Supporting Information

Synthesis and Studies of Covalently Linked (BODIPY)$_2$-3-Pyrrolyl BODIPY Triads

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MATERIALS AND METHODS

Materials:

The chemicals were obtained from reliable vendors like Merck and TCI. These suppliers supplied BF_3•OEt_2, 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ), terepthaldehyde, 4-formyl phenyl boronic acid, trifluoroacetic acid (TFA), NBS, MnO_2, $NaBH_4$, TEMPO, and so on. All other compounds used in the synthesis were of reagent grade quality unless specified differently. To ensure the purity and separation of chemicals throughout the purification process, column chromatography was carried out using silica gel (100-200 mesh) and basic alumina.

Methods:

- All the ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 and 500 MHz instruments. The frequencies for the ^{13}C nucleus are 100.06 and 125.77 MHz for 400 and 500 MHz instruments, respectively. Similarly, the frequencies for the ^{11}B and ^{19}F nucleus are 193 and 376 MHz for 400 MHz instruments.
- Absorption and steady-state fluorescence spectra were obtained with PerkinElmer Lambda-35 and electro paramagnetic resonance (EPR) analysis were carried out through Spinscan X.

- Single green block-shaped crystals of compounds **6**, **7**, **9**, and **14** were used as received. Single crystals of compounds **6**, **7**, **9**, and **14** were picked up with nylon loops and were mounted on Bruker Bruker APEX-II CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo-K_α, λ = 0.71073 Å). Crystals with dimensions of 0.3 × 0.2 × 0.2 mm³, 0.4 × 0.3 × 0.2 mm³, 0.4 × 0.2 × 0.2 mm³, and 0.3 × 0.2 × 0.2 mm³ were selected for compounds 6, 7, 9, and 14, respectively. The crystals were maintained at temperatures of 150.15 K (for **6**), 150 K, (for **7** and **9**), and 100.00 K (for **14**) during data collection. The structures were solved by direct methods and subsequent difference Fourier techniques. Low angle, poor intensity diffraction and twin nature of single crystal resulted slightly higher R_1 and wR_2 value than normal range for all the compound. The structures were solved using the Olex2 Solve 1.5 program (Bourhis et al., 2015) with dual-space methods, employing Olex2 1.5-dev (Dolomanov et al., 2009) as the graphical interface. The model was refined using olex2.refine 1.5-dev (Bourhis et al., 2015) with full matrix least squares minimization on F^2. All the crystal parameter of

compounds 6, 7, 9, and 14 are given in Table 1 in the main manuscript. All the relevant bond angle and bond distance parameters are given in Table S1-S8 in the supporting information file. [S1-S2]

- Studies on cyclic voltammetry (CV) were conducted using the BAS electrochemical system, employing a three-electrode configuration: platinum wire for the auxiliary electrode, saturated calomel for the reference electrode, and glassy carbon for the working electrode. As a supporting electrolyte, tetrabutylammonium perchlorate was used in the dry dichloromethane studies. Mass spectra were recorded with a Q-TOF micro mass spectrometer.
- Fluorescence quantum yields were determined in each case by comparing the corrected spectrum with that of Rhodamine 6G (Φ =0.95) in EtOH by taking the area under total emission using the procedure reported earlier.[S3- S4]
- The exponential decay curve of compounds was fitted appropriately with a mono/biexponential equation. The average lifetime (τ_{av}) was calculated following the equations depicted in the literature.[S5]
- DFT was used in a Gaussian 09W programme package to perform quantum chemistry calculations (gas phase/vacuum) for ground state energy minimized structures for triads **6** and **7**. The optimization process for the ground state structure elucidation utilizes 6-311G basis sets and a DFT-based Beck-3 Lee Young Parr (B3LYP) functional. The oscillator strengths were determined using the same basis and functional hybrid set, whereas the vertical excitation energies were determined with the use of TD-DFT methods. In the toluene media, all calculations were performed utilizing the Self-Consistent Reaction Field (SCRF) under the Polarisable Continuum Model (PCM). Based on the optimized structures, TD-DFT with PCM model was used to extensively analyze the oscillator strengths and electronic absorption spectra.[S6]

^{1}H NMR study

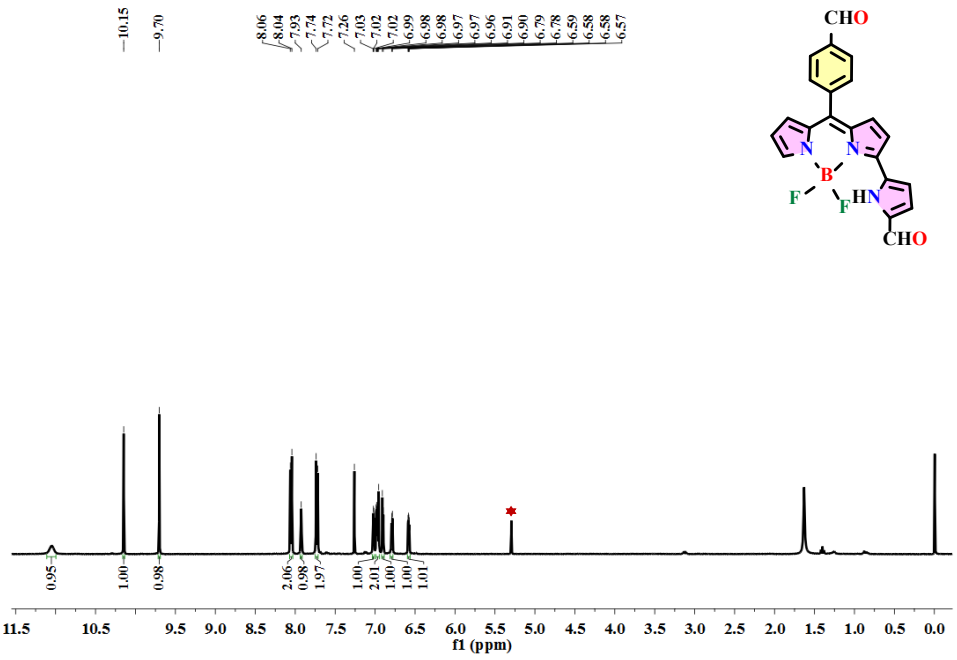

Fig. S1 ^{1}H NMR spectrum of compound **9** in $CDCl_3$ at room temperature.

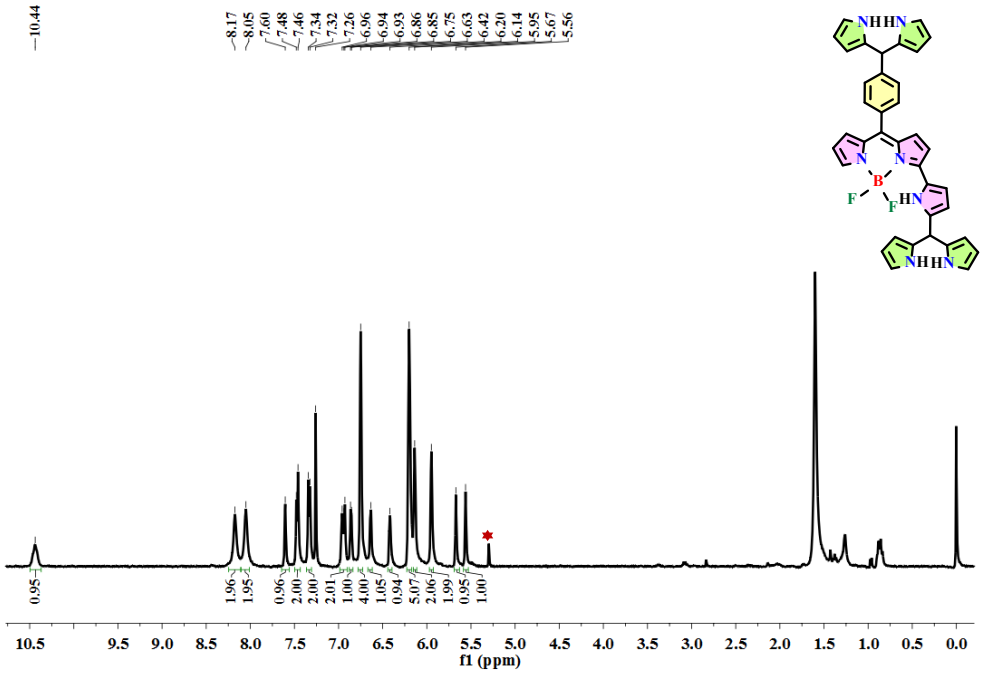

Fig. S2 ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at room temperature.

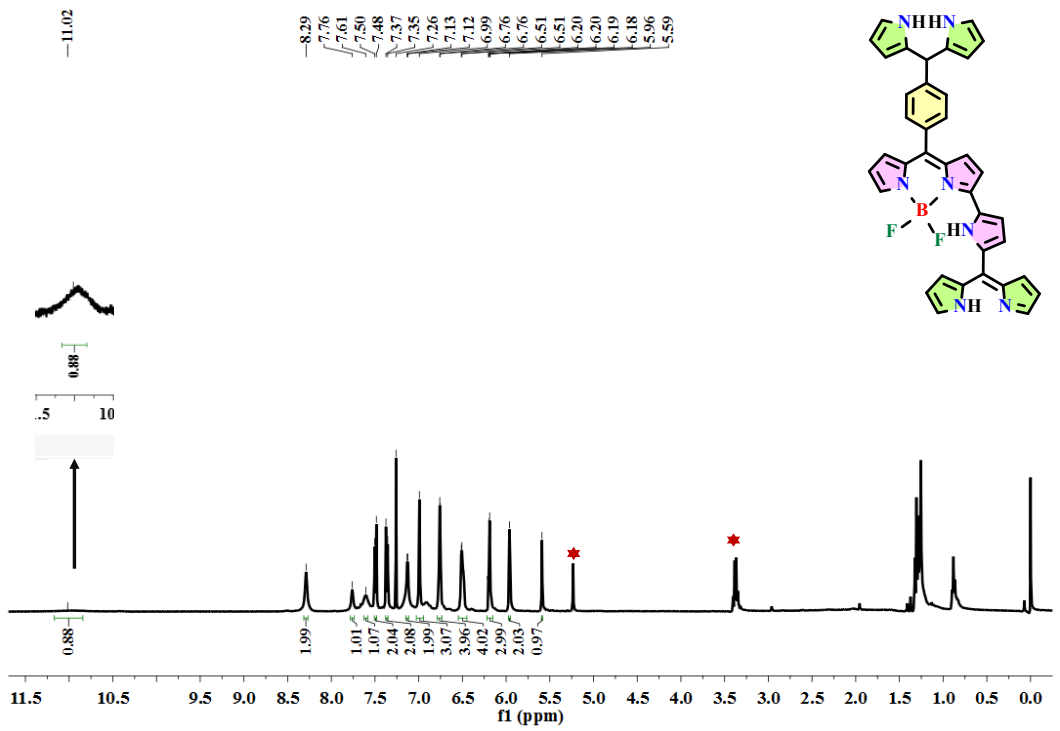

Fig. S3 ^{1}H NMR spectrum of compound **11** in $CDCl_3$ at room temperature.

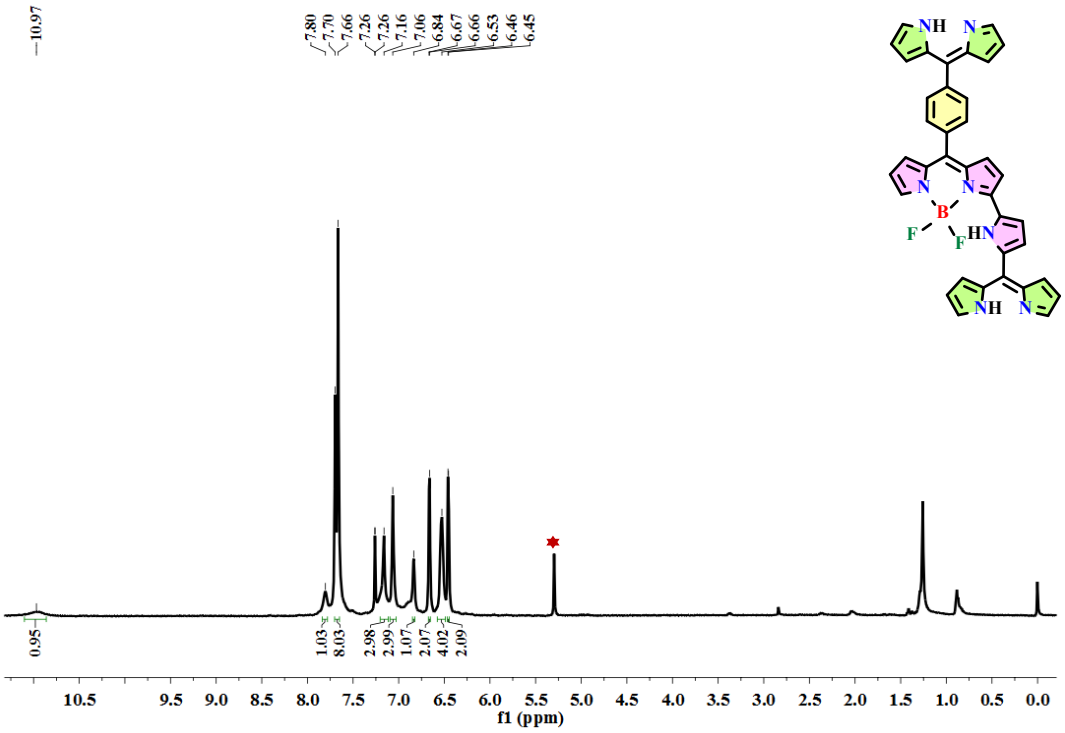

Fig. S4 ^{1}H NMR spectrum of compound **12** in $CDCl_3$ at room temperature.

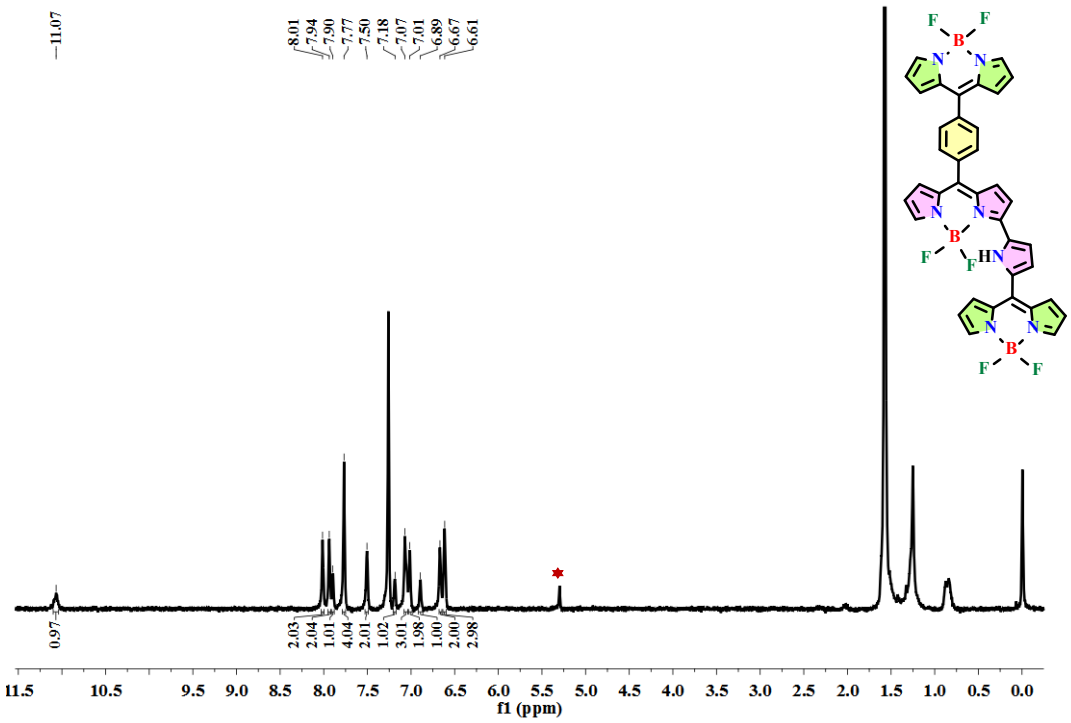

Fig. S5 ^{1}H NMR spectrum of compound **6** in $CDCl_3$ at room temperature.

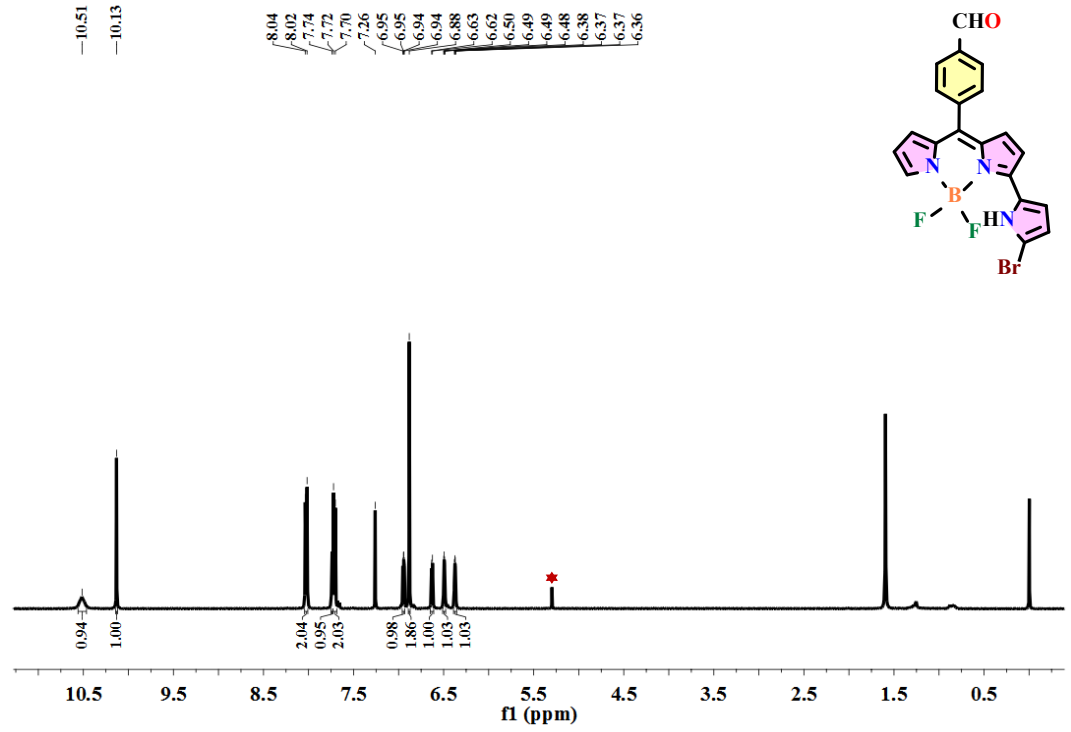

Fig. S6 ^{1}H NMR spectrum of compound **13** in $CDCl_3$ at room temperature.

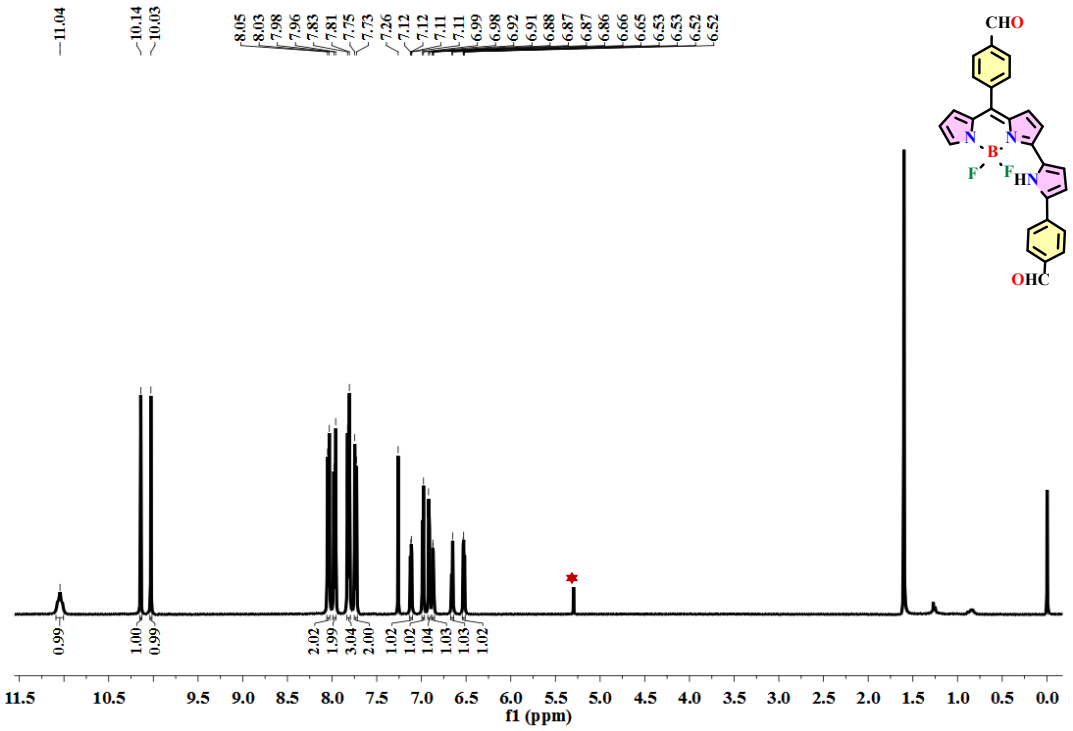

Fig. S7 ^{1}H NMR spectrum of compound **14** in $CDCl_3$ at room temperature.

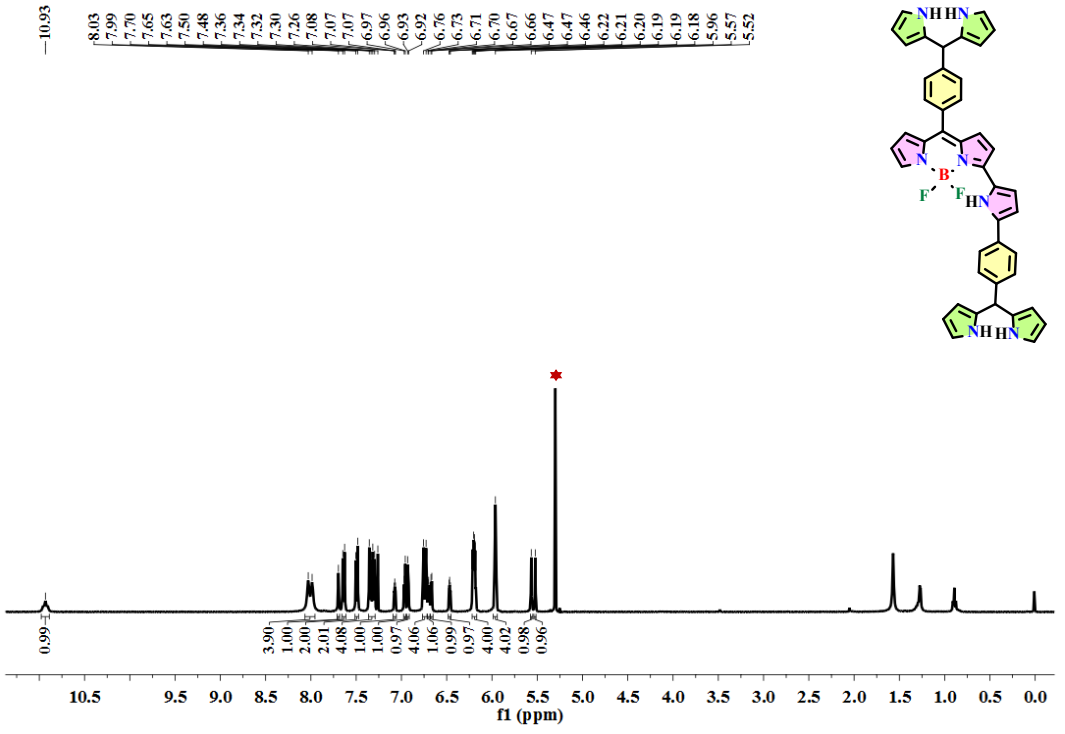

Fig. S8 ^{1}H NMR spectrum of compound **15** in $CDCl_3$ at room temperature.

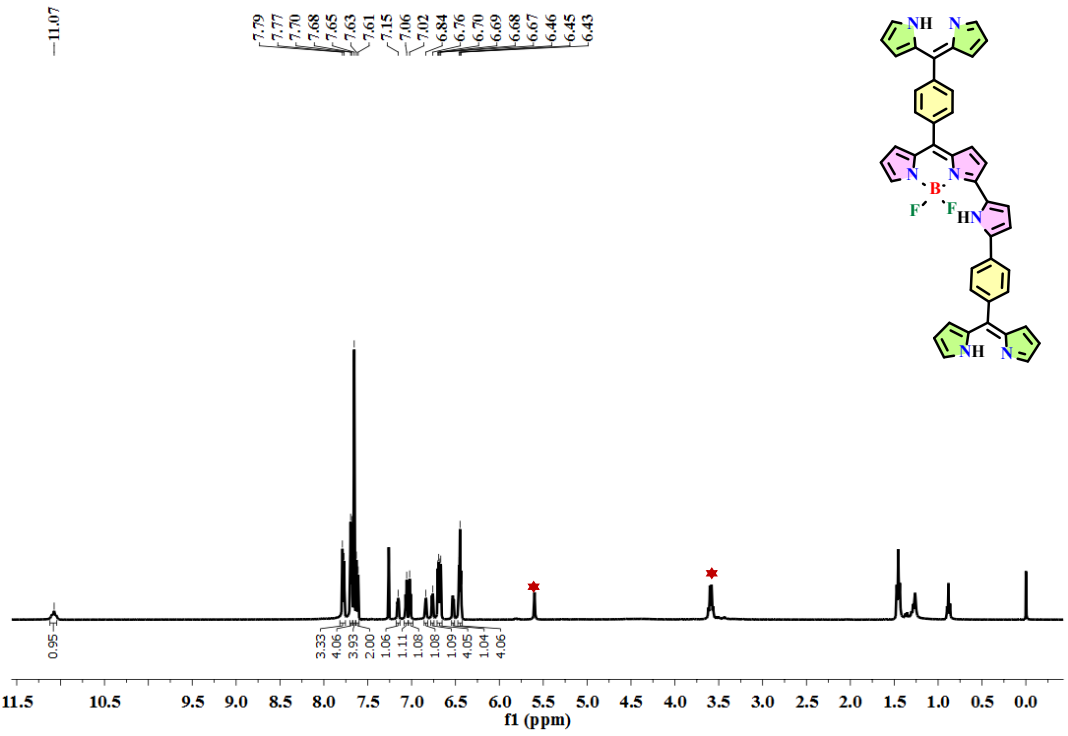

Fig. S9 ^{1}H NMR spectrum of compound **16** in $CDCl_3$ at room temperature.

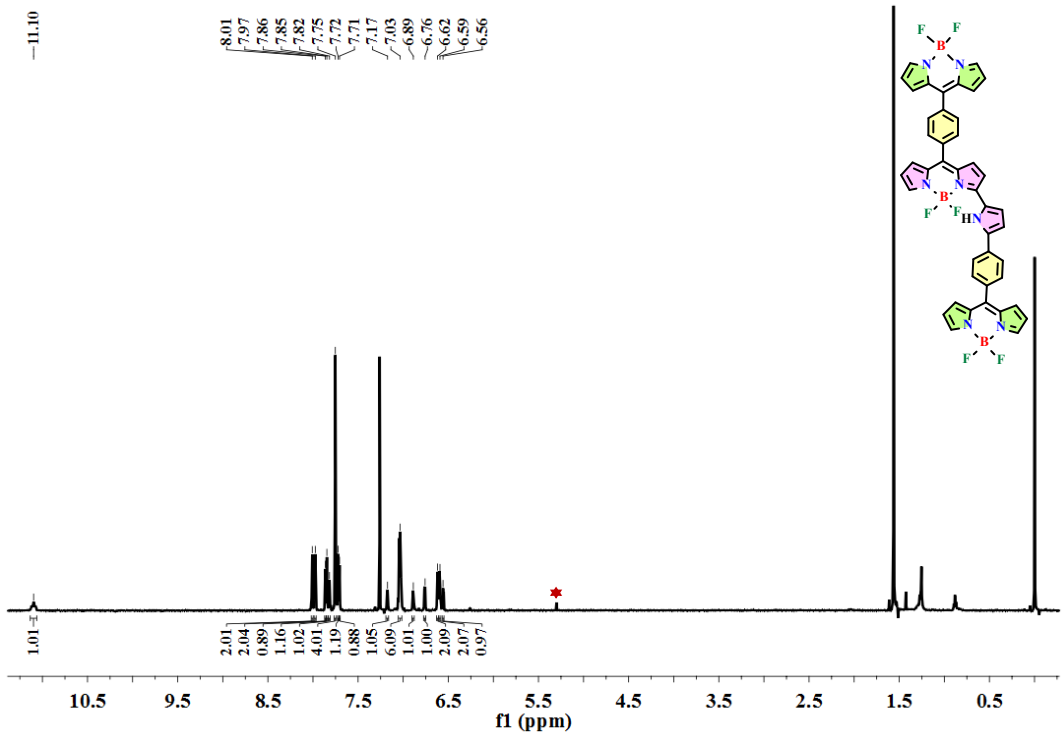

Fig. S10 ^{1}H NMR spectrum of compound **7** in $CDCl_3$ at room temperature.

