Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Efficient cosensitization of new organic dyes containing bipyridine anchors with porphyrin for dye-sensitized solar cells

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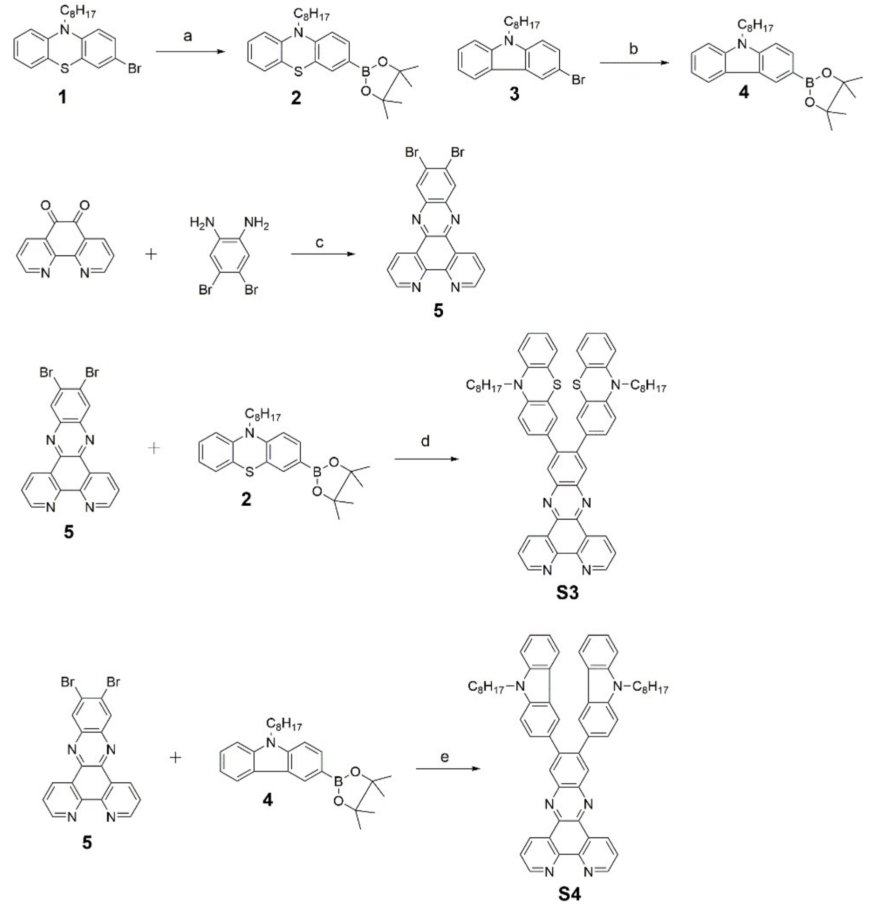
Synthesis of the dyes



Scheme S1 synthesis procedure of **S3** and **S4**. Reagents and conditions: a) bis(pinacolato)diboron, Pd(dppf)Cl_2, KOAc, DMF, 80℃; b) bis(pinacolato)diboron, Pd(dppf)Cl_2, KOAc, DMF, 80℃; c) AcOH, 120℃; d) Pd(PPh_3)$_4$, K_2CO_3, H_2O, THF, 90℃; e) Pd(PPh_3)$_4$, K_2CO_3, H_2O, THF, 90℃.

Synthesis of compound 2

A mixture of compound 1 (5.00 g, 12.80 mmol), bis(pinacolato)diboron (4.88 g, 19.20 mmol) and KOAc (3.78 g, 38.40 mmol) in DMF (80 mL) was added Pd(dppf)Cl_2 (0.60 g) under dinitrogen. The mixture was heated under 80℃ for overnight. The reaction mixture was cooled to room temperature and H_2O (250 mL) was added, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound 2 (4.27 g, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.62-7.65 (m, 2H), 7.14-7.18 (m, 2H), 6.94 (t, *J*=7.5Hz, 1H), 6.87 (d, *J*=8.0Hz, 2H), 3.88 (t, *J*=7.0Hz, 2H), 1.80-1.86 (m, 2H), 1.43-1.47 (m, 2H), 1.24-1.37 (m, 20H), 0.93 (t, *J*=6.5Hz, 3H).

