Electronic Supplementary Information

Porous heterogeneous organic photocatalyst prepared by HIPE polymerization for oxidation of sulfides under visible light

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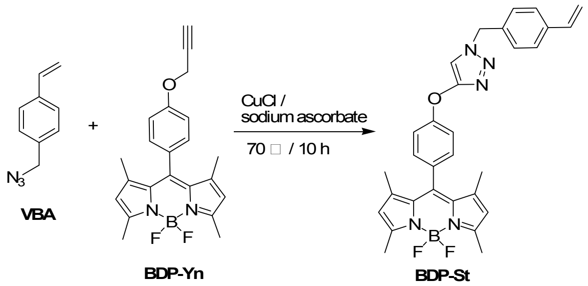
Contents

I. Materials and methods

All reagents were purchased from commercial sources and used without further treatment, unless indicated otherwise. Solvents: Petroleum ether (PE) used was the fraction boiling in the range 60–90 °C. Methanol was purified over magnesium and then distilled under vacuum. *N*,*N*-Dimethylformamide (DMF) and dichloromethane (DCM) were predried over calcium hydride and then distilled under vacuum. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, with TMS as internal standard at 25 °C on a Bruker AV 300M spectrometer. Matrix-Assisted Laser-Desorption-Ionization Time-of-flight (MALDI-ToF) mass spectra were obtained on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer in positive ionization mode with dithranol as a matrix. A JEOL JXA-840 scanning electron microscope was used to observe the morphology of the porous materials under an accelerating voltage of 15 kV. Fluorescence emission spectra were recorded on a LS-55 fluorophotometer. Varian Cary 500 UV-vis-NIR spectrophotometer equipped with an integration sphere was used to record the UV-vis DRS spectra. The sample median pore diameter and porosity were characterized by mercury porosimetry (Micromeritics Instrument Corporation, AutoPore IV 9500).

II. Synthesis of BDP-St



Scheme S1. Synthesis of BDP-St.

Synthesis of 4,4-difluoro-8-[4-O-[1-(4-vinylbenzyl)-4-methyl-1H-1,2,3-triazole]phenyl]-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BDP-St): In a 25 ml round bottomed flask were added BDP-Yn (756 mg, 2.0 mmol), VBA (334 mg, 2.1 mmol), sodium ascorbate (79 mg, 0.4 mmol, 0.2 equiv) and dissolved in dry DMF (10 mL). The solution was purged with argon for 15 min. To the mixture was then added CuCl (9.9 mg, 0.1 mmol, 0.05 equiv) and the reaction mixture was stirred under argon atmosphere at 70 °C for 10 h. After completion of the reaction, the reaction mixture was poured into saturated aqueous NaCl (50 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with water (3 × 20 mL), brine (20 mL), dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude product was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 2:1) to give **BDP-St** (963 mg, 92% yield) as a pink solid. ^{1}H NMR (300 MHz, $CDCl_3$) (Fig. S2): δ 7.56 (s, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 6.4 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.71 (dd, J_1 = 17.6 Hz, J_2 = 10.8 Hz, 1H), 5.97 (s, 2H), 5.77 (d, J = 17.5 Hz, 1H), 5.54 (s, 2H), 5.30 (d, J = 10.8 Hz, 1H), 5.22 (s, 2H), 2.54 (s, 6H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (Fig. S3): δ 158.59, 155.04 (2C), 143.73, 142.94, 141.46, 137.93, 135.70 (2C), 133.63, 131.53, 129.00 (2C), 128.17 (2C), 127.26, 126.66 (2C), 122.66 (2C), 120.98 (2C), 115.18 (2C), 114.80, 61.73, 53.68, 14.33 (4C); MALDI-TOF-MS m/z (Fig. S4): calcd for $C_{31}H_{30}BF_2N_5O$ [M]: 537.25, found 537.3, calcd for $C_{31}H_{30}BFN_5O$ [M-F]: 518.25, found 518.3.

III. Measurement of the optical properties of BDP-St

UV-vis absorption spectra were recorded on a UV-2450 spectrometer at 25 °C, and Fluorescence emission spectra were recorded on a LS-55 spectrometer at 25 °C (Fig. S1).

