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SUPPORTING INFORMATION

Reversible Supramolecular Self-assembly via the Deprotonation-Protonation Strategy

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1. General Consideration

All chemicals and solvents were purchased commercially from Sigma-Aldrich and Sisco Research Laboratories Pvt. Ltd. (SRL) - India, used without purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz and at 100 MHz NMR spectrometer, respectively using DMSO-d_6 and $CDCl_3$ solvents at room temperature and TMS as the internal standard. High-resolution mass spectra were obtained by using the Electron Spray Ionization method (ESI) Agilent QTOF 6538. UV–visible spectral measurements were obtained from JASCO spectrophotometer V730 in the range of 200 to 800 nm and fluorescence measurements from JASCO Spectrofluorometer FP-8300 from 425 nm to 900 nm at 25 ^{O}C.

2. Synthetic procedures

Synthesis of (*E*)-5-(diethylamino)-2-(((4-nitrophenyl)imino)methyl)phenol **(1)**:

Compound **1** was synthesized using a reported procedure.[1] 4-(Diethylamino)-2-hydroxybenzaldehyde (1 g, 5.17 mmol) was dissolved in ethanol (4 mL) at room temperature under stirring, and 4-nitroaniline (0.714 g, 5.17 mmol) was added into the solution. The resulting mixture was then stirred for 26 h. After the completion of the reaction, the mixture was diluted with cold water. The resultant precipitate was filtered off and washed several times with cold ethanol to get the pure compound (**1**) as a dark red solid (Yield = 90%).

Synthesis of *N,N*-diethyl-2,2-difluoro-3-(4-nitrophenyl)-2H-2l4,3l4-benzo[e][1,3,2]oxazaborinin-7-amine **(B-NO_2)**:

Compound **B-NO_2** was synthesized using a reported procedure and confirmed by ^{1}H NMR.[1] The compound **1** (1 g, 3.19 mmol) was dissolved in dry dichloromethane (20 mL) under an N_2 atmosphere. Boron trifluoride diethyl ether (0.98 mL, 7.98 mmol) was added dropwise to the solution and stirred at room temperature for the next 30 min. After the precipitate appeared, DIPEA (1.38 mL, 7.98 mmol) was added and stirred for 19h. Once the starting material was completely consumed, the reaction mixture was diluted with DCM, washed with water, and dried over $NaSO_4$. The dried residue was purified *via* chromatography with silica gel (Petroleum ether: $CHCl_3$=1:3) to afford the boron complex as an orange solid (60% yield). ^{1}H NMR (400 MHz, DMSO- d_6) δ 8.80 (s, 1H), 8.35 (d, *J* = 9.1 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.2 Hz, 1H), 6.62 (dd, *J* = 9.2, 2.1 Hz, 1H), 6.20 (d, *J* = 1.8 Hz, 1H), 3.53 (q, *J* = 7.0 Hz, 4H), 1.17 (t, *J* = 7.0 Hz, 6H).

Synthesis of 3-(4-aminophenyl)-*N,N*-diethyl-2,2-difluoro-2H-2l4,3l4-benzo[e][1,3,2]oxazaborinin-7-amine **($B\text{-}NH_2$)**:

Compound **$B\text{-}NH_2$** was synthesized using a reported procedure and confirmed by ^1H NMR.[1] A solution of **$B\text{-}NO_2$** (500 mg, 1.38 mmol) in toluene was degassed with argon and Pd/C 5% (7.34 mg) was added. H_2 was bubbled through the solution for 15 min. and the mixture was stirred under H_2 atmosphere overnight at room temperature. Once the starting material was completely consumed, the reaction mixture was diluted with DCM and filtered over celite and the solvent was removed under vacuum. Yellow powder. Yield: 90%. ^1H NMR (600 MHz, DMSO- d_6) δ 8.42 (s, 1H), 7.38 (d, *J* = 9.1 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 6.41 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.05 (d, *J* = 2.3 Hz, 1H), 5.28 (s, 2H), 3.39 (q, *J* = 7.0 Hz, 4H), 1.07 (t, *J* = 7.0 Hz, 6H).

Synthesis of *N*-(4-(7-(diethylamino)-2,2-difluoro-2H-2l4,3l4-benzo[e][1,3,2]oxazaborinin-3-yl)phenyl)-4-methylbenzenesulfonamide **(BS-1)**:

$B\text{-}NH_2$ (200 mg, 0.6030 mmol) in a round bottom flask equipped with a magnetic stir bar is dissolved in 25 mL CH_2Cl_2. A CH_2Cl_2 solution (25 mL) of para-toluene sulfonyl chloride (172.44 mg, 0.90 mmol) is then added at 0 °C, followed by the addition of a catalytic amount of pyridine (73.7 μL, 0.90 mmol) and the reaction is stirred 24h at room temperature. The solvent is evaporated off and the reaction mixture is extracted with 1 N HCl solution and ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Methanol: $CHCl_3$=2%) to afford the **BS-1** as a yellow solid (60% yield). ^1H NMR (400 MHz, DMSO-d_6) δ 10.45 (s, 1H), 8.56 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.35 (m, 5H), 7.17 (d, *J* = 8.9 Hz, 2H), 6.52 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.14 (d, *J* = 2.1 Hz, 1H), 3.48 (q, *J* = 7.0 Hz, 4H), 2.35 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 161.22, 159.78, 156.29, 143.95, 139.12, 137.30, 137.03, 135.24, 130.28, 127.20, 124.12, 120.62, 107.15, 97.14, 44.94, 21.43, 12.95. ^{11}B NMR (193 MHz, DMSO- d_6) δ 0.73, 0.64, 0.55. ESI-MS: m/z calcd for $C_{24}H_{26}BF_2N_2O_3S$, $[M+H]^+$, 486.1834; found 486.1919.

Synthesis of *N-(4-(7-(diethylamino)-2,2-difluoro-2H-2l4,3l4-benzo[e][1,3,2]oxazaborinin-3-yl)phenyl)methanesulfonamide* **(BS-2)**:

$B\text{-}NH_2$ (200 mg, 0.6030 mmol) in a round bottom flask equipped with a magnetic stir bar is dissolved in 25 mL CH_2Cl_2. A CH_2Cl_2 solution (25 mL) of methyl sulfonyl chloride (103.11 mg, 0.90 mmol) is then added at 0 °C, followed the addition of catalytic amount of pyridine (73.7 μL, 0.90 mmol) and the reaction is stirred 30 h at room temperature. The solvent is evaporated off and the reaction mixture is extracted with 1 N HCl solution and ethyl acetate. The combined organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (Methanol: $CHCl_3$=2%) to afford the **BS-1** as a yellow solid (55% yield). ^1H NMR (400 MHz, DMSO-d_6) δ 9.93 (s, 1H), 8.61 (s, 1H), 7.48 (t, *J* = 9.2 Hz, 3H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.54 (dd, *J* = 9.1, 2.1 Hz, 1H), 6.16 (s, 1H), 3.48 (dd, *J*

= 13.1, 6.1 Hz, 4H), 3.03 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, DMSO- *d*$_6$) δ 161.27, 159.85, 156.29, 139.16, 137.92, 135.25, 124.29, 120.70, 107.13, 97.18, 79.63, 44.94, 22.56, 12.97.ESI-MS: m/z calcd for $C_{18}H_{22}BF_2N_2O_3S$, $[M+2Na]^{+2}$, 227.5619; found 227.5609.

Synthesis of *N-benzyl-N-(4-(7-(diethylamino)-2,2-difluoro-2H-2l4,3l4-benzo[e][1,3,2]oxazaborinin-3-yl)phenyl)-4-methylbenzenesulfonamide* **(BS-3)**:

A **BS-1** (20 mg, 0.041 mmol) was added to DMSO (0.5 mL), followed by the addition of NaOCl (6.14 mg, 0.082 mmol) at room temperature and stirred for 5 min. The whole mixture was cooled to 0 °C and benzyl bromide (7.04 mg, 0.0824 mmol) was added. The cooling bath was removed, and the resulting mixture was stirred for 16 h at rt. After completion of the reaction, the mixture was diluted with DCM, washed with water, and dried over $NaSO_4$. The dried residue was purified *via* chromatography with silica gel (Solvent: $CHCl_3$) to afford the boron complex as a yellow solid (55% yield). ^{1}H NMR (400 MHz, DMSO- *d*$_6$) δ 8.63 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.44 (dd, *J* = 13.9, 8.9 Hz, 5H), 7.32 – 7.25 (m, 4H), 7.21 (d, *J* = 8.9 Hz, 3H), 6.54 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.14 (d, *J* = 2.1 Hz, 1H), 4.81 (s, 2H), 3.48 (q, *J* = 7.0 Hz, 4H), 2.44 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMSO- *d*$_6$) δ 161.42, 160.09, 156.53, 144.22, 142.01, 137.83, 136.59, 135.50, 135.33, 130.39, 129.43, 128.88, 128.46, 127.96, 127.86, 123.40, 107.37, 106.95, 97.09, 53.58, 44.98, 21.54, 12.98. ESI-MS: m/z calcd for $C_{31}H_{32}BF_2N_2O_3S$, $[M^+]$, 575.2225; found 575.2267.

3. Photophysical Studies

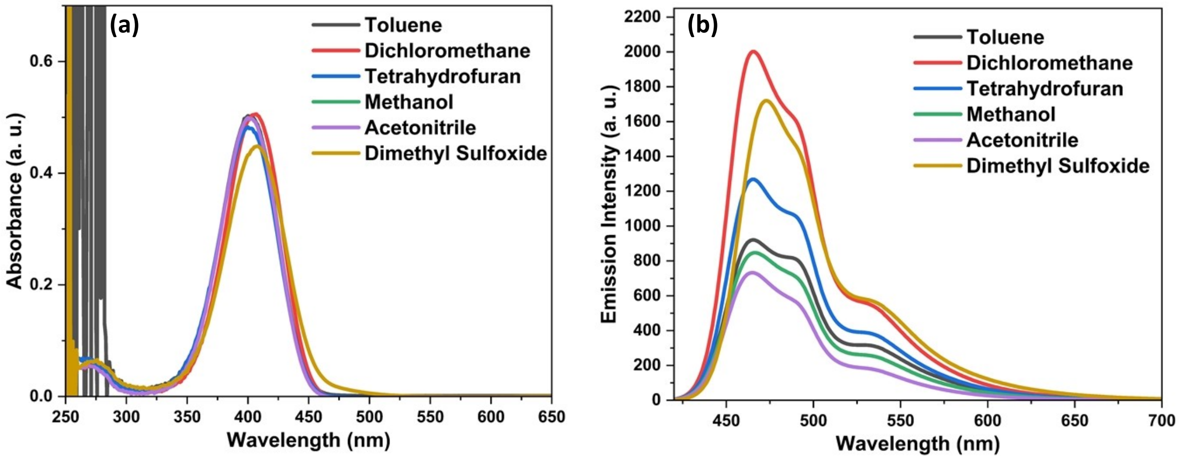


Figure. S1. UV–vis absorption (a) and PL spectra (b) of **BS-1** excited at 406 nm in different solvents (10.0×10^{-6} mol L^{-1}).

