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SUPPORTING INFORMATION

FOR

Unexpected Formation of α-Formylated BOPHY in the Reaction with Copper Salts

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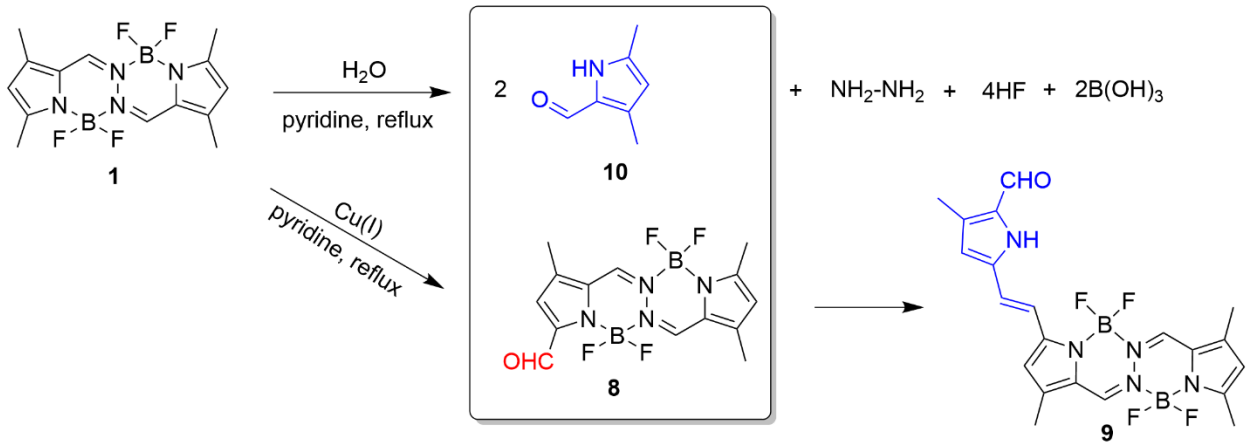


Scheme S1. Possible reaction mechanism for the formation of BOPHY **9**.

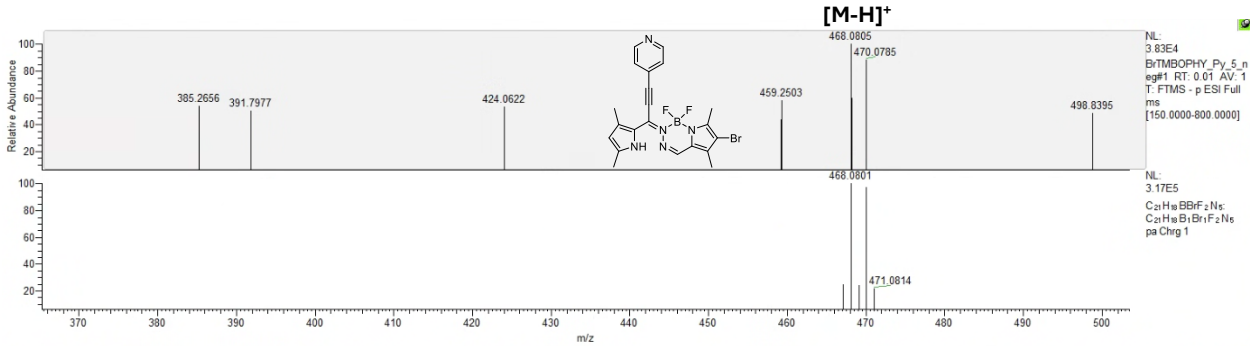


Figure S1. Mass spectrum of BOPHY **4**.

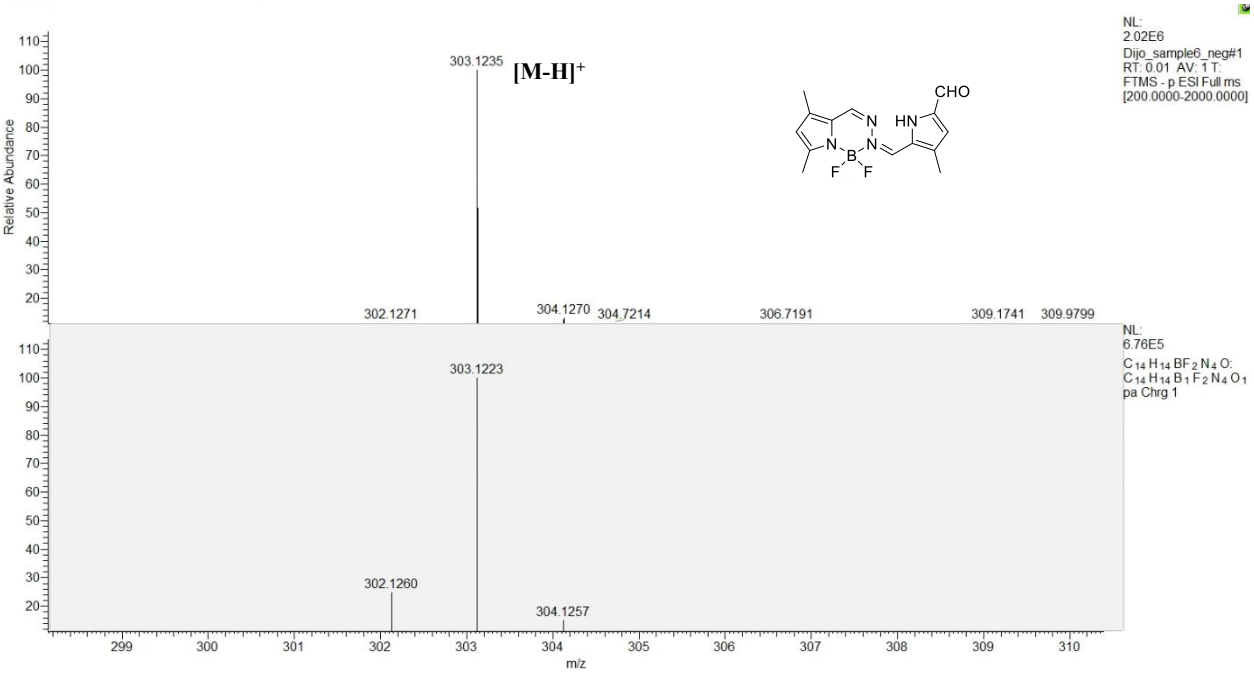


Figure S2. Mass spectrum of half-BOPHY **6**.

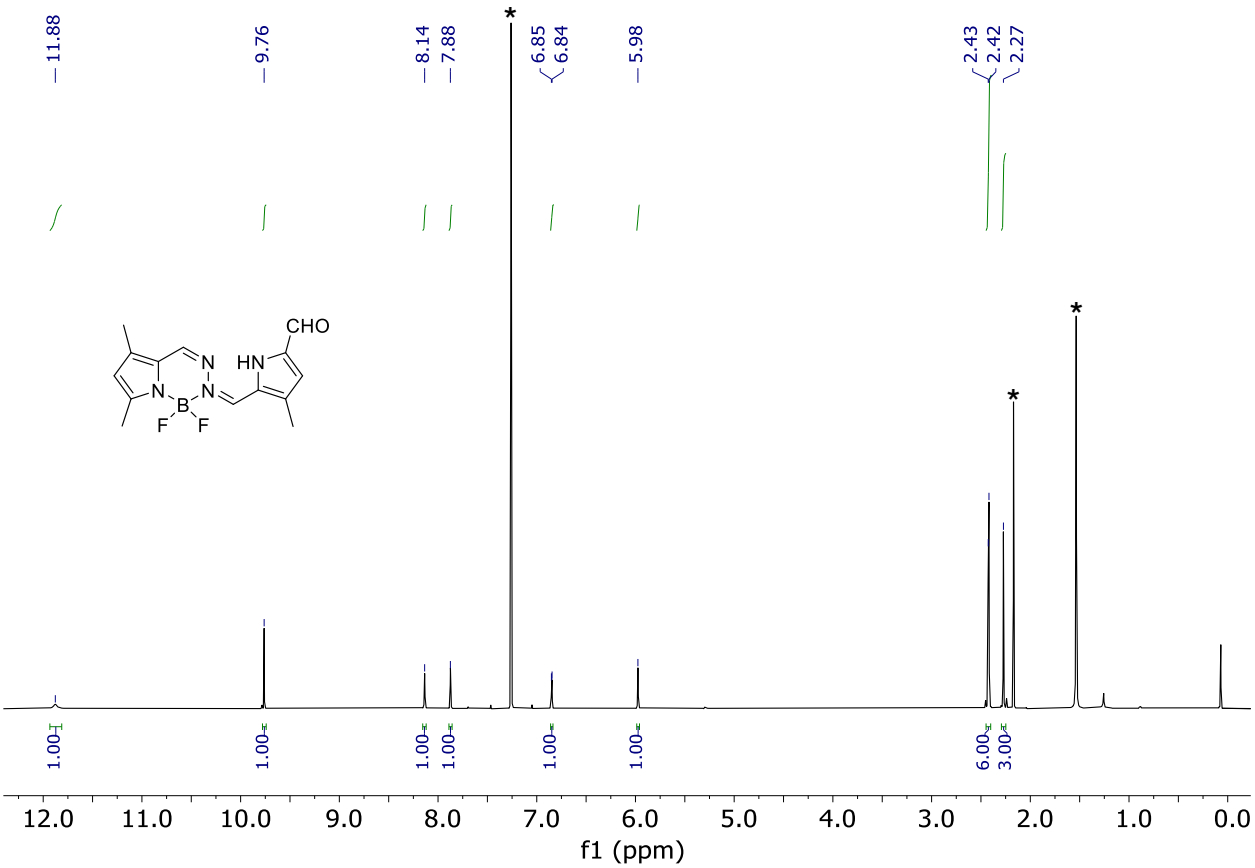


Figure S3. ^{1}H NMR spectrum of half-BOPHY **6** in $CDCl_3$. The solvent peaks are marked with asterisk.