Synthesis of compound 4

The preparation method was the same as that of compound 2. δ_H ^{1}H NMR ($CDCl_3$, 400 MHz) 8.60 (s, 1H), 8.12 (d, *J*=7.6Hz, 1H), 7.91 (d, *J*=8.0Hz, 1H), 7.43-7.47 (m, 1H), 7.38 (d, *J*=8.4Hz, 2H), 7.21-7.25 (m, 1H), 4.27 (t, *J*=7.2Hz, 2H), 1.83-1.87 (m, 2H), 1.40 (s, 12H), 1.25-1.34 (m, 10H), 0.84 (t, *J*=6.8Hz, 3H).

Synthesis of compound 5

Under the protection of nitrogen, 4, 5-dibromo-1,2-phenylenediamine,4 (1 g, 3.76 mmol) and 1,10-phenanthroline-5,6-dione (0.79 g, 3.76 mmol) were added to glacial acetic acid (30 mL). Then the reaction solution was heated to 120℃ for overnight, then cooled to room temperature, added a large amount of ice water and precipitated out. After filtration, water and ethanol were used to wash the filter cake. 1.38 g of compound 5 was obtained after drying, and the yield was 84%. Anal. calcd for [$C_{18}H_8Br_2N_4$] (%): C, 49.12; H, 1.83; N, 12.73. Found (%): C, 49.41; H, 2.22; N, 12.47. MS (ESI) $[M]^+$: calcd for $C_{18}H_8Br_2N_4$, 440.10; found, 440.25.

Synthesis of compound S3

Compound 5 (0.5 g, 1.14 mmol), compound 2 (1.49 g, 3.41 mmol), potassium carbonate (0.63 g, 4.54 mmol) were added to THF (30 mL) and water (5 mL).

$Pd(PPh_3)_4$ (50 mg) was added under nitrogen protection. The mixture was heated to 90℃ for 12 hours, then the reaction stopped and cooled to room temperature. Then the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (DCM/PE=6/1) to obtain 0.73 g red S3 with a yield of 72%. ^1H NMR ($CDCl_3$, 400 MHz), δ_H 9.56 (d, *J*=8.0Hz, 2H), 9.28-9.29 (m, 2H), 8.25 (s, 2H), 7.78-7.81 (m, 2H), 7.30-7.31 (m, 2H), 7.11-7.19 (m, 4H), 6.92-6.94 (m, 4H), 6.85 (d, *J*=8.0Hz, 2H), 6.71 (d, *J*=8.0Hz, 2H), 3.81 (t, *J*=6.8Hz, 4H), 1.77-1.84 (m, 4H), 1.40-1.43 (m, 4H), 1.25-1.28 (m, 16H), 0.87 (t, *J*=6.8Hz, 6H). HRMS (ESI, m/z): $[M+H]^+$. Calcd for $C_{58}H_{56}N_6S_2$: 901.2480. Found: 901.4068.

Synthesis of compound S4

The preparation method was the same as that of S4. δ_H ^1H NMR ($CDCl_3$, 400 MHz) δ_H 9.59 (d, *J*=8.0Hz, 2H), 9.25-9.26 (m, 2H), 8.57 (s, 2H), 8.28 (s, 2H), 7.95 (d, *J*=7.6Hz, 2H), 7.73-7.77 (m, 2H), 7.41-7.45 (m, 2H), 7.35 (d, *J*=8.0Hz, 2H), 7.25-7.27 (m, 2H), 7.17-7.19 (m, 2H), 7.12-7.15 (m, 2H), 4.20 (t, *J*=7.2Hz, 4H), 1.77-1.84 (m, 4H), 1.21-1.33 (m, 20H), 0.85 (t, *J*=7.2Hz, 6H). HRMS (ESI, m/z): $[M-C_2H_5+H]^+$. Calcd for $C_{56}H_{51}N_6$: 808.0660. Found: 809.2544.