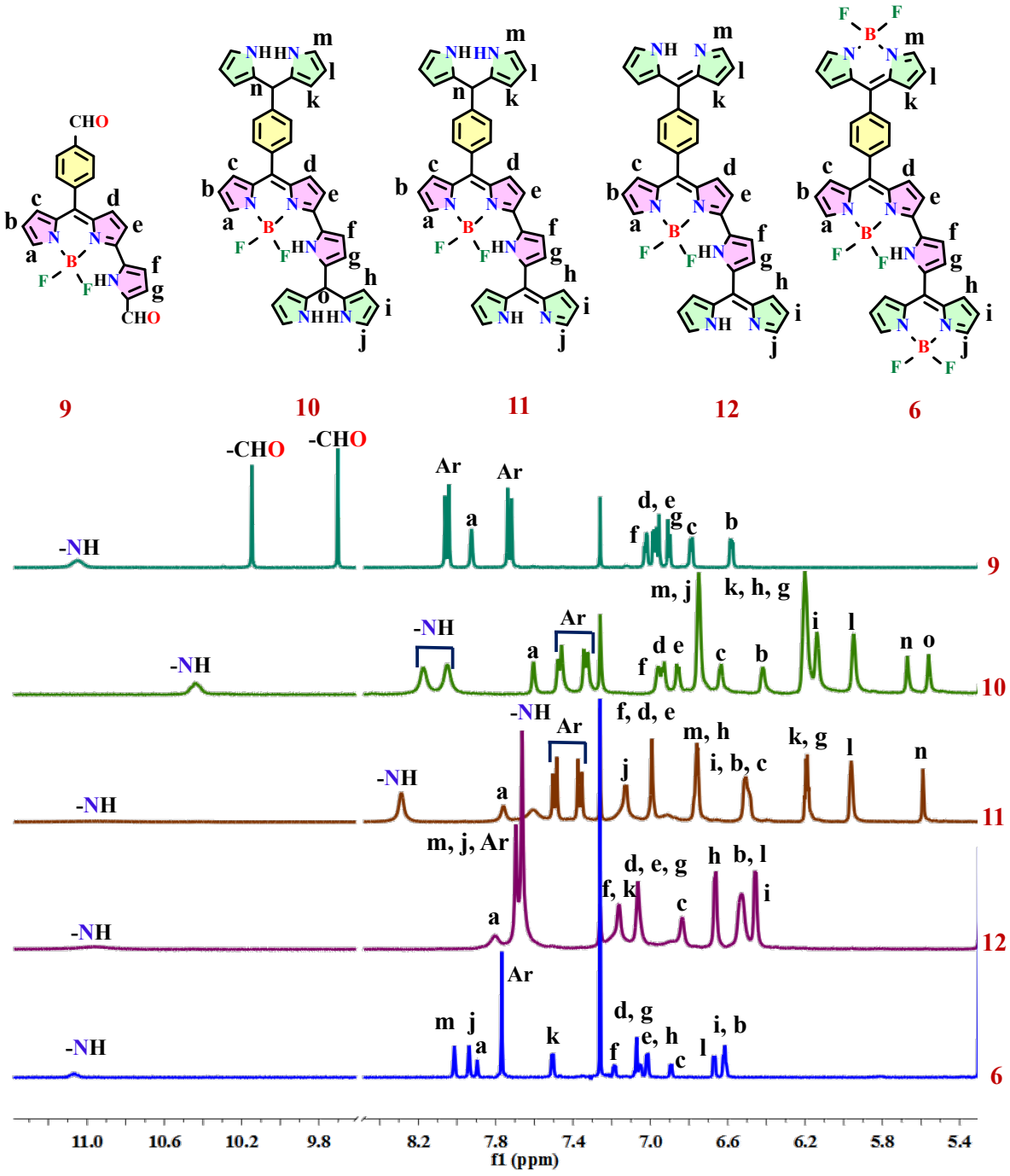

Fig. S11 Partial ^{1}H NMR spectra of **6,** and **9-12** recorded in $CDCl_3$ at 25 °C.

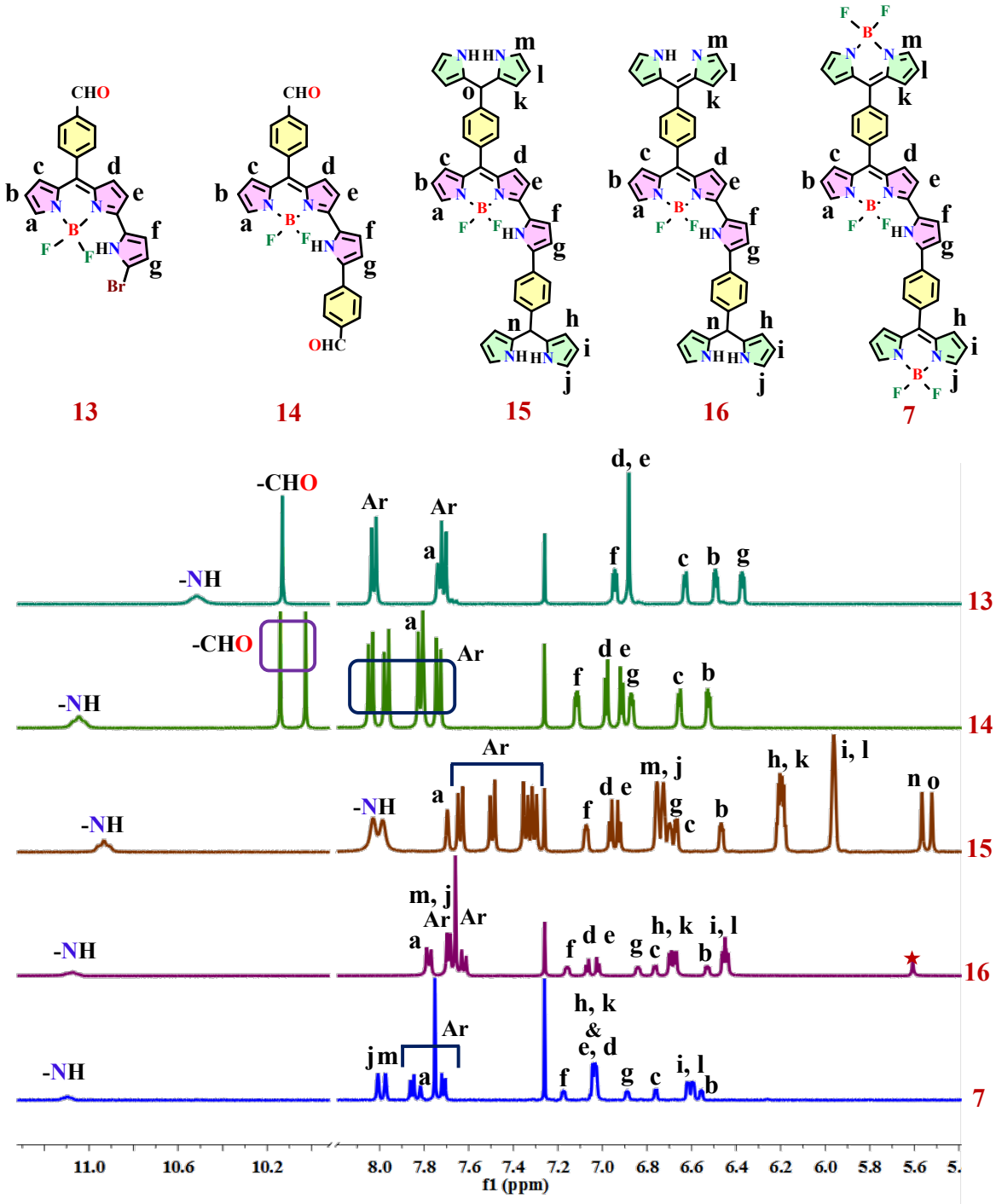

Fig. S12 Partial ^{1}H NMR spectra of triad **7** and **13-16** recorded in $CDCl_3$ at 25 °C.

^{13}C NMR study

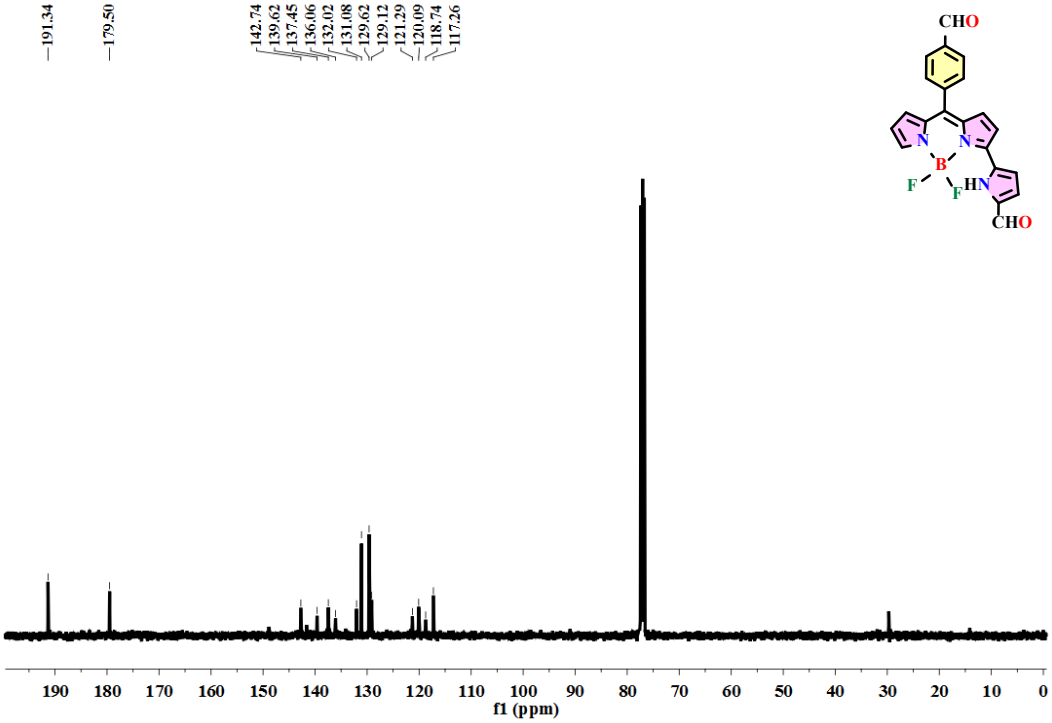

Fig. S13 ^{13}C NMR spectrum of the compound **9** recorded in $CDCl_3$.

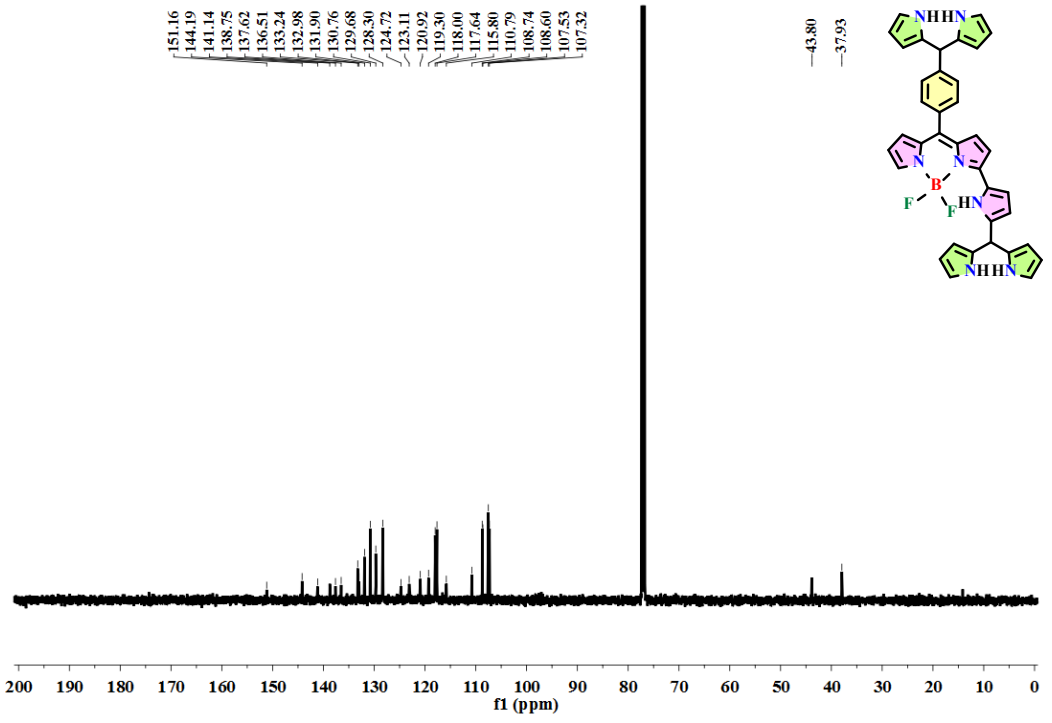

Fig. S14 ^{13}C NMR spectrum of the compound **10** recorded in $CDCl_3$.

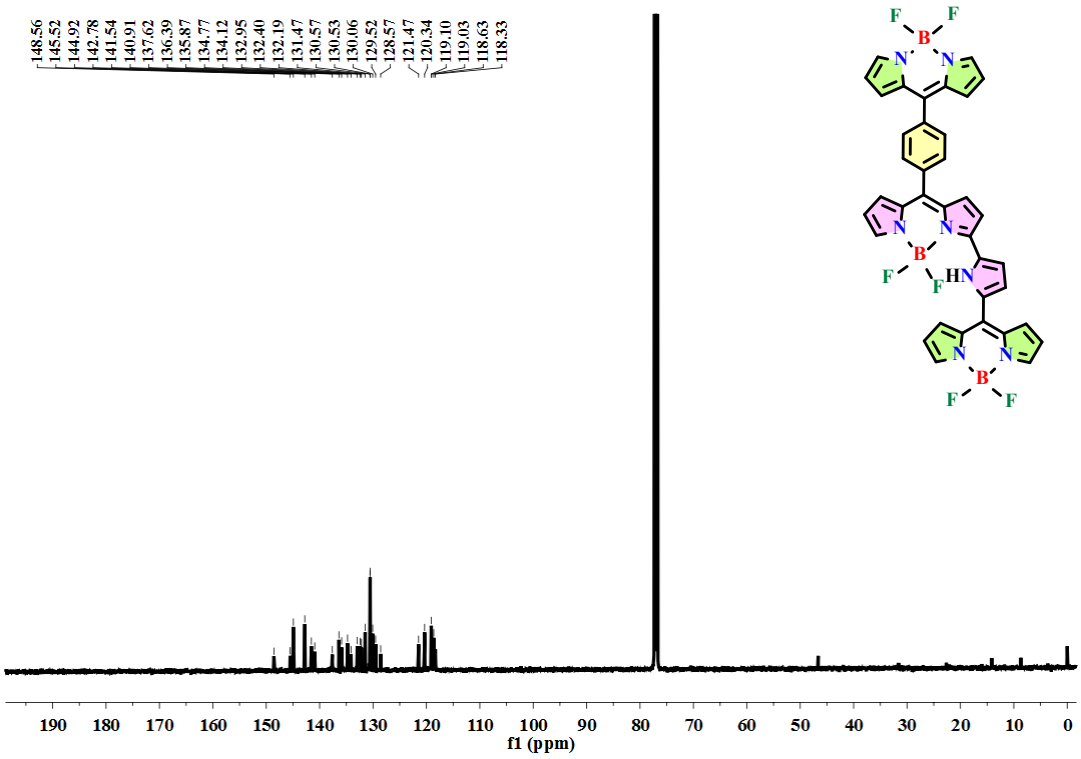

Fig. S15 ^{13}C NMR spectrum of the compound **6** recorded in $CDCl_3$.

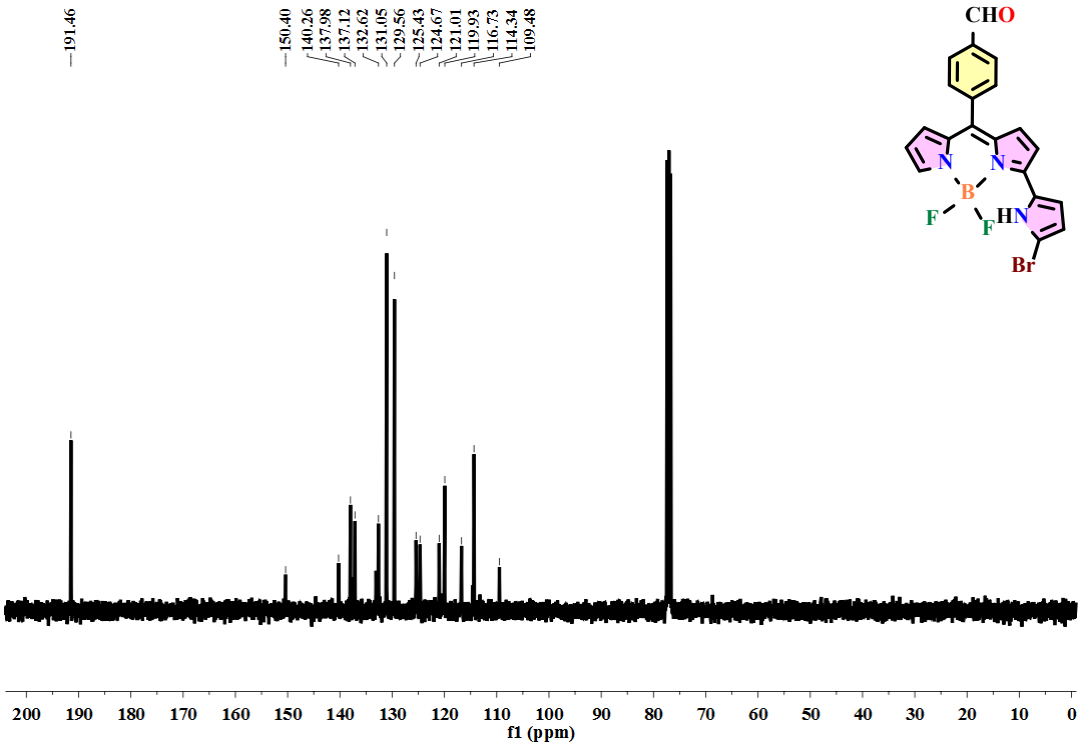

Fig. S16 ^{13}C NMR spectrum of the compound **13** recorded in $CDCl_3$.

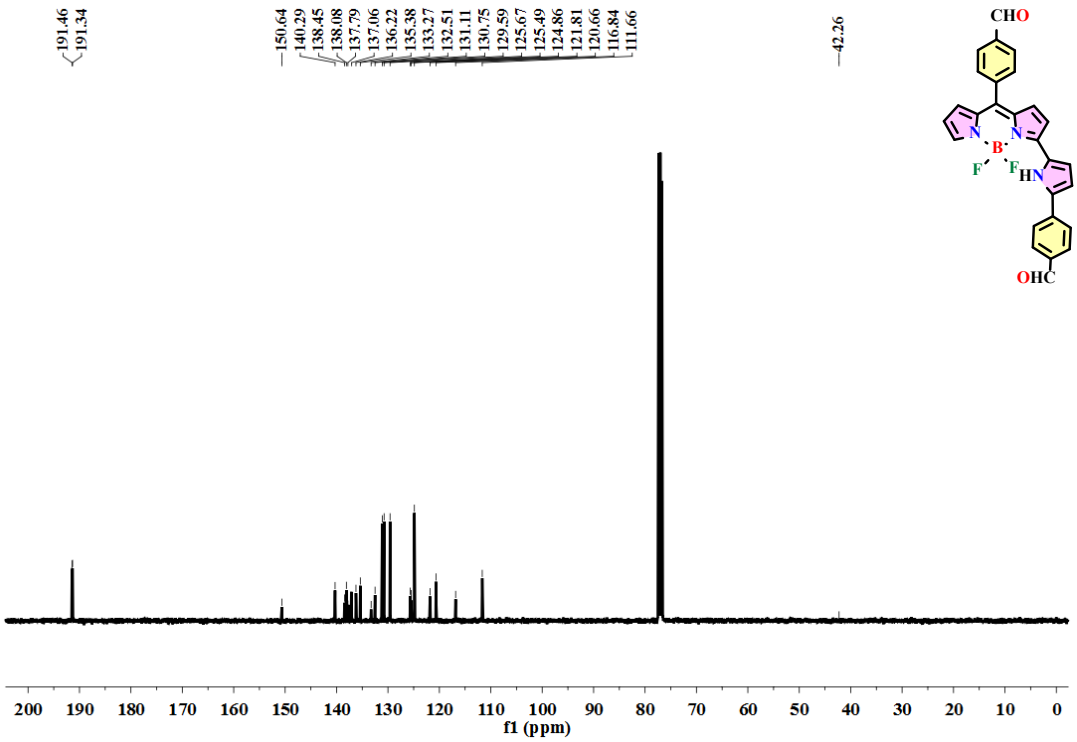

Fig. S17 ^{13}C NMR spectrum of the compound **14** recorded in $CDCl_3$.

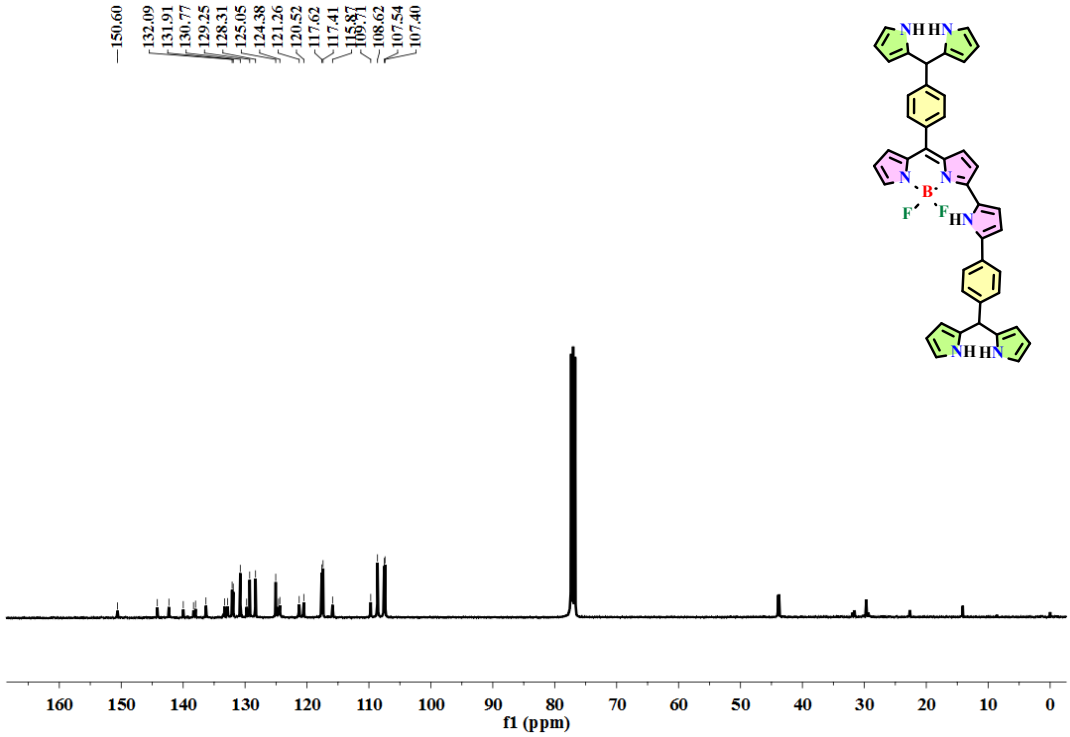

Fig. S18 ^{13}C NMR spectrum of the compound **15** recorded in $CDCl_3$.

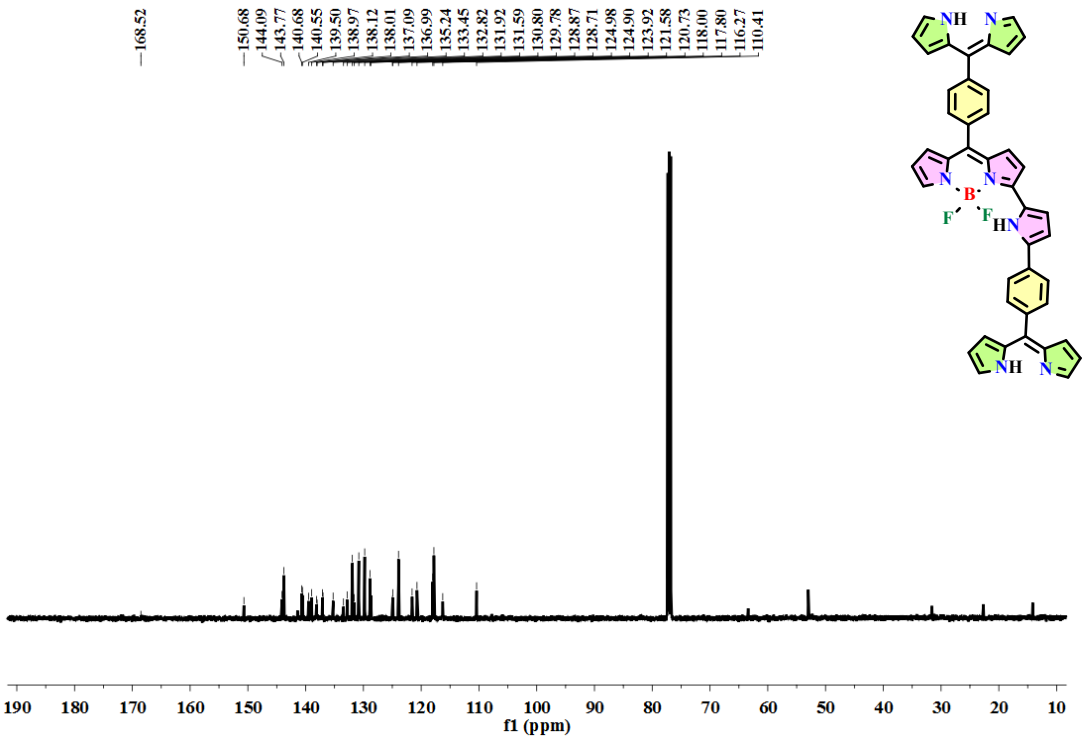

Fig. S19 ^{13}C NMR spectrum of the compound **16** recorded in $CDCl_3$.

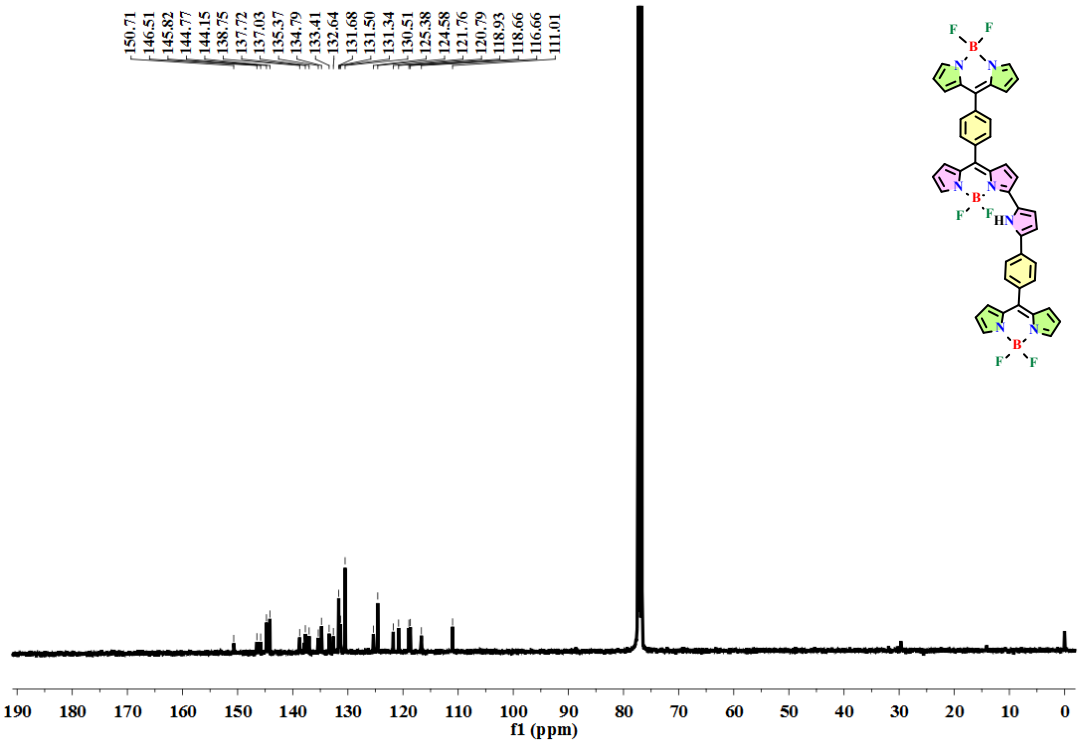

Fig. S20 ^{13}C NMR spectrum of the compound **7** recorded in $CDCl_3$.