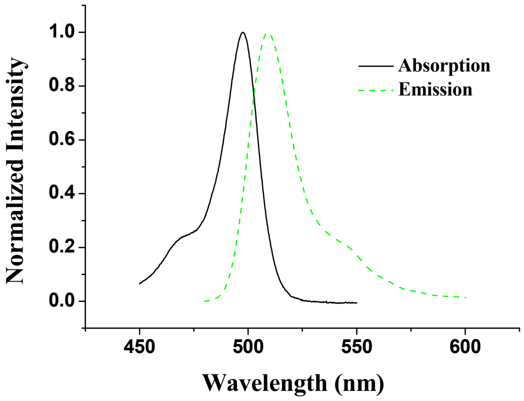


Fig. S1. Normalized absorption (left) and fluorescence emission (right, λ_{ex}= 470 nm) spectra of BDP-St in methanol.

Measurements for the extinction coefficients were performed according to the following protocol. Around 1 mg of dye was weighed using a digital scale (Δw = 0.01 mg), and dissolved into 100 mL of methanol. A number of further diluted solutions with different dye concentrations (10^{-7} to 10^{-6} M) were prepared from this stock solution. The absorption spectra of these diluted solutions were measured, and the absorbance (A) and the concentration (C) were plotted on a graph of A versus C to determine the extinction coefficient (from the gradient). This protocol was performed 5 times, and the average value of the extinction coefficient, the standard deviation (s.d.), and the coefficient of variance (C.V.) were calculated (Table S1).

Measurements of quantum yields were performed by following the method recommended by Horiba Jobin Yvon (see: http://www.jp.jobinyvon.horiba.com/product_j/spex/quantum_yields.pdf). A number of diluted solutions of different dye concentrations (A< 0.05, to prevent reabsorption) were prepared and the absorbance (A) and the integrated fluorescence intensity (F) at each concentration were recorded at 470 nm excitation wavelength. Quantum yield Φ was calculated using the following equation:

$$\Phi_S = \Phi_R \left(\frac{n_S}{n_R}\right)^2 \left(\frac{F_S}{F_R}\right)\left(\frac{A_R}{A_S}\right)$$

The subscripts R and S denote the reference dye and the sample, respectively. n is the refractive index of the solvent. The 1,3,5,7-tetramethyl-8-phenyl-4,4-difluoro- boradiazaindacene (Chart S1) was used as reference dye (Φ = 0.65 in metanol).[1]

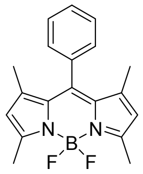


Chart S1. Chemical structure of the reference dye.

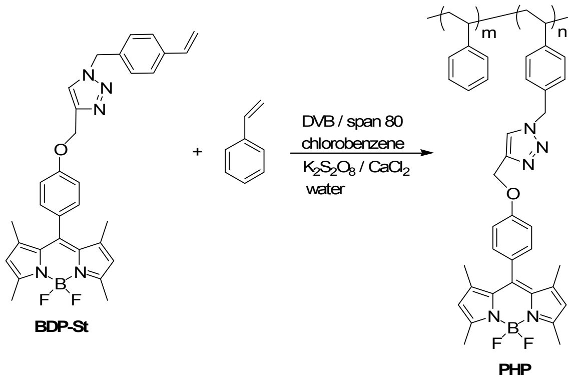
This protocol was performed 3 times, and the average value of the quantum yield, the standard deviation (s.d.), and the coefficient of variance (C.V.) were calculated.

Table S1. Values of extinction coefficients and quantum yields of BDP-St

Dye	ε^{c} ($M^{-1}cm^{-1}$)	C.V. (%)	n^{a}	Φ	C.V. (%)	n^{a}
BDP-St	65000 ± 2860	4.4	5	0.72 ± 0.03	4.2	3

[a] number of measurements

IV. Preparation of PHP by HIPE polymerization



Scheme S2. Synthesis of PHP.

