Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Regulating the activity of boronate moiety to construct fluorescent probes for detection of $ONOO^-$ *in vitro* and *in vivo*

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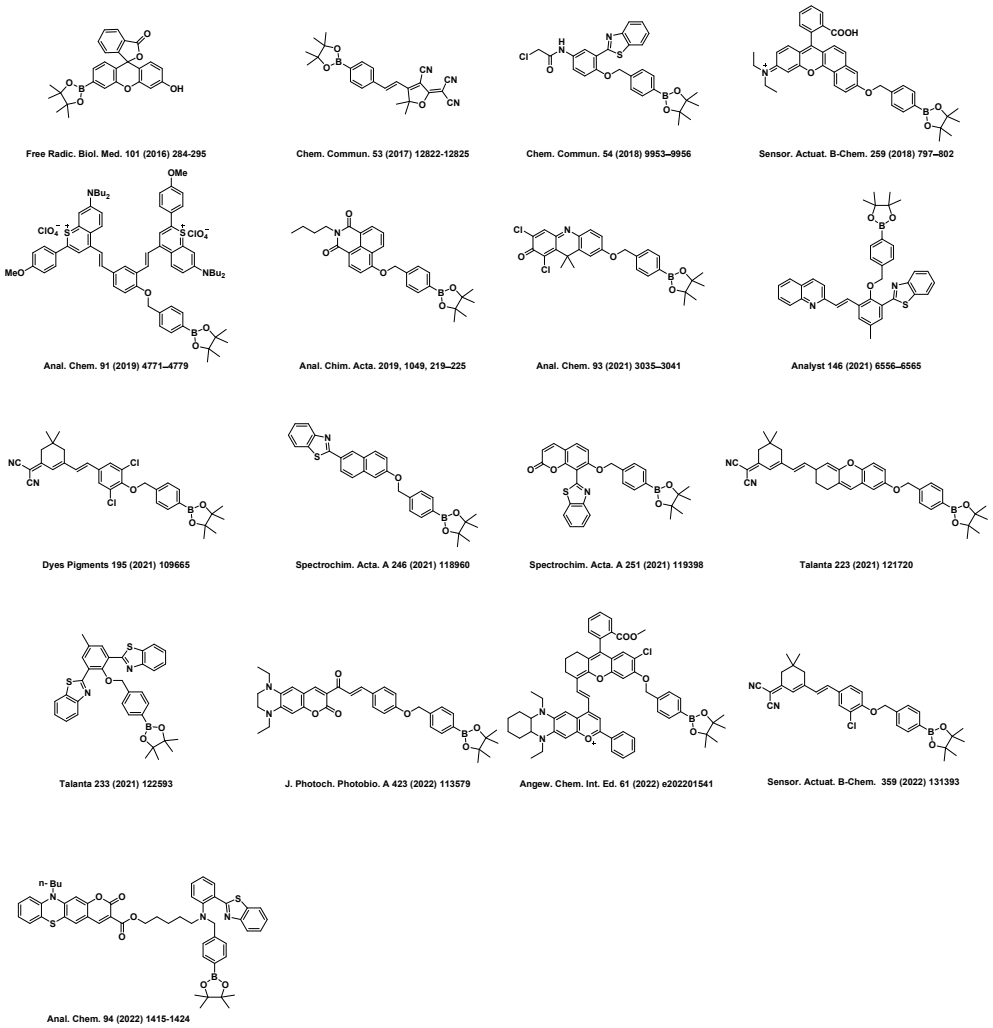
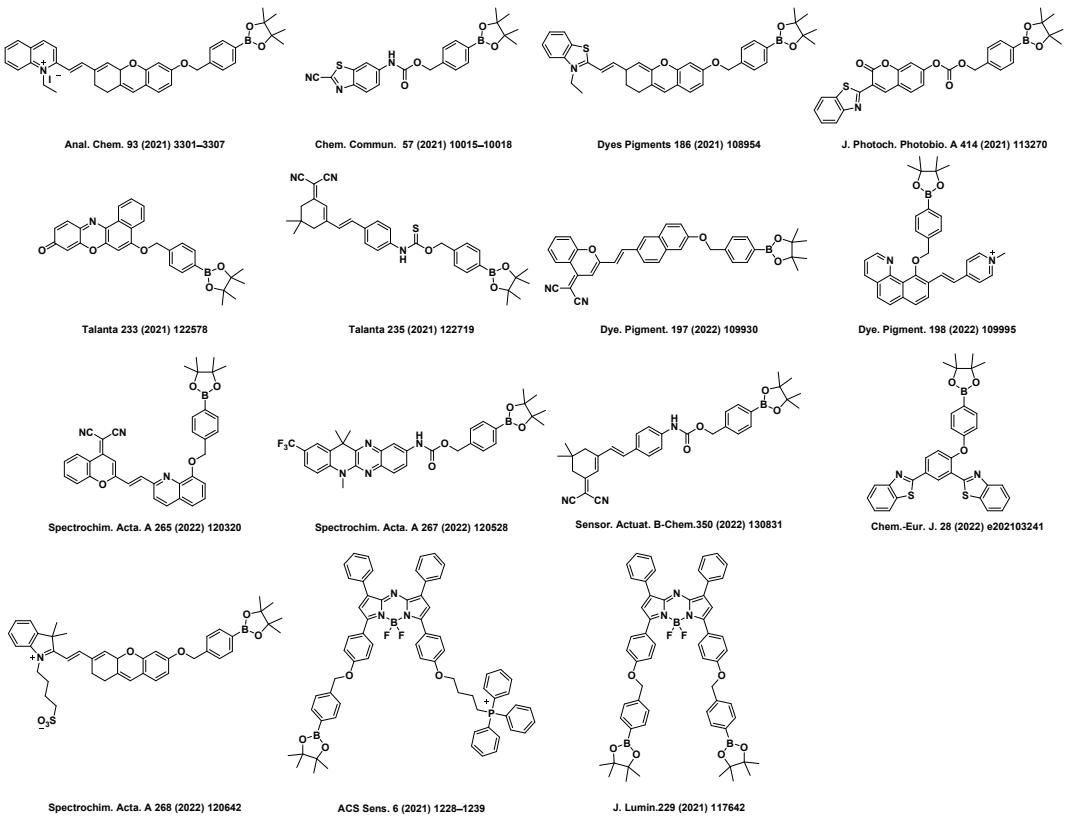
Apparatus and reagents

All reagents were purchased from commercial suppliers and used without further purification. DMSO in chromatographic purity was used in detection. Anhydrous solvents were acquired by standard methods prior to use. TLC analysis was performed on silica gel plates GF254 and chromatography was carried out on 200−300 mesh silica gel (Qingdao Haiyang Chemical, China). ^{1}H NMR spectra were recorded on a Varian Model Mercury 600 MHz spectrometer.^{1}H NMR chemical shifts (δ) are given in ppm (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet) downfield from Me_4Si. ^{13}C NMR spectra were recorded on a Varian Model Mercury 600 MHz spectrometer. Spectrometer UV-vis spectra were acquired on a Lengguang 759S UV-visible spectrophotometer (Lengguang Tech, China). Fluorescence spectra were measured by Lengguang F98 fluorescence spectrophotometer (Lengguang Tech, China). Electrospray ionization (ESI) mass spectra were acquired with Agilent 1100Series LC/MSD and AB SCIEX Triple TOFTM 5600+ mass spectrometer. HRMS (high resolution mass spectrometry, DART positive) spectra were obtained on Thermo Fisher Scientific LTQ FT Ultra. All spectra were recorded at room temperature, except for the confocal laser scanning microscopic images.

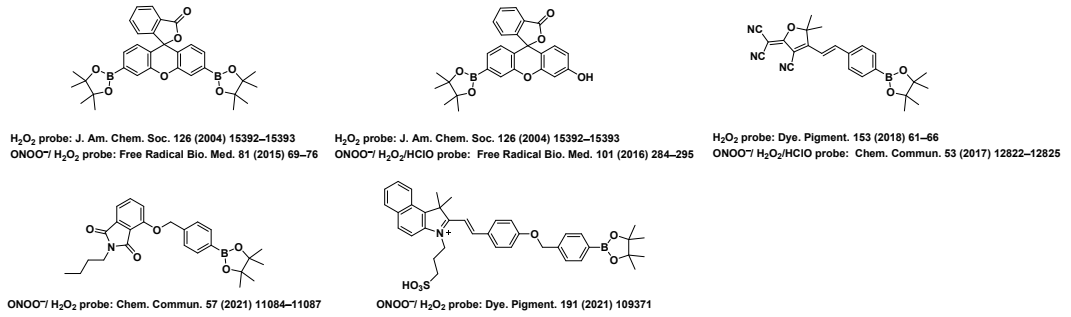
Supplementary schemes



Scheme S1 Examples of fluorescent probes containing arylboronic acid pinacol ester for $ONOO^-$.

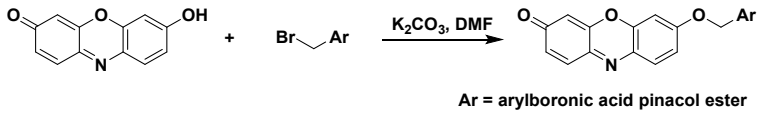


Scheme S2 Examples of fluorescent probes containing arylboronic acid pinacol ester for H_2O_2.



Scheme S3 Examples of fluorescent probes containing arylboronic acid pinacol ester for $ONOO^-$ and/or H_2O_2

Synthetic method



Scheme S4. A general pathway for the synthesis of probes.

The borate ester derivatives were synthesized according to the procedure reported.[1,2]

General procedure for the probes' synthesis: Resorufin (106 mg, 0.5 mmol) was dissolved in DMF (5 mL), and arylboronic acid pinacolate self-eliminating linker (0.6 mmol) and K_2CO_3 (138 mg, 1 mmol) were added. The reaction mixture was purged with nitrogen and stirred at room temperature for 30 min. The crude mixture was poured out in dichloromethane, washed with aqueous Na_2CO_3, and the organic layer was evaporated to dryness. The product was obtained after filtration over silica gel column chromatography.

***p*-Borate:** Orange solid; yield: 68%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.40 (s, 1H), 7.00 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.89 – 6.73 (m, 2H), 6.31 (d, *J* = 1.9 Hz, 1H), 5.20 (s, 2H), 1.34 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ= 186.32, 162.59, 149.81, 145.71, 145.59, 138.46, 135.27, 134.71, 134.26, 131.61, 128.51, 126.53, 114.32, 106.77, 101.16, 83.97, 70.77, 24.88 ppm; MS(ESI): Calculated for $C_{25}H_{24}BNO_5$ $[M+H]^+$: 430.2, measured: 430.2; HRMS (ESI): Calculated for $[M+H]^+$: 430.1856, measured: 430.1854.

***o*-Borate:** Orange solid; yield: 63%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 7.3 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 (d, *J* = 9.8 Hz, 1H), 7.37 (ddd, *J* = 7.5, 5.2, 3.5 Hz, 1H), 7.01 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.94 (d, *J* = 2.6 Hz, 1H), 6.84 (dd, *J* = 9.8, 2.0 Hz, 1H), 6.33 (d, *J* = 2.0 Hz, 1H), 5.46 (s, 2H), 1.29 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.31, 163.32, 149.94, 145.71, 145.36, 141.58, 136.45, 134.70, 134.13, 131.48, 131.39, 128.33, 128.01, 127.77, 114.54, 106.66, 100.92, 83.92, 70.55, 24.89 ppm; MS(ESI): Calculated for $C_{25}H_{24}BNO_5$ $[M+H]^+$: 430.2, measured: 430.1; HRMS(ESI): calculated for $[M+H]^+$: 430.1856, measured: 430.1834.