^{11}B NMR study

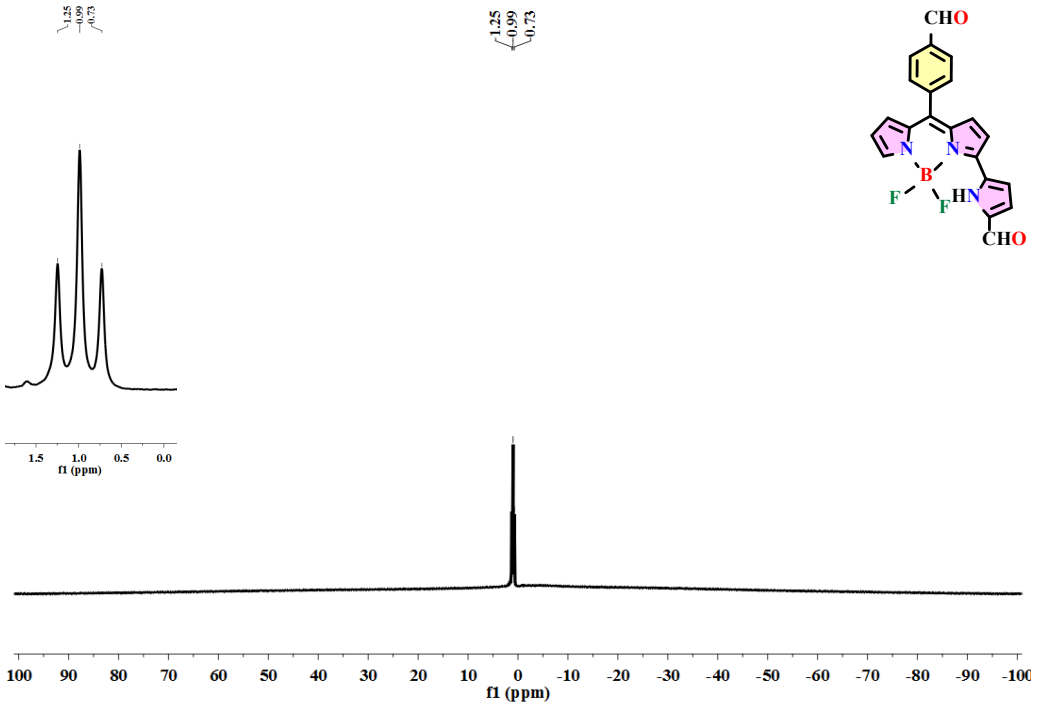

Fig. S21 ^{11}B NMR spectrum of **9** in $CDCl_3$ at room temperature.

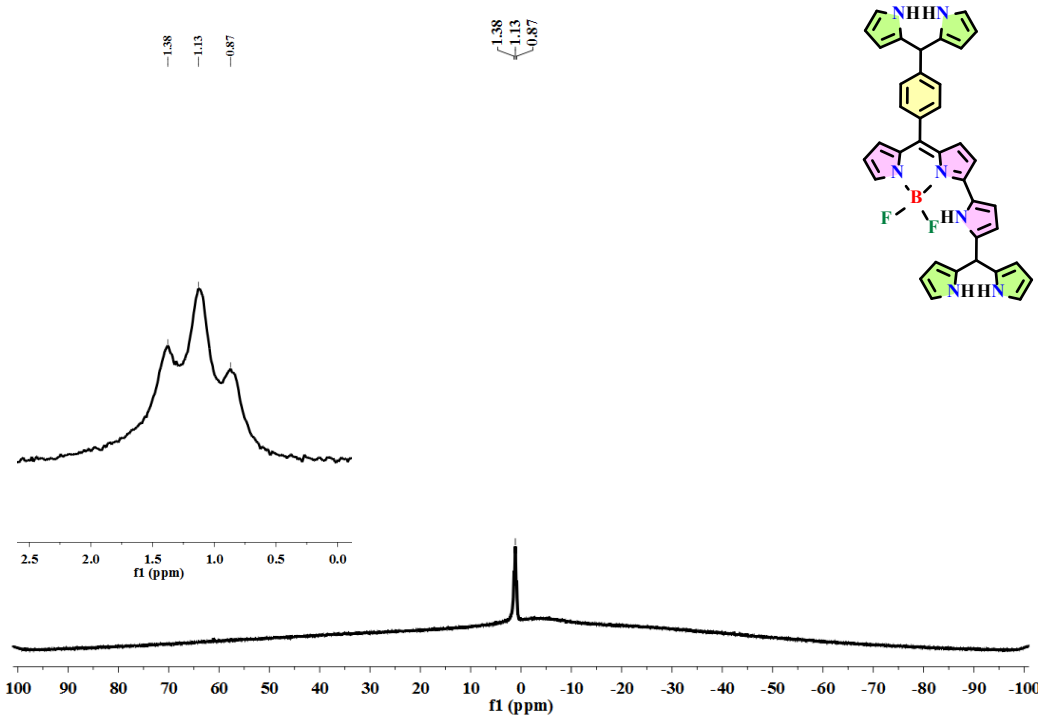

Fig. S22 ^{11}B NMR spectrum of **10** in $CDCl_3$ at room temperature.

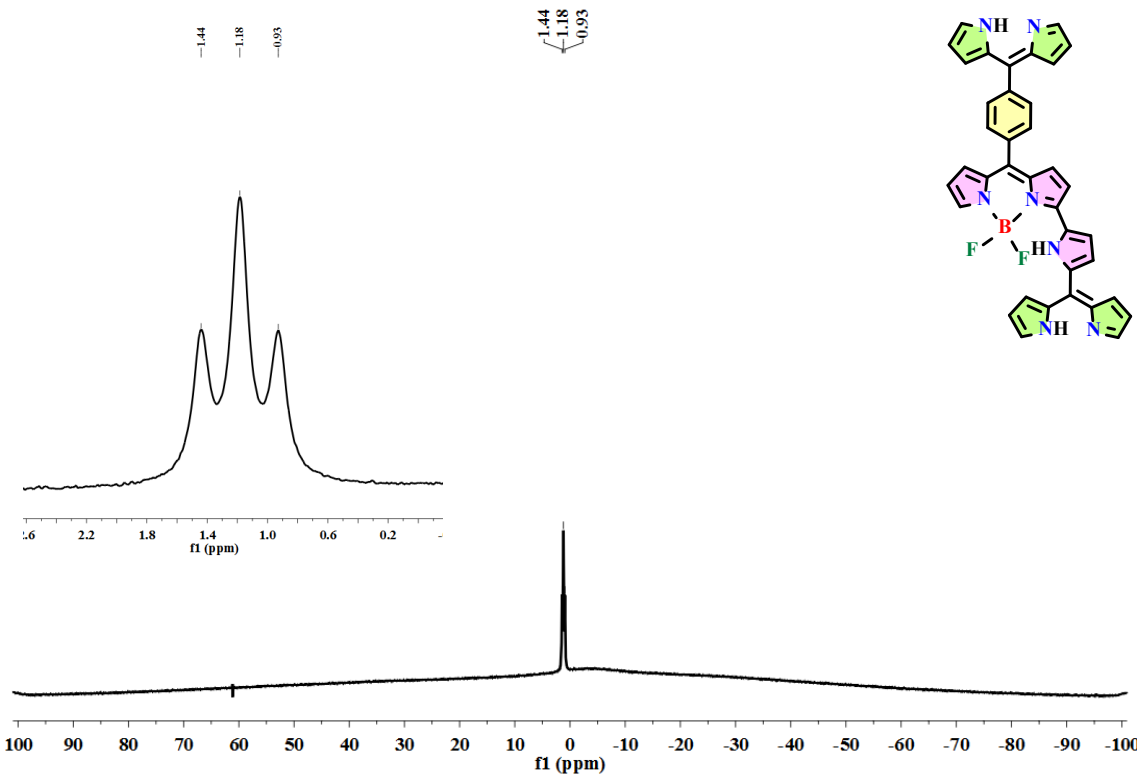

Fig. S23 ^{11}B NMR spectrum of **12** in $CDCl_3$ at room temperature.

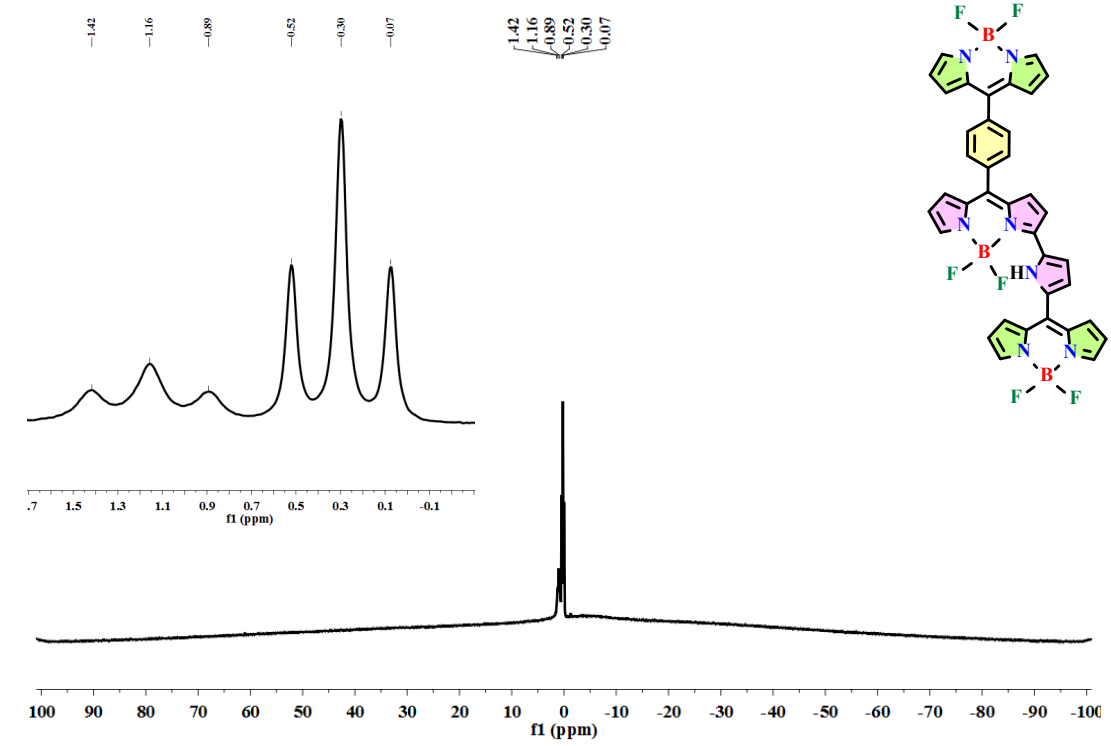

Fig. S24 ^{11}B NMR spectrum of **6** in $CDCl_3$ at room temperature.

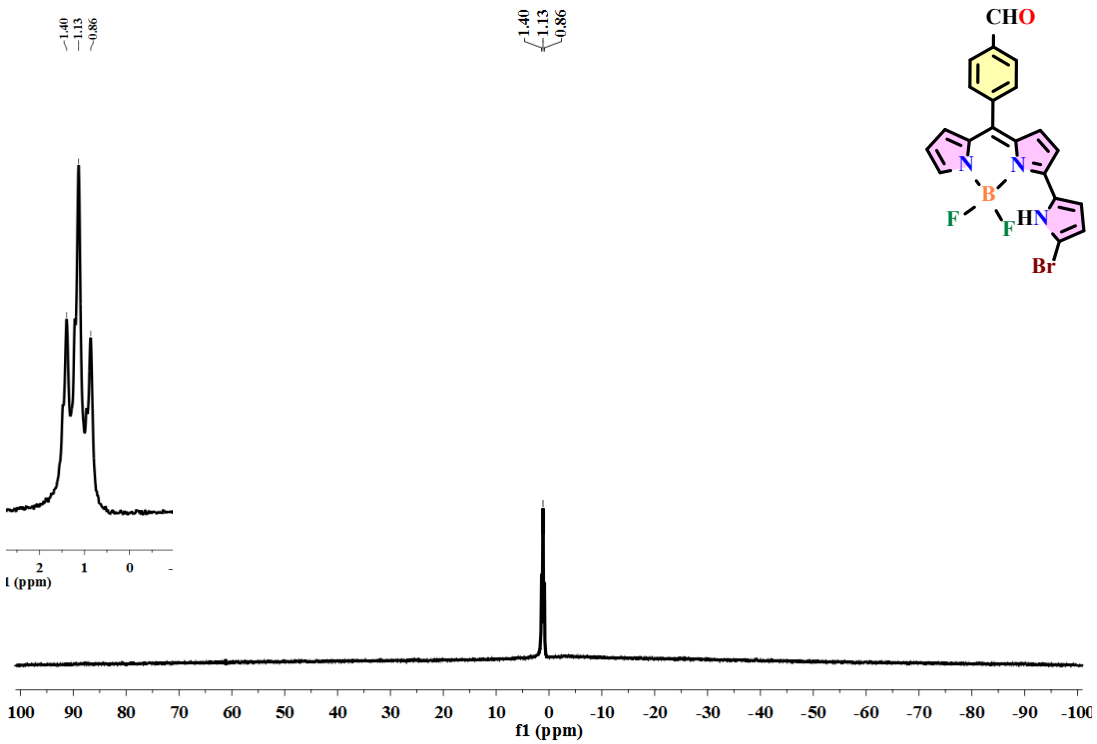

Fig. S25 ^{11}B NMR spectrum of **13** in $CDCl_3$ at room temperature.

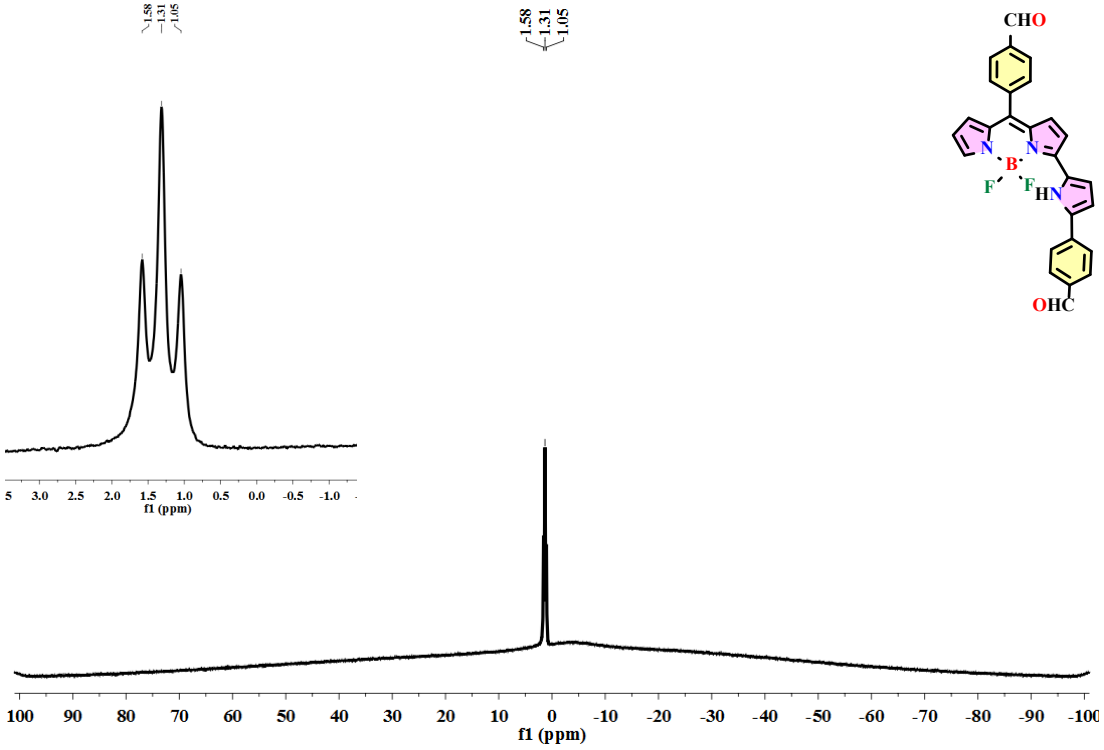

Fig. S26 ^{11}B NMR spectrum of **14** in $CDCl_3$ at room temperature

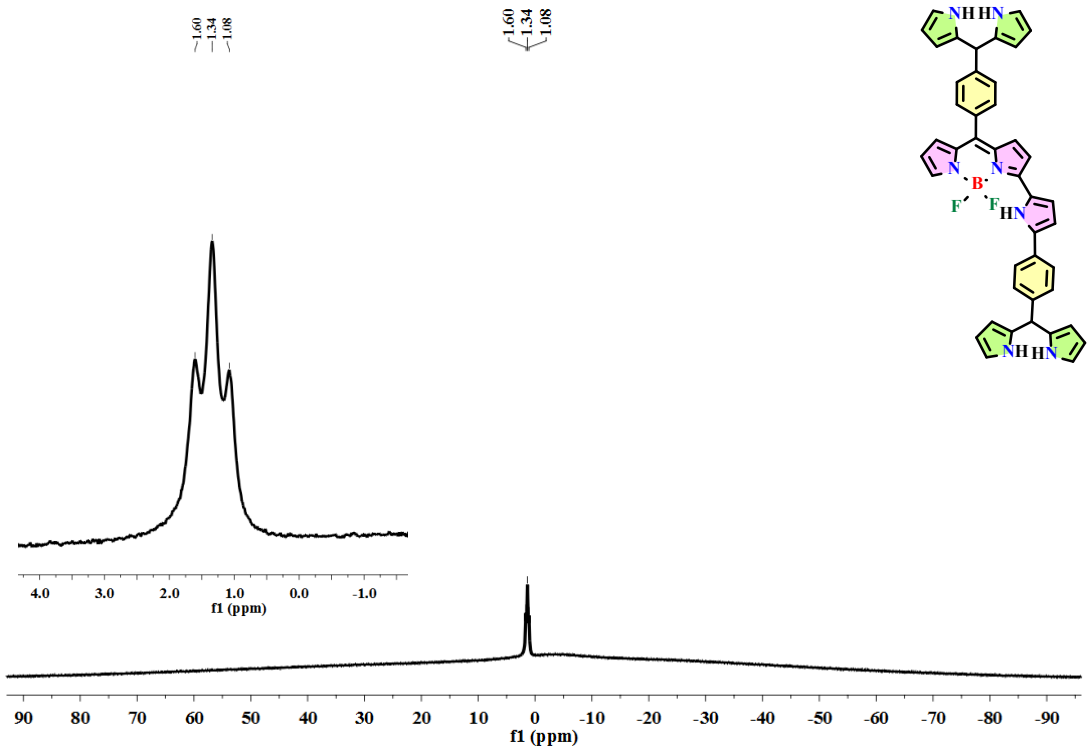

Fig. S27 ^{11}B NMR spectrum of **15** in $CDCl_3$ at room temperature.

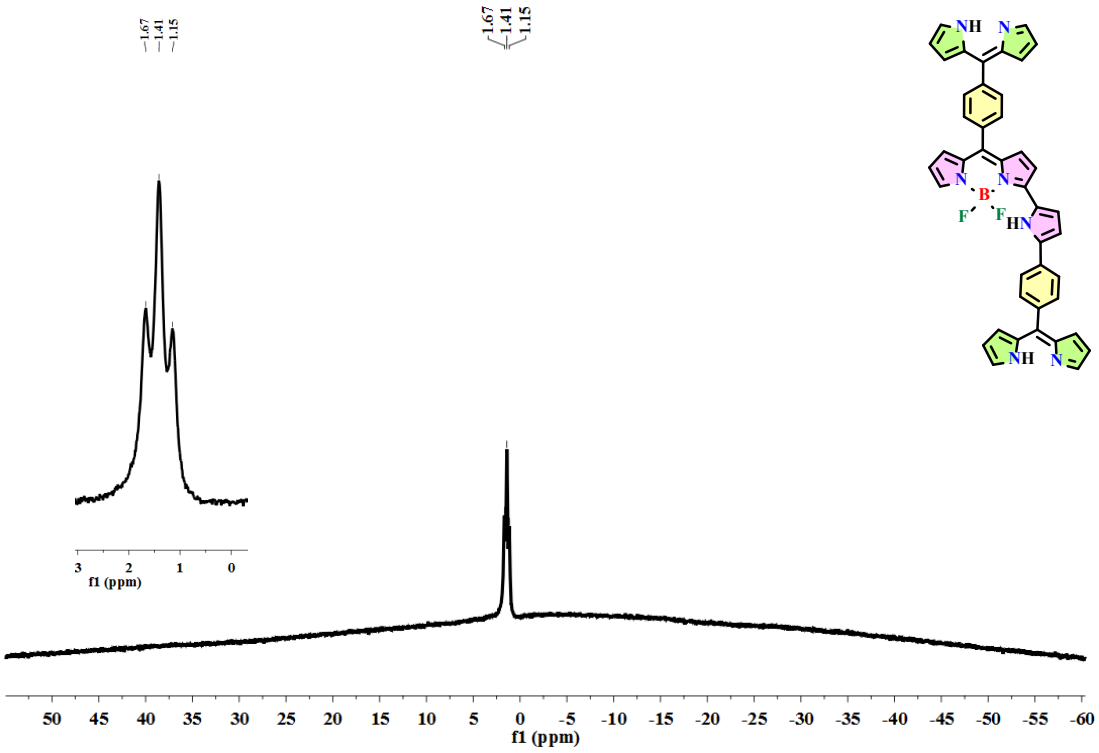

Fig. S28 ^{11}B NMR spectrum of **16** in $CDCl_3$ at room temperature.

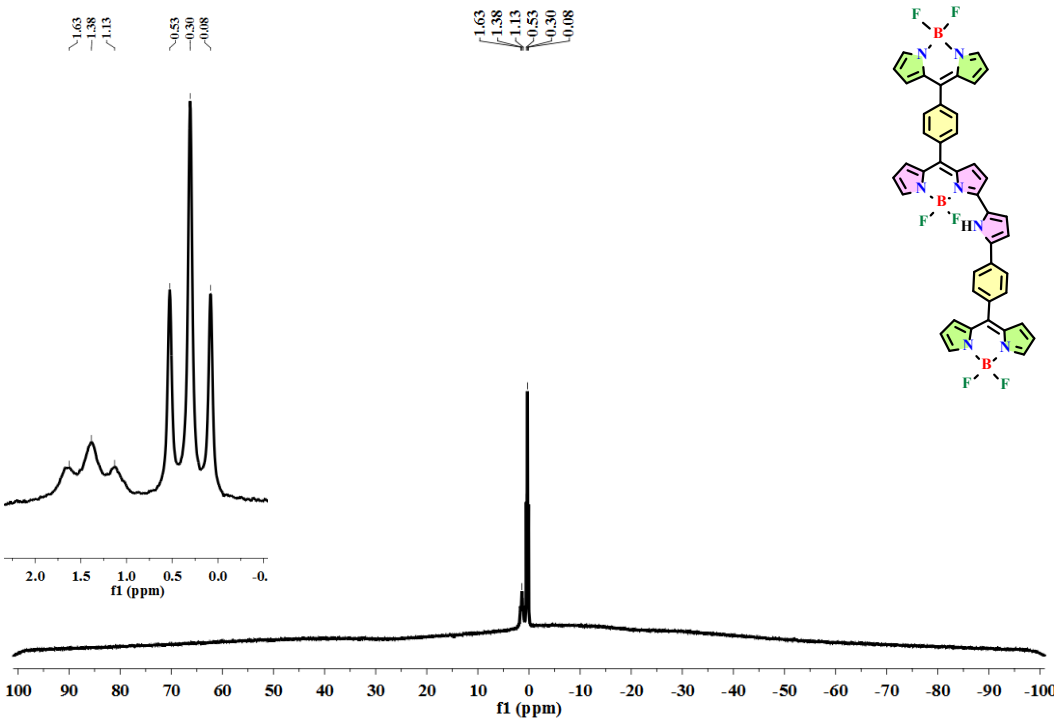

Fig. S29 ^{11}B NMR spectrum of **6** in $CDCl_3$ at room temperature.

^{19}F NMR study

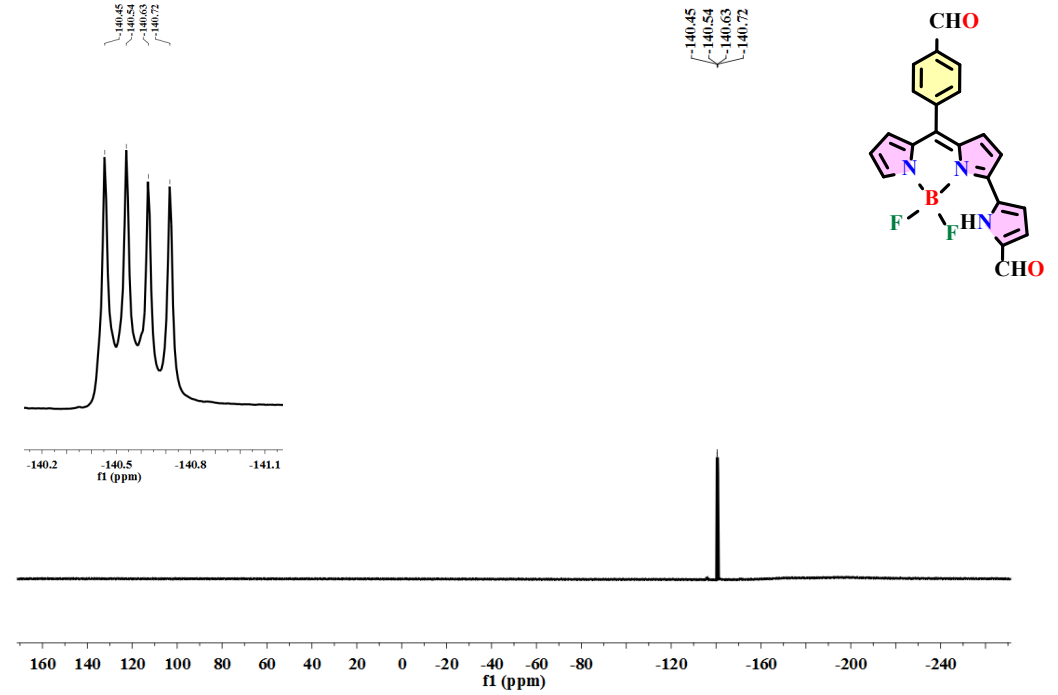

Fig. S30 ^{19}F NMR spectrum of **9** in $CDCl_3$ at room temperature.

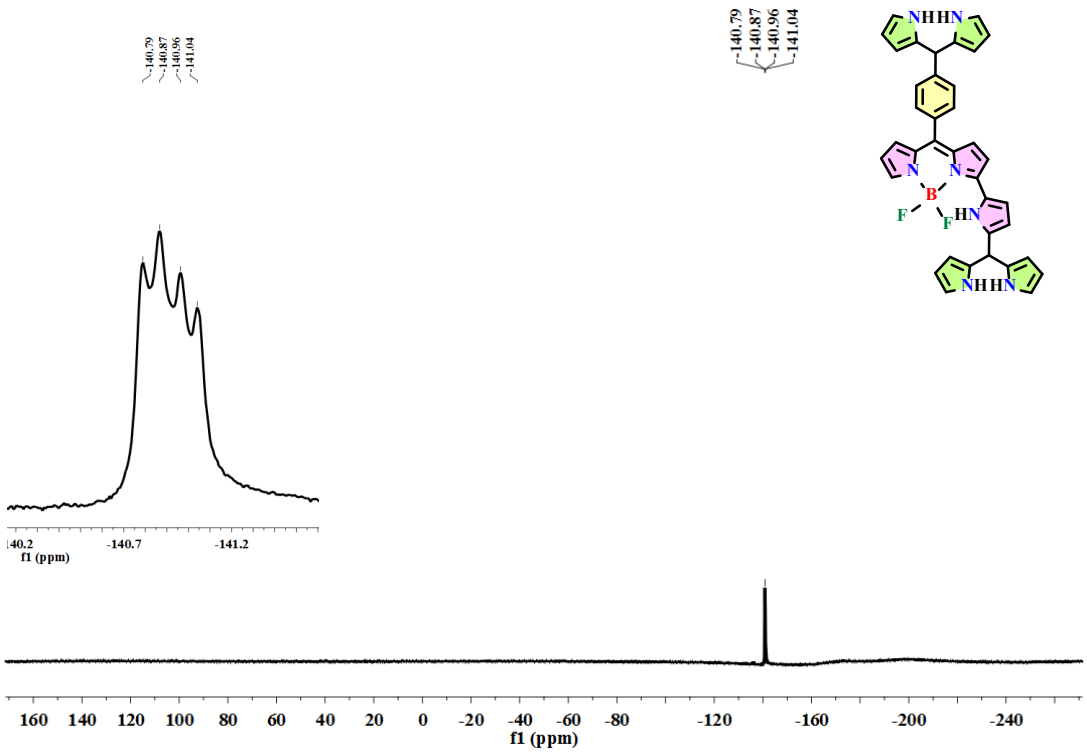

Fig. S31 ^{19}F NMR spectrum of **10** in $CDCl_3$ at room temperature.

