Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Phosphinate-Based Near-Infrared Fluorescence Probe for Imaging the Superoxide Radical Anion In *In Vitro* and *In Vivo*

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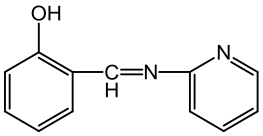
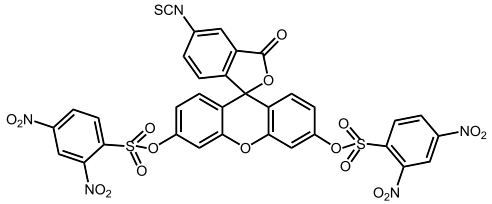
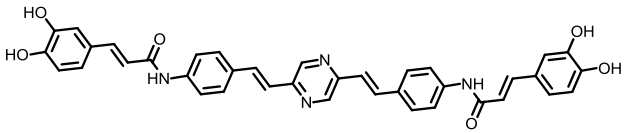
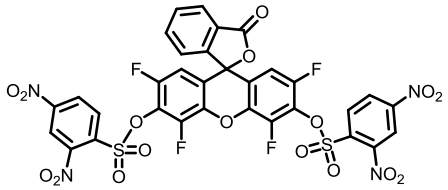
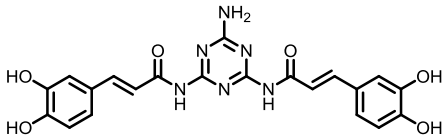
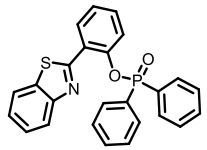
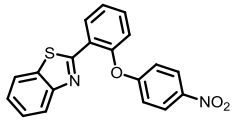
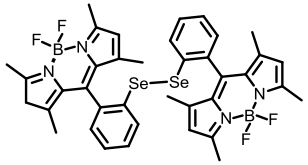
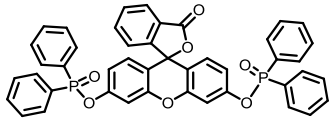
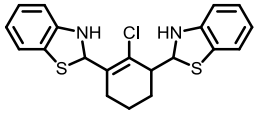
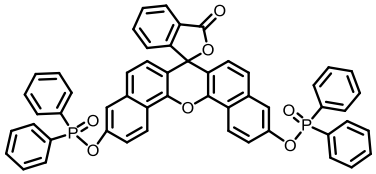
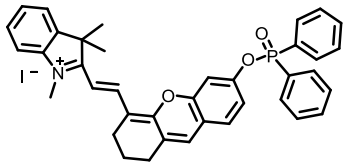
Table S1. Comparison of fluorescent probes for $O_2^{\bullet-}$. (OP: One-photon, TP: Two-photon)

Probe	Ex/Em	Dection system	Range of linear correlation / μM	LOD	Time	Application	ref
	294/355	EtOH/Tris 1:17	2-500 μM	1.38 μM	30 min	Determination of SOD activity in Garlic, Papaya, and Spinach.	10a
	494/520	PBS	0-25 μM	-	10 min	Determination of $O_2^{\bullet-}$ in PBS Buffer and Living Cells.	10g
	OP: 400/520 TP: 800/520	Tris	0-10μM	3.2 nM	1 s	Determination of $O_2^{\bullet-}$ in Tris Buffer, Living Cells, and mouse tumor model.	10f
	485/515	DMSO/ HEPES 1:1	-	1.0 pM	10 min	Not Mentioned	10i
	OP: 491/515 TP: 800/515	Tris	0.01-20μM	2.3 nM	1s	Determination of $O_2^{\bullet-}$ in Tris Buffer, Living Cells, and Mouse.	10b

	310/460	DMSO / HEPES 1:1	-	3.0 mM	10 min	Not Mentioned	10h
	310/460	DMSO / HEPES 1:1	-	63.8 μM	10 min		
	504/514	ACN/ H2O 7:3	6.67-100μM	12.9 μM	30 min	Determination of $O_2^{\bullet-}$ in ACN/H_2O and Living Cells	10c
	490/530	DMSO/ PBS 1/9	0-8μM	4.6 pM	5 min	Determination of $O_2^{\bullet-}$ in PBS Buffer and Living Cells	10j
	485/559	DMSO / HEPES 1:9	0.00503-3.33 μM	1.68 nM	10 min	Determination of $O_2^{\bullet-}$ in HEPES Buffer and Living Cells	10d
	602/662	DMSO / HEPES 1:9	0-0.5 μM	0.1 nM	5 min	Determination of $O_2^{\bullet-}$ in HEPES Buffer and Living Cells	10k
	675/704	DMSO / PBS 1:19	0-7.5μM	9.9 nM	10 min	Determination of $O_2^{\bullet-}$ in HEPES Buffer, Living Cells, Mouse, and Zebrafish.	**This work**

1. Materials, Instrumentation and Cell celture.

Materials Diphenylphosphinyl chloride ($Ph_2P(O)Cl$) was purchased from J&K (Beijing, China). GSH were purchased from Sangon Biotech. Co., LTD. (Shanghai, China). Xanthine oxidase (XO), xanthine (X), 4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron), superoxide dismutase (SOD), 1,4-hydroquinone (HQ), 3-morpholinosydnonimine hydrochloride (SIN-1), 3-(aminopropyl)-1-hydroxy-3-isopropyl-2-oxo-1-triazene (NOC-5), and vitamine C (VC) were purchased from Yuanye Biotech. Co., LTD. (Shanghai, China), Tert-butyl hydroperoxide (^{t}BuOOH, 70% aqueous solution), sodium hypochlorite (NaOCl, 5% aqueous solution), Hydrogen peroxide (H_2O_2, 30% aqueous solution), 2-methoxyestradiol (2-ME), and KO_2 were purchased from Aladdin (Shanghai, China). Ultra-pure water was produced from the ALH-6000-U (Aquapro International Company, USA) purification system. HPLC-grade acetonitrile (ACN) was from Dima Technology (RichmondHill, USA). Anhydrous dichloromethane (CH_2Cl_2) was pretreated with CaH_2 and fractional distilled before use. All other chemicals were obtained from qualified reagent suppliers with analytical reagent grade.

Instrumentation Fluorescence spectra were measured by a Fluorescence spectrometer (RF-5301pc, Japan) with a Xenon lamp and 1.0-cm quartz cells at the slits of 5/5 nm. The fluorescence quantum yields were determined on Fluorescence spectrometer FLSP920 (Edinburgh Instruments Ltd., U.K). Absorption spectra were measured on a UV-visible spectrophotometer (TU-1810, China). The mass spectrum was obtained by Bruker Daltonics APEX II 47e FT-ICR high resolution TOF MS system (America) and Bruker micrOTOF II system (America). NMR spectra were

determined by 400 MHz using a JEOL NMR instruments (Japan). All ^{1}H NMR chemical shifts (δ) are reported relative to residual $CHCl_3$ (δ = 7.27 ppm), and all ^{13}C NMR chemical shifts (δ) are reported relative to $CHCl_3$ (δ = 77.00 ppm). The pH values were measured using a digital pH-meter (PHSJ-3F, Leici, Shanghai, China). The fluorescence images of cells and zebrafish were taken using a confocal laser scanning microscope (TCS SP5, Leica, Germany) with an oil lens (×40) and a dry lens (×5), respectively. Mice imaging was performed with an IVIS Spectrum (Carestream Health, Canada) in epifluorescence mode equipped with 620 and 720 nm filters for excitation and emission, respectively. Measurements of the fluorescence signal were made with Molecular Imaging Software 5.0.6.20.

Sample preparation The stock solution of **CyR** was prepared at 1.0 mM in dimethyl sulfoxide (DMSO). Solutions of XO (1.0 U/mL), SOD (1000 U/mL), GSH (1.0 mM), H_2O_2 (1.0 mM), NaClO (1.0 mM), ^{t}BuOOH (1.0 mM), $FeSO_4$ (1.0 mM), SIN-1 (1.0 mM), VC (1.0 mM), and HQ (1.0 mM) were prepared with H_2O. NOC-5 was prepared as a solution (1.0 mM) in aqueous NaOH (10.0 mM). 2-ME (1.0 mM) and KO_2 were used as a solution (1.0 mM) in DMSO. The hydroxyl radical was produced by treatment of H_2O_2 (20 μM) with Fe^{2+} (200 μM). Single oxygen ($^{1}O_2$) was obtained by addition NaOCl (50 μM) to H_2O_2 (50 μM). Peroxynitrite and nitric oxide were gennerated by using 3-morpholinosydnonimine hydrochloride (SIN-1) and 3-(aminopropyl)-1-hydroxy-3-isopropyl-2-oxo-1-triazene (NOC-5), respectively.

General Procedure for Spectra Measurement Different concentrations of xanthine plus xanthine oxidase or KO_2 were added to PBS buffer (3.8 mL, 10 mM)

and **CyR** (20.0 μL, 0.1 mM) in a 5.0 mL centrifugal tube, and the mixture was added the corresponding volume of DMSO until 4.0 mL, which containing 5% DMSO. The resulting solution was equilibrated then laid aside at 25 ℃ for 10 min before measurement. The fluorescence spectrum was recorded with the excitation and emission wavelengths at 675/704 nm.

