Supplementary Data

Remarkable photocytotoxicity of a novel triazole–linked cationic porphyrin–*β*–carboline conjugate

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General Methods

All reactions were performed in oven-dried glass apparatus unless otherwise mentioned. Bulk grade hexanes, chloroform ($CHCl_3$), methanol and ethyl acetate (EtOAc) for chromatography were distilled prior to use. Tetrahydrofuran (THF), dimethylformamide (DMF), acetonitrile (MeCN) and diethyl ether (Et_2O) were degassed with nitrogen and dried by passing though activated alumina. Triethylamine (NEt_3), dichloromethane (DCM) and chloroform ($CHCl_3$) were distilled from CaH_2 under nitrogen before use. Acetone was distilled over potassium permanganate prior to use. All laboratory grade reagents were obtained commercially from Aldrich (India), S. D. Fine Chemicals, Pvt Ltd, India and Spectrochem, India. The reactions were monitored by thin layered chromatography using Merck pre-coated plates 60 F_{254}. Developed TLC plates were visualized under UV light and/or appropriate strains (potassium permanganate, iodine vapors or sulphuric acid). Column chromatography was performed using silica–gel (100–200 or 230–400 mesh size) purchased from Merck. Fourier transform–infrared (FTIR) were performed on Shimadzu IRPrestige–21 spectrometer. ^1H NMR spectra were recorded at Bruker Advance II 400 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard unless otherwise mentioned. Data are presented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*) in Hertz (Hz) and integration. Matrix–assisted laser desorption ionization–time of flight MS (MALDI–TOF MS) spectrometry was performed using 2,5-dihyrdoxybenzoic acid (DHB) as the matrix. Waters high performance liquid chromatography (HPLC) system with sunfire C18 column was used to ascertain purity of the porphyrin conjugate, mobile phase: isocratic (0.05% TFA)/acetonitrile, rate: 1 mL/min.

DNA Cleavage Assay

Photoirradiation was carried out using a high pressure Xe–arc though a band–path filter (UTVAF–36U, Sigma-Koki, Tokyo, Japan) (λ = 300–390 nm, 4 mW, UV–A) or a white LED light source (ISL–150×150–WW, CCS, Kyoto, Japan) (λ = 400–800 nm, 2 mW, visible). A gel electrophoresis apparatus (Mupid–exu, Advance, Tokyo, Japan) was used for agarose gel electrophoresis. DNA cleavage studies were performed by the use of supercoiled, covalently closed, circular ΦX174 RF I DNA (Form I) (New England Biolabs, USA). Typically, solution of ΦX174 RF I DNA (0.5 μg) and the drugs in 20 mM Tris–HCl buffer (pH 7.2) containing 20 mM NaCl and 2.5 vol% DMSO (total volume 20 μL) was exposed to UV–A or visible light at ambient temperature. The resultant mixtures were then

analyzed by gel electrophoresis (1% agarose gel, ethidium bromide stain). DNA cleavage was determined by the formation of relaxed circular DNA (Form II) and linear DNA (Form III). The gels were visualized on a UV transilluminator (λ_{ex} = 312 nm, ETX–35.M, Vilber–Lourmat, France).

Cell Viability Assay

A549, a human epithelial cell line derived from a lung carcinoma (doubling time; 20–24 h),was obtained from American Type Culture Collection. A549 were grown in Dulbecco's modified Eagle medium with high concentrations of glucose (Invitrogen, Carlsbad, CA, USA) containing 10% fetal bovine serum (FBS), 100 U/mL penicillin and 100 μg streptomycin. Cell line was incubated at 37 °C in a humidified atmosphere consisting of 5% CO_2/air. Porphyrins were dissolved in DMSO (final concentration: 0.1% DMSO in culture medium). A549 cells were seeded (5000 cells/well) on a 96 well plates the day before chemicals treatment. After 24 h of incubation in the presence of the porphyrins (0–5 μM), cells were washed with PBS, and incubated in new PBS for 10 min at 37 °C. Cells were exposed to UV–A or visible light for 10 min, and then PBS was replaced to FBS containing medium. After 48 h incubation in the dark, cell viability was determined by the Cell Counting Kit-8 (Dojin, Kumamoto, Japan) using a spectrophotometer (xMark; Bio-Rad, Hercules, CA, USA). IC_{50} values were determined using 4–parameter equations.

Nuclear Staining

A549 cells were seeded (1×10^5 cells/well) on a 12 well plate the day before chemical treatment. After 24 h of incubation in the presence of the porphyrins (1 μM), cells were rinsed with PBS and then incubated in new PBS for 10 min. Cells were photoexposed to UV–A or visible light for 10 min, and then PBS was replaced to FBS containing medium. After 24 h incubation in the dark, cells were washed twice with PBS, then stained with Hoechst 33342 (Dojin, Kumamoto, Japan), and imaged by a fluorescence microscope (Keyence BZ–8000, Osaka, Japan).