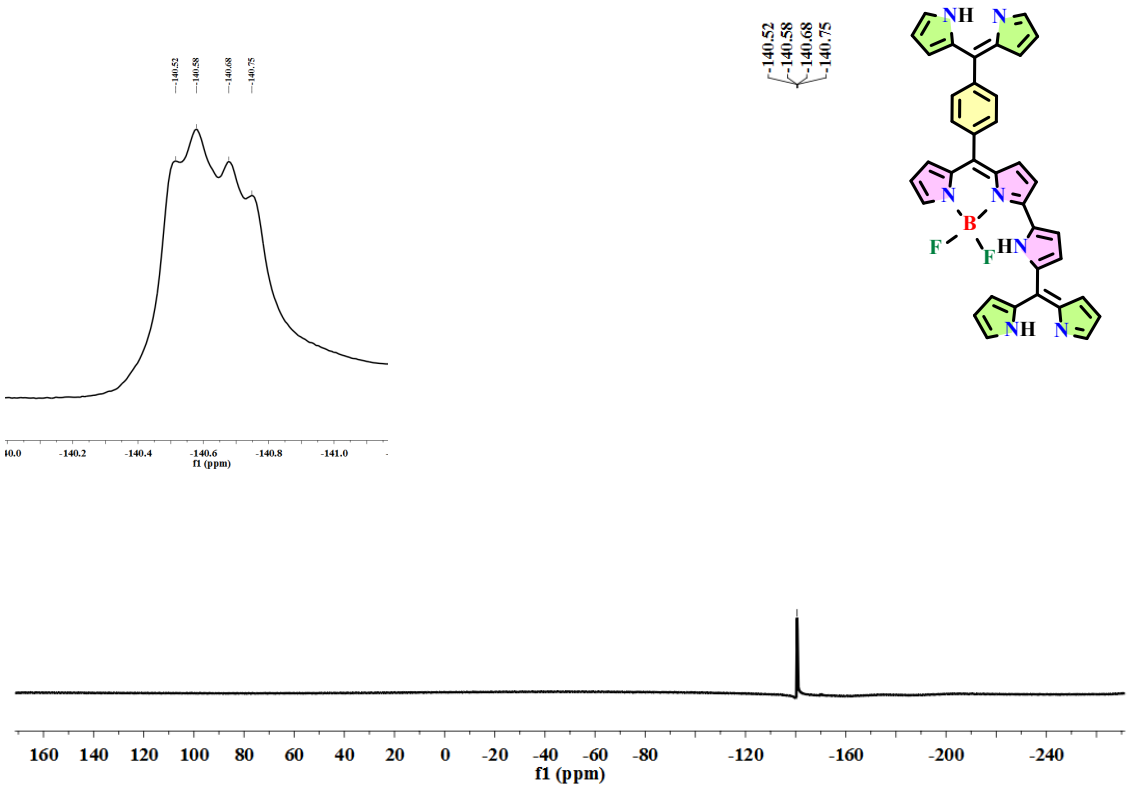

Fig. S32 ^{19}F NMR spectrum of **12** in $CDCl_3$ at room temperature.

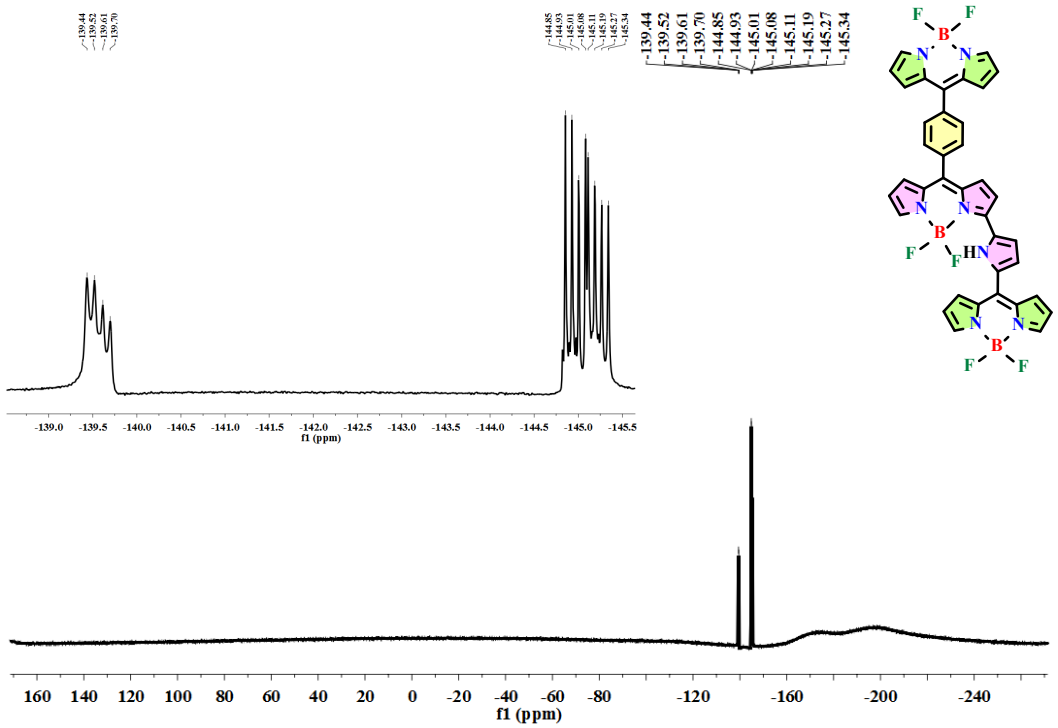

Fig. S33 ^{19}F NMR spectrum of **6** in $CDCl_3$ at room temperature.

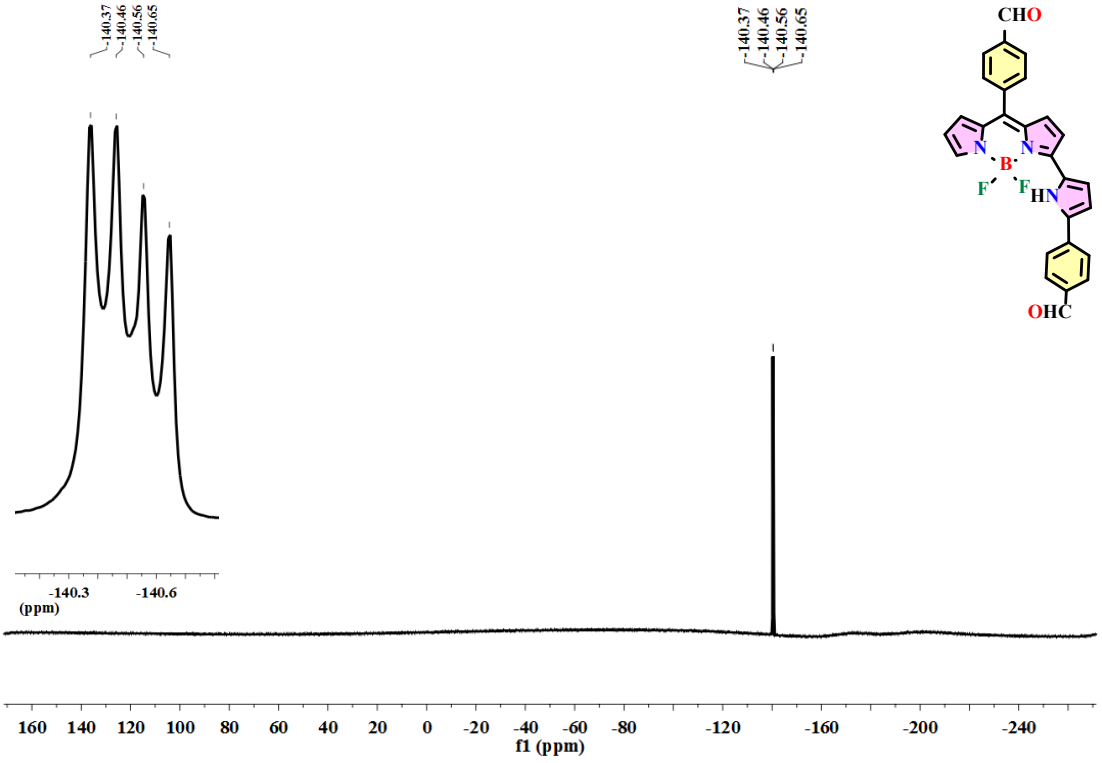

Fig. S34 ^{19}F NMR spectrum of **14** in $CDCl_3$ at room temperature.

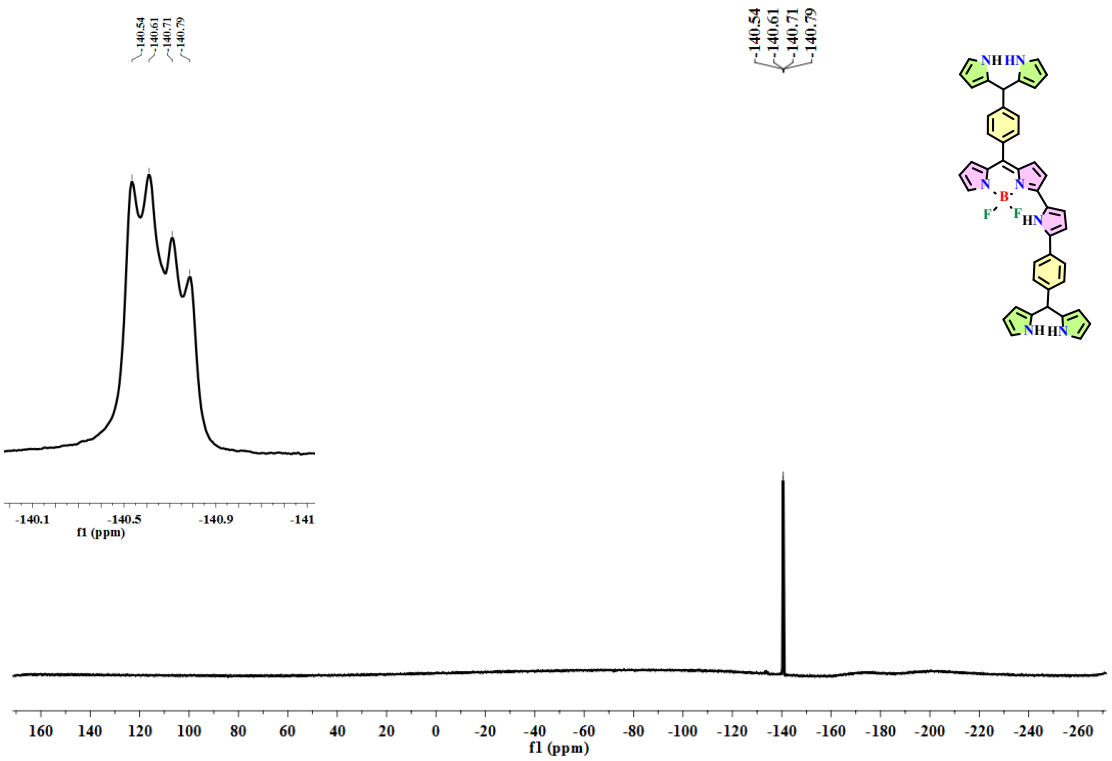

Fig. S35 ^{19}F NMR spectrum of **15** in $CDCl_3$ at room temperature.

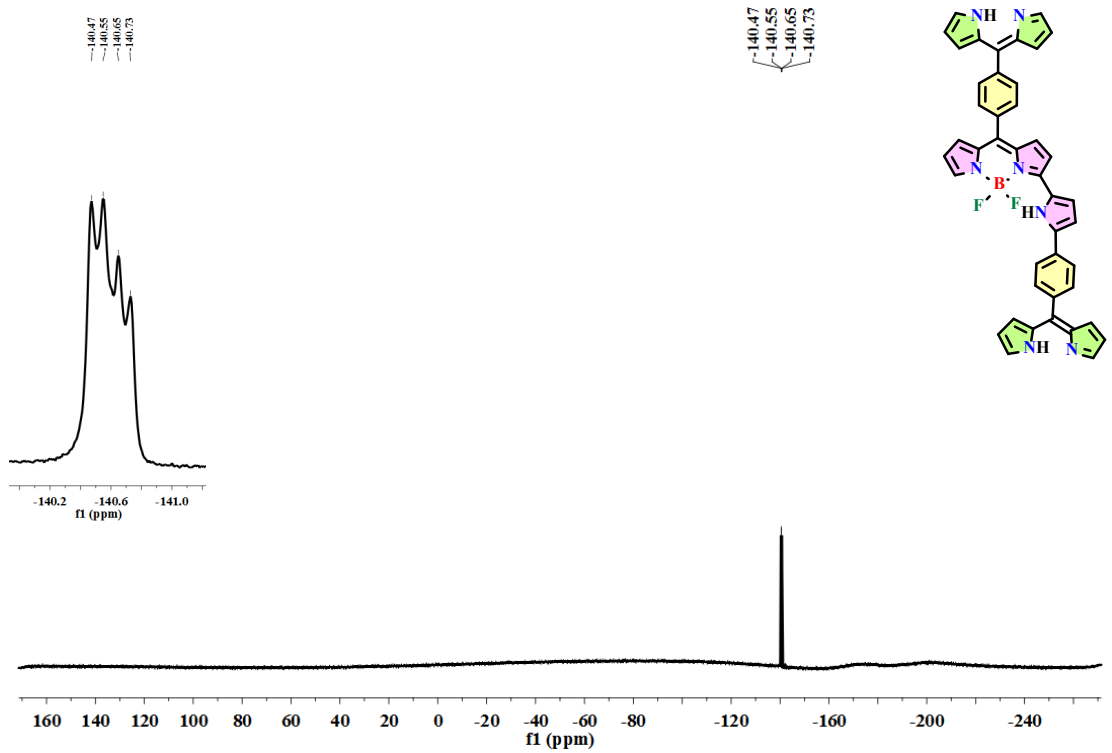

Fig. S36 ^{19}F NMR spectrum of **16** in $CDCl_3$ at room temperature.

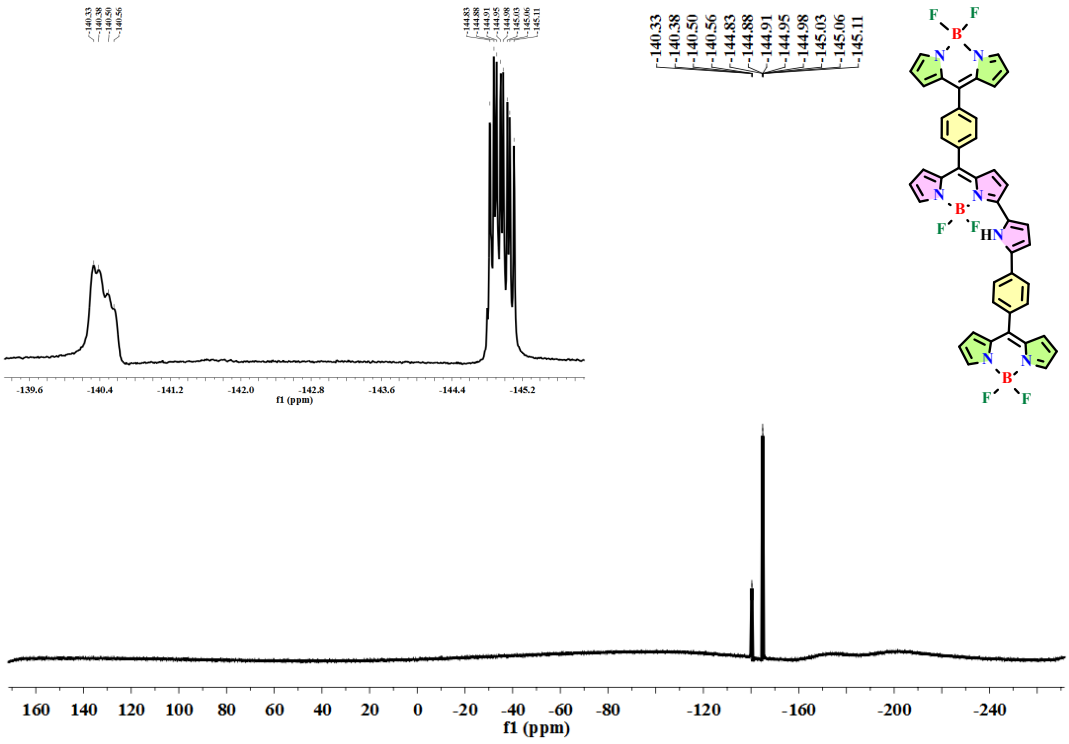

Fig. S37 ^{19}F NMR spectrum of **7** in $CDCl_3$ at room temperature.

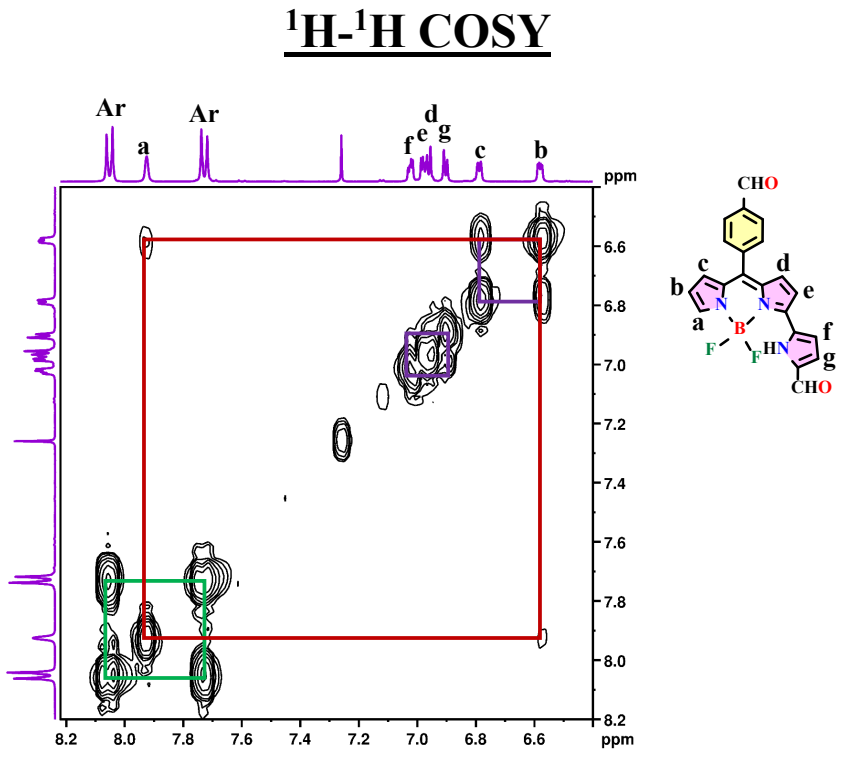

Fig. S38 ^{1}H-^{1}H COSY spectrum of the **9** in $CDCl_3$ at room temperature.

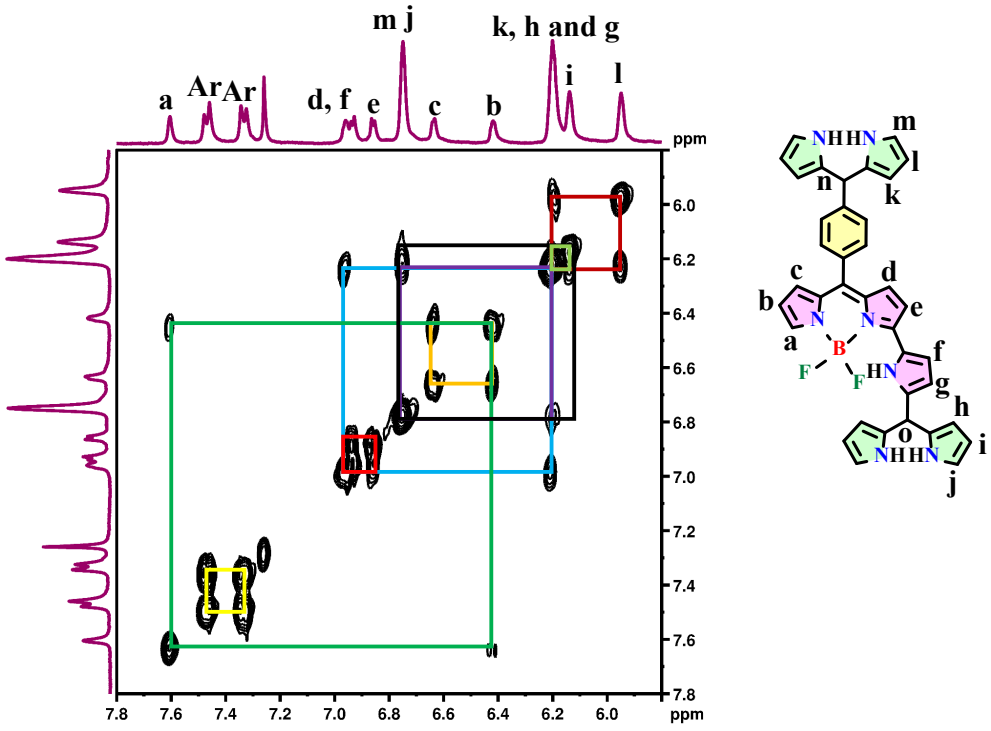

Fig. S39 ^{1}H-^{1}H COSY spectrum of the **10** in $CDCl_3$ at room temperature.

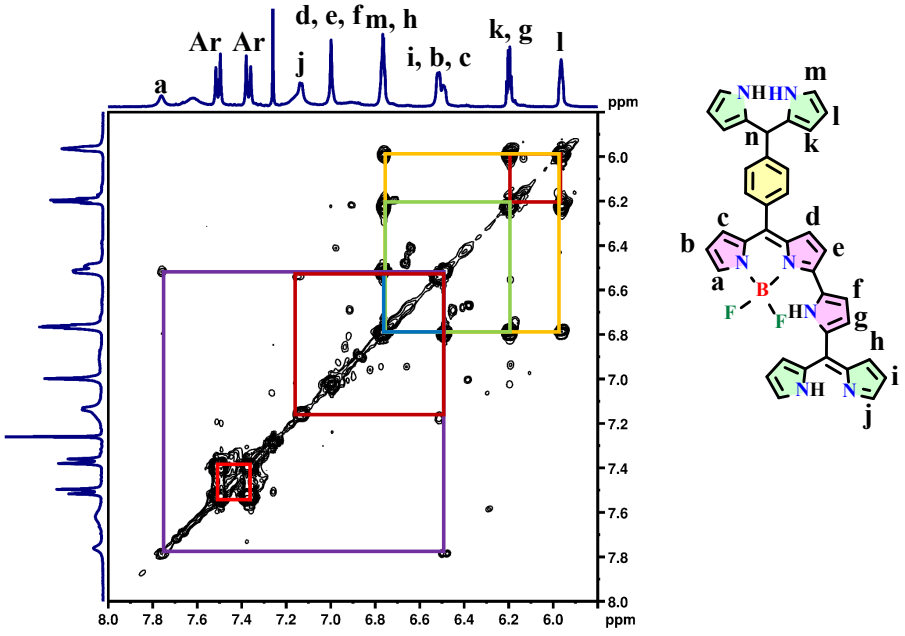

Fig. S40 ^{1}H-^{1}H COSY spectrum of the **11** in $CDCl_3$ at room temperature.

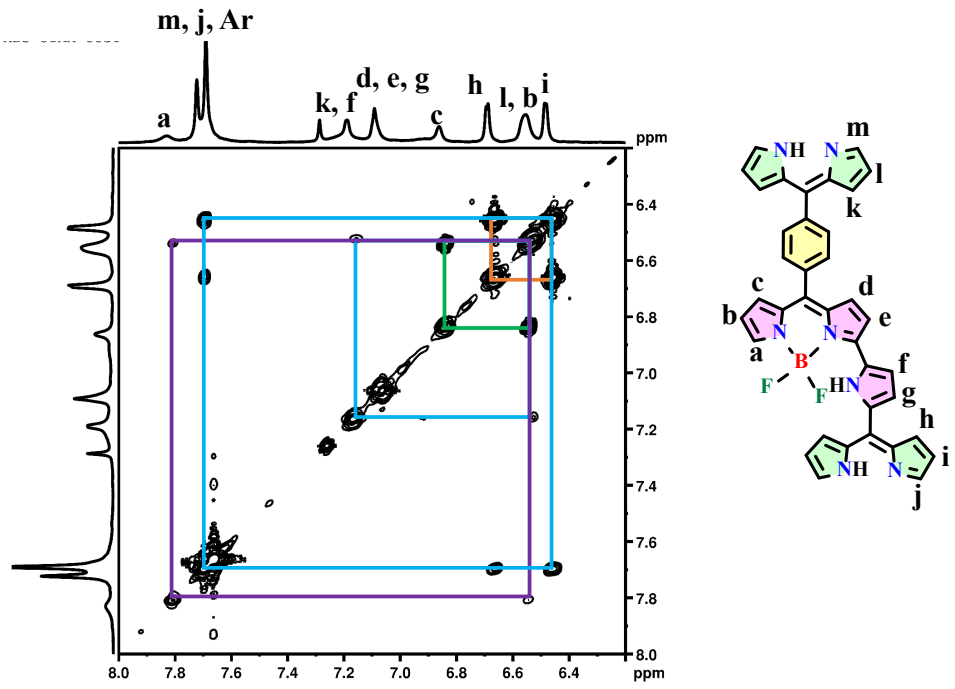

Fig. S41 ^{1}H-^{1}H COSY spectrum of the **12** in $CDCl_3$ at room temperature.

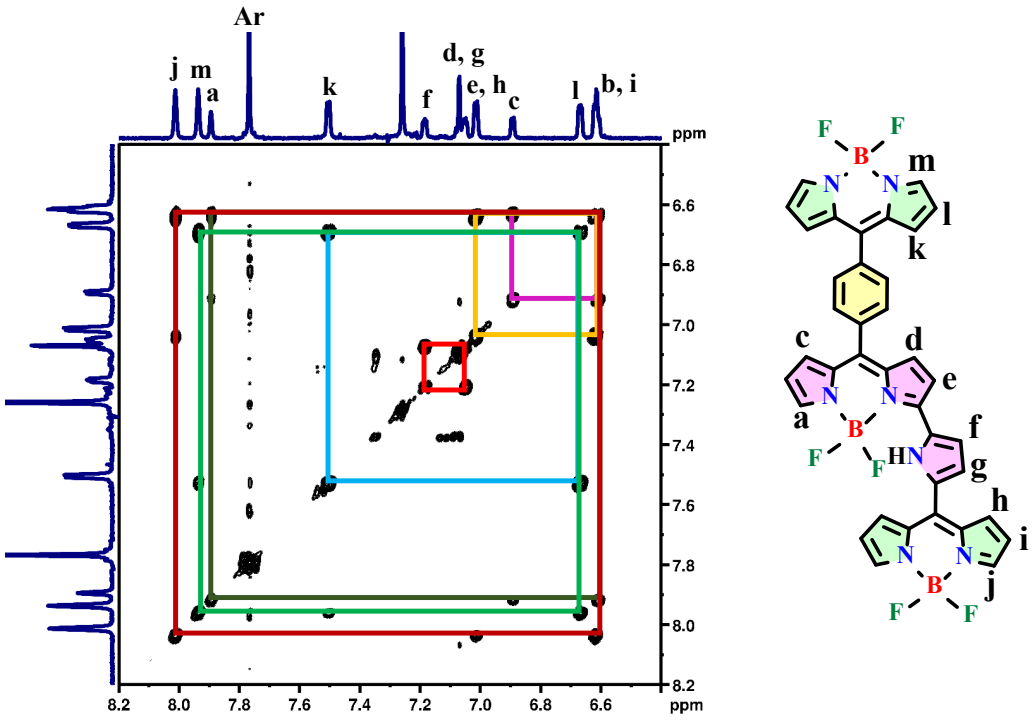

Fig. S42 ^{1}H-^{1}H COSY spectrum of the **6** in $CDCl_3$ at room temperature.