Preparation of PHP: To prepare **PHP3** by HIPE polymerization, the following steps were performed: (with PHP3 as an example) (1) Preparation of the organic phase: BDP-St (0.09 g) was dissolved in chlorobenzene (4.8 mL) in a three-necked round bottomed flask equipped with a mechanical stirrer and a dropping funnel, followed by addition of styrene (4.8 mL), DVB (0.4 mL) and span 80 (3 mL). The solution was stirred at 400 rpm and purged with argon for 20 min at room temperature; (2) Preparation of the high internal phase emulsion: potassium persulfate (0.2 g) and calcium chloride (1.0 g) were dissolved in 90 mL water, which was purged with argon for 20 min. The volume ratio of the aqueous phase to organic phase was 9 : 1. The aqueous phase was placed in the dropping funnel and added dropwise to the organic phase. After complete addition of the of the $K_2S_2O_8$/$CaCl_2$/water solution, the emulsion was kept stirring for additional

5 min; (3) Polymerization of the emulsion: After stirring, the emulsion was immediately transferred into a polyethylene bottle, the neck of the bottle was covered with a polyethylene film to reduce evaporative losses. The bottle was placed in an oven at 60 °C for 24 h. (4) Washing the reaction product: After this period the polyethylene bottle was cut away from the reaction product. The product was then exhaustively extracted with hot ethanol to remove the water and residual organic compounds.[2] Finally, the product was dried under vacuum at room temperature to give **PHP3** as a yellow monolithic material.

V. Measurement of the optical properties of PHP

DRS spectra in the range of 200-800 nm were taken on a Varian Cary 500 UV-vis-NIR spectrophotometer equipped with an integration sphere at room temperature, using $BaSO_4$ as a reference (Fig. 1c in text). Solid fluorescence emission spectra were recorded on a LS-55 spectrometer at room tempreture.

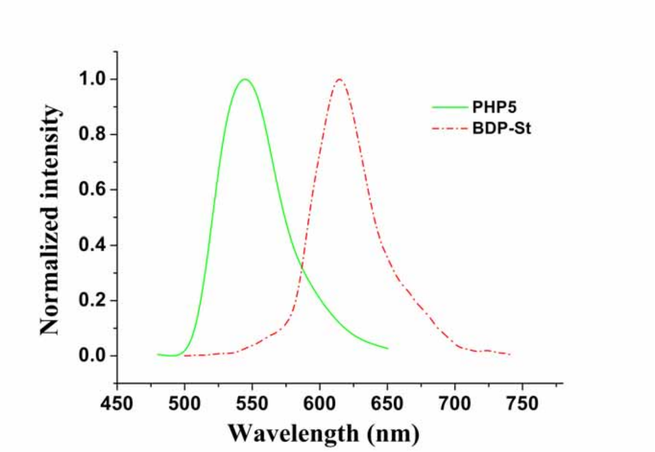
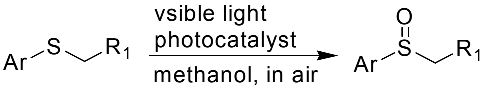


Fig. S2. Normalized fluorescence emission (λ_{ex}= 470 nm) spectra of PHP5 and BDP-St in solid state.

VI. Sulfide oxidation catalyzed by PHP



Scheme S3. Oxidation reaction of sulfidess.

Take oxidation of thioanisole as an example: To a flame-dried 10 mL vial equipped with a magnetic stir bar were added PHP5 (65.2 mg, containing BDP-St 10 μmol, 0.02 equiv) or BDP-St (1.3 mg, 2.5 μmol, 0.005 equiv) catalyst, thioanisole (62 μL, 0.5 mmol, 1.0 equiv), and methanol (2.0 mL). A 24 W household fluorescent light bulb with a highpass filter (λ = 395 nm) was used as the visible light source.[3] The reaction mixture was stirred at room temperature in air at a distance of *ca.* 5 cm from the lamp (the irradiance is about 17.5 W/m^2 for the distance). After the reaction was completed, the PHP5 was then removed by centrifugation and the supernatant was collected. ^{1}H NMR was taken of the reaction mixture, and the integrated area ratio between the ^{1}H NMR peaks of the substrate and product was used to calculate the conversion yields.[4]

Table S2. Control sulfides oxidation reactions[a]

entry	conditions	time (h)	conversion(%)[b]
1	No catalyst	60	0
2	No light	60	0
3	Under N_2 protection	60	4
4	The supernatant[c]	60	3

[a] Reactions were run in methanol with thioanisole as substrate.
[b] Conversion yields were determined by ^{1}H NMR.
[c] The supernatant of the PHP5 reaction mixture, which be used directly to the oxidation of another substrate without any other catalyst added.