Table S1 Optical and electrochemical properties of dyes

Dye	$^{a}\lambda_{max}$/nm ($\varepsilon \times 10^4$ M^{-1} cm^{-1})	$^{b}E_{OX}$/V (NHE)	$^{c}E_{0\text{-}0}$/eV	$^{d}E^{*}_{OX}$/V (NHE)
S3	456 (1.49)	0.94	2.37	-1.43
S4	440 (1.46)	0.96	2.40	-1.44

^{a}Absorption maximum in DCM solution (1×10^{-5} M), ^{b}the ground state oxidation potentials, $^{c}E_{0\text{-}0}$ was estimated from the intersection of emission and absorption spectra, $^{d}E^{*}_{OX}$ was calculated by the formula: $E^{*}_{OX} = E_{OX}\text{-}E_{0\text{-}0}$.

Table S2 Photovoltaic parameters of the DSSCs obtained from the J-V curves

Dye	Rs (Ω cm^{-2})	Rsh (Ω cm^{-2})	Jsc (mA cm^{-2})	Voc (mV)	FF (%)	η (%)
^{a}S3	98	20444	8.25±0.17	723±1.33	68.00±0.28	4.06±0.08
^{a}S4	74	38989	6.46±0.15	686±1.33	73.02±0.12	3.23±0.07
^{b}JA3	59	20577	12.23±0.06	801±1.00	63.55±0.17	6.23±0.01
^{a}JA3+S3	77	12242	15.46±0.06	821±0.67	64.55±0.17	8.20±0.01
^{a}JA3+S4	64	17925	13.08±0.02	819±0.67	66.12±1.35	7.20±0.01

^{a}The size of the active area for each cell is 0.196 cm^2, three devices are assembled in parallel with each dye, the DSSCs were all measured under standard global AM 1.5G solar irradiation. ^{b}The DSSC based on JA3 was reported in ref. 30.

Table S3 Parameters obtained by fitting the EIS of the DSSCs with JA3, JA3+S3, and JA3+S4 using the equivalent circuit

Dye	Rs (Ω cm^{-2})	R_{Pt} (Ω cm^{-2})	R_{ct} (Ω cm^{-2})
JA3	36.21	16.13	117
JA3+S3	42.60	23.47	596
JA3+S4	39.32	22.10	568

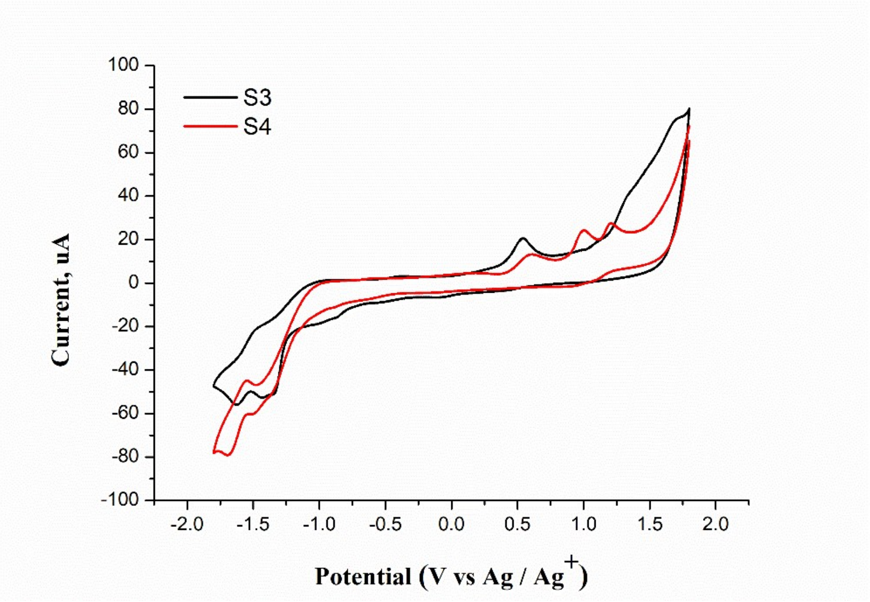


Fig. S1 Cyclic voltammogram of **S3** and **S4** in DCM, 0.1 M TBAPF$_6$, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag$^+$ as reference electrode, scan rate: 100 mV s^{-1}, calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an external reference.