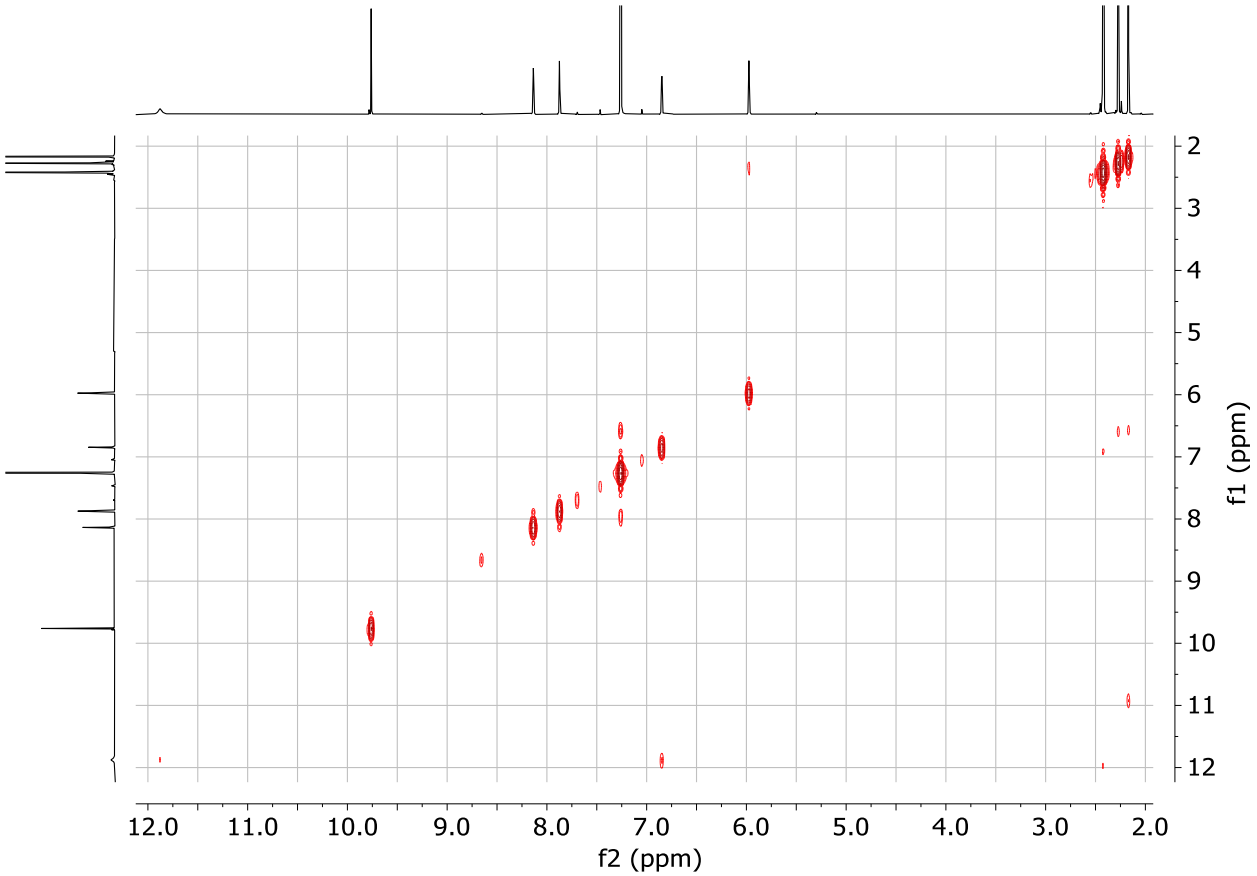


Figure S4. ^{1}H-^{1}H COSY NMR spectrum of half-BOPHY **6** in $CDCl_3$.

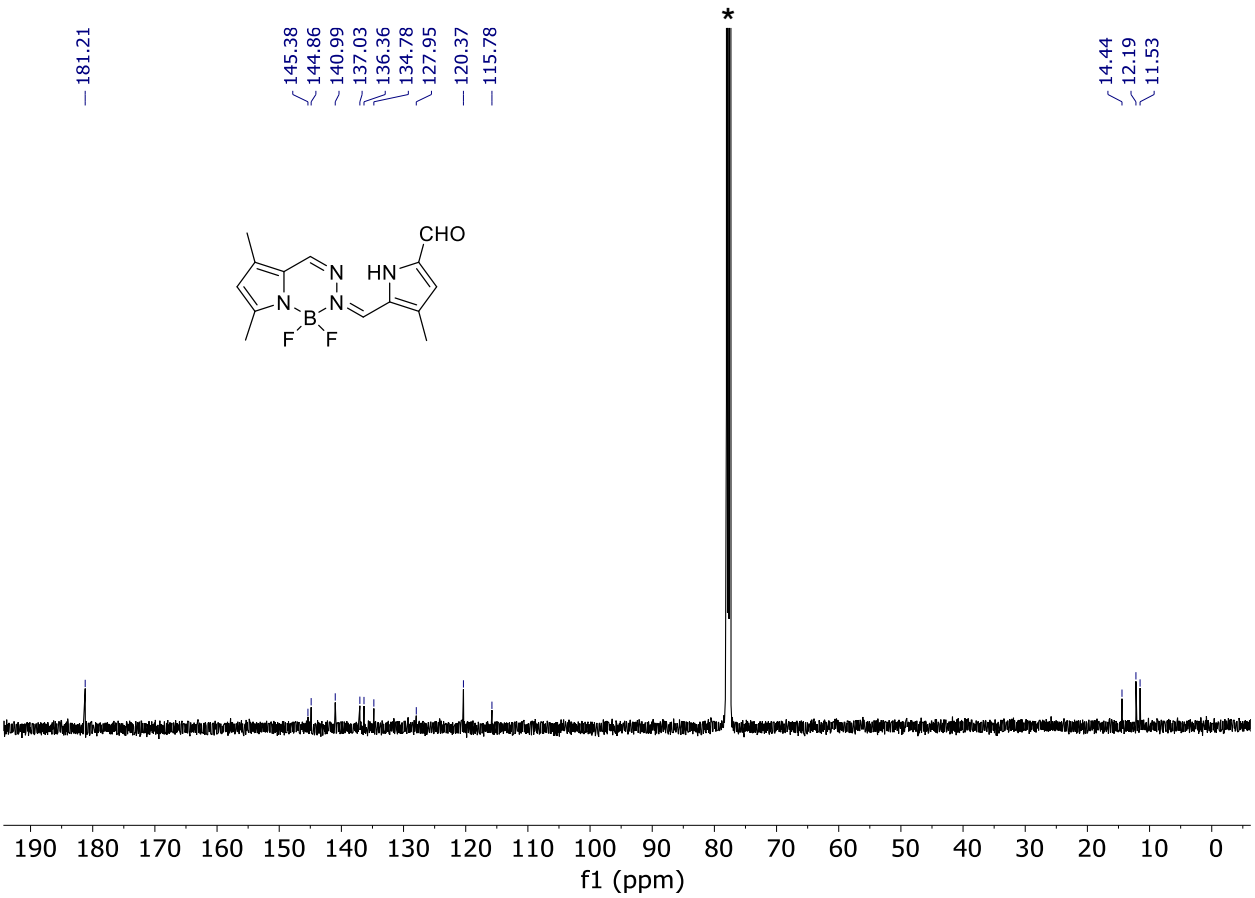


Figure S5. ^{13}C NMR spectrum of half-BOPHY **6** in $CDCl_3$. The solvent peak is marked with asterisk.

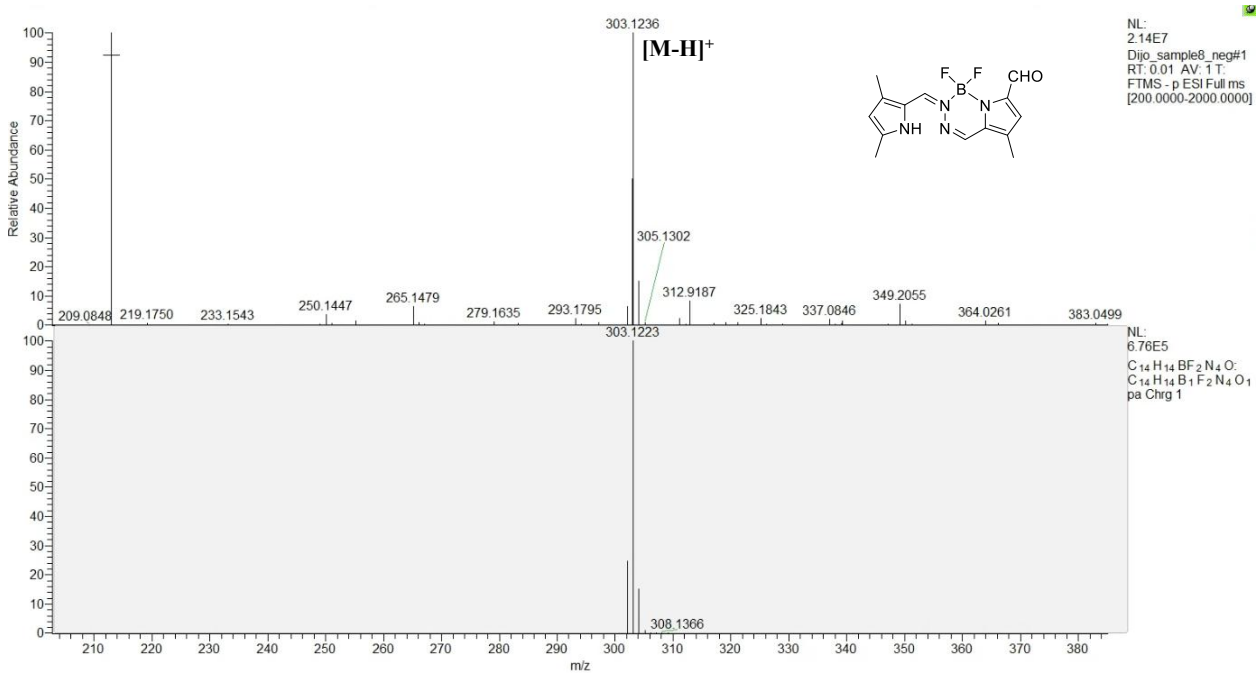


Figure S6. Mass spectrum of half-BOPHY **7**.

