Supporting Information

Cationic Halogenated BODIPYs as Water-soluble Photosensitizers for Photodynamic Therapy

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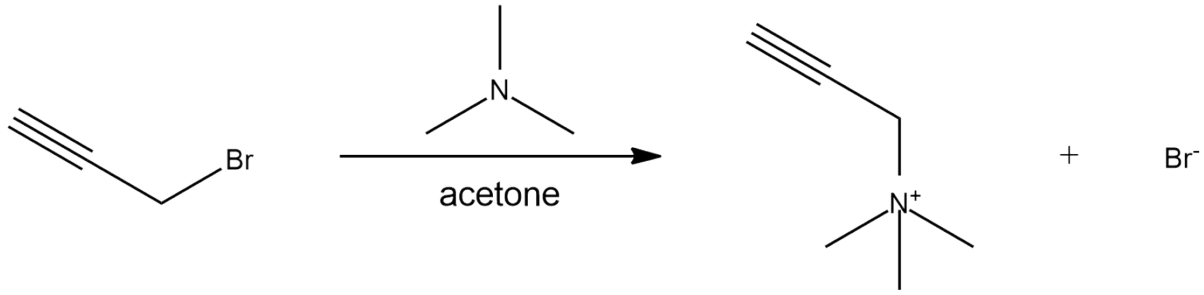
S1. Synthesis of N,N,N-trimethylprop-2-yn-1-aminium bromide.



Scheme S 1. Synthesis of N,N,N-trimethylprop-2-yn-1-aminium bromide.

Propargyl bromide (0.8 mL) was dissolved in acetone (5 mL) in a 100 mL round-bottomed flask under an argon atmosphere. Trimethylamine (2 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 5 minutes under argon. A white precipitate formed upon stirring. The solid was collected by filtration, washed with acetone (3×), and dried to afford a white powder (689.6 mg, 36.22% yield).

^{1}H NMR (400 MHz, D_2O) δ 4.79 (s, 2H), 3.13 (s, 9H), 2.04 (s, 1H).

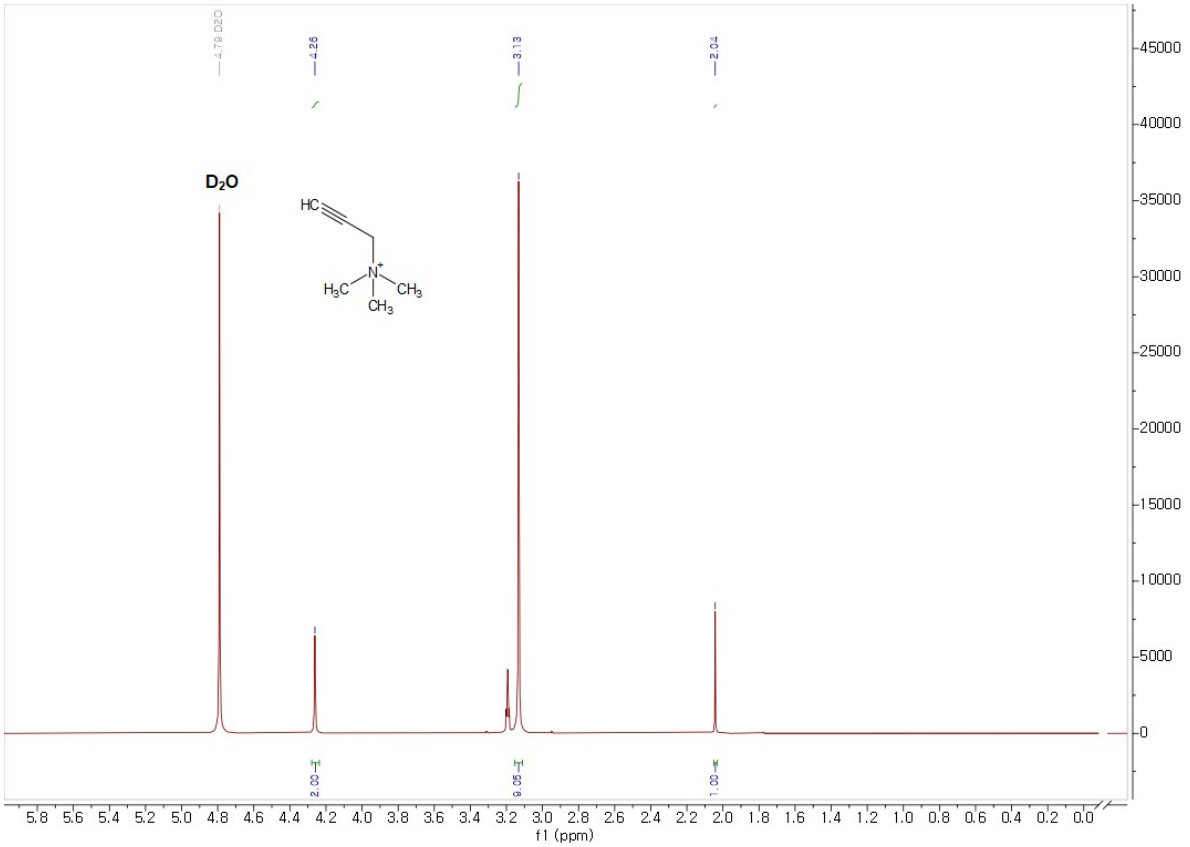


Figure S 1. ^{1}H NMR (400 MHz) spectrum of N,N,N-trimethylprop-2-yn-1-aminium bromide in D_2O.

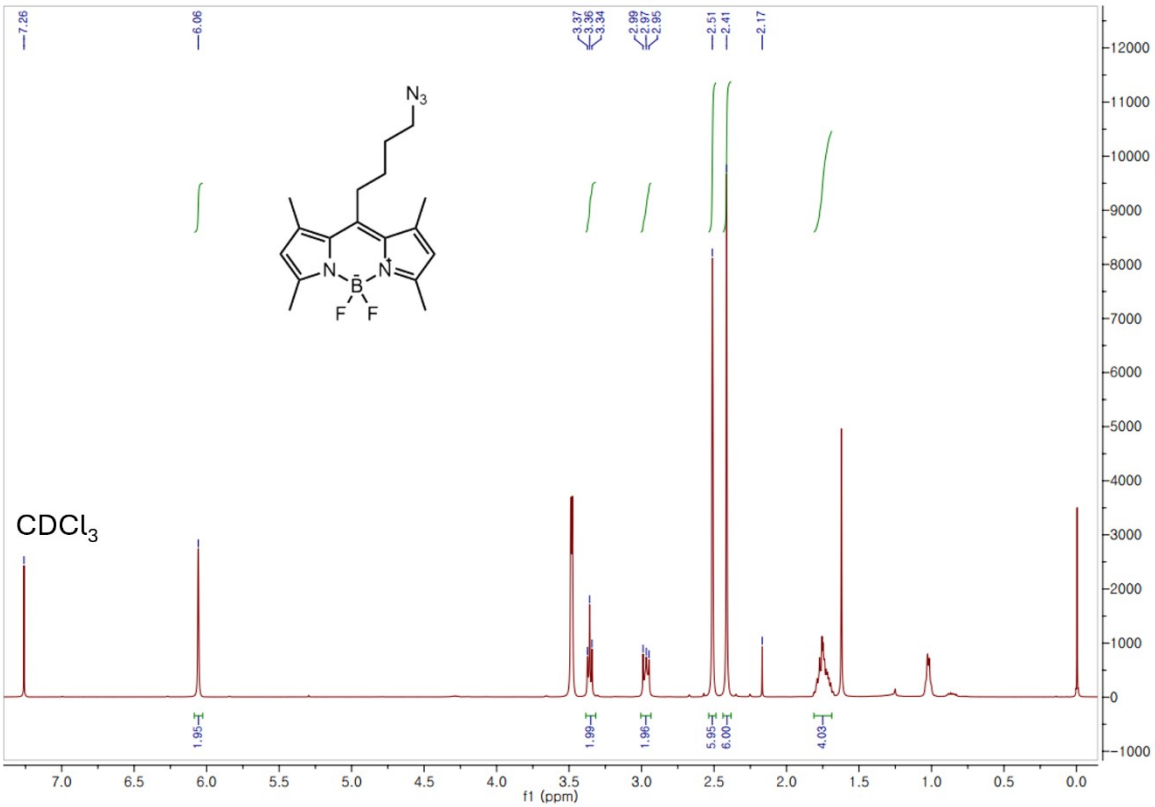


Figure S 2. ^{1}H-NMR (400 MHz) spectrum of Compound 2 in $CDCl_3$.