***m*-Borate**: Orange solid; yield: 54%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (s, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 9.8 Hz, 1H), 6.32 (s, 1H), 5.16 (s, 2H) 1.36 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.32, 162.72, 149.83, 145.65, 135.02, 134.69, 134.24, 133.97, 131.59, 130.50, 128.48, 128.27, 114.28, 106.74, 101.04, 84.04, 70.92, 24.88 ppm; MS(ESI): Calculated for $C_{25}H_{24}BNO_5$ $[M+H]^+$: 430.2, measured: 430.2; HRMS(ESI): Calculated for $[M+H]^+$: 430.1856, measured: 430.1845

***p*-Borate-*o*-OMe:** Orange solid; yield: 33%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.9 Hz, 1H), 7.44 (dd, *J* = 12.5, 5.3 Hz, 2H), 7.42 (s, 1H), 7.35 (s, 1H), 7.03 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.84 (dd, *J* = 9.8, 2.0 Hz, 1H), 6.32 (d, *J* = 5.5 Hz, 1H), 5.26 (s, 2H), 3.95 (s, 3H), 1.36 (s,

12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.71, 162.32, 155.54, 149.26, 145.03, 144.86, 134.07, 133.55, 130.91, 127.82, 126.99, 126.78, 126.31, 115.23, 113.85, 106.06, 100.43, 83.37, 65.37, 54.94, 24.24 ppm; MS(ESI): Calculated for $C_{26}H_{26}BNO_6$ $[M+H]^+$: 460.2, measured: 460.2; HRMS(ESI): Calculated for $[M+H]^+$: 460.1926, measured: 460.1922.

***p*-Borate-*m*-OMe:** Orange solid; yield: 36%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 (s, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.42 (d, *J* = 9.8 Hz, 1H), 7.03 – 6.98 (m, 1H), 6.91 (s, 1H), 6.86 – 6.81 (m, 1H), 6.32 (d, *J* = 1.8 Hz, 1H), 5.18 (s, 1H), 3.85 (s, 1H), 1.35 (s, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.69, 164.97, 162.90, 150.16, 146.11, 145.93, 140.40, 137.60, 135.06, 134.64, 131.95, 128.88, 119.23, 114.66, 109.38, 107.14, 101.58, 83.98, 71.18, 56.26, 25.17.ppm; MS(ESI): Calculated for $C_{26}H_{26}BNO_6$ $[M+H]^+$: 460.2, measured: 460.2; HRMS(ESI): Calculated for $[M+H]^+$: 460.1926, measured: 460.1922.

***p*-Borate-*o*-F:** Orange solid; yield: 48%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 10.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 9.8 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.89 (s, 1H), 6.83 (d, *J* = 9.8 Hz, 1H), 6.32 (s, 1H), 5.26 (s, 1H), 1.34 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.49, 162.44, 161.03, 159.39, 149.94, 146.00, 145.75, 134.86, 134.47, 131.80, 130.85, 129.01, 128.76, 121.45, 121.33, 114.26, 106.97, 101.25, 84.42, 64.71, 25.00 ppm; MS(ESI): Calculated for $C_{25}H_{23}BFNO_5$ $[M+H]^+$: 448.2, measured: 448.1; HRMS(ESI): Calculated for $[M+H]^+$: 448.1762, measured: 448.1720.

***p*-Borate-*m*-F:** Orange solid; yield: 59%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 (t, *J* = 6.8 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.42 (d, *J* = 9.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 9.5 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.83 (d, *J* = 9.3 Hz, 2H), 6.32 (s, 1H), 5.19 (s, 2H), 1.36 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.67, 167.63, 165.96, 161.56, 149.13, 145.31, 144.94, 140.82, 136.81, 134.09, 133.71, 131.04, 128.00, 121.39, 113.52, 106.20, 100.58, 83.44, 69.21, 24.19 ppm; MS(ESI): Calculated for $C_{25}H_{23}BFNO_5$ $[M+H]^+$: 448.2, measured: 448.1; HRMS(ESI): Calculated for $[M+H]^+$: 448.1762, measured: 448.1720.

***o*-Borate-*m*-F:** Orange solid; yield: 43%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 8.1, 6.6 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.45 (d, *J* = 9.8 Hz, 1H), 7.25 (dd, *J* = 10.0, 2.2 Hz, 1H), 7.05 (ddd, *J* = 11.4, 8.6, 2.4 Hz, 2H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.86 (dd, *J* = 9.8, 1.9 Hz, 1H), 6.35 (d, *J* = 1.9 Hz, 1H), 5.49 (s, 2H), 1.33 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.66, 165.27, 163.60, 162.20, 149.24, 145.05, 144.54, 138.23, 138.17, 134.08, 133.59, 130.94, 127.83, 114.02, 113.92, 113.76, 106.09, 100.38, 83.42, 69.00, 24.27 ppm; MS(ESI): Calculated for $C_{25}H_{23}BFNO_5$ $[M+H]^+$: 448.2, measured: 448.2; HRMS(ESI): Calculated for $[M+H]^+$: 448.1762, measured: 448.1720.

***o*-Borate-*m*-NO_2:** Orange solid; yield: 48%; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 8.18 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 8.8, 5.9 Hz, 1H), 7.43 (dd, *J* = 9.7, 3.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 9.8, 1.7 Hz, 1H), 6.33 (d, *J* = 1.7 Hz, 1H), 5.51 (s, 2H), 1.34 (s, 12H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.65, 161.76, 149.31, 149.17,

145.27, 145.01, 143.27, 136.85, 134.10, 133.70, 132.45, 131.06, 129.27, 127.98, 121.39, 113.59, 106.19, 100.36, 84.17, 68.65, 24.28 ppm; MS(ESI): Calculated for $C_{25}H_{23}BN_2O_7$ $[M+H]^+$: 475.1, measured: 475.2; HRMS(ESI): Calculated for $[M+H]^+$: 475.1671, measured: 475.1668.

Generation of various ROS species

All analytes involved were prepared according to the related literature, and concentrations of analytes were determined by measuring their absorption or diluting them. [3–6]

$ONOO^-$: To a vigorously stirred solution of $NaNO_2$ (0.6 M, 10 mL) and H_2O_2 (0.7 M, 10 mL) in deionized H_2O at 0 °C was added HCl (0.6 M, 10 mL), immediately followed by the rapid addition of NaOH (1.5 M, 20 mL). Excess hydrogen peroxide was removed by passing the solution through a short column of MnO_2. The concentration of $ONOO^-$ was determined by UV analysis with the extinction coefficient at 302 nm ($\varepsilon = 1670\ M^{-1}\ cm^{-1}$) in 0.1 M NaOH. Aliquots of the solution were stored at – 20 °C for use.

H_2O_2: H_2O_2 solution was prepared by diluting commercial H_2O_2 solutions with PBS (10 mM, pH 7.4) to make 10 mM stock solutions. The concentration of H_2O_2 was determined by UV analysis with the extinction coefficient at 240 nm ($\varepsilon = 39.4\ M^{-1}\ cm^{-1}$) in water.

$^1O_2$: $NaMoO_4$ (10 mM) and H_2O_2 (10 mM) was prepared in PBS (10 mM, pH 7.4). Equal aliquots of these solutions were then mixed to yield $^1O_2$ of 5 mM.

ClO^-: ClO^- solution was prepared by diluting commercial NaClO solutions with PBS (10 mM, pH 7.4) to make 10 mM stock solutions. The concentration of ClO^- was determined by UV analysis with the extinction coefficient at 292 nm ($\varepsilon = 350\ M^{-1}\ cm^{-1}$) in 0.1 M NaOH.

$O_2^{\bullet-}$: $O_2^{\bullet-}$ (100 μM) also can be generated from enzymatic reaction of xanthine (300 μM) and xanthine oxidase (0.01 U/mL).

•OH: •OH was generated by Fenton reaction. To a solution of H_2O_2 (1.0 mM, 1.0 mL) in PBS (10 mM, pH 7.4) was added $FeSO_4$ solution (1.0 mM, 100 μL) at ambient temperature (stock solution 0.1 mM).

ROO•: ROO• was generated from 2, 2'-azobis(2-amidinopropane)dihydrochloride, which was dissolved in PBS (10 mM, pH 7.4) 1 h before use to make a stock solution of 10 mM.

Cell incubation

Cell culture. Raw 264.7 cells, HepG2 cells and HeLa cells were cultured in Dulbecco's Modified Eagle Medium supplemented with 10% FBS at 37 °C in a humidified 5% CO_2 atmosphere, and the culture medium was refreshed every day. The cells were seeded in glass bottom cell culture dishes (Nest, New Jersey, USA) at a density of 4.5×10^4 cells per well and divided into 3 batches. Culture medium was removed and the cells were incubated with different substances at 37 °C. All the batches were rinsed three times with PBS buffer, and then imaged under the Laser Scanning Confocal Microscopy (LSCM, Carl Zeiss LSM710, Zeiss, Jena, Germany).

Toxicity determination. CCK-8 experiment was performed in 96-well plate to assess the cytotoxicity of ***p*-Borate**. The CCK-8 assay in cells with probe concentrations from 0 to 10 μM was in comparison with the blank and negative control. Cells were plated on cell plates at 4×10^3 cells per well and allowed to incubate for 24 h. ***p*-Borate** in various concentrations was added to the well and

incubated for 24 h followed by classical CCK-8 treatment and data acquiring.

A stock solution of probe (1 mM) was prepared in DMSO and working solution was diluted to desired concentration in Dulbecco's Modified Eagle Medium supplemented with 10% FBS.

Exogenous $ONOO^-$ imaging experiments in live cells. The HepG2 cells were incubated with ***p*-Borate** (10 μM) for 20 min, followed by treated with SIN-1 (10 μL, 10 mM) for 0, 2, 4, 6, 8, 10, 12 minute. Confocal microscopy imaging was carried out after washing the cells with PBS for three times.

Endogenous $ONOO^-$ imaging experiments in live cells. The Raw 264.7 cells were incubated with bacterial products lipopolysaccharide (LPS, bacterial endotoxin, 1 μg/mL) and gamma interferon (IFN-γ, pro-inflammatory cytokine, 50 ng/mL) for 12 h, and then were incubated with ***p*-Borate** (10 μM) for another 20 min at 37 °C. Confocal microscopy imaging was carried out after washing the cells with PBS for three times.

LPS-induced inflammation in mice.

Animal experiments involving mice were conducted in Fudan University's Experimental Animal Centre in compliance with ethical guidelines. A stock solution of probe (1 mM) was prepared in DMSO and working solution was diluted to desired concentration in PBS buffer. LPS (200 μL, 1 mg/mL) was injected into the tibiotarsal joints of 6–8 week-old nude mice to induce acute inflammation. The tibiotarsal joints of mouse were divided into two groups. (I) LPS (200 μL, 1 mg/mL) was injected into the left tibiotarsal joints of the mice. (II) PBS (200 μL) was injected into the right tibiotarsal joints of the mouse. 12 hours later, probe (10 μM) was injected into region I and II.