Cell Culture and Fluorescence Imaging. *HepG2* cells, which were obtained from the Institute of Chinese Medical Sciences of University of Macau (Macao, China), were grown in Dulbecco's Modified Eagle Medium (DMEM) supplemented with heat-inactivated fetal bovine serum (10%), penicillin (100 U/mL), and streptomycin (100 U/mL) at 37 °C in a 95% humidity atmosphere under 5% CO_2 environment. The *HepG2* cells were treated with **CyR** (5 μM) for 15 min at 37 °C. After being washed with Dulbecco's phosphate-buffered saline (DPBS) twice to remove free probe **CyR**, the cells were excited by a soild state laser (638 nm, 20 mW) and imaged by using a confocal laser scanning microscope (TCS SP5, Leica, Germany) at 690−750 nm. Two control experiments were performed. In the first control experiment, the cells were pretreated first with Tiron (200 μM) for 20 min at 37 °C, followed by washing with DPBS twice. Then they were incubated with **CyR** (5 μM) for another 15 min. In the second control experiment, the cells were pretreated with Tiron (200 μM) for 20 min at 37 ℃ and washed with DPBS twice. After that, they were treated with 2-ME (100 μM) for 30 min. and then **CyR** (5 μM) for 15 min. All the cells in the control experiments were washed with DPBS twice before imaging.

Cytotoxicity Assay The cytotoxic effect of **CyR** was determined by MTT (3-(4, 5-dimethyl-2-thiazolyl)-2, 5-diphenyl-2-H-tetrazolium bromide) assays.[49] *HepG2* cells (1×10^4 cells/well) were placed in a flatbottom 96-well plate in 100 μL culture medium and incubated in 5% CO_2 at 37 °C for 4 h incubation. The cells were incubated for 24 h upon different concentrations **CyR** of 0, 2.5, 5.0, 10.0, 20.0, 40.0, and 60.0 μM, respectively. MTT solution (5.0 mg/mL, HEPES) was then added into each well (10 μL/well, 0.5 mg/mL) and the residual MTT solution was removed after 4 h, and then 100 μL of DMSO was added to each well to dissolve the formazan crystals. After shaking for 10 min, the absorbance values of the wells were recorded using a microplate reader at 490 nm. The cytotoxic effect (VR) of **CyR** was assessed using the following equation: $VR = A/A_0 \times 100\%$, where A and A_0 are the absorbance of the experimental group and control group, respectively. The assays were performed in twelve sets for each concentration.

***In Vivo* Imaging.** Kunming mice (KM, female, 7-8 weeks old) were obtained from GanSu University of Chinese Medicine. All animal experiments were performed in accordance with the guidelines issued by The Ethical Committee of GanSu University of Chinese Medicine. Eight kunming mice were divided into four group, the first group was untreated as a control group; The second group was given an inyraperitoneal (i.p.) injection of saline (400 μL); The third group was given an i.p. injection of Tiron (400 μL, 100 μM in saline); The last group was given an i.p. injection of LPS (0.5 mg in 400 μL). Animals were anesthetized by i.p. injection of chloral hydrate (0.1 mL, 10% in saline) and abdominal fur was removed using a razor.

The saline, Tiron, and LPS treated mice were injected i.p. with **CyR** (25 μL, 10 μM in PBS buffer) after 6h. The mice were imaged as quadruplets, one from each group, at the same time after **CyR** injection (20 min after **CyR** injection), using an IVIS Spectrum (Carestream Health, Canada) in fluorescence mode equipped with 620 and 720 nm filters for excitation and emission, respectively. Photographs were taken using a fixed exposure time.

For liver imaging, the mice were euthanized, the livers were dissected and directly incubated with or without lipopolysaccharides (LPS, 1 mg/mL in saline) for 6h, then washed with PBS twice for 2 min. After that, the livers were dipped into **CyR** (10 μM in PBS buffer) for 20 min, then washed with PBS twice to remove free **CyR**. The treated or untreated (control) liver was mounted on a glass slide and then imaged using an IVIS Spectrum with the same conditions as that for *in vivo* imaging.

Imaging in zebrafish. The wild-type Tuebingen (TU) strain of zebrafish, obtained from the Institute of Chinese Medical Sciences of University of Macau (Macao, China), was used in current study. Zebrafish embryos were generated by natural pair-wise mating and raised in standard embryo medium at 28.5 °C. Three days post-fertilization (3dpf) embryos were collected and then divided into four groups. The first group receiving with 0.2 % DMSO was served as a vehicle control. The second group was incubated with a medium solution containing 5 μM **CyR** for 15 min, and then washed with phosphate-buffered saline (PBS) solution three times to remove free probe **CyR**. The third group was pretreated with Tiron (200 μM) for 20 min, followed by washing with PBS for three times. Then embryos were incubated

with **CyR** (5 μM) for another 15 min and washed with PBS. The last group was pretreated with Tiron (200 μM) for 20 min and washed with PBS three times. After that, it was treated with 2-ME (100 μM) for 30 min, and then **CyR** (5 μM) for 15 min. All the zebrafishes were washed with PBS for three times to remove free probe **CyR** and immobilized by methyl cellulose mounting (6%, wt/vol) in the center of a 35-mm glass-bottom dish before imaging operation. Photographs were taken imaged by a confocal laser scanning microscope (TCS SP5, Leica, Germany) using fixed imaging parameters. For probe imaging, the zebrafish was excited by a soild state laser (638 nm, 20 mW) and captured at 690−750 nm.

Synthesis.

Compound **1** was prepared according to the literatures[S1].

Synthesis of **CyOH** To a stirred solution of resorcinol (660 mg, 6.0 mmol) in CH_3CN (40 mL) was added K_2CO_3 (830 mg, 6.0 mmol) at room temperature under nitrogen atmosphere and the resulting mixture was stirred for 30 min. Then, a solution of compound **1** (1.83 g, 3.0 mmol) in CH_3CN (25 mL) was added to the above mixture via a syringe, and the reaction mixture was heated at 50 °C for 5 h. Eventually the solvent was evaporated under reduced pressure, and the crude product was purified by neutral aluminium oxide column chromatography using CH_2Cl_2/ 0-20% methanol as eluent to afford desired products **CyOH** as a blue-green solid (1.21 g, yield 79%). mp 189-191 ^oC; IR (film): ν_{max} = 3429, 2924, 1629, 1580, 1492, 1439, 1361, 1213, 1292, 1258, 1219, 1191, 1143, 1126, 1062, 1030, 978, 913, 804, 727, 563

[S1] Zhang, J.; Yu, B.; Ning, L.; Zhu, X.; Wang, J.; Chen, Z.; Liu, X.; Yao, X.; Zhang, X.; Zhang, H. *Eur. J. Org. Chem.* 2015, **2015**, 1711-1718.

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 13.2 Hz, 1H), 7.31 (s, 1H), 7.28 (s, 1H), 7.26 (s, 1H), 7.20 (d, *J* = 9.2 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.74 (dd, *J* = 1.9, 9.2 Hz, 1H), 6.52 (s, 1H), 5.55 (d, *J* = 13.6 Hz, 1H), 3.33 (s, 3H), 2.66 (t, *J* = 5.8 Hz, 2H), 2.62 (d, *J* = 6.2 Hz, 2H), 1.89 (t, *J* = 6.0 Hz, 2H), 1.66 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 159.6, 159.1, 143.9, 140.0, 139.5, 131.7, 129.8, 128.1, 127.9, 122.0, 121.9, 116.8, 116.4, 116.0, 107.6, 103.6, 94.1, 47.2, 30.0, 29.7, 28.6, 27.9, 24.5, 21.4 ppm; HRMS (ESI) Calcd. for $[C_{26}H_{26}INO_2\text{-}I^{-}]$: 384.1958, found: 384.1965.

Synthesis of **CyR** To a stirred solution of **CyOH** (102.2 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added triethylamine (Et_3N, 56.0 μL, 0.4 mmol, 2.0 equiv) and diphenylphosphinyl chloride (46.0 μL, 0.24 mmol, 1.2 equiv) at 25 °C. After 10 min, the reaction mixture was concentrated under reduced pressure to give crude solid, which was purified by neutral aluminium oxide column chromatography using CH_2Cl_2/ 0-10% methanol as eluent to afford desired products. Yield: 119 mg (84%).