VII. NMR and MS spectra

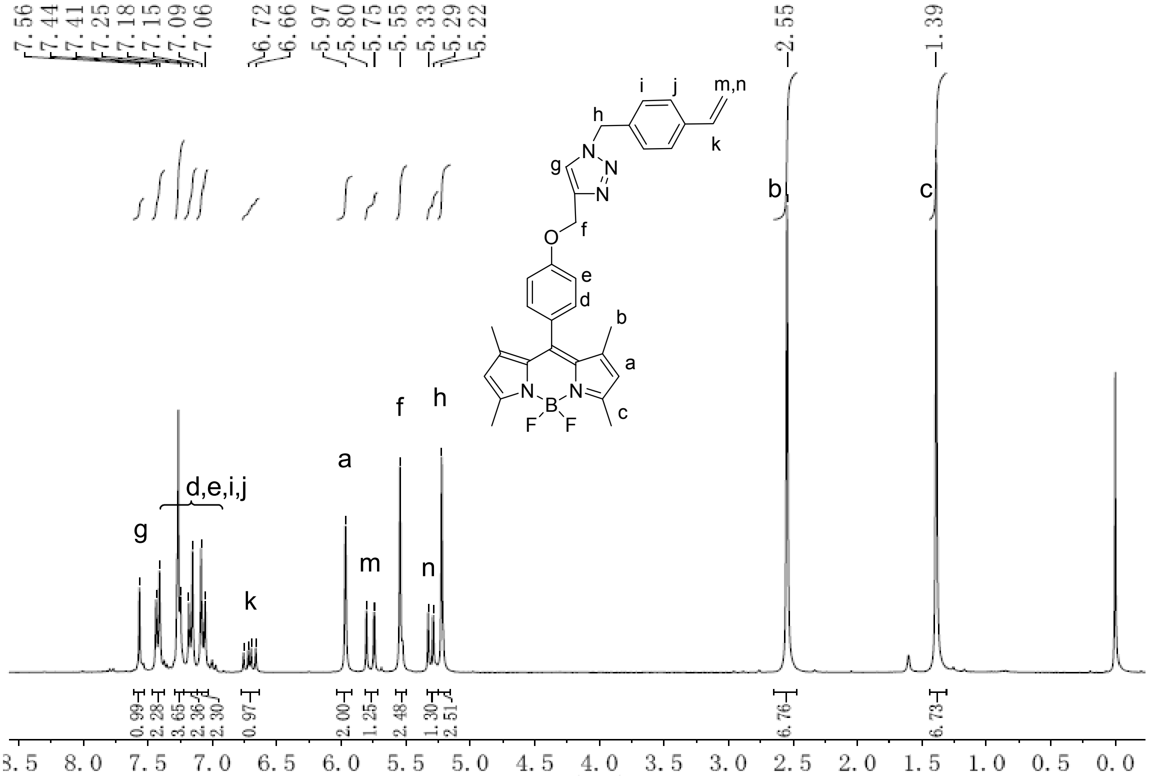


Fig. S3. ^{1}H NMR of BDP-St in $CDCl_3$.