Supplementary optical spectra

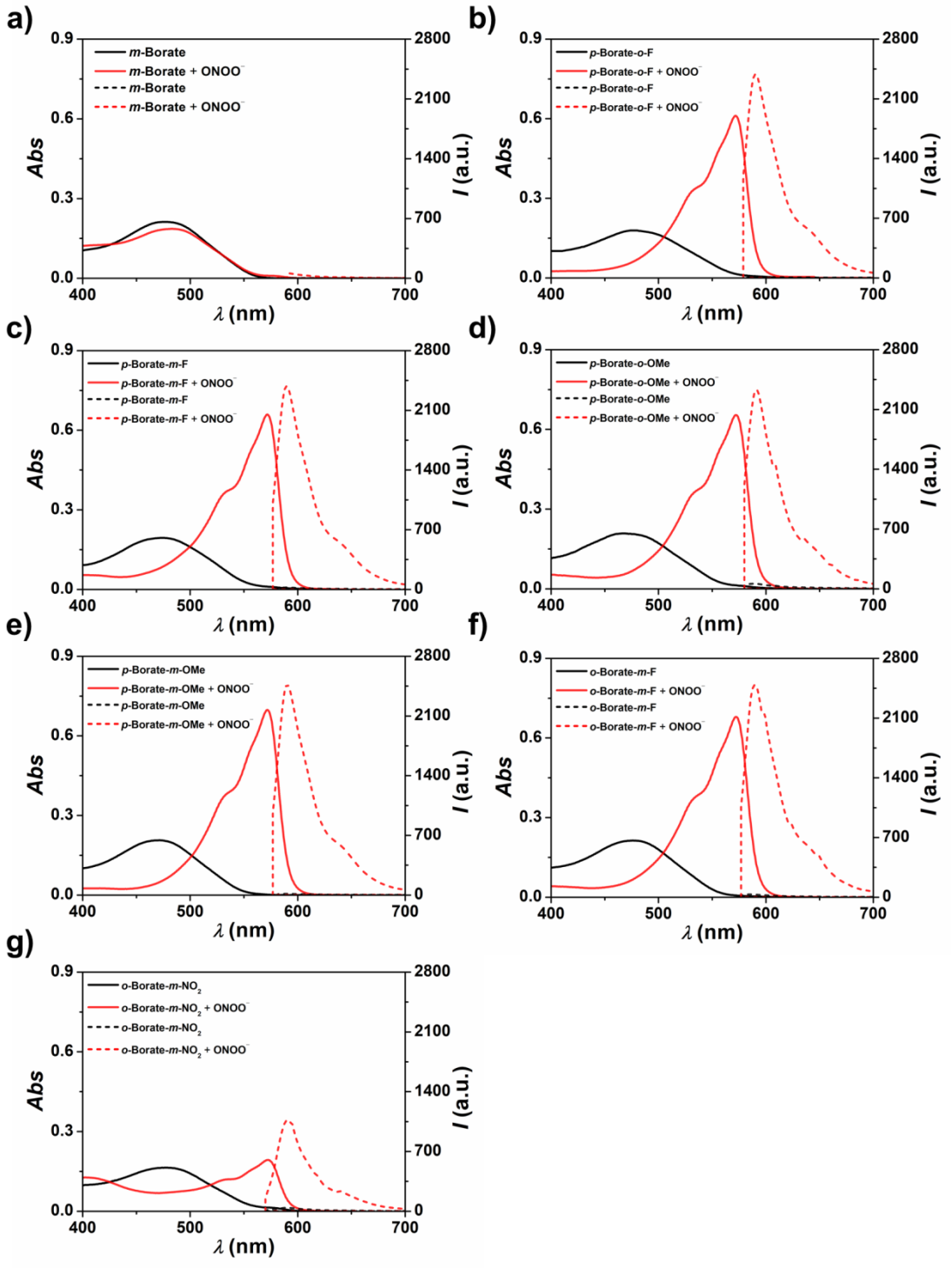


Figure S1. Absorption (solid line) and fluorescence (dashed line, λ_{ex} = 560 nm, slit: 2/5 nm) spectra of probes ((a) ***m*-Borate,** (b) ***p*-Borate-*o*-F**, (c) ***p*-Borate-*m*-F,** (c) ***p*-Borate-*o*-OMe,** (d) ***p*-Borate-*m*-OMe**, (e) ***o*-Borate-*m*-F** and (f) ***o*-Borate-*m*-NO_2** 10 μM, black curve) prior to and after treatment with 100 μM of $ONOO^-$ (red curve) for 10 min, respectively. Conditions: PBS buffer, 10 mM, pH 7.4, containing 20% MeCN, 25 °C.

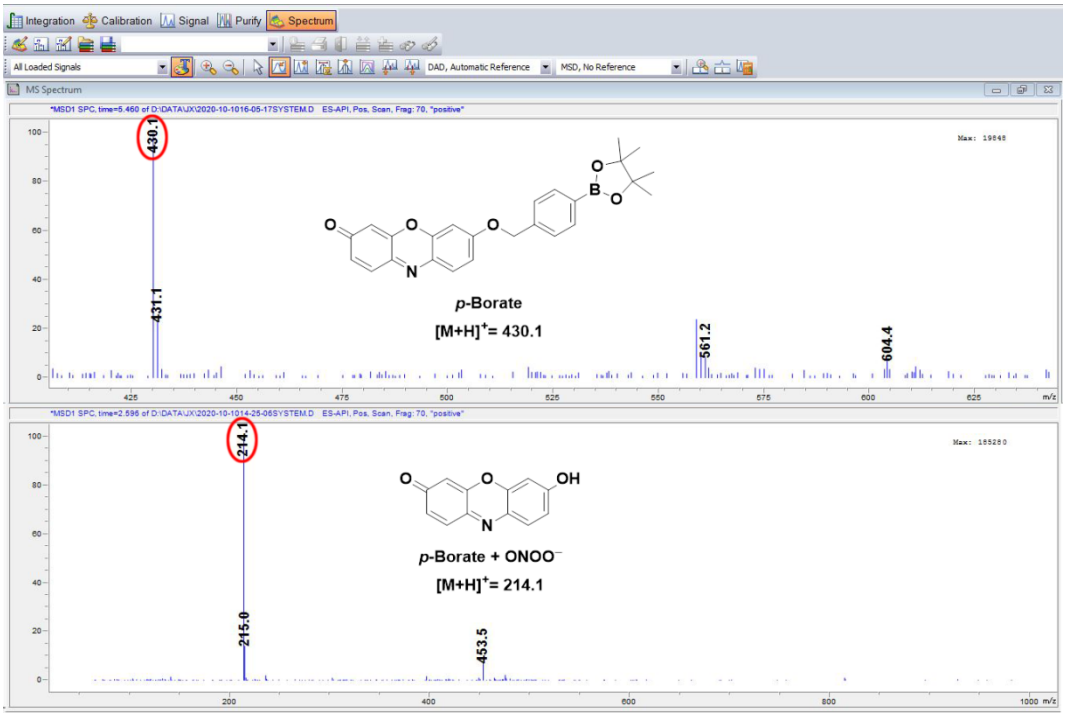


Figure S2. MS spectra of fluorescent ***p*-Borate** prior to and after addition of $ONOO^-$ for 10 min, respectively.

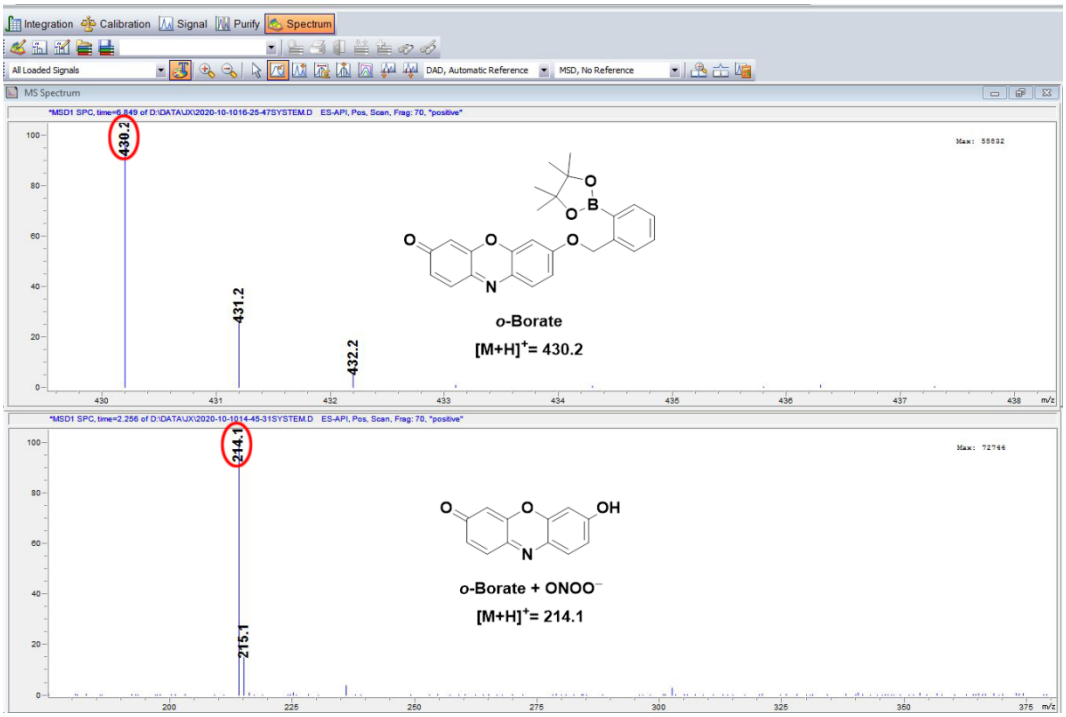


Figure S3. MS spectra of fluorescent ***o*-Borate** prior to and after addition of $ONOO^-$ for 10 min, respectively.

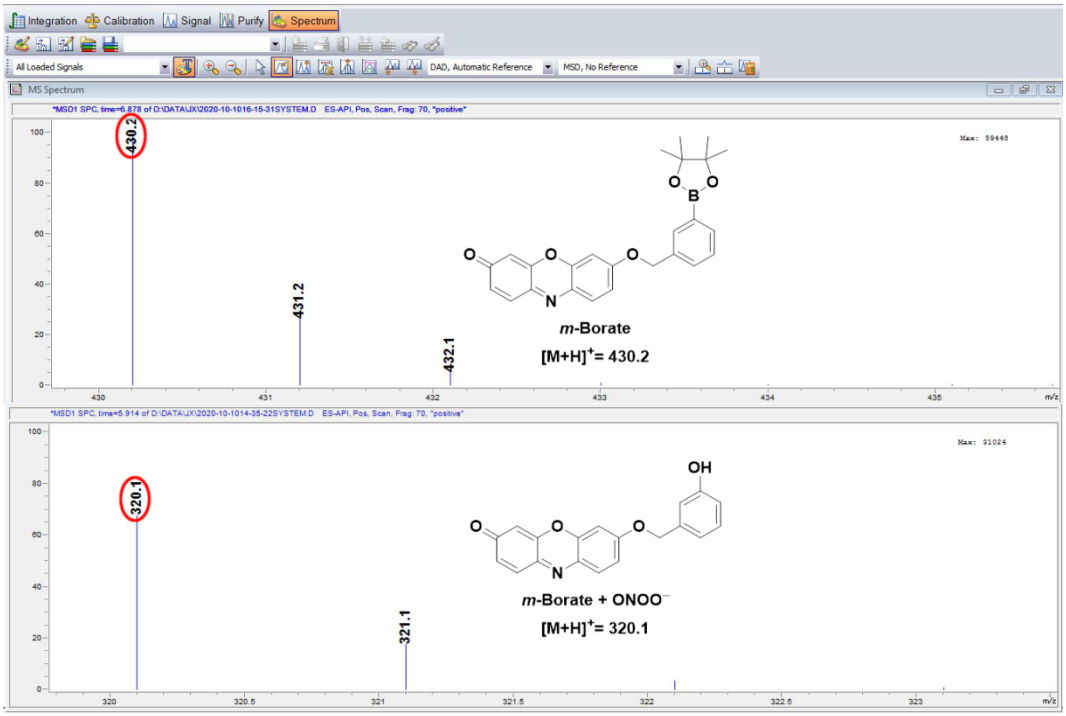


Figure S4. MS spectra of fluorescent ***m*-Borate** prior to and after addition of $ONOO^-$ for 10 min, respectively.

