Selective Sensing of DNA, Live/Dead Cell and Histological Imaging based on Perylene Derivative

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S1. Experimental sections

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 600 MHz and a 400 MHz spectrometers. High-resolution mass spectroscopy (HRMS) was recorded on a MALDI-TOF model. UV-vis spectra were recorded in a quartz cell (light path 10 mm). Fluorescence spectra were obtained in a quartz cell (light path 10 mm). The absolute fluorescence quantum yield was determined by an absolute method using an integrating sphere excited at 633 nm using a 150 W Xenon lamp on an Edinburgh Analytical Instruments FLS980 spectrometer. The fluorescence imaging of tissue stained with a confocal laser scanning microscopy. The H&E images, **PMI-Man** based images and **PMI-Man** with eosin (P&E) based images were scanned using a light microscopy. The sequences of A-T DNA and G-C DNA are $p(dA{\cdot}dT)_2$ and $p(dG{\cdot}dC)_2$, respectively. Ct-DNA is a natural DNA. The sequences of ssDNA are 5'-CCAGTTCGTAGTAACCC-3'. Ct-DNA, AT DNA, GC DNA, ssDNA, poly A and Heparin are all purchased from Sigma-Aldrich.

Fluorescence imaging of PMI-Man with MCF-7 cells. MCF-7 cells (1×10^5 cells) and HepG2 cells (1×10^5 cells) were incubated overnight in a confocal dish at 37 °C. Afterward, **PMI-Man** (10 μM) was added. The cells were further incubated for 1 h. Then the cells were washed four times with PBS buffer.

Calcein AM and PI cell staining assay. MCF-7 cells (1×10^5 cells) were incubated overnight in a confocal dish at 37 °C. Afterward, **PMI-Man** (10 μM) was added. Then, calcein AM and PI dyes were used to stain the cells. The cells were further incubated for 1 h and then washed four times with PBS buffer. For the fluorescence imaging of the dead cells, **PMI-Man** (10 μM) was added to the cells, and then the calcein AM and PI dyes were used to stain the cells. The cells were first incubated for 0.5 h and frozen for 5 min, then further incubated for 30 min at 37 °C.

Stains. Stains were applied directly to tissue sections and intact tissues without further modification.

Tissue collection and processing. Formalin-fixed paraffin embedded tissue sections were obtained from the First Central Hospital of Baoding. We conducted histological staining experiments according to the principles of the Declaration of Helsinki, and all patients provided written informed consent. The protocol (NO.2018061) was approved by the Institutional Review Board of the First Central Hospital of Baoding. The tissues were cut into 4 μm thick sections and mounted on microscope slides. They were stored at room temperature until immediately prior to staining, at which point the sections were deparaffinized, stained according to the protocol below and imaged with confocal fluorescence microscopy and light microscopy.

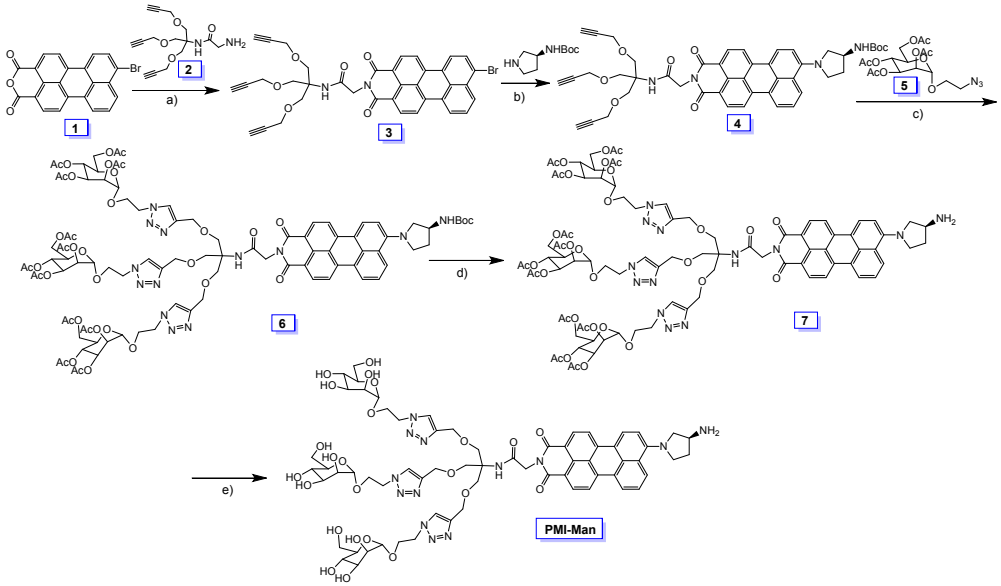
Tissue section staining with PMI-Man or costaining of PMI-Man and eosin. A section of tissue was deparaffinized by xylene twice for 30 min and 20 min, and then soaked in alcohol, 95% alcohol, 80% alcohol, 75% alcohol and water for 10 min. Then, the section of tissue was exposed to **PMI-Man** (100 μM) for 30 min, and dried in air. For staining with **PMI-Man** and eosin, the tissue was briefly exposed to **PMI-Man** (100 μM) for 30 min, followed by 2% eosin in ethanol for 5 min, and thoroughly rinsed with water to remove any excess stain.

For fluorescence imaging, tissue stained by **PMI-Man** or costained with **PMI-Man** and eosin was excited at 633 nm for **PMI-Man** and 488 nm for eosin, respectively, with a confocal laser scanning microscope (Zeiss Company).

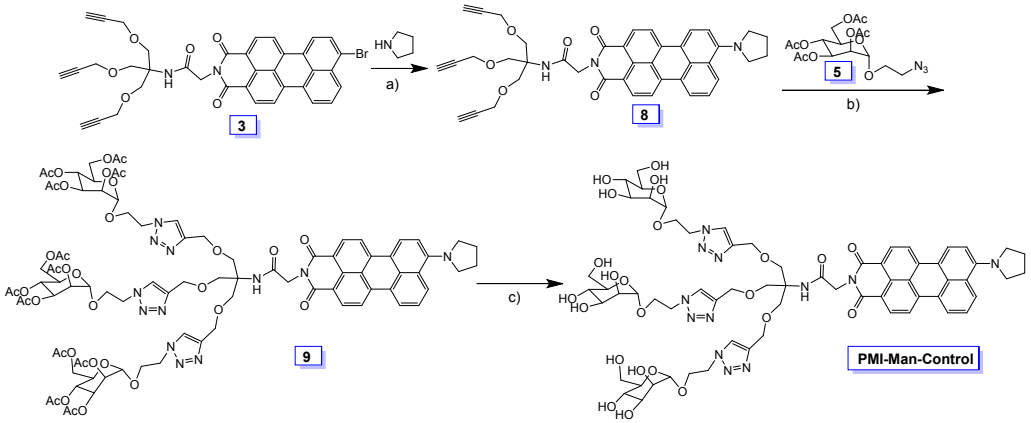
The H&E images, **PMI-Man** based images and **PMI-Man** with eosin (P&E) based images were scanned at 20X with a slide scanner using Olympus BX43 microscopy.

Synthesis.

Triple mannose moieties and a 3-aminopyrrolidine modified perylene monoimide derivative (**PMI-Man**) were synthesized in five steps (Scheme S1) from 9-bromo-perylene-3,4-dicarboxylic acid anhydride (**1**). Then perylene monoimide derivative **3** was obtained by reacting compound **1** with tripropargylated intermediate **2**. Furthermore, compound **4** was synthesized by substitution of 9-bromine with (*R*)-3-(Boc-amino)pyrrolidine. After that, **PMI-AcMan** conjugated with acetyl mannose was obtained by the click reaction of compound **4** with compound **5**. Finally, the target compound **PMI-Man** was produced by the deprotection of the Boc group and the acetyl group. In addition, **PMI-Man-Control** with pyrrolidine modification was synthesized as a control molecule (Scheme S2). The intermediates and the target molecule **PMI-Man** were fully characterized (Fig. S1-S24).



Scheme S1. (a) $Zn(AcO)_2$, pyridine; (b) K_2CO_3, NMP; (c) $CuSO_4 \cdot 5H_2O$, sodium ascorbate, THF/H_2O (1/1); (d) TFA, CH_2Cl_2; (e) MeONa, MeOH.



Scheme S2. (a) K_2CO_3, NMP; (b) $CuSO_4 \cdot 5H_2O$, sodium ascorbate, THF/H_2O (1/1); (c) MeONa, MeOH.

Compound 3: A mixture of compound **1** (100 mg, 0.31 mmol), compound **2** (136 mg, 0.47 mmol), and $Zn(OAc)_2$ (85.4 mg, 0.47 mmol) was dissolved in 20 mL of pyridine. The mixture was reacted at 115 °C for 12 h in a N_2 atmosphere. When the reacted solution was cooled to room temperature, the pyridine solvent was evaporated *in vacuo*. The sample was purified by silica gel column chromatography with the eluent $CH_2Cl_2/CH_3COOCH_2CH_3$ (v/v = 20/1) to give compound **3** (128 mg) in 69.2% yield. m.p. 166.4-167.2 °C. ^{1}H NMR (CF_3COOD, 600 MHz): δ 2.45 (s, 3H, -C≡CH), 4.07 (s, 6H, -CH_2), 4.30 (s, 6H, -CH_2), 5.16 (2H, -CH_2), 7.29 (t, J = 12.6 Hz, 1H), 7.37 (d, J = 12.0 Hz, 1H), 7.47 (d, J = 12.0 Hz, 1H), 7.66 (d, J = 12.0 Hz, 1H), 7.78 (d, J = 12.6 Hz, 1H), 7.85 (d, J = 9.6 Hz, 2H), 8.09 (d, J = 11.4 Hz, 1H), 8.14 (d, J = 12.0 Hz, 1H); ^{13}C NMR (CF_3COOD, 150 MHz): δ 36.75, 52.04, 54.15, 61.57, 68.71, 70.03, 105.54, 106.57, 108.35, 109.39, 110.73, 112.87, 113.18, 117.24, 117.70, 118.20, 119.67, 119.89, 120.15, 120.38, 120.65, 121.83, 123.51, 123.79, 124.55, 125.85, 130.68, 130.82, 158.15, 164.26; HRMS (MALDI-TOF): calcd. for $C_{37}H_{27}BrN_2NaO_6$, 697.0950, found 697.0927.

Compound 4: In a 50 mL flask, 100 mg (0.15 mmol) of compound **3** was dissolved in 20 mL of *N*-methyl pyrrolidone (NMP). Then 270 mg (1.48 mmol) of (*R*)-3-(Boc-amino)pyrrolidine was added, and 41 mg (0.30 mmol) of K_2CO_3 was further added. The mixture was reacted at 110 °C for 24 h under a N_2 atmosphere. After the mixture was cooled to room temperature, 200 mL of HCl (1.0 mol/L) was added, and the precipitate was filtered and washed with water. The obtained solid was

purified by column chromatography with the eluent $CH_2Cl_2/CH_3COOCH_2CH_3$ (v/v = 10/1) to afford pure compound **4** with a yield of 35.0%. m.p. >250 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.48 (s, 9H, -Boc), 2.06 (M, 1H), 2.37 (M, 1H), 2.41 (T, J = 2.4 Hz, -CH), 3.50 (m, 1H), 3.55 (m, 1H), 3.81 (m, 1H), 3.87 (m, 1H), 3.91 (s, 6H, -CH_2), 4.17 (d, J = 2.4 Hz, 6H), 4.44 (br, 1H), 4.85 (d, J = 3.0 Hz, 2H), 5.18 (br, 1H, -NH), 6.12 (s, 1H, Ar-H), 6.86 (d, J = 9.0 Hz, Ar-H), 7.45 (t, J = 8.4 Hz, 1H, Ar-H), 7.97 (d, J = 8.4 Hz, 1H, Ar-H), 8.11 (d, J = 8.4 Hz, Ar-H), 8.14 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H, Ar-H), 8.28 (d, J = 7.8 Hz, 1H, Ar-H), 8.36 (dd, J = 1.8 Hz, 7.8 Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 26.91, 28.54, 31.87, 43.31, 50.45, 50.85, 58.79, 59.73, 68.65, 74.76, 79.75, 110.91, 116.39, 117.96, 118.43, 119.12, 123.97, 125.21, 125.30, 125.71, 128.08, 128.48, 129.70, 130.67, 131.32, 137.49, 137.99, 149.82, 155.69, 163.61, 167.52; HRMS (MALDI-TOF): calcd. for $C_{46}H_{44}N_4O_8$, 780.3139, found 780.3159.