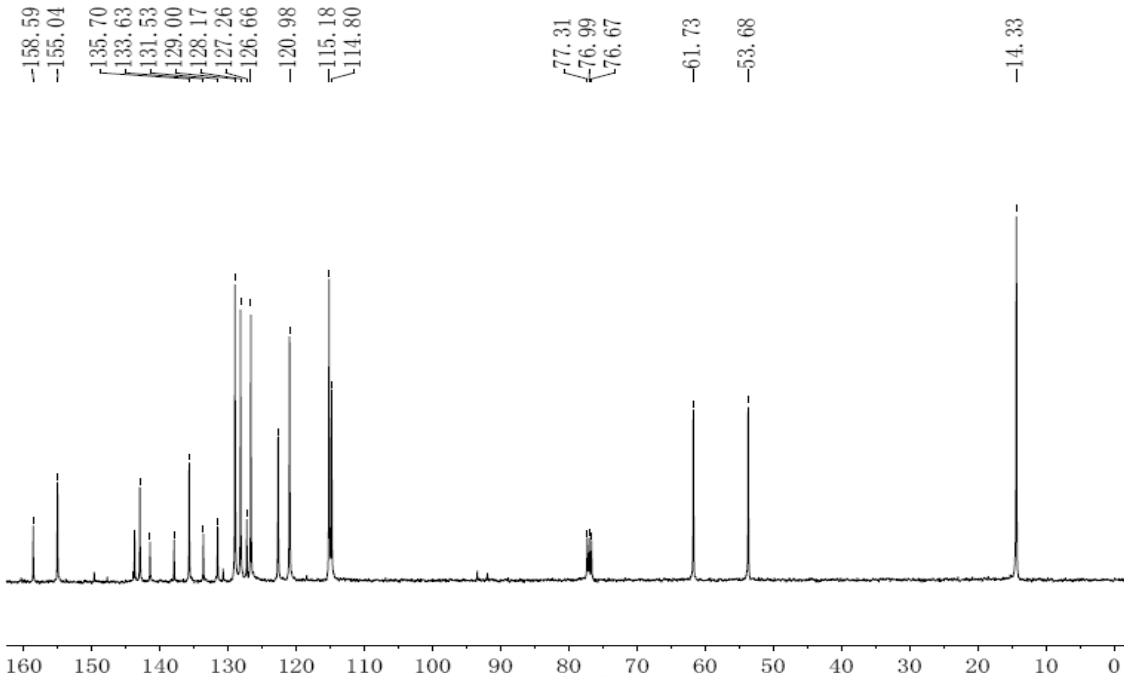


Fig. S4. ^{13}C NMR of BDP-St in $CDCl_3$.

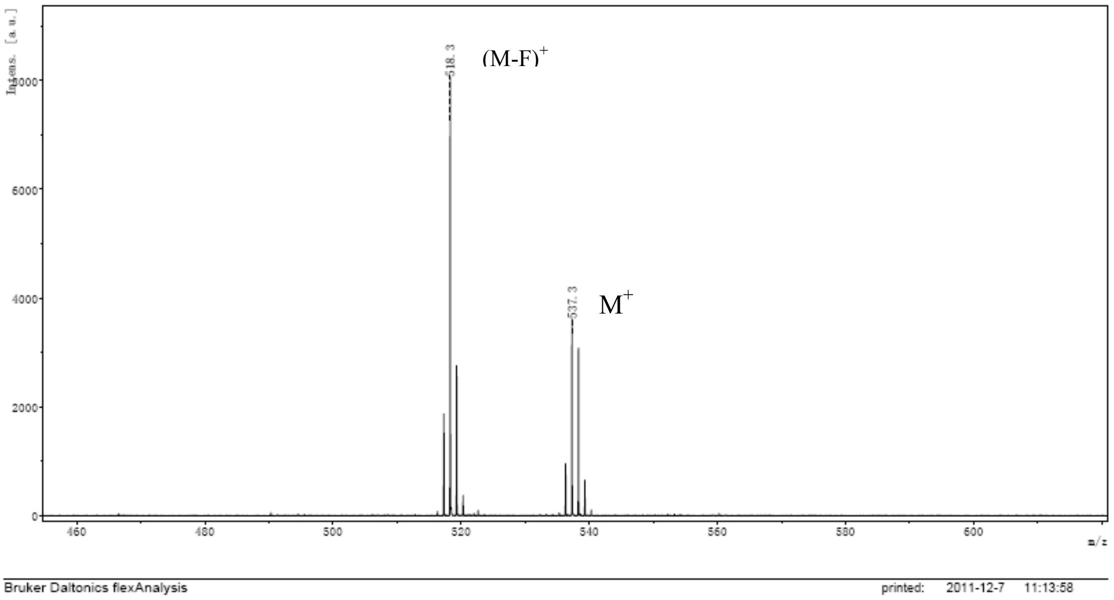


Fig. S5. TOF-MS of BDP-St.