CyR: mp 146-148 °C; IR (film): ν_{max} = 3402, 3047, 2977, 2925, 2850, 2622, 2497, 1618, 1575, 1536, 1503, 1459, 1439, 1411, 1398, 1365, 1312, 1257, 1231, 1187, 1173, 1126, 1109, 1058, 1039, 1019, 995, 974, 901, 800, 723, 635, 587, 353 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 15.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 12.7 Hz, 4H), 7.58 (t, *J* = 7.5 Hz, 3H), 7.54–7.46 (m, 7H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 6.6 Hz, 1H), 7.05 (s, 1H), 7.02 (dt, *J* = 1.08, 8.5 Hz, 1H), 6.74 (d, *J* = 15.1 Hz, 1H), 4.15 (s, 3H), 2.78 (t, *J* = 5.7 Hz, 2H), 2.67 (t, *J* = 5.7 Hz, 2H), 1.88 (t, *J* = 5.9 Hz, 2H), 1.76 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 153.3, 153.1, 153.0, 146.3,

142.1, 141.9, 133.1, 131.9(2C), 131.8(2C), 131.5, 131.1, 130.8, 129.8, 129.5, 129.4, 129.0(2C), 128.9(2C), 128.6, 127.9, 122.3, 118.9, 118.2, 115.7, 113.5, 108.6, 106.7, 50.9, 29.8, 29.5, 28.1(2C), 24.4, 20.2 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.7 ppm; HRMS (ESI, m/z) Calcd. for [$C_{38}H_{35}NO_3P–I^-$]: 584.2349, found: 584.2353.

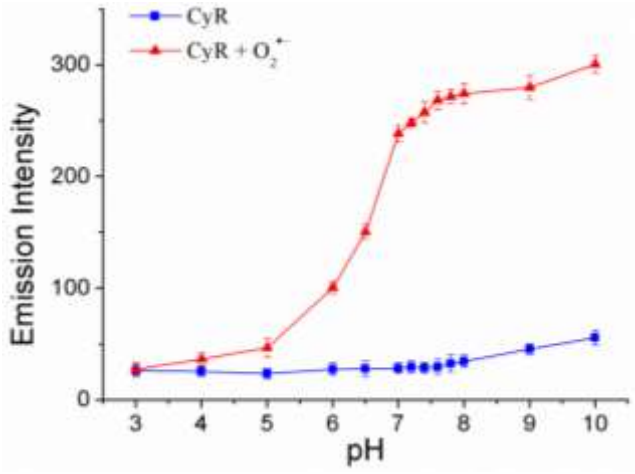


Figure S1. Fluorescence intensity of **CyR** (■) and **CyR** (5 μM) with $O_2^{\bullet-}$ (20 μM, ▲) in 10 min at various pH values, respectively. The data were reported as the mean ± standard deviation of triplicate experiments.

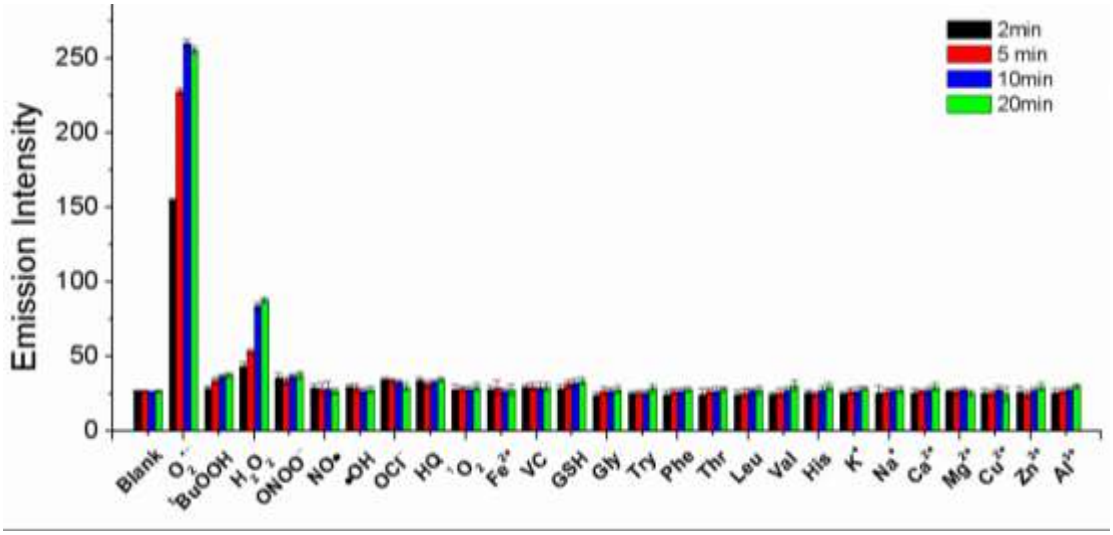


Figure S2. Fluorescence responses of **CyR** (5 μM, in 10 mM PBS, pH 7.4) to various ROS, amino acids, metal ions, and reductants. Data shown are for 20 μM $O_2^{\bullet-}$, H_2O_2, and ^{t}BuOOH, and 50 μM others. All data were obtained after incubation at 25 °C. Collected emission was integrated at 704 nm (λ_{ex} = 675 nm), and bars in each group represent the relative fluorescence responses at 2, 5, 10, and 20 min (from left to right) after addition of the appropriate ROS or others. The data were

reported as the mean ± standard deviation of triplicate experiments.

Figure S3. The color change of **CyR** (5 μM) upon addition of $O_2^{\bullet-}$ in PBS (10 mM, pH = 7.4) containing 5% DMSO. Each sample was recorded at 10 min after the addition of XA/XO (**1-10**: 0/0, 0.3/0.3, 1.0/1.0, 3.0/3.0, 8.0/8.0, 15.0/15.0, 20.0/20.0, 30.0/30.0, 45.0/45.0 μM/mU).

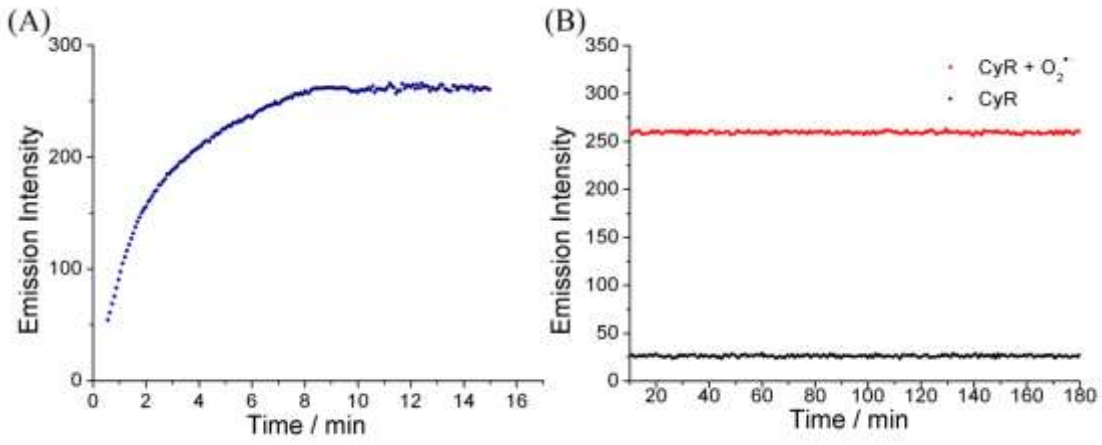


Figure S4. (A) Time-dependent fluorescence changes of **CyR** (5 μM) upon addition of $O_2^{\bullet-}$ (20 μM) in PBS (10 mM, pH 7.4) containing 5% DMSO. (B) Black line: 5 μM **CyR**. Red line: the system of 5 μM **CyR** and 20 μM $O_2^{\bullet-}$, λ_{ex} = 675 nm, λ_{em} = 704 nm.

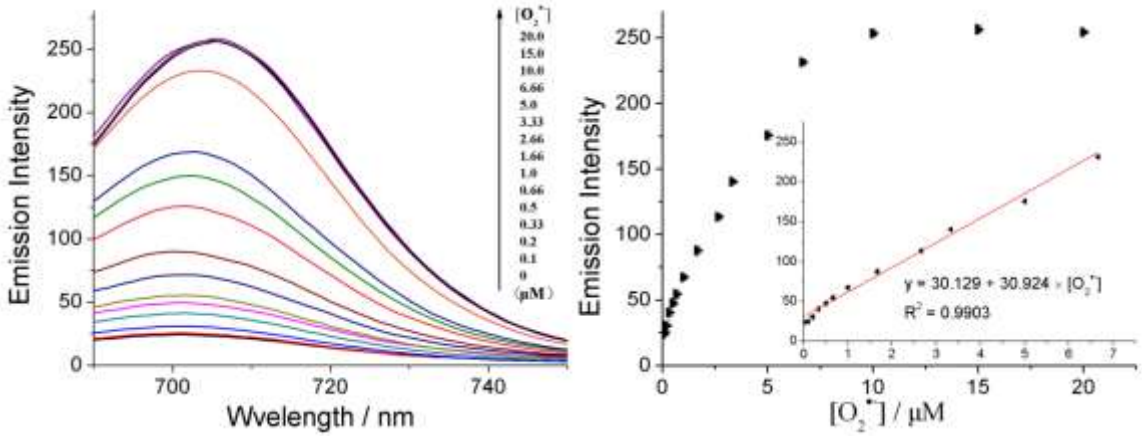


Figure S5. Emission spectra (λ_{ex} = 675 nm) of **CyR** (5 μM) in the presence of various concentrations of $O_2^{\bullet-}$ (0–20.0 μM) at 25 °C in PBS buffer (10 mM, pH 7.4). Spectra were obtained in 10 min after the addition of different concentrations X/XO (final concentration: 0/0, 0.3/0.3, 0.6/0.6, 1.0/1.0, 1.5/1.5, 2.0/2.0, 3.0/3.0, 5.0/5.0, 8.0/8.0, 10.0/10.0, 15.0/15.0, 20.0/20.0, 30.0/30.0, 45.0/45.0, 60.0/60.0 μM/mU) to the solution of **CyR**.