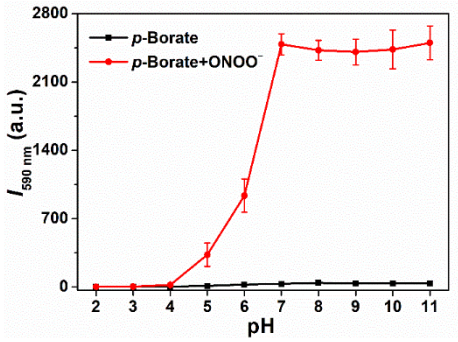


Figure S5. The fluorescent intensities of ***p*-Borate** (10 μM) prior to and after addition of 100 μM of $ONOO^-$ at various pH values for 10 min incubation at 25 °C ($\lambda_{ex}/\lambda_{em}$ = 560/590 nm, slit: 2/5 nm).

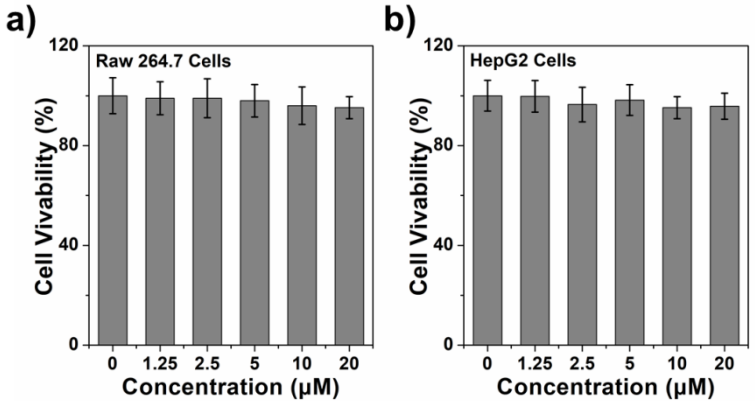


Figure S6. Cytotoxicity assays of ***p*-Borate** in living Raw 264.7 cells and HepG2 cells.

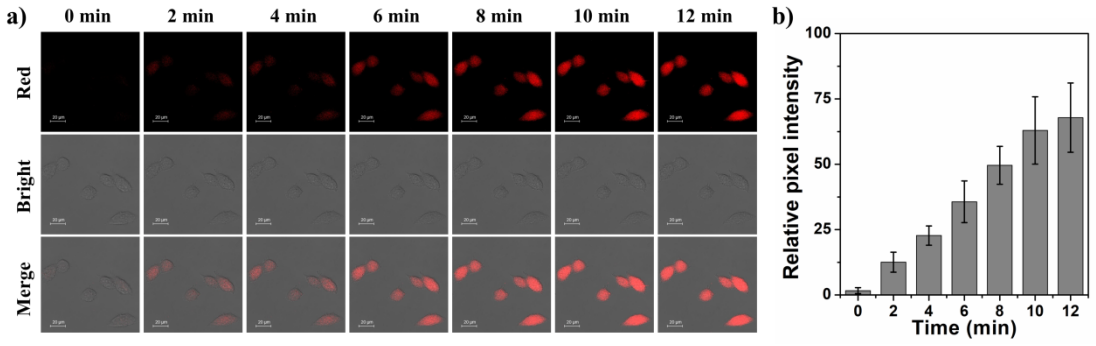


Figure S7. Confocal lasing scanning microscopy and red channel images of HepG2 cells. (a) Fluorescence image of HepG2 cells treated with ***p*-Borate** (10 μM) for 20 min at 37 °C, and then incubated with **SIN-1** (1 mM) for 0 min, 2 min, 4 min, 8 min, 10 min and 12 min. (b) Relative pixel intensity of the corresponding fluorescence images. Scale: 20 μm.

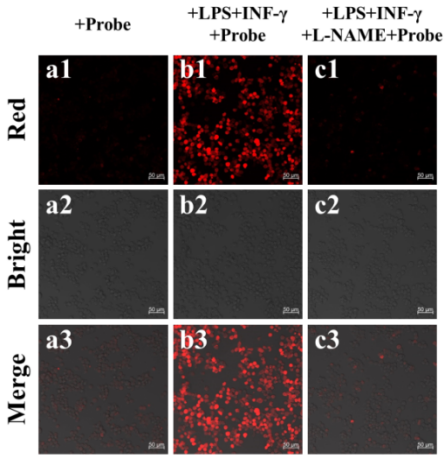


Figure S8. Confocal lasing scanning microscopy and red channel images of Raw 264.7 cells under various treatments. (a) Fluorescence image of Raw 264.7 cells treated with ***p*-Borate** (10 μM) for 20 min at 37 °C. (b) Fluorescence image of Raw 264.7 cells pretreated with LPS (1 μg·mL^{-1}) and IFN-γ (50 ng·mL^{-1}) for 12 h and then incubated with ***p*-Borate** (10 μM, 20 min). (c) Fluorescence image of Raw 264.7 cells pretreated with NOS inhibitor L-NAME (3 mM, 12 h) during stimulation with LPS (1 μg•mL^{-1}) and IFN-γ (50 ng•mL^{-1}) for 12 h, subsequently incubated with probe ***p*-Borate** (10 μM, 20 min). Scale: 50 μm.

Supplementary table

Table S1 Photophysical properties of the synthesized probes

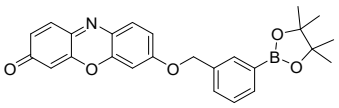
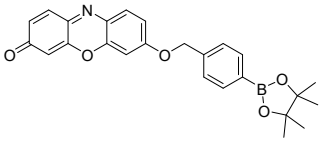
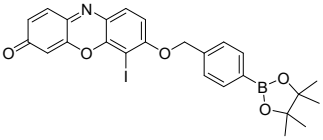
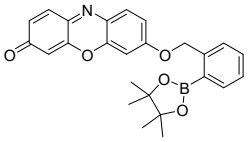
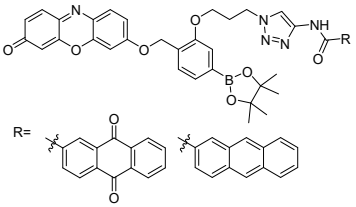
No.	Sensors	Analytes	Solution system	Saturation Time	Ref.
1		150 U mL^{-1} tyrosinase	PBS buffer (2% DMSO)	10 h	*Anal. Chem.*, 2018, 90, 855–858
2		1000 eq. H_2O_2	PBS buffer	12 min	*Chem. – Eur. J.*, 2015, 21, 15167 – 15172
3		10 eq. H_2O_2	PBS buffer 1% DMSO	2 h	*Dyes Pigm.*, 2021, 193, 109499
4		10 eq. BPO	PBS buffer 10% EtOH	10 min	*Chem. Commun.*, 2012,48, 2809-2811
5		50 eq. H_2O_2	PBS buffer 10% DMSO	1 h	*Chem. Asian J.*, 2017, 12, 2656 – 2659

Table S2 Photophysical properties of the synthesized probes

Probes	$\lambda_{abs}/\lambda_{fl}$ (nm) [a, c]	$\lambda_{abs}/\lambda_{fl}$ (nm) [a, d]	ε ($10^4 M^{-1}cm^{-1}$) [a, c]	t ($ONOO^-$) [a]	Φ_{fl}[a]
***p*-Borate**	470/- [b]	572/590	1.9	1 min	0.0075
***m*-Borate**	472/- [b]	477/- [b]	2.1	- [b]	0.0055
***o*-Borate**	477/- [b]	572/590	2.1	＜20 s	0.0051
***p*-Borate-*o*-F**	473/- [b]	572/590	1.9	3 min	0.0069
***p*-Borate-*m*-F**	476/- [b]	572/590	1.9	10 min	0.0061
***p*-Borate-*o*-OMe**	477/- [b]	572/590	2.1	＜20 s	0.0073
***p*-Borate-*m*-OMe**	474/- [b]	572/590	2.1	1 min	0.0060
***o*-Borate-*m*-F**	473/- [b]	572/590	2.1	1 min	0.0051
***o*-Borate-*m*-NO_2**	473/- [b]	572/590	2.0	＞10 min	0.0050

[a] Measured in 10 mM of PBS buffer (pH 7.4, 20% CH_3CN). [b] Undetectable. Wavelength changes of probe prior to[c] and after treatment with[d] $ONOO^-$ for 10 min, respectively. [e] Φ_{fl} is the relative fluorescence quantum yield estimated by using **Resorufin** (Φ_{fl} = 0.63 in alcohol) as a fluorescence standard [7].

Copies of NMR spectroscopic data

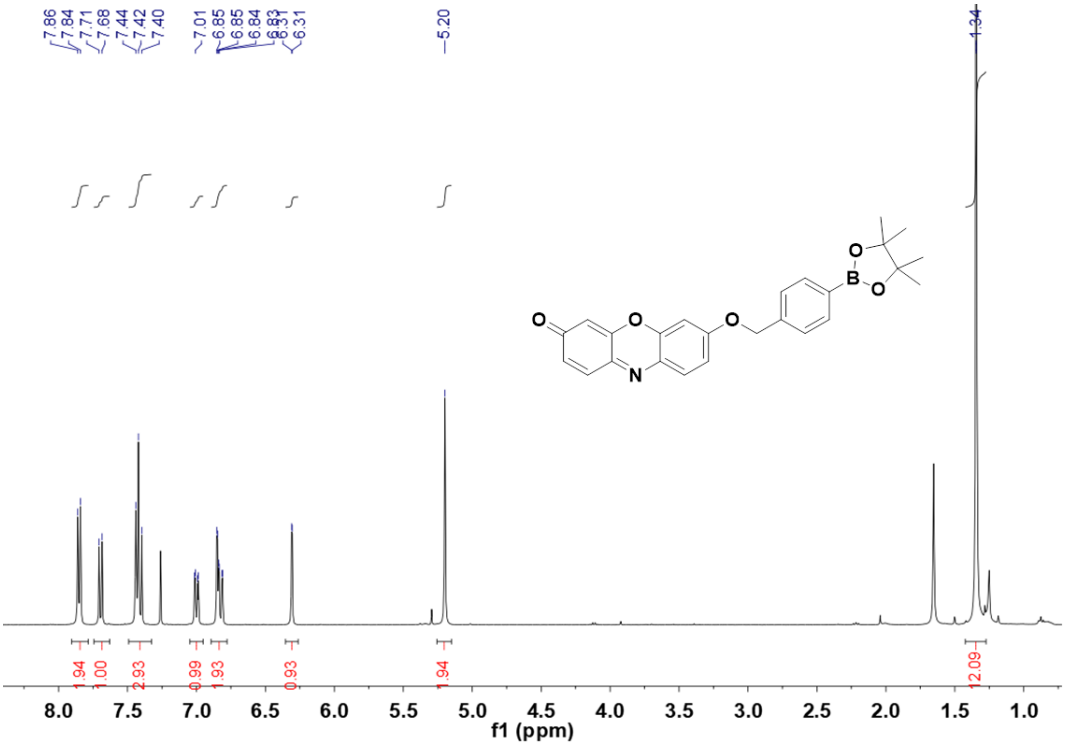


Figure S9: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***p*-Borate**.