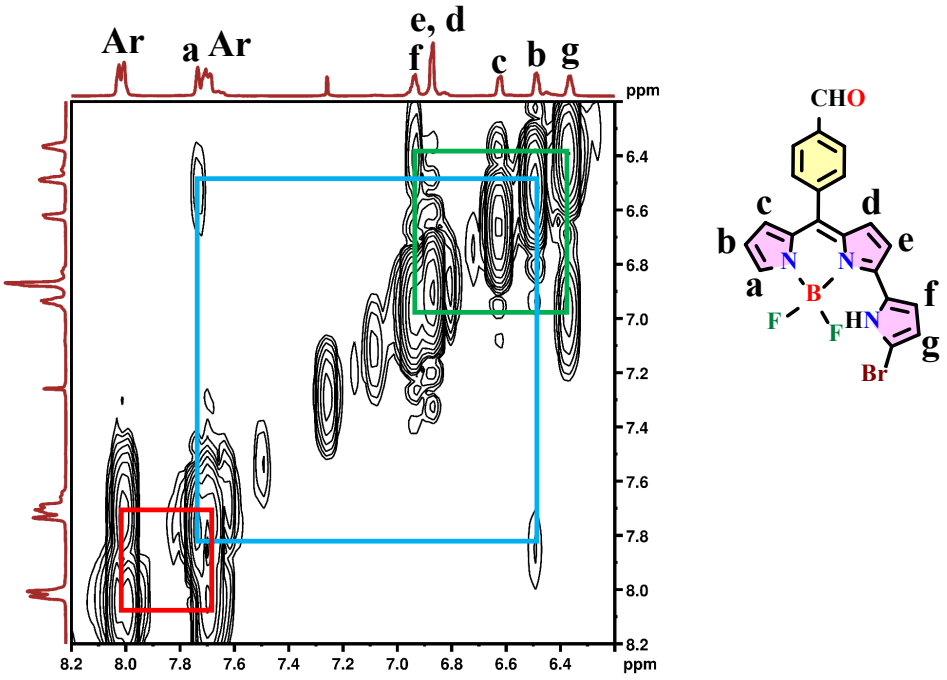

Fig. S43 ^{1}H-^{1}H COSY spectrum of the **13** in $CDCl_3$ at room temperature.

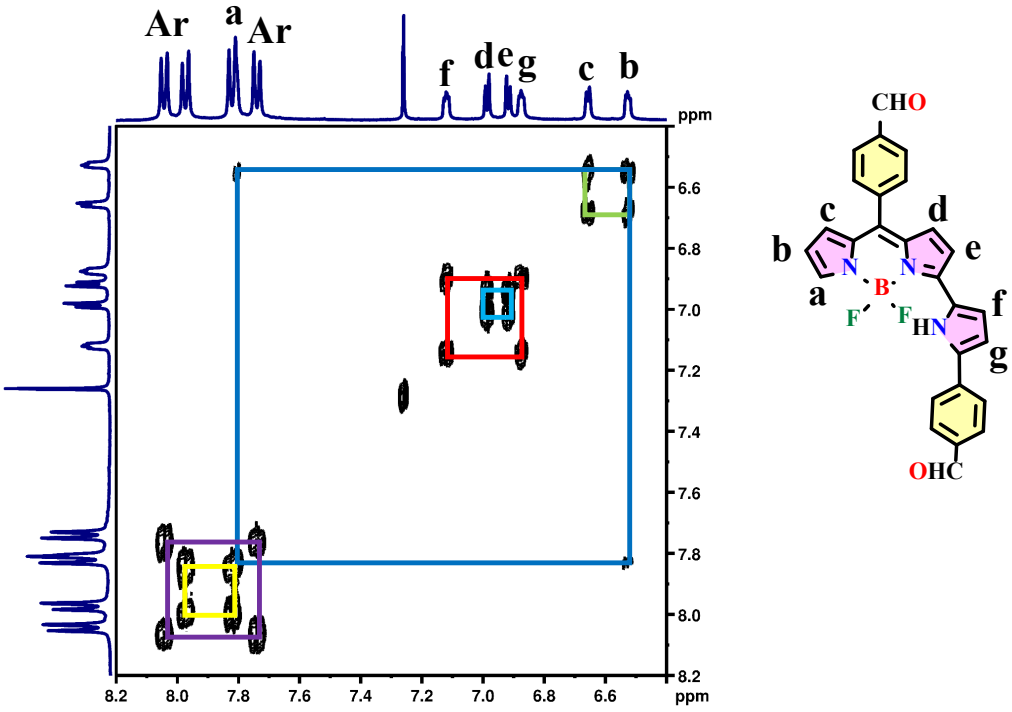

Fig. S44 ^{1}H-^{1}H COSY spectrum of the **14** in $CDCl_3$ at room temperature.

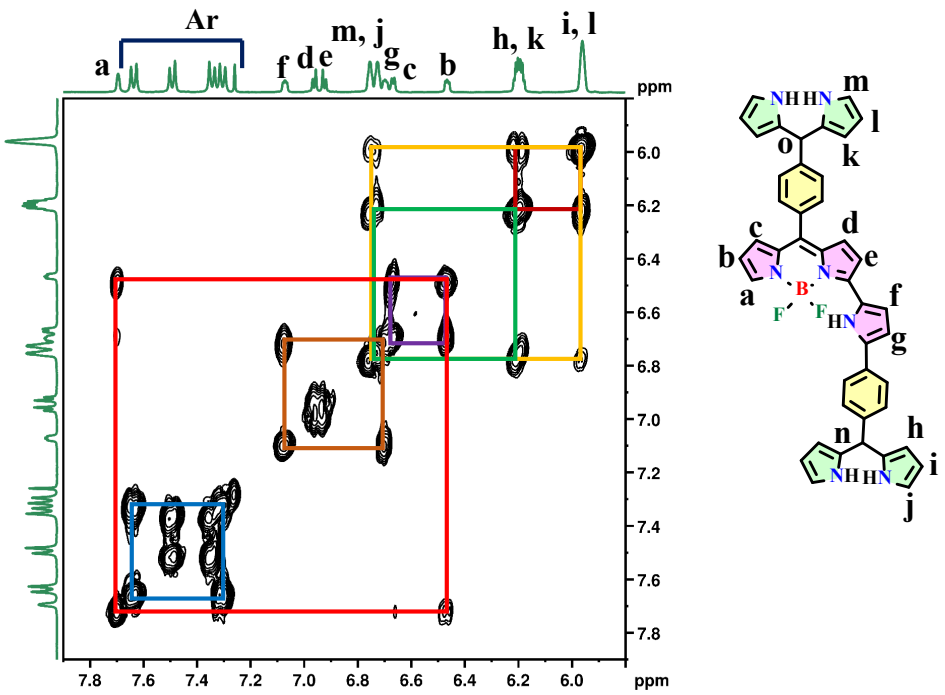

Fig. S45 ^{1}H-^{1}H COSY spectrum of the **15** in $CDCl_3$ at room temperature.

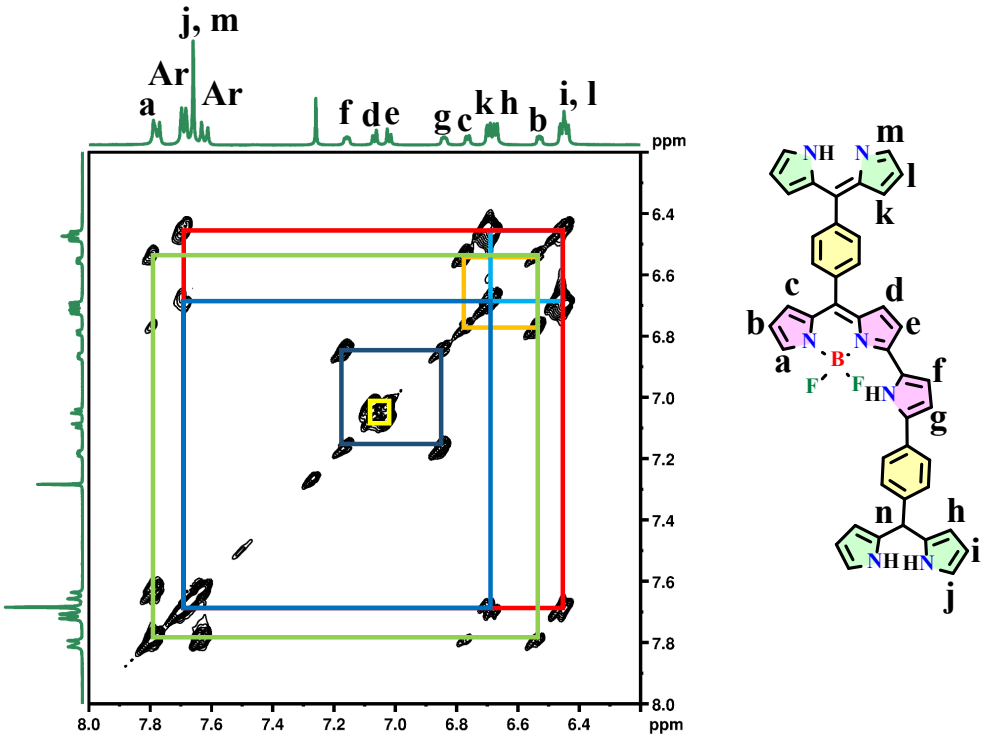

Fig. S46 ^{1}H-^{1}H COSY spectrum of the **16** in $CDCl_3$ at room temperature.

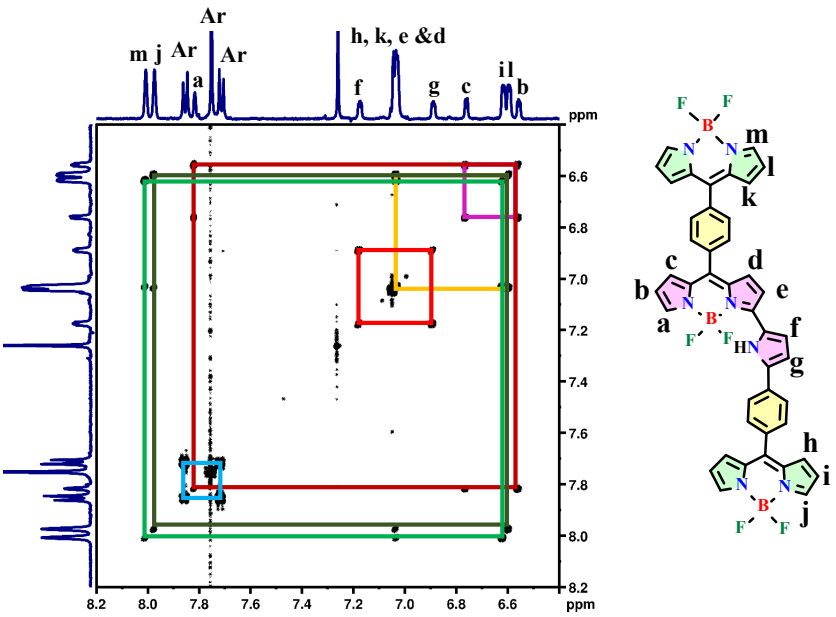

Fig. S47 ^{1}H-^{1}H COSY spectrum of the **7** in $CDCl_3$ at room temperature.

ESI-MS mass spectra study

Department of Chemistry I.I.T. (B)

Agilent Trusted Answers

Sample Information

Name	MR-ABS-2CHO	Data File Path	D:\MassHunter\Data\SEPT-23\MR-ABS-2CHO.d
Sample ID		Acq. Time (Local)	18-09-2023 12.58.35 PM (UTC+05:30)
Instrument	LCMS QTOF	Method Path (Acq)	D:\MassHunter\Methods\6545XT checkout\Methods\TRAINING\MS SCAN_AB_POS_100-1000_4000-100-120.m
MS Type	QTOF	Version (Acq SW)	6200 series TOF/6500 series Q-TOF B.09.00 (B9044.0)
Inj. Vol. (ul)	0.5	IRM Status	Success
Position	P1-C5	Method Path (DA)	D:\MassHunter\Report Templates\REPORT METHOD\HRMS_IITB_1.m
Plate Pos.		Target Source Path	
Operator		Result Summary	1 qualified (1 targets)

Sample Spectra

Compound Details

Cpd. 1: C21 H14 B F2 N3 O2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C21 H14 B F2 N3 O2	390.1203	390.120328098013	-2.01563268700511	-5.1933455655049	88.93

Compound Spectra (Zoomed)

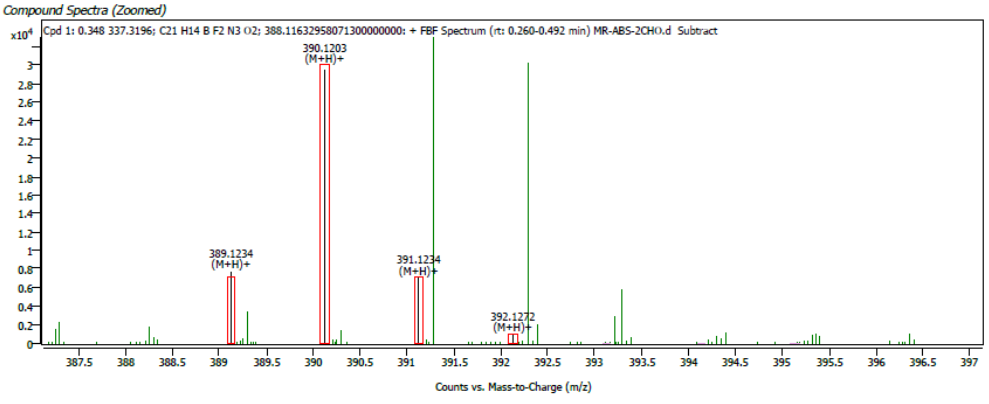

Fig. S48 High resolution mass spectrum of **9**.

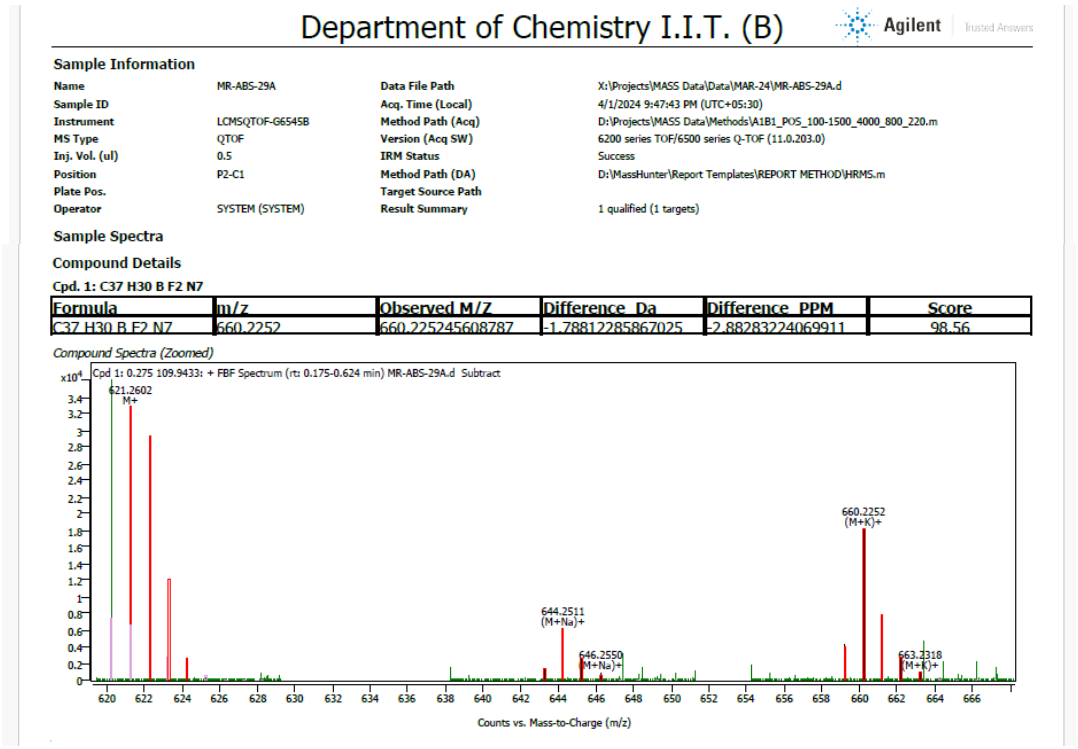

Fig. S49 High resolution mass spectrum of **10**.

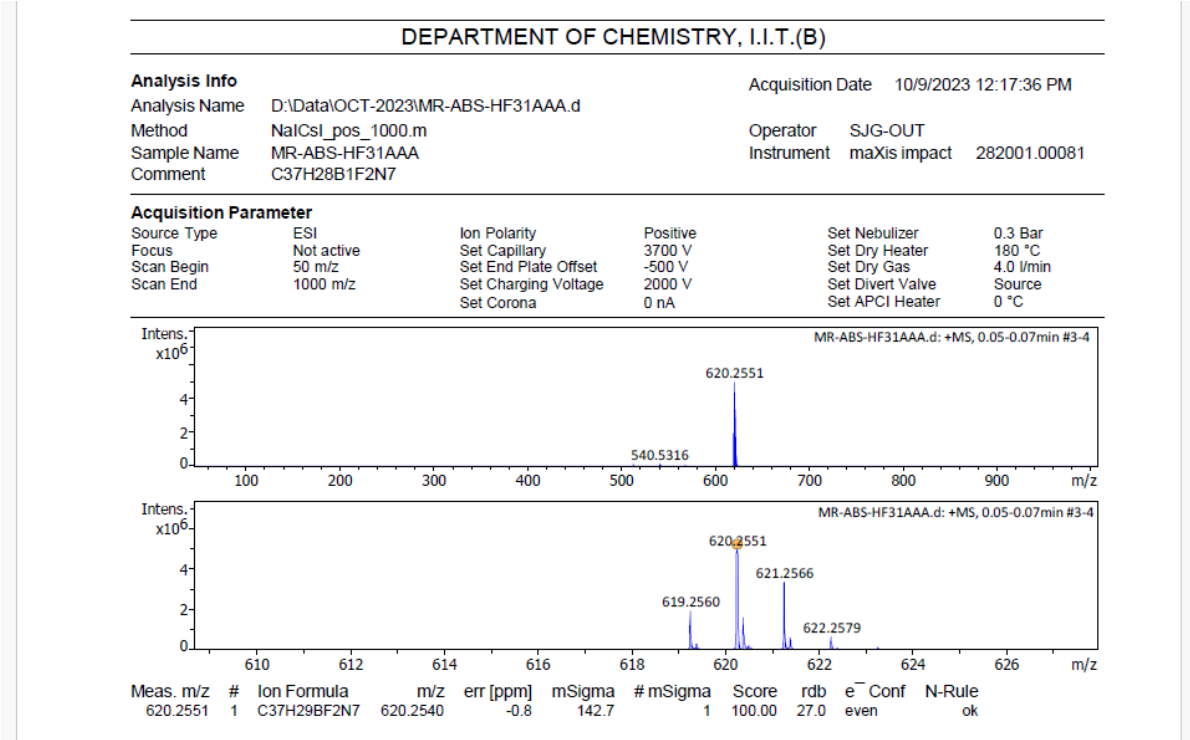

Fig. S50 High resolution mass spectrum of **11**.

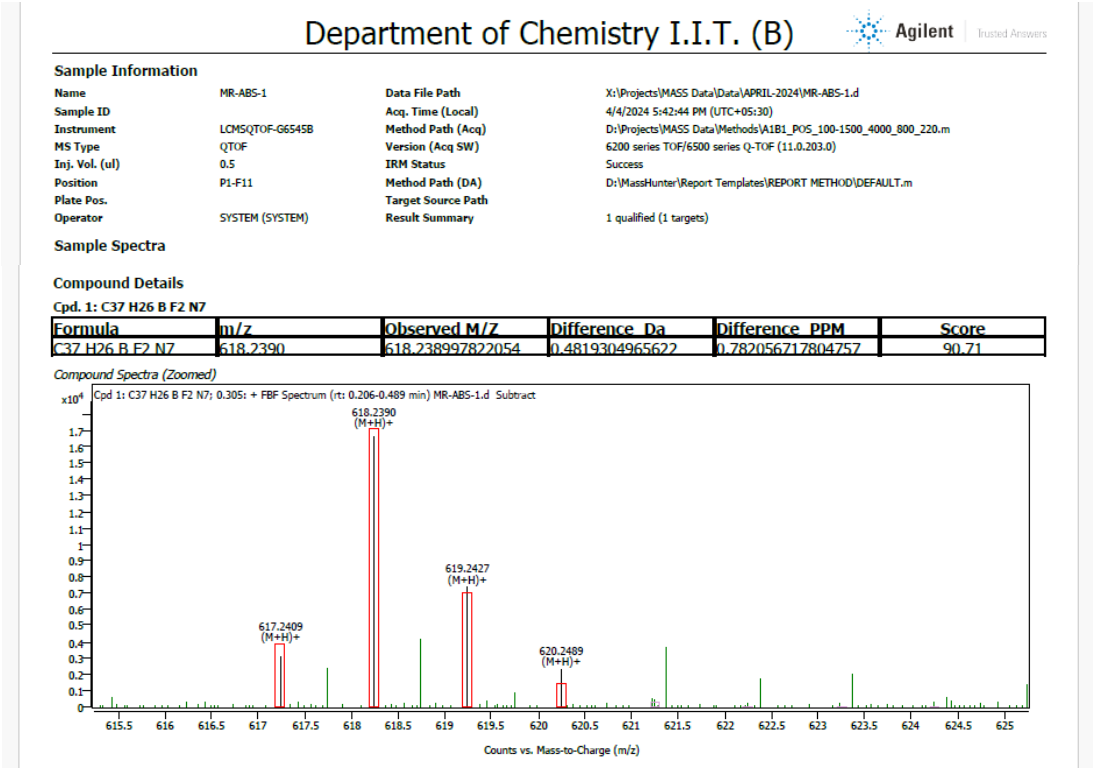

Fig. S51 High resolution mass spectrum of **12**.

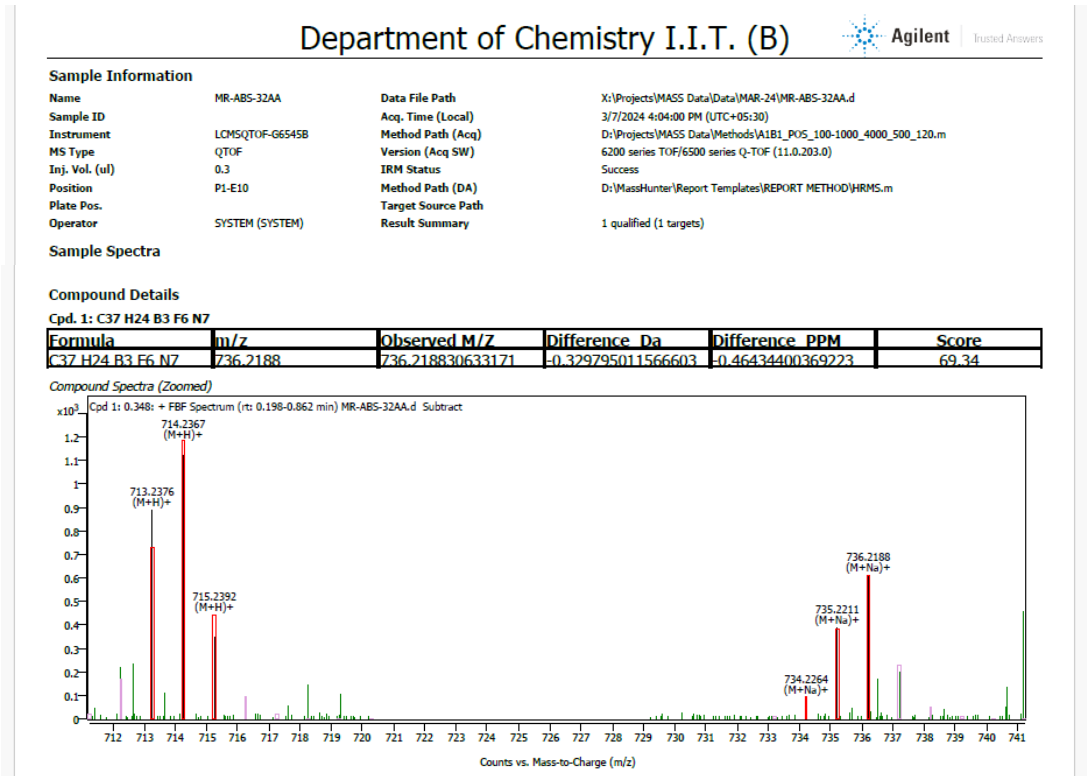

Fig. S52 High resolution mass spectrum of **6**.

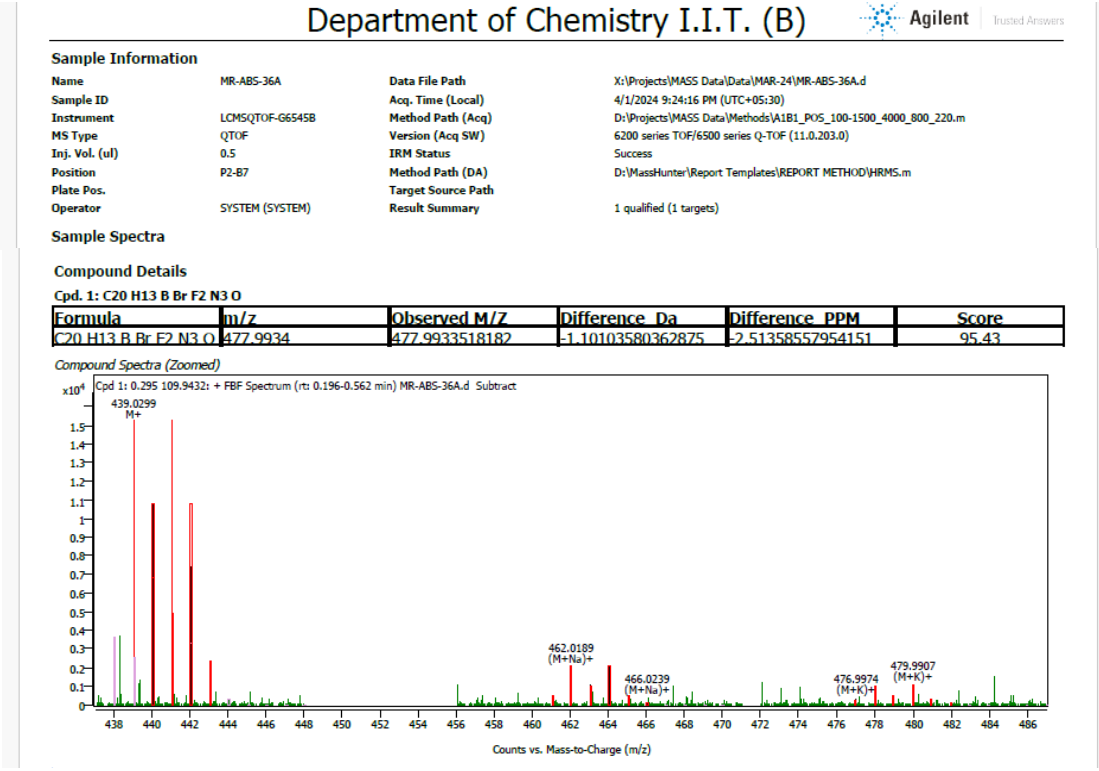

Fig. S53 High resolution mass spectrum of **13**.

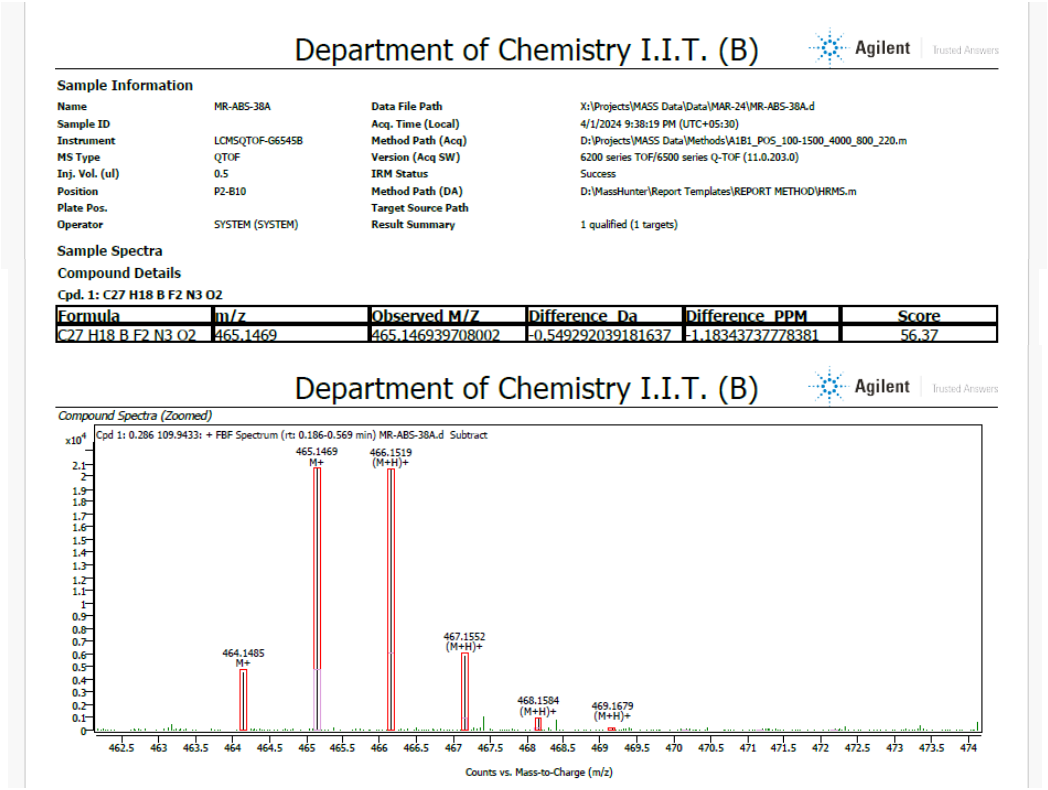

Fig. S54 High resolution mass spectrum of **14**.