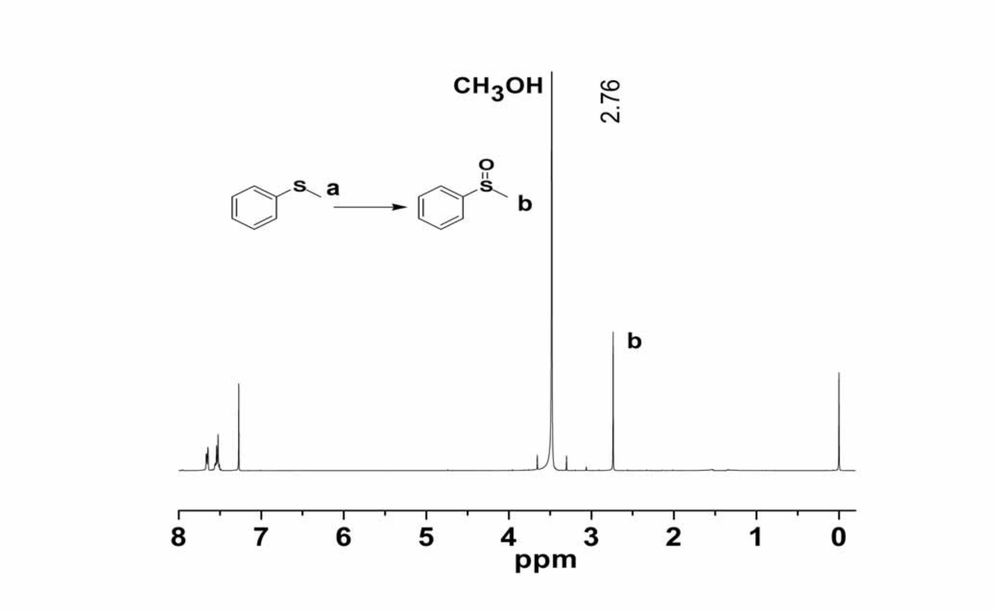


Fig. S6. ^{1}H NMR for Table 3 entry 1 in $CDCl_3$, PHP5 as the catalyst, the peak at 2.76 ppm of the product and the peak at 2.47 ppm of the substrate were used to calculate the conversion.

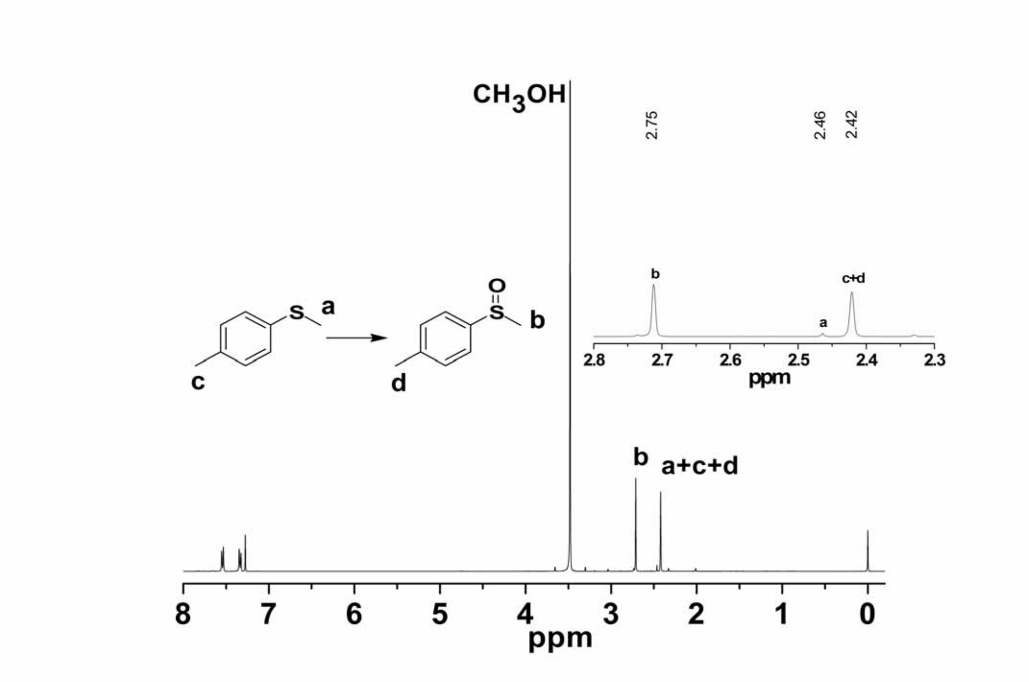


Fig. S7. ^{1}H NMR for Table 3 entry 2 in $CDCl_3$, PHP5 as the catalyst, the peak at 2.75 ppm of the product and the peak at 2.46 ppm of the substrate were used to calculate the conversion.