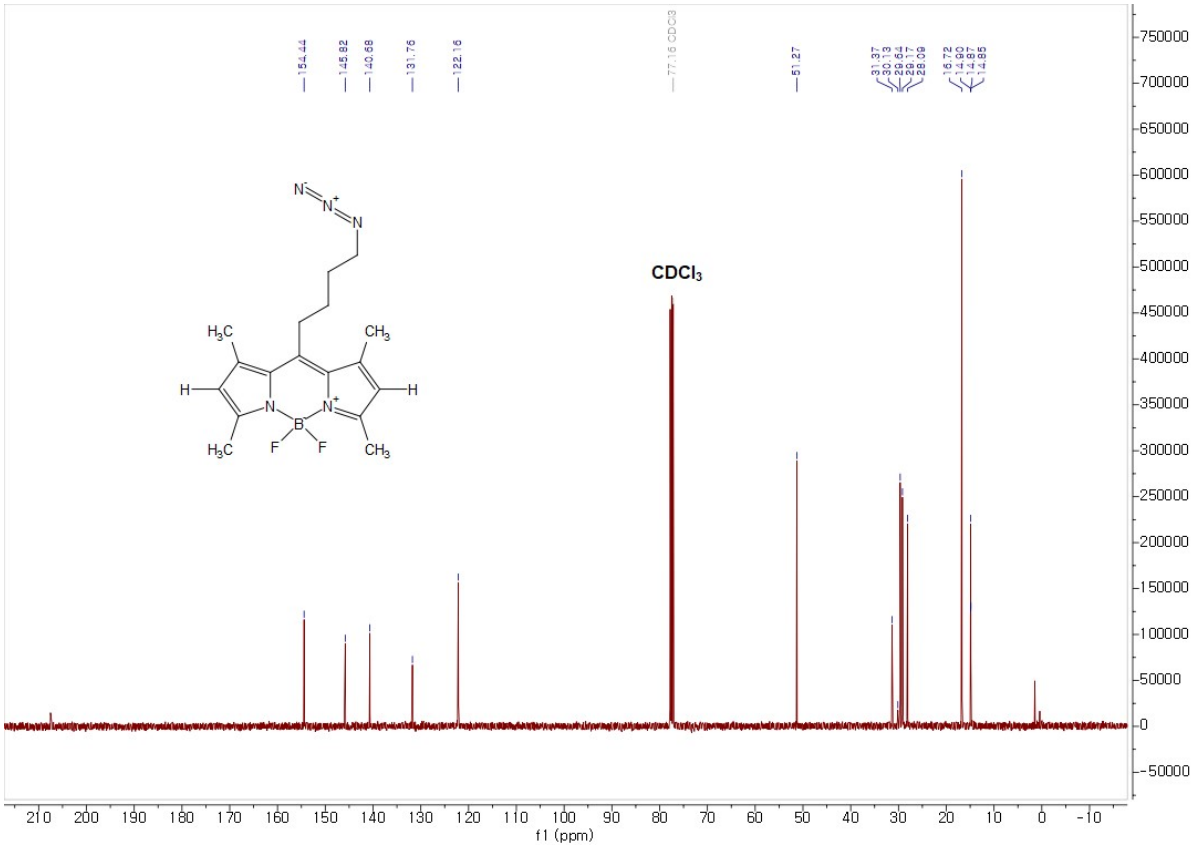


Figure S 3. ^{13}C NMR (101 MHz) spectrum of Compound 2 in $CDCl_3$.

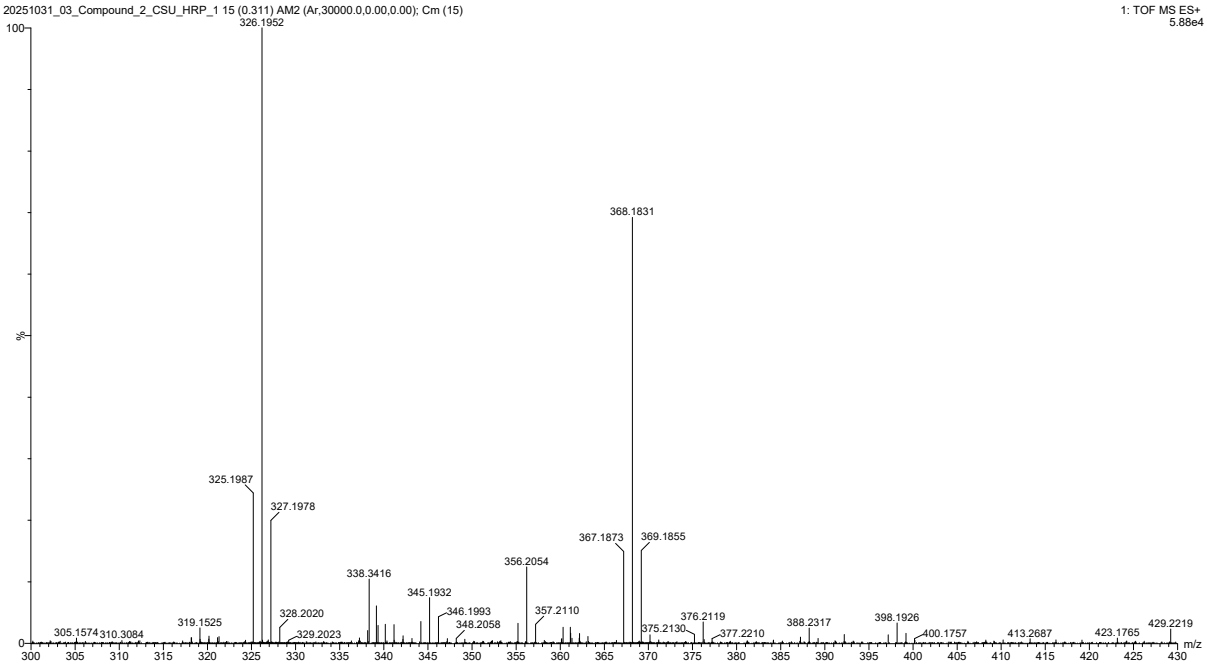


Figure S 4. HR-ESI mass spectrum of Compound 2.

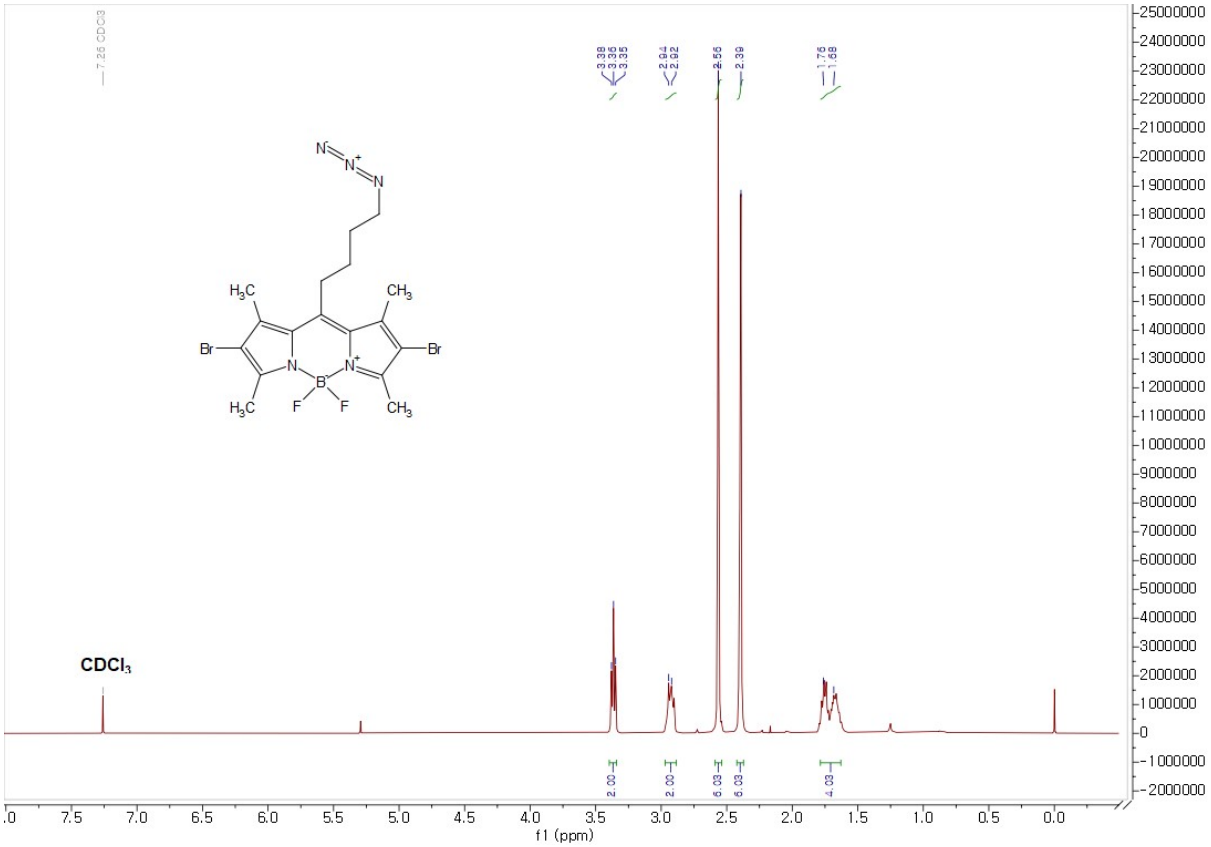


Figure S 5. ^{1}H-NMR (400 MHz) spectrum of Compound 3 in $CDCl_3$.