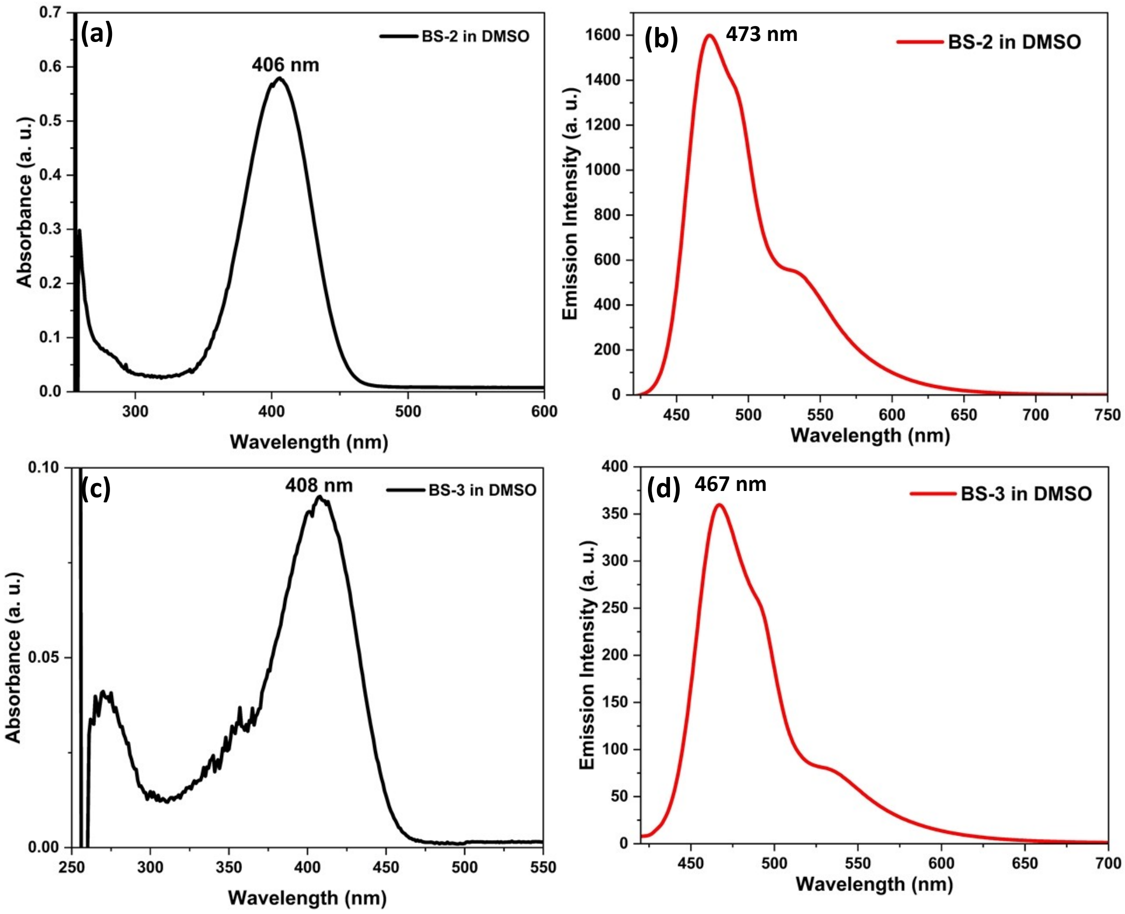


Figure. S2. UV–vis absorption (a,c) and PL spectra (b, d) of **BS-2** and **BS-3** excited at 406 nm in DMSO (15.0×10^{-6} mol L^{-1}).

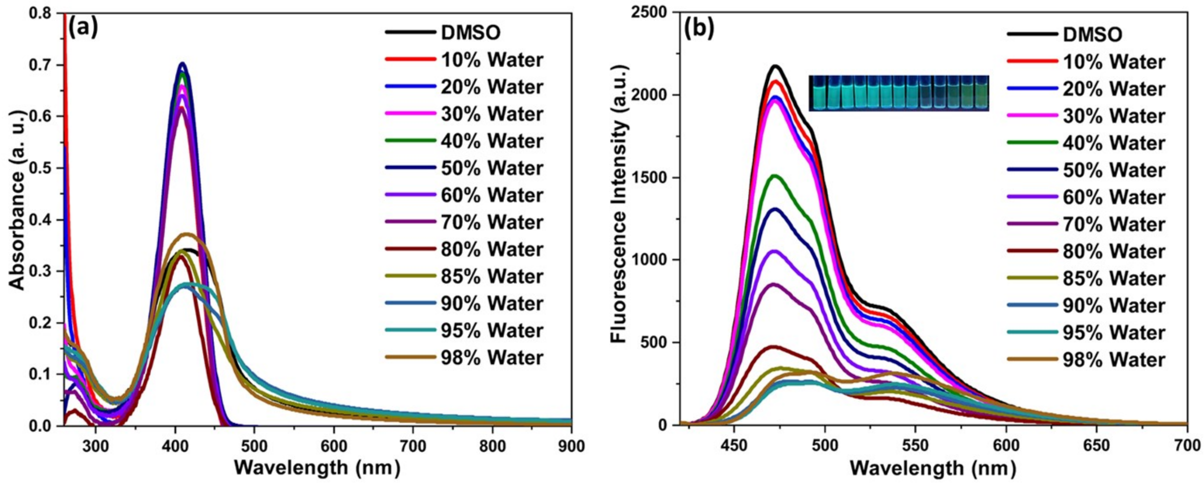


Figure S3. (a) Absorbance and (b) Fluorescence spectra of **BS-1** (15.0×10^{-6} mol L^{-1}) in DMSO-Water with water fractions (0 to 98%, λ_{ex} = 406 nm).

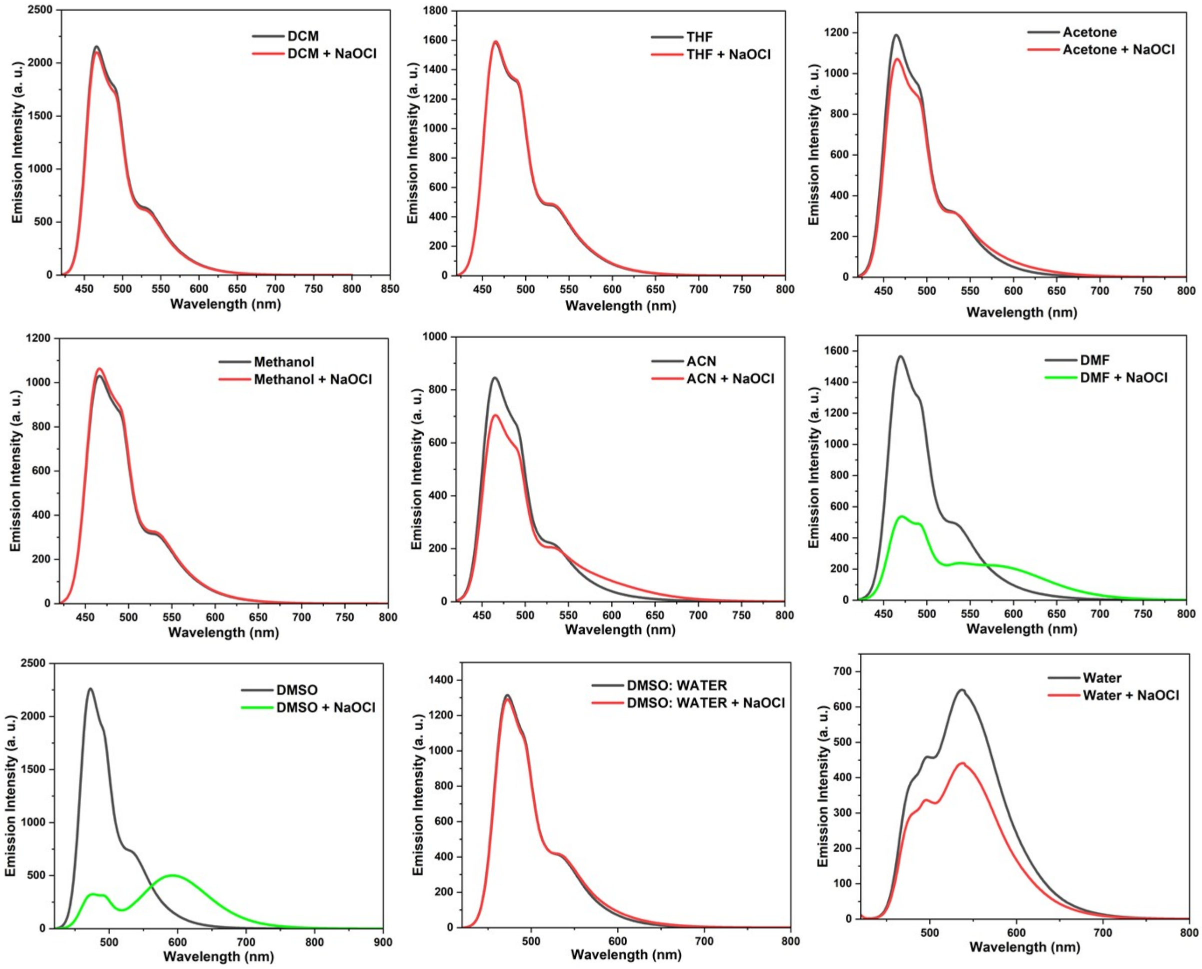


Figure S4. Fluorescence spectra of **BS-1** (15.0×10^{-6} mol L^{-1}) were recorded in different solvents (λ_{ex} = 406 nm).