Compound 6: The mixture of compound **4** (50 mg, 0.064 mmol) and compound **5** (107 mg, 0.26 mM) was dissolved by THF (20 mL). Then, a water solution of $CuSO_4{\cdot}5H_2O$ (13 mg, 0.064 mM) and sodium ascorbate (17 mg, 0.064 mM) was added. The reaction mixture was stirred for 10 h at 55 °C under a N_2 atmosphere. The reaction solvents were evaporated under vacuum. The residue was resolved by CH_2Cl_2 and purified by silica-gel column chromatography using CH_2Cl_2/CH_3OH (v/v = 30/1) as the eluent. Compound **6** (84 mg) was obtained with a yield of 65.0%. m.p. 115.2-116.4 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.47 (s, 9H, Boc), 1.98 (s, 9H, -CH_3), 2.01 (s, 9H, -CH_3), 2.08 (s, 9H, -CH_3), 2.12 (s, 9H, -CH_3), 2.37 (m, 1H), 3.48 (m, 1H), 3.57 (m, 1H), 3.59 (br, 3H), 3.80-3.88 (8H), 3.93 (m, 3H), 4.03 (dd, J = 1.8 Hz, 12.6 Hz, 3H), 4.15 (m, 3H), 4.21 (dd, J = 4.8 Hz, 12.6 Hz, 3H), 4.43 (br, 1H), 4.65 (m, 12H), 4.83 (s, 3H), 4.90 (s, 2H), 4.97 (s, 1H), 5.24 (s, 8H), 6.65 (s, 1H), 6.95 (d, J = 8.4 Hz, 1H, Ar-H), 7.54 (t, J = 7.8 Hz, 1H, Ar-H), 7.84 (s, 3H, Triazole-H), 8.18 (d, J = 8.4 Hz, 1H, Ar-H), 8.23 (d, J = 8.4 Hz, 1H, Ar-H), 8.31 (d, J = 9.0 Hz, 1H, Ar-H), 8.33 (d, J = 8.4 Hz, 1H, Ar-H), 8.45 (t, J = 7.8 Hz, 2H, Ar-H), 8.49 (d, J = 8.4 Hz, 1H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.09, 20.67, 20.72, 20.81, 22.67, 28.43,

29.33, 29.67, 31.90, 49.52, 51.05, 58.81, 60.13, 62.22, 64.85, 65.71, 66.30, 68.88, 68.98, 69.19, 79.77, 97.53, 111.29, 117.37, 117.48, 118.88, 119.28, 120.16, 124.06, 124.49, 125.98, 128.08, 128.76, 129.10, 130.21, 131.24, 131.72, 138.07, 138.51, 145.33, 150.24, 155.54, 163.86, 163.92, 167.29, 169.67, 169.97, 170.03, 170.60; HRMS (MALDI): calcd. for $C_{94}H_{113}N_{13}NaO_{38}$, 2055.7241, found 2055,7209.

Compound 7: In a 25 mL flask, 100 mg (0.052 mmol) of compound **6** was dissolved in 5 mL of CH_2Cl_2. Five milliliters of CF_3COOH was carefully added at a temperature of 0 °C. The mixture was stirred for 2 h. Then, the solvent was removed under reduced pressure. The solid was dissolved in 50 mL of CH_2Cl_2, washed with $NaHCO_3$ aqueous solution, and dried with anhydrous sodium sulfate. The sample was obtained without any purification. m.p. 153.7-155.1 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.96 (s, 9H, -$COCH_3$), 2.00 (s, 9H, -$COCH_3$), 2.07 (s, 9H, -$COCH_3$), 2.11 (s, 9H, -$COCH_3$), 2.28 (brs, 1H), 2.78 (brs, 2H, -NH_2), 3.52 (m, 2H), 3.54 (m, 3H), 3.83-3.93 (12H), 4.01 (m, 1H), 4.04 (m, 2H), 4.10-4.21 (6H), 4.64 (m, 12H), 4.82 (s, 3H), 4.87 (m, 2H), 5.22-5.23 (9H), 6.72 (d, J = 12.0 Hz, 1H), 6.83 (s, 1H), 7.35 (m, 1H), 7.79 (m, 1H), 7.84 (s, 3H, triazole-H), 7.98 (m, 2H), 8.13-8.17 (4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.65, 20.69, 20.78, 42.98, 49.52, 51.23, 60.19, 62.23, 64.86, 65.76, 66.31, 68.92, 68.97, 69.22, 97.57, 110.98, 116.99, 117.19, 118.66, 119.06, 119.60, 123.99, 124.29, 124.43, 125.84, 126.05, 128.26, 128.60, 129.04, 130.13, 131.09, 131.64, 138.04, 138.51, 145.33, 150.44, 163.79, 163.84, 167.33, 169.61, 169.89, 169.93, 170.52; HRMS (MALDI): calcd. for $C_{89}H_{106}N_{13}O_{36}$ 1932.6863, found 1932.6852.

Compound PMI-Man: Compound **7** (100 mg, 0.052 mM) and MeONa (67 mg, 1.24 mmol) were dissolved in anhydrous MeOH (10 mL). The reaction mixture was stirred at room temperature for 10 h. The reaction mixture was placed in a cellulose dialysis tube (cutoff 800) and dialyzed against water for 2 d. The compound **PMI-Man** (67 mg) was obtained through lyophilization with a yield of 90.1%. m.p. 133.5-135.3 °C. ^{1}H NMR (DMSO-d_6+D_2O, 600 MHz): δ 1.81 (m, 1H), 2.13 (m, 1H), 3.19 (t, J = 7.8 Hz, 3H), 3.43-3.44 (5H), 3.56 (s, 3H), 3.62-3.68 (12H), 3.83 (m, 6H), 3.97

(m, 4H), 4.54 (brs, 10H), 4.59-4.62 (4H), 4.65 (s, 3H), 4.73 (br, 3H), 6.84 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.53 (t, *J* = 6.6 Hz, 1H), 8.07 (s, 3H, Triazole-H), 8.13 (d, *J* = 7.2 Hz, 1H, Ar-H), 8.22 (d, *J* = 7.2 Hz, 1H, Ar-H), 8.28 (d, *J* = 7.2 Hz, 1H, Ar-H), 8.31-8.37 (3H, Ar-H), 8.54 (d, *J* = 6.0 Hz, 1H, Ar-H); ^{13}C NMR (DMSO-d_6+D_2O, 100 MHz): δ 29.75, 34.19, 42.59, 49.79, 51.11, 51.36, 60.31, 61.43, 64.64, 65.35, 67.06, 68.41, 70.41, 71.12, 74.36, 100.21, 110.38, 115.61, 116.91, 117.25, 118.23, 118.91, 124.31, 124.66, 125.38, 127.47, 127.56, 127.87, 128.72, 129.24, 129.87, 130.91, 130.97, 131.49, 137.95, 138.00, 138.64, 144.54, 150.87, 163.28, 163.40, 167.40; HRMS: calcd. for $C_{65}H_{85}N_{13}NaO_{24}$, 1450.5415, found 1450.5432.

Compound 8: The reaction and purification processes of compound **8** were similar with compound **4** with a yield of 35.0%. m.p. 98.3-100.1 °C. ^{1}H NMR (CF_3COOD, 600 MHz): δ 2.27 (s, 3H, -C≡CH), 2.36 (m, 4H, -CH_2), 3.77 (m, 2H), 3.93 (s, 6H, -CH_2), 4.14 (s, 6H, -CH_2), 4.25 (m, 2H), 4.99 (s, 2H, -CH_2), 7.76 (m, 2H, Ar-H), 7.98 (d, J = 8.4 Hz, 1H, Ar-H), 8.35 (d, J = 5.4 Hz, 1H, Ar-H), 8.42 (m, 3H, Ar-H), 8.45 (d, J = 8.4 Hz, 1H, Ar-H), 8.50 (d, J = 8.4 Hz, Ar-H); ^{13}C NMR (CF_3COOD, 150 MHz): δ 16.21, 16.59, 16.93, 39.81, 43.25, 51.93, 52.78, 53.98, 61.48, 68.47, 68.52, 69.90, 104.82, 114.71, 115.14, 116.91, 118.93, 119.18, 119.32, 121.52, 122.39, 122.70, 124.57, 126.47, 130.28, 130.41, 131.05, 142.94, 143.42, 158.70, 158.76, 164.17; HRMS (MALDI-TOF): calcd. for $C_{41}H_{35}N_3NaO_6$, 688.2424, found 688.2429.

Compound 9: The reaction and purification processes of compound **9** were similar with compound **6** with a yield of 66.0%. m.p. 105.1-106.3 °C. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.96 (s, 9H, -$COCH_3$), 1.99 (s, 9H, -$COCH_3$), 2.06 (13H, -$COCH_3$, -CH_2), 2.10 (s, 9H, -$COCH_3$), 3.61 (m, 6H), 3.83-3.92 (9H), 4.00 (d, J = 16.8 Hz, 3H), 4.11-4.20 (6H), 4.62 (s, 12H), 4.81-4.86 (3H), 5.21-5.27 (10H), 6.66 (s, 1H), 6.81 (d, J = 11.4 Hz, 1H), 7.43 (m, 1H), 7.83 (s, 3H), 7.97 (d, J = 9.0 Hz, 1H), 8.15 (m, 2H), 8.24 (d, J = 12.6 Hz, 1H), 8.31-8.36 (3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 20.64, 20.68, 20.76, 25.84, 29.64, 42.95, 49.49, 53.13, 53.42, 60.11, 62.22, 64.89, 65.74, 66.30, 68.89, 68.97, 69.21, 97.54, 110.48, 116.91, 117.01, 118.68, 119.00,

119.17, 123.98, 124.57, 125.75, 126.11, 126.41, 128.60, 128.71, 129.34, 130.42, 131.23, 131.78, 138.34, 138.91, 145.38, 151.04, 163.82, 163.92, 167.28, 169.63, 169.89, 169.94, 170.53; HRMS (MALDI-TOF): calcd. for $C_{89}H_{105}N_{12}O_{36}$, 1918.6788, found 1918.6707.

Compound PMI-Man-Control: The reaction and purification processes of compound **PMI-Man-Control** were similar with compound **PMI-Man** with a yield of 89.5%. m.p. 145.1-146.7 °C. ^{1}H NMR (DMSO-d6, 600 MHz): δ 1.90 (s, 4H), 3.12 (s, 4H), 3.39-3.63 (25H), 3.93 (s, 3H), 4.50-4.62 (19H), 6.41 (s, 1H), 7.22 (s, 1H), 7.49 (m, 1H), 7.69-8.03 (9H); ^{13}C NMR (DMSO-d6, 150 MHz): δ 25.93, 42.58, 49.78, 53.23, 60.30, 61.40, 64.60, 65.34, 67.00, 68.36, 70.39, 71.08, 74.33, 100.16, 110.54, 110.56, 115.63, 116.91, 117.31, 118.22, 118.94, 124.29, 124.66, 125.42, 127.47, 127.87, 129.27, 129.90, 130.93, 131.47, 138.05, 138.69, 144.52, 150.82, 163.28, 163.40, 167.35; HRMS (MALDI-TOF): calcd. for $C_{65}H_{81}N_{12}O_{24}$, 1413.5487, found 1413.5455.