HPLC was carried out using a C18 column (Hedera·ODS-2, 5 μm, 250 mm × 4.6mm) with a Varian 210 HPLC system. The mobile phase was a mixture of acetonitrile and ammonium acetate buffer (25 mM, pH = 6.0) (8:2, v/v). The flow rate was 1 mL/min and detection at 600 nm. The reaction solutions of **CyR** (5 μM) and KO_2 (2.5 μM, 10 μM) in PBS buffer (10 mM, pH = 7.4) was as the samples.

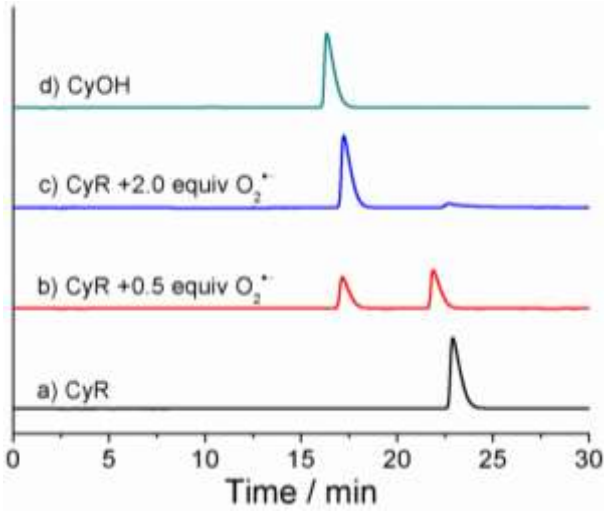


Figure S6. HPLC chromatograms of **CyR** (a), the reaction solutions of **CyR** with different amount of $O_2^{\bullet-}$ (b, c), and **CyOH** (d). Conditions: incubation for 10 min at room temperature in PBS (10 mM, pH = 7.4) containing 5% DMSO.

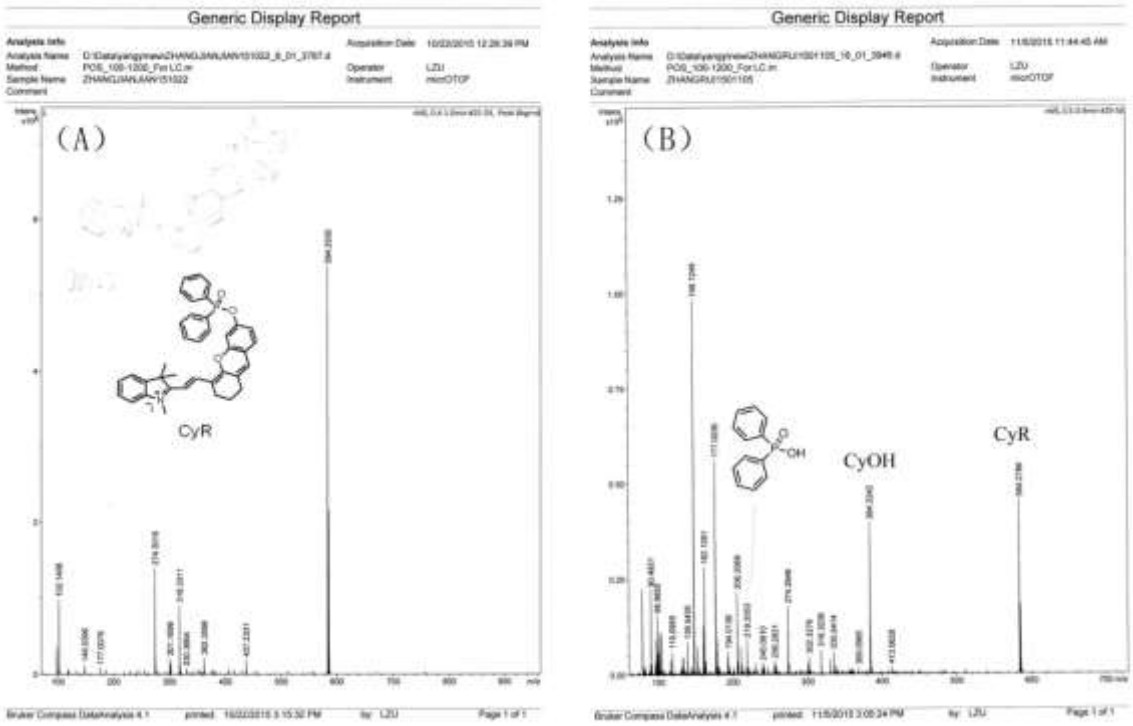


Figure S7. The micrOTOF mass spectra of **CyR** treating with KO_2. (A) **CyR**; (B) **CyR** + 1.0 equiv KO_2**.**

To better understand the mechanism of NIR fluorescence from the hemicyanine chromophore, the structures of **CyR** and **CyOH** were optimized and their frontier molecular orbital profiles were optimized by the DFT calculations at the B3LYP/6-311G level in a suite of Gaussian 09 programs. (Figure S8). The indolium moiety was substantially coplanar and conjugated with the 2,3-dihydro-1H-xanthene (DHX) core in **CyOH**, which resulted in a fluorescence emission. In addition, the π electrons of **CyOH** were mainly located on the whole π-conjugated DHX-indolium skeleton on both the HOMO and the LUMO. In addition, the π electrons on the HOMO of **CyR** were mainly located on the DHX-indolium skeleton, while on the LUMO of **CyR** were mainly situated in the diphenyl phosphinate group. The possible photoinduced electron transfer (PET) process in **CyR** was supported by the LUMO and HOMO levels. The electron transfer from the DHX-indolium skeleton (PET donor) to the diphenyl phosphinate group (PET acceptor) quenched the fluorescence of the primordial fluorophore. However, the PET process was prevented in **CyOH**,

and the fluorescence was “turn on”. The energy gaps (HOMO − LUMO) of **CyR** and **CyOH** were calculated as 1.38 and 1.37 eV, respectively. From these results, the theory calculations are support the experimental results, which rationalize the PET process.

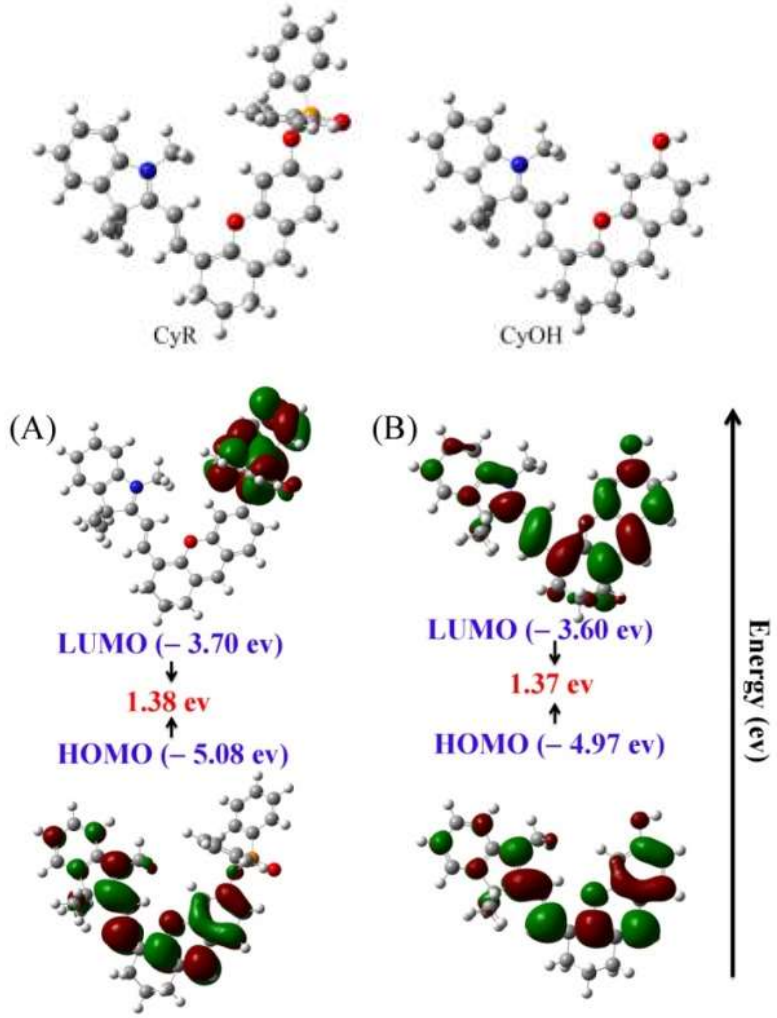


Figure S8. The optimized conformation of **CyR** and **CyOH** . In the ball-and-stick model, carbon, oxygen and nitrogen atoms are colored in gray, red and blue, respectively. Density functional theory (DFT) optimized structures and frontier molecular orbitals (MOs) of (A) **CyR** and (B) **CyOH**. Calculations were based on ground state geometry by DFT at the B3LYP/6-311G (d, p)/level using Gaussian 09.

