Electronic Supplementary Information

Preparation of Unsymmetrical Distyryl BODIPY Derivatives and Effects of the Styryl Substituents on their *in vitro* Photodynamic Properties

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Contents

Experimental Section

Experimental details regarding the purification of solvents, spectroscopic and photophysical measurements and *in vitro* studies are described elsewhere unless otherwise stated.[1] Diiodo BODIPY **6** was prepared by our previously described procedure.[2] Benzaldehydes **7**[3] and **12**[4] were prepared as described.

Monostyryl BODIPY 8. A mixture of diiodo BODIPY **6** (0.29 g, 0.4 mmol), bis(triethylene glycol)-substituted benzaldehyde **7** (0.17 g, 0.4 mmol), glacial acetic acid (0.4 mL, 7.0 mmol) and piperidine (0.5 mL, 5.1 mmol) in toluene (40 mL) was refluxed for 2 h. The water formed during the reaction was removed azeotropically with a Dean-Stark apparatus. The mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using $CHCl_3$ as the eluent, followed by size exclusion chromatography with Bio-beads S-X1 beads using THF as the eluent. The purple fraction was collected and rotary evaporated to afford a purple solid (78 mg, 17%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.05 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.47 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.23 (dd, *J* = 2.0, 8.4 Hz, 1 H, ArH), 7.19 (d, *J* = 8.8 Hz, 2 H, ArH), 7.17 (d, *J* = 2.0 Hz, 1 H, ArH), 7.09 (d, *J* = 8.8 Hz, 2 H, ArH), 6.96 (d, *J* = 8.4 Hz, 1 H, ArH), 4.19-4.25 (m, 6 H, OCH_2), 3.85-3.89 (m, 6 H, OCH_2), 3.69-3.73 (m, 6 H, OCH_2), 3.59-3.65 (m, 12 H, OCH_2), 3.49-3.53 (m, 6 H, OCH_2), 3.35 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 2.66 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 159.9, 156.9, 150.4, 149.1, 146.2, 145.2, 140.4, 139.1, 132.8, 132.4, 130.5, 129.4, 127.2, 122.1, 117.1, 115.6, 114.3, 113.6, 86.2, 82.5, 72.1, 71.0, 70.8, 70.7, 69.9, 69.8, 69.1, 68.8, 67.7, 59.2, 17.8, 17.4, 16.3 (some of the signals are overlapped). MS (ESI): two isotopic clusters peaking

at *m/z* 1173 {100%, $[M + Na]^+$} and 1189 {45%, $[M + K]^+$}. HRMS (ESI): *m/z* calcd for $C_{47}H_{63}BF_2I_2N_2NaO_{12}$ $[M + Na]^+$: 1173.2424, found:1173.2430.

Distyryl BODIPY 1. According to the procedure described for **8**, monostyryl BODIPY **8** (100 mg, 87 μmol) was treated with benzaldehyde (**9**) (92 mg, 0.87 mmol), glacial acetic acid (0.45 mL, 7.9 mmol) and piperidine (0.63 mL, 6.4 mmol) in toluene (30 mL) to give **1**, which was purified by silica gel column chromatography using $CHCl_3$ as the eluent, followed by size exclusion chromatography using THF as the eluent. The product was collected as a green solid (21 mg, 20%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.15 (d, *J* = 16.4 Hz, 1 H, CH=CH), 8.11 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.69 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.66 (d, *J* = 7.2 Hz, 2 H, ArH), 7.55 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.43 (t, *J* = 7.2 Hz, 2 H, ArH), 7.35-7.38 (m, 1 H, ArH), 7.28 (dd, *J* = 1.6, 8.4 Hz, 1 H, ArH), 7.22 (d, *J* = 8.8 Hz, 2 H, ArH), 7.20 (d, *J* = 1.6 Hz, 1 H, ArH), 7.10 (d, *J* = 8.8 Hz, 2 H, ArH), 6.98 (d, *J* = 8.4 Hz, 1 H, ArH), 4.20-4.26 (m, 6 H, OCH_2), 3.86-3.89 (m, 6 H, OCH_2), 3.70-3.72 (m, 6 H, OCH_2), 3.57-3.66 (m, 12 H, OCH_2), 3.48-3.54 (m, 6 H, OCH_2), 3.35 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 1.54 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 159.9, 151.1, 150.6, 149.9, 149.1, 146.5, 145.6, 139.7, 139.3, 139.2, 136.9, 133.6, 133.3, 130.5, 129.6, 129.2, 128.9, 127.7, 127.4, 122.1, 119.0, 117.2, 115.6, 114.4, 113.9, 83.3, 82.8, 72.1, 71.0, 70.8, 70.7, 69.9, 69.8, 69.2, 68.9, 67.7, 59.2, 17.9, 17.8 (some of the signals are overlapped). MS (ESI): two isotopic clusters peaking at *m/z* 1261 {100%, $[M + Na]^+$} and 1277 {30%, $[M + K]^+$}. HRMS (ESI): *m/z* calcd for $C_{54}H_{67}BF_2I_2N_2NaO_{12}$ $[M + Na]^+$: 1261.2737, found:1261.2757.

Distyryl BODIPY 2. According to the procedure described for **8**, monostyryl BODIPY **8** (0.13 g, 0.11 mmol) was treated with naphthaldehyde (**10**) (0.17 g, 1.1 mmol), glacial acetic acid (0.57 mL, 10.0 mmol) and piperidine (0.79 mL, 8.0 mmol) in toluene (40 mL) to give **2**, which was purified by silica gel column chromatography using $CHCl_3$ as the eluent, followed by size exclusion chromatography using THF as the eluent. The product was collected as a green solid (20 mg, 14%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.02 (d, *J* = 16.8 Hz, 1 H, CH=CH), 8.36 (d, *J* = 8.0 Hz, 1 H, ArH), 8.14 (d, *J* = 16.8 Hz, 1 H, CH=CH), 8.00 (d, *J* = 7.2 Hz, 1 H, ArH), 7.90-7.93 (m, 2 H, ArH), 7.78 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.54-7.62 (m, 4 H, CH=CH and ArH), 7.28 (dd, *J* = 1.6, 8.4 Hz, 1 H, ArH), 7.24 (d, *J* = 8.8 Hz, 2 H, ArH), 7.20 (d, *J* = 1.6 Hz,1 H, ArH), 7.11 (d, *J* = 8.8 Hz, 2 H, ArH), 6.97 (d, *J* = 8.4 Hz, 1 H, ArH), 4.20-4.23 (m, 6 H, OCH_2), 3.86-3.90 (m, 4 H, OCH_2), 3.82 (t, *J* = 4.8 Hz, 2 H, OCH_2), 3.47-3.72 (m, 24 H, OCH_2), 3.36 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 1.58 (s, 3 H, CH_3), 1.56 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 159.9, 151.1, 150.6, 150.0, 149.1, 146.6, 145.6, 139.8, 139.3, 135.9, 134.4, 133.9, 133.7, 133.4, 131.8, 130.5, 129.6, 128.8, 127.4, 126.8, 126.1, 126.0, 124.5, 124.0, 122.1, 121.2, 117.2, 115.6, 114.3, 113.8, 83.4, 83.2, 72.0, 71.0, 70.9, 70.8, 70.7, 70.6, 69.8, 69.7, 69.1, 68.8, 67.7, 59.2, 59.1, 17.9, 17.8 (some of the signals are overlapped). MS (ESI): two isotopic clusters peaking at *m/z* 1311 {100%, $[M + Na]^+$} and 1327 {40%, $[M + K]^+$}. HRMS (ESI): *m/z* calcd for $C_{58}H_{69}BF_2I_2N_2NaO_{12}$ $[M + Na]^+$: 1311.2893, found:1311.2891.

Distyryl BODIPY 3. According to the procedure described for **8**, monostyryl BODIPY **8** (0.11 g, 0.10 mmol) was treated with 4-dimethylaminobenzaldehyde (**11**) (0.15 g, 1.0 mmol), glacial acetic acid (0.52 mL, 9.1 mmol) and piperidine (0.73 mL, 7.4 mmol) in

toluene (30 mL) to give **3**, which was purified by silica gel column chromatography using $CHCl_3$ as the eluent, followed by size exclusion chromatography using THF as the eluent. The product was collected as a green solid (36 mg, 29%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.25 (d, *J* = 16.4 Hz, 1 H, CH=CH), 8.02 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.56 (d, *J* = 8.8 Hz, 2 H, ArH), 7.54 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.51 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.27 (dd, *J* = 2.0, 8.4 Hz, 1 H, ArH), 7.21 (d, *J* = 8.4 Hz, 2 H, ArH), 7.19 (d, *J* = 2.0 Hz, 1 H, ArH), 7.08 (d, *J* = 8.4 Hz, 2 H, ArH), 6.98 (d, *J* = 8.4 Hz, 1 H, ArH), 6.74 (d, *J* = 8.8 Hz, 2 H, ArH), 4.19-4.27 (m, 6 H, OCH_2), 3.86-3.89 (m, 6 H, OCH_2), 3.70-3.72 (m, 6 H, OCH_2), 3.57-3.65 (m, 12 H, OCH_2), 3.49-3.54 (m, 6 H, OCH_2), 3.35 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 3.05 (s, 6 H, NCH_3), 1.53 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 159.7, 151.8, 151.5, 150.1, 149.0, 148.8, 146.5, 144.1, 140.8, 138.0, 137.4, 133.7, 132.9, 130.9, 129.8, 129.6, 127.7, 124.9, 121.7, 117.7, 115.5, 114.5, 114.1, 113.9, 112.2, 83.4, 82.2, 72.0, 71.0, 70.8, 70.7, 70.6, 69.9, 69.8, 69.7, 69.1, 68.8, 67.6, 59.2, 59.1, 40.4, 18.0, 17.6 (some of the OCH_2 signals are overlapped). MS (ESI): two isotopic clusters peaking at *m/z* 1304 {100%, $[M + Na]^+$} and 1320 {40%, $[M + K]^+$}. HRMS (ESI): *m/z* calcd for $C_{56}H_{72}BF_2I_2N_3NaO_{12}$ $[M + Na]^+$: 1304.3159, found:1304.3165.

