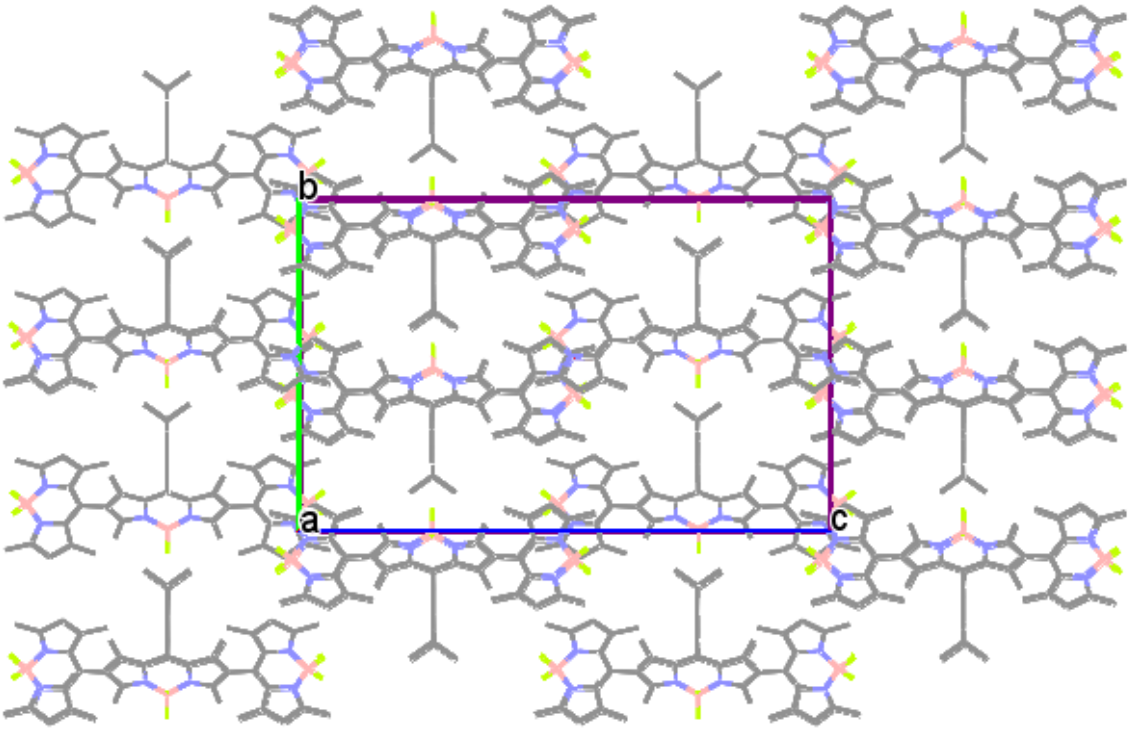


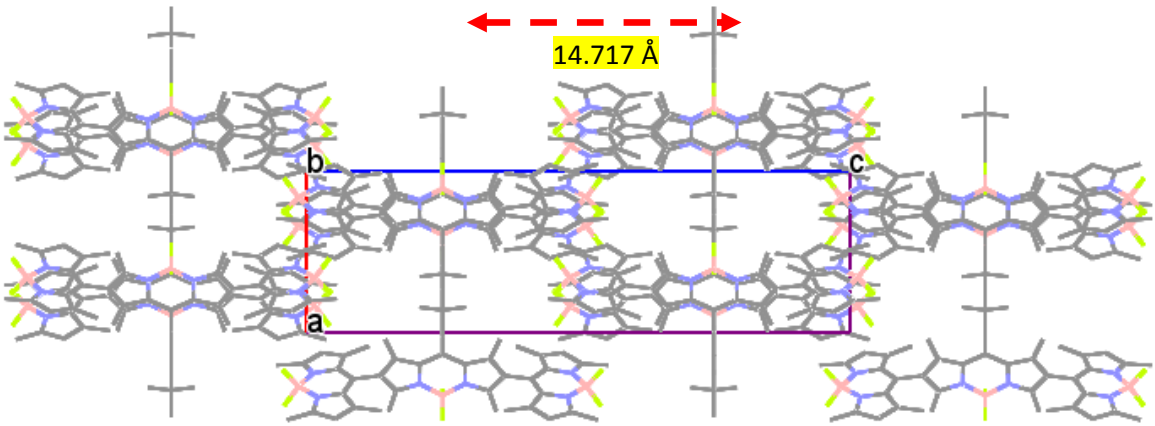
Figure 32. Molecule diagram of the title compound **5a** view along the (a) plane-A and (b) plane-B, (c) plane C and D.

Table S5. Dihedral angle between the planes

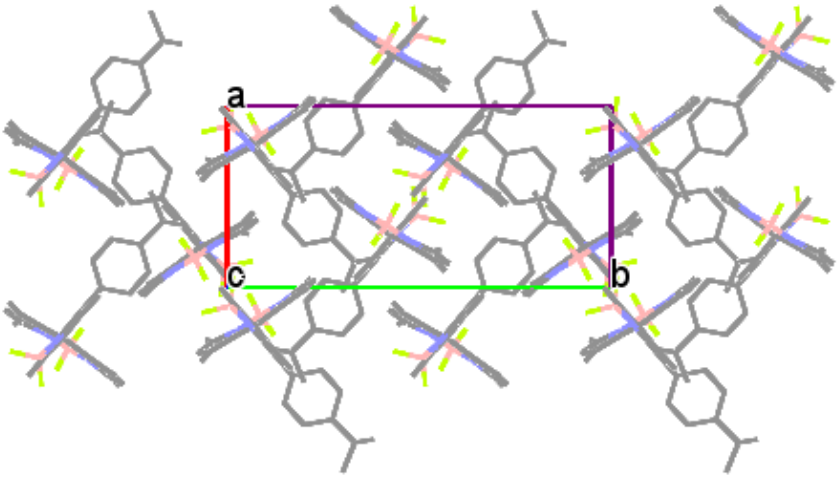
Plane 1	Plane 2	Angle (°)
A	B	90.00
A	C	84.11
A	D	84.11
B	C	81.86
B	D	81.86
C	D	11.79



View along a-axis



View along b-axis



View along c-axis

Figure 33. Molecular packing diagrams of compound **5a**.

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