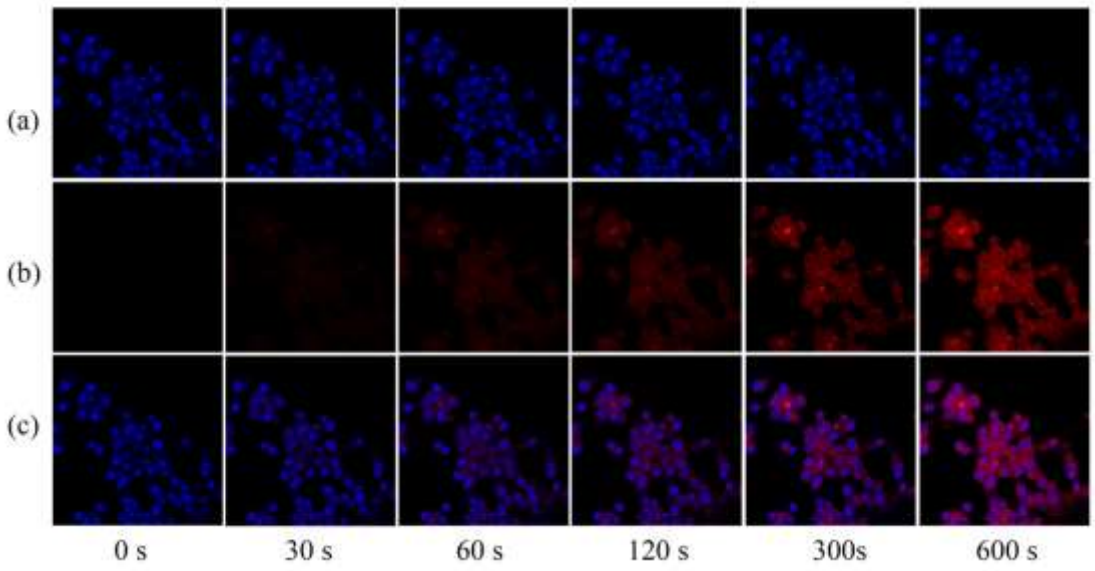


Figure S9. Confocal fluorescence images of Tiron-pretreated *HepG2* cells recorded at different time points after treated with **CyR** (5 μM), followed by stimulated with 2-ME (100 μM). (a) Fluorescence images for cells co-stained with 4′, 6-diamidino-2-phenylindole (DAPI) to identify cell nuclei (blue dots); (b) Fluorescence images from **CyR**; (c) Merge.

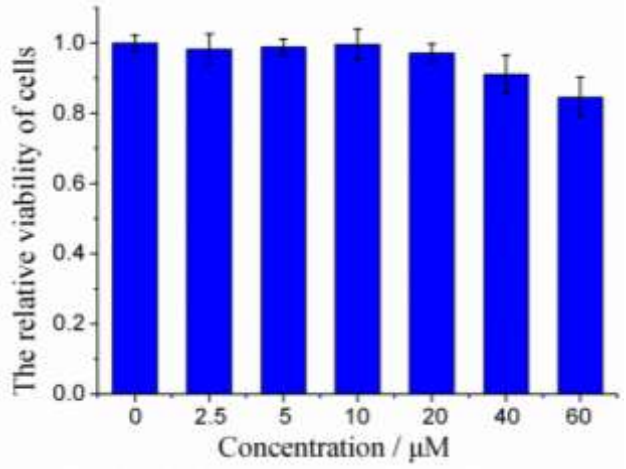


Figure S10. MTT assay for the relative viability of *HepG2* cells treated with various concentrations of **CyR** for 24 h. Error bars represent the standard deviations of 12 trials.

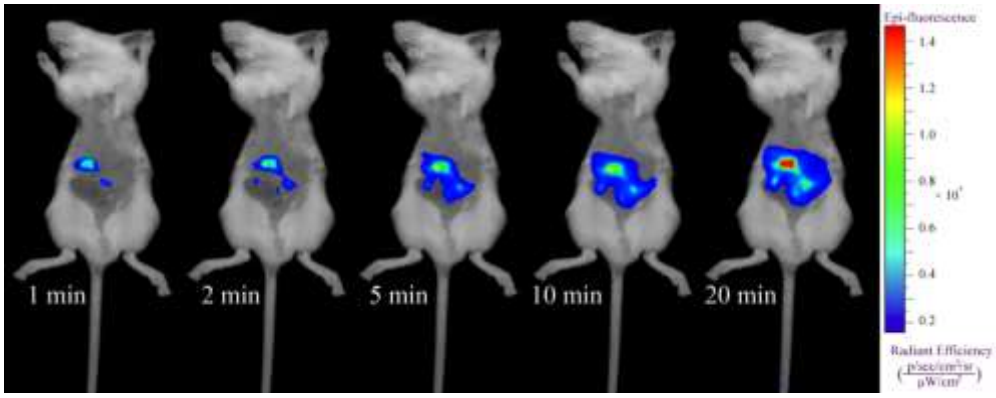


Figure 11. Representative fluorescence images (pseudocolor) of a Kunming mouse given an i.p. injection of LPS (0.5 mg in 400 μL saline), followed by i.p. injection of **CyR** (25 μL, 10 μM in PBS buffer) after 6 h. Images were taken after incubation for 1, 2, 5, 10, and 20 min, respectively.

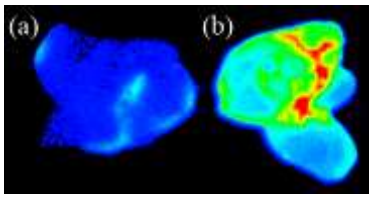


Figure S12. In vivo images of ROS production from the liver of mice with **CyR**. Fluorescence images of (a) liver from mouse only incubated with **CyR** (50 μM); (b) Liver from mouse incubated with **CyR** (50 μM) after being preincubated with LPS (1 mg in 400 μL saline) for 6 h. Each was imaged in 20 min after **CyR** incubated.