Distyryl BODIPY 4. According to the procedure described for **8**, monostyryl BODIPY **8** (96 mg, 84 μmol) was treated with 4-(2-dimethylaminoethyoxy)benzaldehyde (**12**) (0.16 g, 0.83 mmol), glacial acetic acid (0.5 mL, 8.7 mmol) and piperidine (0.73 mL, 7.4 mmol) in toluene (30 mL) to give **4**, which was purified by silica gel column chromatography using $CHCl_3$ as the eluent, followed by size exclusion chromatography using THF as the eluent. The product was collected as a green solid (31 mg, 28%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ

8.15 (d, *J* = 16.8 Hz, 1 H, CH=CH), 8.07 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.61 (d, *J* = 8.8 Hz, 2 H, ArH), 7.56 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.53 (d, *J* = 16.4 Hz, 1 H, CH=CH), 7.28 (dd, *J* = 1.6, 8.4 Hz, 1 H, ArH), 7.21 (d, *J* = 8.8 Hz, 2 H, ArH), 7.19 (d, *J* = 1.6 Hz, 1 H, ArH), 7.09 (d, *J* = 8.8 Hz, 2 H, ArH), 6.98 (d, *J* = 8.4 Hz, 1 H, ArH), 6.96 (d, *J* = 8.8 Hz, 2 H, ArH), 4.20-4.26 (m, 6 H, OCH_2), 4.12 (t, *J* = 5.6 Hz, 2 H, OCH_2), 3.88 (t, *J* = 4.4 Hz, 6 H, OCH_2), 3.70-3.72 (m, 6 H, OCH_2), 3.57-3.66 (m, 12 H, OCH_2), 3.47-3.54 (m, 6 H, OCH_2), 3.35 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 2.73 (t, *J* = 5.6 Hz, 2 H, NCH_2), 2.32 (s, 6 H, NCH_3), 1.53 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 160.1, 159.8, 150.6, 150.4, 150.3, 149.0, 146.0, 145.7, 139.2, 139.1, 138.7, 133.4, 133.3, 130.5, 129.7, 129.3, 127.5, 121.9, 117.3, 116.8, 115.6, 115.0, 114.3, 114.0, 82.9, 72.0, 71.0, 70.8, 70.7, 70.6, 69.9, 69.8, 69.7, 69.1, 68.8, 67.7, 66.1, 59.2, 59.1, 58.3, 46.0, 17.9, 17.8 (some of the signals are overlapped). MS (ESI): an isotopic cluster peaking at *m/z* 1326 {95%, $[M + H]^+$}. HRMS (ESI): *m/z* calcd for $C_{58}H_{77}BF_2I_2N_3O_{13}$ $[M + H]^+$: 1326.3601, found:1326.3592.

Distyryl BODIPY 5. A mixture of **4** (48 mg, 36 μmol) and iodomethane (2 mL, 32 mmol) in $CHCl_3$ (15 mL) was stirred at room temperature for 30 min. Diethyl ether (50 mL) was added for precipitation. The green precipitate was filtered, then washed with diethyl ether and dried *in vacuo* (33 mg, 62%). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.14 (d, *J* = 16.8 Hz, 1 H, CH=CH), 8.09 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.65 (d, *J* = 8.8 Hz, 2 H, ArH), 7.59 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.54 (d, *J* = 16.8 Hz, 1 H, CH=CH), 7.26 (dd, *J* = 1.6, 8.4 Hz, 1 H, ArH), 7.20-7.23 (m, 3 H, ArH), 7.10 (d, *J* = 8.8 Hz, 2 H, ArH), 7.03 (d, *J* = 8.8 Hz, 2 H, ArH), 6.98 (d, *J* = 8.4 Hz, 1 H, ArH), 4.56 (br s, 2 H, NCH_2), 4.20-4.26 (m, 6 H, OCH_2), 4.03-4.05 (m, 2 H, OCH_2), 3.87-3.89 (m, 6 H, OCH_2), 3.70-3.72 (m, 6 H, OCH_2), 3.59-3.64 (m, 12 H,

OCH_2), 3.50-3.54 (m, 6 H, OCH_2), 3.37 (s, 9 H, OCH_3), 3.35 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 1.54 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 159.8, 158.1, 150.5, 150.1, 148.9, 146.1, 145.9, 139.3, 139.0, 138.4, 133.4, 133.3, 130.8, 130.3, 129.6, 129.3, 127.3, 121.7, 117.5, 117.2, 115.6, 115.0, 114.3, 114.2, 83.1, 82.9, 72.0, 71.9, 70.9, 70.8, 70.7, 70.6, 70.5, 69.8, 69.7, 69.2, 68.8, 67.6, 65.1, 62.4, 59.1, 59.0, 54.5, 54.4, 17.8, 17.7 (some of the signals are overlapped). MS (ESI): an isotopic cluster peaking at *m/z* 1340 {100%, $[M - I]^+$}. HRMS (ESI): *m/z* calcd for $C_{59}H_{79}BF_2I_2N_3O_{13}$ $[M - I]^+$: 1340.3758, found: 1340.3780.

Photocytotoxicity Assay. Distyryl BODIPYs **1-5** were first dissolved in DMF to give 1.6 mM solutions, which were diluted to 80 μM with an aqueous solution of Tween 80 (Arcos, 0.5% by volume in these 80 μM solutions). The solutions were filtered with a 0.22 μm filter, then diluted with the culture medium to appropriate concentrations. The remaining steps are the same as described previously.[1]

Intracellular Fluorescence Studies. About 1.2×10^5 HT29 cells in the culture medium (2 mL) were seeded on a coverslip and incubated overnight at 37 °C under 5% CO_2. The medium was removed, then the cells were incubated with the solutions of distyryl BODIPYs **1-5** in the medium (2 μM, 2 mL) for 2 h under the same conditions. The cells were rinsed with phosphate buffered saline (PBS) and then viewed with a Leica SP5 confocal microscope equipped with a 633 helium neon laser. Emission signals from 650-720 nm (gain = 750 V) were collected and the images were digitised and analysed by Leica Application Suite Advanced Fluorescence. The intracellular fluorescence intensities (a total of 50 cells for each sample) were also determined.

Subcellular Localisation Studies. About 1.2×10^5 HT29 cells in the culture medium (2 mL) were seeded on a coverslip and incubated overnight at 37 °C under 5% CO_2. The medium was then removed. The cells were incubated with a solution of **4** or **5** in the medium (1 μM, 2 mL) for 2 h under the same conditions. For the study using ER-Tracker, the cells were incubated with ER-Tracker Green (Molecular Probe, 0.2 μM in PBS) under the same conditions for a further 30 min. For the study using LysoTracker and MitoTracker, the cells were incubated with LysoTracker Green DND 26 (Molecular Probe, 4 μM in the medium) or MitoTracker Green FM (Molecular Probe, 1 μM in the medium) for a further 10 min. For all the cases, the cells were then rinsed with PBS and viewed with a Leica SP5 confocal microscope equipped with a 488 nm argon laser and a 633 helium neon laser. All the Trackers were excited at 488 nm and monitored at 510-560 nm, whereas compounds **4** and **5** were excited at 633 nm and monitored at 675-720 nm. The images were digitised and analysed using Leica Application Suite Advanced Fluorescence. The subcellular localisation of **4** and **5** was revealed by comparing the intracellular fluorescence images caused by the ER-Tracker, LysoTracker or MitoTracker and these dyes.

References

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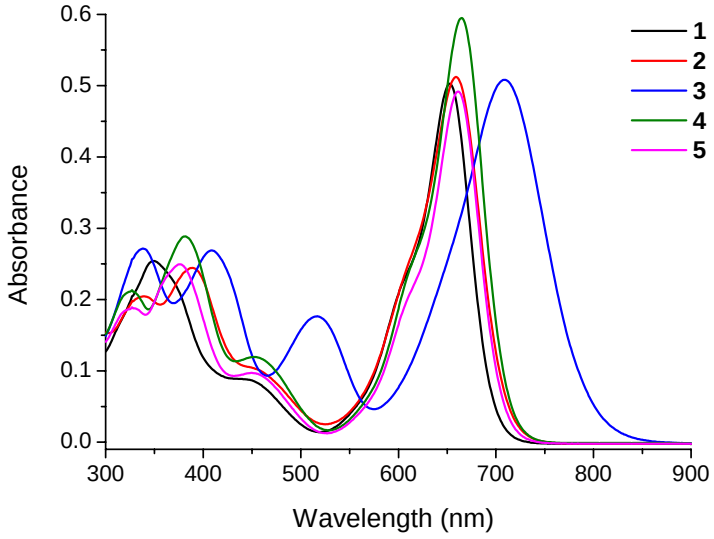

Fig. S1 Electronic absorption spectra of **1**-**5** (8 μM) in DMF.