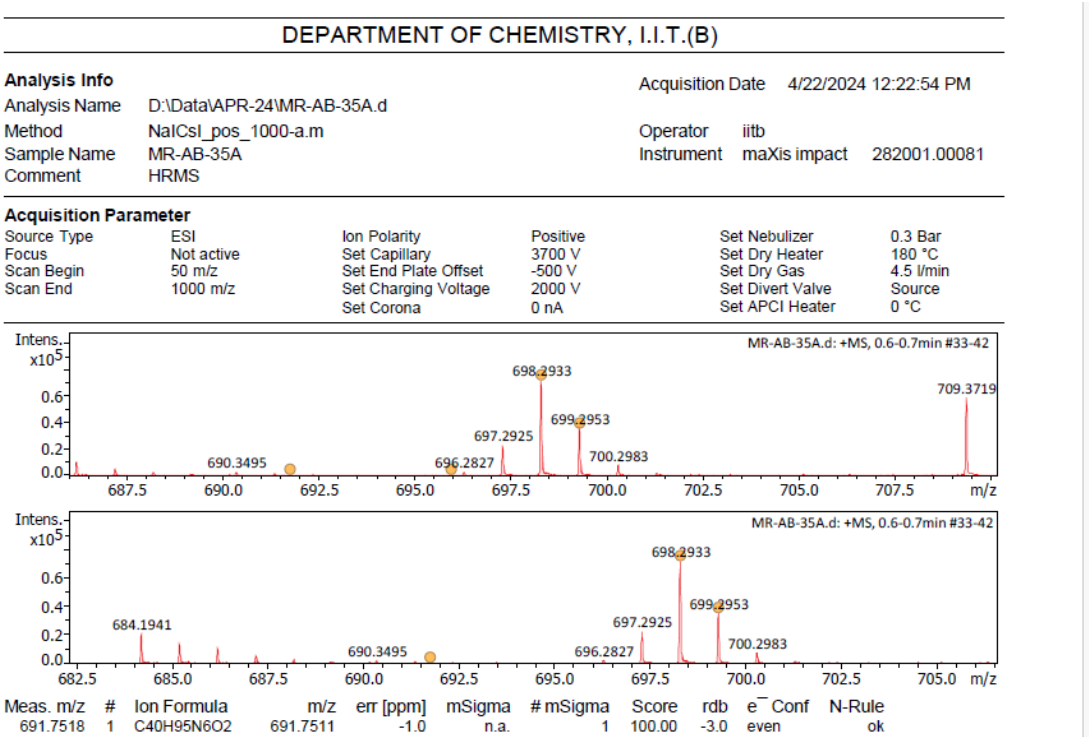

Fig. S55 High resolution mass spectrum of **15**.

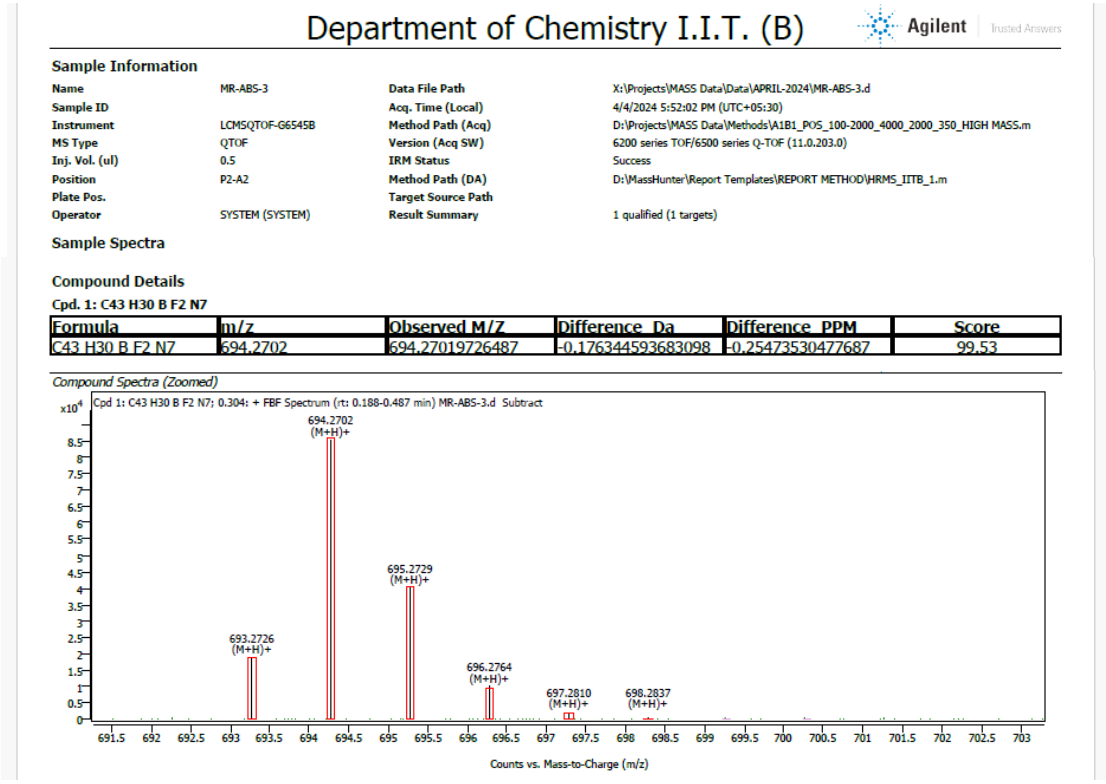

Fig. S56 High resolution mass spectrum of **16**.

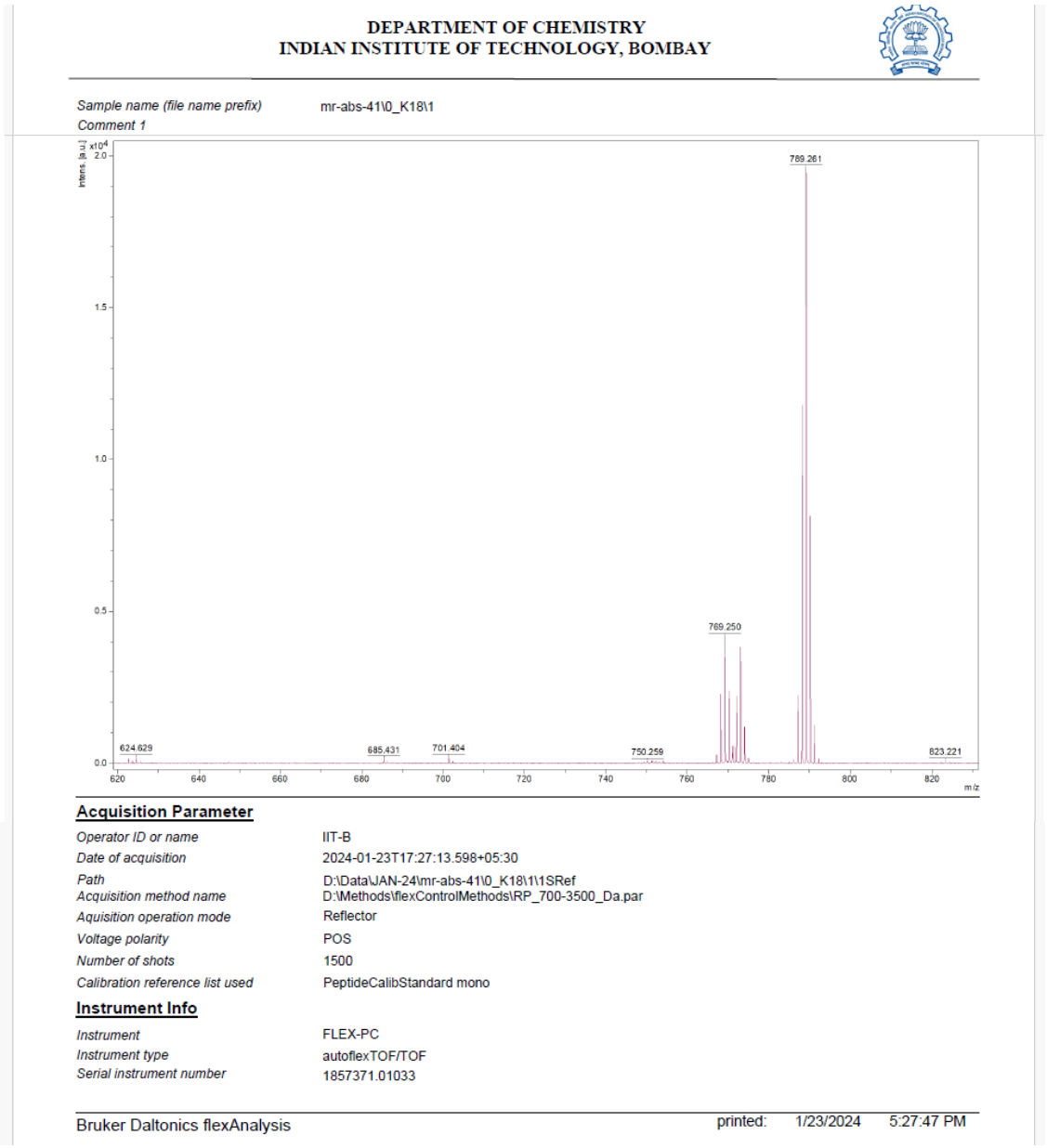

Fig. S57 High resolution mass spectrum of **7**.

Crystallographic Data

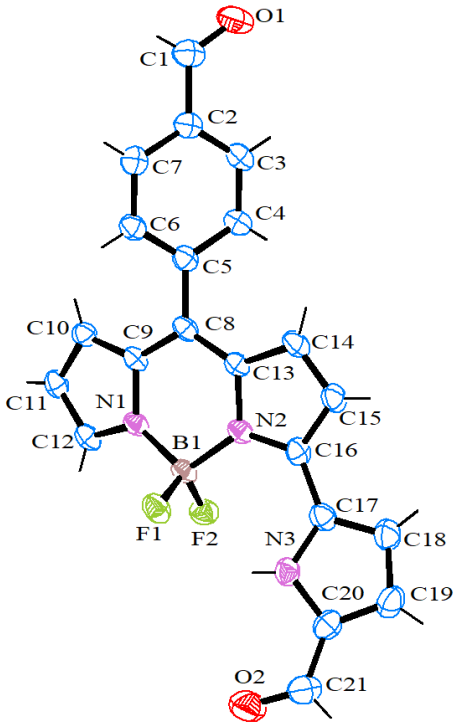

Fig. S58 ORTEP drawing (ellipsoids at 50% probability) of complex **9.**

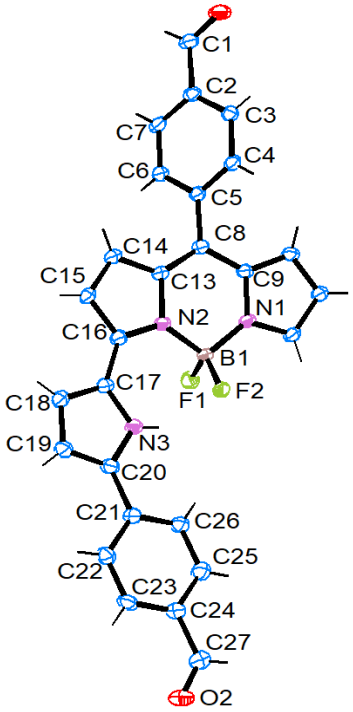

Fig. S59 ORTEP drawing (ellipsoids at 50% probability) of complex **14.**

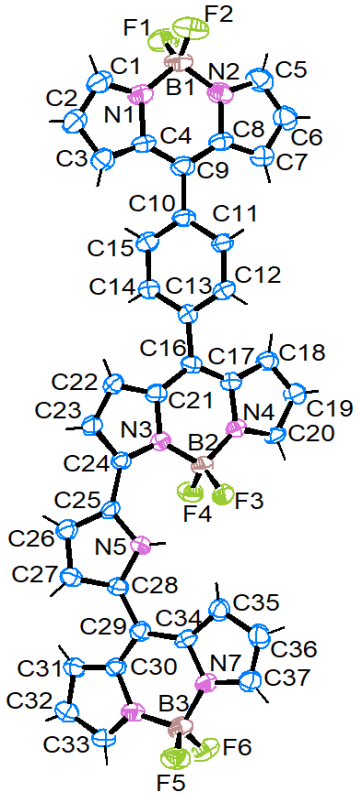

Fig. S60 ORTEP drawing (ellipsoids at 50% probability) of complex **6.**

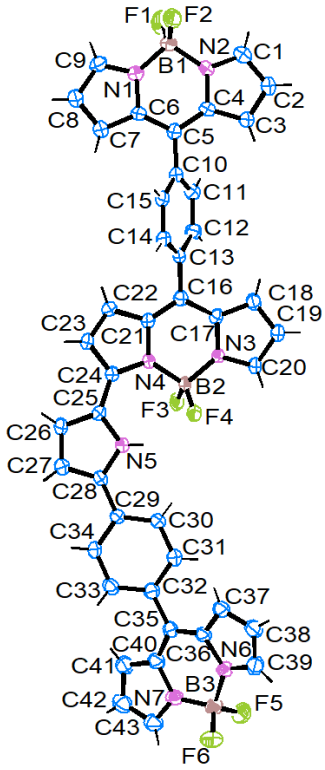

Fig. S61 ORTEP drawing (ellipsoids at 50% probability) of complex **7.**

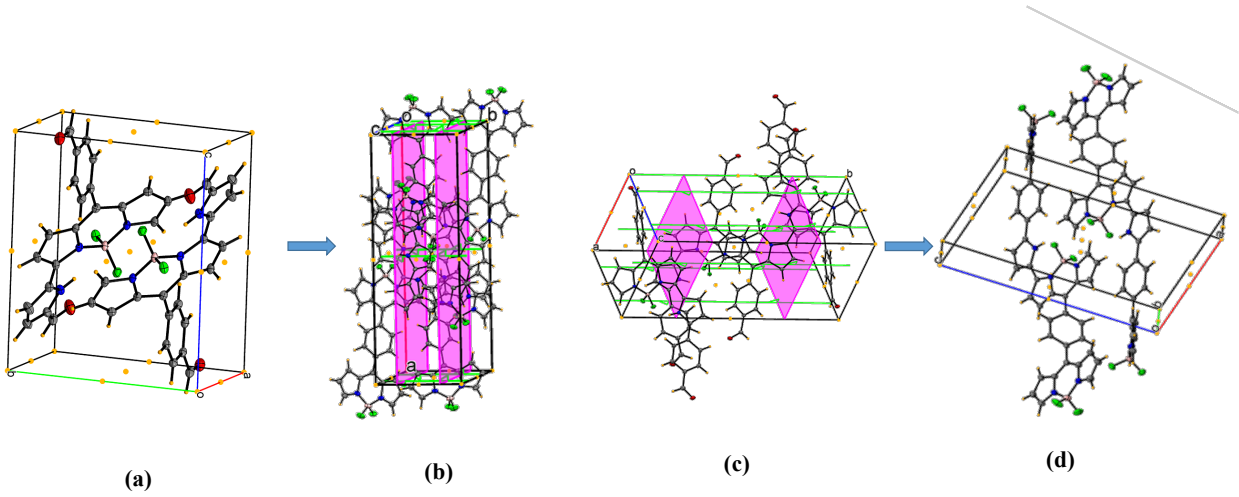

Fig. 62. Symmetry operation in the unit cell of compounds (a) **6**, (b) **7** (c) **9,** and (d) **14**.

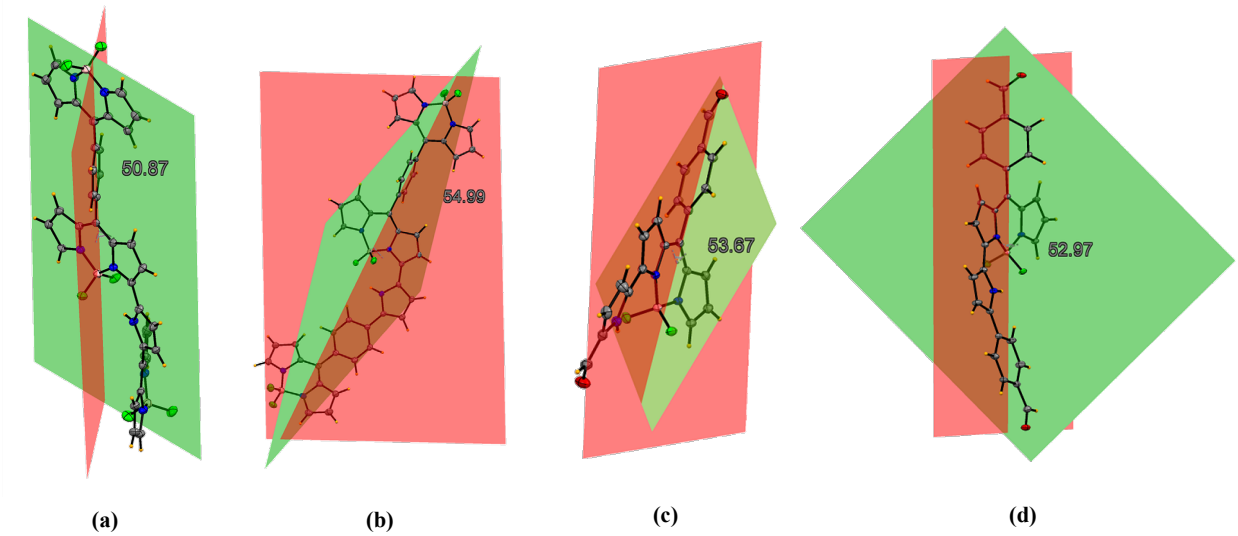

Fig. 63 Orientation of *meso*-phenyl ring with respect to the 3-pyrrolyl dipyrrin unit plane in the compounds (a) **6**, (b) **7** (c) **9**, and (d) **14**.

Table S1 Crystallographic data and processing parameters of compounds **6**, **7**, **9**, and **14**.

Compounds	**6**	**7**	**9**	**14**
CCDC	2349801	2349802	2349799	2349800
Empirical formula	$C_{37}H_{24}B_3F_6N_7$	$C_{43}H_{28}B_3F_6N_7$	$C_{21}H_{14}BF_2N_3O_2$	$C_{27}H_{18}BF_2N_3O_2$
Formula weight	713.06	789.212	389.16	465.284
Temperature/k	150.15	150.00	150.00	100.00
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	P-1	$P2_1/c$
a/Å	22.3780(11)	8.9117(14)	7.786(3)	11.489(2)
b/Å	7.7085(4)	12.6161(17)	10.093(3)	19.692(3)
c/Å	18.3524(8)	17.867(3)	11.219(4)	9.7156(18)
α/°	90	108.165(5)	87.523(9)	90
β/°	90.338(5)	98.751(6)	85.753(10)	108.980(7)
γ/°	90	101.583(6)	77.440(8)	90
Volume/$Å^3$	3165.7(3)	1819.4(5)	857.8(5)	2078.5(7)
Z	4	2	2	4
$\rho_{calc}g/cm^3$	1.496	1.441	1.507	1.487
μ/mm^{-1}	0.115	0.107	0.113	0.107
F(000)	1456.0	808.6	400.3	960.7
Crystal size/mm^3	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.4 × 0.2 × 0.2	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ	4.43 to 49.99	4.8 to 50	4.14 to 50	4.14 to 50
Index ranges	-26 ≤ h ≤ 26, -9 ≤ k ≤ 7, -21 ≤ l ≤ 21	-10 ≤ h ≤ 10, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14	-15 ≤ h ≤ 15, -28 ≤ k ≤ 28, -13 ≤ l ≤ 13
Reflections collected	24138	39010	11611	74928
Independent reflections	5382 [R_{int} = 0.1530, R_{sigma} = 0.1739]	6398 [R_{int} = 0.1234, R_{sigma} = 0.0924]	3016 [R_{int} = 0.0931, R_{sigma} = 0.1001]	3645 [R_{int} = 0.0927, R_{sigma} = 0.0627]
Data/restraints/ parameters	5382/0/478	6398/0/532	3016/0/262	3645/0/317
Goodness-of-fit F^2	0.900	1.142	1.078	1.059
Final R indexes [i>=2σ (i)]	R_1 = 0.0761, wR_2 = 0.1431	R_1 = 0.0622, wR_2 = 0.1560	R_1 = 0.0647, wR_2 = 0.1619	R_1 = 0.0545, wR_2 = 0.1191
Final R indexes [all data]	R_1 = 0.2035, wR_2 = 0.1841	R_1 = 0.1224, wR_2 = 0.1977	R_1 = 0.0972, wR_2 = 0.1840	R_1 = 0.0597, wR_2 = 0.1218
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.34	0.62/-0.49	0.38/-0.43	0.87/-0.31

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.
[c] wR2 = $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2+bP]$, $P = (F_o^2+2F_c^2)/3$

Coordination bond lengths (Å) and angles (°)

Table S2 Bond Lengths for **9.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.395(4)	C7	C6	1.385(4)
F2	B1	1.380(4)	C7	C2	1.390(4)
N1	C9	1.396(4)	C6	C5	1.392(5)
N1	C12	1.352(4)	C14	C15	1.367(5)
N1	B1	1.541(4)	C12	C11	1.387(4)
O1	C1	1.216(4)	C2	C3	1.392(5)
N2	C13	1.406(4)	C2	C1	1.485(4)
N2	C16	1.359(4)	C16	C15	1.401(4)
N2	B1	1.555(4)	C16	C17	1.450(4)
N3	C20	1.381(4)	C11	C10	1.369(4)
N3	C17	1.353(4)	C5	C4	1.401(4)
O2	C21	1.218(4)	C4	C3	1.384(4)
C13	C8	1.384(4)	C20	C19	1.384(5)
C13	C14	1.422(4)	C20	C21	1.412(5)
C9	C8	1.405(4)	C17	C18	1.382(5)
C9	C10	1.416(4)	C18	C19	1.383(5)

Table S3 Bond Angles for **9.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N1	C9	106.7(3)	C17	C16	C15	122.6(3)
B1	N1	C9	126.5(2)	C10	C11	C12	107.6(3)
B1	N1	C12	126.8(3)	C6	C5	C8	120.7(3)
C16	N2	C13	107.9(2)	C4	C5	C8	120.2(3)
B1	N2	C13	123.0(3)	C4	C5	C6	119.1(3)
B1	N2	C16	128.9(3)	C3	C4	C5	120.8(3)
C17	N3	C20	109.4(3)	C11	C10	C9	107.1(3)
C8	C13	N2	123.1(3)	C4	C3	C2	119.8(3)
C14	C13	N2	107.0(3)	C19	C20	N3	107.2(3)
C14	C13	C8	129.8(3)	C21	C20	N3	123.1(3)
C8	C9	N1	119.9(3)	C21	C20	C19	129.6(3)
C10	C9	N1	108.0(3)	C16	C15	C14	108.2(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	C9	C8	131.6(3)	C16	C17	N3	126.2(3)
C9	C8	C13	119.7(3)	C18	C17	N3	107.7(3)
C5	C8	C13	119.6(3)	C18	C17	C16	125.9(3)
C5	C8	C9	120.7(3)	C2	C1	O1	123.7(4)
C2	C7	C6	120.8(3)	C19	C18	C17	108.2(3)
C5	C6	C7	120.0(3)	C18	C19	C20	107.5(3)
C15	C14	C13	107.7(3)	C20	C21	O2	126.1(4)
C11	C12	N1	110.5(3)	F2	B1	F1	107.7(3)
C3	C2	C7	119.6(3)	N1	B1	F1	110.7(3)
C1	C2	C7	119.6(3)	N1	B1	F2	110.6(2)
C1	C2	C3	120.8(3)	N2	B1	F1	109.8(2)
C15	C16	N2	109.2(3)	N2	B1	F2	111.7(3)
C17	C16	N2	128.2(3)	N2	B1	N1	106.4(2)

Table S4 Bond Lengths for **14.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F2	B1	1.403(3)	C20	C19	1.381(4)
F1	B1	1.384(3)	C9	C10	1.399(3)
O2	C27	1.206(3)	C16	C17	1.433(3)
O1	C1	1.213(3)	C16	C15	1.425(3)
N3	C20	1.354(3)	C17	C18	1.386(4)
N3	C17	1.366(3)	C4	C3	1.376(3)
N2	C16	1.357(3)	C2	C3	1.398(4)
N2	C13	1.408(3)	C2	C7	1.389(4)
N2	B1	1.560(3)	C2	C1	1.477(3)
N1	C9	1.382(3)	C12	C11	1.393(3)
N1	C12	1.360(3)	C13	C14	1.422(3)
N1	B1	1.527(3)	C6	C7	1.387(3)
C21	C20	1.459(3)	C14	C15	1.349(3)
C21	C22	1.398(3)	C11	C10	1.390(3)
C21	C26	1.388(4)	C22	C23	1.371(4)
C5	C8	1.485(3)	C24	C23	1.387(4)
C5	C4	1.397(3)	C24	C27	1.471(3)
C5	C6	1.393(3)	C24	C25	1.383(4)
C8	C9	1.421(3)	C26	C25	1.383(4)
C8	C13	1.383(3)	C18	C19	1.389(4)

Table S5 Bond Angles for **14.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C17	N3	C20	111.0(2)	C1	C2	C3	120.6(2)
C13	N2	C16	107.49(19)	C1	C2	C7	120.1(2)
B1	N2	C16	129.9(2)	C11	C12	N1	109.5(2)
B1	N2	C13	122.07(19)	C2	C3	C4	120.1(2)
C12	N1	C9	108.0(2)	C8	C13	N2	121.8(2)
B1	N1	C9	126.19(19)	C14	C13	N2	107.7(2)
B1	N1	C12	125.70(19)	C14	C13	C8	130.1(2)
C22	C21	C20	120.1(2)	C7	C6	C5	120.3(2)
C26	C21	C20	122.0(2)	C15	C14	C13	107.7(2)
C26	C21	C22	117.9(2)	C10	C11	C12	106.9(2)
C4	C5	C8	120.5(2)	C11	C10	C9	107.7(2)
C6	C5	C8	120.5(2)	C14	C15	C16	108.3(2)
C6	C5	C4	118.9(2)	C23	C22	C21	121.0(2)
C9	C8	C5	119.5(2)	C27	C24	C23	121.4(2)
C13	C8	C5	120.1(2)	C25	C24	C23	118.8(2)
C13	C8	C9	120.3(2)	C25	C24	C27	119.8(2)
C21	C20	N3	122.5(2)	C6	C7	C2	120.5(2)
C19	C20	N3	106.8(2)	C24	C23	C22	120.7(2)
C19	C20	C21	130.7(2)	C2	C1	O1	123.9(2)
C8	C9	N1	119.7(2)	C24	C27	O2	125.9(3)
C10	C9	N1	108.0(2)	C25	C26	C21	121.0(2)
C10	C9	C8	132.2(2)	C19	C18	C17	107.9(2)
C17	C16	N2	127.8(2)	C18	C19	C20	108.1(2)
C15	C16	N2	108.8(2)	C26	C25	C24	120.6(2)
C15	C16	C17	123.3(2)	F1	B1	F2	107.9(2)
C16	C17	N3	126.6(2)	N2	B1	F2	111.0(2)
C18	C17	N3	106.3(2)	N2	B1	F1	109.8(2)
C18	C17	C16	127.0(2)	N1	B1	F2	108.7(2)
C3	C4	C5	120.9(2)	N1	B1	F1	112.1(2)
C7	C2	C3	119.3(2)	N1	B1	N2	107.34(19)