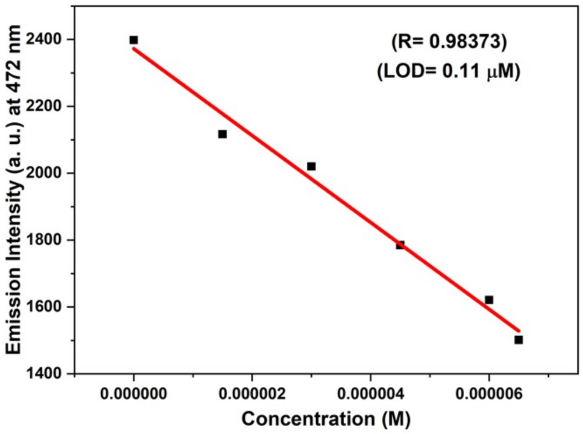


Figure S5. The detection limit of the probe **BS-1** towards NaOCl.

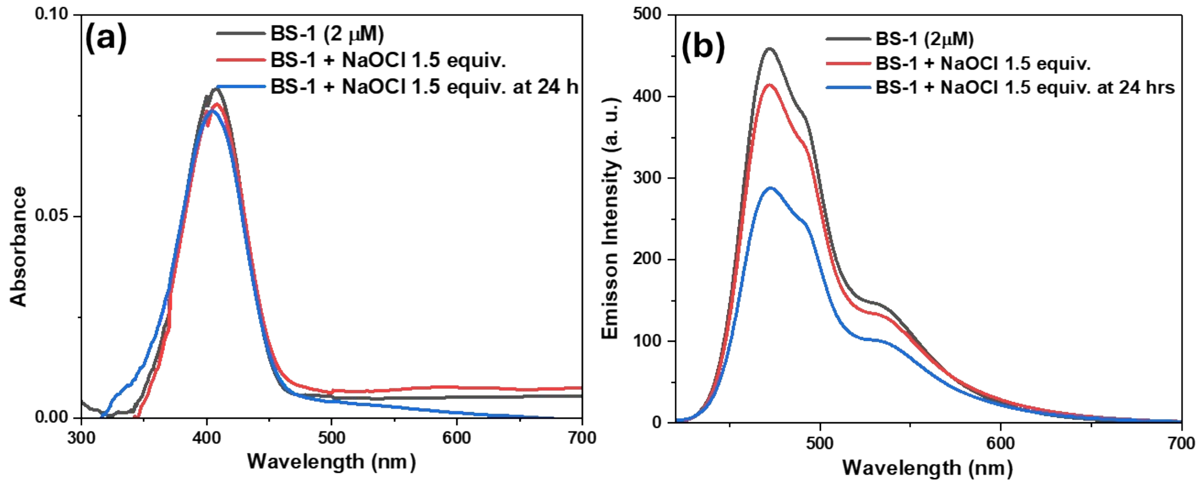


Figure S6. The absorbance and fluorescence responses of **BS-1** (2 μM) in DMSO.

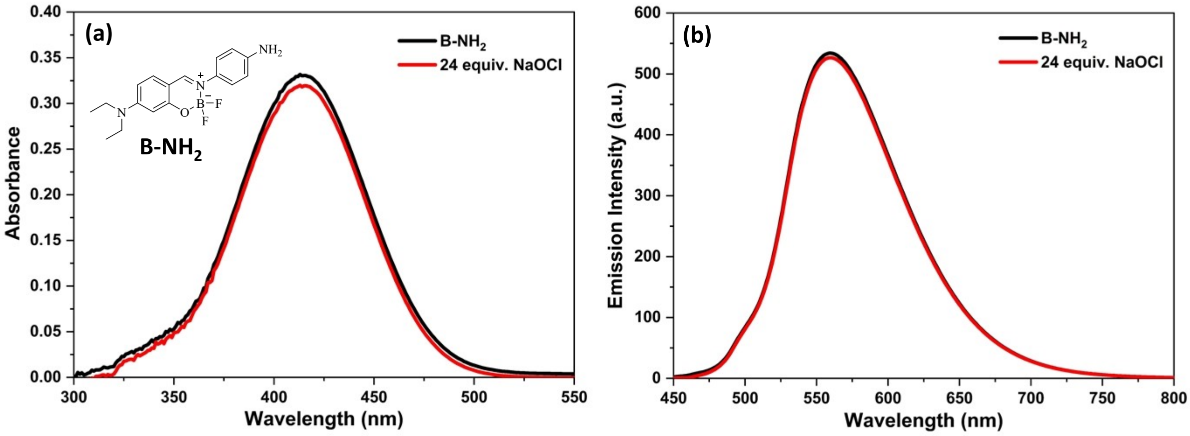


Figure S7. UV–vis absorption (a) and PL spectra (b) of **B-NH$_2$** upon the addition of hypochlorite (24 equiv.) in DMSO. (λ_{ex}= 406 nm; Concentration= 15.0 × 10^{-6} mol L^{-1}).

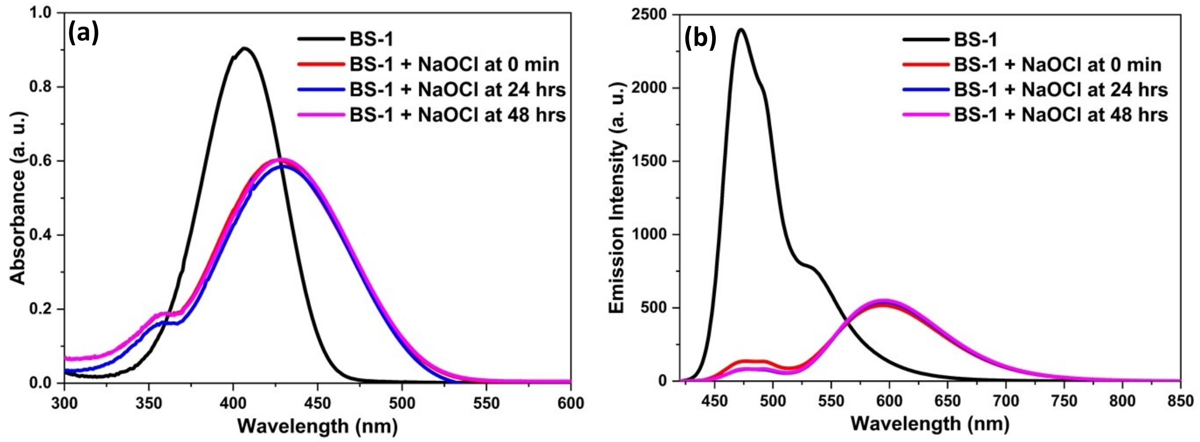


Figure S8. Stability testing of formed aggregates in DMSO at 0min, 24 hrs, and 48 hrs. (**BS-1**= 15.0 × 10^{-6} mol L^{-1}; λ_{ex}= 406 nm; Hypochlorite= 1.5 equiv.).

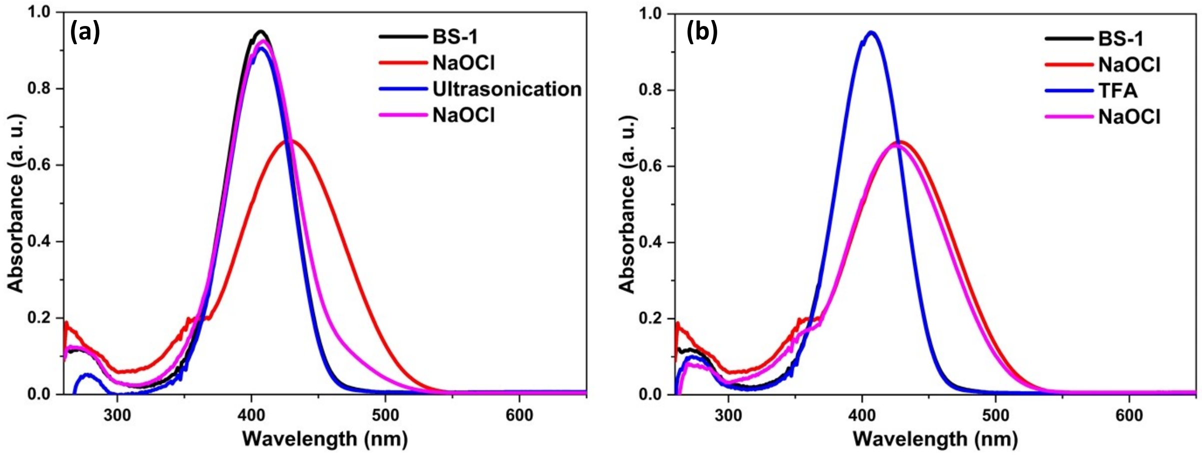


Fig. S9. Changes in the absorption spectra of reversibility study **BS-1** in DMSO using ultrasonication and TFA as a proton source (**BS-1**= 15.0 × 10^{-6} mol L^{-1}; TFA= 1.5 equiv.; Hypochlorite= 1.5 equiv.).

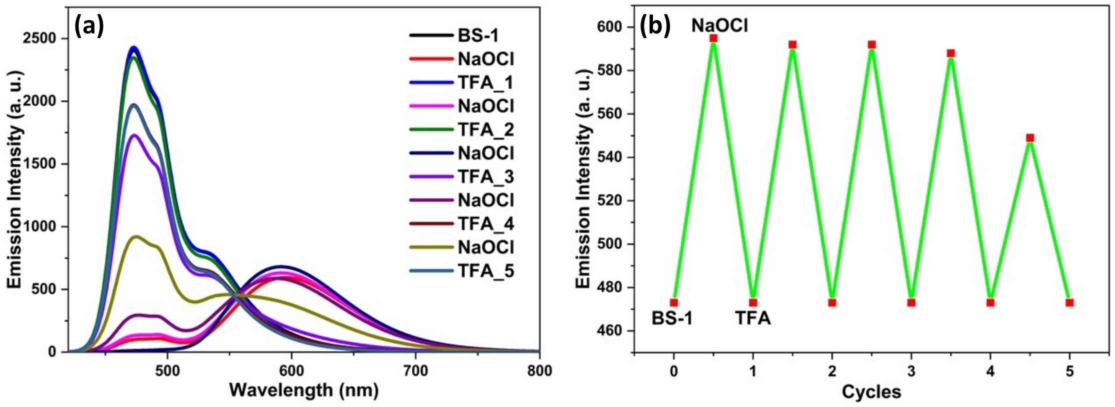


Figure S10. Reversibility cycle study **BS-1** in DMSO using NaOCl and TFA.