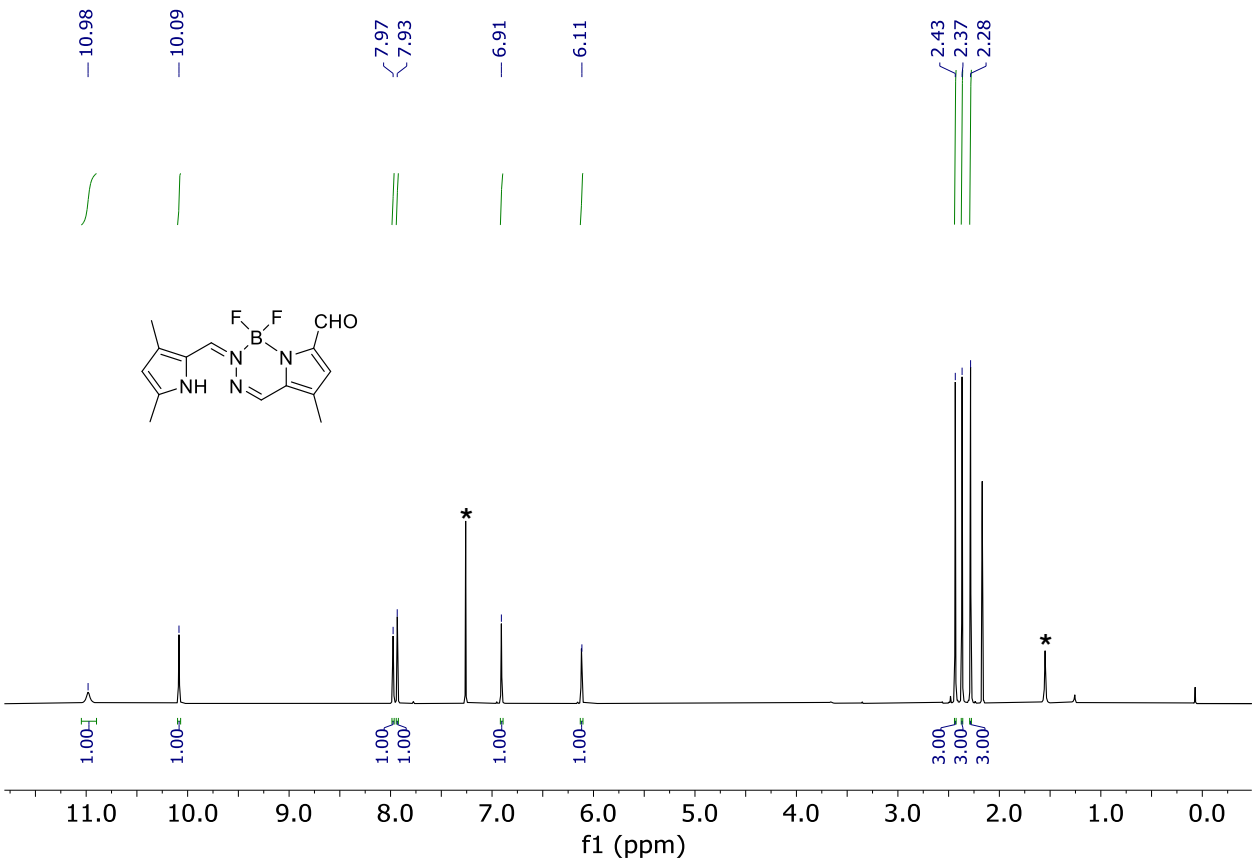


Figure S7. ^{1}H NMR spectrum of half-BOPHY **7** in $CDCl_3$. The solvent peaks are marked with asterisk.

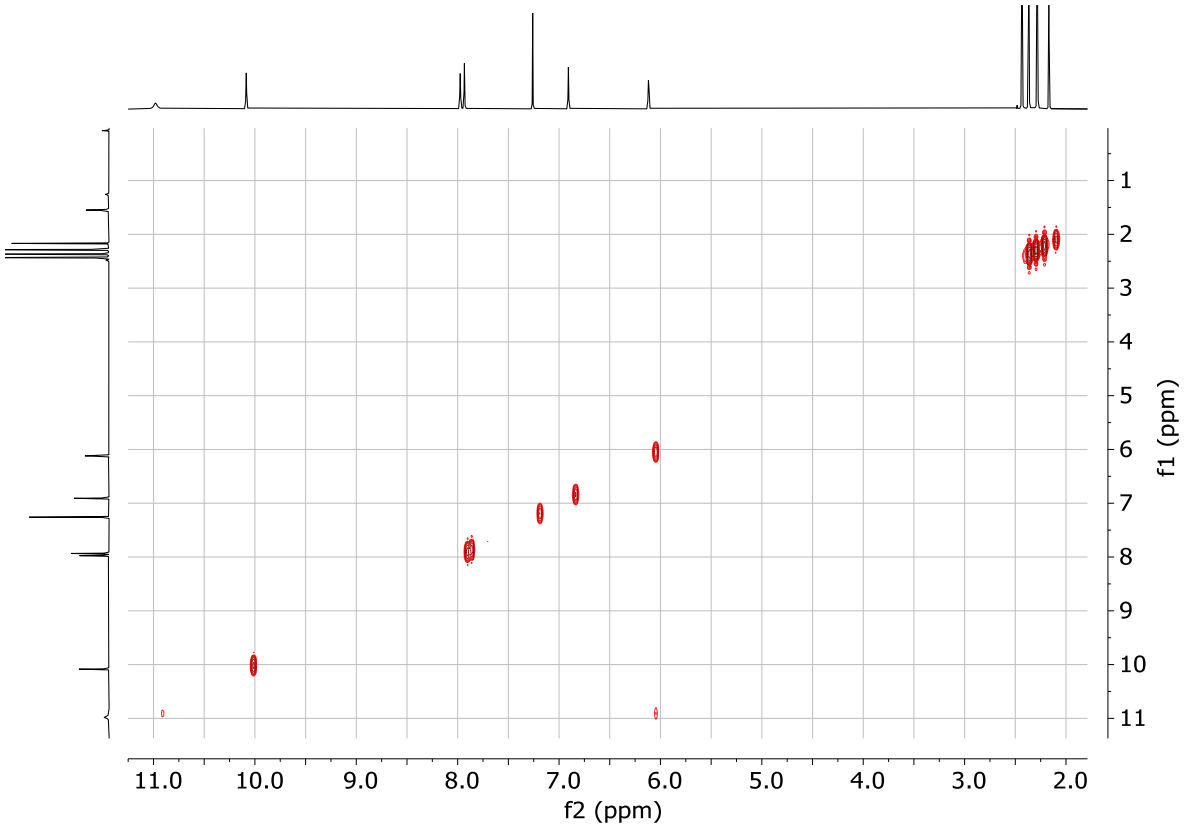


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of half-BOPHY **7** in $CDCl_3$.

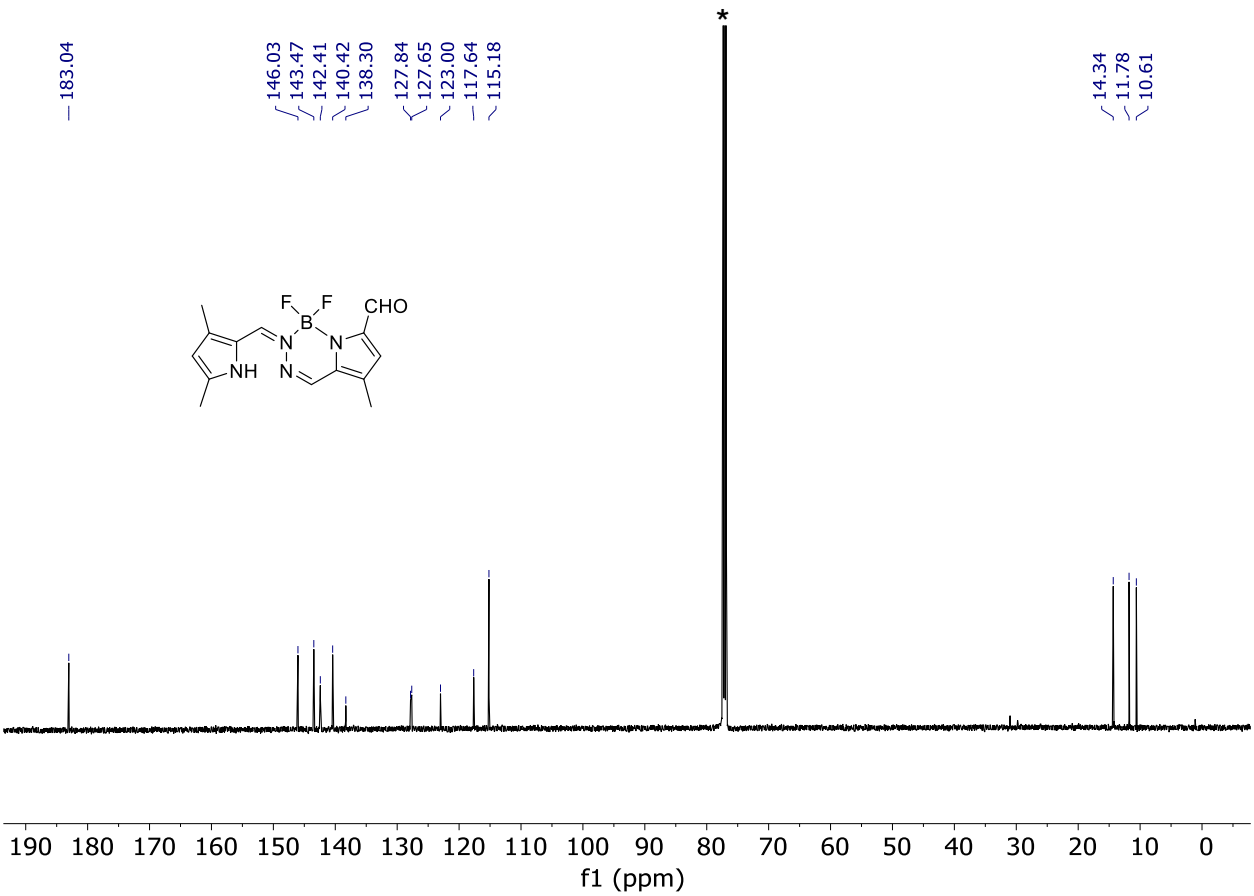


Figure S9. ^{13}C NMR spectrum of half-BOPHY **7** in $CDCl_3$. The solvent peak is marked with asterisk.