Table S6 Bond Lengths for **6.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F3	B2	1.402(5)	C16	C21	1.407(5)
F4	B2	1.384(7)	C16	C17	1.389(6)
F5	B3	1.383(6)	C13	C12	1.387(6)
F1	B1	1.382(6)	C13	C14	1.394(5)
F6	B3	1.385(7)	C21	C22	1.401(6)
F2	B1	1.374(8)	C34	C29	1.408(5)
N3	C24	1.355(5)	C34	C35	1.409(6)
N3	C21	1.414(6)	C31	C32	1.384(6)
N3	B2	1.531(7)	C12	C11	1.376(6)
N4	C20	1.347(5)	C23	C22	1.357(6)
N4	C17	1.397(5)	C20	C19	1.395(6)
N4	B2	1.529(6)	C11	C10	1.396(5)
N5	C25	1.367(5)	C10	C15	1.383(6)
N5	C28	1.367(5)	C10	C9	1.487(6)
N6	C30	1.397(5)	C4	C9	1.375(6)
N6	C33	1.324(6)	C4	C3	1.404(6)
N6	B3	1.539(6)	C28	C29	1.450(6)
N7	C34	1.390(5)	C28	C27	1.385(6)
N7	C37	1.344(5)	C27	C26	1.382(6)
N7	B3	1.545(7)	C18	C17	1.404(6)
N1	C4	1.414(5)	C18	C19	1.366(6)
N1	C1	1.323(6)	C37	C36	1.377(7)
N1	B1	1.544(7)	C15	C14	1.384(6)
N2	C8	1.400(6)	C35	C36	1.369(6)
N2	C5	1.349(5)	C33	C32	1.399(6)
N2	B1	1.538(8)	C7	C8	1.409(6)
C24	C25	1.453(6)	C7	C6	1.350(6)
C24	C23	1.407(6)	C8	C9	1.418(6)
C25	C26	1.382(5)	C5	C6	1.393(7)
C30	C31	1.393(6)	C3	C2	1.367(7)
C30	C29	1.395(6)	C1	C2	1.401(6)
C16	C13	1.477(6)			

Table S7 Bond Angles for **6.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	N3	C21	106.3(4)	N5	C28	C29	123.9(4)
C24	N3	B2	128.1(4)	N5	C28	C27	107.2(4)
C21	N3	B2	125.4(4)	C27	C28	C29	128.8(4)
C20	N4	C17	107.3(4)	C30	C29	C34	120.2(4)
C20	N4	B2	125.8(4)	C30	C29	C28	118.6(4)
C17	N4	B2	126.7(4)	C34	C29	C28	121.2(5)
C25	N5	C28	109.8(4)	C26	C27	C28	107.7(4)
C30	N6	B3	125.6(4)	C19	C18	C17	108.4(4)
C33	N6	C30	108.3(4)	N7	C37	C36	110.0(4)
C33	N6	B3	126.1(4)	C23	C22	C21	107.6(5)
C34	N7	B3	125.8(4)	N4	C17	C18	107.2(4)
C37	N7	C34	107.8(4)	C16	C17	N4	119.5(4)
C37	N7	B3	125.4(4)	C16	C17	C18	133.1(5)
C4	N1	B1	126.2(5)	C25	C26	C27	108.3(4)
C1	N1	C4	106.7(4)	C14	C15	C10	121.3(4)
C1	N1	B1	127.0(5)	C36	C35	C34	107.6(5)
C8	N2	B1	127.0(4)	C15	C14	C13	120.2(4)
C5	N2	C8	105.5(5)	N6	C33	C32	110.3(5)
C5	N2	B1	126.6(5)	C6	C7	C8	107.1(5)
N3	C24	C25	126.4(4)	N2	C8	C7	108.8(4)
N3	C24	C23	109.6(4)	N2	C8	C9	118.8(5)
C23	C24	C25	123.9(4)	C7	C8	C9	132.3(5)
N5	C25	C24	126.3(4)	C18	C19	C20	106.8(4)
N5	C25	C26	107.0(4)	C4	C9	C10	120.1(4)
C26	C25	C24	126.7(4)	C4	C9	C8	121.7(5)
C31	C30	N6	107.2(4)	C8	C9	C10	118.0(5)
C31	C30	C29	131.9(4)	C35	C36	C37	107.6(4)
C29	C30	N6	120.9(4)	N2	C5	C6	110.8(5)
C21	C16	C13	119.3(5)	C31	C32	C33	106.1(4)
C17	C16	C13	119.0(4)	C2	C3	C4	108.6(5)
C17	C16	C21	121.7(5)	C7	C6	C5	107.7(5)
C12	C13	C16	119.1(4)	N1	C1	C2	111.8(5)
C12	C13	C14	118.5(5)	C3	C2	C1	105.8(5)
C14	C13	C16	122.4(4)	F3	B2	N3	110.0(4)
C16	C21	N3	119.5(4)	F3	B2	N4	109.9(4)
C22	C21	N3	108.4(4)	F4	B2	F3	108.0(4)
C22	C21	C16	132.1(5)	F4	B2	N3	111.5(4)
N7	C34	C29	120.1(5)	F4	B2	N4	110.4(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N7	C34	C35	107.0(4)	N4	B2	N3	107.1(4)
C29	C34	C35	133.0(5)	F5	B3	F6	108.8(5)
C32	C31	C30	108.1(4)	F5	B3	N6	111.5(4)
C11	C12	C13	121.2(4)	F5	B3	N7	110.2(5)
C22	C23	C24	108.0(4)	F6	B3	N6	109.7(5)
N4	C20	C19	110.2(4)	F6	B3	N7	110.5(4)
C12	C11	C10	120.6(5)	N6	B3	N7	106.1(4)
C11	C10	C9	120.8(4)	F1	B1	N1	111.1(5)
C15	C10	C11	118.3(5)	F1	B1	N2	109.3(5)
C15	C10	C9	121.0(4)	F2	B1	F1	110.0(5)
C9	C4	N1	120.1(4)	F2	B1	N1	110.1(5)
C9	C4	C3	132.7(5)	F2	B1	N2	110.6(5)
C3	C4	N1	107.1(4)	N2	B1	N1	105.7(4)

Table S8 Bond Lengths for **7.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F4	B2	1.401(5)	C13	C14	1.402(5)
F3	B2	1.377(4)	C13	C12	1.385(5)
F5	B3	1.387(5)	C29	C28	1.448(5)
F6	B3	1.383(5)	C29	C30	1.402(5)
F2	B1	1.365(5)	C29	C34	1.391(5)
F1	B1	1.393(6)	C25	C26	1.398(5)
N3	C17	1.382(4)	C23	C22	1.355(5)
N3	C20	1.353(4)	C35	C36	1.405(5)
N3	B2	1.525(5)	C35	C32	1.478(5)
N5	C25	1.381(4)	C35	C40	1.402(5)
N5	C28	1.370(4)	C18	C19	1.389(5)
N4	C21	1.404(4)	C36	C37	1.410(5)
N4	C24	1.361(4)	C6	C7	1.411(5)
N4	B2	1.567(5)	C6	C5	1.405(5)
N6	C36	1.401(4)	C28	C27	1.389(5)
N6	C39	1.344(5)	C12	C11	1.388(4)
N6	B3	1.551(5)	C32	C31	1.398(5)
N1	C6	1.382(4)	C32	C33	1.410(5)
N1	C9	1.338(5)	C30	C31	1.380(5)
N1	B1	1.526(5)	C10	C11	1.394(5)
N2	C4	1.398(4)	C10	C5	1.493(5)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C1	1.327(5)	C34	C33	1.382(5)
N2	B1	1.557(5)	C7	C8	1.375(5)
N7	C40	1.402(4)	C4	C5	1.383(5)
N7	C43	1.349(4)	C4	C3	1.406(5)
N7	B3	1.541(6)	C19	C20	1.392(5)
C15	C14	1.377(4)	C37	C38	1.366(5)
C15	C10	1.392(5)	C27	C26	1.392(5)
C16	C17	1.425(5)	C8	C9	1.398(5)
C16	C21	1.379(5)	C3	C2	1.377(5)
C16	C13	1.487(4)	C38	C39	1.383(5)
C17	C18	1.401(5)	C40	C41	1.409(5)
C21	C22	1.419(5)	C41	C42	1.383(5)
C24	C25	1.418(4)	C43	C42	1.401(6)
C24	C23	1.422(4)	C1	C2	1.397(5)

Table S9 Bond Angles for **7.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	N3	C17	108.1(3)	C27	C28	C29	131.1(3)
B2	N3	C17	127.2(3)	C11	C12	C13	120.8(3)
B2	N3	C20	124.7(3)	C31	C32	C35	119.7(3)
C28	N5	C25	110.6(3)	C33	C32	C35	122.4(3)
C24	N4	C21	107.8(3)	C33	C32	C31	117.9(3)
B2	N4	C21	122.9(3)	C31	C30	C29	121.2(3)
B2	N4	C24	128.6(3)	C11	C10	C15	118.7(3)
C39	N6	C36	107.4(3)	C5	C10	C15	120.5(3)
B3	N6	C36	125.9(3)	C5	C10	C11	120.8(3)
B3	N6	C39	126.5(3)	C33	C34	C29	121.5(3)
C9	N1	C6	107.9(3)	C8	C7	C6	107.6(3)
B1	N1	C6	126.3(3)	C10	C11	C12	120.7(3)
B1	N1	C9	125.7(3)	C5	C4	N2	121.4(3)
C1	N2	C4	107.9(3)	C3	C4	N2	107.2(3)
B1	N2	C4	124.6(3)	C3	C4	C5	131.2(3)
B1	N2	C1	127.5(3)	C10	C5	C6	119.1(3)
C43	N7	C40	107.7(3)	C4	C5	C6	120.1(3)
B3	N7	C40	126.3(3)	C4	C5	C10	120.7(3)
B3	N7	C43	125.6(3)	C20	C19	C18	107.0(3)
C10	C15	C14	120.4(3)	C19	C20	N3	109.6(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	C16	C17	120.1(3)	C38	C37	C36	107.6(3)
C13	C16	C17	119.2(3)	C26	C27	C28	108.4(3)
C13	C16	C21	120.6(3)	C30	C31	C32	121.0(4)
C16	C17	N3	119.5(3)	C34	C33	C32	120.5(3)
C18	C17	N3	108.0(3)	C9	C8	C7	106.5(3)
C18	C17	C16	132.3(3)	C2	C3	C4	107.7(3)
C16	C21	N4	122.6(3)	C27	C26	C25	108.0(3)
C22	C21	N4	107.6(3)	C39	C38	C37	107.7(4)
C22	C21	C16	129.7(3)	C38	C39	N6	110.2(4)
C25	C24	N4	127.8(3)	C35	C40	N7	120.3(3)
C23	C24	N4	108.5(3)	C41	C40	N7	107.2(3)
C23	C24	C25	123.7(3)	C41	C40	C35	132.4(4)
C14	C13	C16	120.1(3)	C42	C41	C40	108.2(4)
C12	C13	C16	121.7(3)	C42	C43	N7	110.4(3)
C12	C13	C14	118.2(3)	C8	C9	N1	110.4(3)
C13	C14	C15	121.2(3)	C43	C42	C41	106.5(4)
C30	C29	C28	121.1(3)	C2	C1	N2	110.5(3)
C34	C29	C28	121.1(3)	C1	C2	C3	106.6(4)
C34	C29	C30	117.8(3)	F3	B2	F4	108.7(3)
C24	C25	N5	125.7(3)	N3	B2	F4	109.4(3)
C26	C25	N5	106.3(3)	N3	B2	F3	112.1(3)
C26	C25	C24	128.1(3)	N4	B2	F4	110.2(3)
C22	C23	C24	108.3(3)	N4	B2	F3	109.4(3)
C32	C35	C36	118.1(3)	N4	B2	N3	107.0(3)
C40	C35	C36	119.9(3)	F6	B3	F5	109.1(3)
C40	C35	C32	122.0(3)	N6	B3	F5	109.9(3)
C23	C22	C21	107.8(3)	N6	B3	F6	110.9(3)
C19	C18	C17	107.4(3)	N7	B3	F5	110.9(3)
C35	C36	N6	120.7(3)	N7	B3	F6	110.5(3)
C37	C36	N6	107.1(3)	N7	B3	N6	105.5(3)
C37	C36	C35	132.2(3)	F1	B1	F2	109.5(3)
C7	C6	N1	107.6(3)	N1	B1	F2	110.8(4)
C5	C6	N1	120.7(3)	N1	B1	F1	110.0(4)
C5	C6	C7	131.6(3)	N2	B1	F2	110.8(4)
C29	C28	N5	122.1(3)	N2	B1	F1	109.2(4)
C27	C28	N5	106.8(3)	N2	B1	N1	106.5(3)

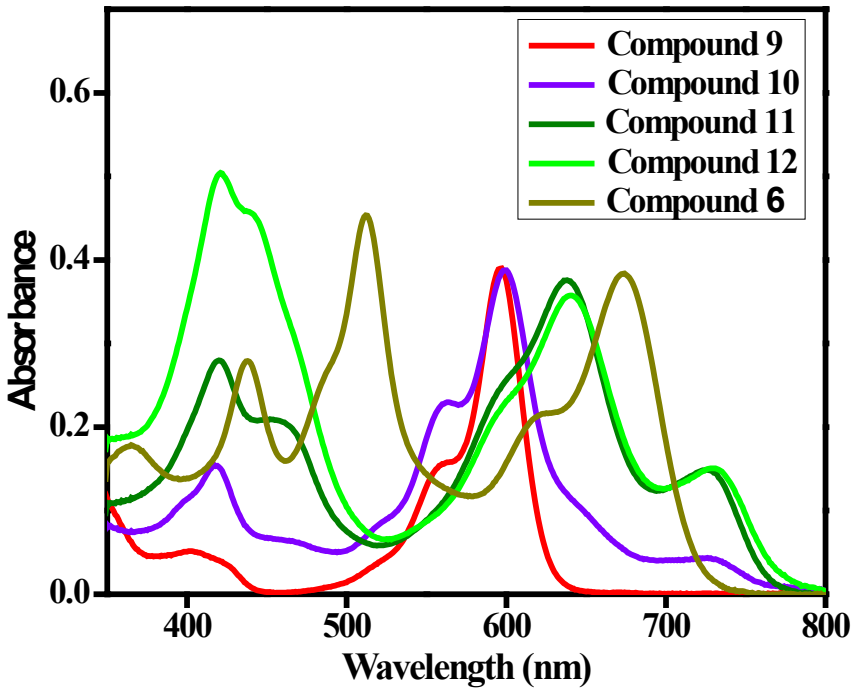

Fig. S64 Absorption spectra of **9, 10, 11, 12** and **6.** *Condition:* **[9-12]** = **[6]=** 10μM in Toluene.

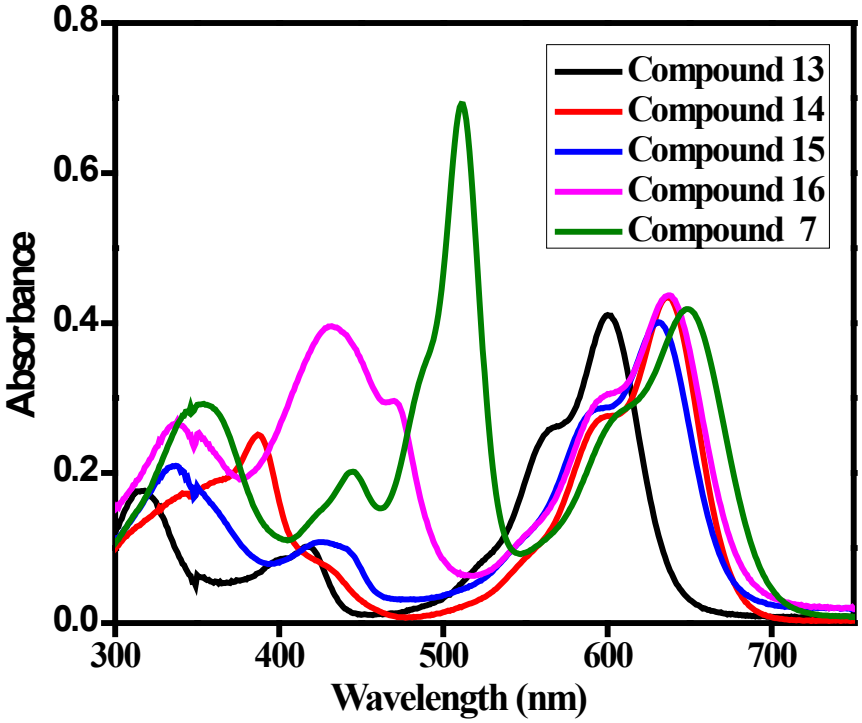

Fig. S65 (a) Absorption spectra of **13, 14, 15, 16** and **7.** *Condition:* **[13-16]** = **[7] =** 10μM in toluene.

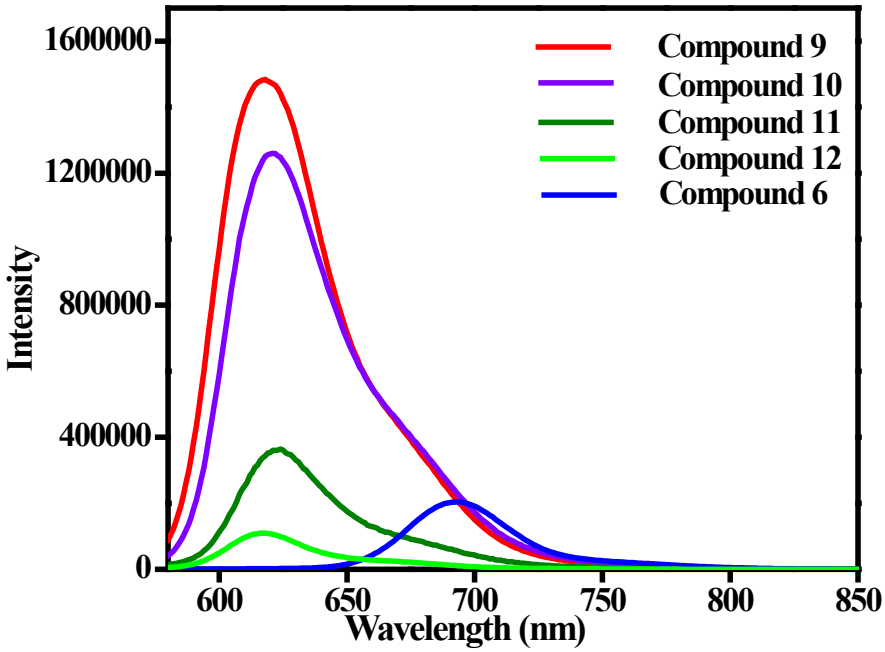

Fig. S66 Emission spectra of **9, 10, 11, 12** and **6.** *Condition:* **[9-12]** = **[6] =** 1μM in Toluene.

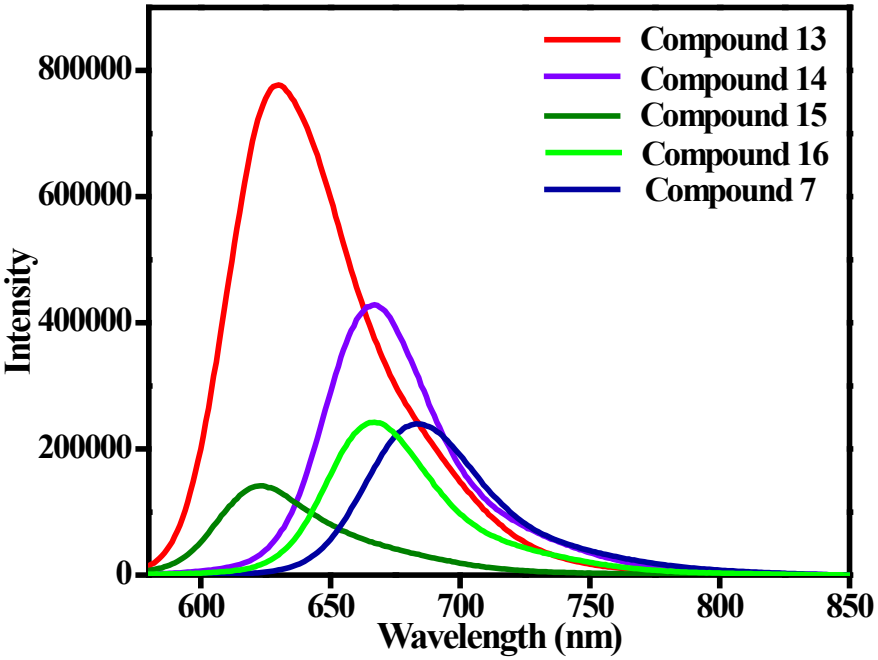

Fig. S67 emission spectra of **13-16** and **7**. *Conditions:* **[13-16] and [7]** = 1μM in Toluene.

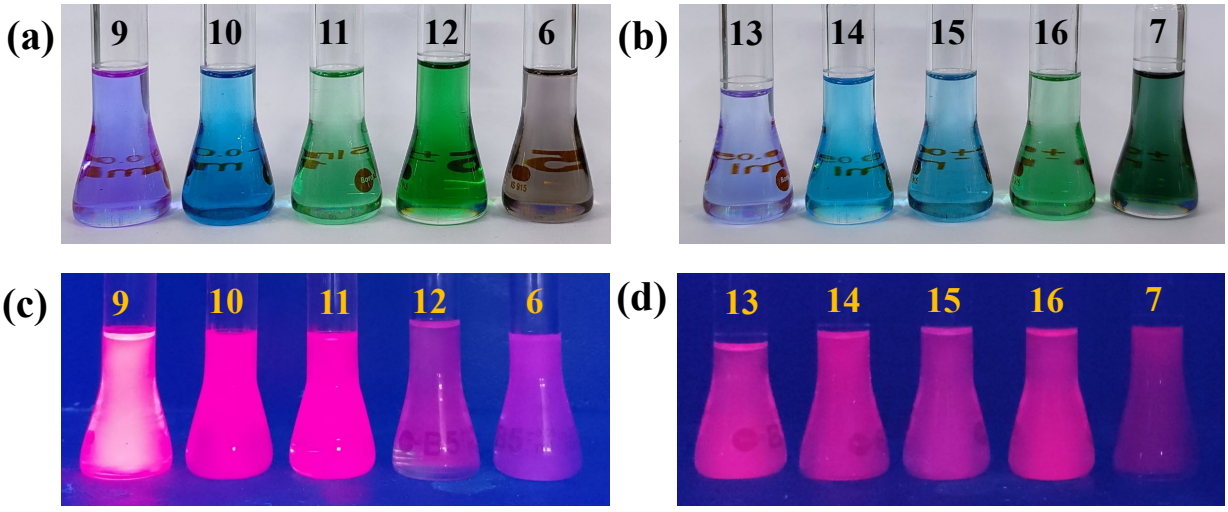

Fig. S68 Photograph depicting the color of solutions of compounds **9**, **10**, **11**, **12,** and **6** (leftside) and **13**, **14**, **15**, **16** and **7** (rightside) in (a, b) naked eye (c, d) UV light.

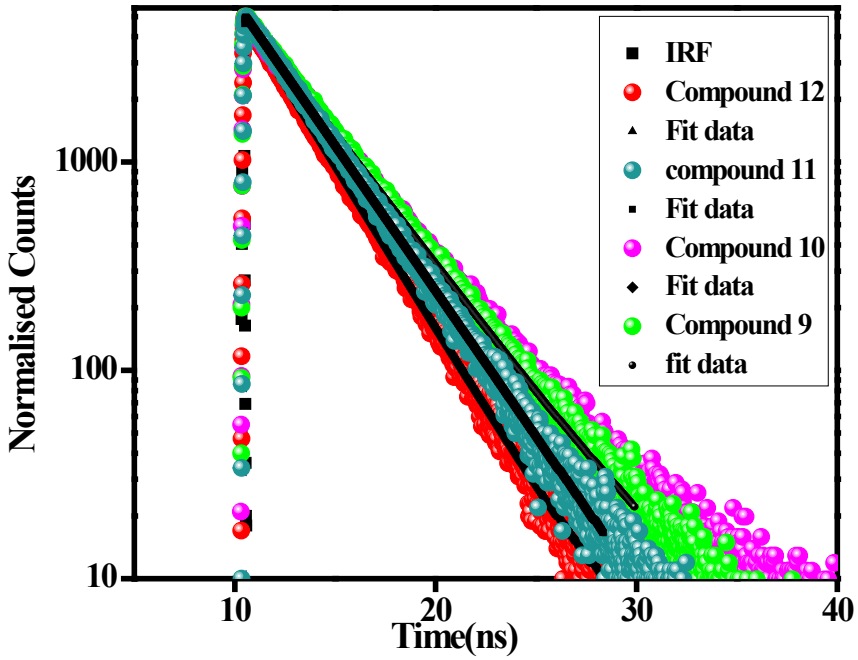

Fig. S69 Excited-state lifetime decay profiles of compound **9-12** recorded in toluene medium. $\lambda_{ex.}$= 520 nm.

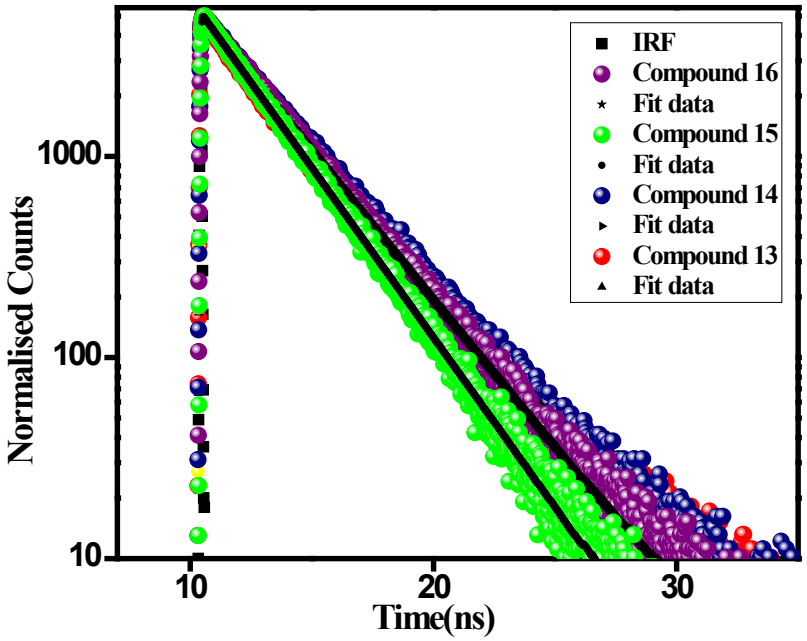

Fig. S70 Excited-state lifetime decay profiles of compound **13-16** recorded in toluene medium. $\lambda_{ex.}$= 520 nm.

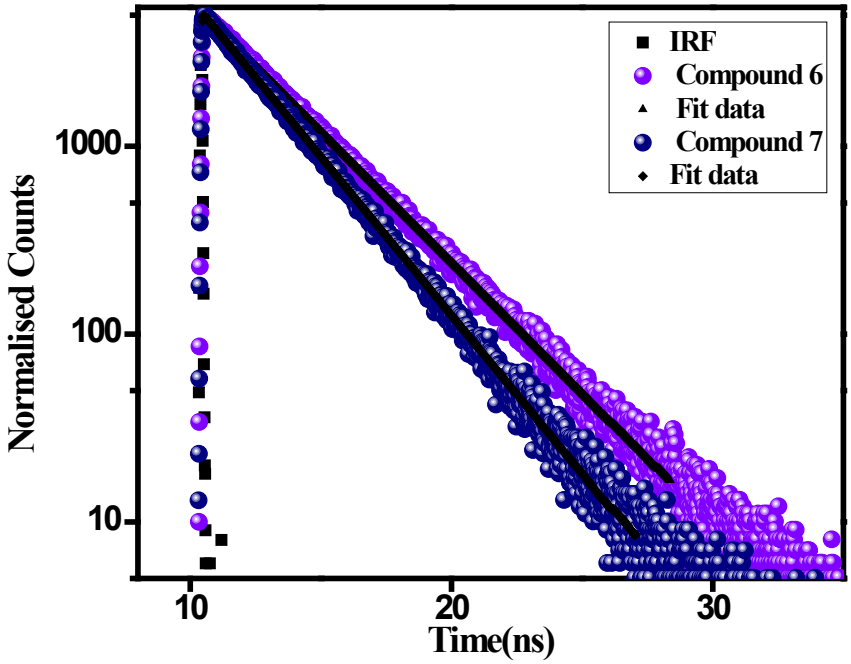

Fig. S71 Excited-state lifetime decay profiles of compound **6** and **7** recorded in toluene medium. $\lambda_{ex.}$= 520 nm.