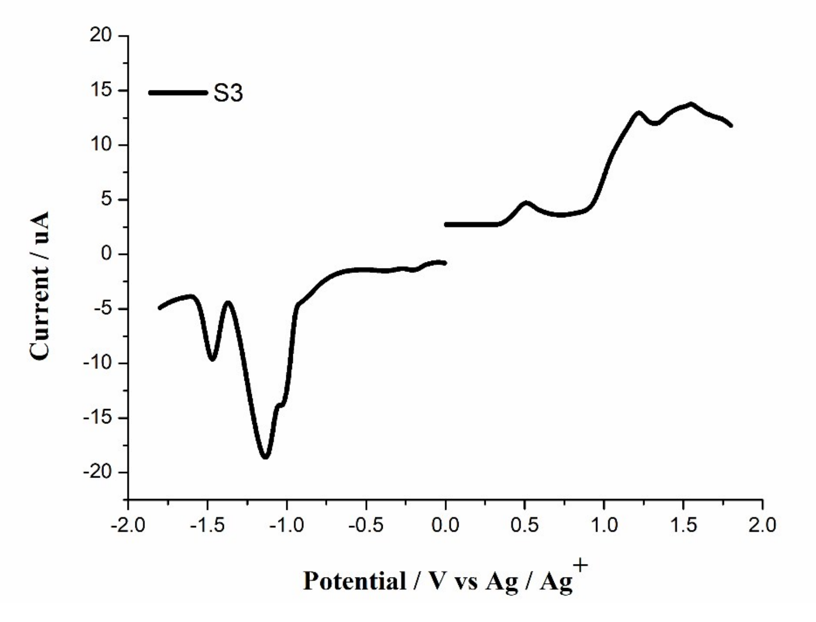


Fig. S2 Differential pulse voltammetry (DPV) of **S3** in DCM, 0.1 M TBAPF$_6$, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag$^+$ as reference electrode.

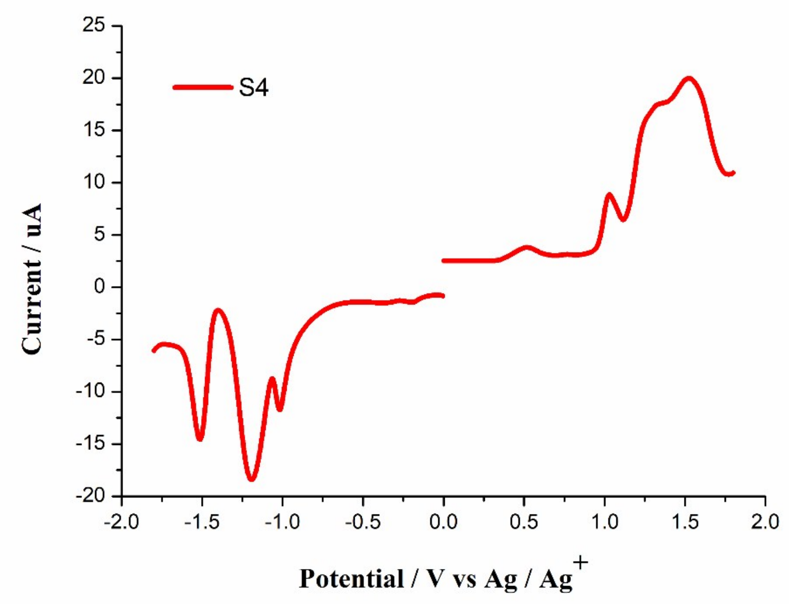


Fig. S3 Differential pulse voltammetry (DPV) of **S4** in DCM, 0.1 M TBAPF$_6$, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag$^+$ as reference electrode.