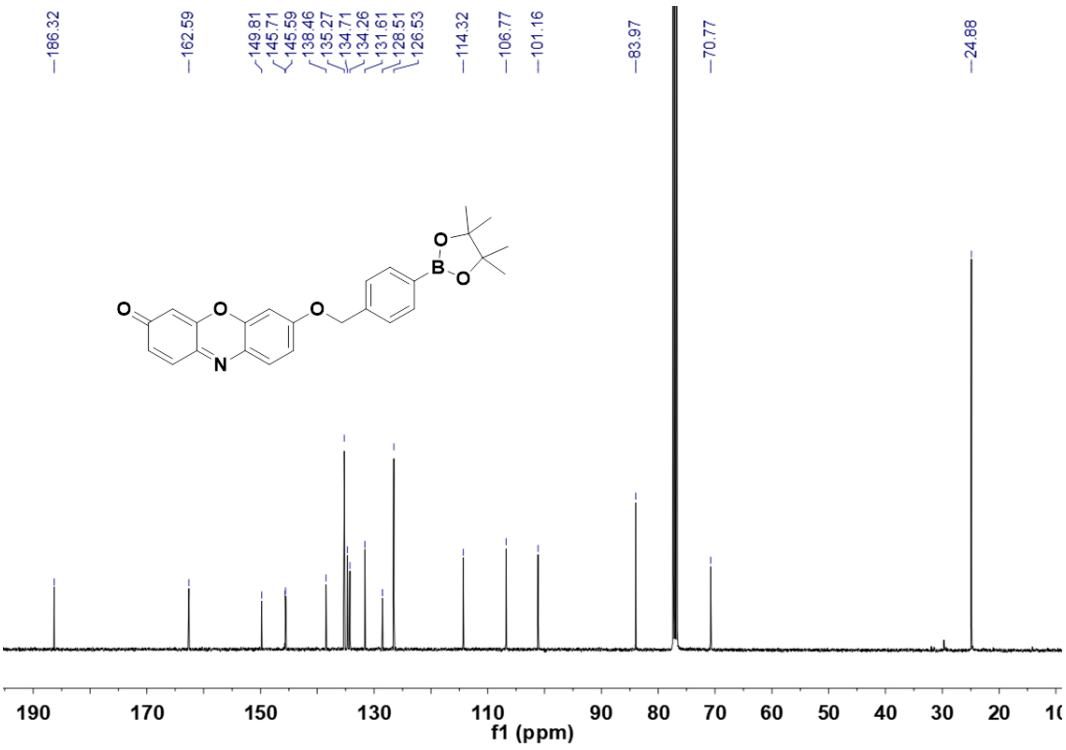


Figure S10: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***p*-Borate**.

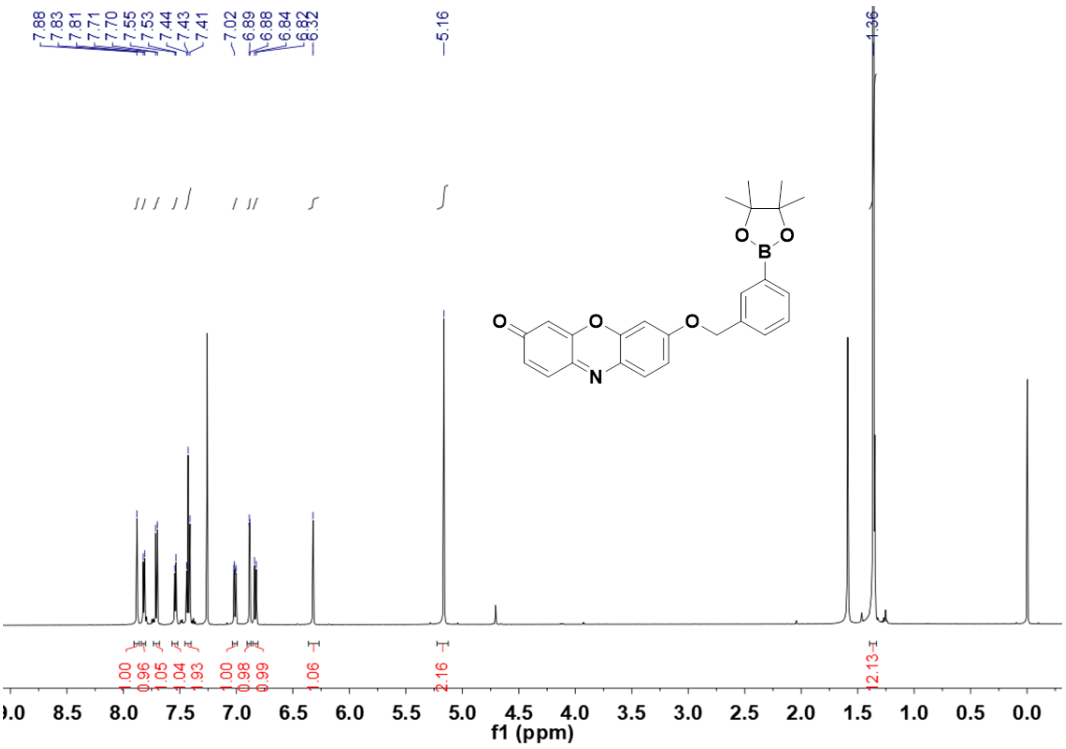


Figure S11: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***m*-Borate**.

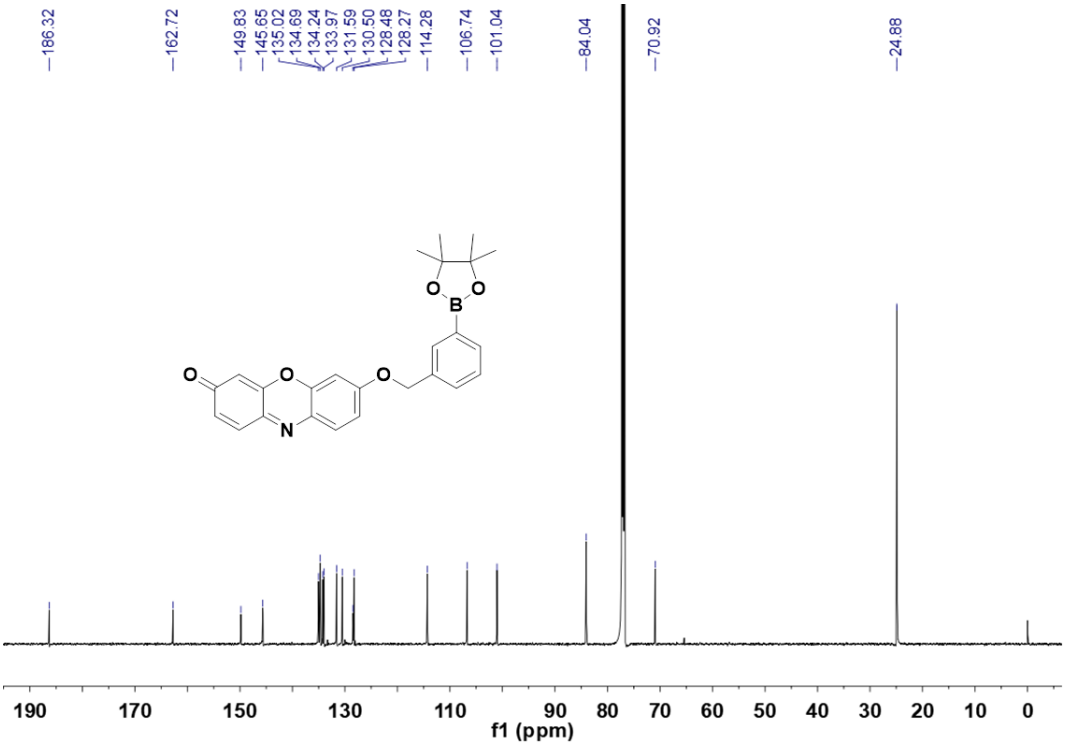


Figure S12: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***m*-Borate**.

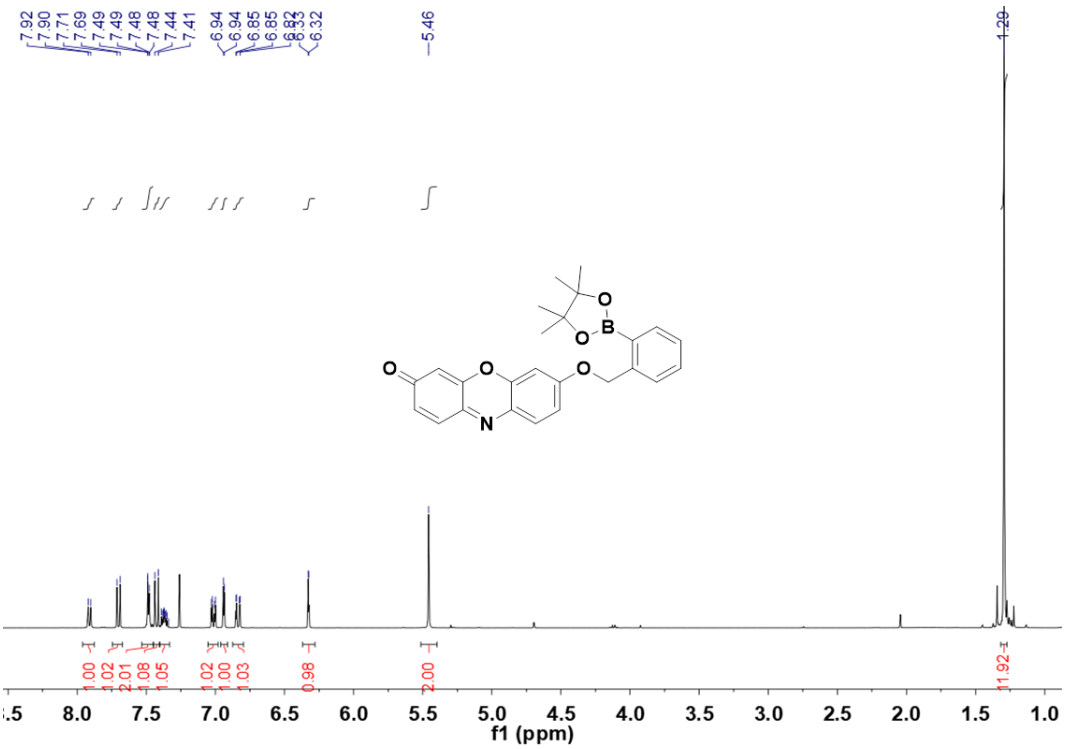


Figure S13: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***o*-Borate**.