S2. Additional Figures

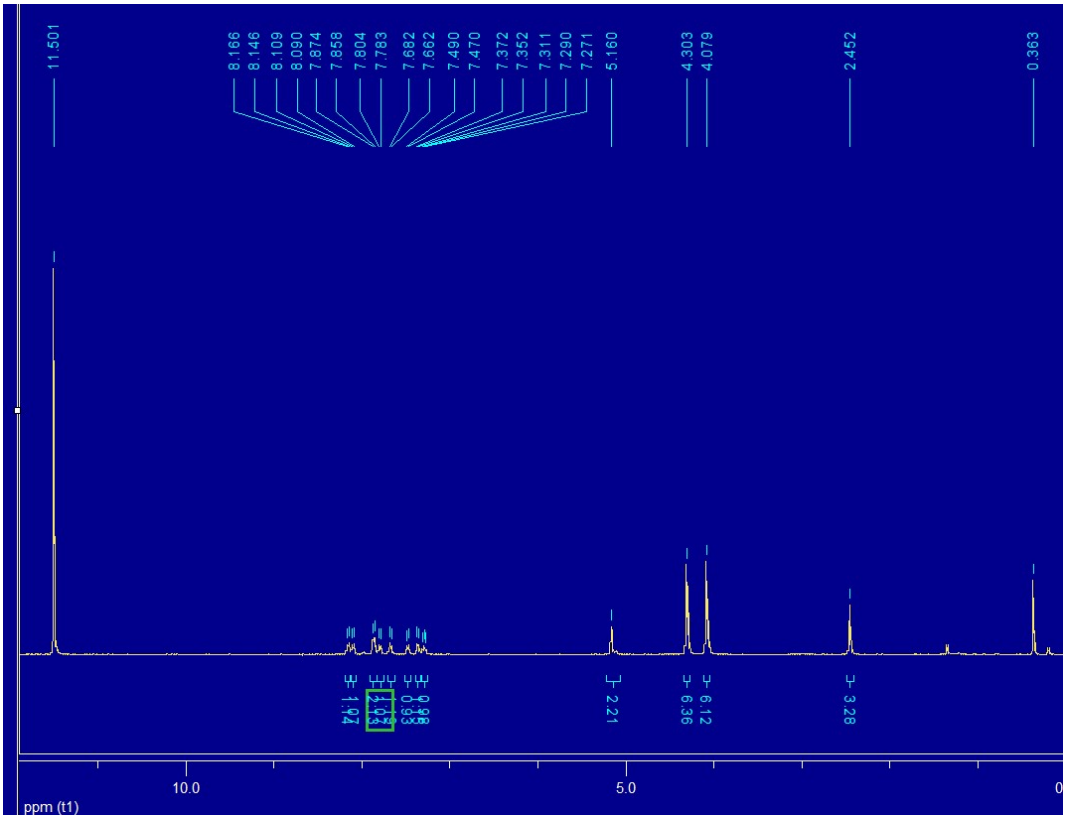


Fig. S1 ^{1}H NMR (CF_3COOD, 600 MHz) of compound **3**.

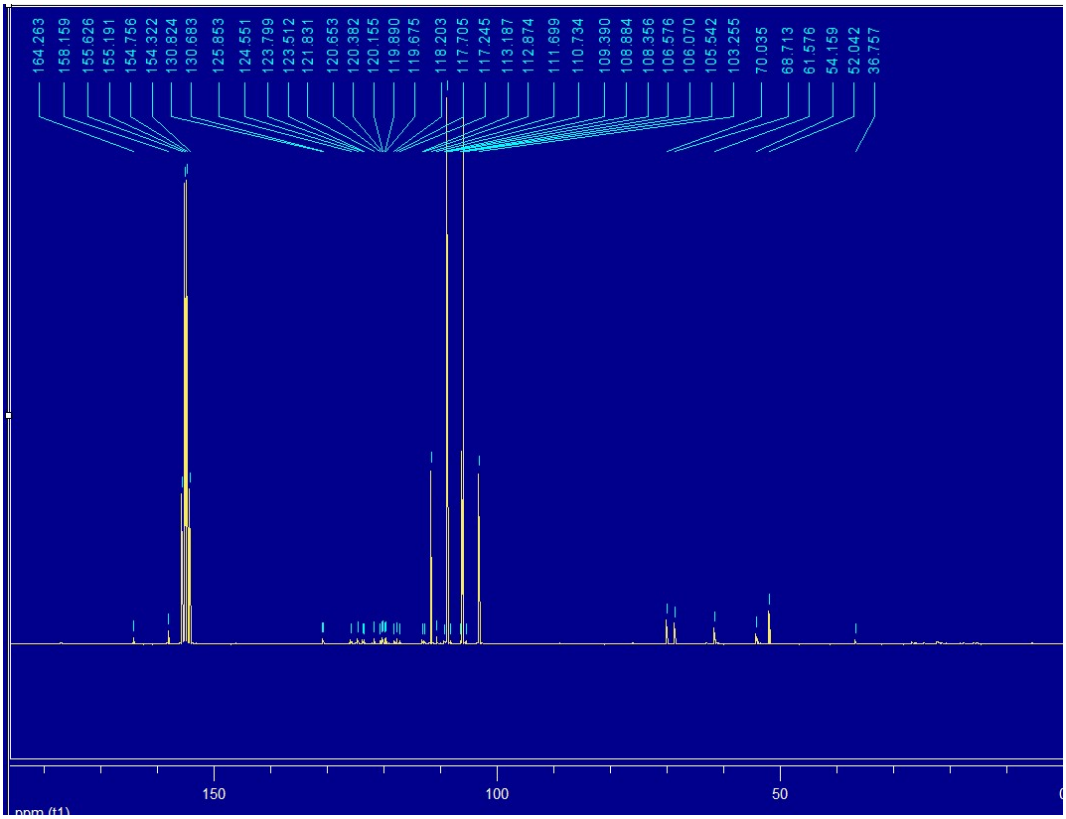
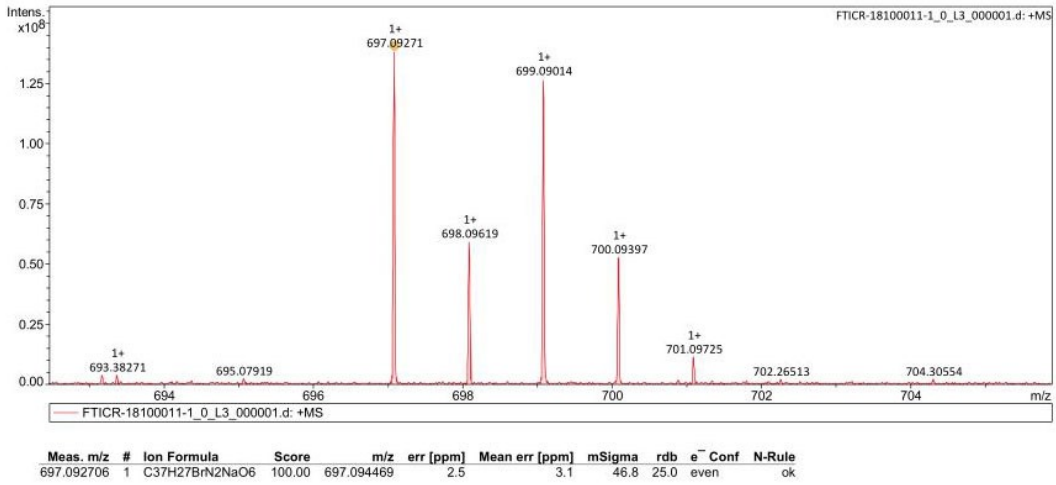


Fig. S2 ^{13}C NMR (CF_3COOD, 150 MHz) of compound **3**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
697.092706	1	C37H27BrN2NaO6	100.00	697.094469	2.5	3.1	46.8	25.0	even	ok

Fig. S3 HRMS (MALDI-TOF) of compound **3**.

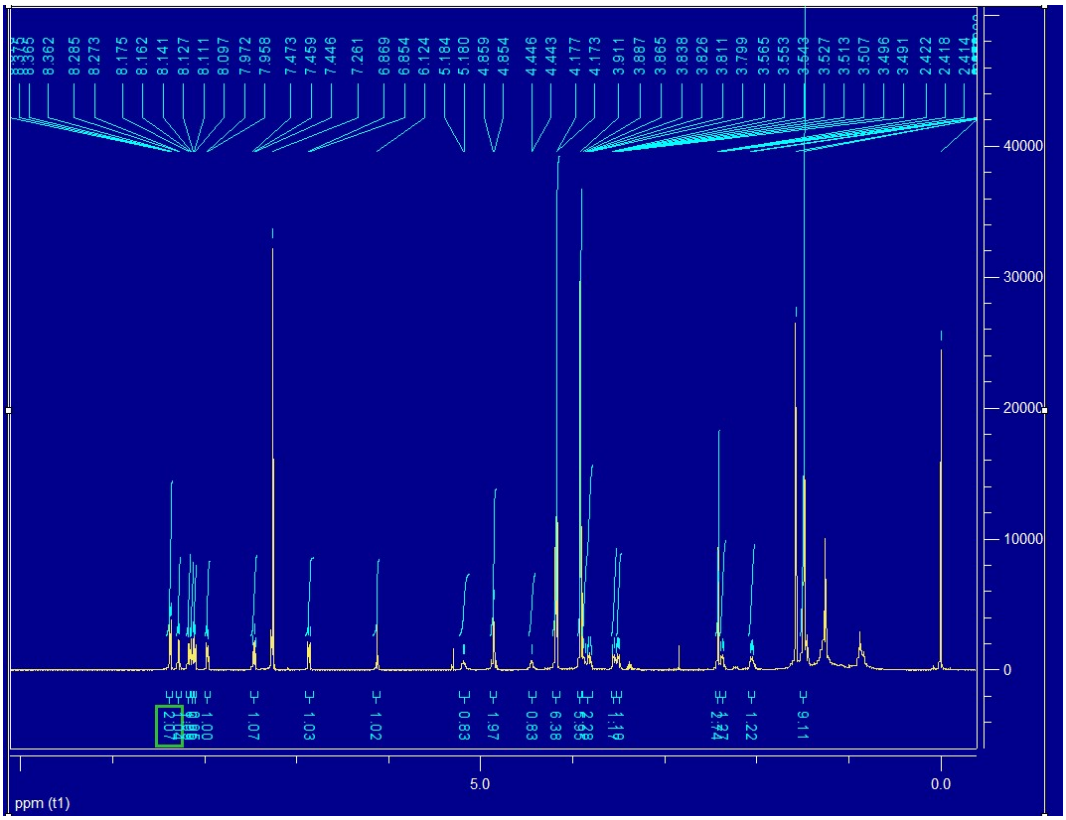


Fig. S4 ^{1}H NMR ($CDCl_3$, 600 MHz) of compound **4**.