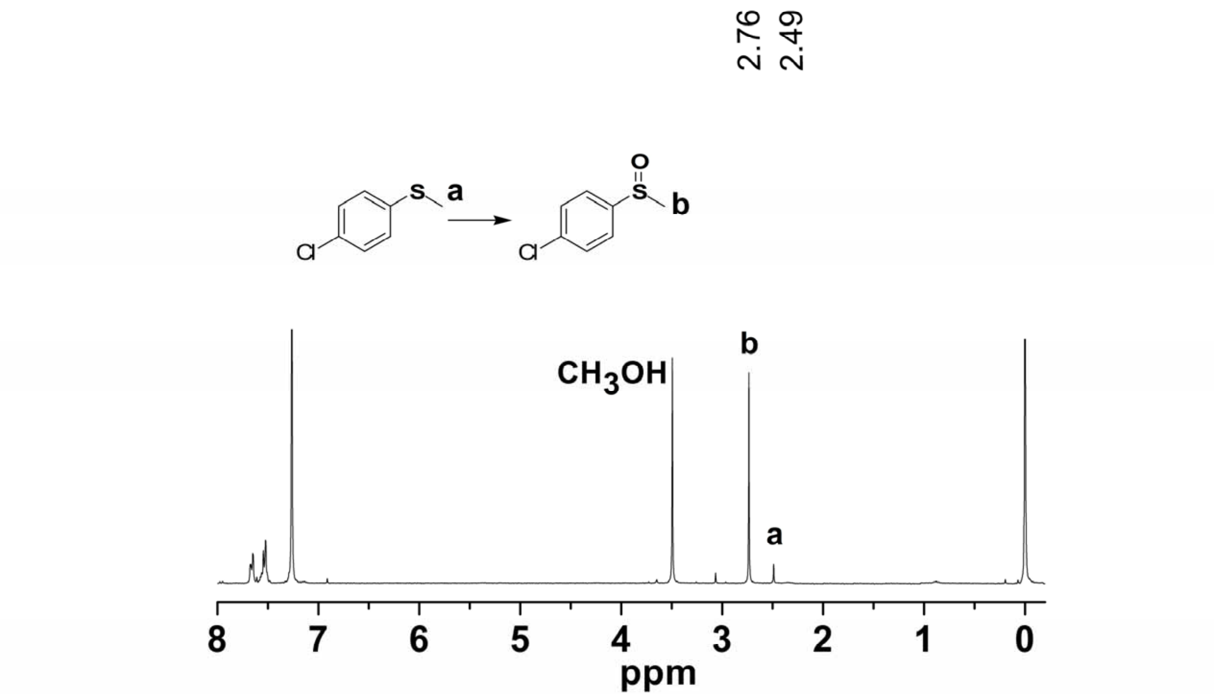


Fig. S8. ^{1}H NMR for Table 3 entry 3 in CDCl$_3$, PHP5 as the catalyst, the peak at 2.76 ppm of the product and the peak at 2.49 ppm of the substrate were used to calculate the conversion.