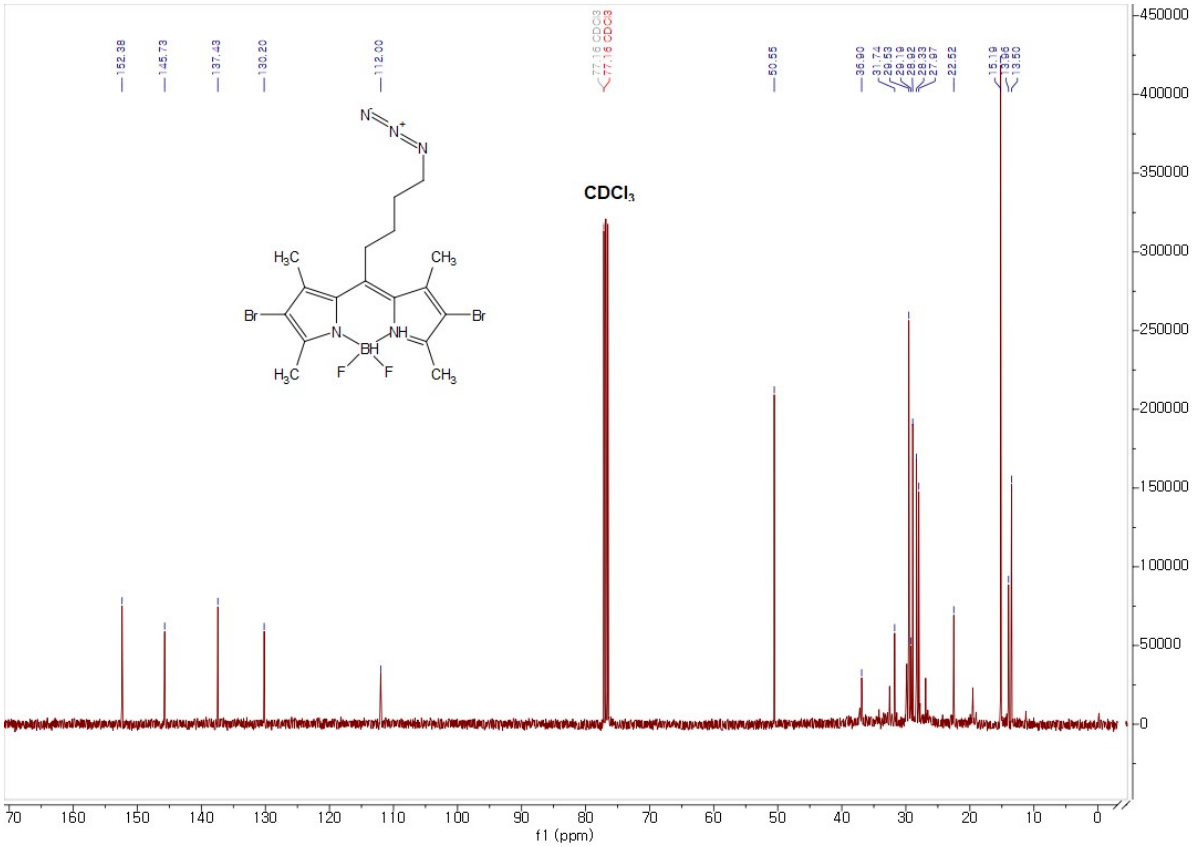


Figure S 6. ^{13}C NMR (101 MHz) spectrum of Compound 3 in $CDCl_3$.

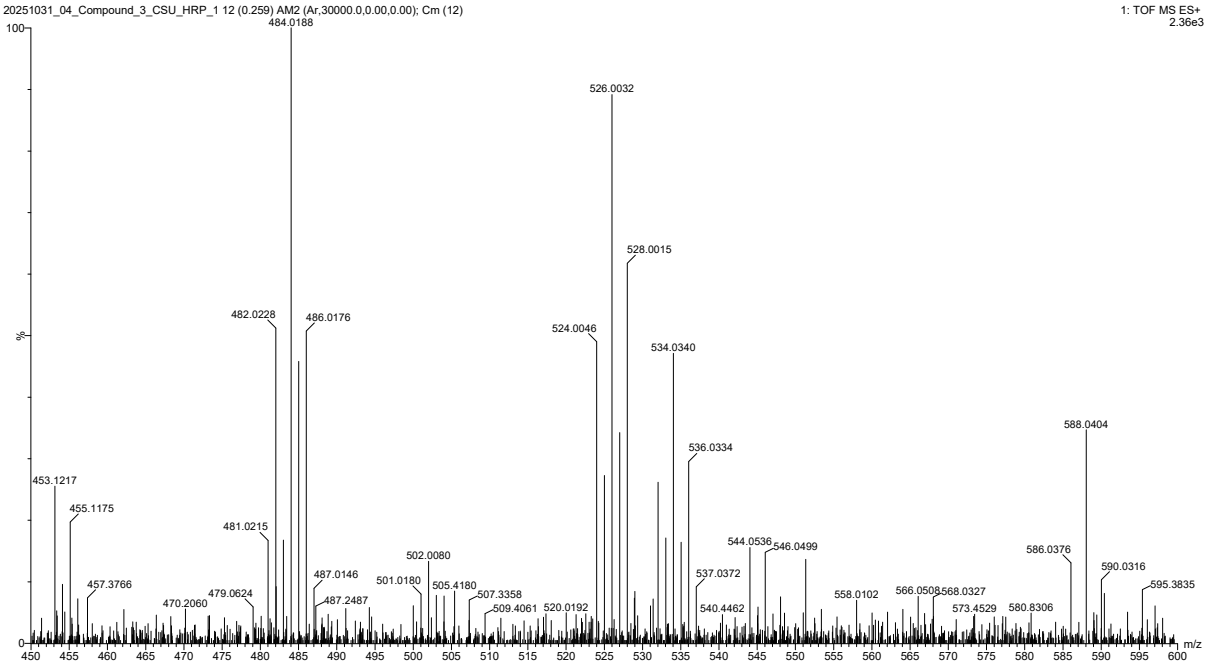


Figure S 7. HR-ESI mass spectrum of Compound 3.

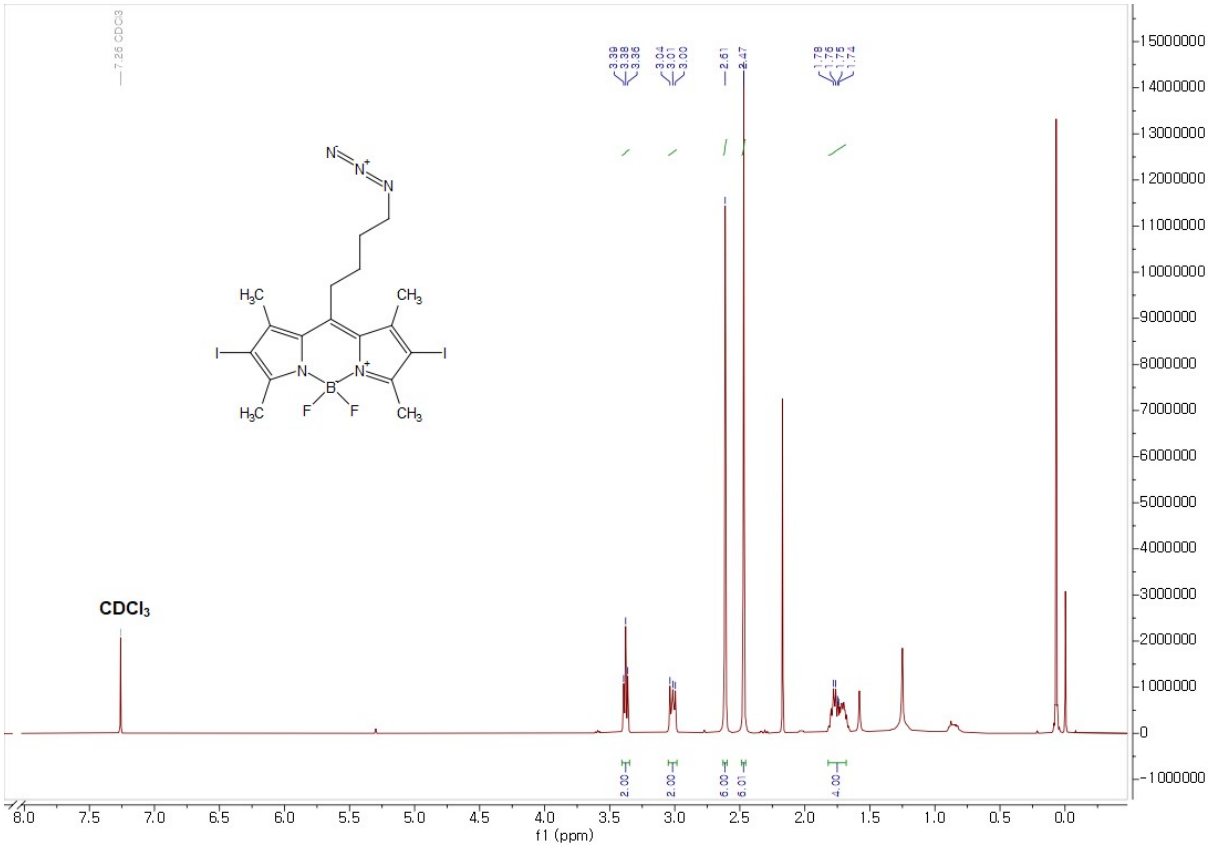


Figure S 8. ^{1}H-NMR spectrum (400 MHz) spectrum of Compound 4 in $CDCl_3$.