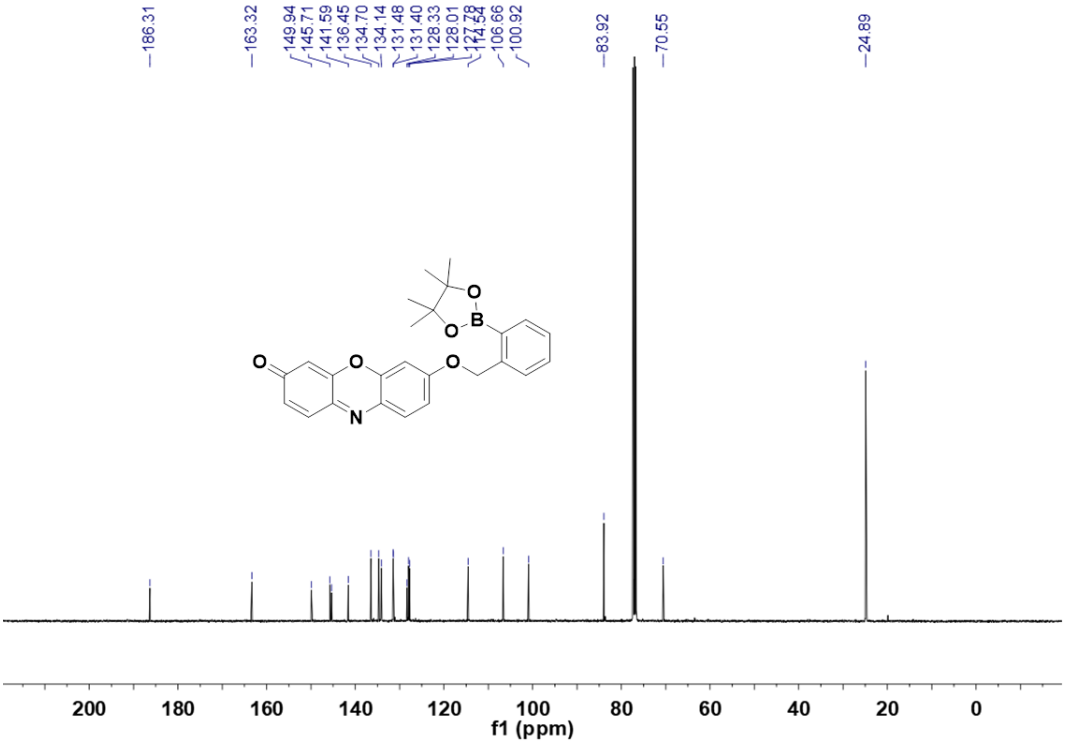


Figure S14: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***o*-Borate**.

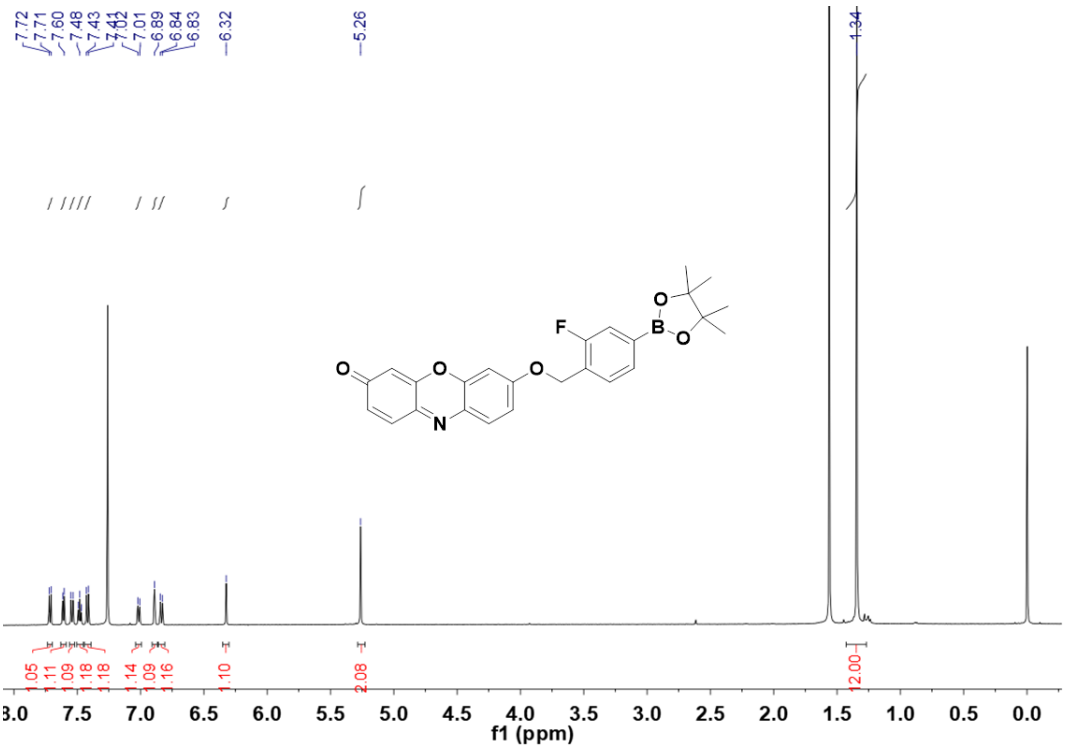


Figure S15: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***p*-Borate-*o*-F**.

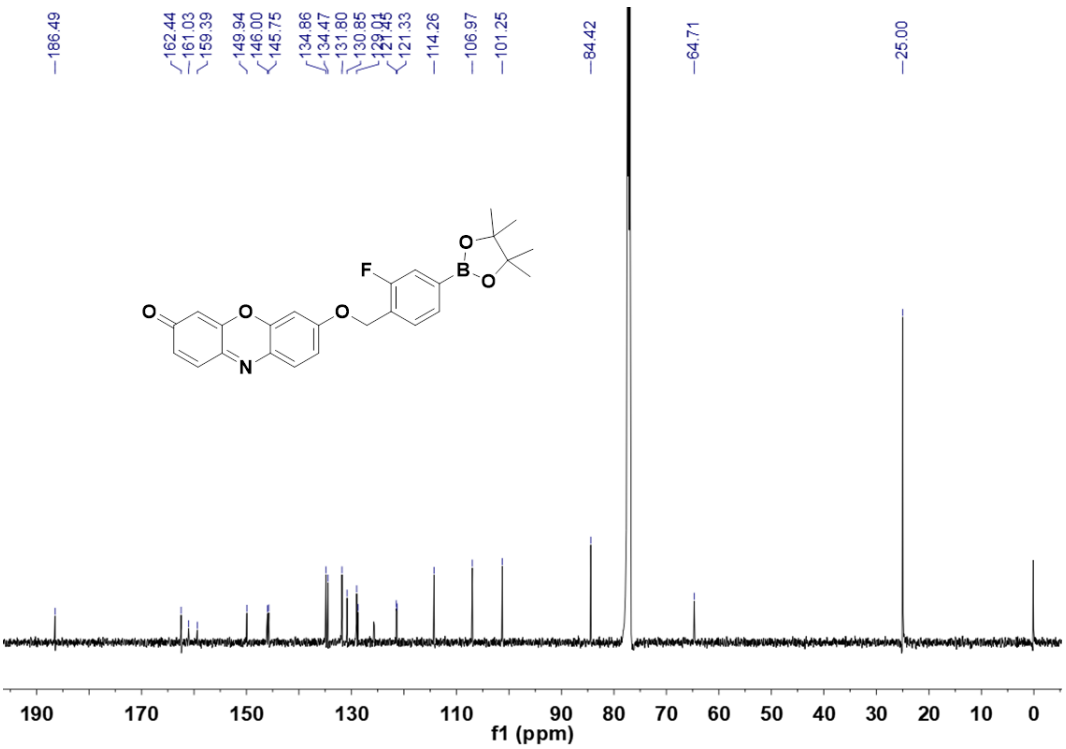


Figure S16: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***p*-Borate-*o*-F**.

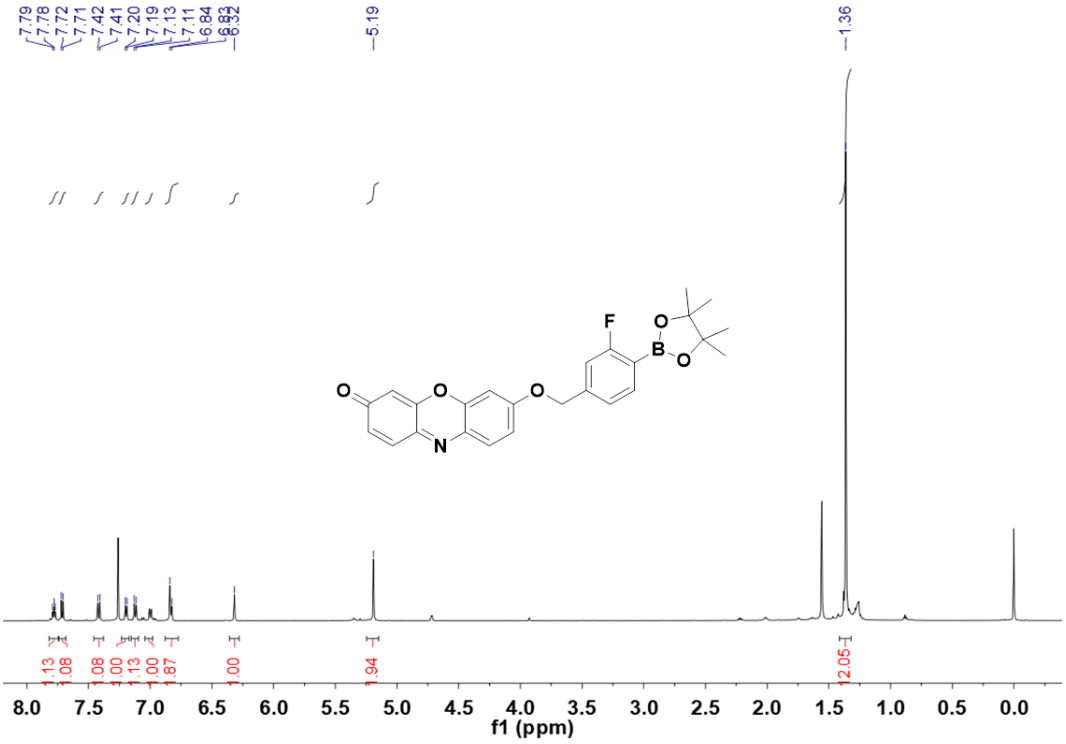


Figure S17: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***p*-Borate-*m*-F**.