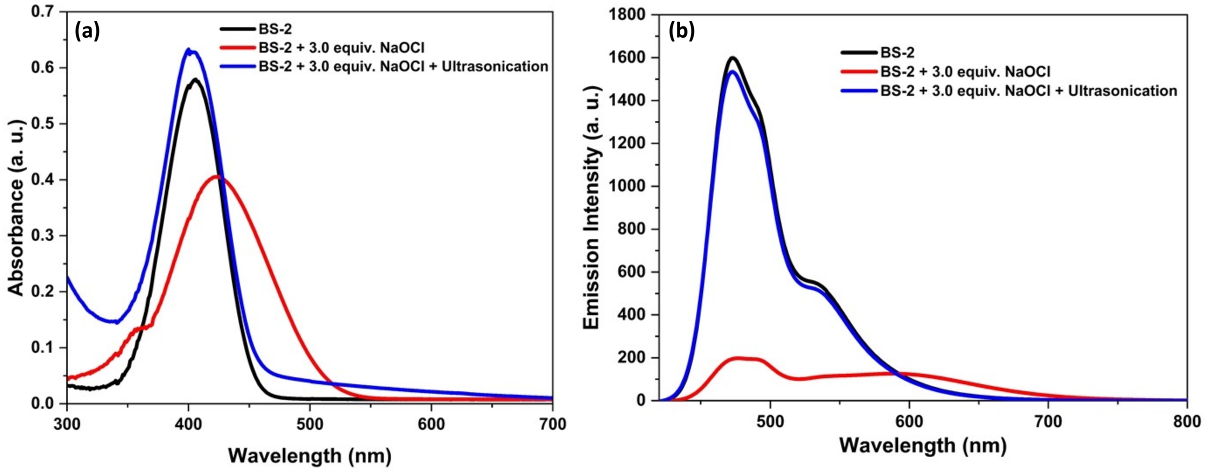


Figure S11. Reversibility study **BS-2** in DMSO using ultrasonication (**BS-2**= 15.0 × 10^{-6} mol L^{-1}; Hypochlorite= 3.0 equiv.).

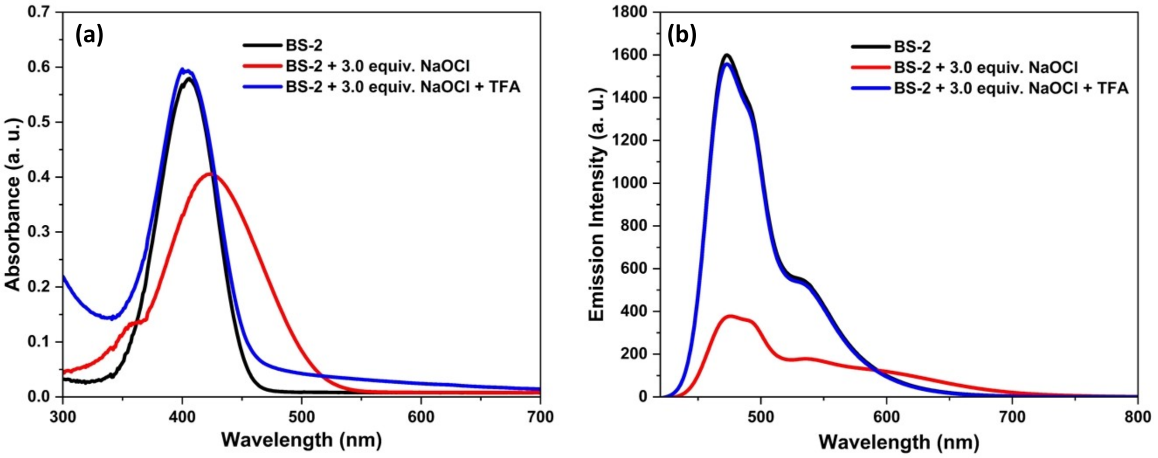


Figure S12. Reversibility study **BS-2** in DMSO using TFA as a proton source (**BS-2**= 15.0 × 10^{-6} mol L^{-1}; TFA= 3.0 equiv.; Hypochlorite= 3.0 equiv.).

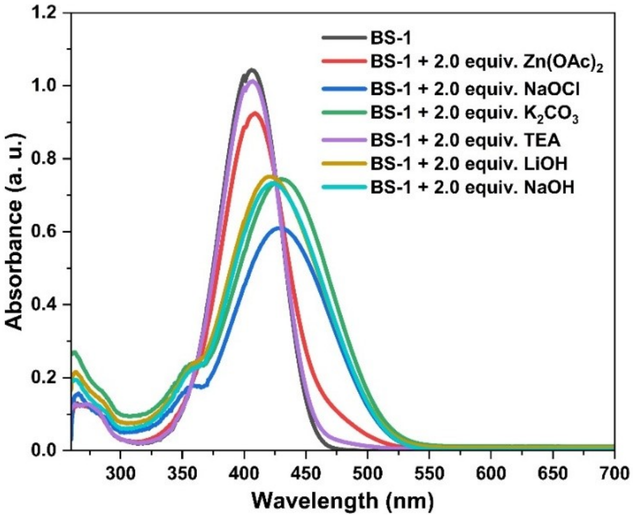


Figure S13. Changes in the absorption spectra of the **BS-1** (15.0 × 10^{-6} mol L^{-1}) upon the addition of various bases.

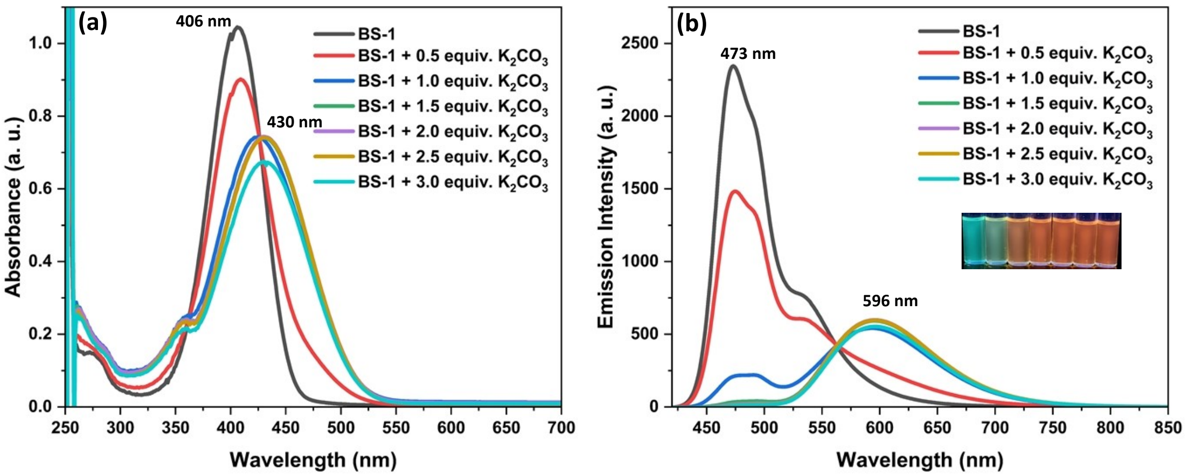


Figure S14. UV–vis absorption (a) and PL spectra (b) of **BS-1** upon the increasing concentration of K_2CO_3 (0–3.0 equiv.) in DMSO. (**BS-1**: λ_{ex}= 406 nm; Concentration= 15.0×10^{-6} mol L^{-1}).

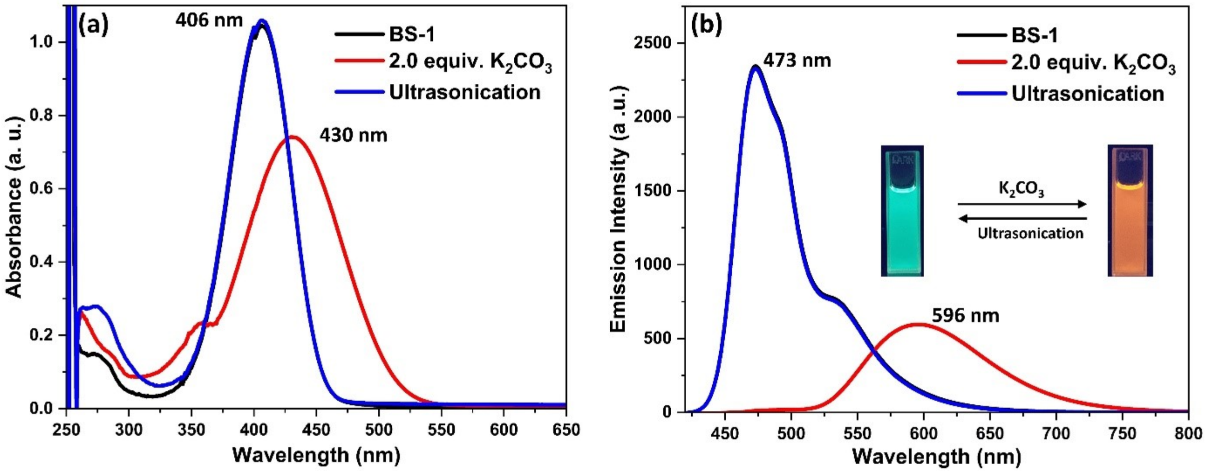


Figure S15. Reversibility study **BS-1** in DMSO using ultrasonication (**BS-1**= 15.0×10^{-6} mol L^{-1}; K_2CO_3= 2.0 equiv.).

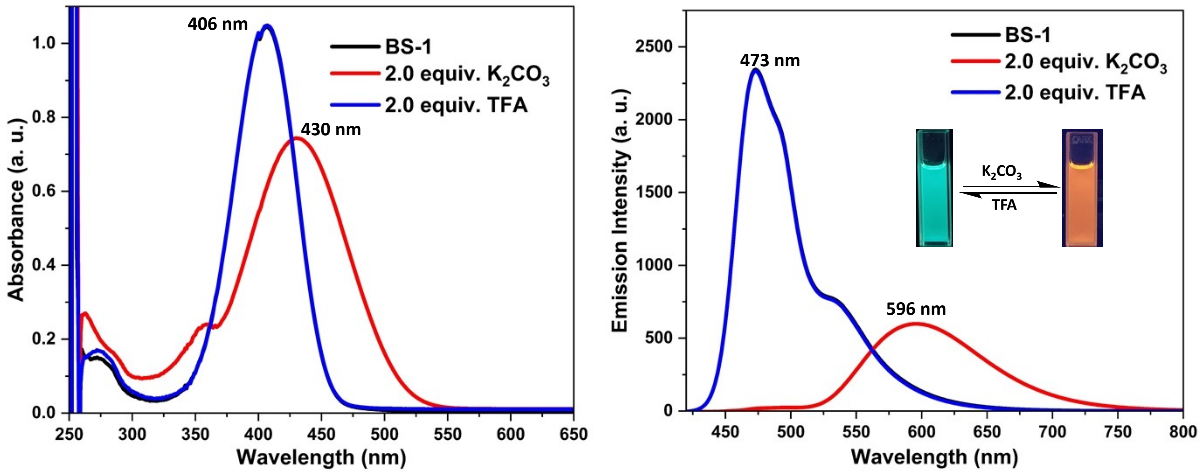


Figure S16. Reversibility study **BS-1** in DMSO using TFA as a proton source (**BS-1**= 15.0 × 10^{-6} mol L^{-1}; K_2CO_3= 2.0 equiv., TFA= 2.0 equiv.).