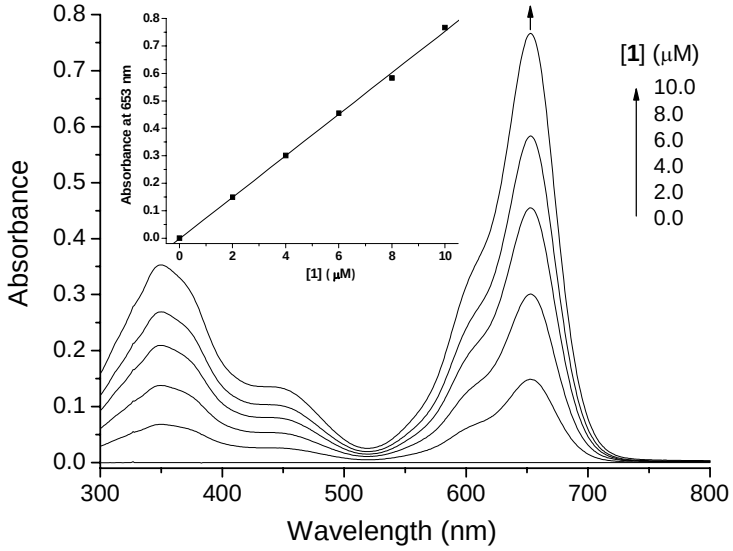

Fig. S2 Electronic absorption spectra of **1** at various concentrations in DMF. The inset plots the Q-band absorbance *vs.* the concentration of **1**.

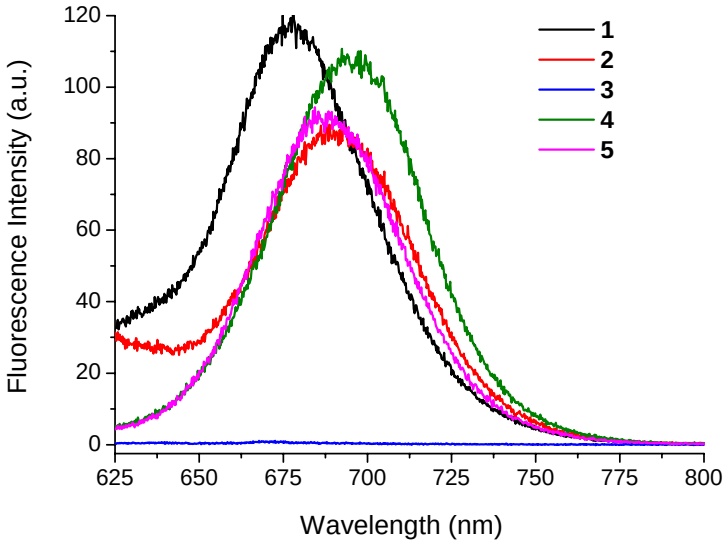

Fig. S3 Fluorescence emission spectra of **1**-**5** (8 μM) in DMF.

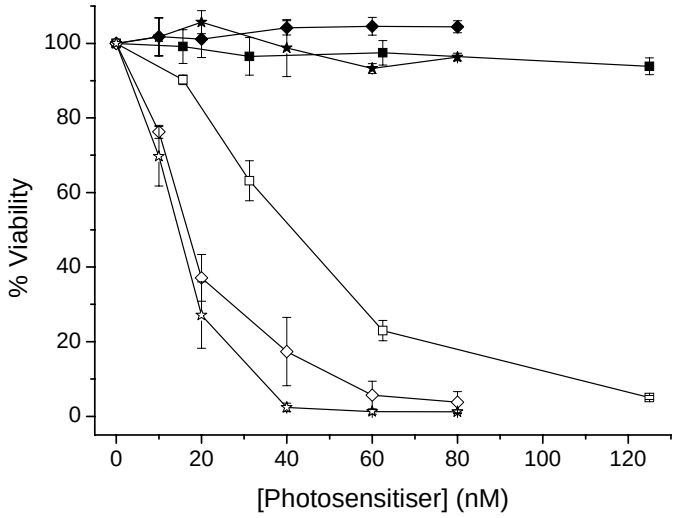

Fig. S4 Comparison of the cytotoxic effects of **1** (squares), **4** (rhombus) and **5** (stars) on HT29 cells in the absence (closed symbol) and presence (open symbol) of light (λ > 610 nm, 40 mW cm^{-2}, 48 J cm^{-2}). Data are expressed as mean value ± standard error of the mean value (SEM) of three independent experiments, each performed in quadruplicate.

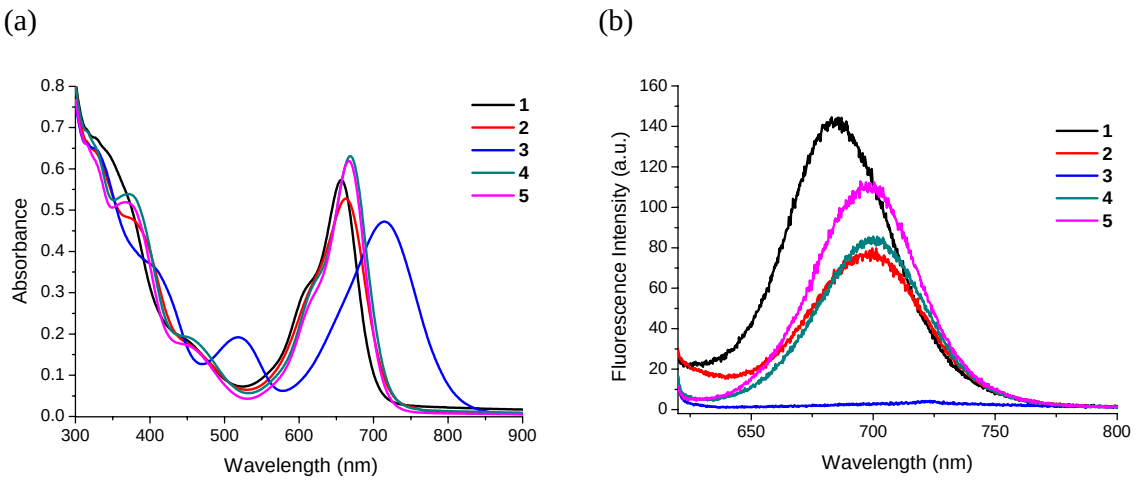

Fig. S5 (a) Electronic absorption and (b) fluorescence emission spectra of **1-5** (8 μM) formulated with Tween 80 (0.05% by volume) in the DMEM culture medium.

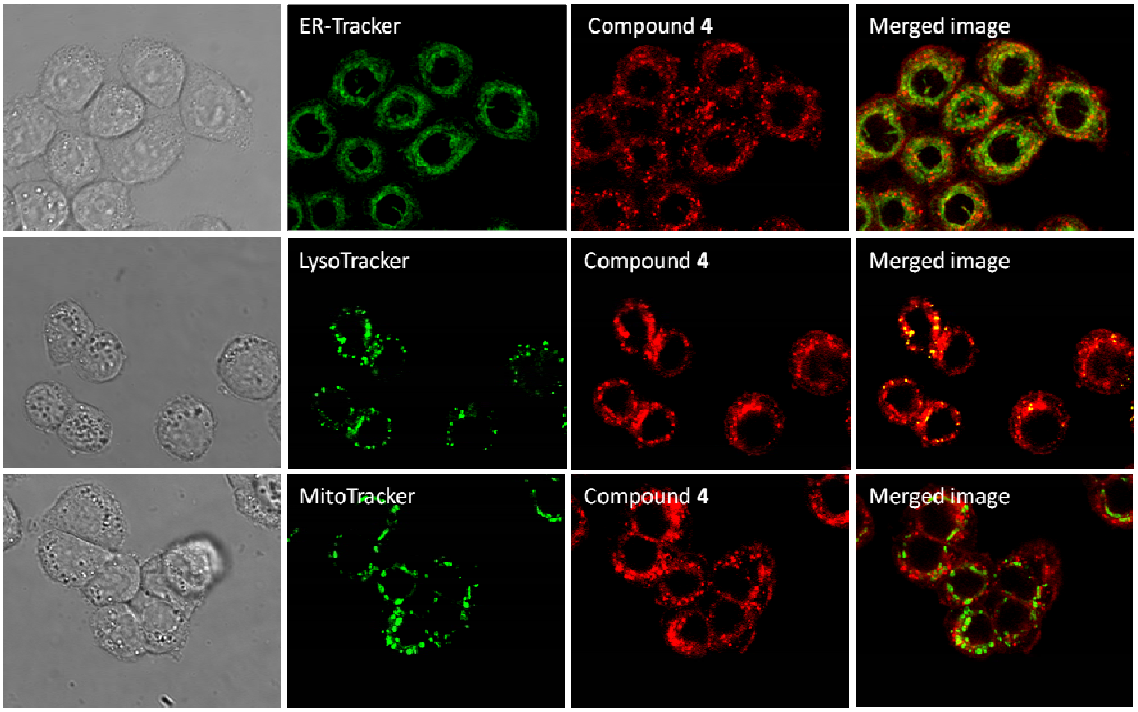

Fig. S6 Visualisation of the intracellular fluorescence of HT29 by using filter sets specific for compound **4** (in red, column 3) and ER-Tracker, LysoTracker or MitoTracker (in green, column 2). The corresponding superimposed and bright field images are given in columns 4 and 1 respectively.