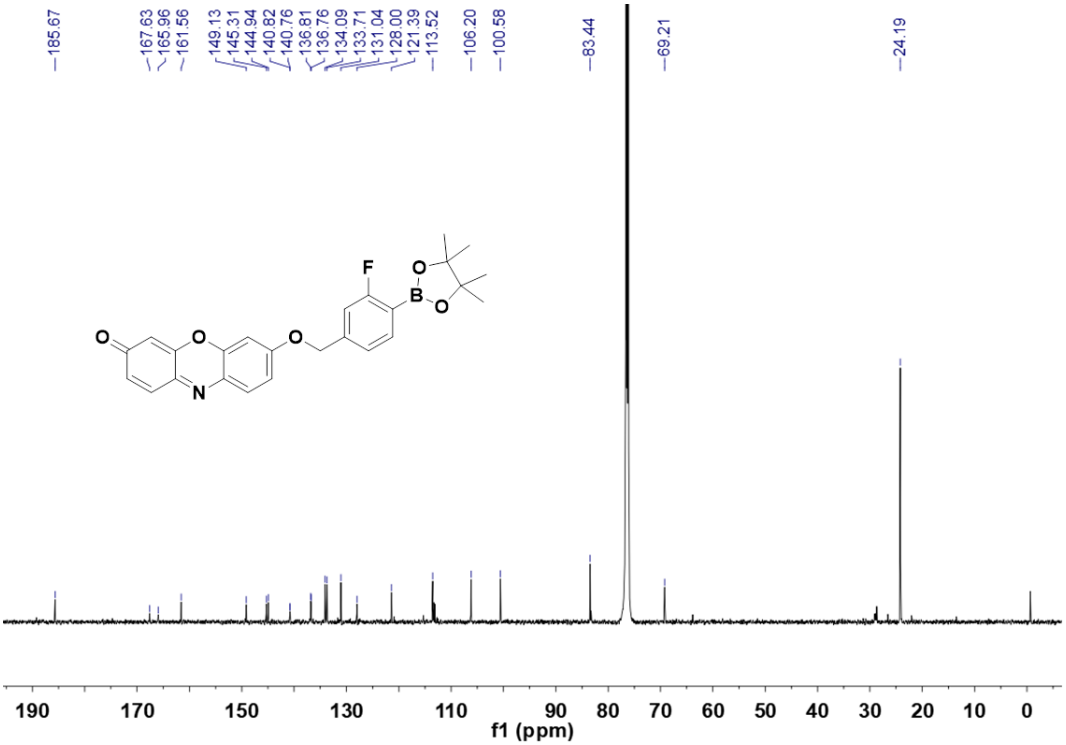


Figure S18: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***p*-Borate-*m*-F**.

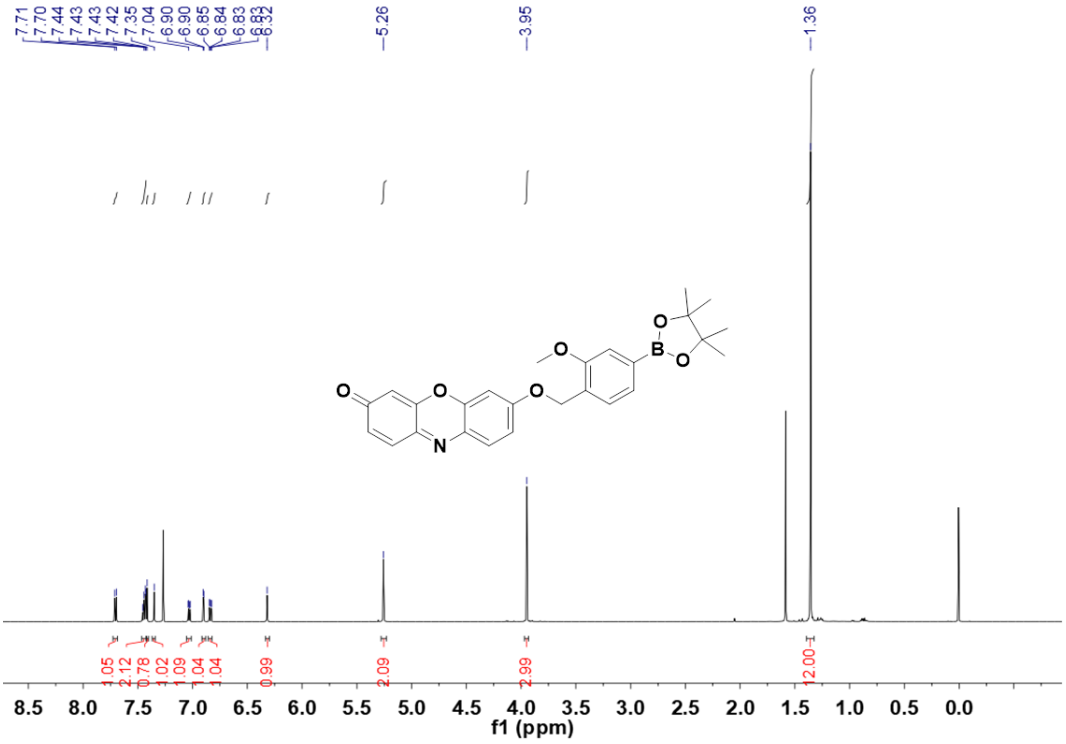


Figure S19: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***p*-Borate-*o*-OMe**.

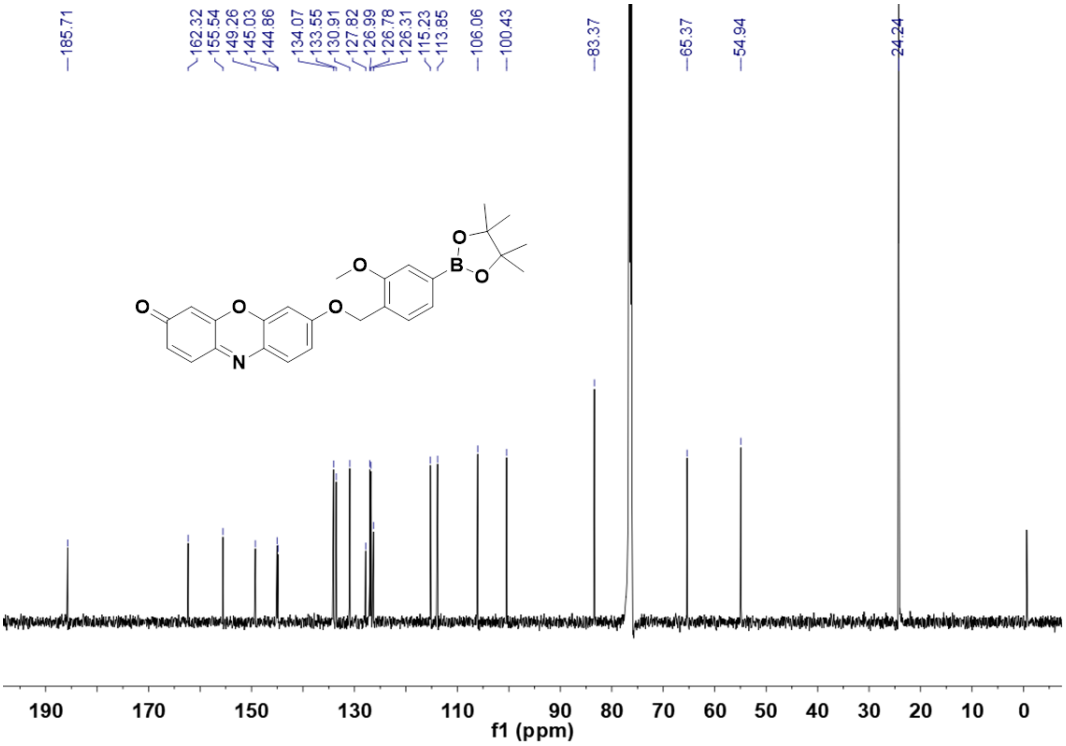


Figure S20: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***p*-Borate-*o*-OMe**.

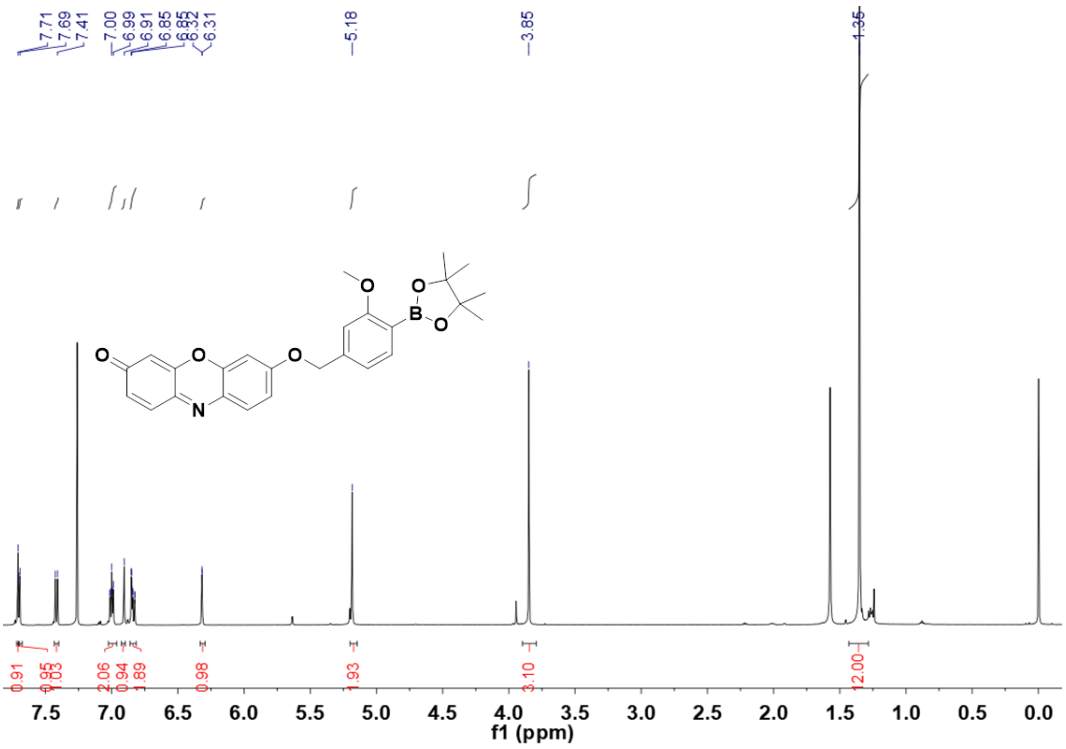


Figure S21: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***p*-Borate-*m*-OMe**.

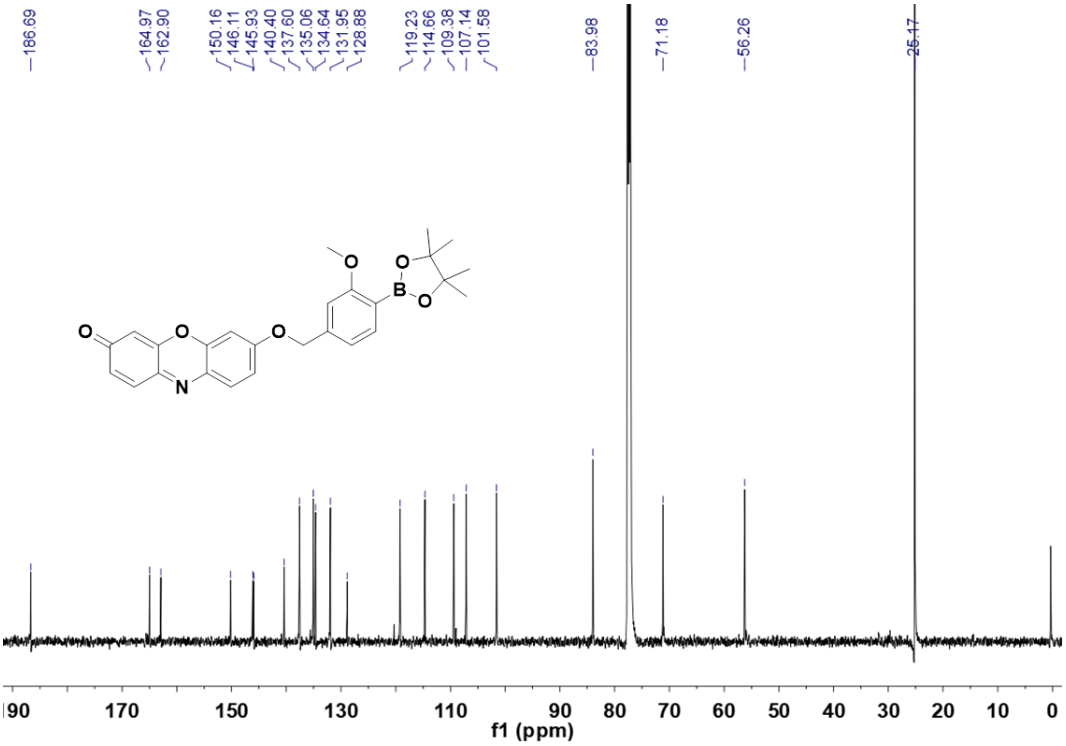


Figure S22: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***p*-Borate-*m*-OMe**.