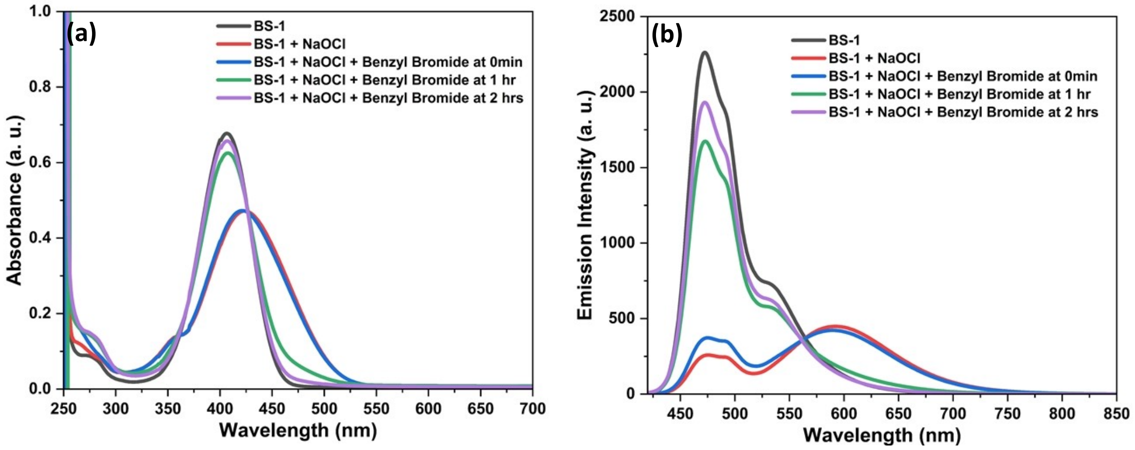


Figure S17. Changes in the absorption and emission spectra of the **BS-1** (15.0 × 10^{-6} mol L^{-1}) upon the sequential addition of NaOCl (2.0 equiv.) and benzyl bromide (2.0 equiv.) at different time intervals.

4. NMR Titration

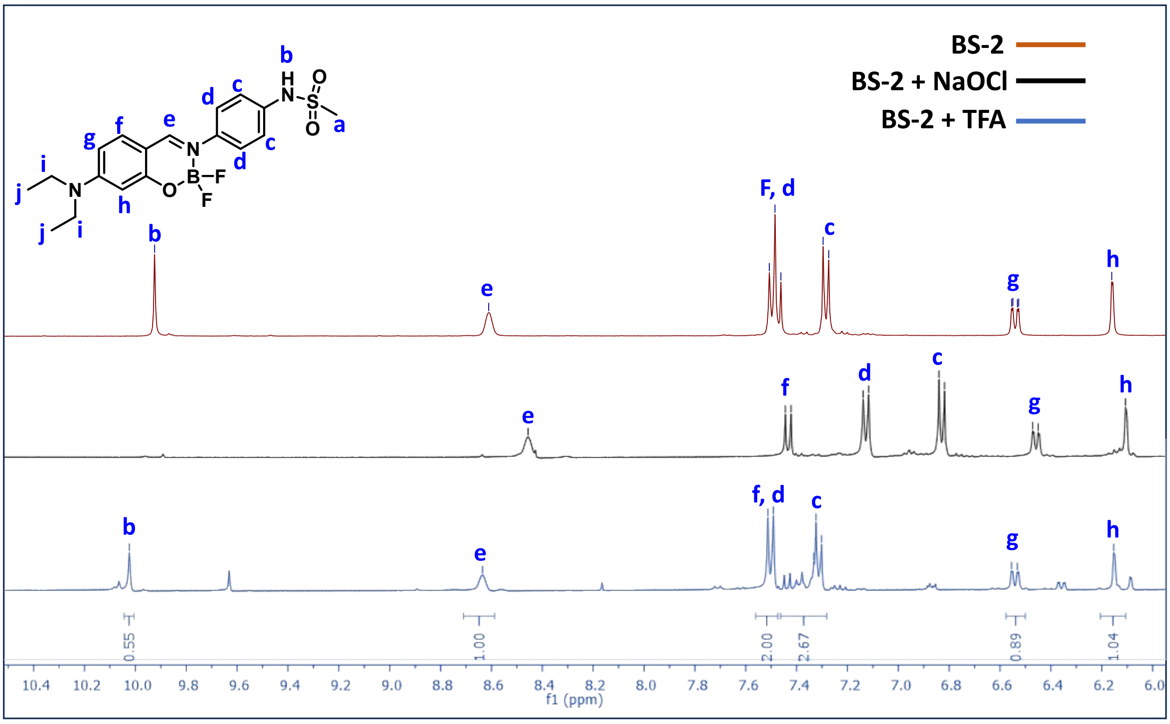


Figure S18. Overlay ^{1}H NMR spectra of **BS-2** in DMSO-d_6 upon addition of NaOCl (2.0 equiv.) and TFA (2.0 equiv.).

5. SEM Images

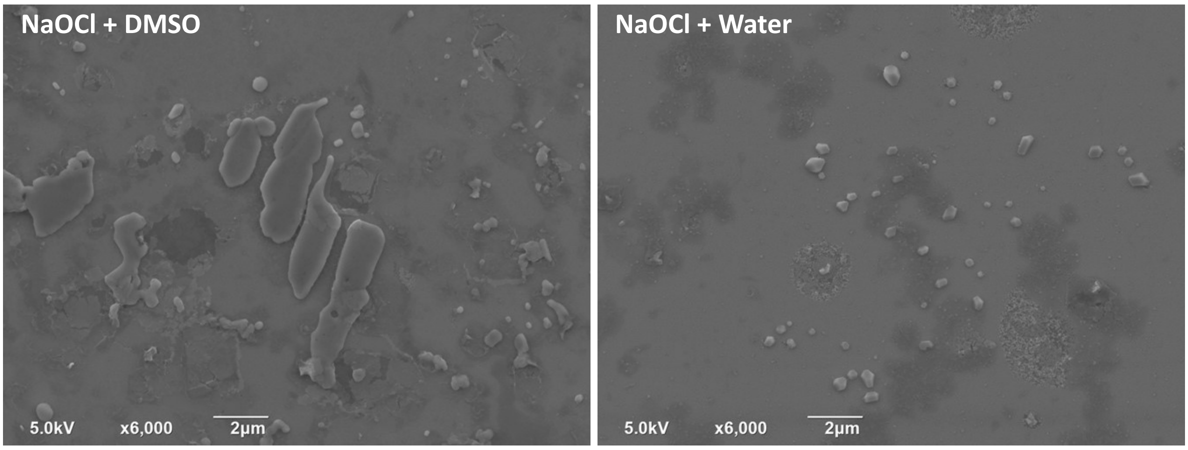


Figure S19. SEM images of the self-assembly of NaOCl (45 μM) in DMSO and water.

Table S1. Photophysical data of **BS-1**, **BS-2,** and **BS-3**.

Sr. No.	**Compound**	**Solvents**	**λ_{abs} (nm)**	**λ_{em} (nm)**	**Stokes shift cm^{-1} (nm)**	**Φ_F ^{a}**
1	**BS-1**	Toluene	400	465	3,495 (65)	0.111
		Dichloromethane	406	465	3,125 (59)	0.067
		Tetrahydrofuran	400	465	3,495 (65)	0.080
		Methanol	400	467	3,589 (67)	0.053
		Acetonitrile	408	465	3,004 (57)	0.045
		Dimethyl Sulfoxide	400	472	3,814 (72)	0.110
2	**BS-2**	Dimethyl Sulfoxide	406	473	3,489 (67)	-
3	**BS-3**	Dimethyl Sulfoxide	408	467	3,096 (59)	-

[a] The fluorescence quantum yield (ΦF) measured using coumarin in ethanol (Φ_F = 0.38) as standard.

6. List of NMR and HR-MS

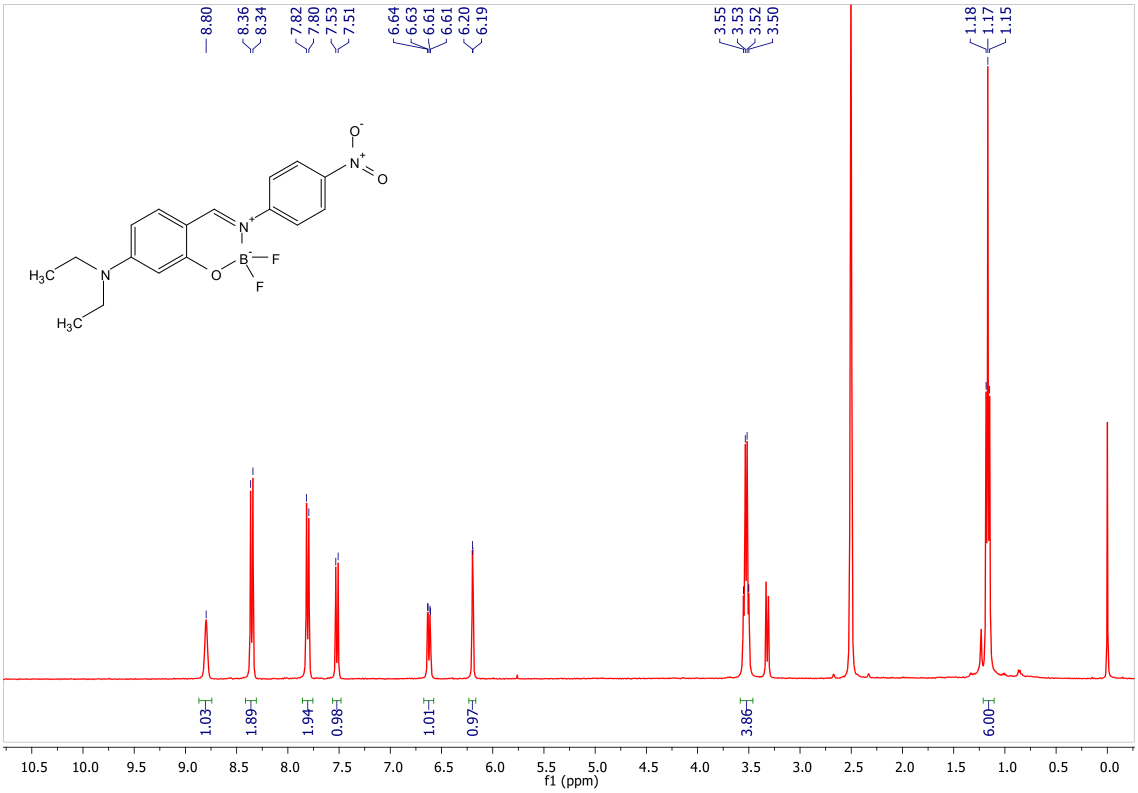


Figure S20. ^{1}H NMR spectrum of **B-NO$_2$** in DMSO-d_6 solution.