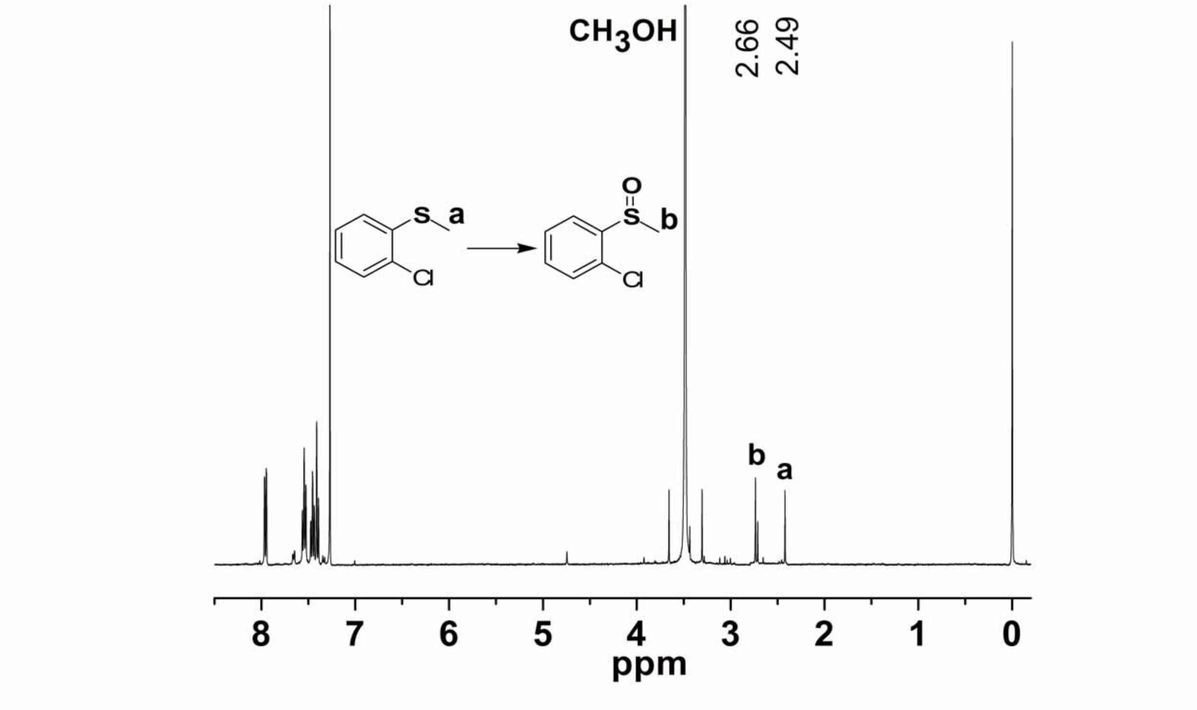


Fig. S9. ^{1}H NMR for Table 3 entry 4 in CDCl$_3$, PHP5 as the catalyst, the peak at 2.66 ppm of the product and the peak at 2.49 ppm of the substrate were used to calculate the conversion.

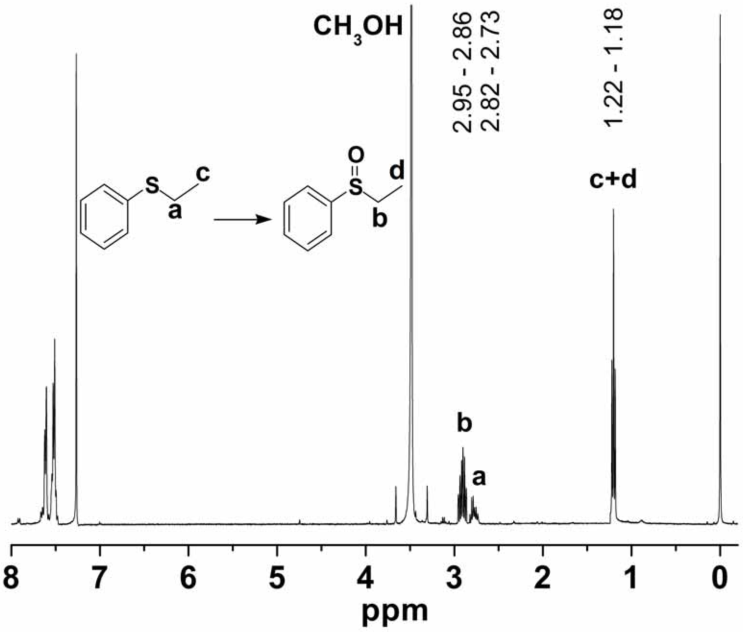


Fig. S10. ^{1}H NMR for Table 3 entry 5 in $CDCl_3$, PHP5 as the catalyst, the peak at 2.95-2.86 ppm of the product and the peak at 2.82-2.73 ppm of the substrate in the ^{1}H NMR were used to calculate the conversion.

VIII. References:

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