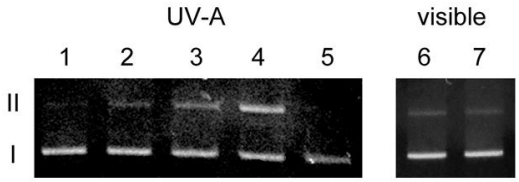


Figure S1. Photoinduced DNA cleavage by **11**. *Φ*X174 supercoiled DNA (0.5 μg) was incubated with **11** (100 μM) in 20 μl of Tris–HCl (20 mM, pH 7.2) containing NaCl (20 mM), DMSO (2.5 vol%) at ambient temperature in the dark for 30 min, and then exposed to (lanes 2–4) UV–A or (lanes 6) visible light. Lanes 1 and 7, DNA + **11**; lane 2, DNA + **11** + $h\nu$ 15 min; lane 3, DNA + **11** + $h\nu$ 30 min; lanes 4 and 6, DNA + **11** + $h\nu$ 60 min; lane 5, DNA alone.

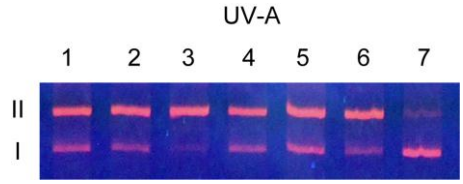


Figure S2. Photoinduced DNA cleavage by **11**. *Φ*X174 supercoiled DNA (0.5 μg) was incubated with **11** (100 μM) in 20 μl of Tris–HCl (20 mM, pH 7.2) containing NaCl (20 mM), DMSO (2.5 vol%), and various scavengers at ambient temperature in the dark for 30 min, and UV–A irradiated for 90 min. Lane 1, DNA + **11** + $h\nu$; lane 2, DNA + sodium azide (20 mM) + **11** + $h\nu$; lane 3, DNA + TMP (20 mM) + **11** + $h\nu$; lane 4, DNA + mannitol (20 mM) + **11** + $h\nu$; lane 5, DNA + catalase (100 U/ml) + **11** + $h\nu$; lane 6, DNA + SOD (100 U/ml) + **11** + $h\nu$; lane 7, DNA + **11**.

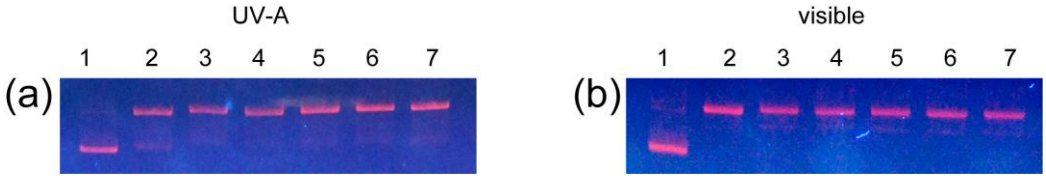


Figure S3. Photoinduced DNA cleavage by **12**. *Φ*X174 supercoiled DNA (0.5 μg) was incubated with **12** (100 μM) in 20 μl of Tris–HCl (20 mM, pH 7.2) containing NaCl (20 mM), DMSO (2.5 vol%), and various scavengers at ambient temperature in the dark for 30 min, and exposed to (a) UV–A or (b) visible light for 90 min. Lanes 1, DNA + **12**; lanes 2, DNA + sodium azide (20 mM) + **12** + $h\nu$; lanes 3, DNA + TMP (20 mM) + **12** + $h\nu$; lanes 4, DNA + mannitol (20 mM) + **12** + $h\nu$; lanes 5, DNA + catalase (100 U/ml) + **12** + $h\nu$; lanes 6, DNA + SOD (100 U/ml) + **12** + $h\nu$; lanes 7, DNA + **12** + $h\nu$.

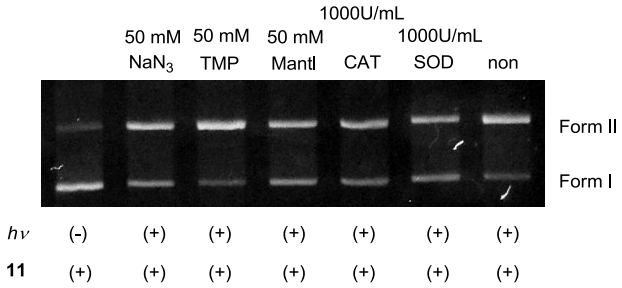


Figure S4. The presence of reactive oxygen species was investigated by carrying out the photoinduced DNA cleavage experiments in the presence of singlet oxygen quenchers like NaN_3 (1-20 mM), TMP (1-20 mM), hydroxyl radical scavenger like mannitol (1-20 mM), H_2O_2 quencher like catalase (10-100 U/mL), and single oxygen quencher like superoxide dismutase (10-100U/mL). Even in the presence of high concentrations of the quenchers (up to 20 mM or 100U/mL) no remarkable quenching effect was observed.