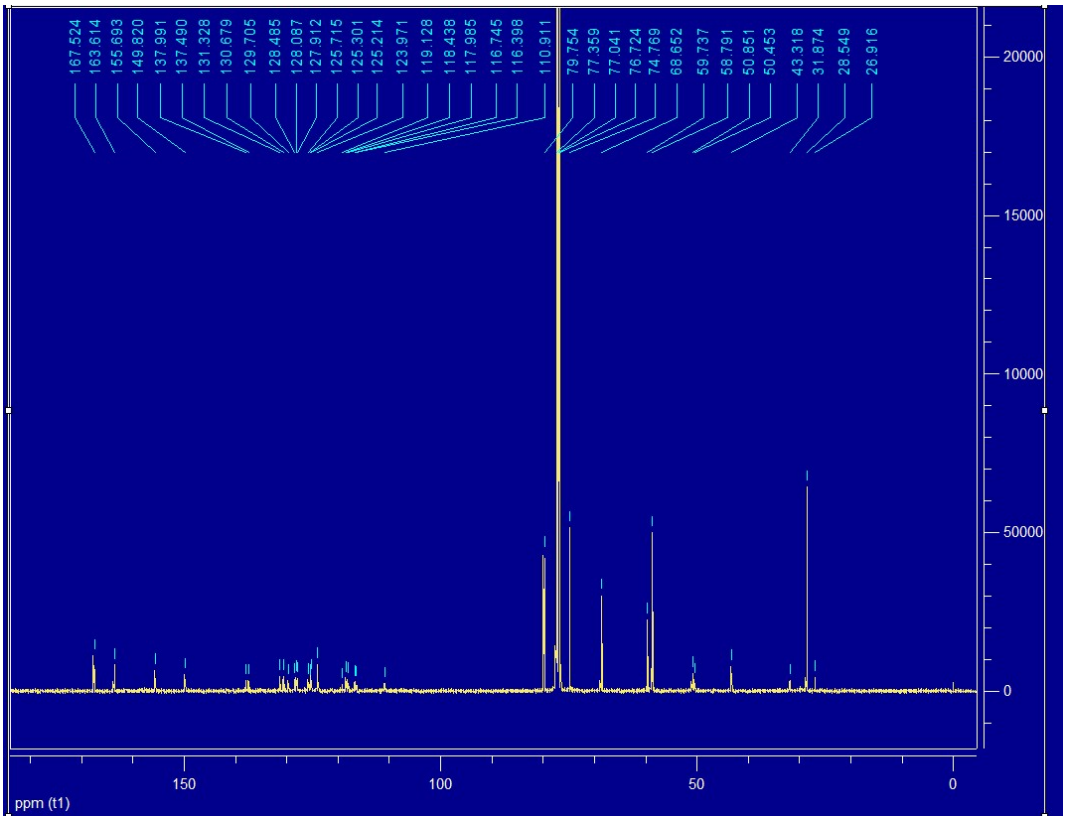
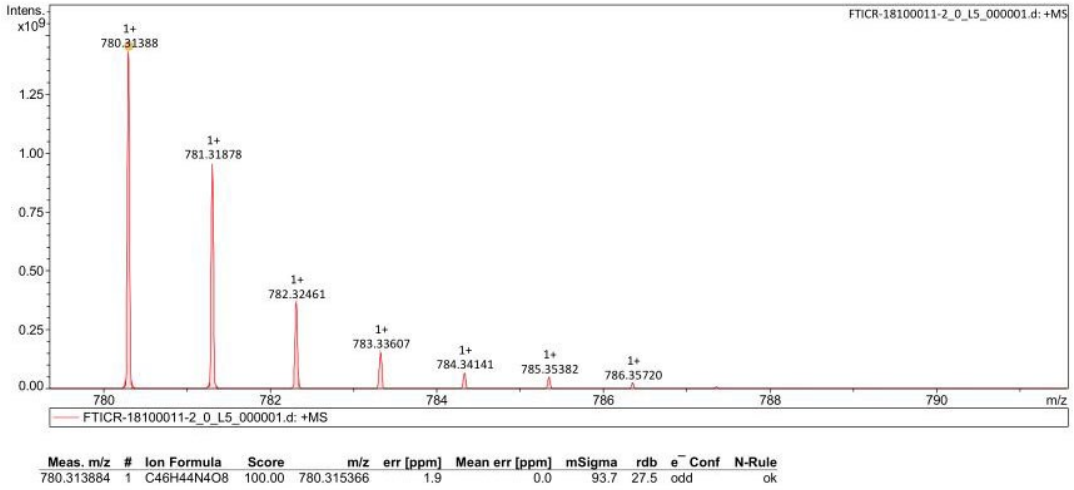


Fig. S5 ^{13}C NMR ($CDCl_3$, 150 MHz) of compound **4**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
780.313884	1	C46H44N4O8	100.00	780.315366	1.9	0.0	93.7	27.5	odd	ok

Fig. S6 HRMS (MALDI-TOF) of compound **4**.

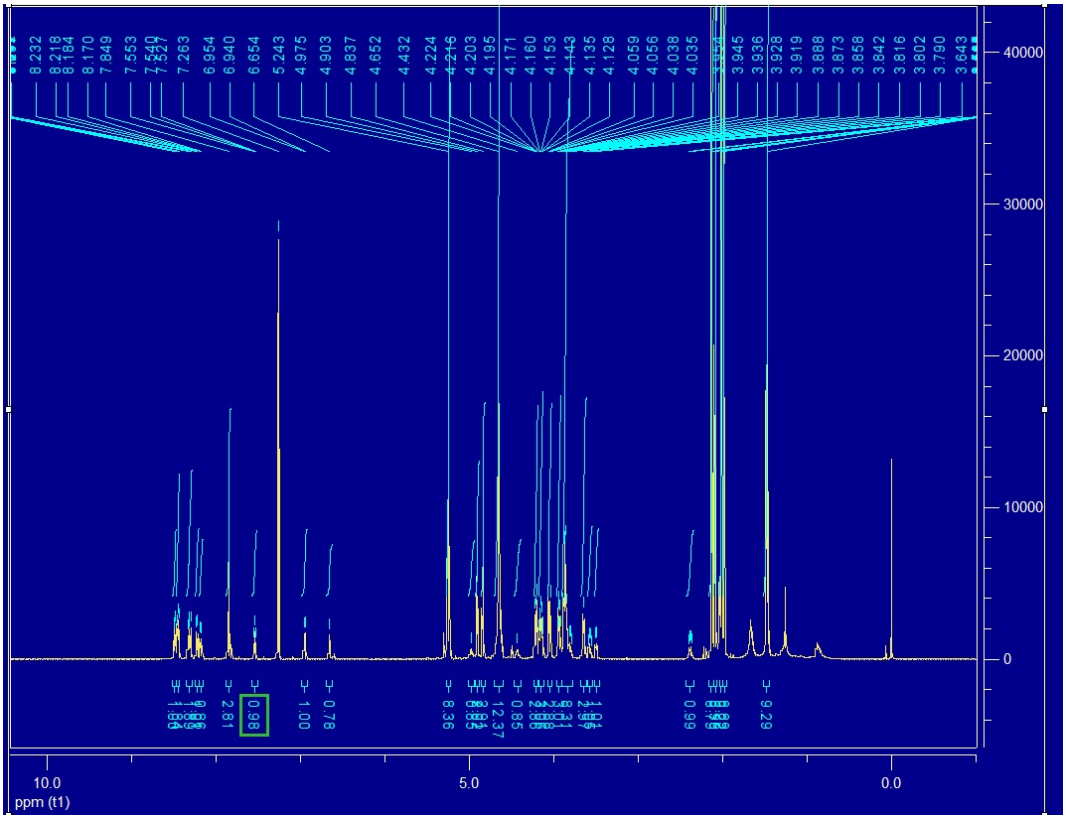


Fig. S7 ^{1}H NMR ($CDCl_3$, 600 MHz) of compound **6**.

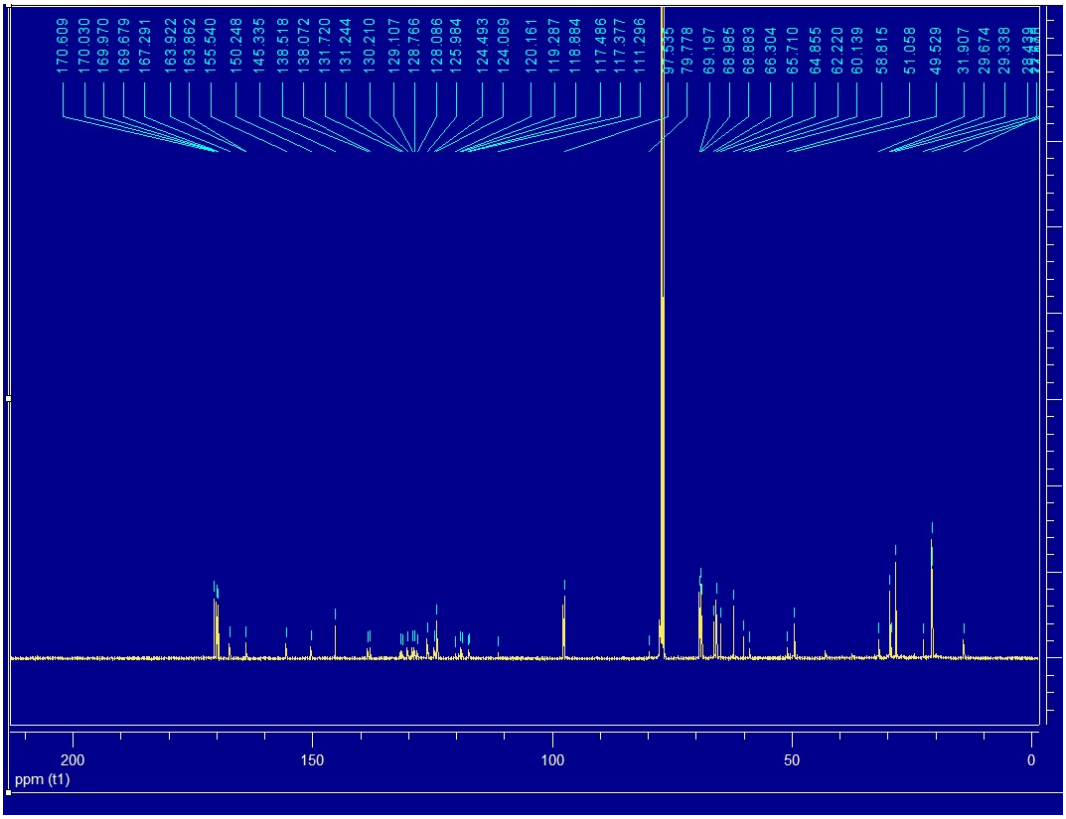


Fig. S8 ^{13}H NMR ($CDCl_3$, 100 MHz) of compound **6**.

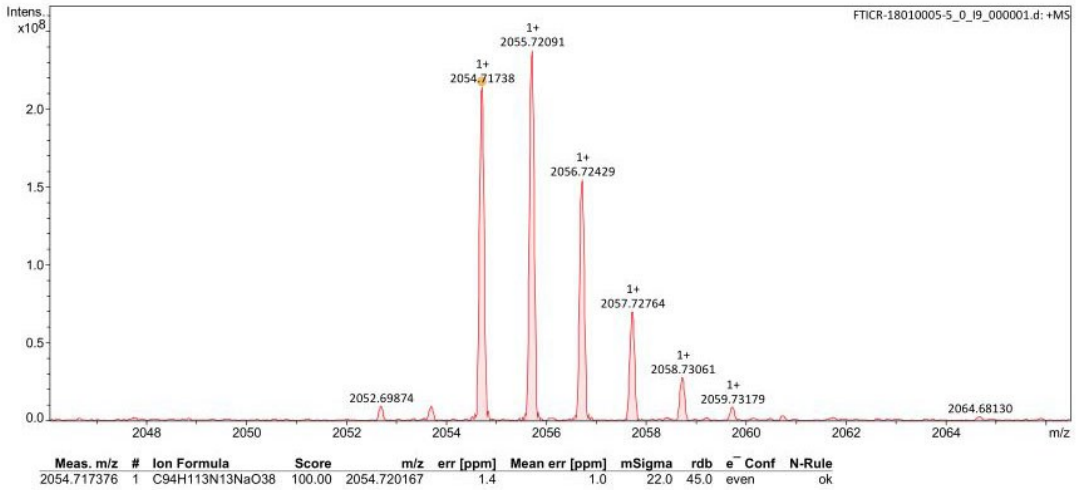


Fig. S9 HRMS (MALDI-TOF) of compound **6**.

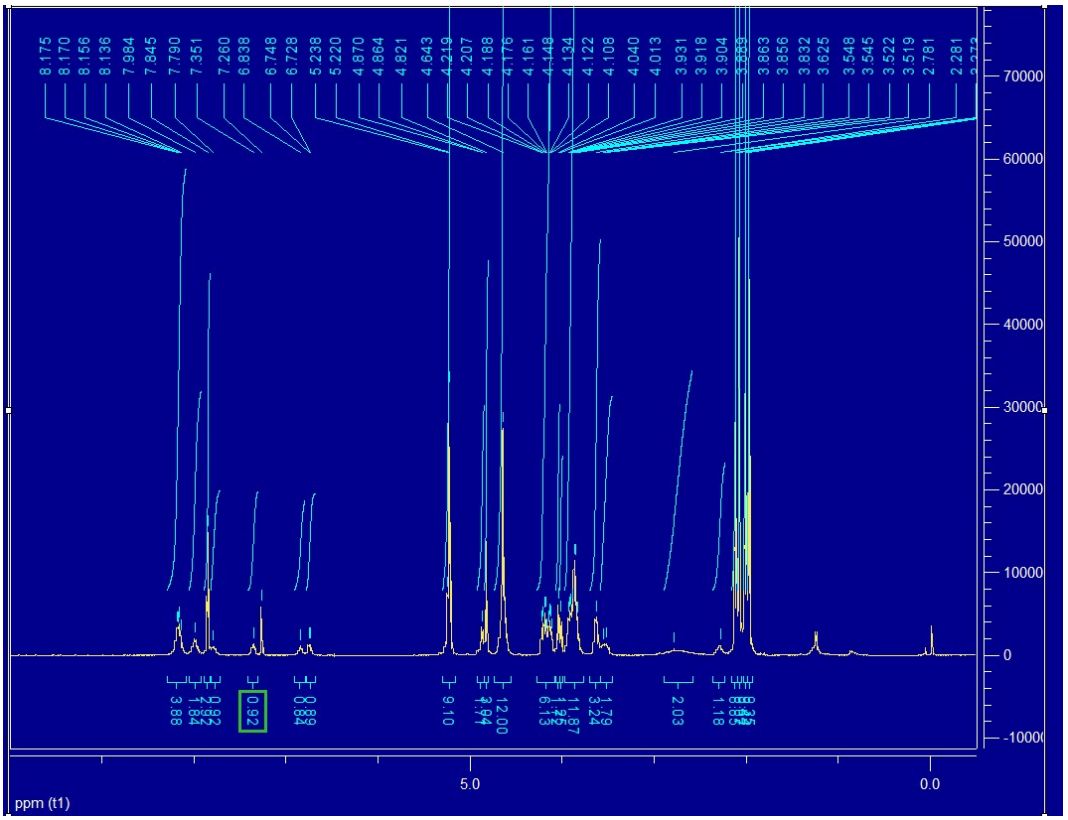


Fig. S10 ^{1}H NMR (DMSO-d_6, 600 MHz) of compound **7**.