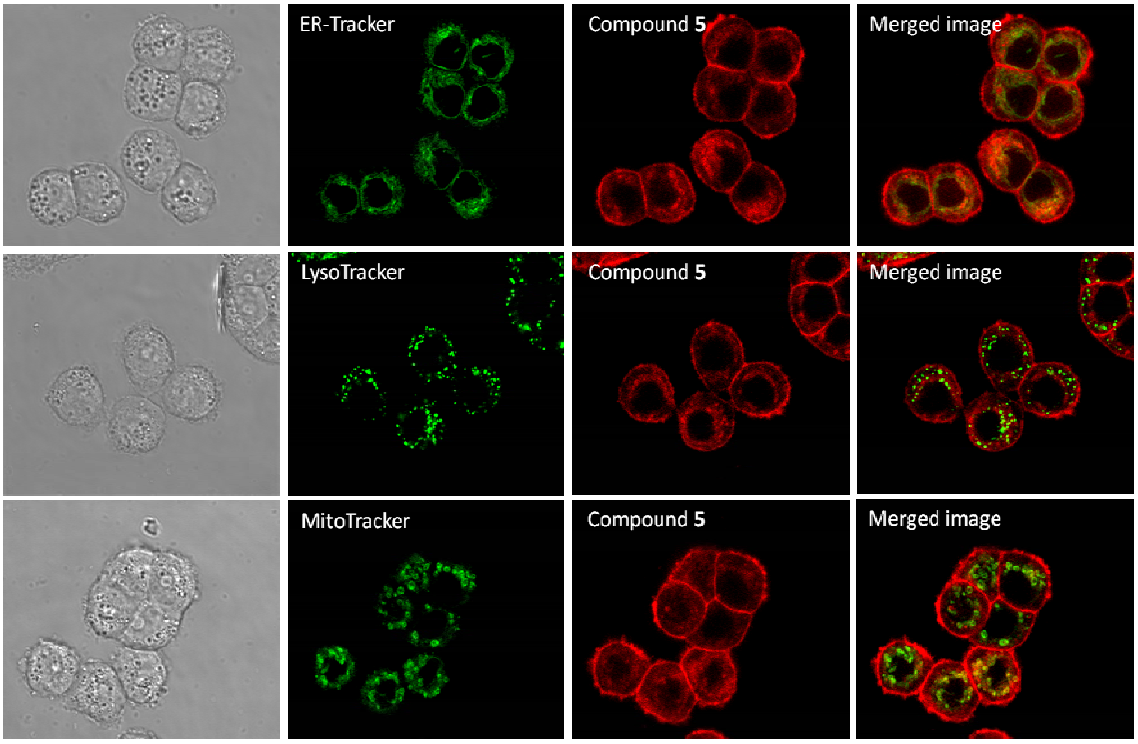

Fig. S7 Visualisation of the intracellular fluorescence of HT29 by using filter sets specific for compound **5** (in red, column 3) and ER-Tracker, LysoTracker or MitoTracker (in green, column 2). The corresponding superimposed and bright field images are given in columns 4 and 1 respectively.

In all the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, (residual) solvent signals are marked with asterisks.

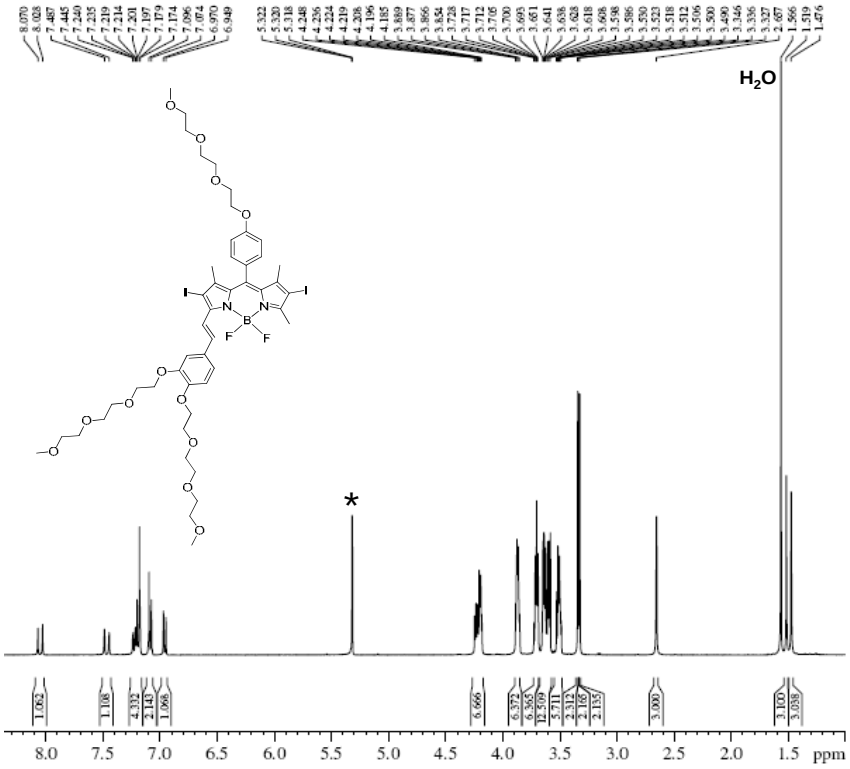

Fig. S8 ^{1}H NMR spectrum of **8** in CD_2Cl_2.

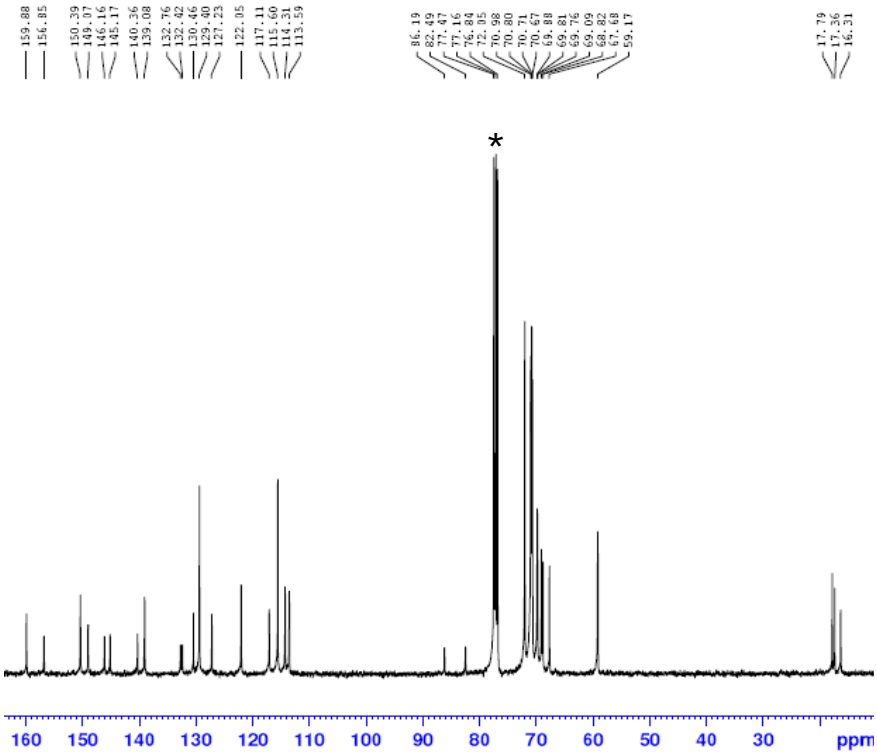

Fig. S9 $^{13}C\{^{1}H\}$ NMR spectrum of **8** in $CDCl_3$.