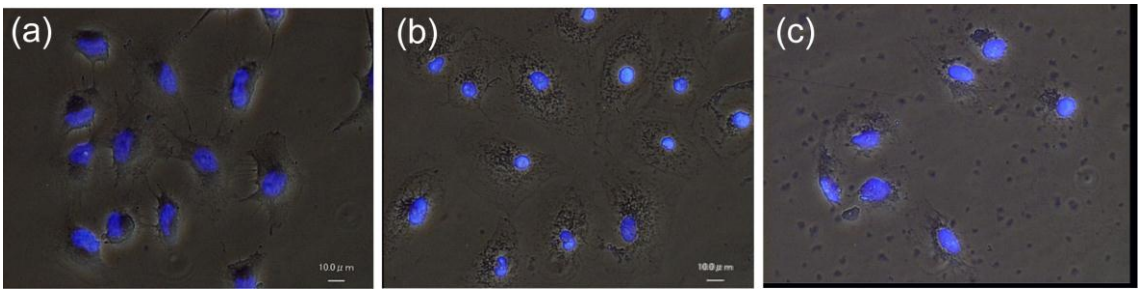


Figure S5. Hoechst 33342 staining of TMPyP (1 μM) treated A549 cells to identify nuclear morphology: (a) incubated in the dark, (b) exposed to UV-A (4 mW, 10 min), and (c) exposed to visible light (2 mW, 10 min).

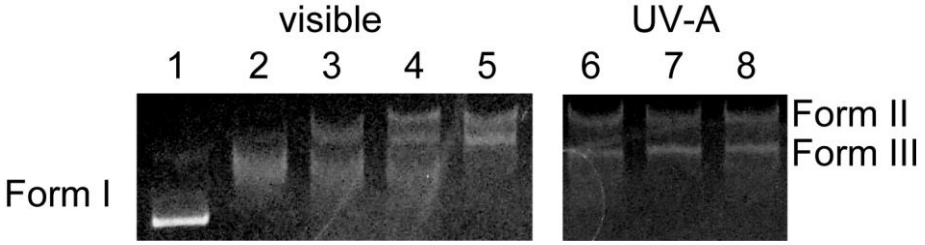
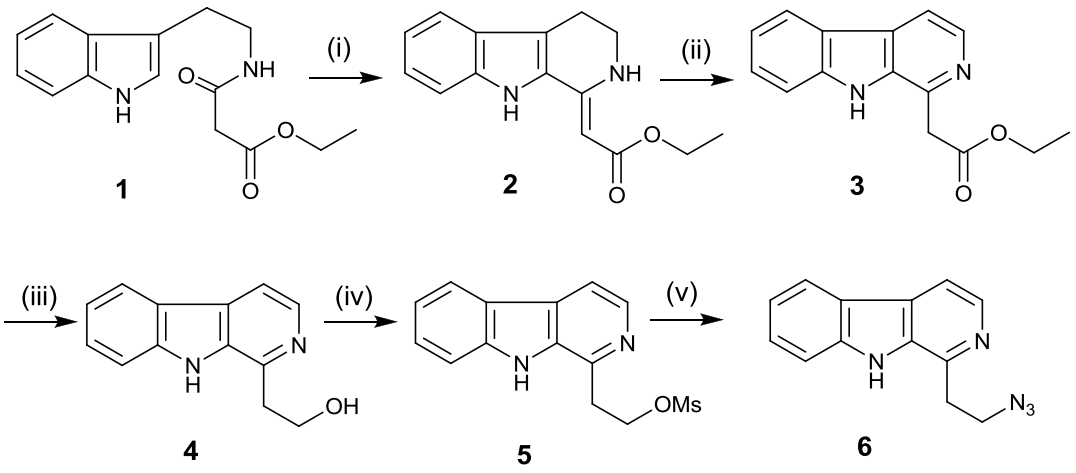


Figure S6. Photoinduced DNA cleavage by TMPyP. ΦX174 supercoiled DNA (0.5 μg) was incubated with TMPyP (20 μM) in 20 mL of Tris-HCl (20 mM, pH 7.2) containing NaCl (20 mM) at ambient temperature in the dark for 30 min, and then exposed to (lanes 3-5) visible light or (lanes 6-8) UV-A light. Lane 1, DNA alone; lane 2, DNA+TMPyP; lanes 3 and 6, DNA+TMPyP+$h\nu$, 15min; lanes 4 and 7, DNA+TMPyP+$h\nu$, 30 min; lanes 5 and 8, DNA+TMPyP+$h\nu$, 60 min.



Scheme S1. Synthesis of *β*–carboline azide **6**; (i) $POCl_3$, rt, 8 h, 57%; (ii) Pd–C (10%), 165 °C, *p*–cymene, 1 h, 45%; (iii) $LiAlH_4$, THF, 0–27 °C, 6 h, 90%; (iv) MsCl, Et_3N, CH_2Cl_2, 0–5 °C, 1 h, 57%; (v) NaN_3, DMF–H_2O, 50 °C, 8 h, 87%.

***N*–(Indol–3–yl–ethyl)–2–ethoxycarbonylacetamide** (**1**) To a stirred solution of tryptamine (5 g, 31.25 mmol) at 0 °C was simultaneously added a solution of ethyl malonyl chloride (5.5 g, 36.5 mmol) in dichloromethane (75 mL) and aqueous sodium hydroxide solution (2 g, 75 mL) over a period of 30 minutes with vigorous stirring. The reaction mixture was stirred at room temperature for another 1 h and then diluted with dichloromethane (50 mL) and added HCl (5%, 10 mL). Organic phase was washed with saturated sodium bicarbonate (2 × 10 mL), dried over sodium sulfate, and concentrated in vacuo to afford a yellow oil which was washed with a mixture of dichloromethane: hexane (1:9) to afford **1** (7.5 g, 88 %). IR (KBr) 3410, 3315, 1735, 1667, 1559 cm^{-1}.