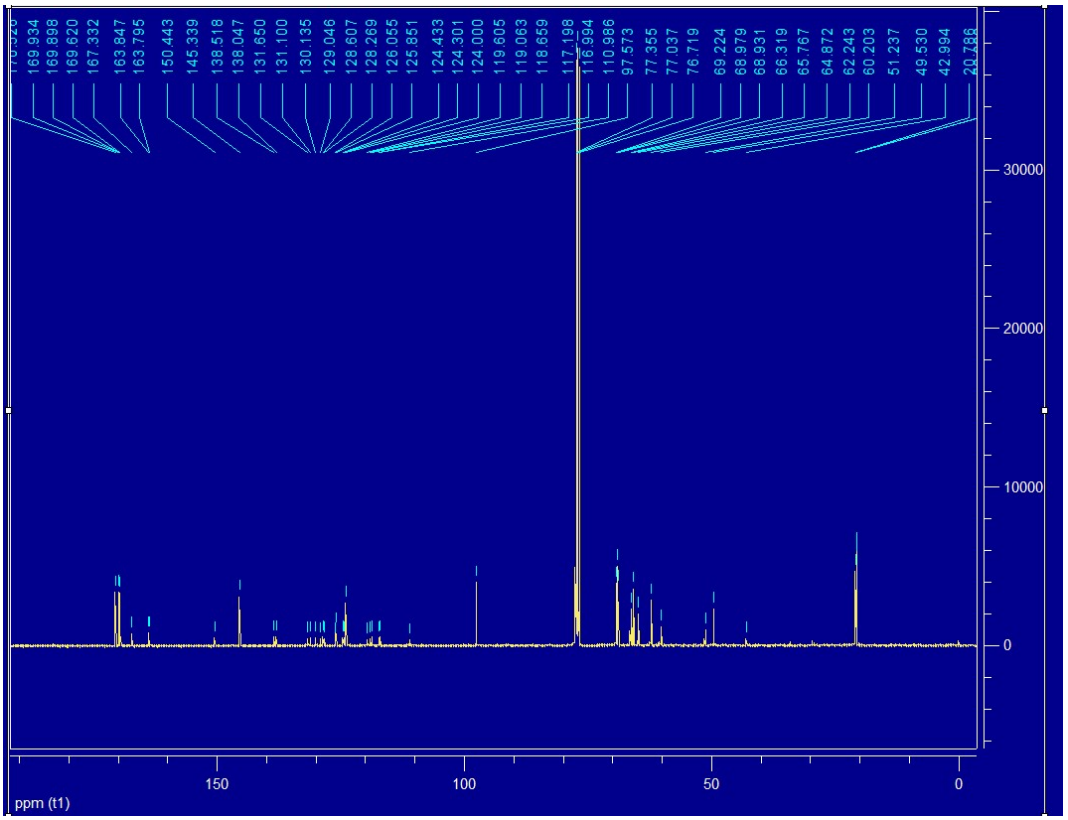


Fig. S11 ^{13}C NMR ($CDCl_3$, 100 MHz) of compound **7**.

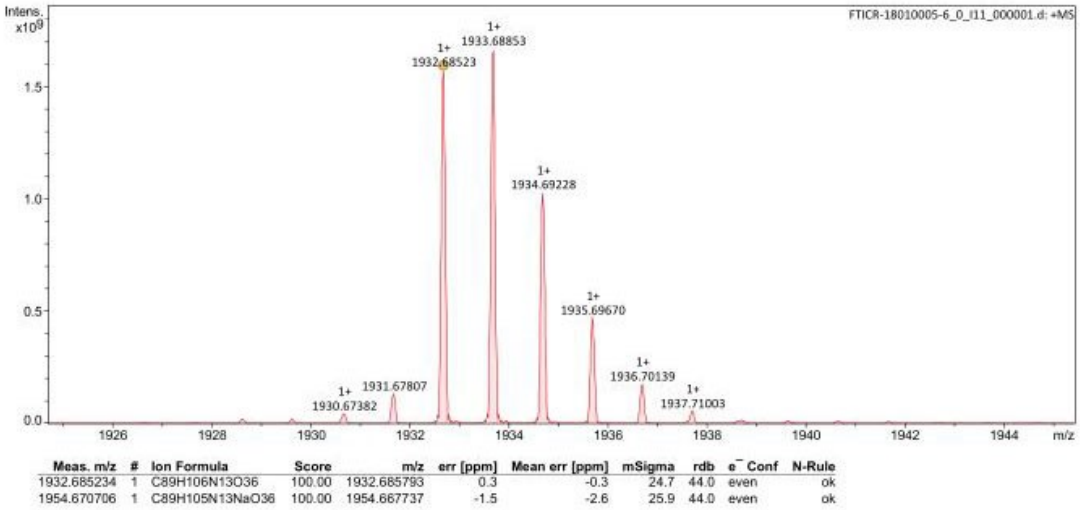


Fig. S12 HRMS (MALDI-TOF) of compound **7**.

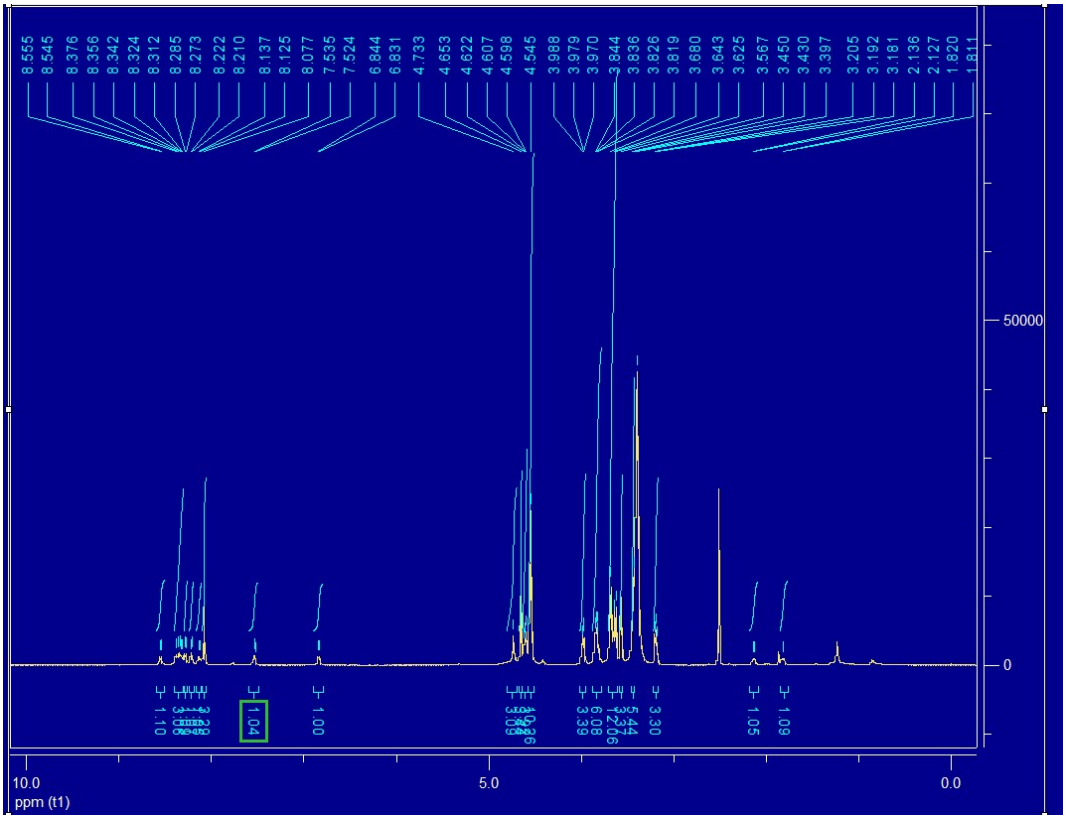


Fig. S13 ^{1}H NMR (DMSO-d_6+D_2O, 600 MHz) of compound **PBI-Man**.

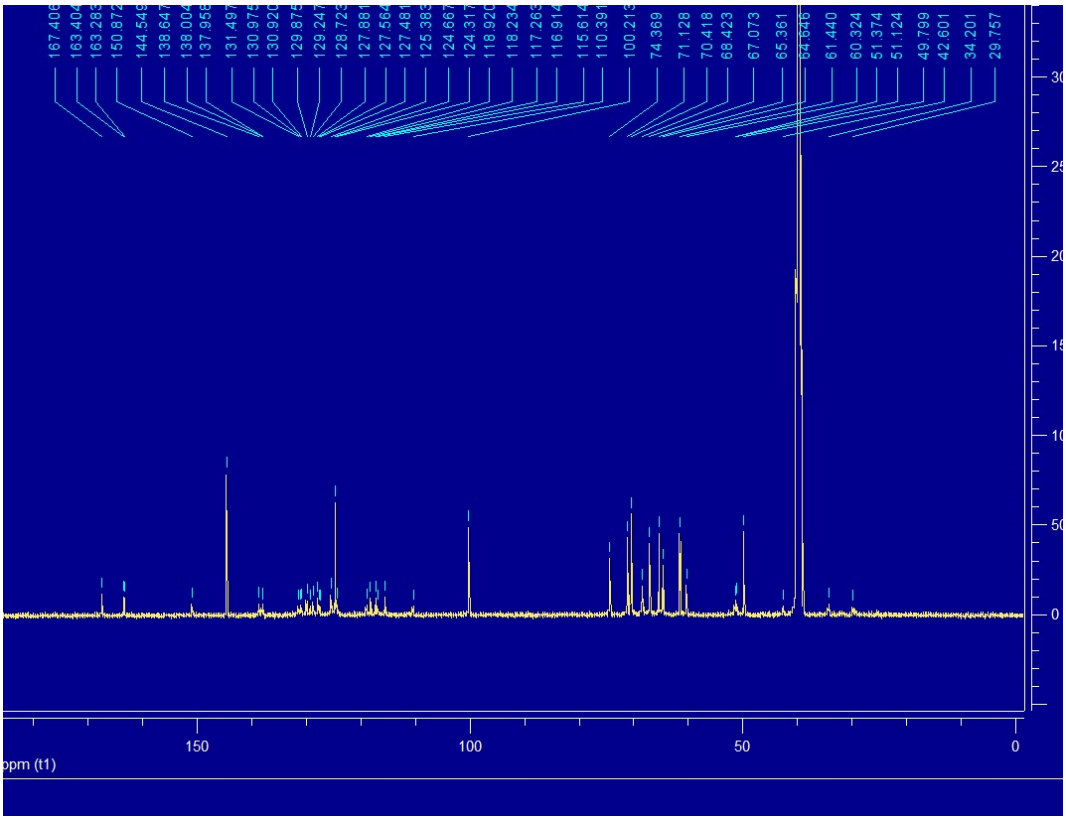
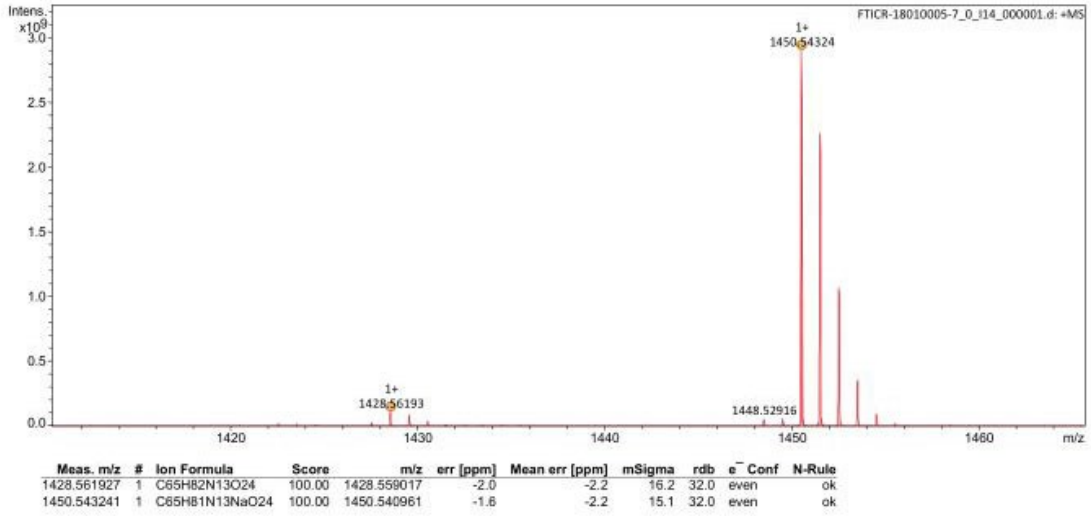