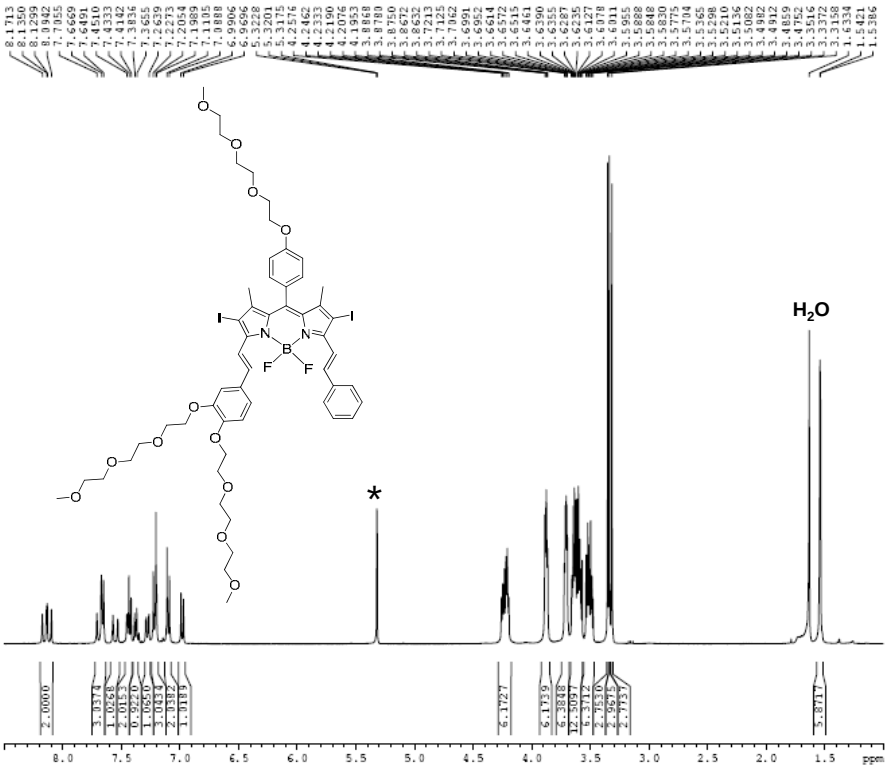

Fig. S10 ^{1}H NMR spectrum of **1** in CD_2Cl_2.

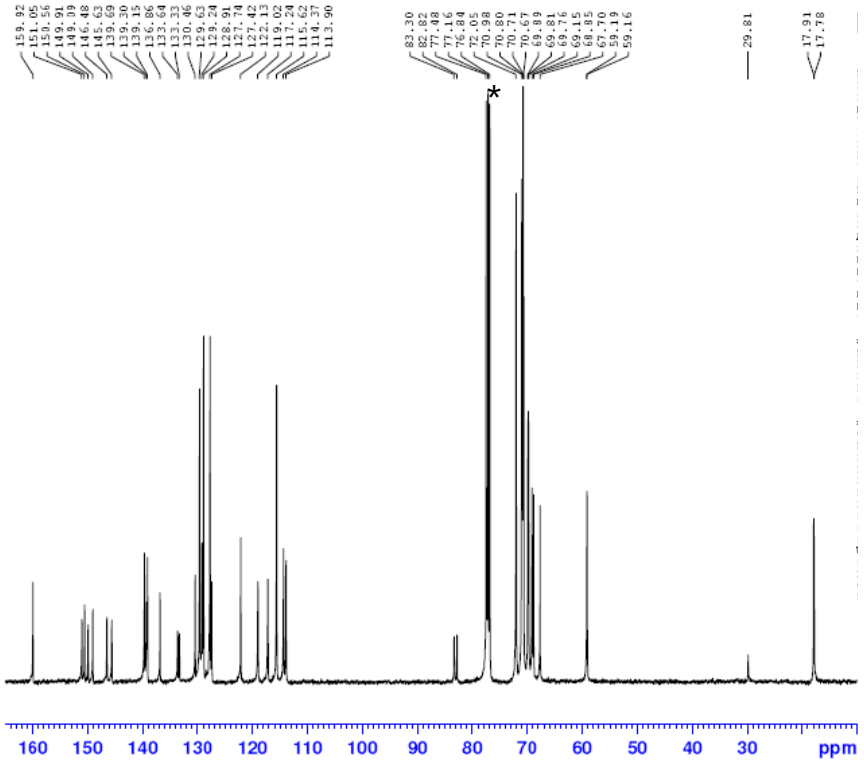

Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$.

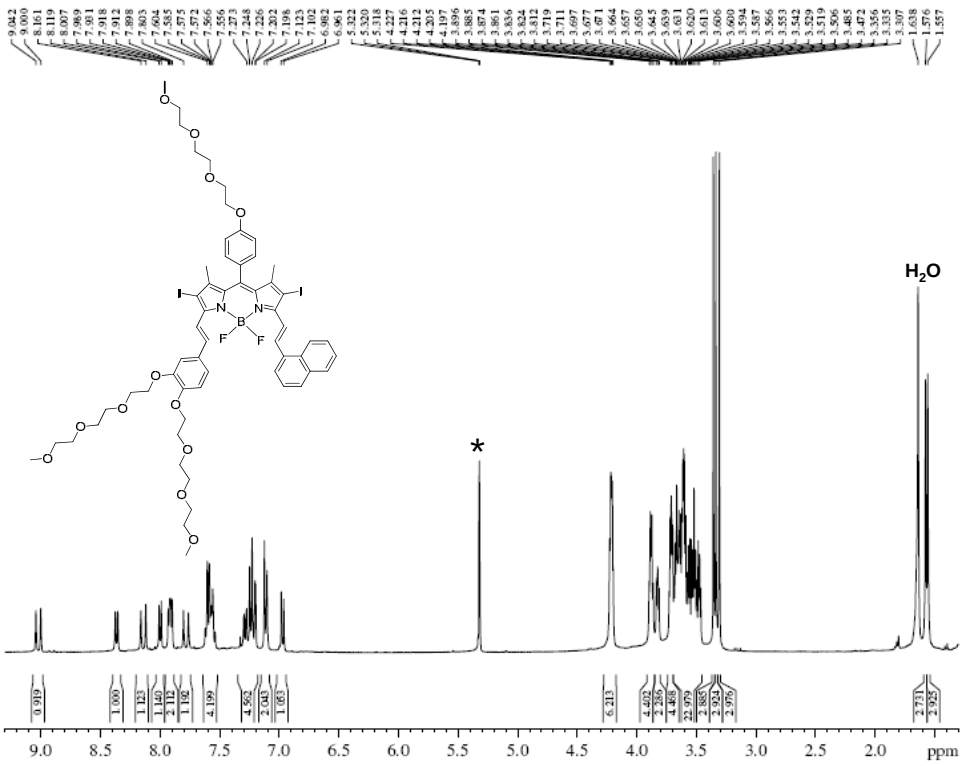

Fig. S12 ^{1}H NMR spectrum of **2** in CD_2Cl_2.

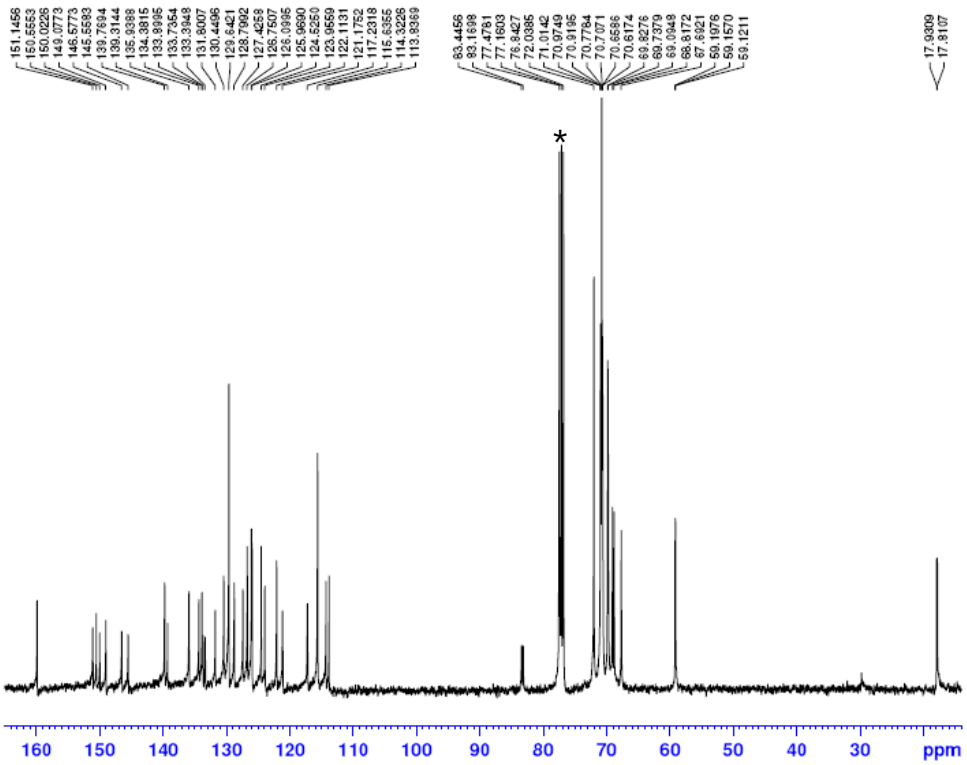

Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$.