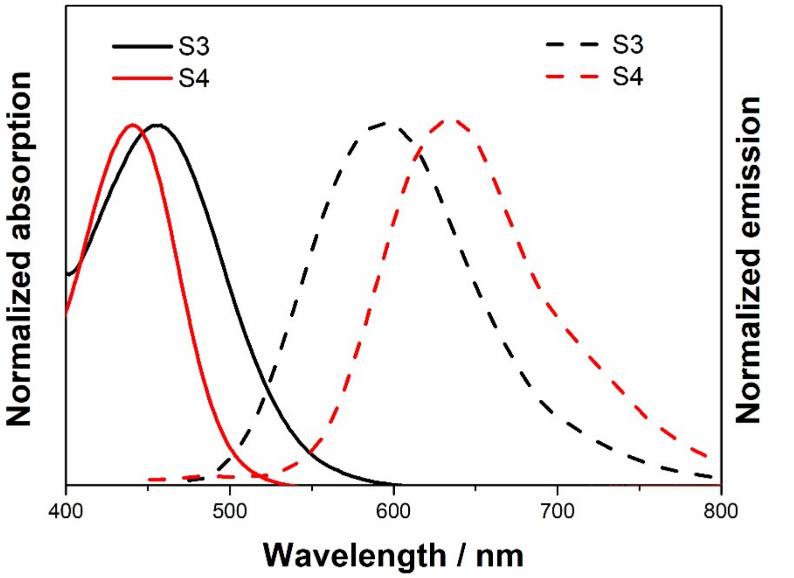


Fig. S4 The normalized absorption and normalized emission spectra of S3 and S4, and the zero-zero excitation energy (E$_{0-0}$) can be estimated by the intersection of emission and absorption.