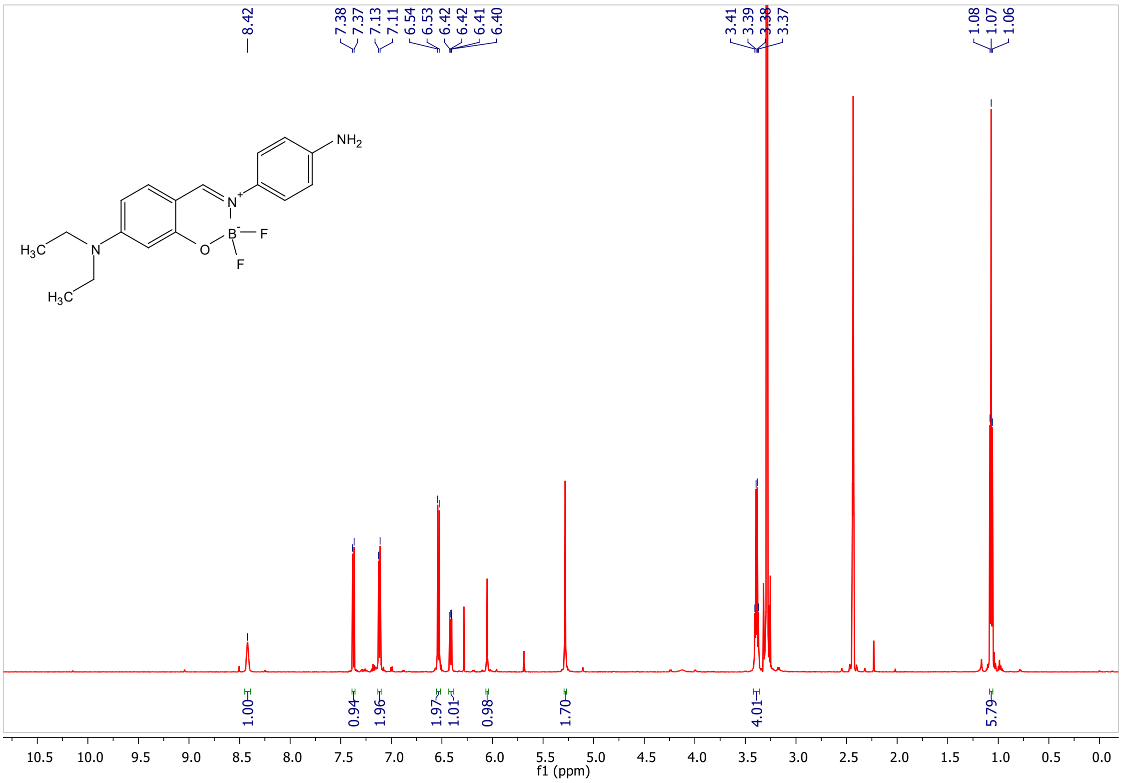


Figure S21. ^{1}H NMR spectrum of **B-NH$_2$** in DMSO-d_6 solution.

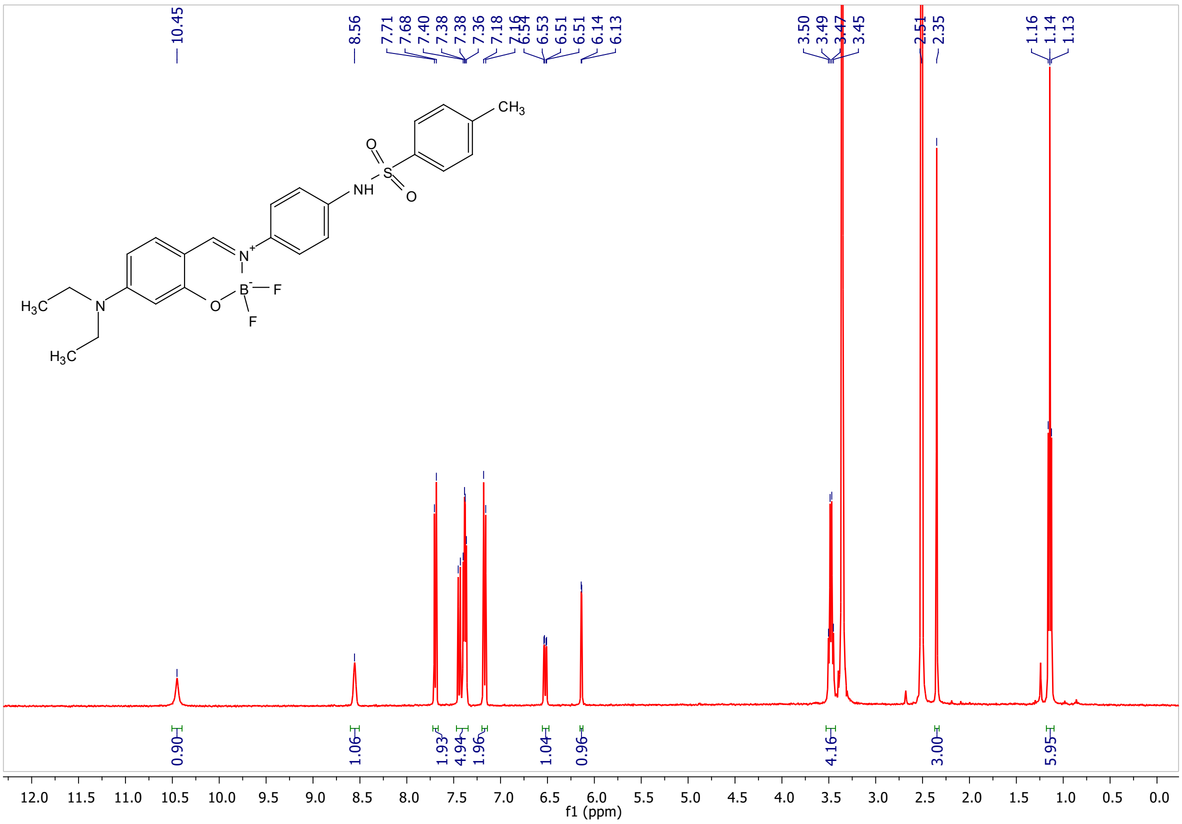


Figure S22. ^{1}H NMR spectrum of **BS-1** in DMSO-d_6 solution.

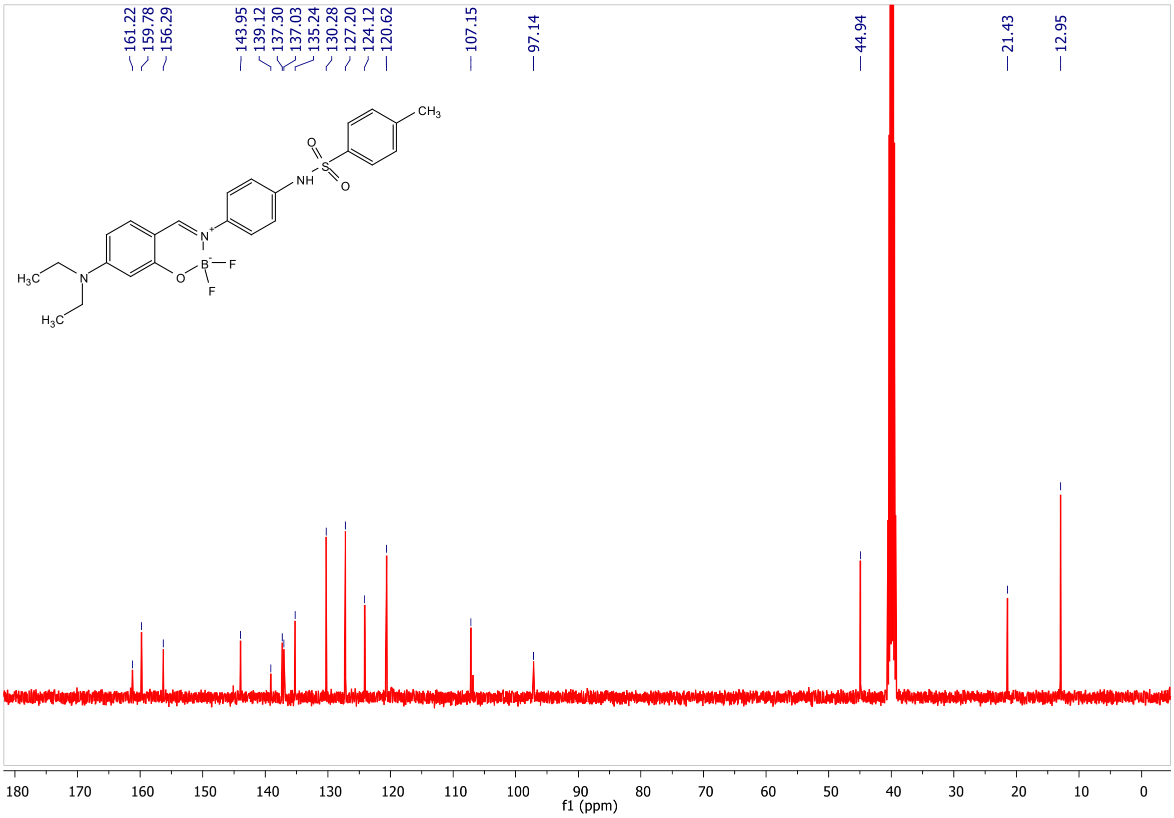


Figure S23. ^{13}C NMR spectrum of **BS-1** in DMSO-d_6 solution.