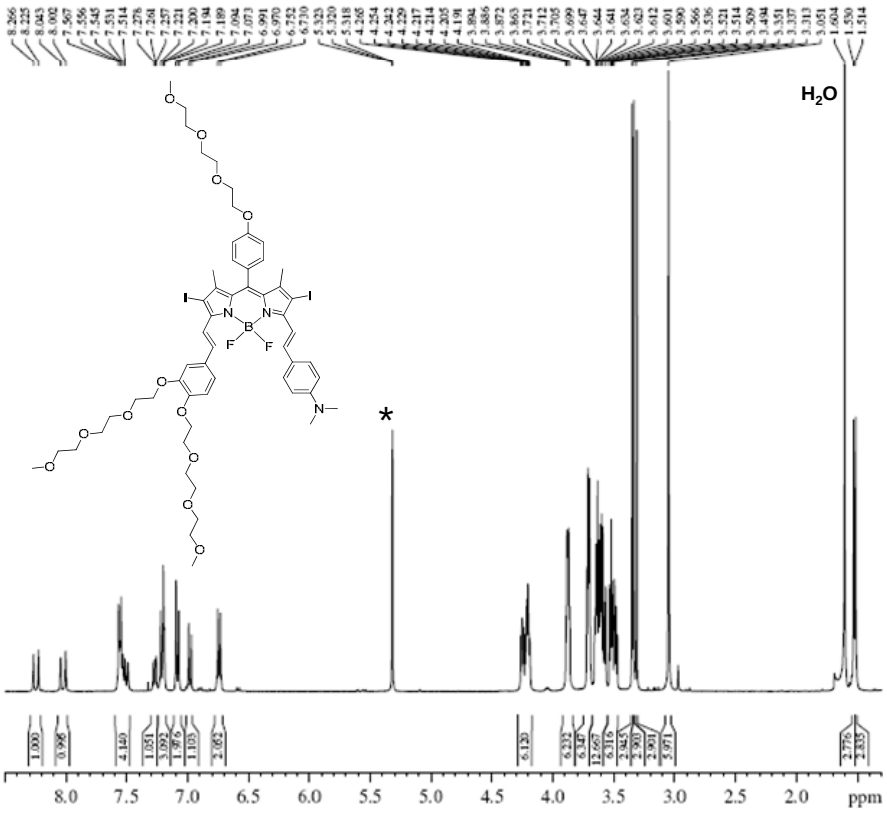

Fig. S14 ^{1}H NMR spectrum of **3** in CD_2Cl_2.

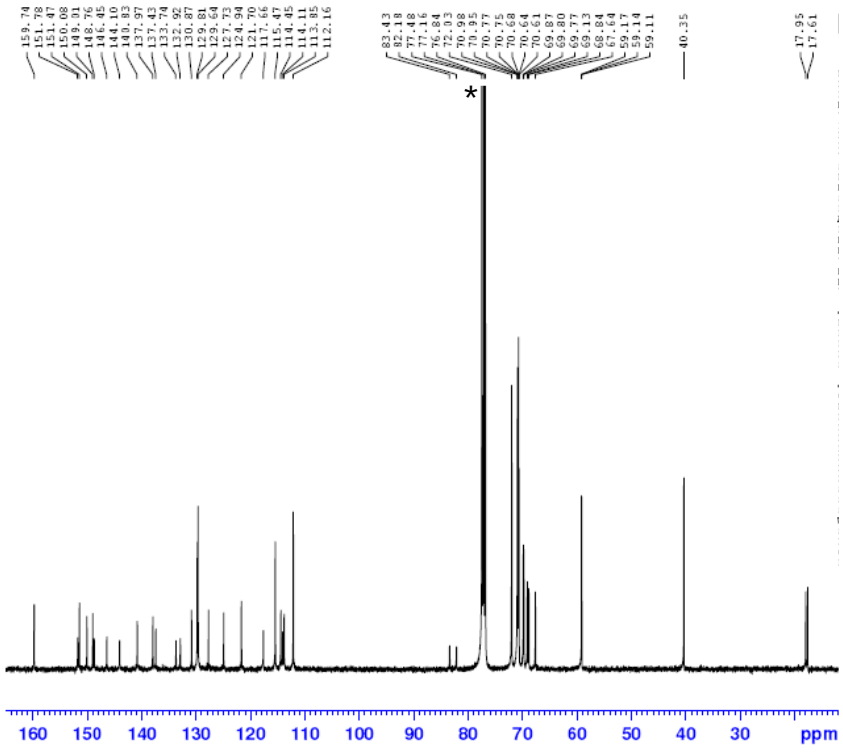

Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $CDCl_3$.

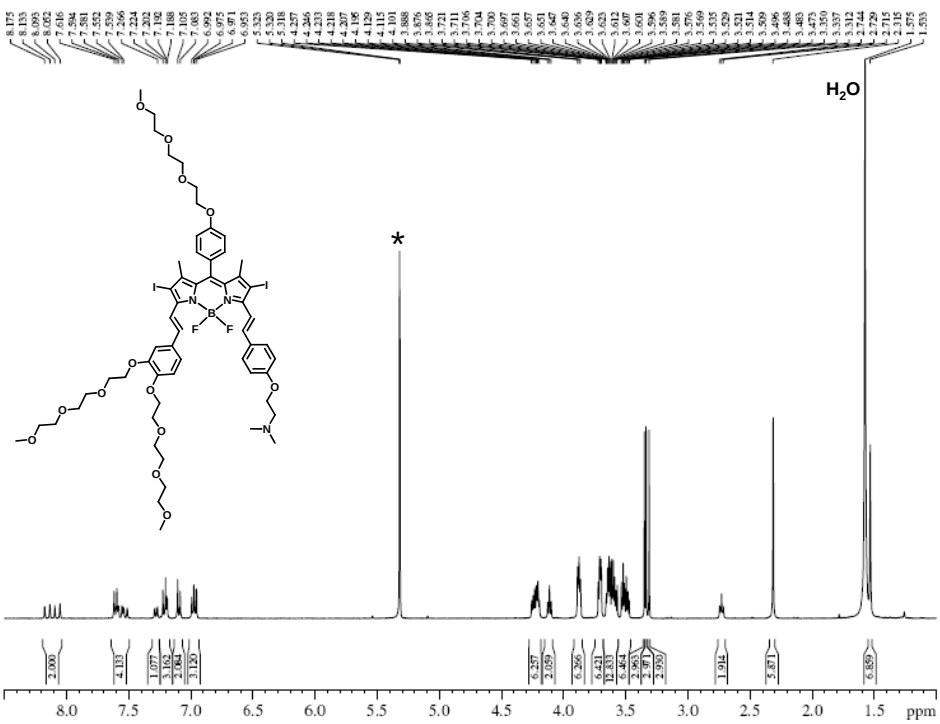

Fig. S16 ^{1}H NMR spectrum of **4** in CD_2Cl_2.

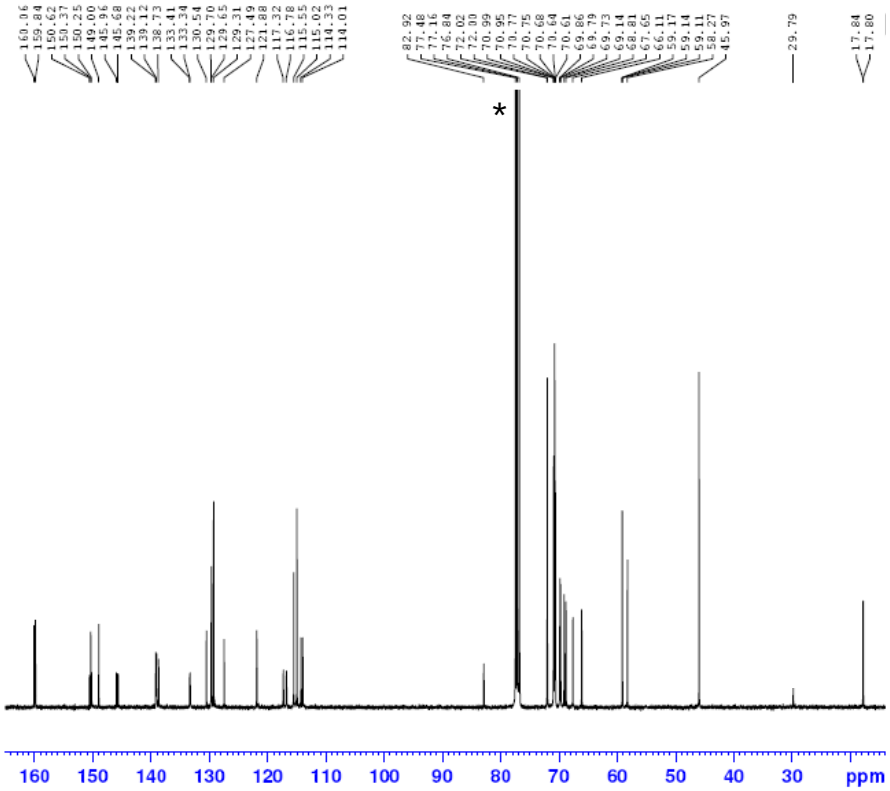

Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

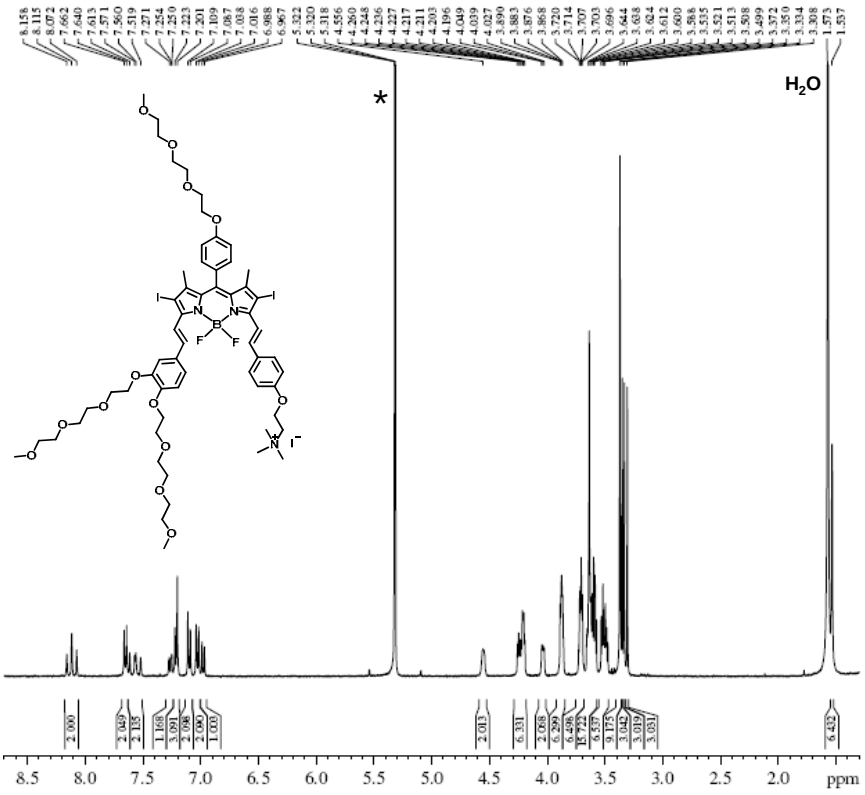

Fig. S18 ^{1}H NMR spectrum of **5** in CD_2Cl_2.