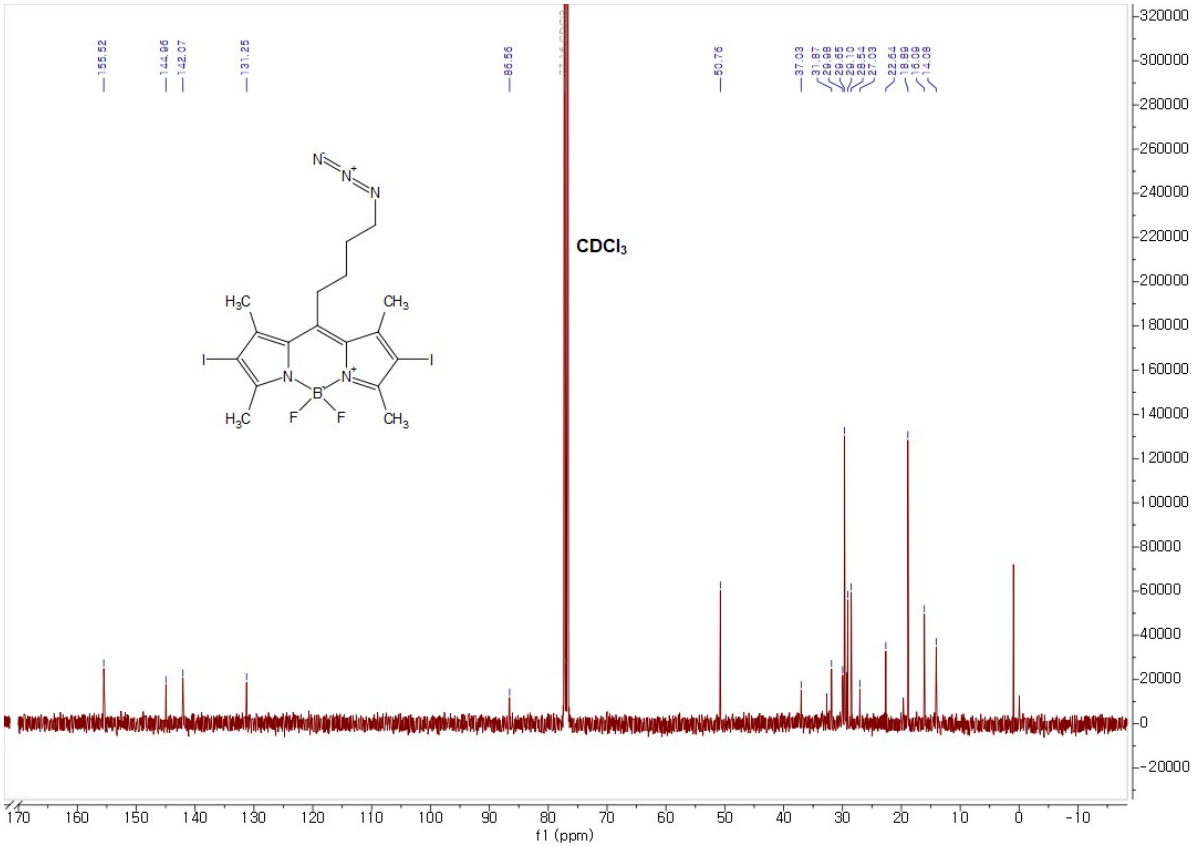


Figure S 9. ^{13}C NMR (101 MHz) spectrum of Compound 4 in $CDCl_3$.

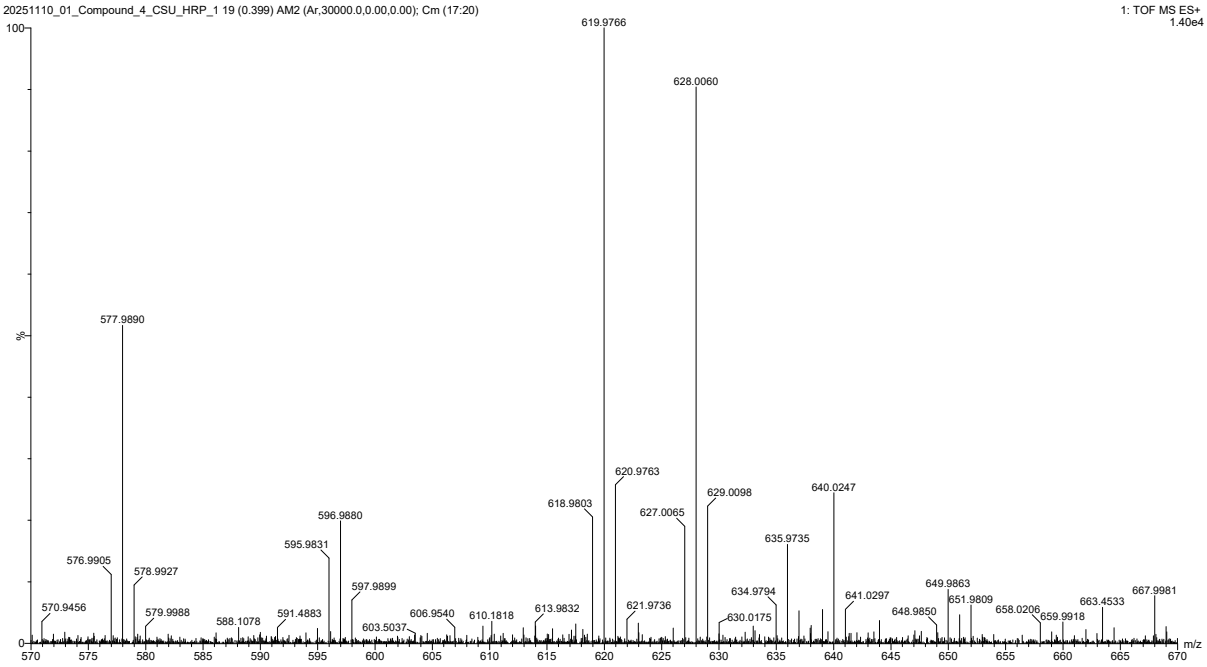


Figure S 10. HR-ESI mass spectrum of Compound 4.

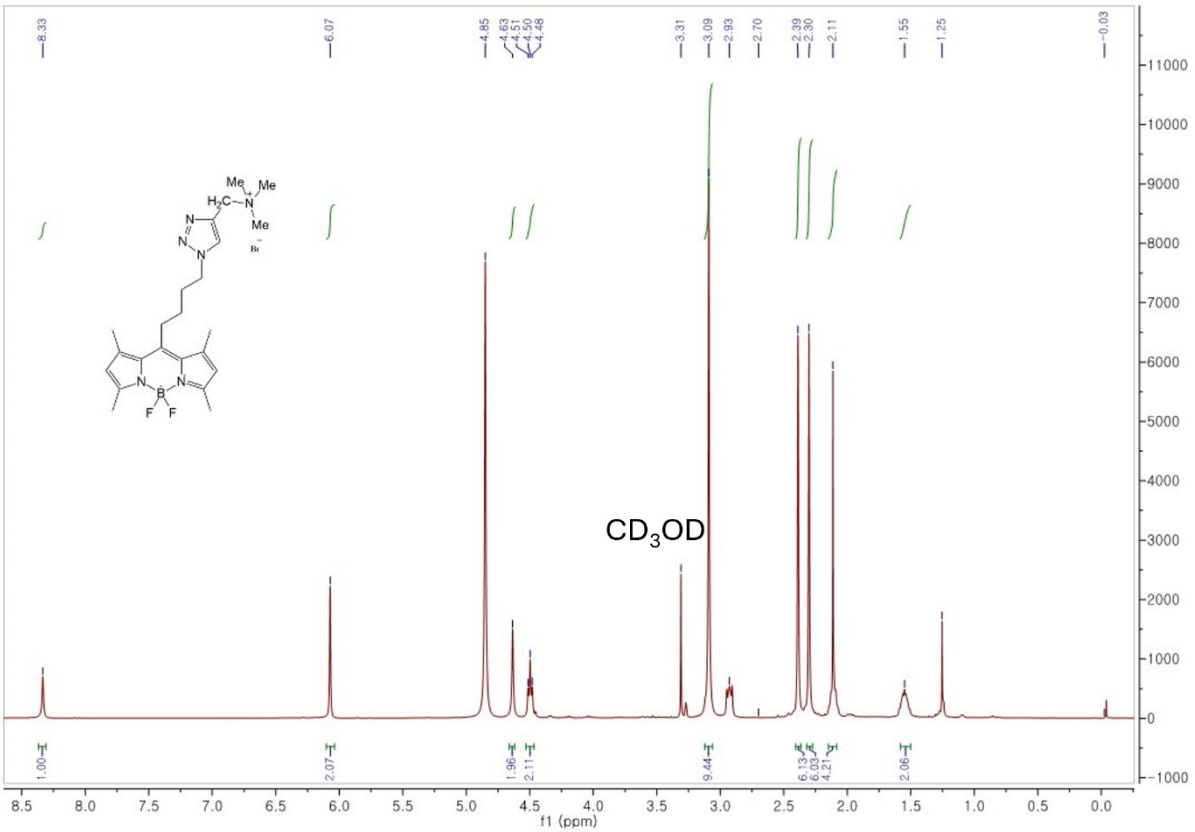


Figure S 11. ^{1}H-NMR (400 MHz) spectrum of **BHTM** in CD_3OD.