1–(Ethoxycarbonylmethylidene)–tetrahydro–*β*–carboline (**2**) The amide ester **1** (7.0 g, 25.5 mmol) in phosphorus oxychloride (30 mL) was stirred at room temperature for 7 h. Excess of phosphorus oxychloride was distilled in vacuo and the residue so obtained was basified with saturated sodium bicarbonate and extracted with dichloromethane. After removal of dichloromethane, the resulting crude was washed with a mixture of dichloromethane/hexane to afford **2** as yellow oil (3.7 g, 57 %). IR (KBr) 3348, 1631, 1607, 1538 cm^{-1}.

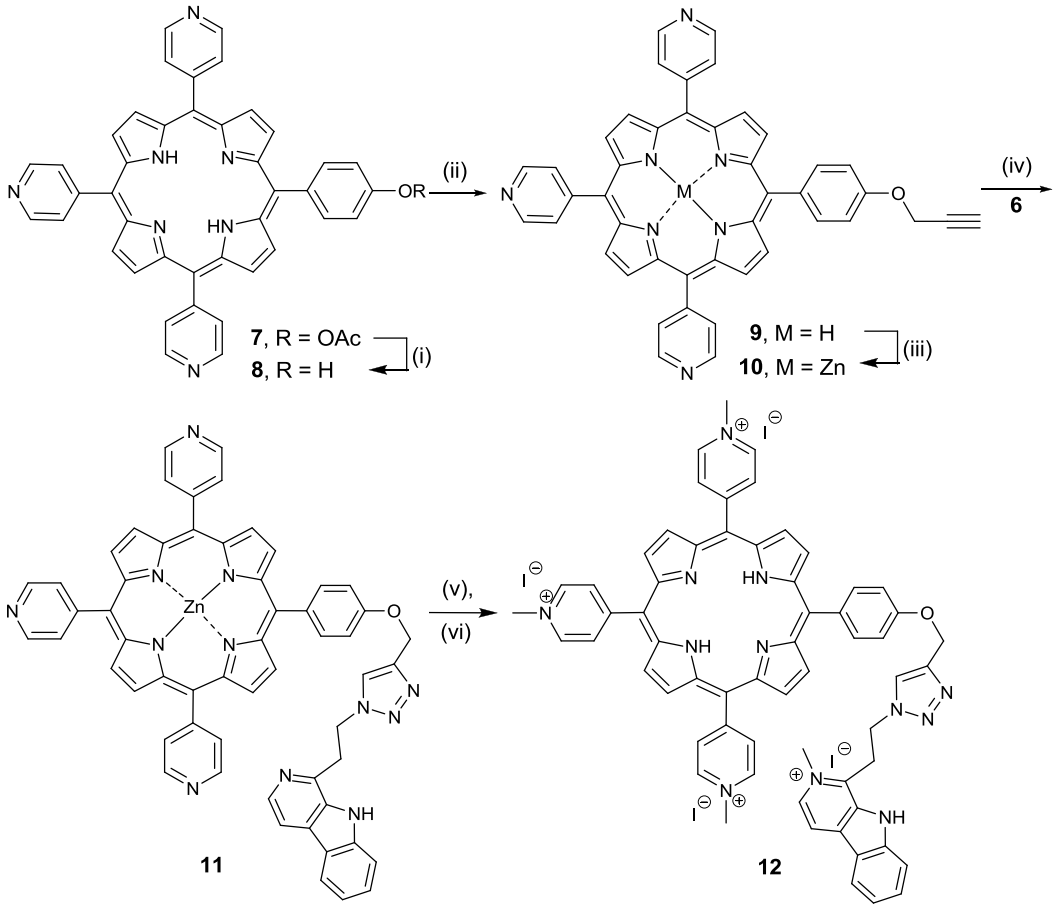
1–(Ethoxycarbonylmethyl)–*β*–carboline: (**3**) To a solution of the enaminoester **2** (3.5 g, 13.7 mmol) in *p*-cymene (180 mL) at 40 °C was added 10% Pd-C (6.0 g) in one portion and the resulting mixture was immediately kept in a heated oil bath at 165 °C for 15 min. After completion of the reaction, the mixture was diluted with ethyl acetate (100 mL), filtered and distilled off under vacuo. The crude product so obtained was purified by column

chomatography using ethyl acetate:hexane (1:5; v/v) as eluent to afford *β*-carboline ester **3** (1.6 g, 45 %). IR (KBr) 3507, 1738, 1635 cm^{-1}.

l–(2–Hydroxyethyl)–*β*–carboline 4: To a stirred suspension of lithium aluminium hydride (1.0 g. 3.9 mmol) in tetrahydrofuran (20 mL) was added 20 mL solution of the *β*–carboline ester **3** (0.84 g, 22.3 mmol) in tetrahydrofuran at room temperature and the resulting mixture was allowed to stir at same temperature for 2 h. The mixture was cooled in an ice–bath, quenched with aqueous sodium hydroxide (1 g, 1 mL) and stirred for another 30 min. Reaction contents were diluted with ethyl acetate (30 mL), dried over anhydrous sodium sulfate, filtered and washed with ethyl acetate. After removal of organic solvent, the crude product obtained was purified by column chromatography using chloroform: methanol (9:1; v/v) to produce alcohol **4** (0.75 g, 90 %). mp 194-196 °C (Lit. m.p. 195.5-197 °C), IR (KBr) 3412, 3177 cm^{-1}.