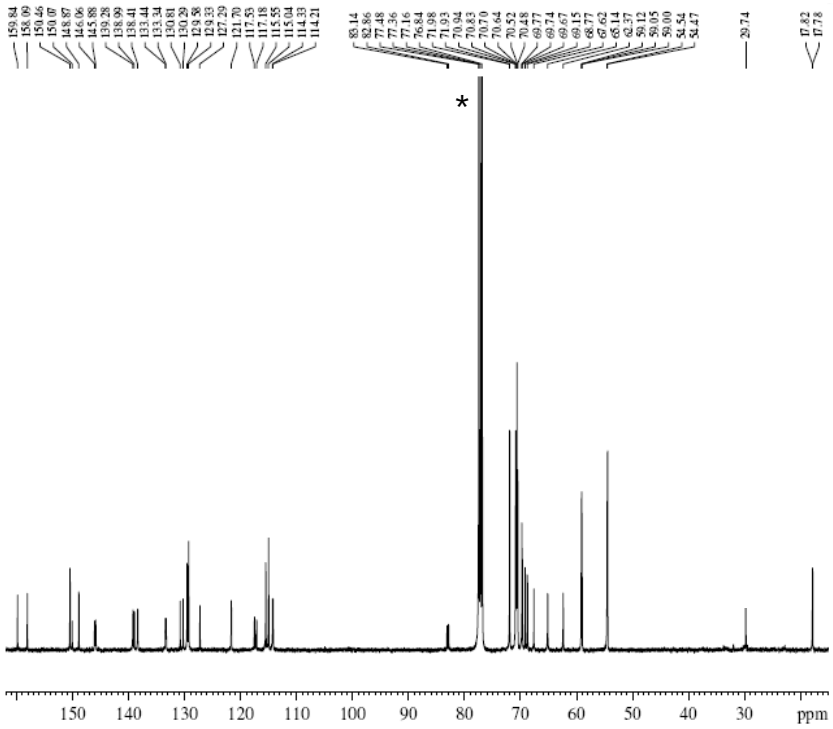

Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

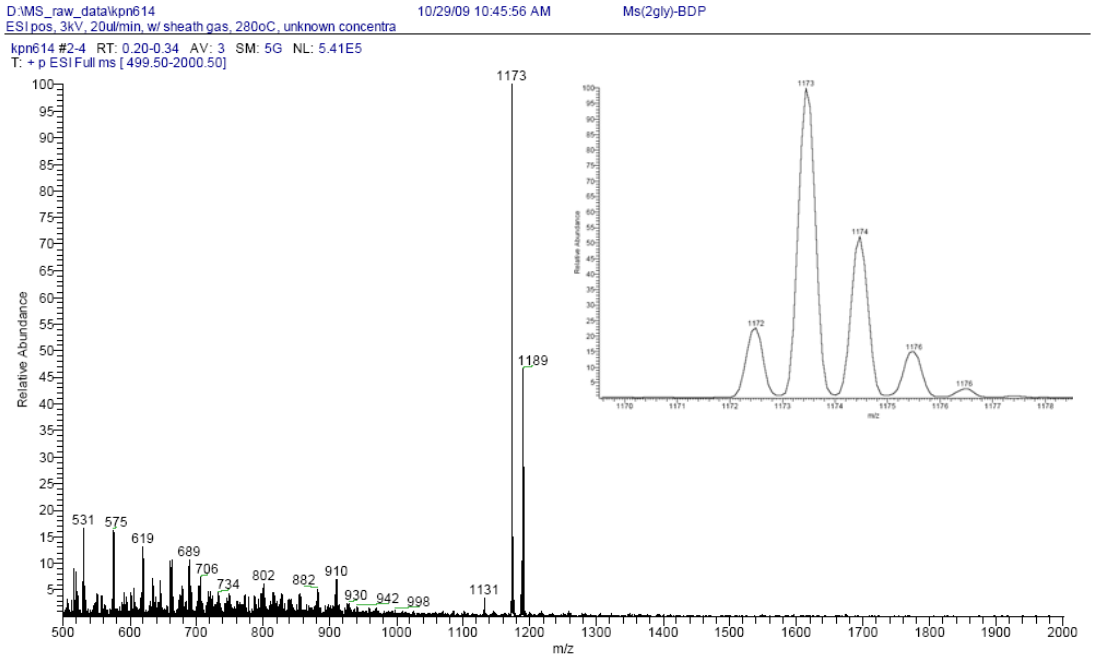

Fig. S20 ESI mass spectrum of **8**.

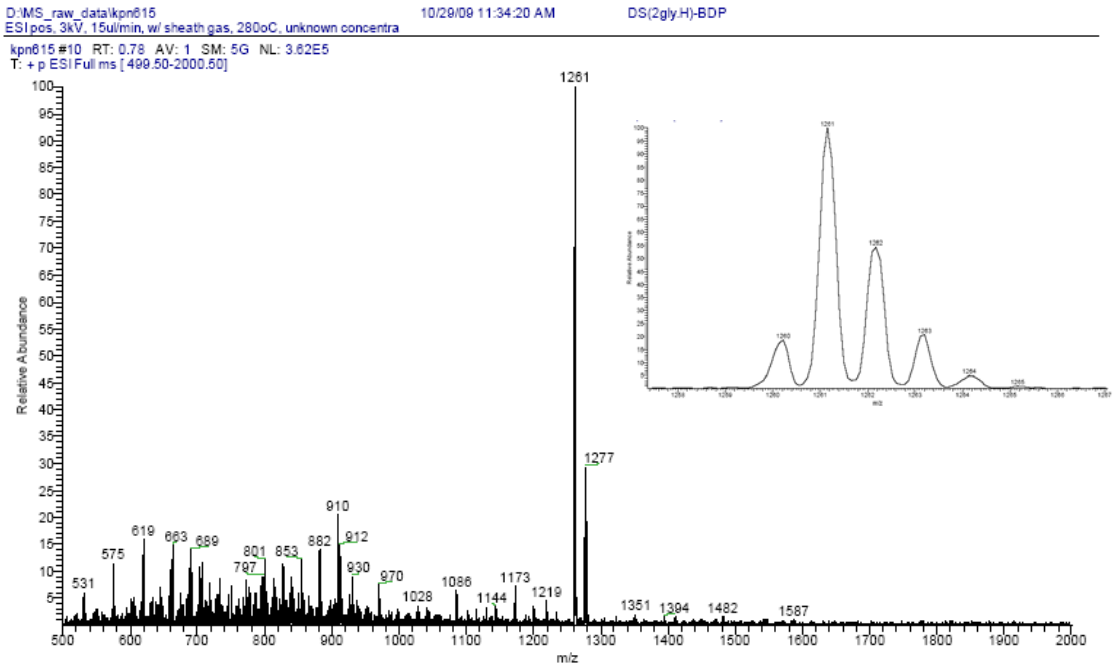

Fig. S21 ESI mass spectrum of **1**.