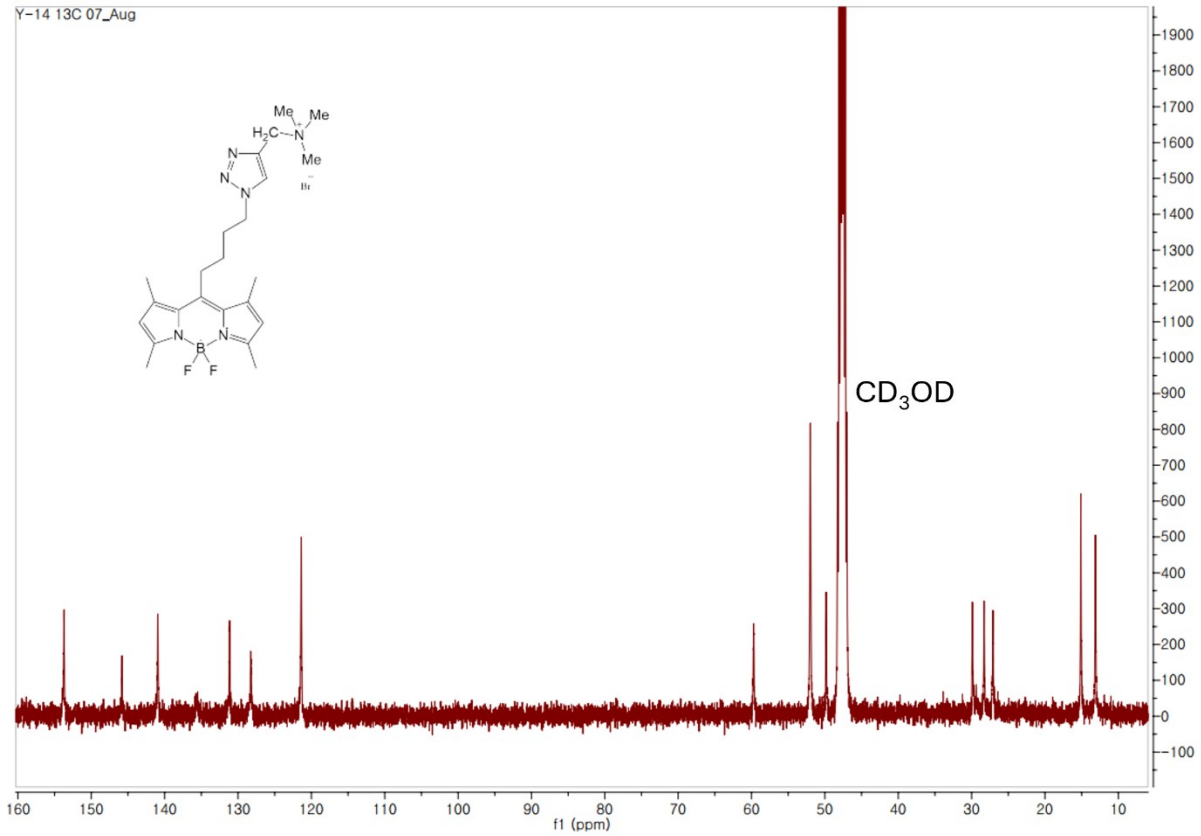


Figure S 12. ^{13}C-NMR spectrum (101 MHz) of **BHTM** in CD_3OD.

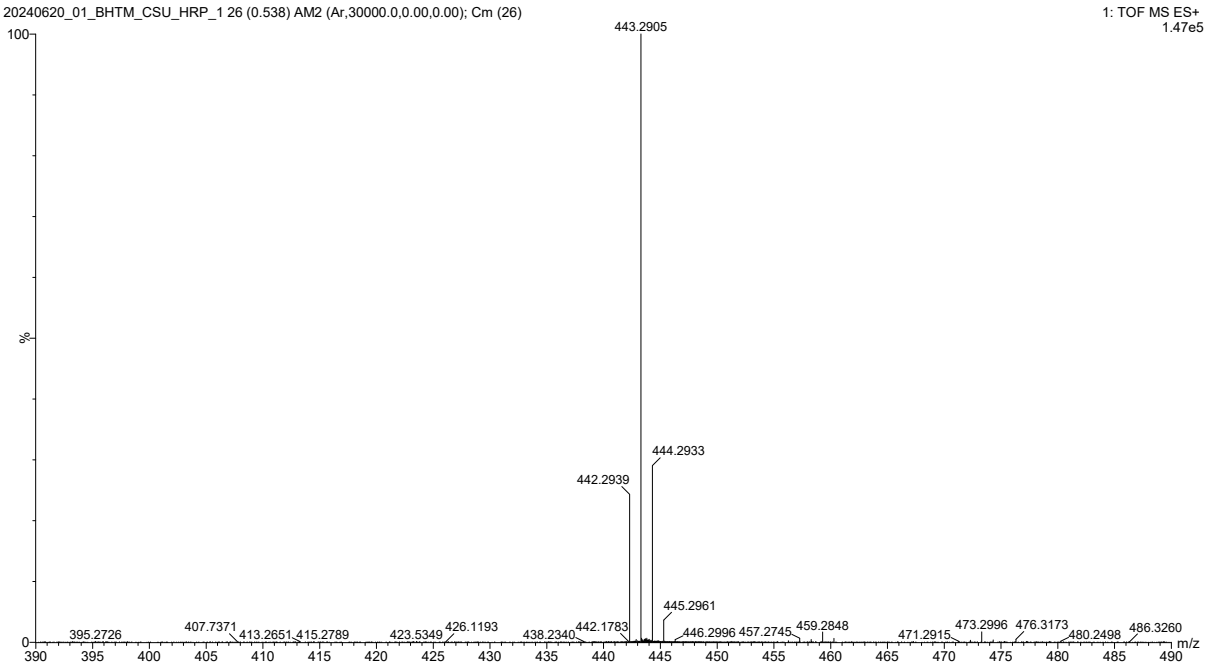


Figure S 13. HR-ESI mass spectrum of **BHTM**.

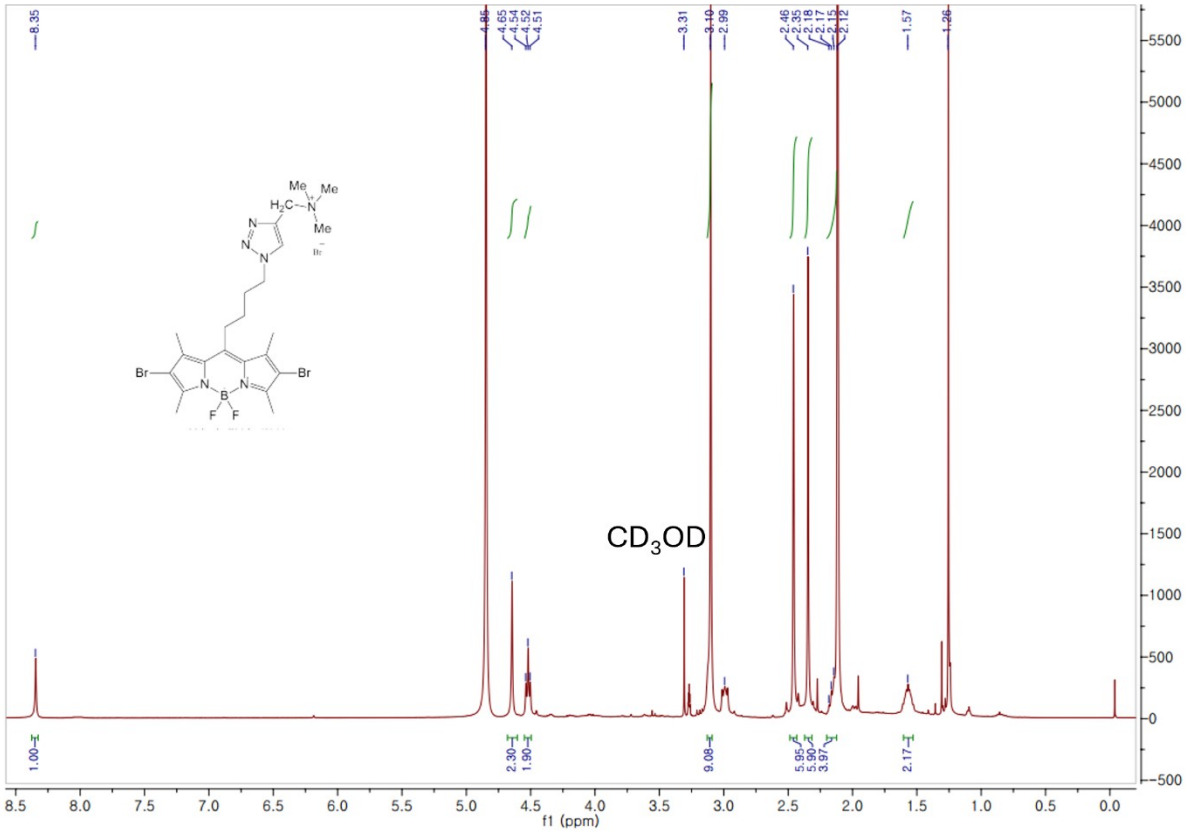


Figure S 14. ^{1}H-NMR (400 MHz) spectrum of **BBrTM** in CD_3OD.