Fig. S14 ^{13}C NMR (DMSO-d_6+D_2O, 100 MHz) of compound **PBI-Man**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1428.561927	1	C65H82N13O24	100.00	1428.559017	-2.0	-2.2	16.2	32.0	even	ok
1450.543241	1	C65H81N13NaO24	100.00	1450.540961	-1.6	-2.2	15.1	32.0	even	ok

Fig. S15 HRMS (MALDI-TOF) of compound **PBI-Man**.

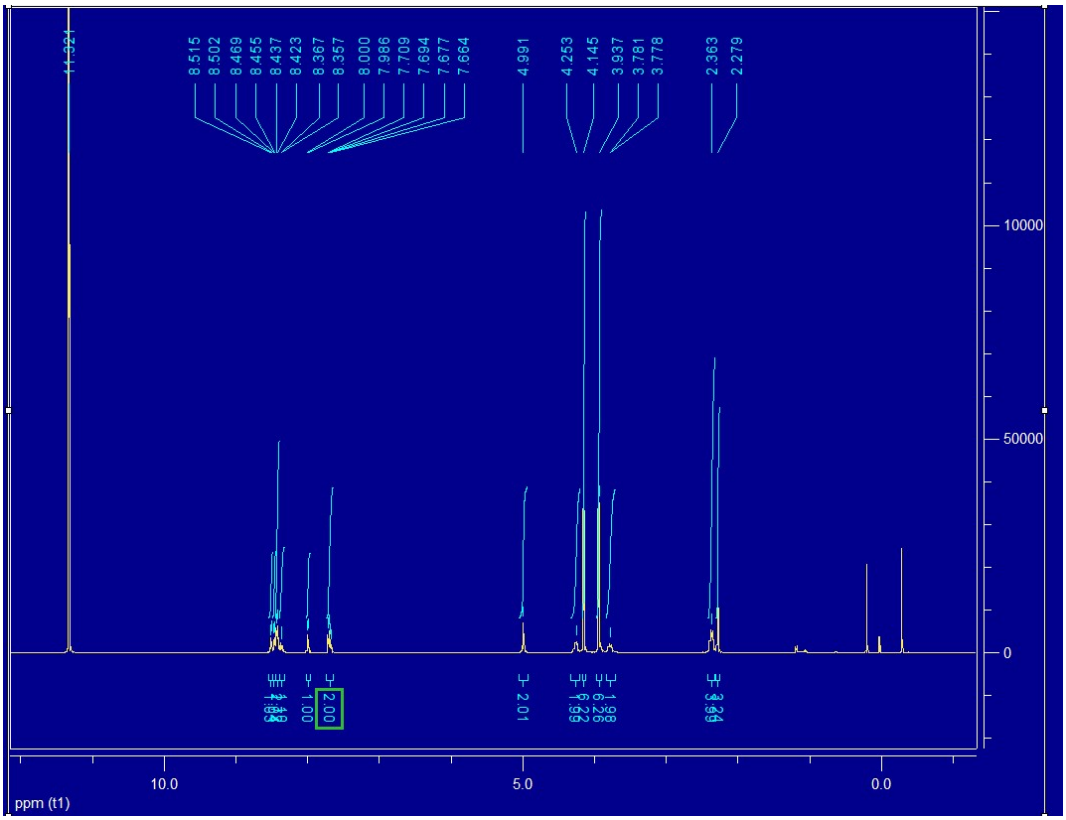


Fig. S16 ^{1}H NMR (CF_3COOD, 600 MHz) of compound **8**.

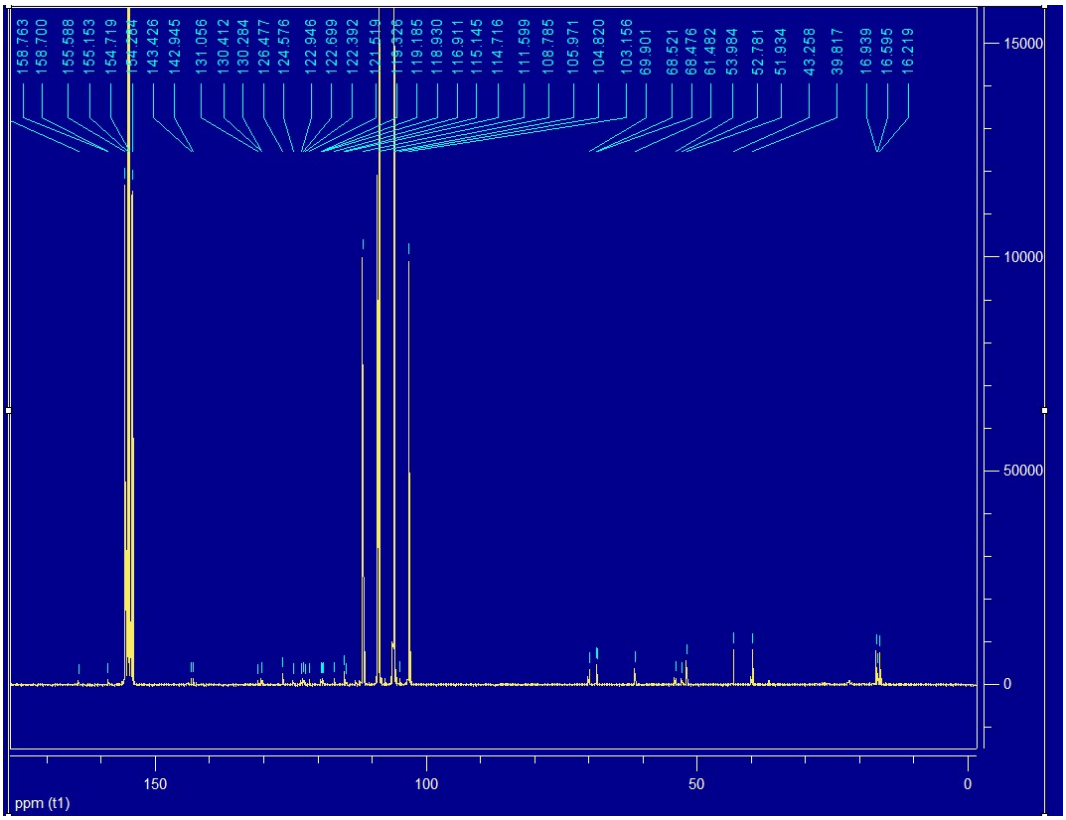
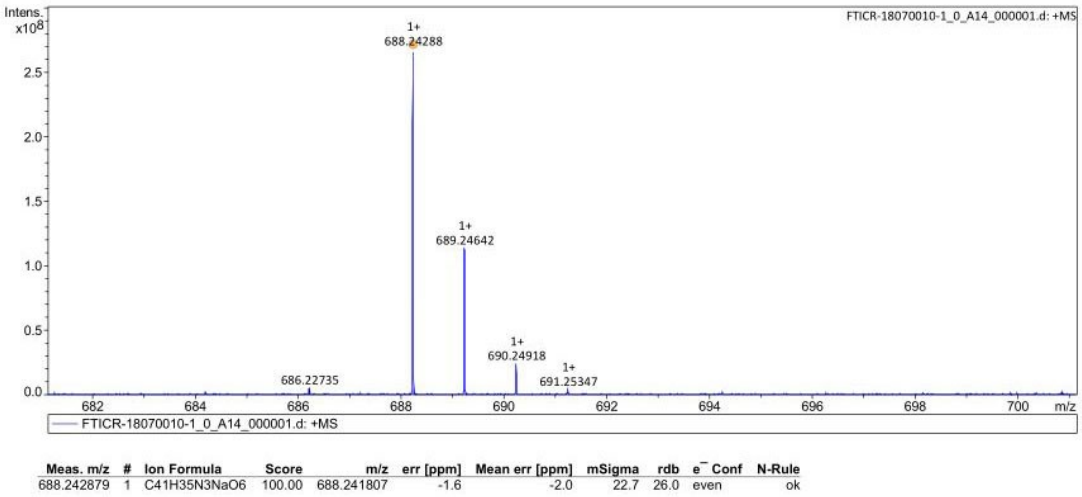


Fig. S17 ^{13}C NMR (CF_3COOD, 150 MHz) of compound **8**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
688.242879	1	C41H35N3NaO6	100.00	688.241807	-1.6	-2.0	22.7	26.0	even	ok

Fig. S18 HRMS (MALDI-TOF) of compound **8**.

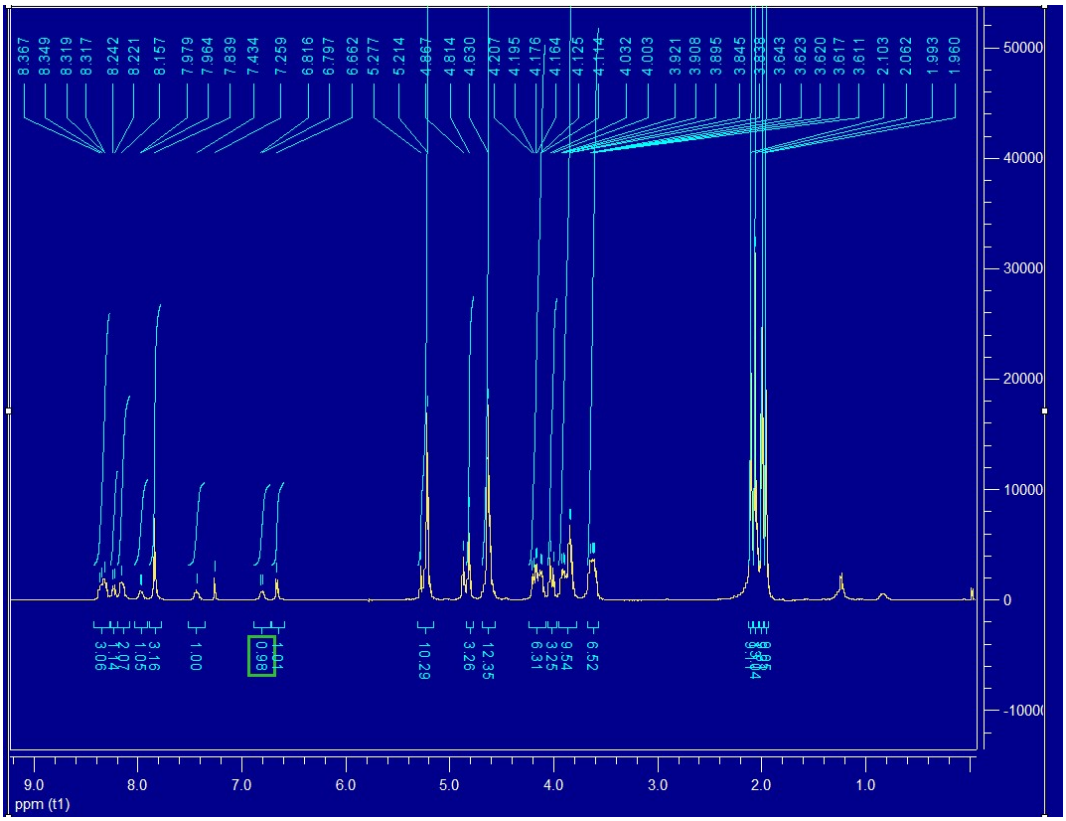


Fig. S19 ^{1}H NMR ($CDCl_3$, 600 MHz) of compound **9**.