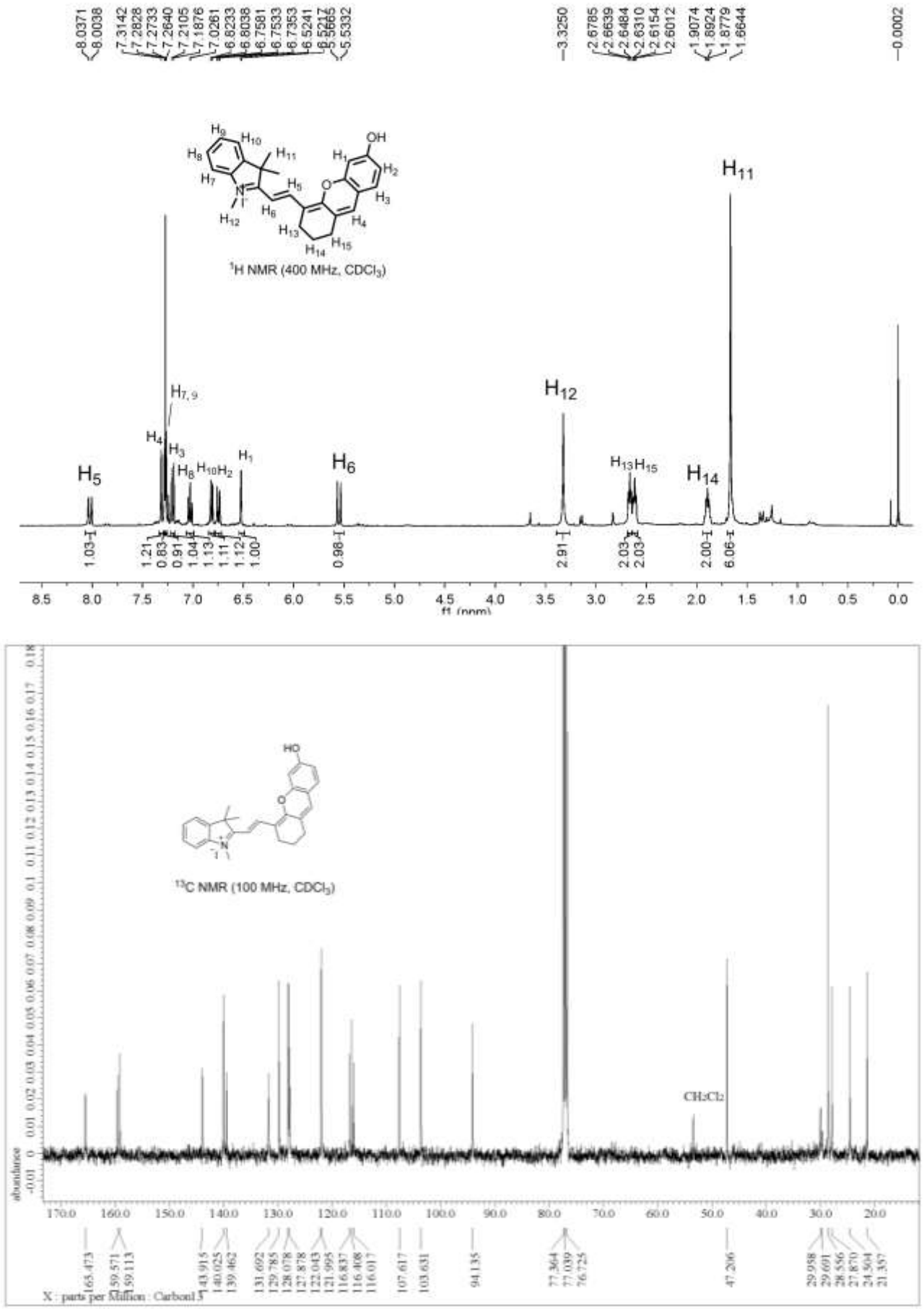
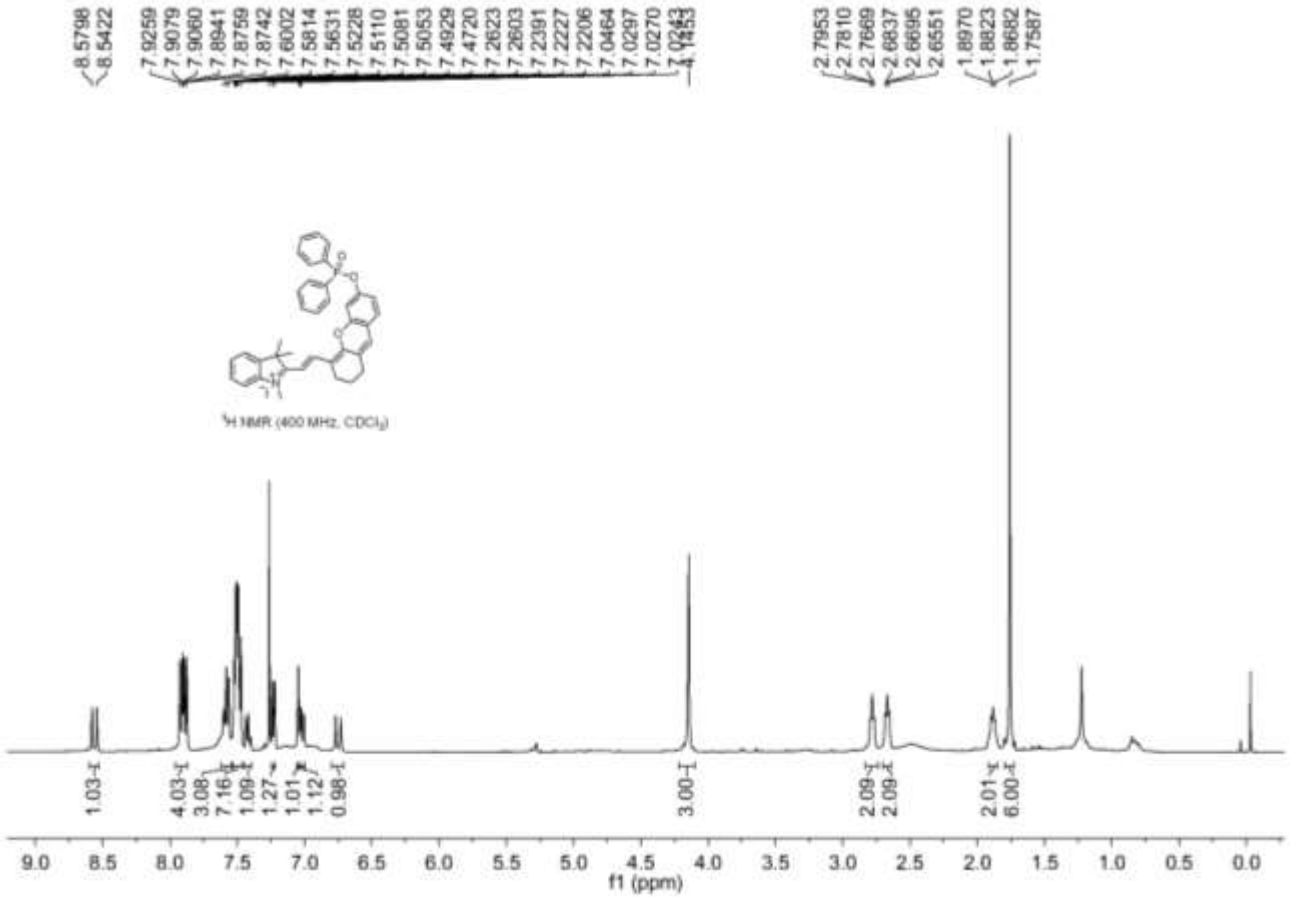
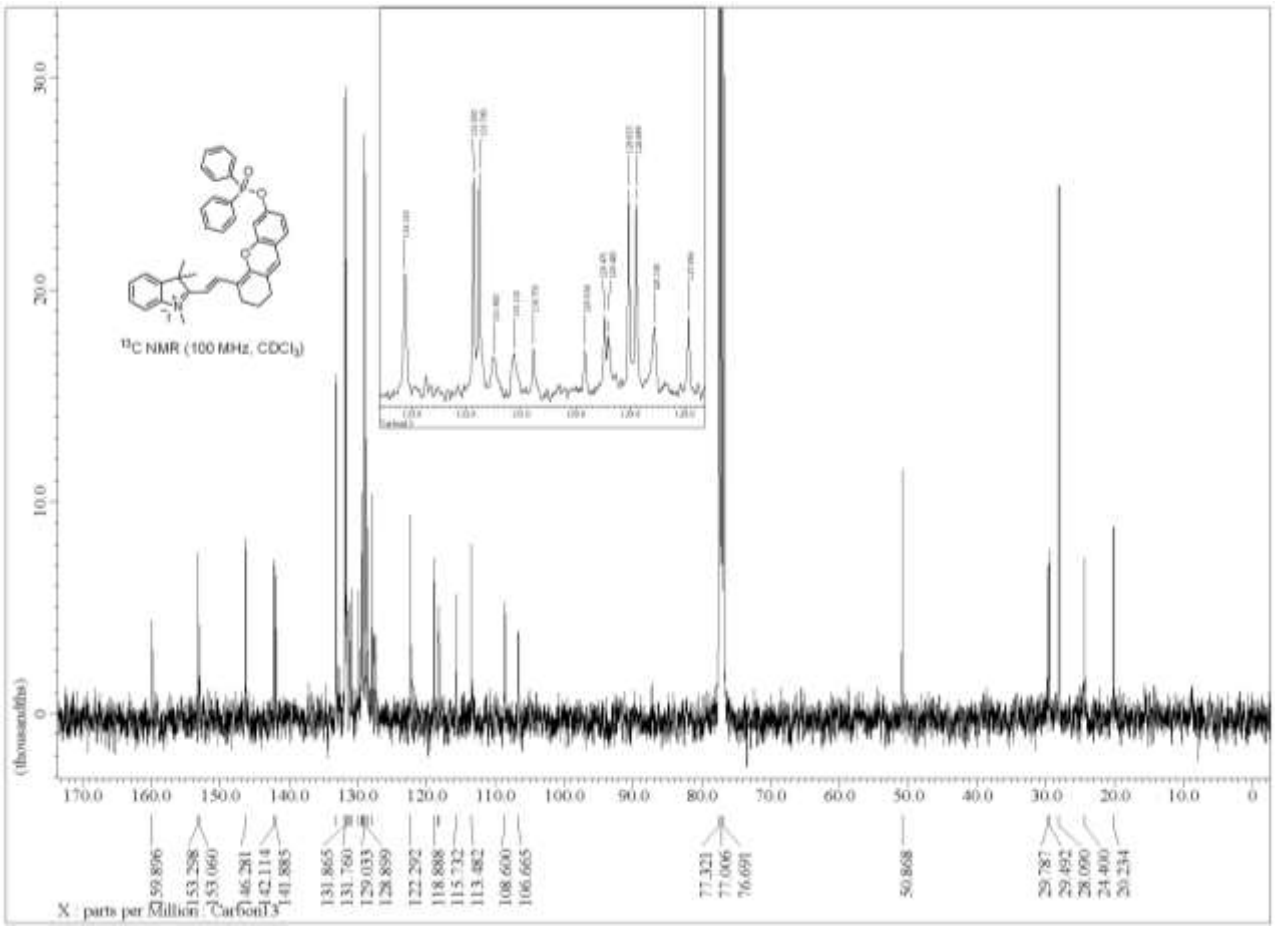


Figure S13. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra of **CyOH** in $CDCl_3$ at 25 °C.