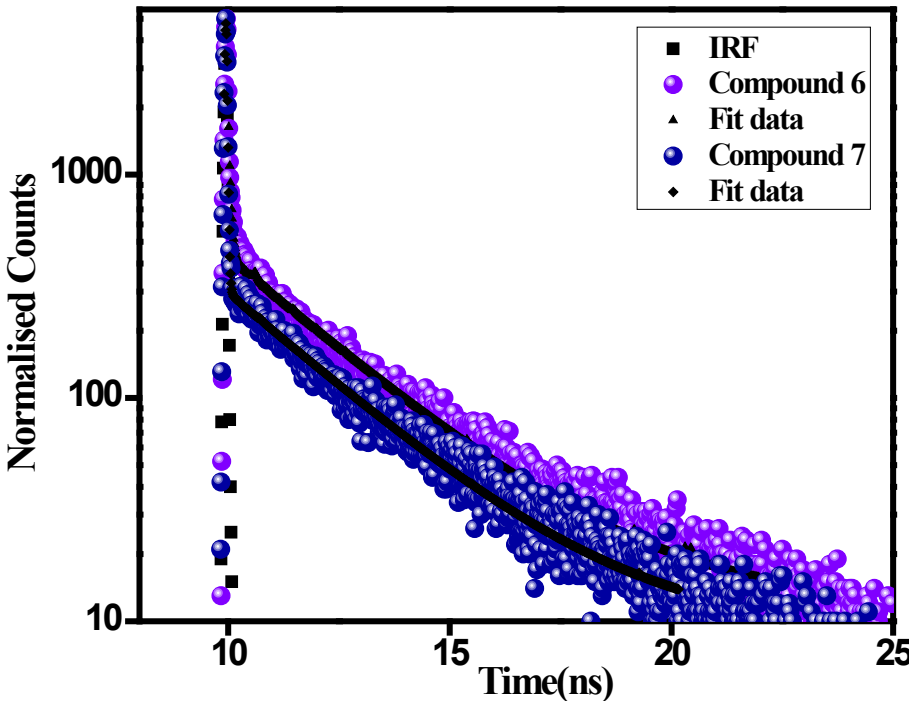

Fig. S72 Excited-state lifetime decay profiles of compound **6** and **7** recorded in toluene medium. $\lambda_{ex.}$= 460 nm.

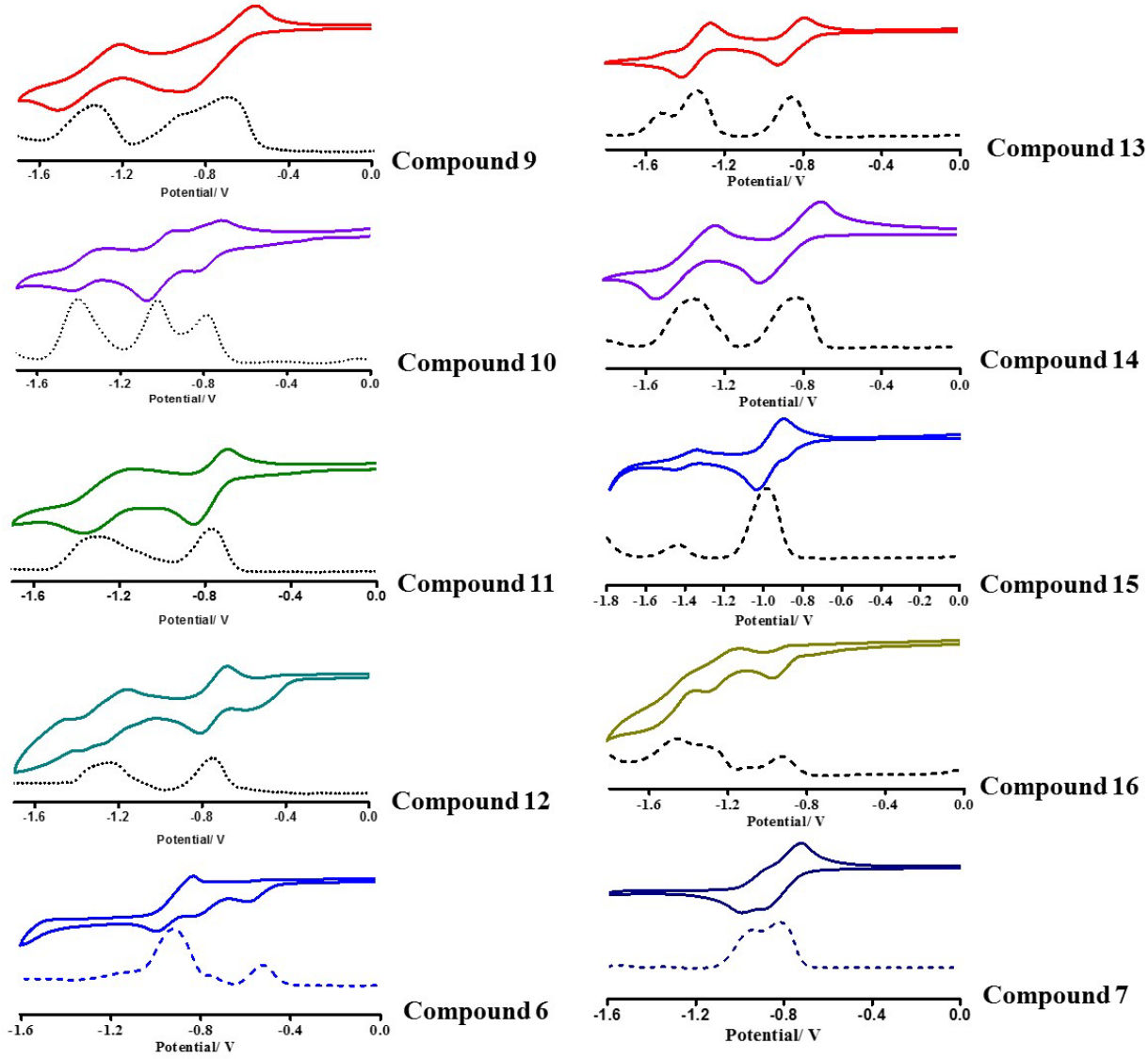

Fig. S73 Cyclic voltammograms of compounds **9-16** and compound **6** and **7** recorded in CH_2Cl_2 containing 0.1 MTBAP as the supporting electrolyte and a saturated calomel electrode as the reference electrode at a scan rate of 50 mV s^{-1}.

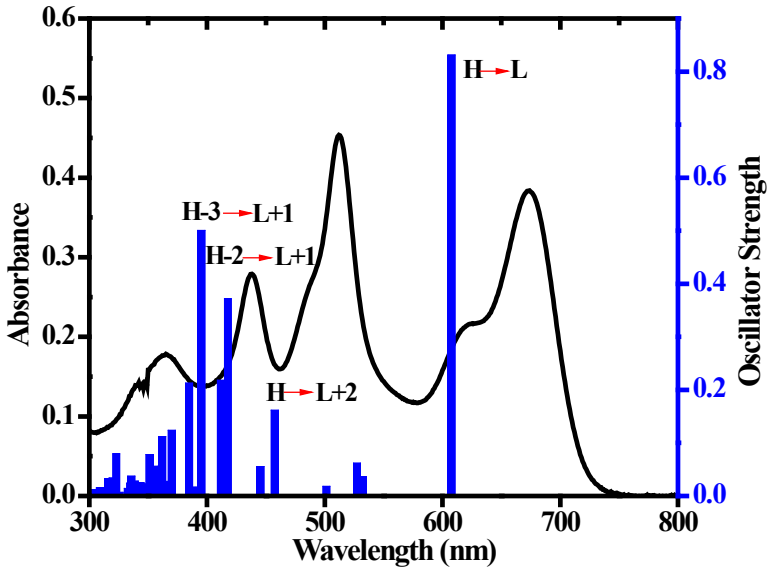

Fig. S74 Calculated excitations (blue vertical lines) and experimental absorption spectrum (black curve) for triad **6**.

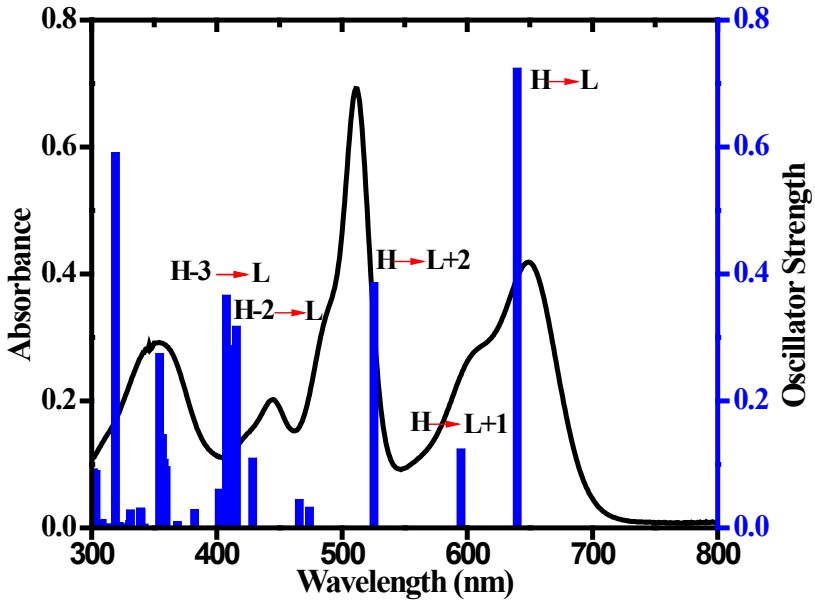

Fig. S75 Calculated excitations (blue vertical lines) and experimental absorption spectrum (black curve) for triad **7**.

Table S10. S_0 optimized geometry of the compound **6** at B3LYP/6-31g (d,p).

Atom	X	Y	Z	Atom	X	Y	Z
F	-2.492644000	1.446836000	1.344321000	F	-2.735872000	1.243204000	0.915306000
F	-9.951975000	1.165326000	1.187392000	F	-10.173454000	0.360350000	0.941653000
F	10.818460000	-0.615965000	0.836243000	F	10.485691000	-0.907719000	1.407499000
N	-0.718302000	2.260879000	0.084361000	N	-4.109191000	-0.856634000	-0.111760000
H	-3.962789000	0.051553000	0.322671000	N	-1.111090000	-0.189665000	-0.197457000
N	-8.004171000	1.167622000	-0.256411000	N	8.776365000	-1.697287000	-0.104447000
N	9.137527000	0.738027000	0.251281000	N	-8.915617000	-0.951573000	0.657817000
C	4.633760000	-0.407364000	-1.039731000	H	5.110847000	-0.910760000	-1.873759000
C	1.157569000	0.720904000	-0.023956000	C	0.652773000	2.030988000	0.103560000
C	0.276325000	-0.358725000	-0.164148000	C	-1.681847000	-1.421248000	-0.321418000
C	2.623225000	0.488277000	-0.005906000	C	3.258784000	-0.192553000	-1.057598000
H	2.673315000	-0.528877000	-1.906813000	C	-3.084033000	-1.721587000	-0.408276000
C	-0.651192000	-2.405879000	-0.363495000	H	-0.815289000	-3.471167000	-0.429127000
C	0.553448000	-1.751974000	-0.255245000	H	1.537571000	-2.194271000	-0.219657000
C	1.302097000	3.283242000	0.233601000	H	2.370763000	3.435406000	0.259687000
C	-6.773295000	0.542258000	-0.450282000	C	7.401782000	-1.467772000	-0.105173000
C	3.409449000	0.952025000	1.062127000	H	2.933085000	1.458925000	1.894564000
C	5.419054000	0.055037000	0.029004000	C	6.750917000	-2.722586000	-0.260485000
H	5.682236000	-2.876051000	-0.279764000	C	4.784532000	0.739681000	1.079000000
H	5.372042000	1.081966000	1.924270000	C	7.756853000	0.921808000	0.211421000
C	6.885545000	-0.169346000	0.049826000	C	0.308308000	4.256363000	0.307152000
H	0.441113000	5.323257000	0.413341000	C	-0.921798000	3.588160000	0.206857000
H	-1.924119000	3.992832000	0.208784000	C	-5.894221000	1.486094000	-1.052716000

H	-4.869063000	1.316762000	-1.347530000	C	-5.058420000	-2.784824000	-0.721198000
H	-5.811545000	-3.503911000	-1.005467000	C	7.742148000	-3.687823000	-0.367427000
H	7.612700000	-4.752269000	-0.499710000	C	7.501446000	2.319414000	0.276848000
H	6.525371000	2.779724000	0.238963000	C	-3.671073000	-2.935522000	-0.804278000
H	-3.136215000	-3.807548000	-1.151020000	C	-6.605478000	2.670974000	-1.191233000
H	-6.247402000	3.602912000	-1.604343000	C	-7.901550000	2.430351000	-0.697284000
H	-8.753768000	3.094601000	-0.655687000	C	-7.658689000	-1.527679000	0.510682000
C	-7.693684000	-2.809033000	1.122021000	H	-6.855464000	-3.483082000	1.212660000
C	-9.699634000	-1.822353000	1.313490000	H	-10.723957000	-1.567335000	1.546862000
C	8.975851000	-3.013499000	-0.261147000	H	9.978707000	-3.417458000	-0.280680000
C	-8.980005000	-2.993395000	1.615329000	H	-9.361911000	-3.851640000	2.149225000
C	9.713049000	1.945053000	0.342348000	H	10.789747000	2.037927000	0.379501000
C	8.730776000	2.956592000	0.365670000	H	8.918658000	4.018768000	0.427010000
B	-1.817937000	1.203701000	-0.153625000	B	-9.343752000	0.468433000	0.160724000
B	9.894421000	-0.634760000	0.188846000	C	-5.317997000	-1.478054000	-0.280129000
C	-6.592906000	-0.806837000	-0.074349000				

DFT optimized XYZ coordinates

Table S11. S_0 optimized geometry of the compound **7** at B3LYP/6-31g (d,p).

Atom	X	Y	Z	Atom	X	Y	Z
F	-1.263684000	-0.792582000	0.161340000	F	-0.754794000	-0.189753000	-1.981336000
F	-11.611856000	-2.340740000	-0.782280000	F	-12.509350000	-1.207820000	0.990373000
F	12.467059000	-0.255652000	1.264620000	F	12.240369000	0.218382000	-0.961815000
N	0.757835000	-1.661616000	-0.787921000	N	-2.291919000	1.683824000	0.042604000
H	-2.213130000	0.676517000	0.158706000	N	0.601139000	0.767876000	-0.216501000
N	-10.154987000	-1.750646000	1.058912000	N	10.577368000	1.088863000	0.555928000
N	10.685387000	-1.340540000	0.042209000	N	-11.012106000	-0.019489000	0.502900000
C	6.246427000	0.248784000	1.060360000	H	6.702595000	0.633134000	1.966416000
C	2.767279000	-0.380061000	-0.318998000	C	2.135317000	-1.606728000	-0.619560000
C	2.000169000	0.774845000	-0.137812000	C	0.167199000	2.049486000	-0.030088000
C	4.244826000	-0.325968000	-0.196560000	C	4.859882000	0.199135000	0.952424000
H	4.244167000	0.543836000	1.776500000	C	-4.760901000	1.803399000	0.100242000
C	-1.190656000	2.503455000	-0.016860000	C	1.297377000	2.898429000	0.166308000
H	1.247572000	3.960348000	0.356716000	C	-8.682649000	0.001511000	0.216670000
C	2.423244000	2.115422000	0.094381000	H	3.449751000	2.435368000	0.190700000
C	2.642014000	-2.922656000	-0.735699000	H	3.677980000	-3.207272000	-0.626788000
C	-8.908681000	-1.129344000	1.024421000	C	9.190320000	1.028808000	0.433002000
C	-3.441618000	2.421049000	0.053921000	C	5.064734000	-0.810694000	-1.229659000
H	4.607995000	-1.202309000	-2.132308000	C	-7.340546000	0.622515000	0.179095000
C	-4.935904000	0.425123000	-0.133841000	H	-4.083594000	-0.200731000	-0.379794000
C	7.064939000	-0.231489000	0.024745000	C	-5.905468000	2.575356000	0.376749000
H	-5.800394000	3.634032000	0.589819000	C	8.677251000	2.336926000	0.650750000

H	7.635463000	2.617144000	0.604917000
H	7.067785000	-1.119907000	-1.939817000
C	8.543302000	-0.183832000	0.135871000
H	1.572319000	-4.832328000	-1.123506000
H	-0.620739000	-3.222296000	-1.159357000
H	-7.054307000	-1.502971000	2.202098000
H	-3.740913000	4.614027000	-0.052939000
H	-6.309474000	-1.212856000	-0.287538000
H	-8.032191000	2.612897000	0.641082000
H	9.742616000	4.220203000	1.138827000
H	7.864888000	-3.051730000	-0.283520000
H	-1.058122000	4.713067000	-0.127626000
H	-8.512188000	-3.479484000	3.328425000
H	-10.974495000	-3.343834000	2.166121000
C	-9.779845000	1.653013000	-1.429395000
C	-11.806789000	0.697591000	-1.310981000
C	10.912760000	2.353916000	0.845606000
C	-11.081926000	1.751219000	-1.902024000
C	11.124558000	-2.600833000	-0.080590000
C	10.038342000	-3.484559000	-0.246762000
B	-0.216156000	-0.465060000	-0.740150000
B	11.584037000	-0.068034000	0.220584000
C	6.451047000	-0.765286000	-1.120834000
C	9.294594000	-1.359260000	-0.039290000
C	1.555550000	-3.761106000	-0.983577000
C	0.413353000	-2.948551000	-1.005386000
C	-8.073101000	-1.778498000	1.973573000
C	-3.065533000	3.772320000	-0.008840000
C	-6.197549000	-0.153183000	-0.084431000
C	-7.168456000	2.000373000	0.405547000
C	9.760144000	3.162428000	0.919425000
C	8.887122000	-2.710346000	-0.215312000
C	-1.668414000	3.825173000	-0.048581000
C	-8.824923000	-2.788747000	2.558686000
C	-10.103709000	-2.733737000	1.969563000
C	-9.738676000	0.546006000	-0.538958000
H	-8.941032000	2.282838000	-1.685260000
H	-12.844606000	0.423768000	1.442198000
H	11.950189000	2.629510000	0.976329000
H	-11.476977000	2.481386000	2.593574000
H	12.182852000	-2.818618000	0.038383000
H	10.107288000	-4.556859000	0.359567000
B	-11.399570000	-1.374849000	0.185031000

Table S12. Major transitions were calculated using TD-DFT studies of **6**.

Wavelength (nm)	Osc. Strength	Major contribs
608.03	0.8209	HOMO->LUMO (97%)
533.65	0.0415	HOMO->L+1 (99%)
527.65	0.0618	H-1->LUMO (96%)
502.22	0.017	H-2->LUMO (97%)
457.40	0.1451	HOMO->L+2 (89%)
446.00	0.0553	H-1->L+1 (97%)
417.72	0.3642	H-2->L+1 (92%)
411.81	0.2156	H-4->LUMO (22%), H-1->L+2 (70%)
395.00	0.4988	H-3->LUMO (79%)
387.59	0.0205	H-2->L+2 (96%)
384.73	0.2144	H-4->LUMO (67%), H-1->L+2 (24%)
369.93	0.1294	H-7->LUMO (85%)
367.02	0.0265	H-6->LUMO (88%)
362.19	0.0943	H-5->LUMO (67%), H-5->L+1 (22%)
354.87	0.0657	H-3->L+1 (81%)
351.60	0.0606	H-8->LUMO (74%)
345.26	0.0099	H-10->LUMO (70%)
343.69	0.0227	H-9->LUMO (60%), H-9->L+1 (25%)
338.56	0.0645	H-11->LUMO (13%), H-5->LUMO (20%), H-5->L+1 (56%)
335.66	0.0319	H-11->LUMO (54%), H-4->L+1 (13%)
334.81	0.0293	H-11->LUMO (17%), H-4->L+1 (47%), H-4->L+2 (23%)
332.85	0.0158	H-12->LUMO (66%), H-3->L+2 (13%)
325.71	0.0109	H-12->LUMO (12%), H-8->L+1 (12%), H-7->L+1 (26%), H-3->L+2 (36%)
323.10	0.0785	H-8->L+1 (10%), H-7->L+1 (36%), H-3->L+2 (34%)
320.24	0.0247	H-9->LUMO (26%), H-9->L+1 (56%)
318.50	0.0119	H-4->L+1 (34%), H-4->L+2 (63%)
317.42	0.0012	H-6->L+1 (50%), H-6->L+2 (23%)
316.33	0.0509	H-11->L+1 (10%), H-8->L+1 (38%), H-7->L+1 (10%), H-6->L+1 (10%)
309.22	0.0066	H-12->L+1 (25%), H-11->L+1 (41%), H-8->L+1 (15%)
303.45	0.0109	H-10->L+1 (45%), H-10->L+2 (40%)
302.22	0.0063	H-6->L+1 (33%), H-6->L+2 (65%)
296.88	0.005	H-7->L+2 (87%)
293.39	0.0008	H-12->L+1 (33%), H-11->L+1 (12%), H-10->L+1 (26%), H-10->L+2 (20%)
291.31	0.014	HOMO->L+3 (85%)
290.27	0.0025	H-5->L+2 (92%)
288.14	0.0142	H-12->L+1 (14%), H-11->L+1 (14%), H-10->L+1 (11%), H-8->L+2 (10%), HOMO->L+4 (39%)
287.93	0.0079	H-12->L+1 (11%), HOMO->L+4 (59%)
286.53	0.0199	H-10->L+2 (19%), H-8->L+2 (52%), HOMO->L+3 (10%)
278.01	0.0152	H-12->L+2 (37%), H-11->L+2 (54%)
277.09	0.0001	H-9->L+2 (93%)
269.48	0.0012	H-12->L+2 (53%), H-11->L+2 (35%)

269.06	0.025	H-2->L+3 (94%)
268.77	0.0448	H-13->LUMO (75%), HOMO->L+5 (16%)
266.47	0.0254	H-2->L+4 (95%)
259.11	0.1247	H-14->LUMO (51%), H-13->LUMO (12%), HOMO->L+5 (30%)
257.96	0.0068	H-1->L+3 (89%)
254.00	0.0003	H-1->L+4 (97%)
251.87	0.1866	H-14->LUMO (39%), H-13->L+1 (11%), HOMO->L+5 (34%)
248.26	0.2189	H-13->L+1 (82%)
245.57	0.0115	H-1->L+5 (90%)

Table S13. Major transitions were calculated using TD-DFT studies of **7**.

Wavelength (nm)	**Osc. Strength**	**Major contribs**
645.48	0.7037	HOMO->LUMO (95%)
596.47	0.1511	HOMO->L+1 (99%)
526.02	0.367	HOMO->L+2 (94%)
476.49	0.0278	H-1->LUMO (97%)
468.23	0.0518	H-2->LUMO (91%)
428.80	0.1172	H-1->L+1 (95%)
415.55	0.2623	H-2->L+1 (88%)
410.73	0.2739	H-1->L+2 (84%)
409.21	0.3817	H-3->LUMO (85%)
401.00	0.0707	H-2->L+2 (90%)
382.44	0.0379	H-3->L+1 (94%)
368.75	0.0134	H-5->LUMO (34%), H-3->L+2 (56%)
359.85	0.0931	H-7->LUMO (11%), H-5->LUMO (42%), H-3->L+2 (29%)
357.84	0.0874	H-4->LUMO (44%), H-4->L+1 (33%), H-4->L+2 (12%)
357.56	0.1683	H-6->LUMO (60%), H-6->L+1 (18%)
356.37	0.2779	H-7->LUMO (76%)
343.36	0.0067	H-8->LUMO (84%)
339.82	0.0513	H-10->LUMO (69%), H-10->L+1 (23%)
339.32	0.0126	H-9->LUMO (44%), H-9->L+1 (36%), H-9->L+2 (14%)
331.68	0.01	H-4->LUMO (49%), H-4->L+1 (25%), H-4->L+2 (21%)
331.19	0.0115	H-12->LUMO (22%), H-11->LUMO (35%), H-11->L+1 (14%)
329.57	0.0174	H-7->L+1 (25%), H-5->L+1 (21%)
328.64	0.0104	H-13->LUMO (31%), H-12->LUMO (17%), H-7->L+1 (20%)
327.37	0.0025	H-13->LUMO (21%), H-12->LUMO (35%), H-5->L+1 (10%)
325.16	0.0058	H-6->LUMO (17%), H-6->L+1 (26%), H-6->L+2 (11%), H-5->L+1 (24%)
322.47	0.0346	H-13->LUMO (23%), H-7->L+1 (10%), H-6->L+1 (21%), H-5->L+1 (15%)
319.75	0.57	H-7->L+1 (11%), HOMO->L+3 (58%)
314.08	0.0052	H-9->LUMO (42%), H-9->L+1 (17%), H-9->L+2 (15%), H-8->L+1 (12%)
313.62	0.0045	H-11->LUMO (23%), H-9->LUMO (10%), H-8->L+1 (34%), H-8->L+2 (10%)
309.80	0.0009	H-5->L+2 (11%), H-4->L+1 (26%), H-4->L+2 (45%)
309.61	0.0042	H-5->L+1 (13%), H-5->L+2 (51%), H-4->L+2 (12%)
307.63	0.0067	H-13->L+1 (21%), H-13->L+2 (11%), H-10->LUMO (10%), H-10->L+1 (20%)

307.28	0.0024	H-13->L+1 (11%), H-10->LUMO (16%), H-10->L+1 (31%), H-10->L+2 (11%)
306.76	0.0016	H-11->LUMO (11%), H-11->L+1 (21%), H-11->L+2 (19%), H-8->L+1 (19%)
305.16	0.0003	H-7->L+1 (10%), H-7->L+2 (45%), HOMO->L+5 (12%)
303.28	0.0211	H-8->L+2 (15%), HOMO->L+4 (65%)
303.16	0.0205	H-8->L+2 (48%), HOMO->L+4 (25%)
301.43	0.1675	HOMO->L+5 (72%)
298.41	0.002	H-6->L+1 (20%), H-6->L+2 (73%)
297.38	0.0015	H-14->LUMO (77%)
294.12	0.014	H-12->L+1 (21%), H-9->L+1 (22%), H-9->L+2 (40%)
294.01	0.012	H-12->L+1 (34%), H-9->L+1 (12%), H-9->L+2 (22%)
292.11	0.0081	HOMO->L+6 (78%)
287.10	0.0074	H-11->L+1 (31%), H-11->L+2 (44%), HOMO->L+6 (11%)
284.79	0.0318	H-1->L+3 (95%)
284.47	0.0014	H-10->L+1 (19%), H-10->L+2 (70%)
284.06	0.0041	H-12->L+1 (11%), H-12->L+2 (66%)
281.55	0.0004	H-14->L+1 (71%)
275.83	0.0034	H-14->L+1 (14%), H-13->L+1 (18%), H-13->L+2 (57%)
273.05	0.0231	H-14->L+2 (83%)

ROS generation property study

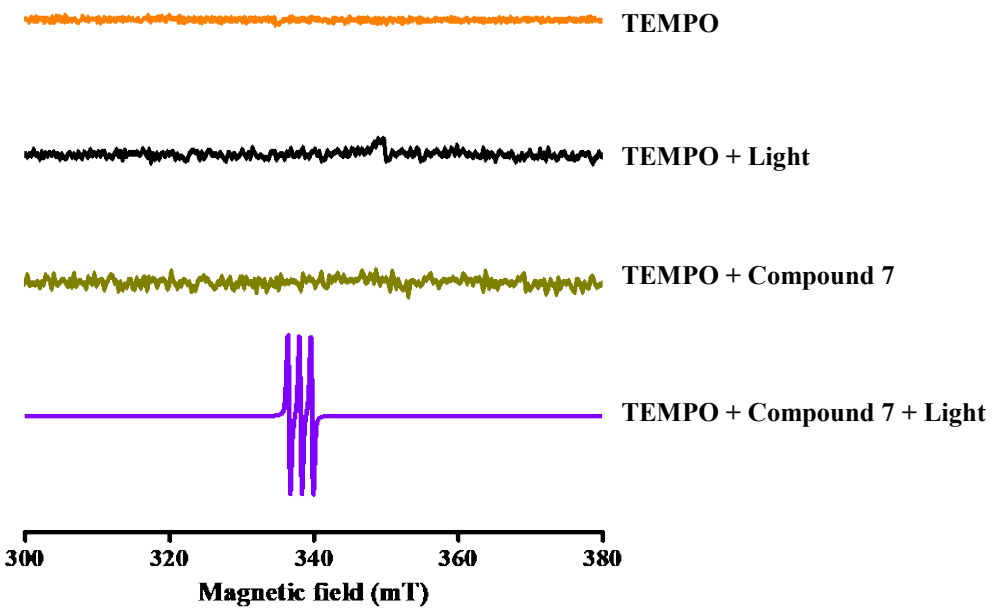

Fig. S76 EPR spectra compound **7** (0.05 mM, in toluene) for $^1O_2$ characterization with TEMP (50 mM) in different conditions.

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