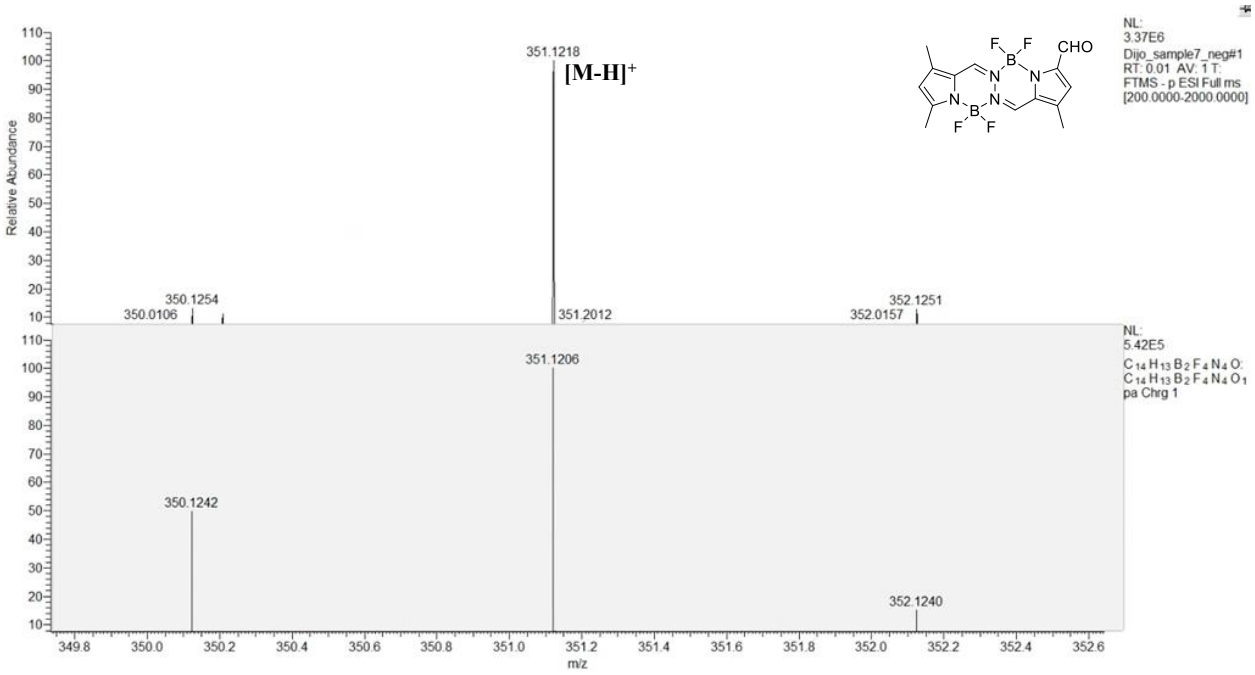


Figure S10. Mass spectrum of BOPHY **8**.

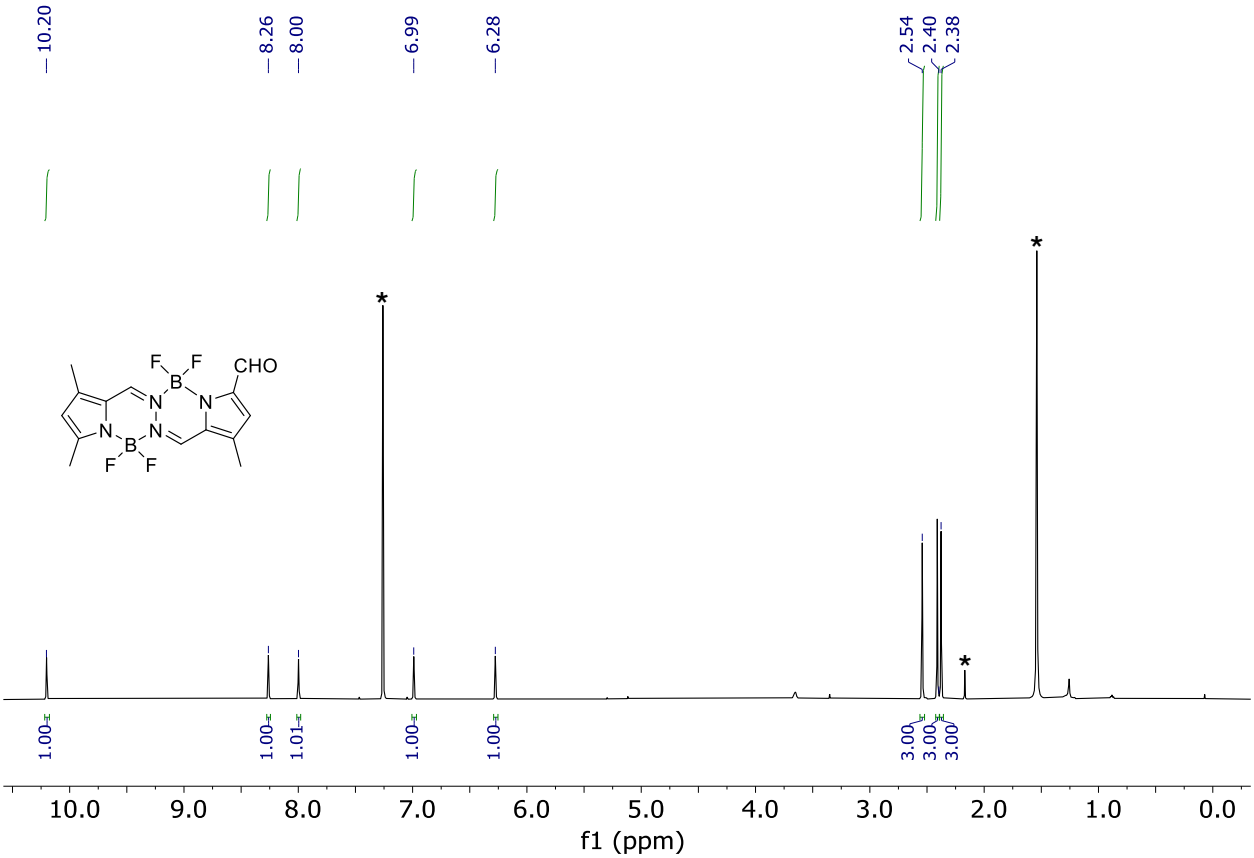


Figure S11. ^{1}H NMR spectrum of BOPHY **8** in $CDCl_3$. The solvent peaks are marked with asterisk.

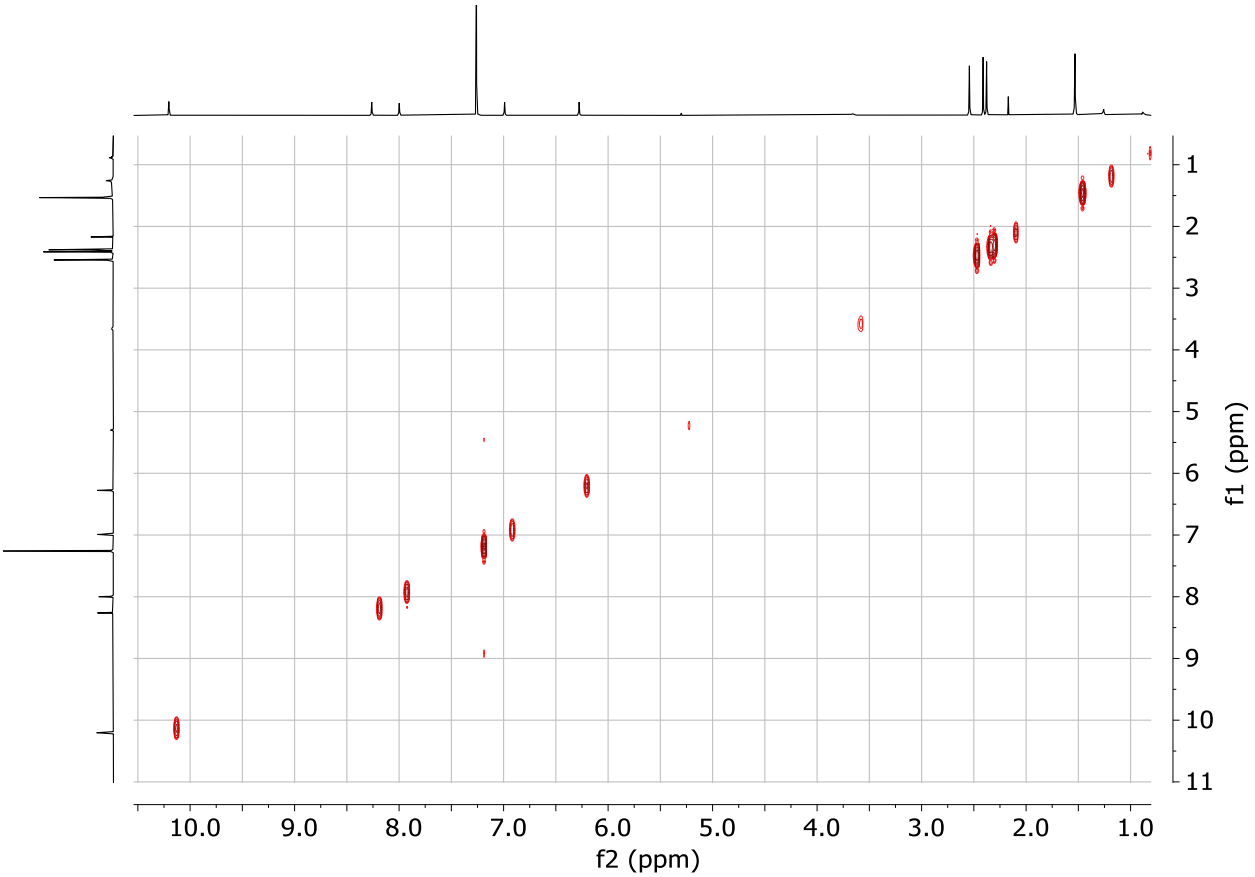


Figure S12. ^{1}H-^{1}H COSY NMR spectrum of BOPHY **8** in $CDCl_3$.