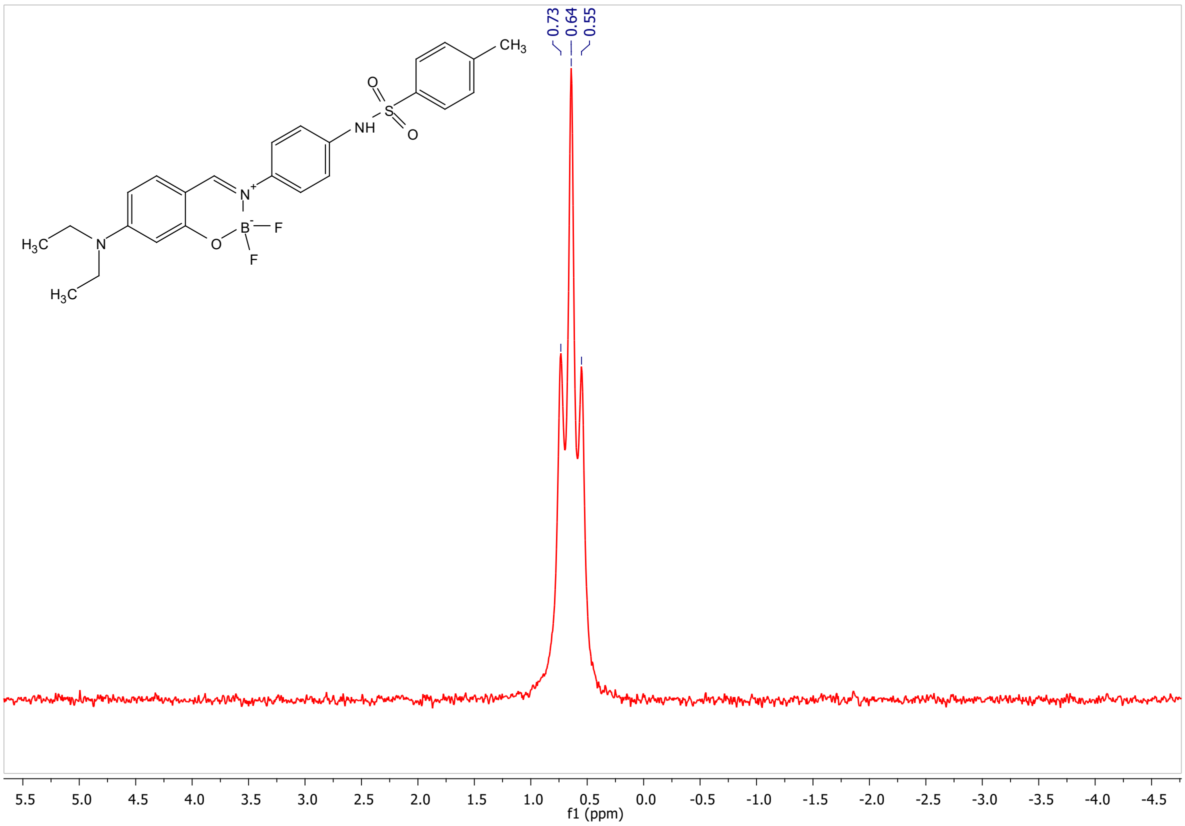
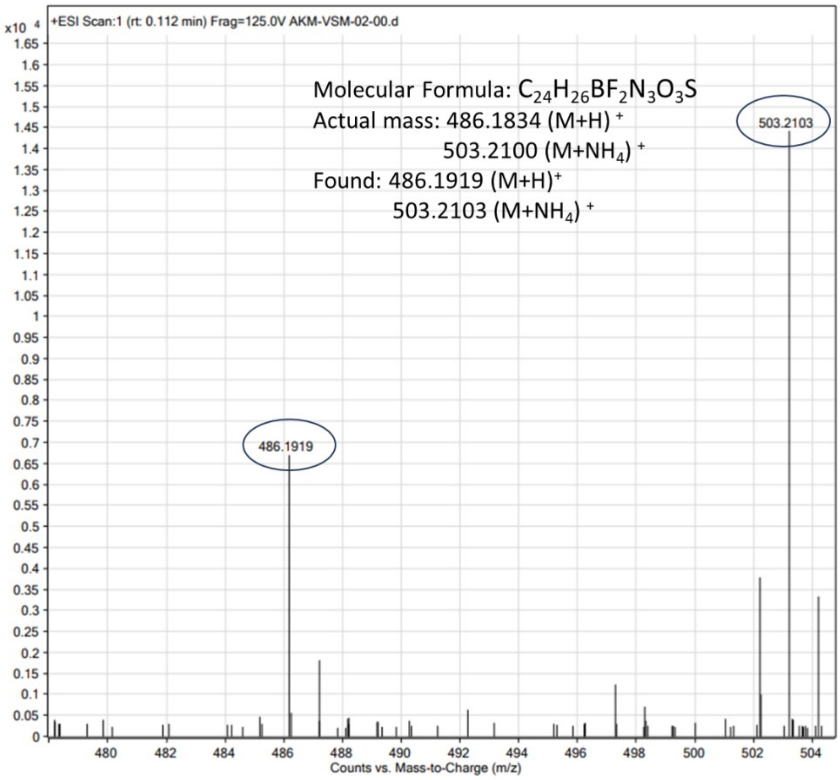


Figure S24. ^{11}B NMR spectrum of **BS-1** in DMSO-*d*$_6$ solution.



Molecular Formula: $C_{24}H_{26}BF_2N_3O_3S$

Actual mass: 486.1834 $(M+H)^+$

503.2100 $(M+NH_4)^+$

Found: 486.1919 $(M+H)^+$

503.2103 $(M+NH_4)^+$

Figure S25. HR-MS spectrum of **BS-1.**

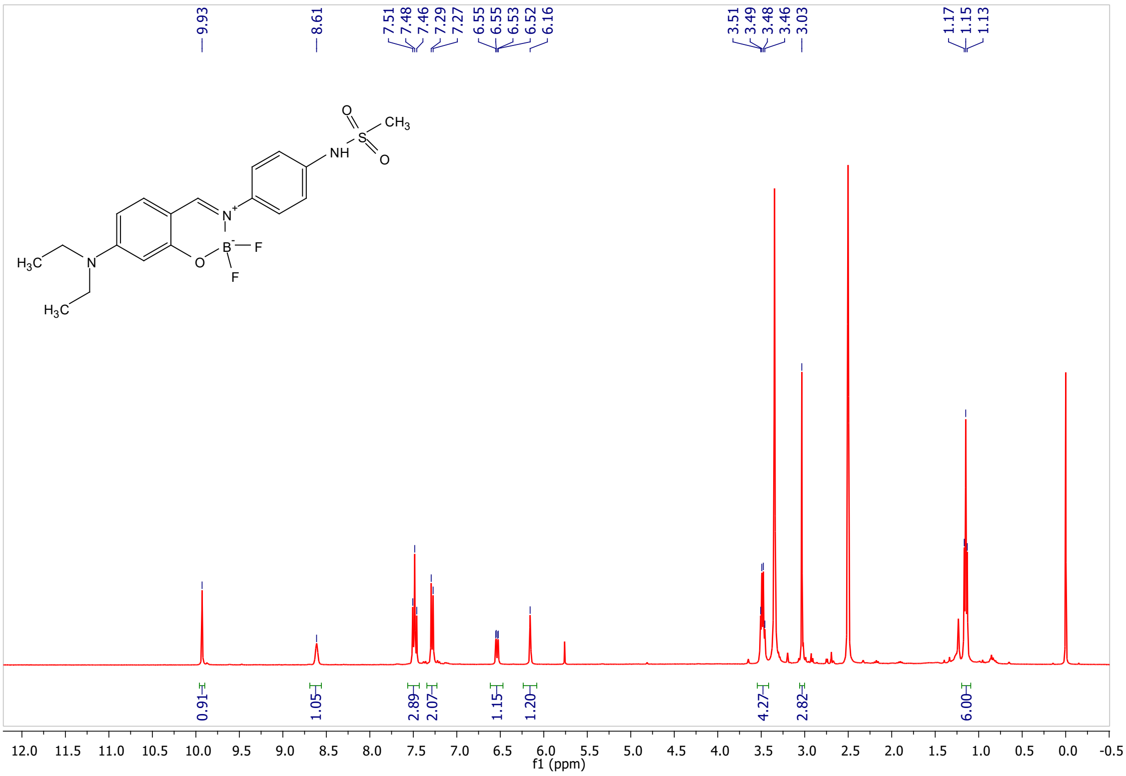


Figure S26. ^{1}H NMR spectrum of **BS-2** in DMSO-d_6 solution.

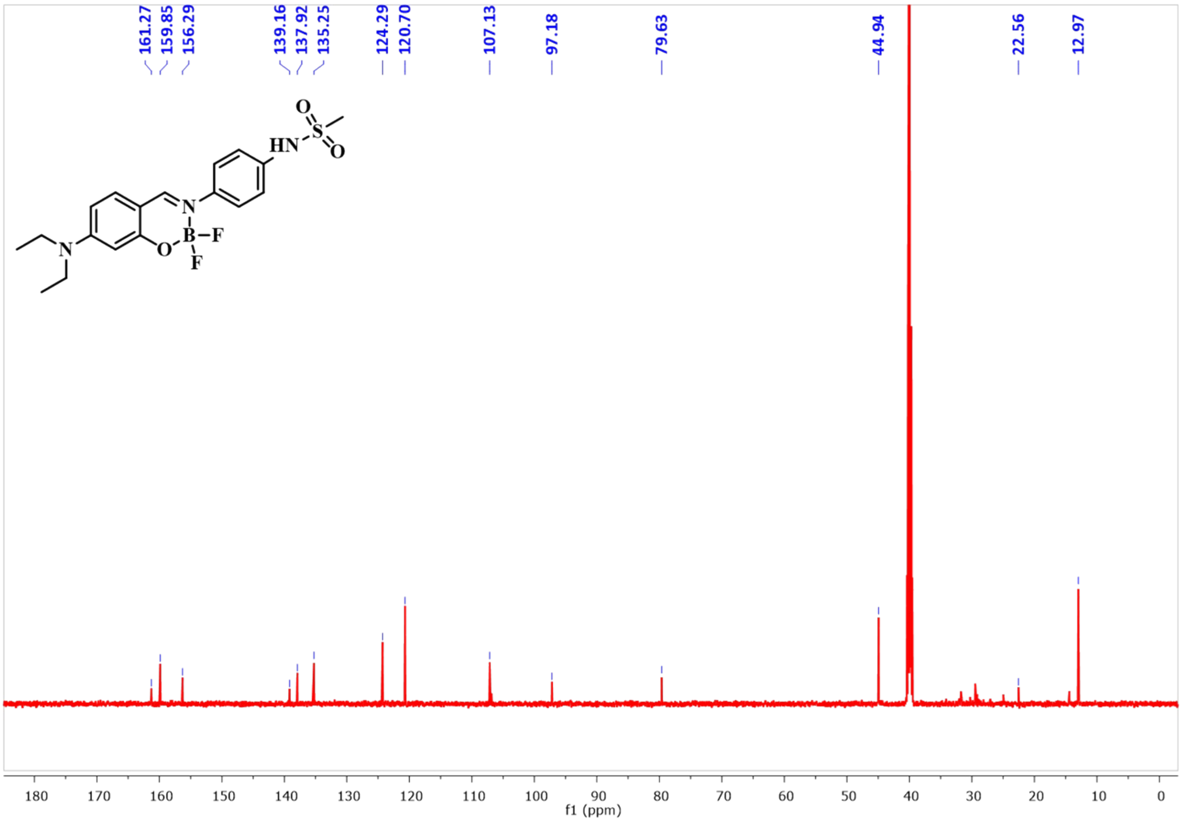


Figure S27. ^{13}C NMR spectrum of **BS-2** in DMSO-d_6 solution.