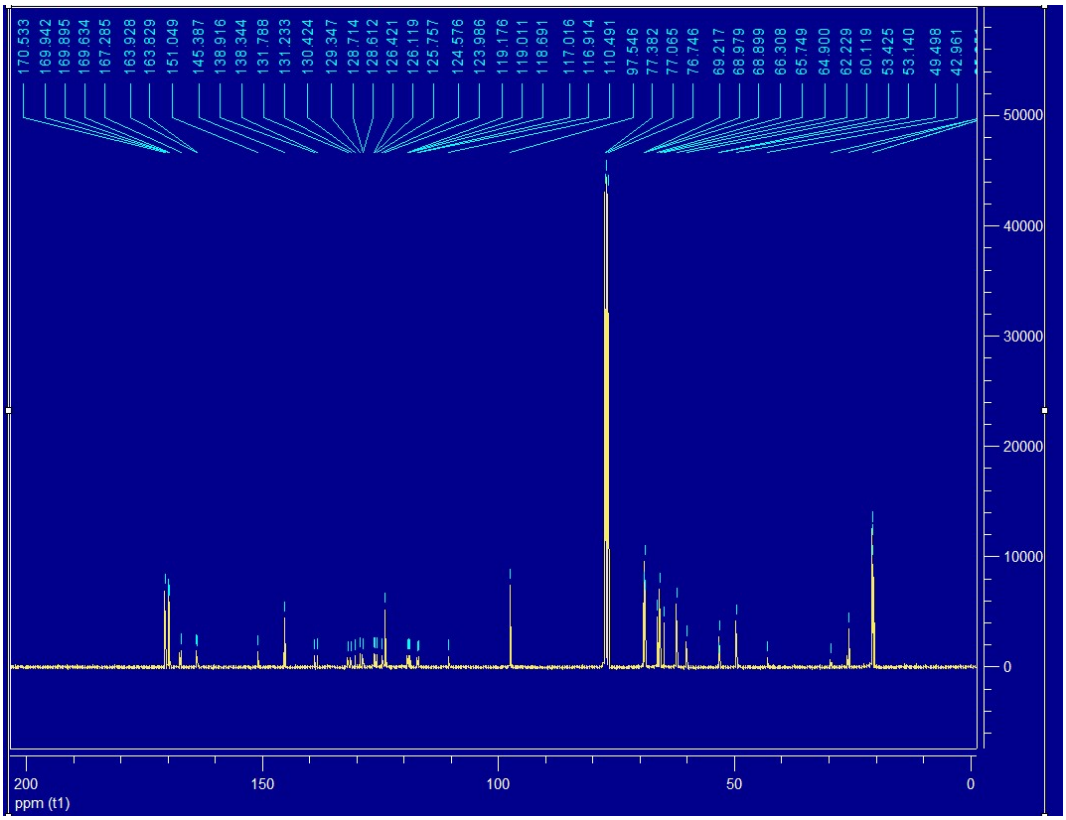
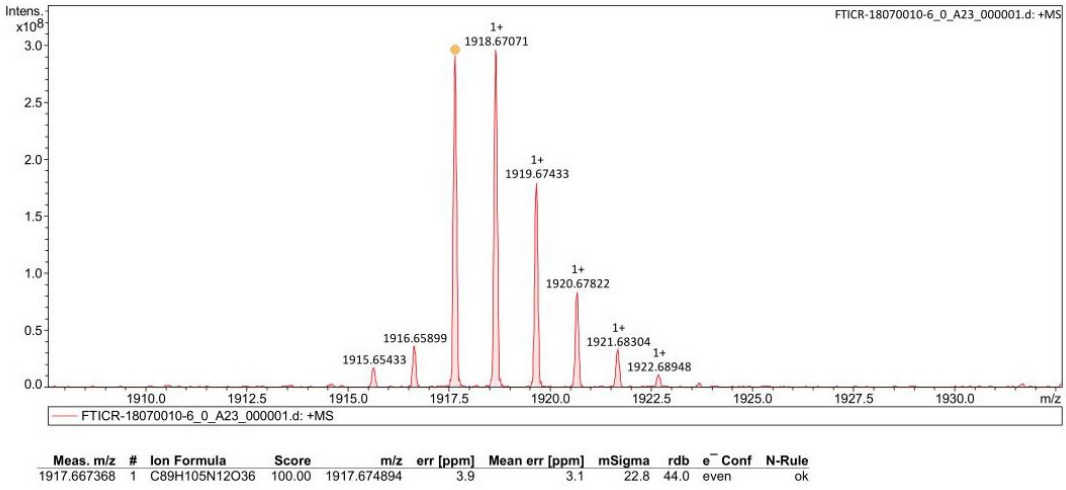


Fig. S20 ^{13}C NMR ($CDCl_3$, 150 MHz) of compound **9**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1917.667368	1	C89H105N12O36	100.00	1917.674894	3.9	3.1	22.8	44.0	even	ok

Fig. S21 HRMS (MALDI-TOF) of compound **9**.

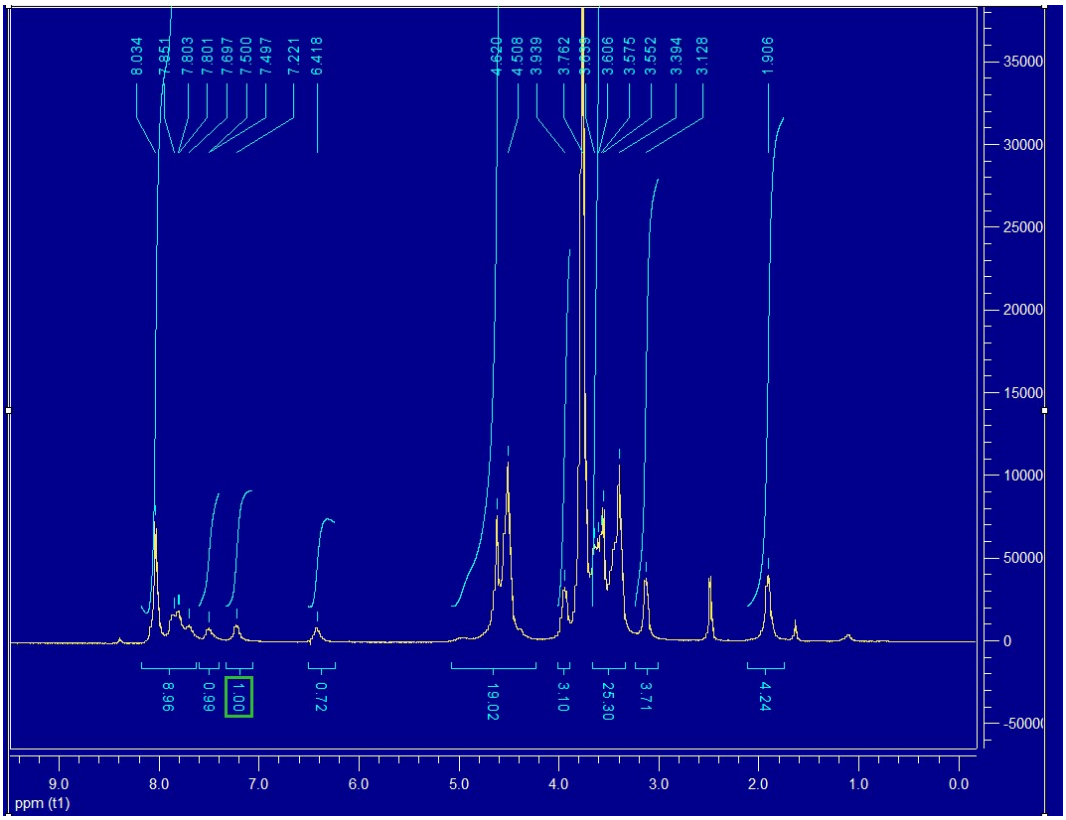


Fig. S22 ^{1}H NMR (DMSO-d_6, 600 MHz) of compound **PMI-Man-Control**.

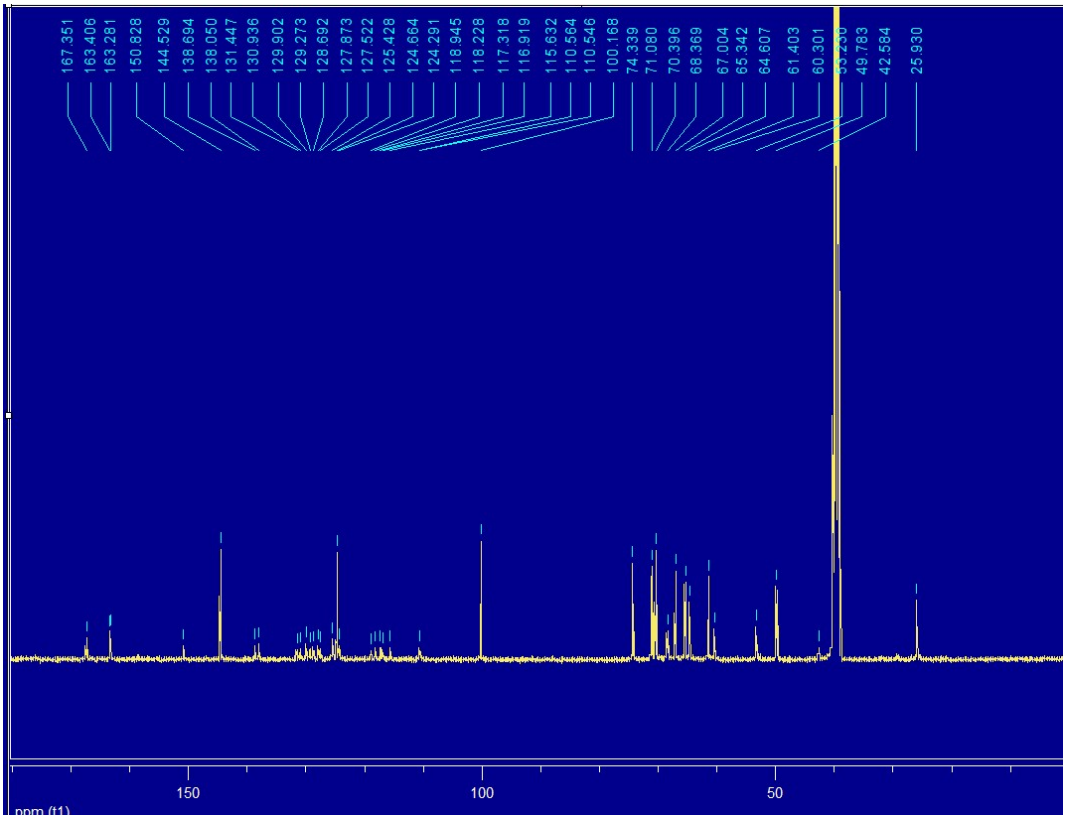
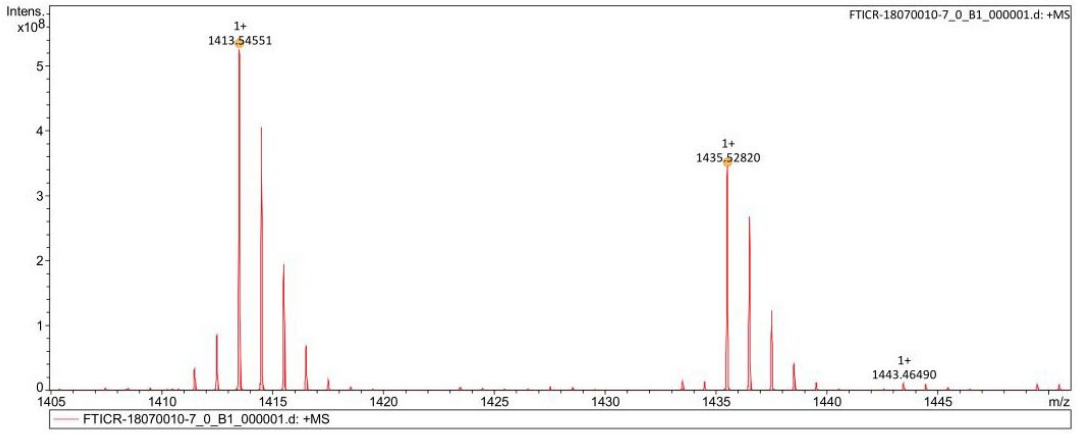


Fig. S23 ^{13}C NMR (DMSO-d_6, 150 MHz) of compound **PMI-Man-Control**.