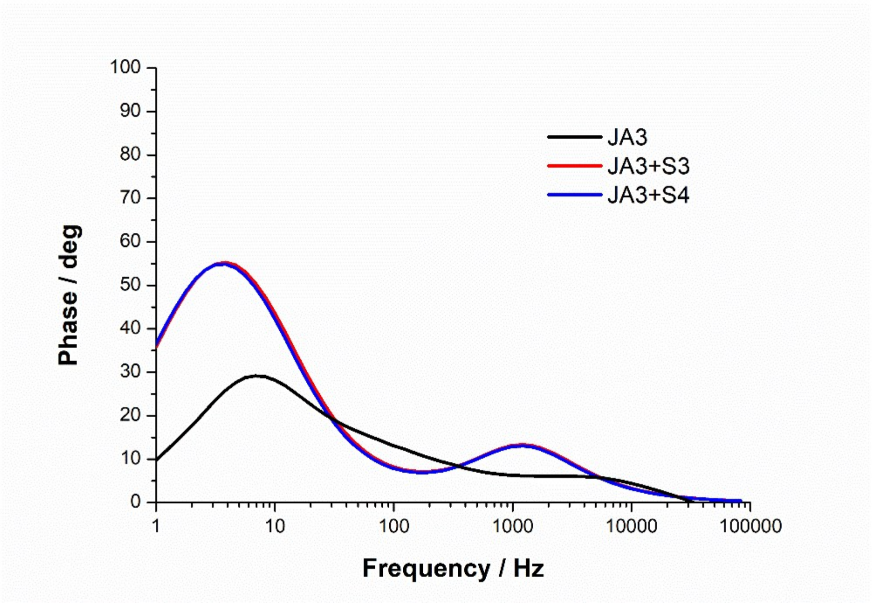


Fig. S5 The Bode Phase of DSSCs

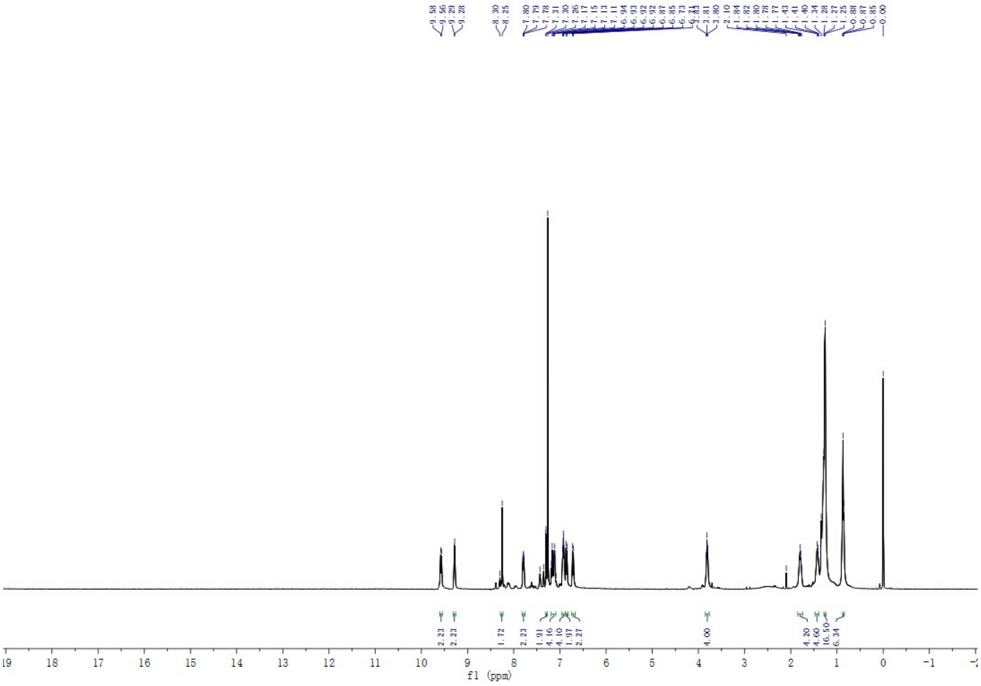


Fig. S6 ^{1}H NMR of S3

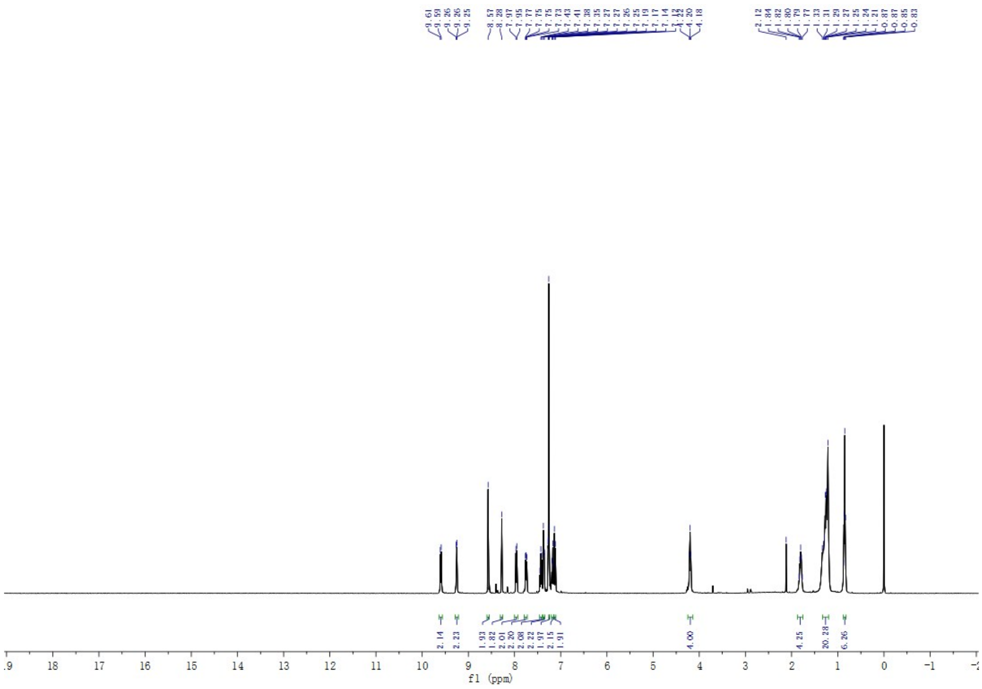