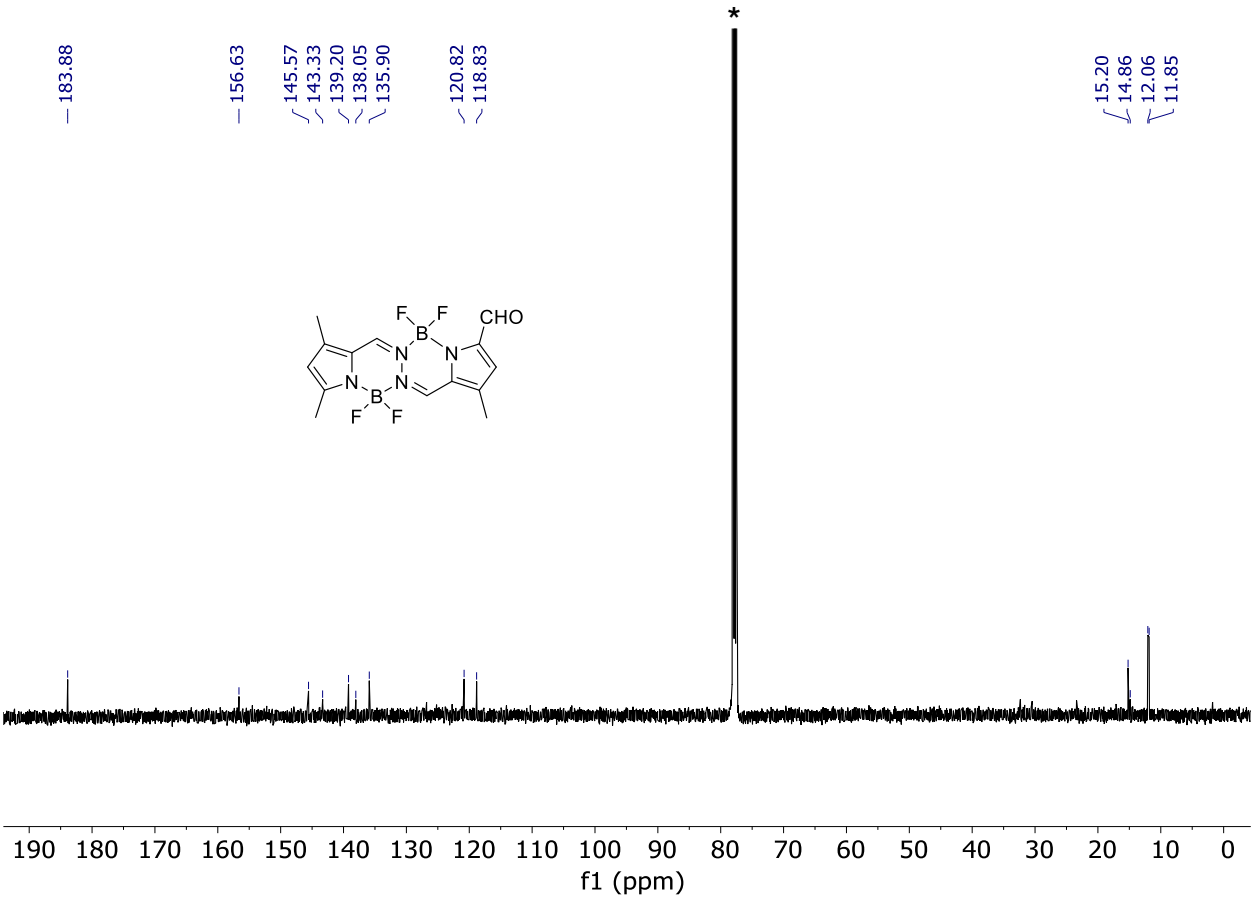


Figure S13. ^{13}C NMR spectrum of BOPHY **8** in $CDCl_3$. The solvent peak is marked with asterisk.

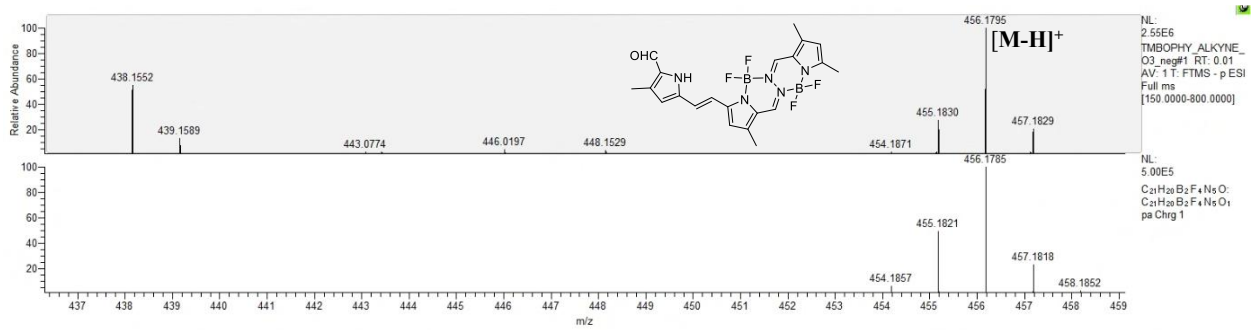


Figure S14. Mass spectrum of compound **9**.

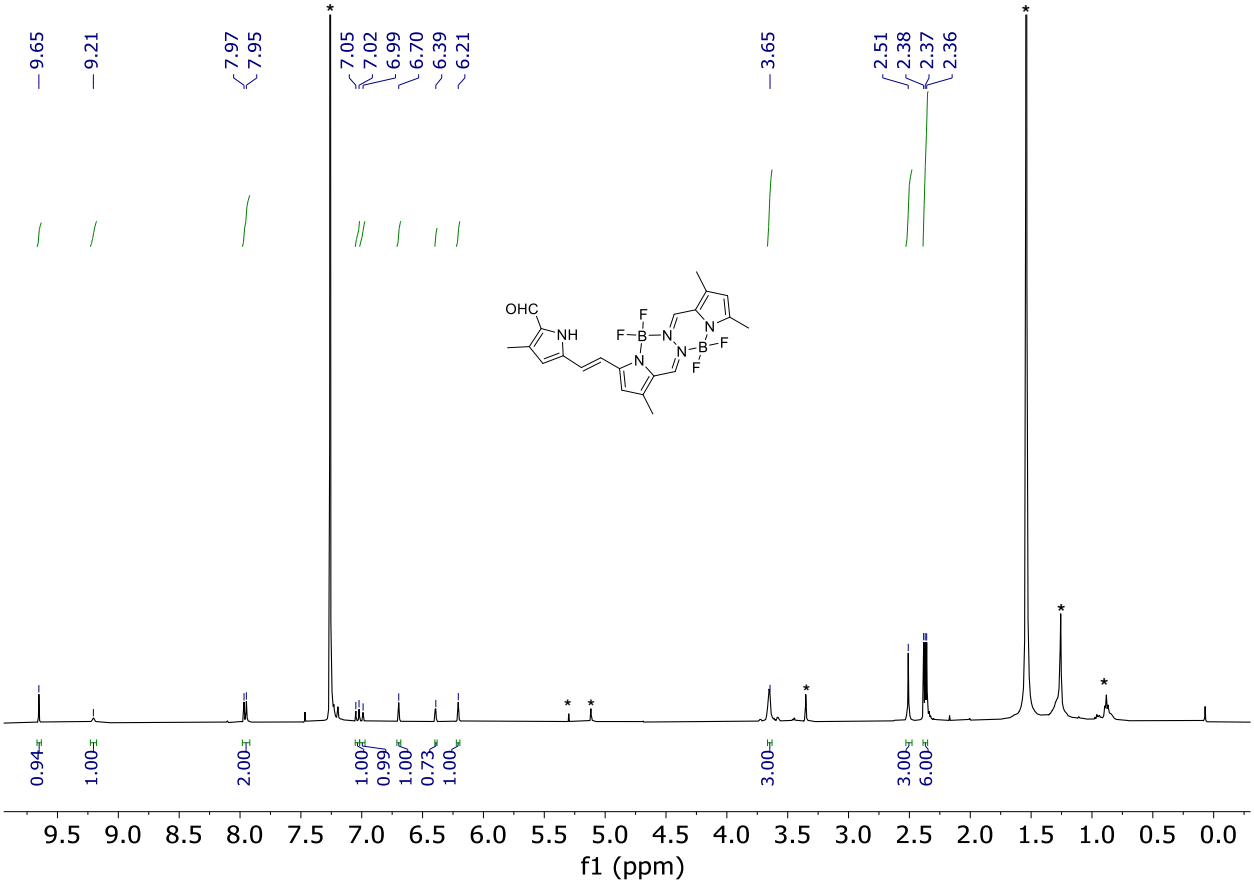
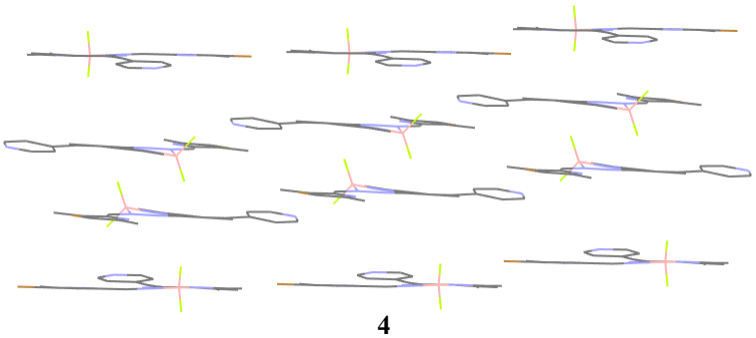


Figure S14. ^{1}H NMR spectrum of compound **9** in $CDCl_3$. The solvent peaks are marked with asterisk.



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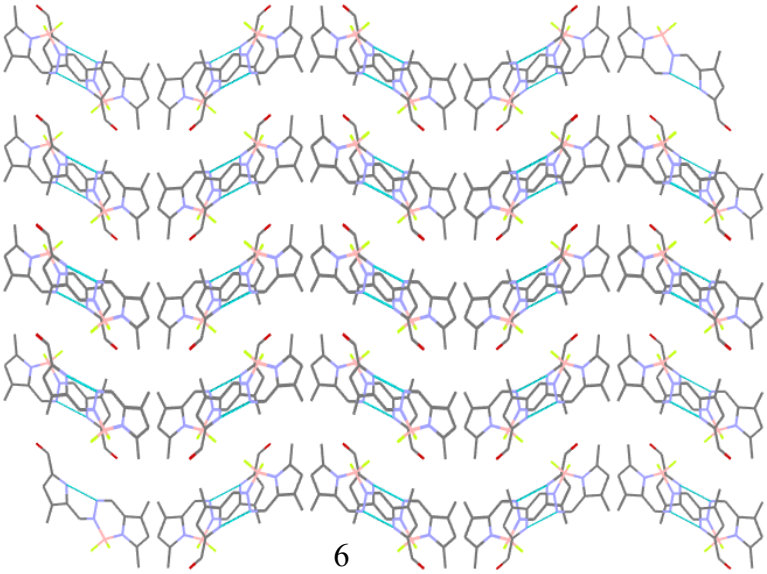

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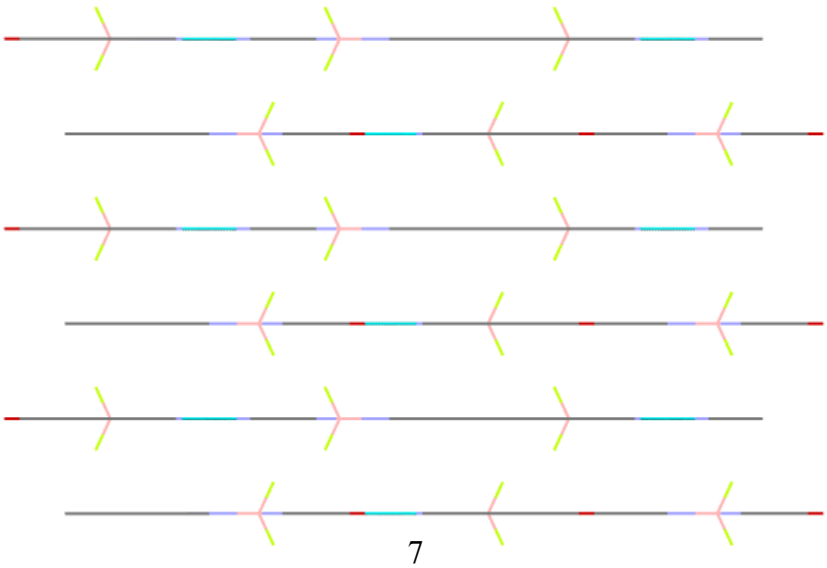