Preparation of *β*–carboline mesylate 5: To a stirred and cooled solution of *β*–carboline alcohol **4** (0.7 g, 3.3 mmol) at 0 °C was added triethylamine (0.53 mL, 3.8 mmol) in dichloromethane (40 mL) followed by methanesulfonyl chloride (0.31 mL, 3.6 mmol). The resulting mixture was stirred at the 0 °C for 20 min. Diluted with dichloromethane (50 mL) and added a saturated solution of sodium bicarbonate. Organic layer was washed with brine (2 × 30 mL), dried over anhydrous sodium sulfate and removed the excess of solvent. The yellow solid so obtained was triturated with a mixture of methanol: diisopropyl ether (6:4, v/v), filtered and dried to afford *β*–carboline mesylate **5** (0.55 g, 57%). IR (KBr) 3512, 2506, 1633, 1355, 1172 cm^{-1}.

Preparation of *β*–carboline azide 6: To a solution of mesylate **5** (0.5 g, 1.7 mmol) in DMF (5 mL) was added sodium azide (0.3 g, 5.1 mmol) and stirred at room temperature for 12 h. The reaction mixture was diluted with dichloromethane (80 mL) and water (40 mL) was added. The aqueous layer was extracted with dichloromethane (2 × 20 mL) and combined organic extract was washed with water, dried over sodium sulfate and distilled off. The residue so obtained was purified by chromatography to afford *β*–carboline azide **6** as lemon yellow solid (0.35 g, 87%). mp: 212–215 °C; IR (KBr) 3517, 2506, 2392, 2098, 1352, 1175 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.09 – 7.05(m, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 3.58 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* = 6.8 Hz, 2H); HRMS-TOF: *m/z* calcd. for $C_{13}H_{12}N_5$ 238.1093, found 238.1105 $[M + H]^+$.



Scheme S2. Synthesis of porphyrin–*β*–carboline conjugate **12**; (i) KOH, MeOH-H_2O, reflux, 5 h; (ii) propargyl bromide (1.2 equiv), K_2CO_3 (1.2 equiv), DMF, 0–27 °C, 24 h; (iii) $Zn(OAc)_2$, $CHCl_3$–MeOH, reflux, 2 h; (iv) $CuSO_4$, sodium ascorbate, DMF–H_2O, 80°C, 7 days; (v) $CHCl_3$, aq HCl (25%), 1 h; (vi) MeI (120 equiv.), $CHCl_3$, rt, 168 h.

5–[4'–(Methylcarbonyloxy)]phenyl]–10,l5,20–tri(4'–pyridyl)porphyrin 7: A mixture of 4-carboxyethylbenzaldehyde (4.25 g, 35 mmol), propionic acid (280 mL), and acetic anhydride (16 mL) was heated at 110 °C with stirring. To this solution were successively and slowly added 4–pyridinecarboxaldehyde (10 mL, 113.6 mmol) and pyrrole (9 mL, 135.7 mmol). The resulting mixture was refluxed for 1.5 h. The volume of solvent was reduced to 50 mL at reduced pressure and the mixture was neutralized with a saturated sodium bicarbonate solution, filtered and washed several times with water. The crude material was extracted with a mixture of dichloromethane: methanol (8.5:1.5, v/v) and purified by chromatography using chloroform: methanol (9.5:0.5; v/v) over silica–gel

neutralized with triethylamine prior to loading compound. Evaporation of solvent afforded 0.57 g of **1** as a purple powder in 5% yield. M.p. >300 °C. IR (KBr) carbonyl at 1740 cm^{-1}.

5–(4'–Hydroxyphenyl)–10,l5,20–tri(4'–pyridyl)porphyrin 8: Porphyrin **7** (0.6 g, 0.89 mmol) was dissolved in 25 mL of ethanol and 45 mL of 2M NaOH solution. The resulting mixture was refluxed for 1 h, cooled to room temperature and 90 mL of 1N HCl was added. The resulting solution (pH = 7) was then extracted with chloroform (4 × 80 mL). After removal of chloroform, obtained pure product **8** in 85% yield (0.49 g) which was used as such without further purification.

5–(4'–Propargyloxyphenyl)–10,15,20–tri(4'–pyridyl)porphyrin 9: To a stirred suspension of **8** (0.3 g, 0.47 mmol) and fused potassium carbonate (0.078 g, 0.57 mmol) at 0 °C in dry DMF (20 mL) was gradually added propargyl bromide (0.064 g, 0.057 mmol) over a period of 15 min. The reaction mixture was allowed to stir at room temperature for 24 h. After completion of the reaction, mixture was cooled to room temperature, diluted with DCM (50 mL), filtered. To the filtrate, 70 mL of water was added and separated organic phase, dried over anhydrous sodium sulfate and concentrated in vacuo. Chromatography (9:1, chloroform: methanol) of the residual mass afforded **9** as purple solid (0.17 g, 55%). M.p. >300 °C; IR (KBr) 3210, 2967, 2945, 2875, 2110 cm^{-1}; ^{1}H NMR (400 MHz, DMSO–d_6) δ 9.00–8.98 (m, 6H), 8.88–8.81 (m, 8H), 8.27–8.26 (m, 6H), 8.17 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 5.10 (s, 2H), 2.88 (s, 1H), −3.02 (s, 2H); ESI-MS: *m/z* calcd for $C_{44}H_{29}N_7O$ 672.24, found 672.30 $[M+H]^+$.