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1413.545508	1	C65H81N12O24	100.00	1413.548118	1.8	0.6	n.a.	32.0	even	ok
1435.528196	1	C65H80N12NaO24	100.00	1435.530062	1.3	0.4	n.a.	32.0	even	ok

Fig. S24 HRMS (MALDI-TOF) of compound **PMI-Man-Control**.

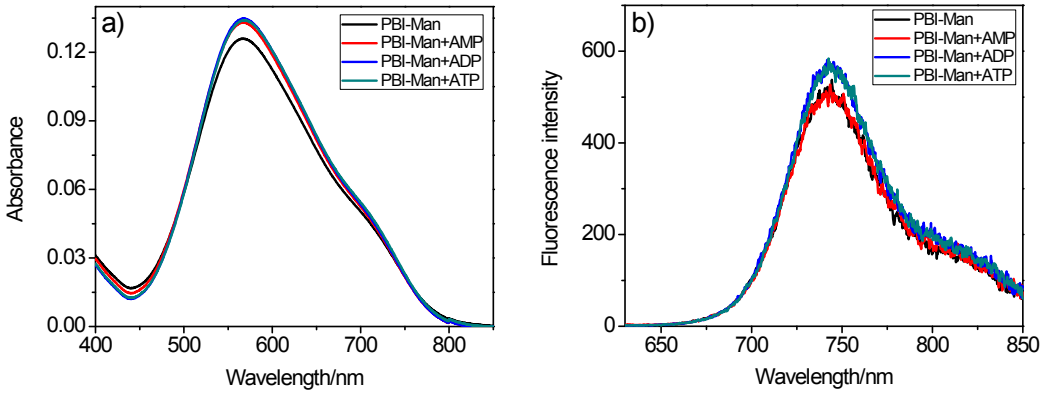


Fig. S25 UV-Vis (a) and fluorescence (b, λ_{ex} = 600 nm) spectra of **PBI-Man** (1×10^{-5} M) upon addition of 1×10^{-4} M of AMP, ADP and ATP in PBS buffer.

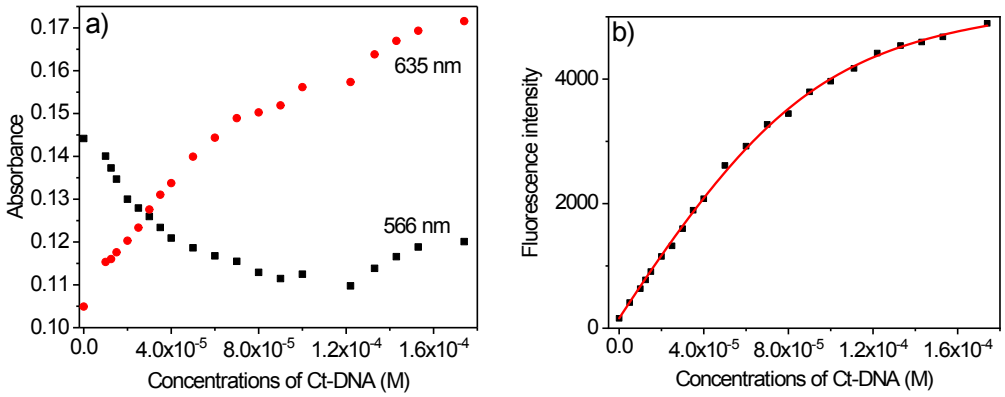


Fig. S26 Absorption changes (a) and fluorescent changes (b) of **PBI-Man** (1×10^{-5} M, λ_{ex} = 630 nm) upon addition of different equivalent of Ct-DNA in PBS buffer.

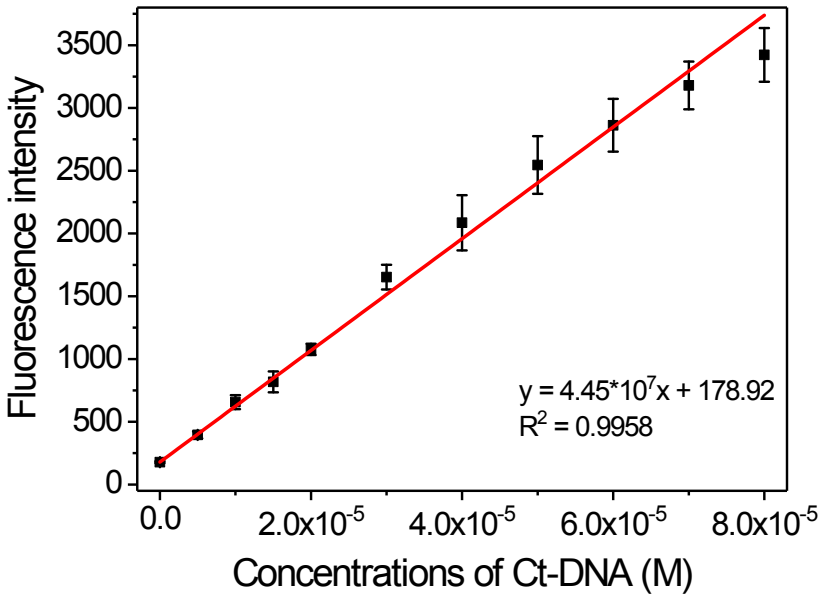


Fig. S27 The detection limit curve of **PMI-Man** towards Ct-DNA at 755 nm of **PBI-Man** (1×10^{-5} M) versus increasing concentrations of Ct-DNA.

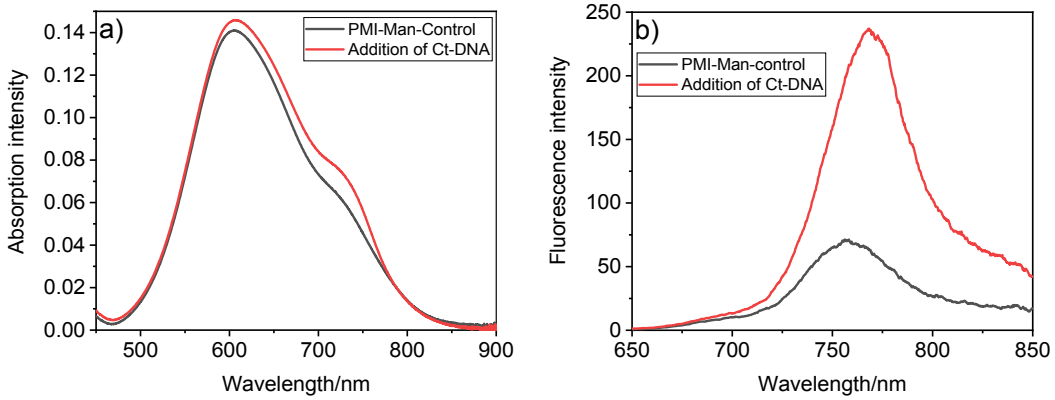


Fig. S28 UV-Vis (a) and fluorescence (b, λ_{ex}=600 nm) spectra of **PBI-Man-Control** (1×10^{-5} M) upon addition of 1×10^{-4} M of Ct-DNA in PBS buffer.

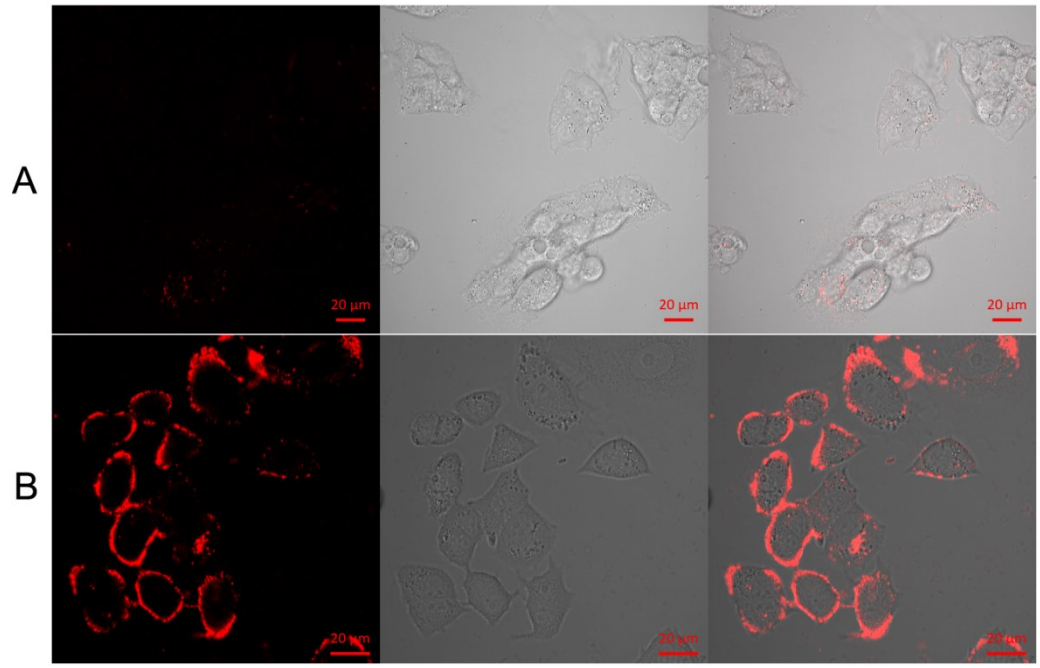


Fig. 29 Fluorescence imaging (λ_{ex} = 633 nm) of **PBI-Man** (10 μM) with HepG2 cells (A) and MCF-7 cells (B) after incubated for 2 h at 37 °C.

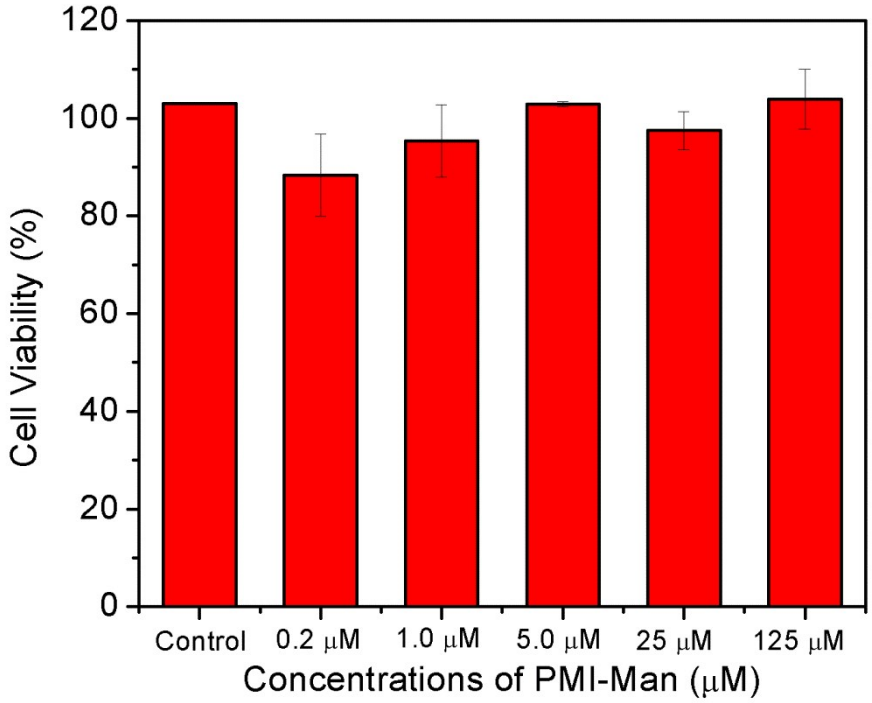


Fig. S30 Cell viability of **PBI-Man** against MCF-7 cells under the concentrations of 0.2, 1.0, 5.0, 25 and 125 μM.