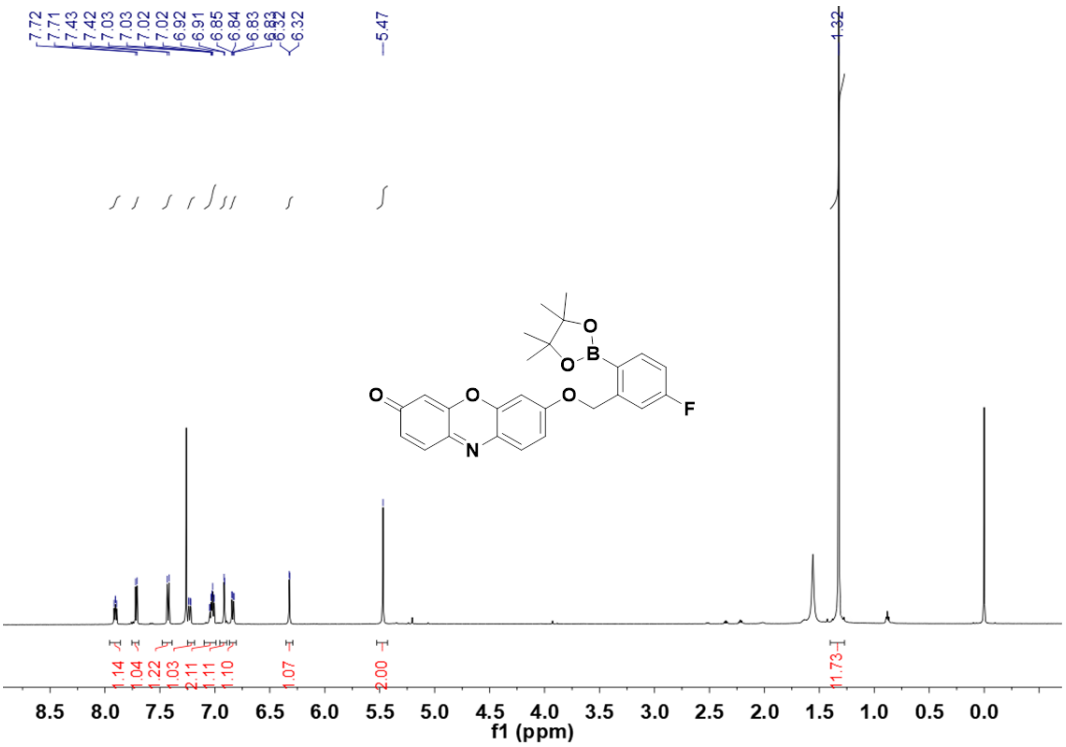


Figure S23: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***o*-Borate-*m*-F**.

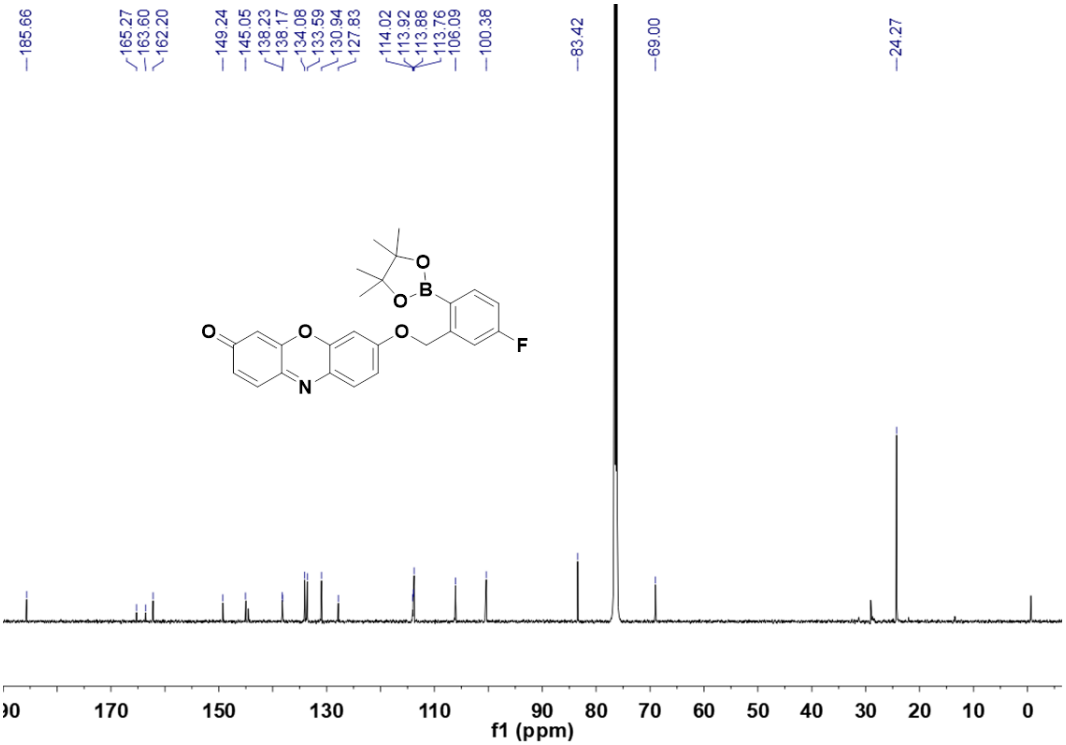


Figure S24: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***o*-Borate-*m*-F**.

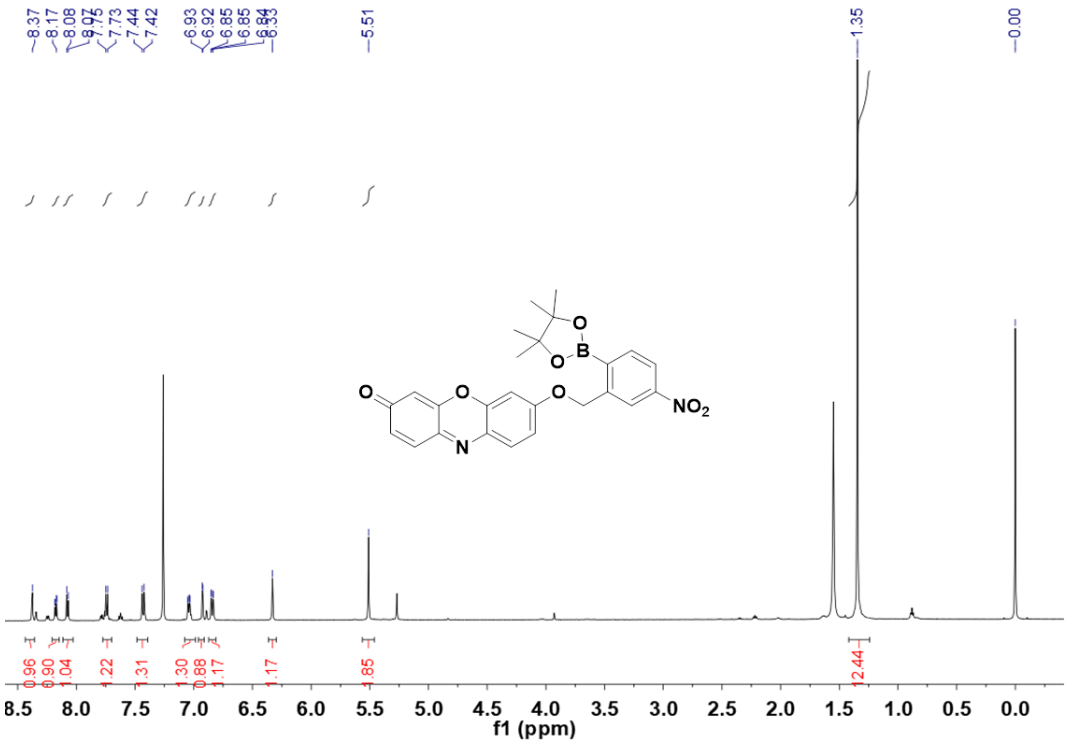


Figure S25: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ***o*-Borate-*m*-NO_2**.

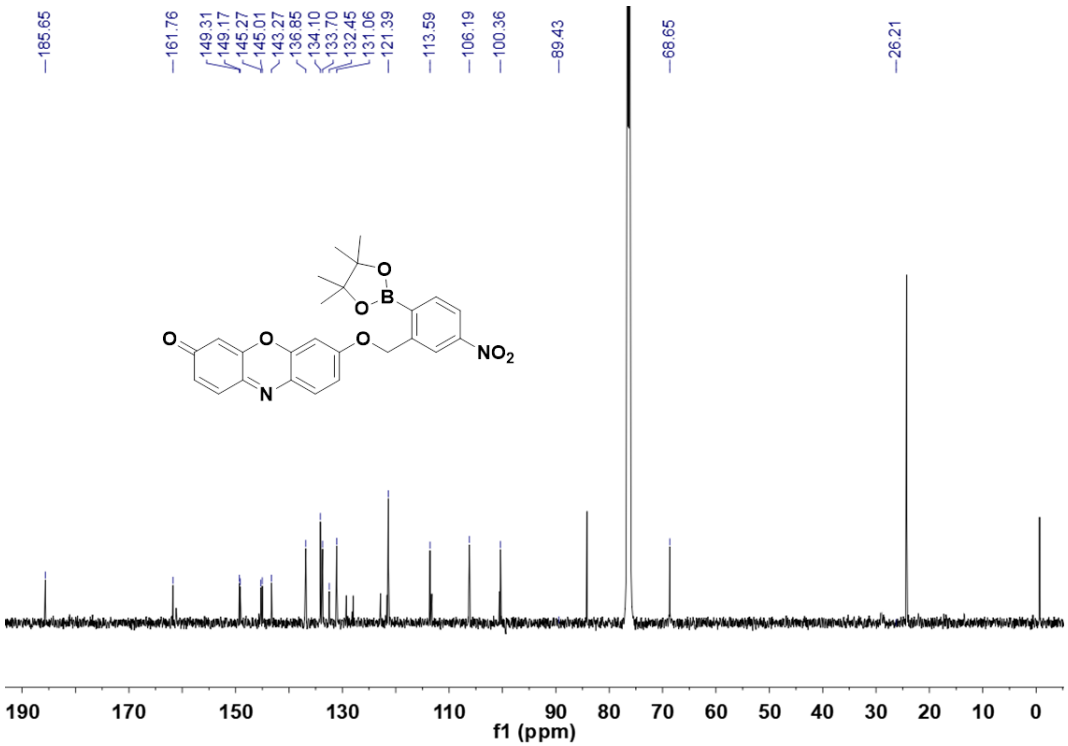


Figure S26: ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of ***o*-Borate-*m*-NO_2**.

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