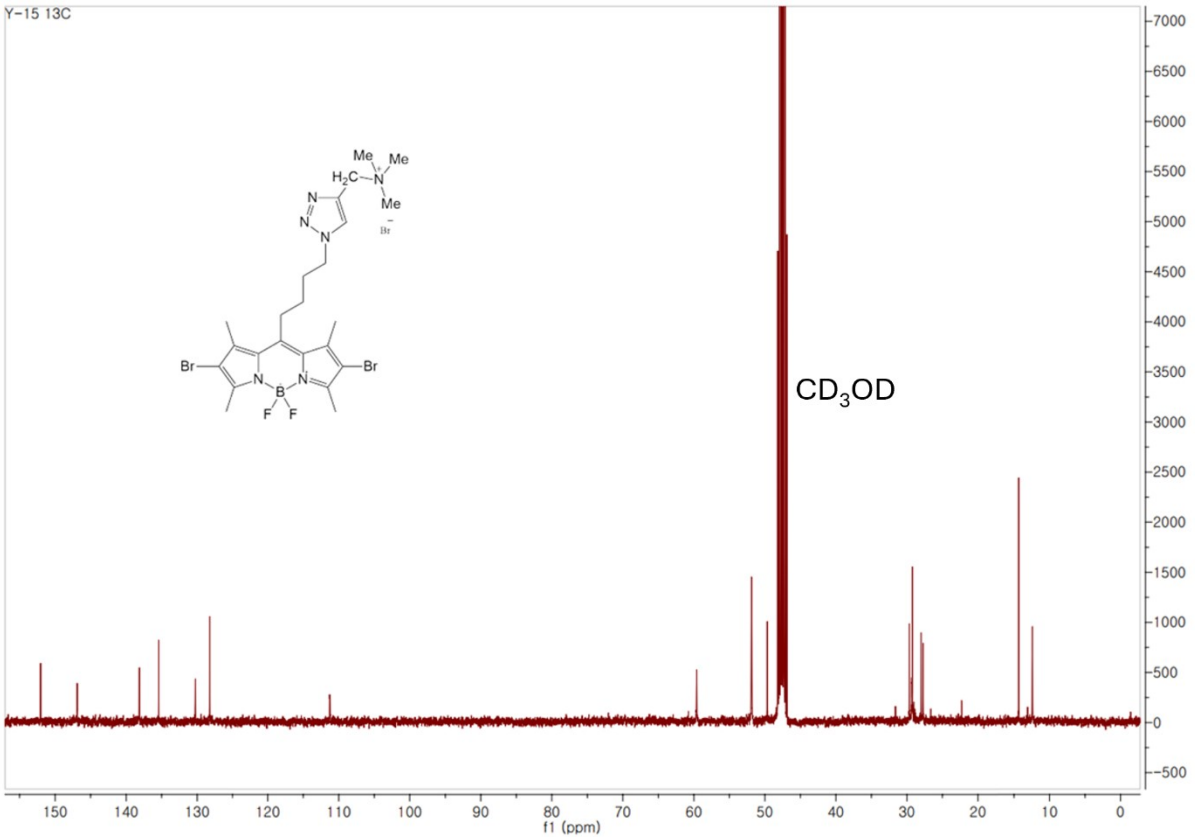


Figure S 15. ^{13}C-NMR (101 MHz) spectrum of **BBrTM** in CD_3OD.

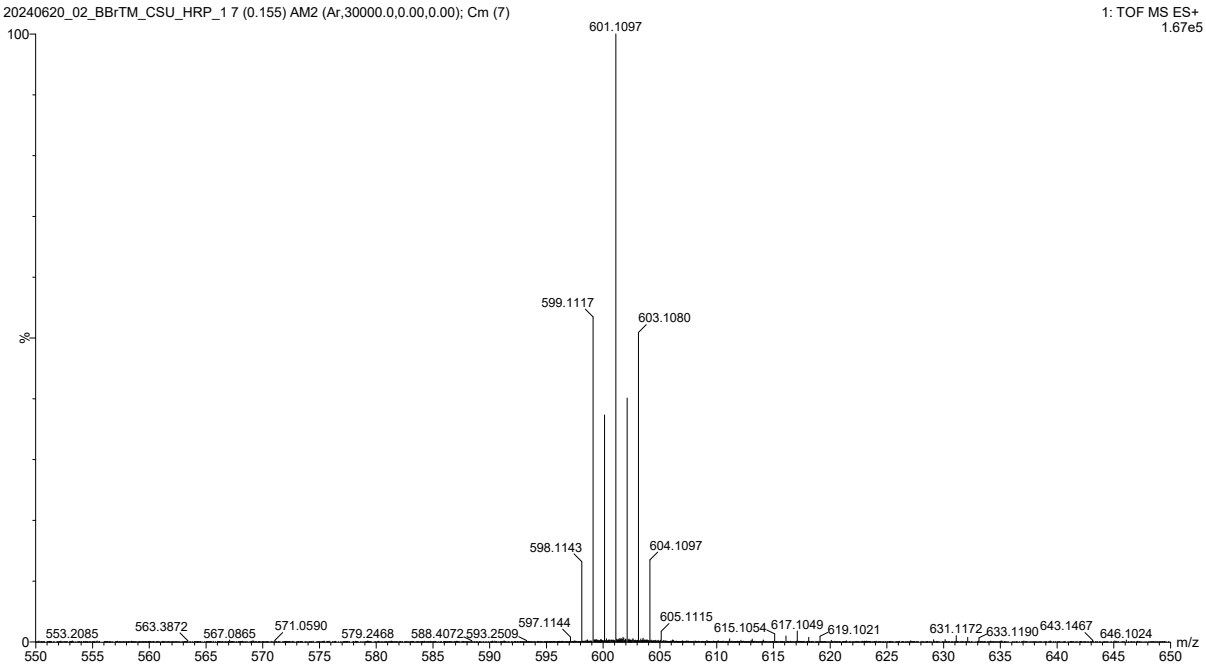


Figure S 16. HR-ESI mass spectrum of **BBrTM**.