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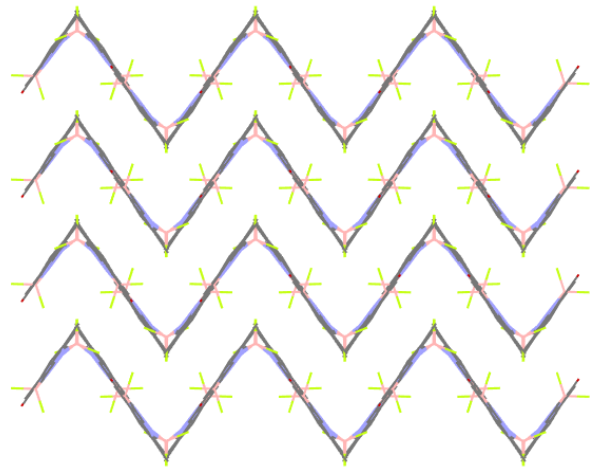

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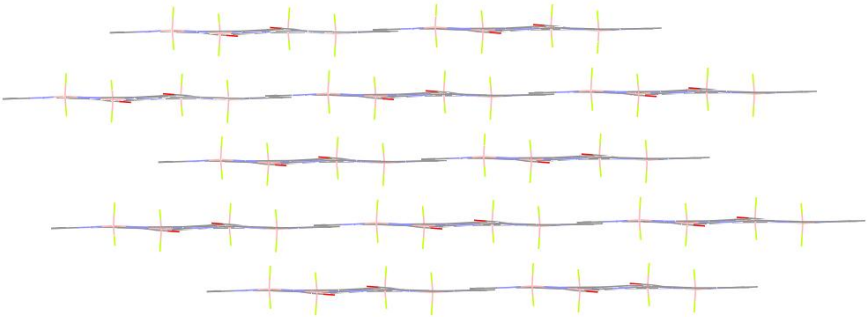

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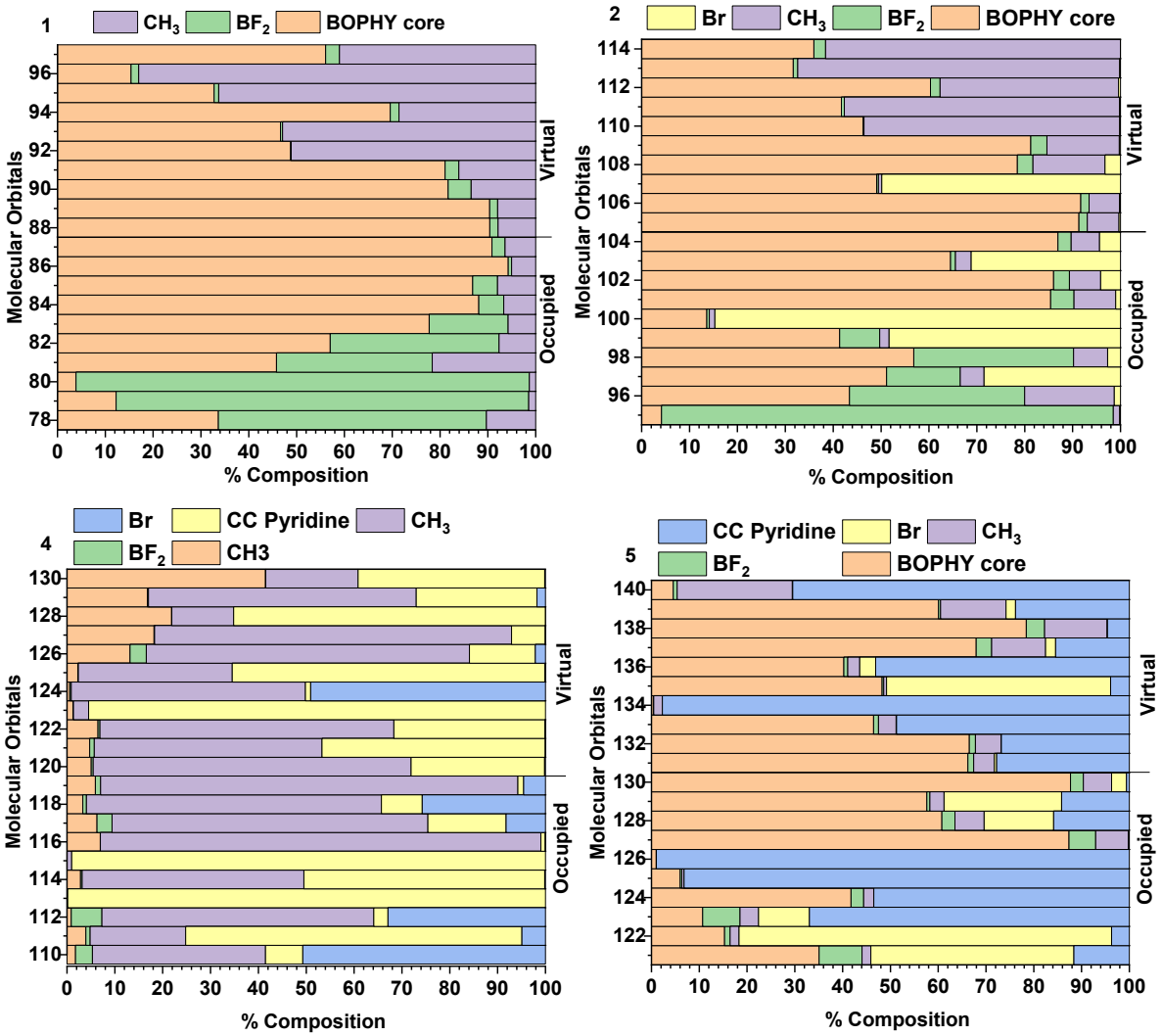
Figure S16. Crystal packing diagram of compounds **4**, **6-9**.

Table S1. Crystal data and structure refinement for compounds **4**, **6**, and **7**.

Compound	4	6	7
Empirical formula	$C_{42}H_{38}B_2Br_2F_5N_{10}$	$C_{14}H_{15}BF_2N_4O$	$C_{14}H_{15}BF_2N_4O$
Formula weight	959.26	304.11	304.123
Temperature (K)	100	100	100
Wavelength (Å)	Cu Kα (λ = 1.54178)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	$P2_1/c$	Pnma
Unit cell dimension	a= 13.1933 (14), b= 13.3860 (13), c= 13.7640 (14); α= 98.094 (6), β= 93.490 (6), γ= 118.563 (5)	a= 7.5311 (4), b= 20.6790 (12), c= 9.2357 (4); α= 90, β= 99.939 (2), γ= 90	a= 16.4025 (19), b= 6.7909 (8), c= 12.6068 (15); α= 90, β=90, γ= 90
Volume ($Å^3$)	2090.6 (4)	1416.74 (13)	1404.2(3)
Z	2	4	4
Density (g cm-3)	1.524	1.426	1.439
Absorption coefficient (mm^{-1})	3.033	0.110	0.111
F(000)	970.0	632.0	632.5
Crystal size (mm × mm × mm)	0.204 × 0.034 × 0.017	0.16 × 0.1 × 0.096	0.90 × 0.140 × 0.996
2θ range for data collection (◦)	10.38 to 101.076	4.892 to 53.458	4.96 to 56.6
Index ranges	-12 ≤ h ≤ 13, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	-9 ≤ h ≤ 9, -26 ≤ k ≤ 26, -11 ≤ l ≤ 9	-21 ≤ h ≤ 21, -9 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	9642	21068	15155
Independent reflections	4192 [R_{int} = 0.0783, R_{sigma} = 0.1032]	3005 [R_{int} = 0.0712, R_{sigma} = 0.0432]	1874 [R_{int} = 0.0901, R_{sigma} = 0.0528]
Absorption correction	Multiscan (SADABS-2016/2)	Multiscan (SADABS-2016/2)	Multiscan (SADABS-2016/2)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4192/0/420	3005/0/206	1874/0/120
Goodness-of-fit on F2	1.078	1.042	1.057
Final R indices [I>2sigma(I)]	R_1 = 0.1107, wR_2 = 0.2536	R_1 = 0.0453, wR_2 = 0.1050	R_1 = 0.1022, wR_2 = 0.2470
R indices (all data)	R_1 = 0.1474, wR_2 = 0.2766	R_1 = 0.0676, wR_2 = 0.1171	R_1 = 0.1309, wR_2 = 0.2682
Largest diff. peak and hole e $Å^{-3}$	2.35/-0.89	0.29/-0.23	0.95/-1.12

Table S2. Crystal data and structure refinement for compounds **8**, and **9**.

Compound	**8**	**9**
Empirical formula	$C_{18}H_{18}B_2F_5N_5O_1$	$C_{21}H_{21}B_2F_4N_5O$
Formula weight	469.21	457.05
Temperature (K)	100	100
Wavelength (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	$P2_1/c$
Unit cell dimension	a= 11.5405 (7), b= 9.9104 (6), c= 25.9429 (16); α= 90, β= 90, γ= 90	a= 9.2716 (15), b= 32.352 (5), c= 7.3861 (10); α= 90, β= 112.817 (4), γ= 90
Volume ($Å^3$)	2967.1(3)	2042.2 (5)
Z	6	4
Density (g cm-3)	1.576	1.487
Absorption coefficient (mm^{-1})	0.135	0.118
F(000)	1440.0	944.0
Crystal size (mm × mm × mm)	0.422 × 0.357 × 0.036	0.422 × 0.357 × 0.036
2θ range for data collection (◦)	4.724 to 56.672	4.766 to 41.594
Index ranges	$-11 \le h \le 15$, $-13 \le k \le 13$, $-32 \le l \le 34$	$-9 \le h \le 9$, $-32 \le k \le 32$, $-6 \le l \le 6$
Reflections collected	30444	6832
Independent reflections	3695 [R_{int} = 0.0595, R_{sigma} = 0.0341]	1920 [R_{int} = 0.0961, R_{sigma} = 0.0828]
Absorption correction	Multiscan (SADABS-2016/2)	Multiscan (SADABS-2016/2)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3695/0/229	1920/0/302
Goodness-of-fit on F2	1.128	1.107
Final R indices [I>2sigma(I)]	R_1 = 0.0559, wR_2 = 0.1418	R_1 = 0.0631, wR_2 = 0.1379
R indices (all data)	R_1 = 0.0658, wR_2 = 0.1477	R_1 = 0.0904, wR_2 = 0.1522
Largest diff. peak and hole e $Å^{-3}$	1.45/-0.44	0.29/-0.23