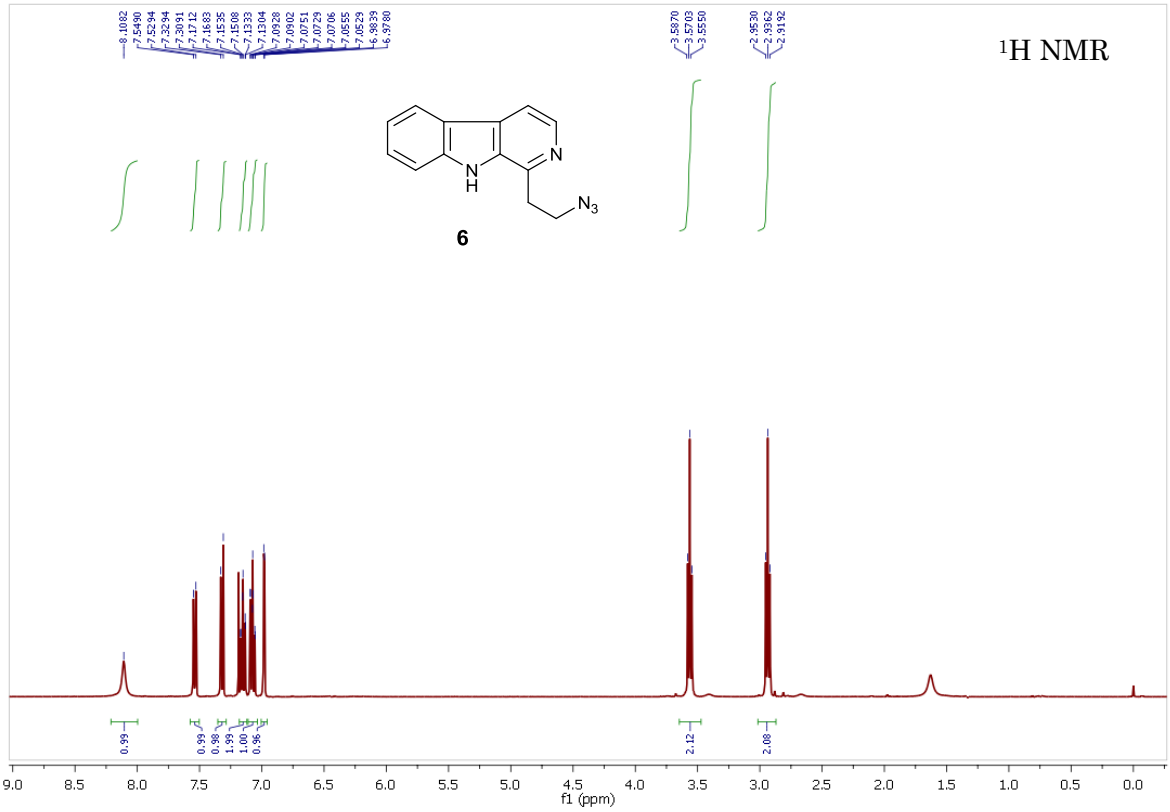
5–(4'–Propargyloxyphenyl)–10,15,20–tri(4'–pyridyl)porphyrinato zinc(II) 10 : To a stirred solution of **9** (0.15 g, 0.22 mmol) in a mixture chloroform: methanol (3:1, 15 mL) was added $Zn(OAc)_2$ (0.051 g, 0.23 mmol) and the contents were refluxed for 1 h. After completion of the reaction, the reaction mixture was diluted with chloroform (30 mL) and saturated sodium bicarbonate (50 mL) (pH = 8). The organic layer was separated, washed with water and dried over Na_2SO_4. The excess of the solvent was distilled off in vacuum to produce **10** (0.15 g, 90%) as purple solid. The compound was sufficiently pure and used for next step without further purification.