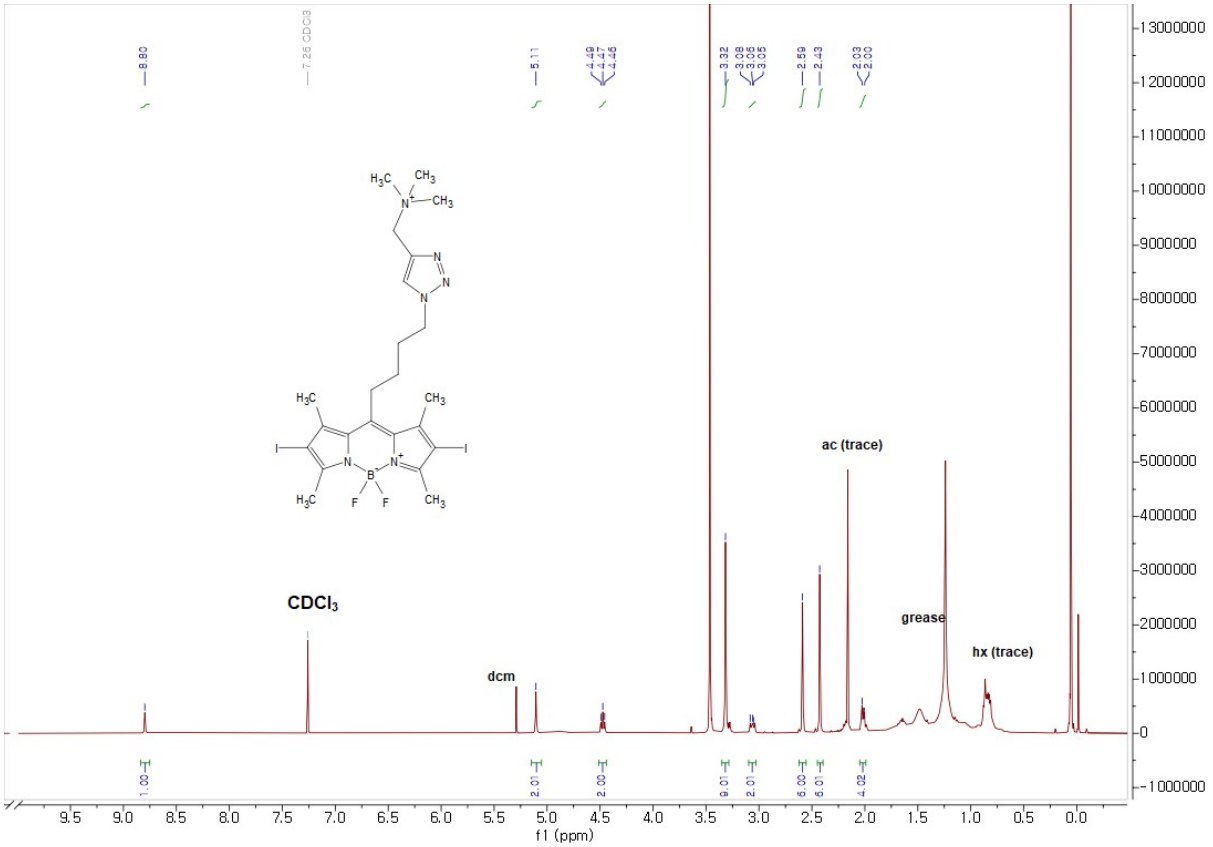


Figure S 17. ^{1}H-NMR spectrum (400 MHz) spectrum of **BITM** in $CDCl_3$.

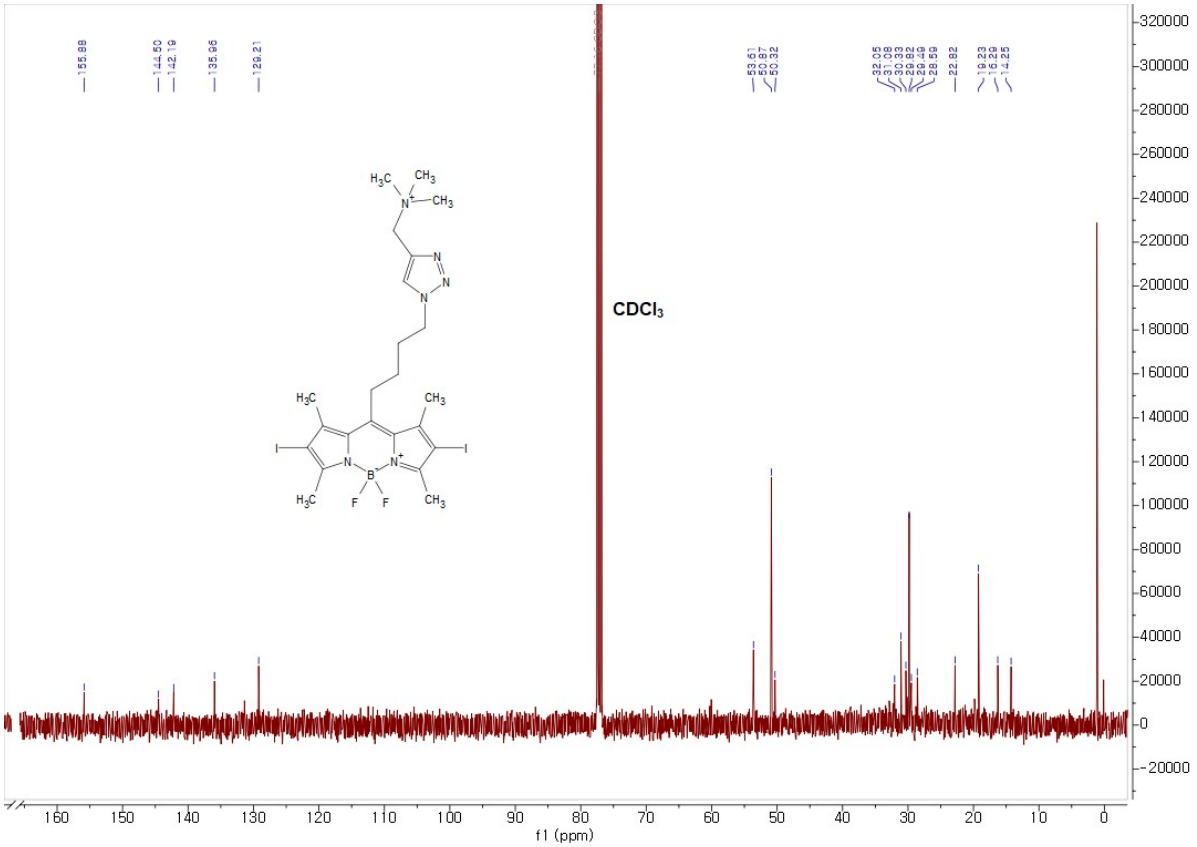


Figure S 18. ^{13}C NMR (101 MHz) spectrum of **BITM** in $CDCl_3$.

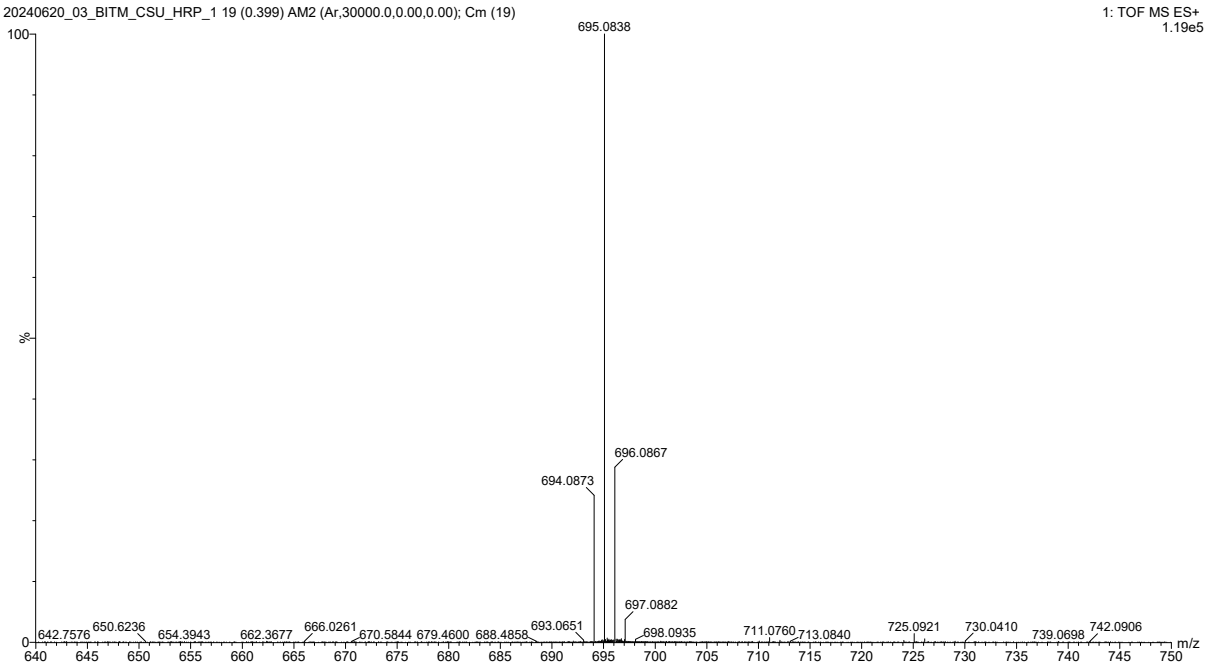


Figure S 19. HR-ESI mass spectrum of **BITM**.