Fig. S7 ^{1}H NMR of S4

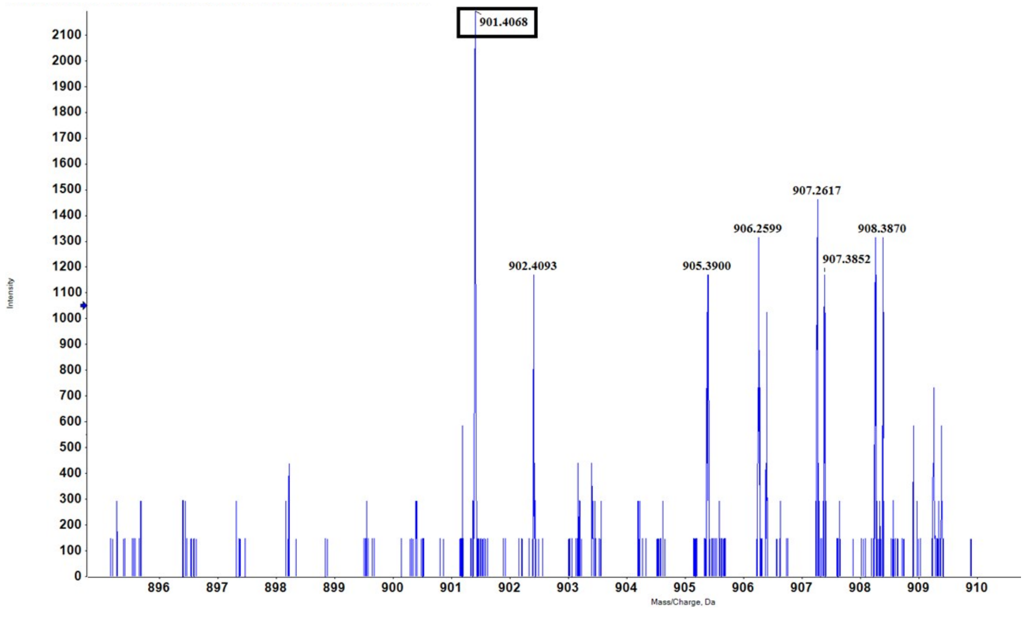


Fig. S8 HRMS of S3

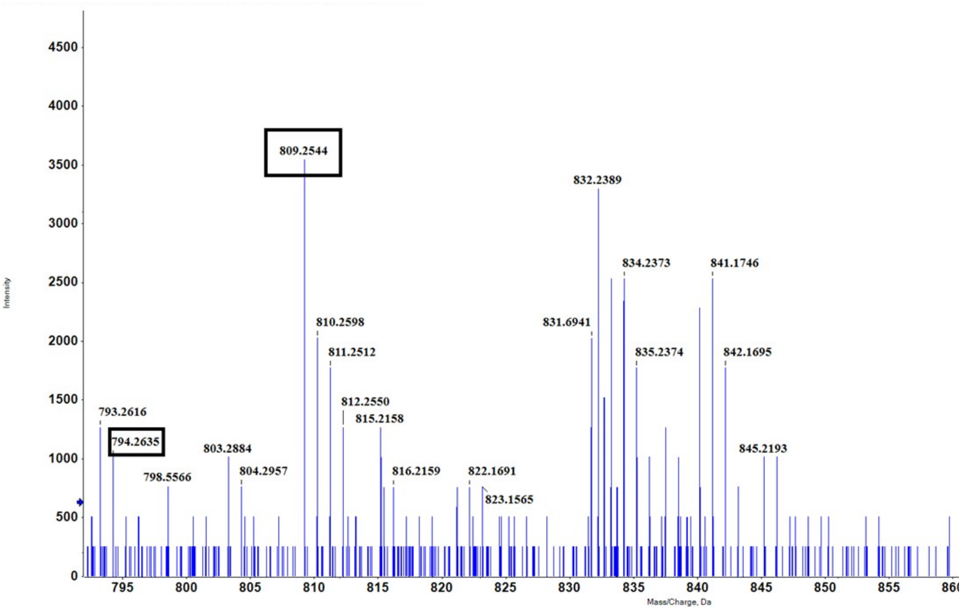


Fig. S9 HRMS of S4