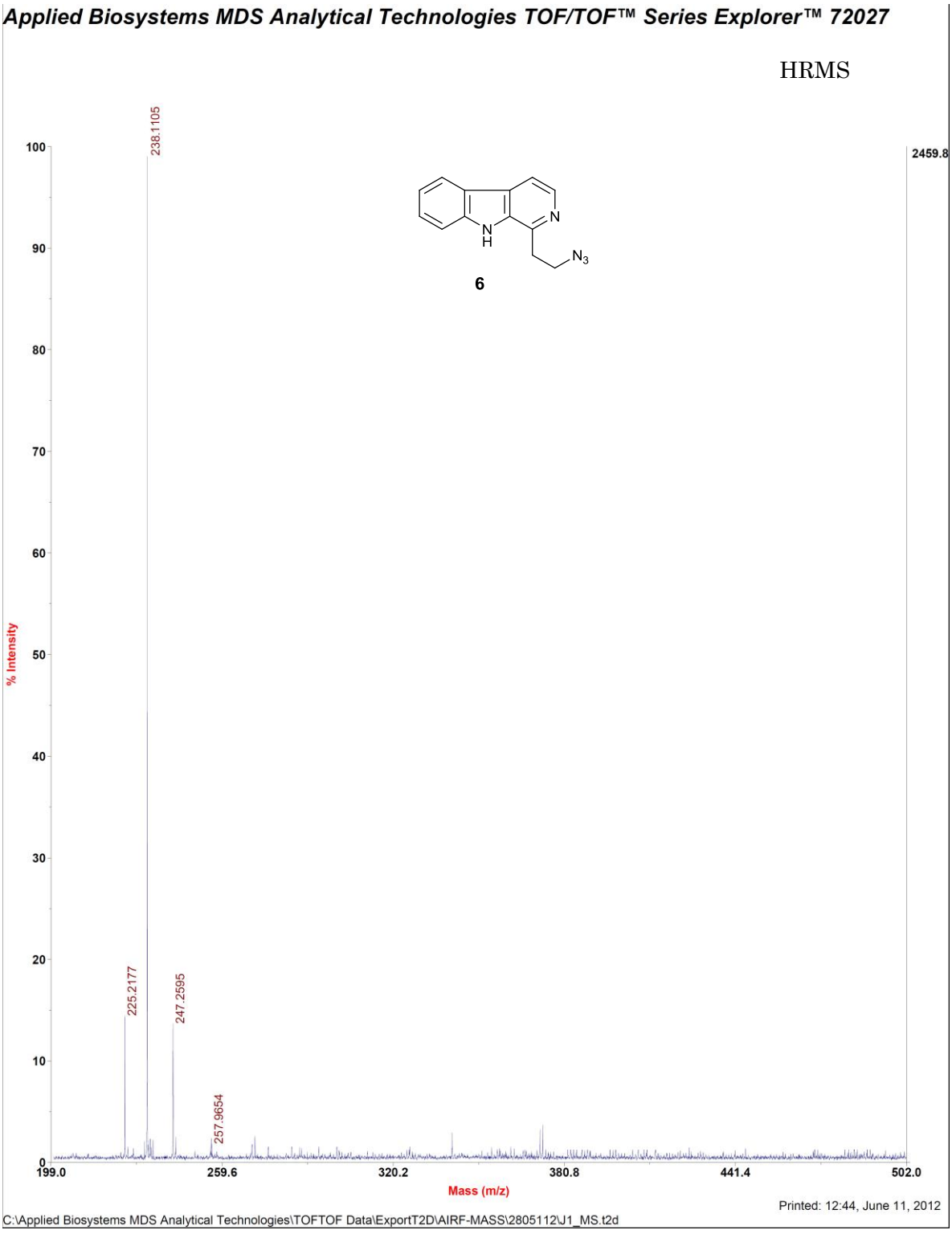
Preparation of porphyrin–*β*–carboline conjugate 11: To a stirred solution of metallated porphyrin **10** (0.15 g, 0.2 mmol) in DMF: H_2O (1:1; 40 mL) was added $CuSO_4.5H_2O$ (0.19

g, 0.8 mmol), sodium ascorbate (0.32 g, 1.6 mmol) followed by *β*–carboline azide **6** (0.097 g, 0.41 mmol). The reaction mixture was heated at 80 °C and stirred for 168 h. After completion of the reaction, the contents were diluted with chloroform (50 mL) and ammonia solution (20%, 15 mL). The resulting solution was filtered over thin celite bed and washed thoroughly with chloroform. The combined organic phase was washed with water, dried over anhydrous sodium sulfate and distilled off under vacuo. The residue so obtained was purified by column chromatography using chloroform: methanol (8:2, v/v) as eluent to afford the porphyrin conjugate **11** (0.115 g, 57%) as dark green solid. M.p. >300 °C; ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.02 (s, 1H), 8.86–8.82 (m, 7H), 8.36 (d, *J* = 5.6 Hz, 1H), 8.23 (s, 1H), 8.19–8.07 (m, 9H), 7.76–7.74 (m, 8H), 7.65-7.59 (m, 2H), 7.34-7.27 (m, 3H), 5.39 (s, 2H), 5.14 (t, *J* = 7.3 Hz, 2H), 4.00 (t, *J* = 7.3 Hz, 2H); HRMS-TOF: *m/z* calcd for $C_{57}H_{39}N_{12}OZn$ 971.2583; found 971.2541 $[M + H]^+$.