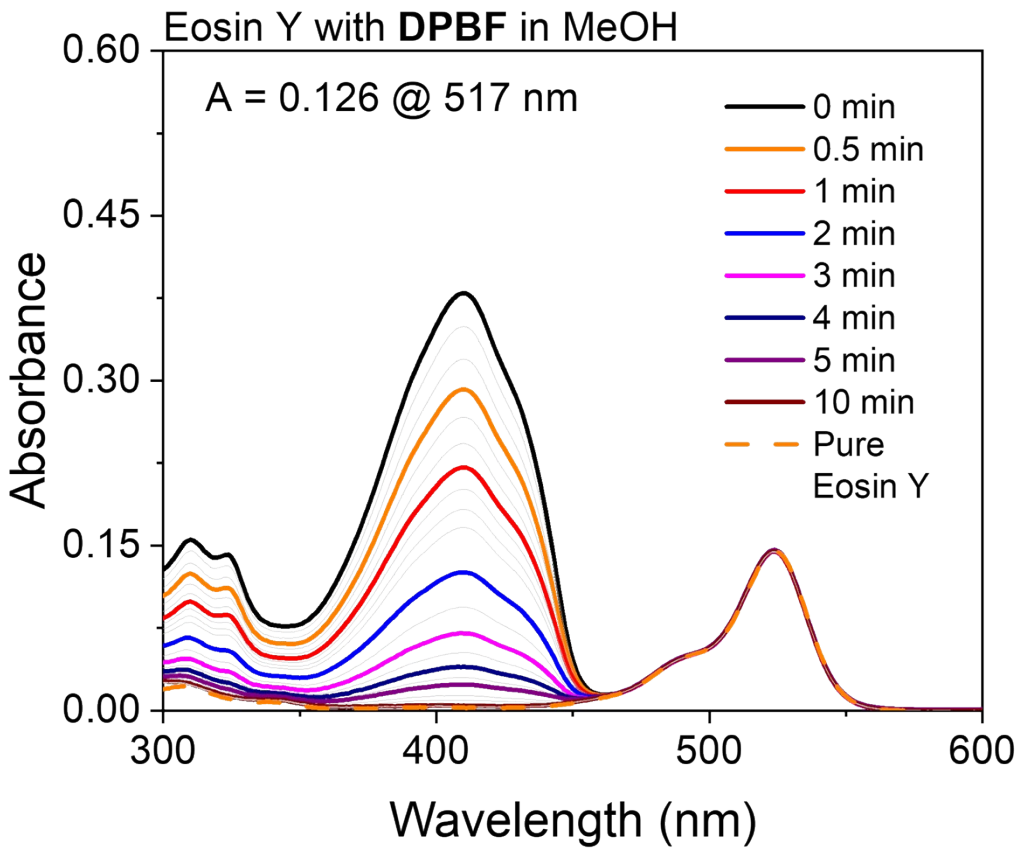
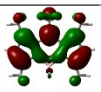
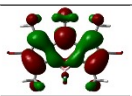
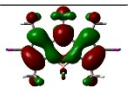
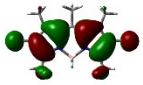
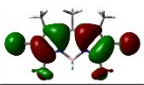
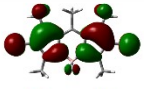
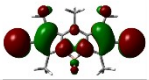
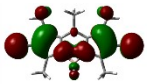
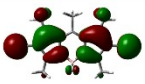
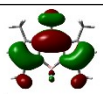
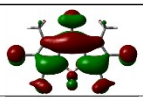
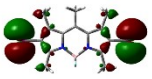
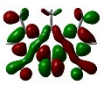
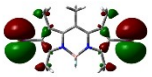


Figure S 20. Time-dependent absorption spectra of 1,3-diphenylisobenzofuran (DPBF) in MeOH with Eosin Y after LED laser irradiation at 517 nm.

	BHTM	BBrTM	BITM
LUMO			
HOMO			
H – 1			
H – 2			
H – 3			
H – 4			

	HOMO – LUMO gap (eV)
BHTM	3.063
BBrTM	2.945
BITM	2.918

S_1 state of **BHTM**
3.0221 eV 410.25 nm f=0.5075
HOMO-1 -> LUMO 4.0%
HOMO -> LUMO 97.1%
HOMO <- LUMO - 2.5%

S_1 state of **BBrTM**
2.7960 eV 443.43 nm f=0.4670
HOMO-1 -> LUMO 9.8% (-0.22138)
HOMO -> LUMO 90.9% (0.67416)

S_1 state of **BITM**
2.7440 eV 451.83 nm f=0.4695
HOMO-1 -> LUMO 11.3% (-0.23803)
HOMO -> LUMO 89.2% (0.66778)

Chart S 1. Frontier molecular orbitals and their corresponding energy levels (eV) of **BHTM**, **BBrTM**, and **BITM**, calculated at the B3LYP/Def2-TZVP level of theory using Gaussian 16.

<BHTM>

Excited State 1: Triplet-A 1.6140 eV 768.18 nm f=0.0000 <S**2>=2.000
HOMO(69) -> LUMO(70) 100.5% (0.70898)
HOMO(69) <- LUMO(70) - 2.3% (0.10638)

Excited State 2: Triplet-A 2.8269 eV 438.59 nm f=0.0000 <S**2>=2.000
HOMO-1(68) -> LUMO(70) 96.1% (0.69323)

Excited State 3: Triplet-A 2.9721 eV 417.16 nm f=0.0000 <S**2>=2.000
HOMO-3(66) -> LUMO(70) 5.1% (-0.15989)
HOMO-2(67) -> LUMO(70) 90.6% (0.67290)
HOMO-1(68) -> LUMO+1(71) 2.1% (-0.10450)

Excited State 4: Singlet-A 3.0221 eV 410.25 nm f=0.5075 <S**2>=0.000
HOMO-1(68) -> LUMO(70) 4.0% (0.14114)
HOMO(69) -> LUMO(70) 97.1% (0.69662)
HOMO(69) <- LUMO(70) - 2.5% (-0.11172)

Excited State 5: Triplet-A 3.4403 eV 360.39 nm f=0.0000 <S**2>=2.000
HOMO-3(66) -> LUMO(70) 91.8% (0.67753)
HOMO-2(67) -> LUMO(70) 0.16377

Excited State 6: Singlet-A 3.5398 eV 350.26 nm f=0.0702 <S**2>=0.000
HOMO-1(68) -> LUMO(70) 95.4% (0.69051)
HOMO(69) -> LUMO(70) 4.2% (-0.14452)

Excited State 7: Singlet-A 3.7593 eV 329.81 nm f=0.0284 <S**2>=0.000
HOMO-2(67) -> LUMO(70) 99.1% (0.70392)

Table S 1. Simulated excited states based on B3LYP/Def2TZVP level in the Gaussian 16 (**BHTM**).

<BBrTM>

Excited State 1:	Triplet-A	1.5748 eV	787.32 nm	f=0.0000 <S**2>=2.000
HOMO-1(102) -> LUMO(104)		3.2% (0.12597)		
HOMO(103) -> LUMO(104)		98.3% (0.70103)		
Excited State 2:	Triplet-A	2.5868 eV	479.30 nm	f=0.0000 <S**2>=2.000
HOMO-1(102) -> LUMO(104)		93.5% (0.68390)		
HOMO(103) -> LUMO(104)		3.0% (-0.12229)		
Excited State 3:	Triplet-A	2.7590 eV	449.37 nm	f=0.0000 <S**2>=2.000
HOMO-2(101) -> LUMO(104)		94.3% (0.68670)		
Excited State 4:	Singlet-A	2.7960 eV	443.43 nm	f=0.4670 <S**2>=0.000
HOMO-1(102) -> LUMO(104)		9.8% (-0.22138)		
HOMO(103) -> LUMO(104)		90.9% (0.67416)		
Excited State 5:	Triplet-A	3.2312 eV	383.71 nm	f=0.0000 <S**2>=2.000
HOMO-3(100) -> LUMO(104)		92.8% (0.68103)		
Excited State 6:	Singlet-A	3.3823 eV	366.56 nm	f=0.2344 <S**2>=0.000
HOMO-1(102) -> LUMO(104)		89.7% (0.66952)		
HOMO(103) -> LUMO(104)		10.2% (0.22616)		
Excited State 7:	Singlet-A	3.4173 eV	362.81 nm	f=0.0376 <S**2>=0.000
HOMO-2(101) -> LUMO(104)		97.8% (0.69935)		

Table S 2. Simulated excited states based on B3LYP/Def2TZVP level in the Gaussian 16 (**BBrTM**).

<BITM>

Excited State 1:	Triplet-A	1.5746 eV 787.41 nm	f=0.0000 <S**2>=2.000
HOMO-2(91) -> LUMO(94)		5.3% (0.16210)	
HOMO(93) -> LUMO(94)		96.1% (0.69334)	
Excited State 2:	Triplet-A	2.5437 eV 487.42 nm	f=0.0000 <S**2>=2.000
HOMO-6(87) -> LUMO(94)		2.8% (-0.11916)	
HOMO-2(91) -> LUMO(94)		90.1% (0.67113)	
HOMO(93) -> LUMO(94)		4.8% (-0.15429)	
Excited State 3:	Triplet-A	2.6883 eV 461.20 nm	f=0.0000 <S**2>=2.000
HOMO-7(86) -> LUMO(94)		2.0% (-0.10101)	
HOMO-5(88) -> LUMO(94)		2.8% (-0.11816)	
HOMO-1(92) -> LUMO(94)		92.6% (0.68038)	
Excited State 4:	Singlet-A	2.7288 eV 454.35 nm	f=0.4775 <S**2>=0.000
HOMO-2(91) -> LUMO(94)		10.8% (-0.23287)	
HOMO(93) -> LUMO(94)		89.6% (0.66947)	
Excited State 5:	Triplet-A	3.2004 eV 387.40 nm	f=0.0000 <S**2>=2.000
HOMO-7(86) -> LUMO(94)		-0.17503	
HOMO-5(88) -> LUMO(94)		0.66123	
HOMO-1(92) -> LUMO(94)		0.10039	
Excited State 6:	Singlet-A	3.2593 eV 380.41 nm	f=0.0303 <S**2>=0.000
HOMO-1(92) -> LUMO(94)		0.70040	
Excited State 7:	Singlet-A	3.3300 eV 372.32 nm	f=0.2972 <S**2>=0.000
HOMO-2(91) -> LUMO(94)		0.66520	
HOMO(93) -> LUMO(94)		0.23790	

Table S 3. Simulated excited states based on B3LYP/Def2TZVP level in the Gaussian 16 (**BITM**).