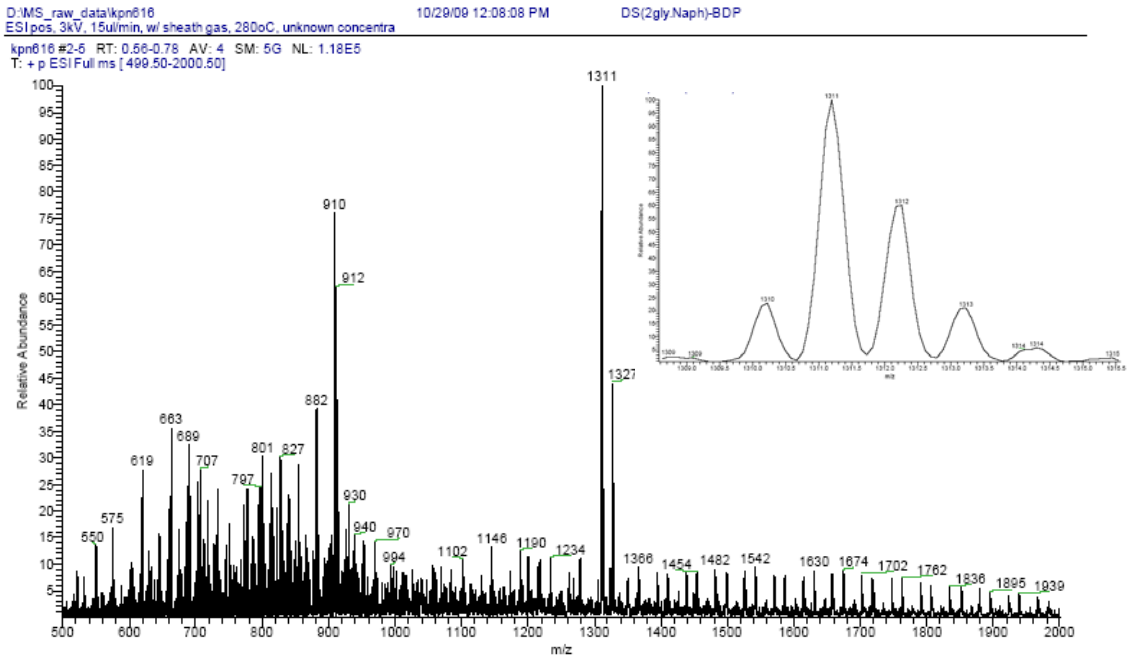

Fig. S22 ESI mass spectrum of **2**.

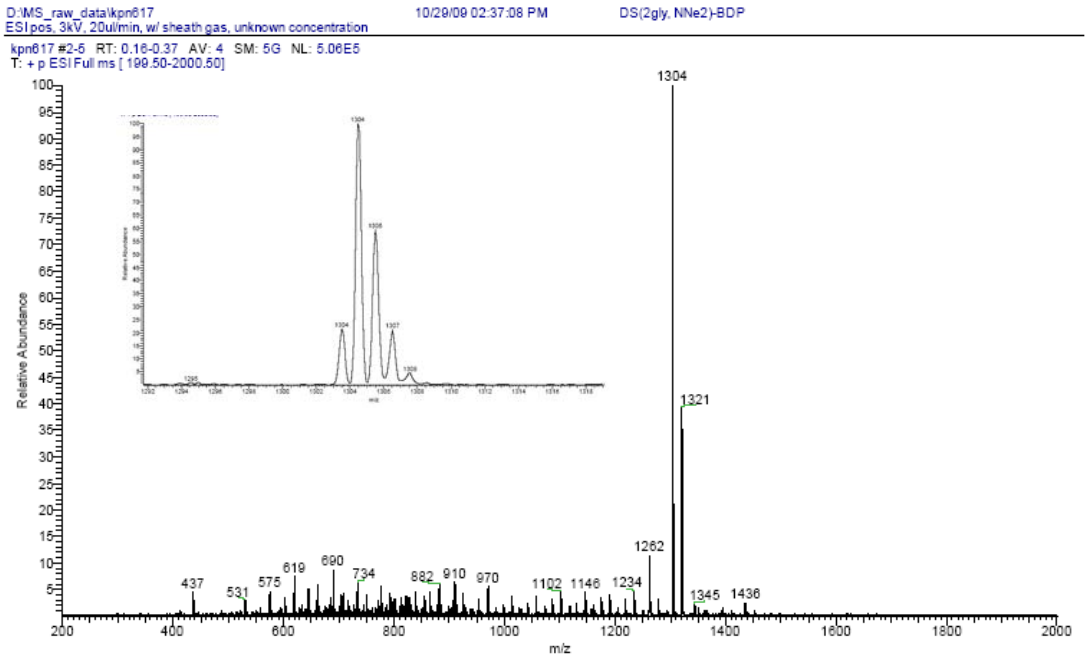

Fig. S23 ESI mass spectrum of **3**.

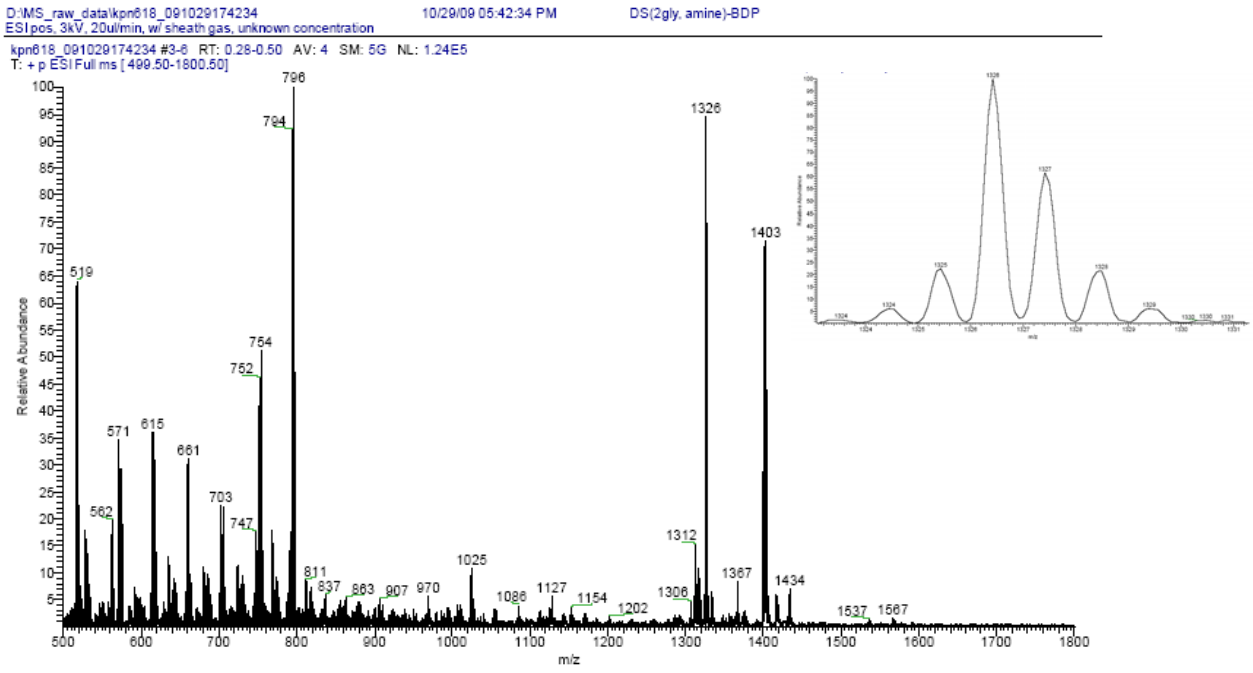

Fig. S24 ESI mass spectrum of **4**.

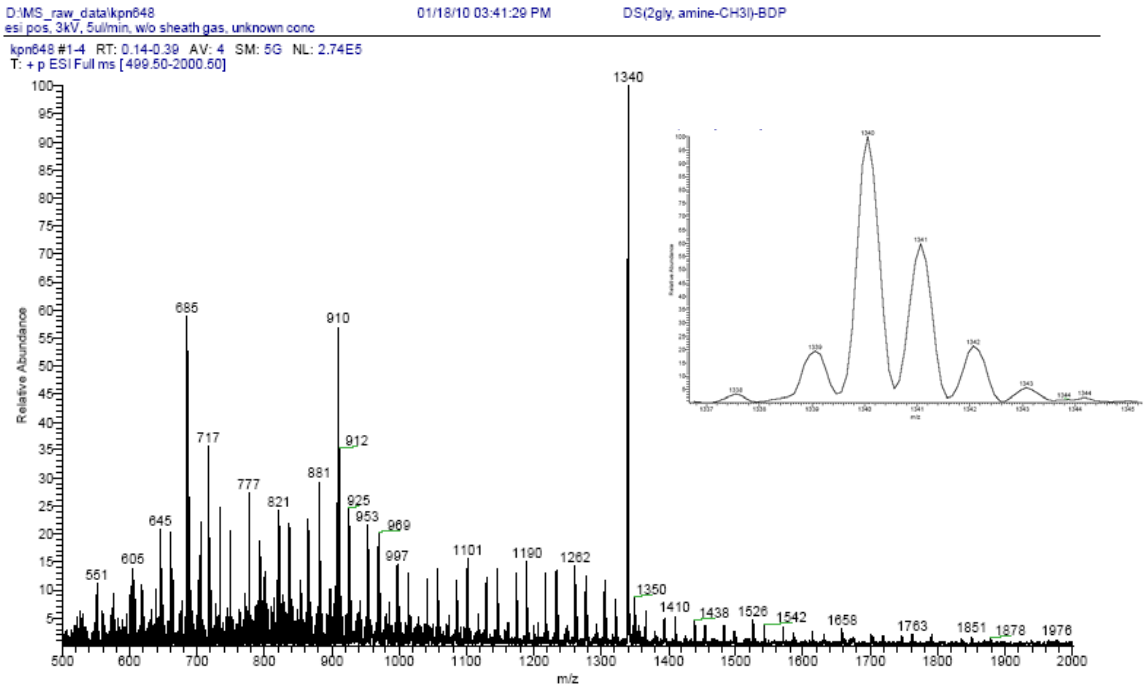

Fig. S25 ESI mass spectrum of **5**.