1
CH3
BF2
BOPHY core
Molecular Orbitals
Virtual
Occupied
% Composition
2
Br
CH3
BF2
BOPHY core
Molecular Orbitals
Virtual
Occupied
% Composition
4
Br
CC Pyridine
CH3
BF2
CH3
Molecular Orbitals
Virtual
Occupied
% Composition
5
CC Pyridine
Br
CH3
BF2
BOPHY core
Molecular Orbitals
Virtual
Occupied
% Composition

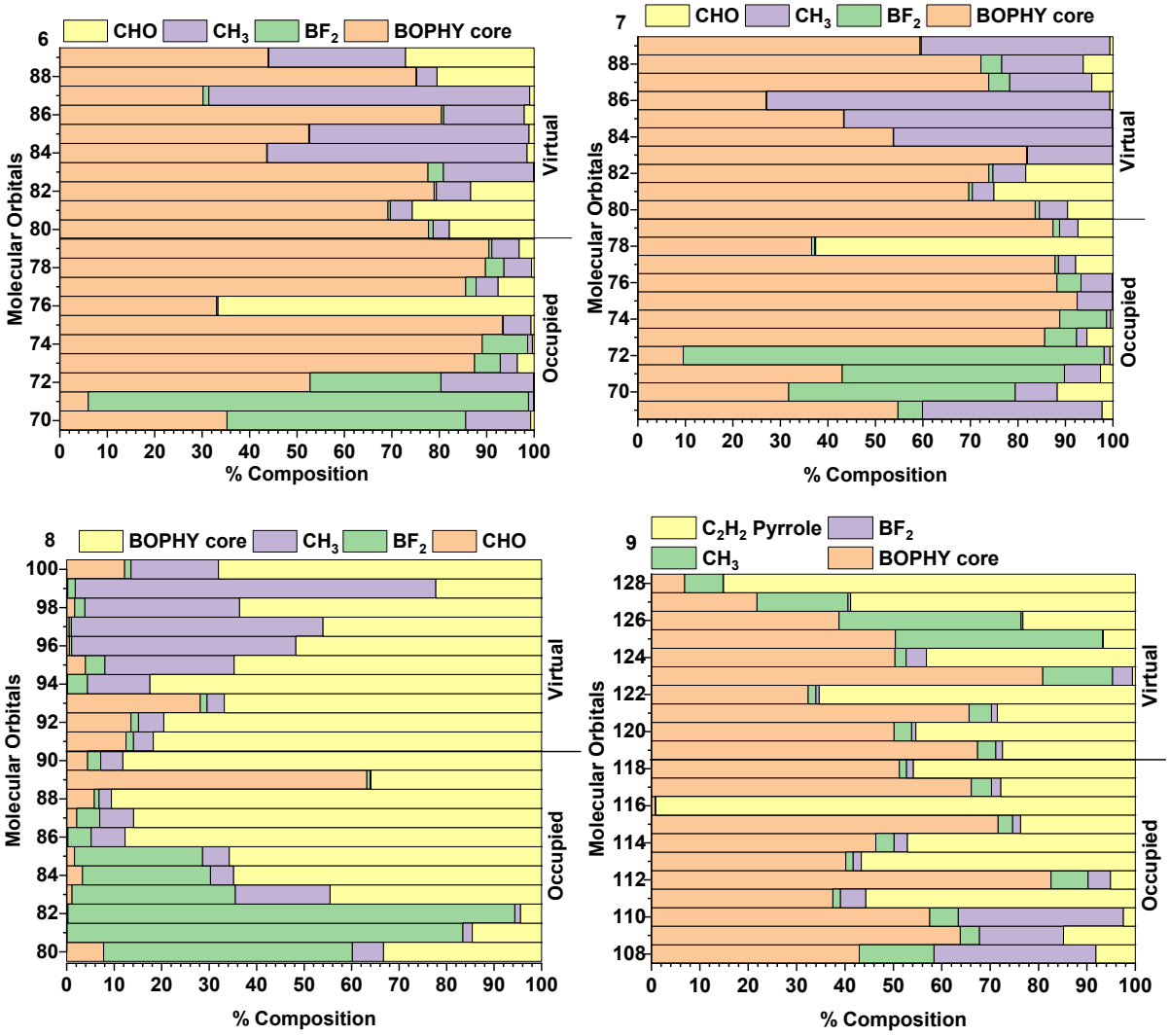
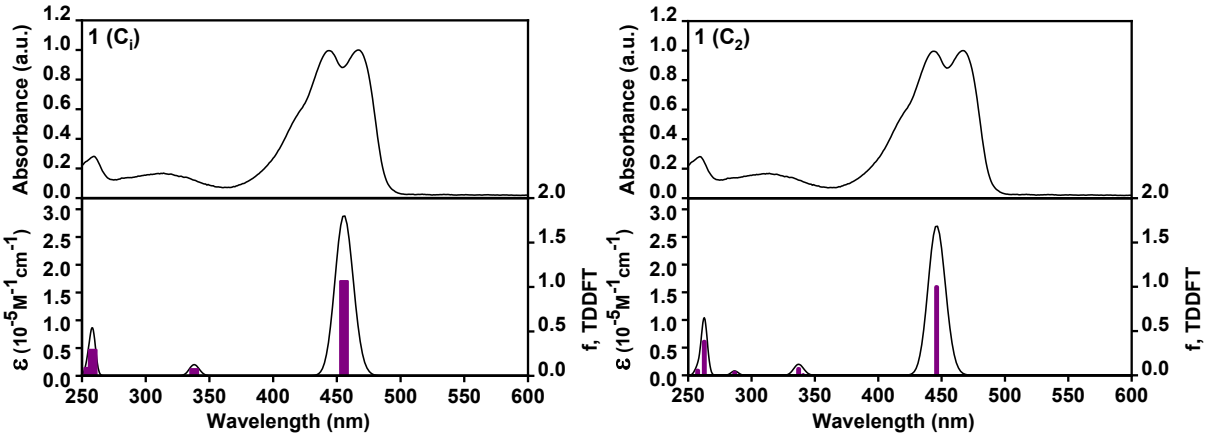


Figure S17. Percentage composition of various fragments in compounds **1**, **2**, and **4-9**.



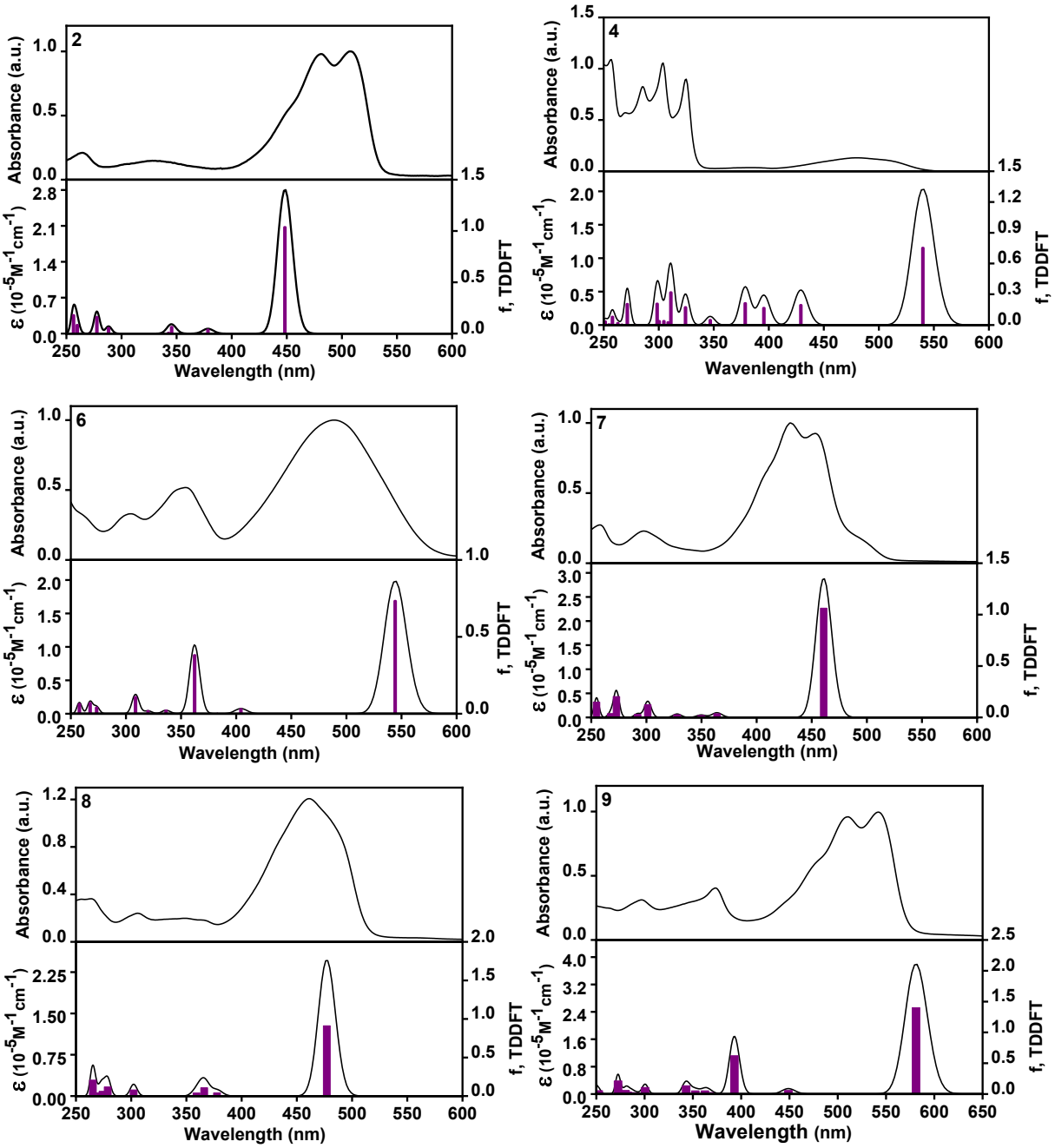


Figure S18. Comparison between experimental (top) and TDDFT at TPSSh level predicted (bottom) UV−vis spectra of compounds **1**, **2**, **4**, **6-9**.

Table S3. Energy, wavelength, oscillator strength, and percentage contribution of transitions for the most intense excited states in compounds **1**, **2**, and **4-9**.