8.5798
8.5422
7.9259
7.9079
7.9060
7.8941
7.8759
7.8742
7.6002
7.5814
7.5631
7.5228
7.5110
7.5081
7.5053
7.4929
7.4720
7.2623
7.2603
7.2391
7.2227
7.2206
7.0464
7.0297
7.0270
2.7953
2.7810
2.7669
2.6837
2.6695
2.6551
1.8970
1.8823
1.8682
1.7587
^{1}H NMR (400 MHz, CDCl$_3$)
1.03
4.03
3.08
7.16
1.09
1.27
1.01
1.12
0.98
3.00
2.09
2.09
2.01
6.00
f1 (ppm)


^{13}C NMR (100 MHz, CDCl$_3$)
(thousands)
X : parts per Million : Carbon13
159.896
153.298
153.060
146.281
142.114
141.885
131.865
131.760
129.033
128.859
122.292
118.888
115.732
113.482
108.600
106.665
77.321
77.006
76.691
50.868
29.787
29.492
28.090
24.490
20.254

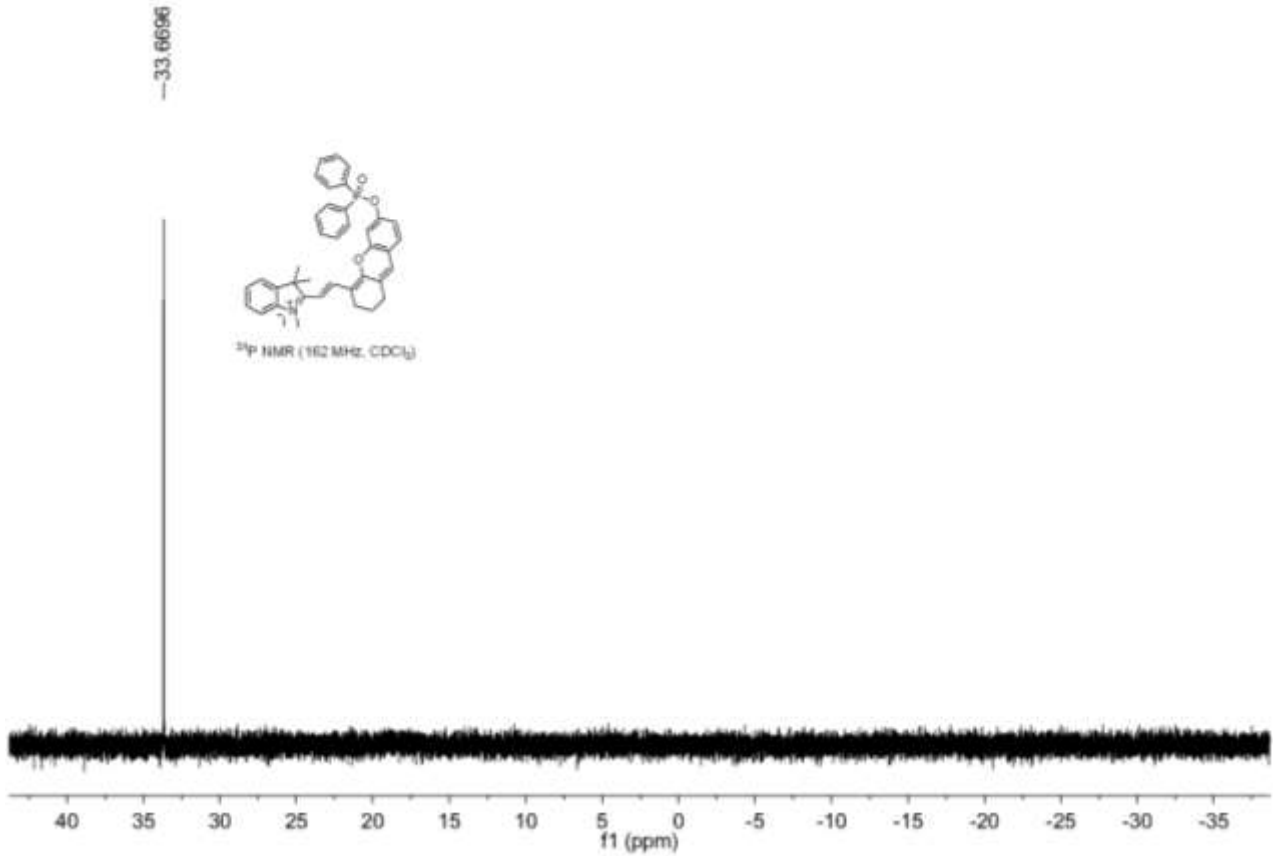
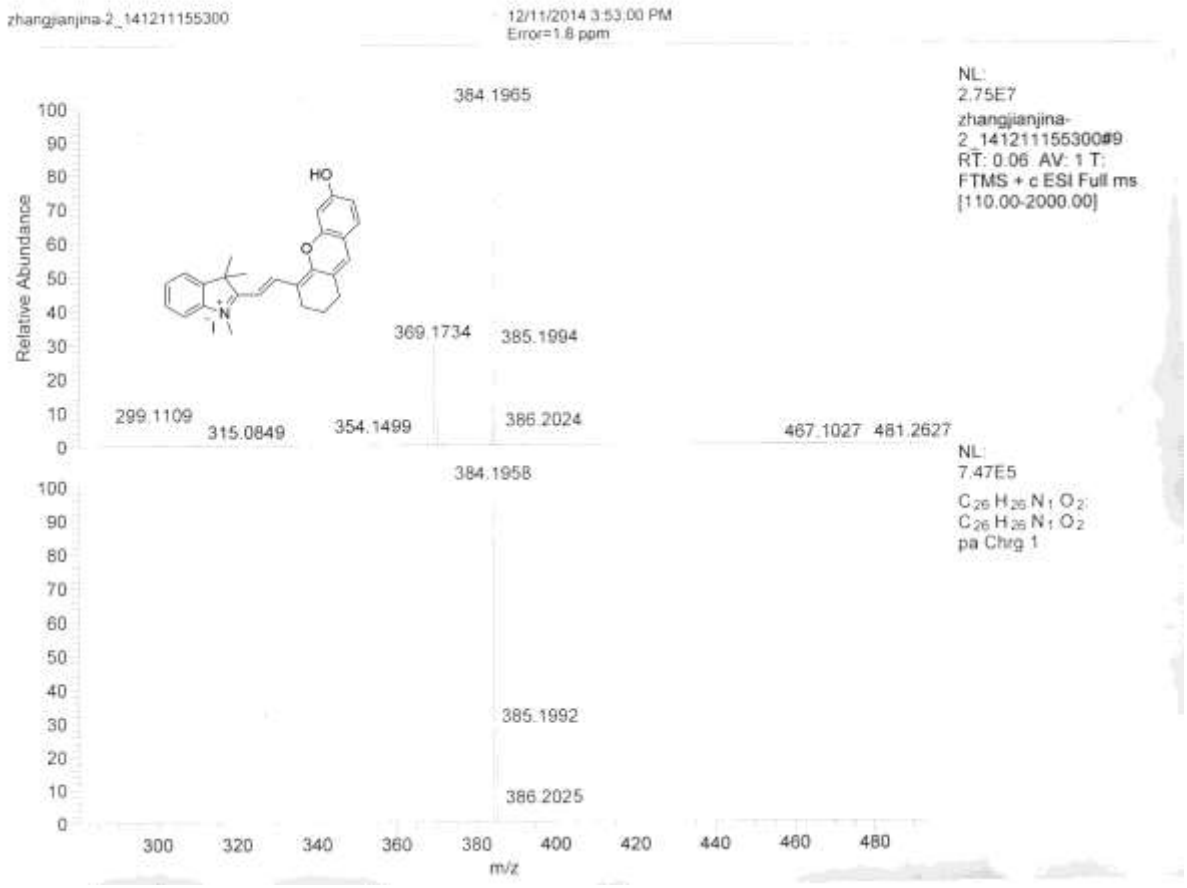


Figure S14. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) spectra of **CyR** in $CDCl_3$ at 25 ℃.