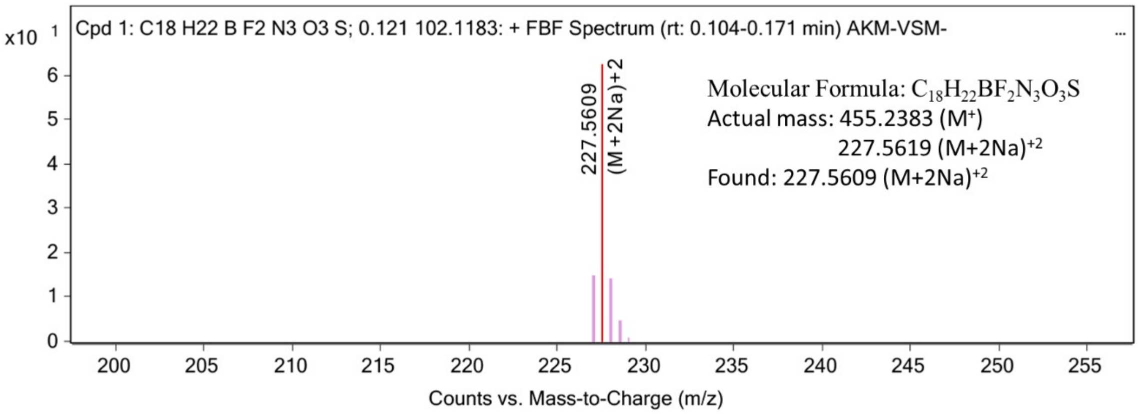


Figure S28. HR-MS spectrum of **BS-2.**

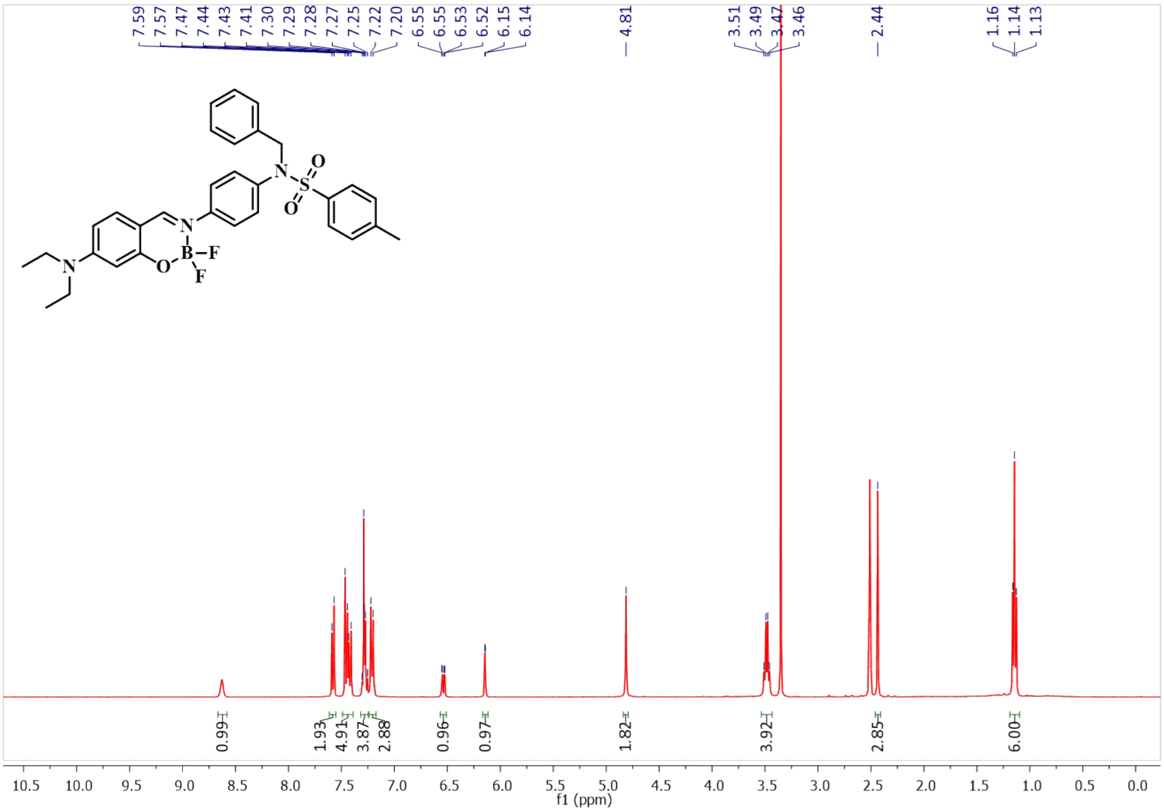


Figure S29. ^{1}H NMR spectrum of **BS-3** in DMSO-d_6 solution.

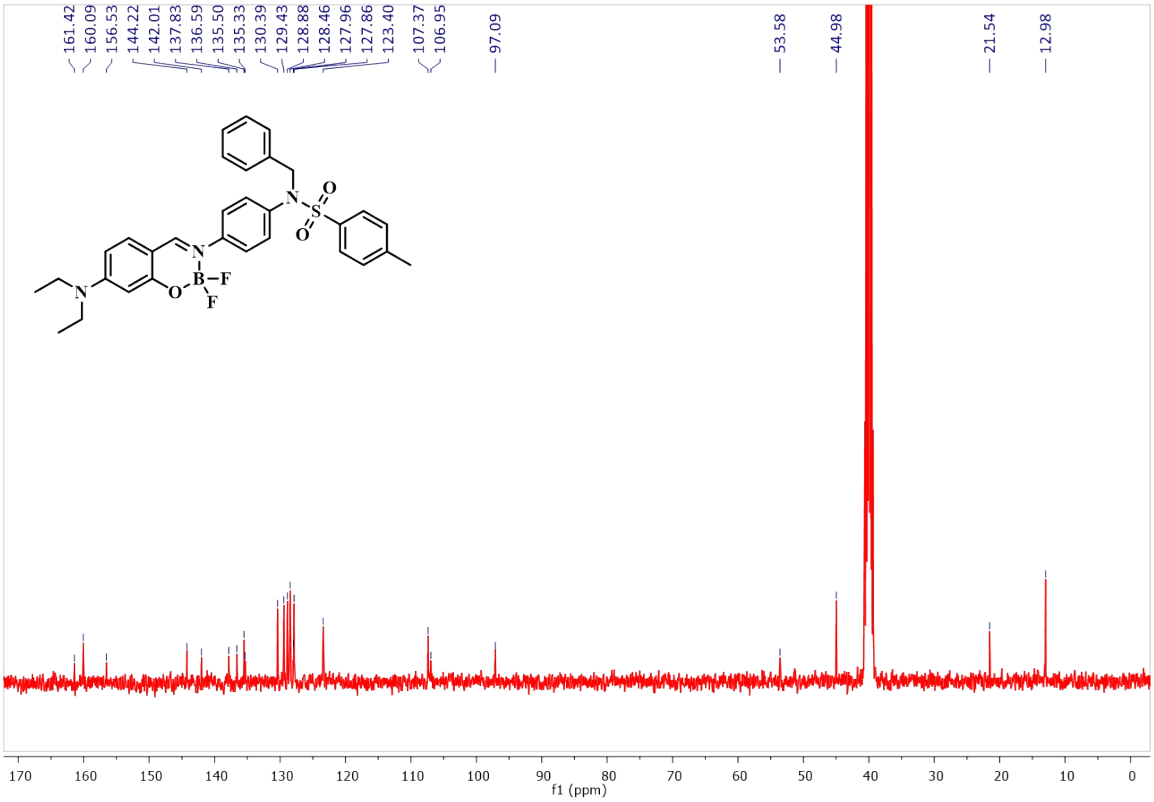


Figure S30. ^{13}C NMR spectrum of **BS-3** in DMSO-d_6 solution.

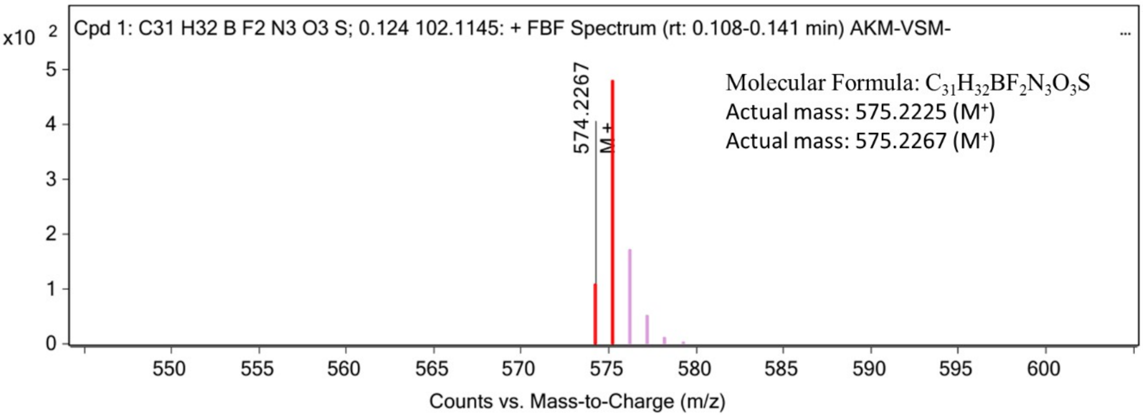


Figure S31. HR-MS spectrum of **BS-3.**

7. Reference

1. D. Frath, S. Azizi, G. Ulrich and R. Ziessel, *Org. Lett.*, 2012, **14**, 4774–4777.