	Excited State	Energy (eV)	Wavelength (nm)	Oscillator Strength	Contributions
1 (C_i)	1	2.72	456	1.0650	100.0% HOMO →LUMO
	4	3.67	338	0.0742	99.0% H-3 → LUMO
	6	4.80	258	0.2913	90.2% H-1 → L+1, 6.73% H-4 → LUMO
	7	4.86	255	0.0874	96.4% H-2 → L+1
	10	5.64	220	0.1151	80.4% H-4 → LUMO, 9.02% HOMO → L+3, 4.42% H-1 → L+1,
	14	6.18	200	0.1106	50.1% HOMO → L+3, 45.3% H-8 → LUMO
	15	6.27	198	0.2645	47.3% H-8 → LUMO, 34.3% HOMO → L+3, 6.98% H-4 → LUMO, 6.36% H-9 → LUMO
	28	6.99	177	0.0875	36.1% H-1 → L+2, 30.5% HOMO → L+6, 17.1% H-2 → L+2
	31	7.11	174	0.2186	49.0% H-1 → L+2, 25.0% HOMO → L+6, 11.3% HOMO → L+7, 9.99% H-2 → L+2
1 (C_2)	1	2.78	446	0.9968	99.8% HOMO → LUMO
	4	3.68	337	0.0726	98.9% H-3 → LUMO
	6	4.72	263	0.3796	94.0% H-1 → L+1
	7	4.82	257	0.0533	96.9% H-2 → L+1
	10	5.75	216	0.0960	82.5% H-4 → LUMO, 9.09% HOMO → L+3
	14	6.24	199	0.1563	63.4% HOMO → L+3, 28.5% H-8 → LUMO
	15	6.32	196	0.1485	65.5% H-8 → LUMO, 18.0% HOMO → L+3, 5.83% H-4 → LUMO
	18	6.49	191	0.0749	82.1% H-11 → LUMO, 7.00% H-5 → L+1
	27	6.97	178	0.1160	51.0% H-1 → L+2, 15.9% H-2 → L+2, 14.9% HOMO → L+6, 5.21% H-17 → LUMO
	30	7.08	175	0.1968	40.7% HOMO → L+6, 33.7% H-1 → L+2, 16.8% H-2 → L+2
2	1	2.77	448	1.0350	99.4% HOMO → LUMO
	3	3.59	346	0.0627	87.7% H-2 → LUMO, 5.82% HOMO → L+1, 5.40% H-3 → LUMO
	5	4.30	288	0.0524	51.9% HOMO → L+1, 16.9% H-3 → LUMO, 15.6% H-1 → L+1, 7.85% H-2 → LUMO, 5.35% H-1 → LUMO
	6	4.47	278	0.1591	80.5% H-1 → L+1, 9.72% HOMO → L+1

	8	4.77	260	0.0820	77.1% H-2 → L+1, 20.4% H-3 → L+1
	9	4.83	256	0.1774	75.2% H-3 → L+1, 17.9% H-2 → L+1
	16	5.97	208	0.0907	77.0% HOMO → L+3, 10.1% H-7 → LUMO
	20	6.23	199	0.0887	59.2% HOMO → L+4, 30.3% H-10 → LUMO
	21	6.29	197	0.1278	60.5% H-10 → LUMO, 17.3% HOMO → L+4, 5.50% H-7 → LUMO
	29	6.66	186	0.0623	81.5% H-15 → LUMO, 12.1% H-1 → L+3
	30	6.67	186	0.4668	76.0% H-1 → L+3, 11.6% H-15 → LUMO
	34	6.8639	181	0.0721	26.1% HOMO → L+6, 21.7% H-2 → L+3, 12.5% H-3 → L+3, 8.80% H-1 → L+4, 8.39% H-17 → LUMO, 6.83% HOMO → L+7
4	1	2.30	540	0.7504	99.8% HOMO → LUMO
	2	2.89	429	0.1930	92.8% H-1 → LUMO
	3	3.13	396	0.1646	85.7% H-2 → LUMO, 11.4% HOMO → L+1
	4	3.27	379	0.2109	80.0% HOMO → L+1, 8.35% H-2 → LUMO
	7	3.82	324	0.1714	68.5% H-5 → LUMO, 20.3% H-1 → L+1, 6.85% HOMO → L+2
	8	3.99	311	0.3169	64.6% H-1 → L+1, 14.4% HOMO → L+2, 6.81% H-7 → LUMO, 6.30% H-2 → L+1, 5.45% H-5 → LUMO
	12	4.15	299	0.2058	51.4% H-2 → L+1, 28.6% HOMO → L+3, 17.4% HOMO → L+2
	15	4.57	271	0.2030	36.2% HOMO → L+2, 21.1% H-2 → L+1, 17.8% H-5 → LUMO, 10.2% H-1 → L+1
	18	4.81	258	0.0780	78.5% H-1 → L+2, 13.4% H-5 → L+1
	28	5.23	237	0.0599	48.1% H-2 → L+3, 40.3% H-6 → L+1
5	1	2.27	547	0.7218	99.2% HOMO → LUMO
	2	2.78	446	0.2763	92.0% H-1 → LUMO, 6.05% H-2 → LUMO
	3	3.06	405	0.2048	89.1% H-2 → LUMO
	4	3.10	399	0.0662	94.8% H-3 → LUMO
	6	3.45	359	0.2906	74.1% HOMO → L+1, 18.0% H-6 → LUMO
	8	3.75	331	0.0753	45.8% H-6 → LUMO, 18.1% H-7 → LUMO, 11.2% HOMO → L+2, 10.4% H-1 → L+1, 8.39% HOMO → L+1
	9	3.82	325	0.0550	77.0% H-7 → LUMO, 9.57% H-6 → LUMO
	10	4.00	310	0.3515	64.2% H-1 → L+1, 33.0% HOMO → L+2
	13	4.43	280	0.2256	29.7% H-2 → L+1, 19.1% HOMO → L+2, 12.9% HOMO → L+3, 9.97% H-1 → L+1, 8.75% H-6 → LUMO, 7.63% HOMO → L+1

6	1	2.28	544	0.7318	99.5% HOMO → LUMO
	4	3.42	362	0.3795	69.0% H-2 → LUMO, 27.2% HOMO → L+1
	7	4.02	309	0.1068	45.0% HOMO → L+1, 18.9% H-2 → LUMO, 13.8% H-5 → LUMO, 10.4% H-4 → LUMO, 9.48% HOMO → L+2
	9	4.63	268	0.0678	97.1% H-1 → L+1
	11	4.81	258	0.0622	70.6% H-2 → L+1, 22.6% H-6 → LUMO
	13	5.33	232	0.3218	50.5% H-6 → LUMO, 13.8% H-5 → L+1, 11.9% H-1 → L+2, 11.1% H-2 → L+1
	15	5.45	228	0.0989	81.9% H-5 → L+1, 8.15% H-6 → LUMO
	16	5.57	222	0.1552	89.3% H-2 → L+2
	20	5.96	208	0.0861	95.1% H-4 → L+2
	24	6.24	199	0.0837	43.8% H-11 → LUMO, 38.4% HOMO → L+3, 5.73% H-6 → L+1
	25	6.26	198	0.0690	46.6% H-11 → LUMO, 32.7% HOMO → L+3, 6.84% H-6 → L+1
	28	6.60	188	0.1481	59.9% H-6 → L+1, 21.6% H-13 → LUMO, 7.19% HOMO → L+3
7	1	2.69	461	1.0630	99.9% HOMO → LUMO
	6	4.12	301	0.1238	54.1% HOMO → L+1, 26.4% H-2 → LUMO, 13.6% H-5 → LUMO
	9	4.54	273	0.2027	75.1% H-2 → L+1, 18.0% HOMO → L+2
	11	4.87	255	0.1486	59.8% HOMO → L+2, 12.5% H-4 → L+1, 10.5% H-2 → L+1, 6.06% H-6 → LUMO, 5.50% H-3 → L+1
	15	5.56	223	0.2109	58.7% H-2 → L+2, 29.4% H-6 → LUMO
	16	5.63	220	0.1242	50.3% H-6 → LUMO, 31.5% H-2 → L+2
	17	5.77	215	0.1632	92.5% H-3 → L+2
	21	6.19	200	0.1928	79.5% HOMO → L+3, 6.18% H-6 → L+1
	38	7.15	173	0.0835	22.2% H-2 → L+3, 18.4% H-3 → L+3, 13.6% HOMO → L+7, 12.7% H-15 → LUMO, 10.6% H-8 → L+1, 10.3% HOMO → L+8, 5.45% H-16 → LUMO
8	1	2.60	477	0.9109	99.1% HOMO → LUMO
	4	3.39	366	0.1078	50.9% H-3 → LUMO, 28.3% HOMO → L+1, 15.6% H-2 → LUMO
	6	4.10	302	0.0790	63.7% HOMO → L+1, 17.8% H-2 → LUMO, 13.9% H-3 → LUMO
	8	4.45	279	0.1178	60.1% H-2 → L+1, 31.7% HOMO → L+2
	9	4.53	274	0.0618	71.7% H-3 → L+1, 14.1% H-2 → L+1, 9.91% HOMO → L+2
	11	4.67	265	0.2068	49.9% HOMO → L+2, 18.7% H-3 → L+1, 16.6% H-2 → L+1

	15	5.47	227	0.0523	70.7% H-3 → L+2, 13.1% H-4 → L+2, 10.9% H-2 → L+2
	16	5.53	224	0.1815	39.6% H-6 → LUMO, 26.5% H-5 → LUMO, 13.4% H-4 → L+2
	17	5.61	221	0.2058	68.2% H-4 → L+2, 9.75% H-6 → LUMO, 5.95% H-5 → LUMO, 5.38% H-2 → L+2
	26	6.32	196	0.0827	53.7% HOMO → L+3, 28.0% H-6 → L+1, 11.5% H-14 → LUMO
	29	6.58	188	0.0693	28.5% H-16 → LUMO, 25.5% H-5 → L+1, 24.1% H-6 → L+1, 13.2% HOMO → L+3
9	1	2.13	581	1.401	99.3% HOMO → LUMO
	3	3.16	393	0.622	57.5% HOMO → L+1, 37.9% H-1 → LUMO
	9	3.61	343	0.1346	46.0% H-1 → L+1, 36.9% H-6 → LUMO, 8.27% HOMO → L+2, 6.36% H-5 → LUMO
	11	4.13	301	0.1065	29.4% H-1 → L+1, 20.3% H-1 → L+2, 19.3% HOMO → L+2, 7.87% H-5 → LUMO, 5.69% H-3 → LUMO, 5.59% H-3 → L+1
	17	4.55	272	0.2126	25.6% H-1 → L+2, 17.2% H-5 → L+1, 15.2% H-7 → LUMO, 11.8% HOMO → L+3, 10.8% H-4 → L+1, 10.2% H-3 → L+1
	21	5.01	247	0.138	69.2% H-5 → L+2, 12.7% H-6 → L+2, 9.00% H-7 → LUMO, 5.83% H-1 → L+3
	29	5.76	215	0.1082	55.5% HOMO → L+4, 24.8% H-3 → L+3, 11.4% H-7 → L+1
	33	5.89	210	0.1093	48.3% H-6 → L+3, 24.4% H-5 → L+3, 17.1% H-7 → L+1