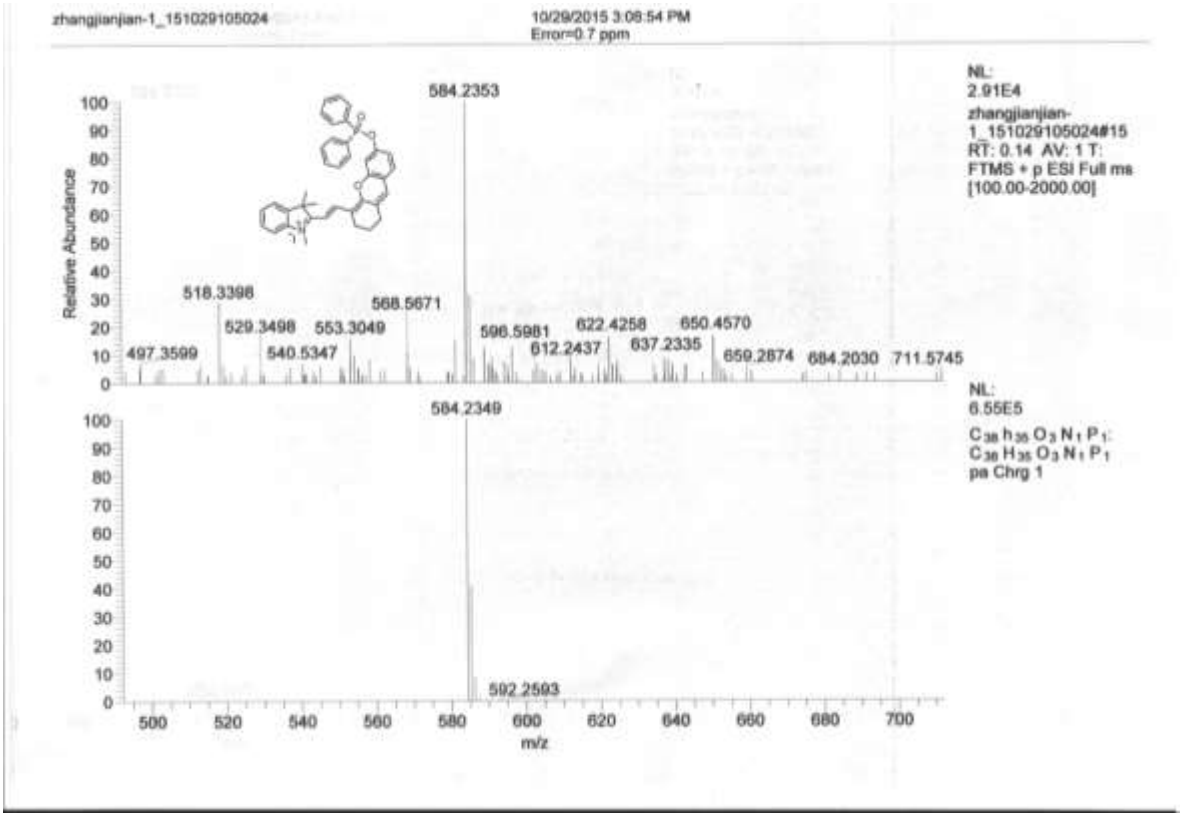
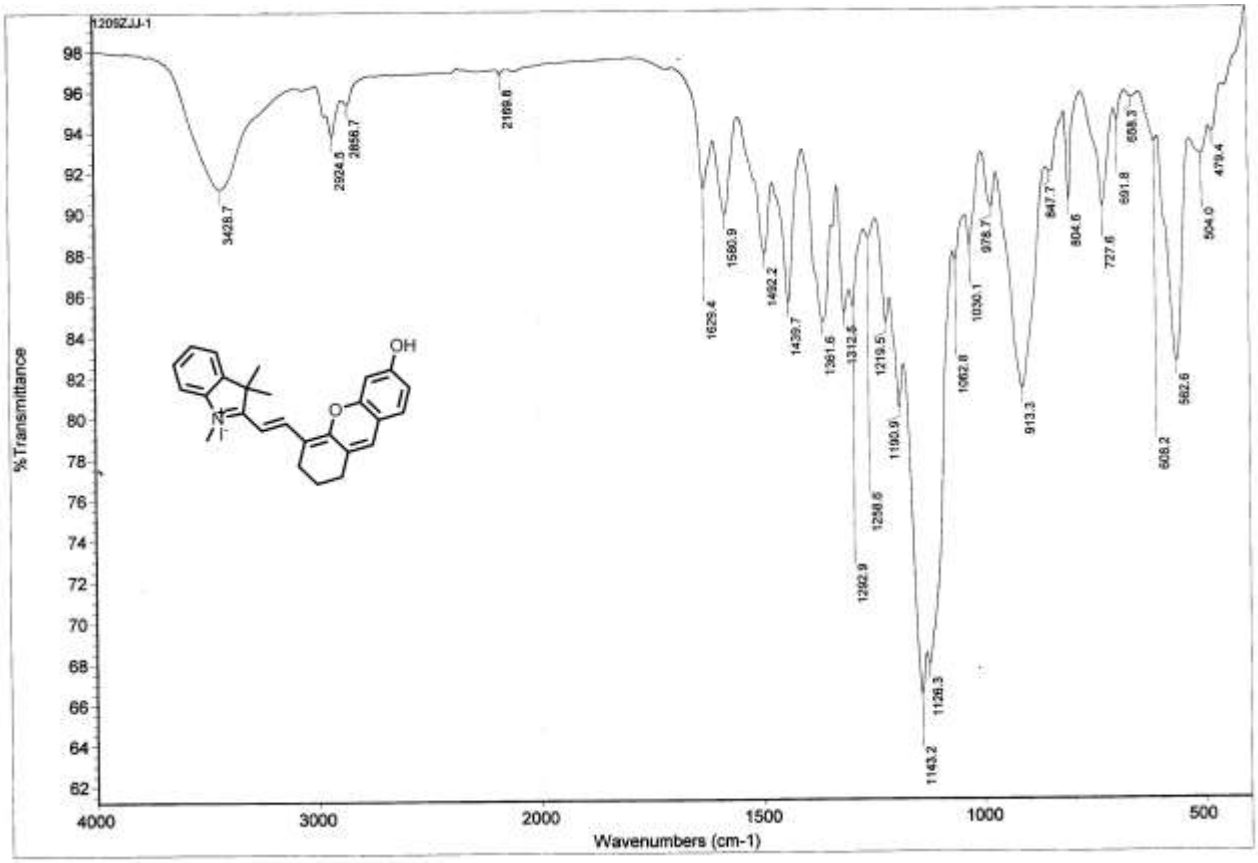


Figure S15 HRMS of **CyOH** and **CyR**.



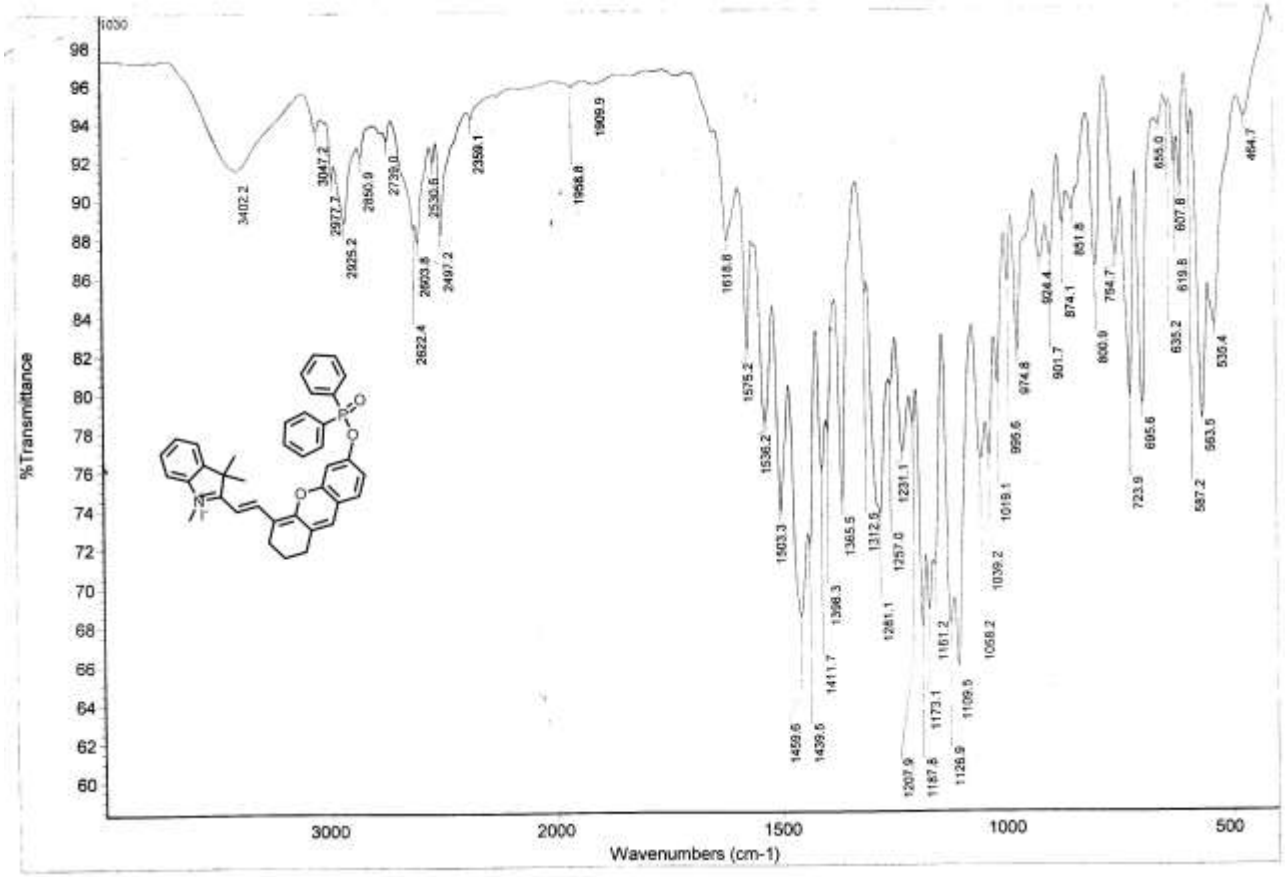


Figure S16 IR of **CyOH** and **CyR**.