Preparation of cationic porphyrin–*β*–carboline conjugate 12: To a stirred solution of metallated conjugate **11** (0.1 g) in chloroform: methanol (19:1, 25 mL) was added hydrochloric acid (25%, 10 mL) and stirred for 1 h. Cooled the reaction mixture, basified with ammonia solution and separated the organic layer, which was dried over anhydrous sodium sulfate and distilled off under vacuo to afford demetallated porphyrin triazole **11a** (0.088 g), which was dissolved in dichloromethane: methanol (9:1), precipitated by adding hexane, filtered, dried and used as such for further reaction. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.83 (s, 1H), 9.03-9.02 (m, 6H), 8.99 – 8.82 (m, 8H), 8.37 – 8.33 (m, 2H), 8.23 – 8.22 (m, 7H), 8.09 – 8.05 (m, 3H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.40 (s, 2H), 5.08 (t, *J* = 7.4 Hz, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), −3.01 (s, 2H); MALDI-TOF: *m/z* calcd for $C_{57}H_{41}N_{12}O$ 909.3526; found: 909.3558 $[M+H]^+$. To a solution of demetallated porphyrin triazole (0.088 g, 0.098 mmol) in dry N,N'-dimethylformamide (20 mL) was added methyl iodide (0.75 mL, 11.73 mmol) and allowed the reaction mixture to stir at room temperature until starting material was consumed (72 h). The solvent was removed in vacuo and methanol (5 mL) was added. The solution was precipitated by adding diethyl ether (15 mL), which was repeated four times to afford compound **12** (0.08 g, 62%) as brown solid. M.p. >300 °C ^{1}H NMR (DMSO–d_6, 500 MHz) δ 9.49 – 9.42 (m, 8H), 9.18 – 8.99 (m, 15H), 8.23 – 8.15 (m, 4H), 7.77 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.16 –7.14 (m, 1H), 5.88 (s, 2H), 5.27 (t, *J* = 7.2 Hz, 2H), 4.95 (t, *J* = 7.3 Hz, 2H) 4.73 (s, 9H), 4.60 (s, 3H), −3.01 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.92, 157.08, 156.89, 148.68, 147.96, 145.84, 144.64, 144.64, 143.54,

139.94, 136.11, 134.46, 132.58, 131.42, 130.21, 126.21, 122.88, 116.92, 115.93, 115.78, 114.78, 114.21, 107.79, 71.56, 58.93, 48.37, 46.47, 31.22; MALDI–TOF: calcd for $C_{61}H_{52}N_{12}O$: 968.4365; found: 968.4357 $[M]^+$; HPLC purity: 99.24%.

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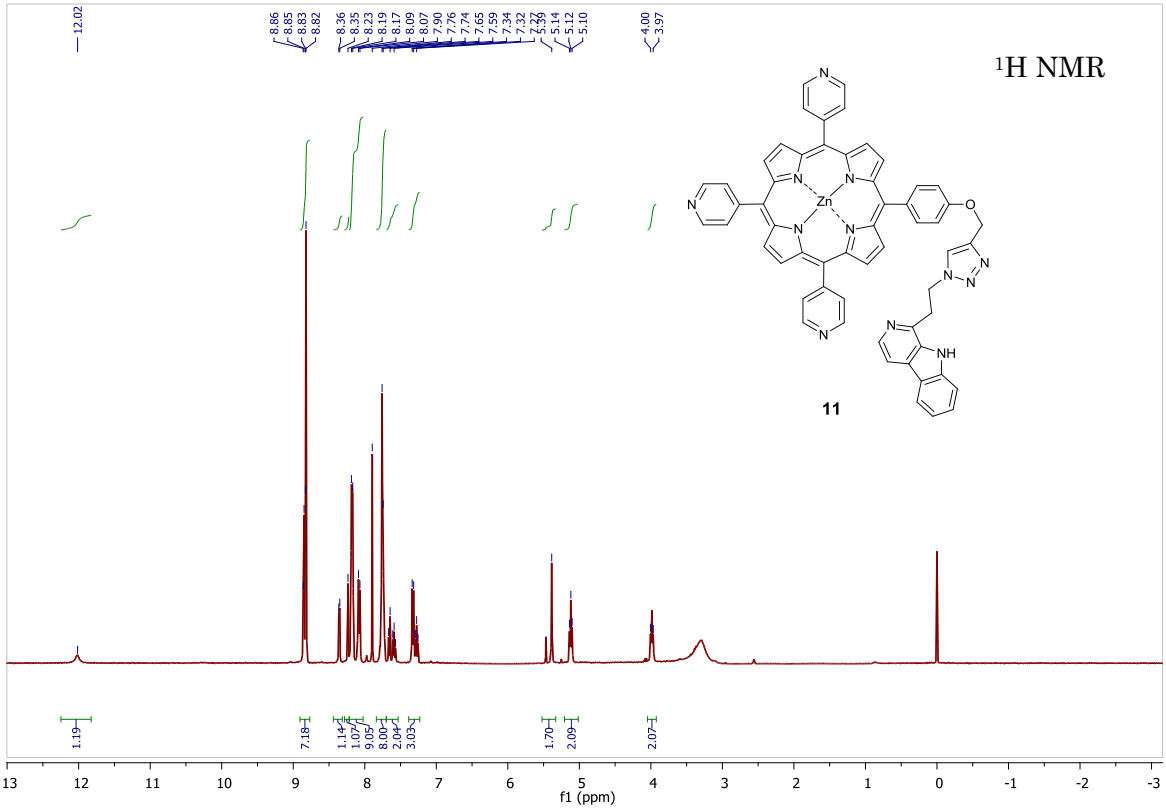
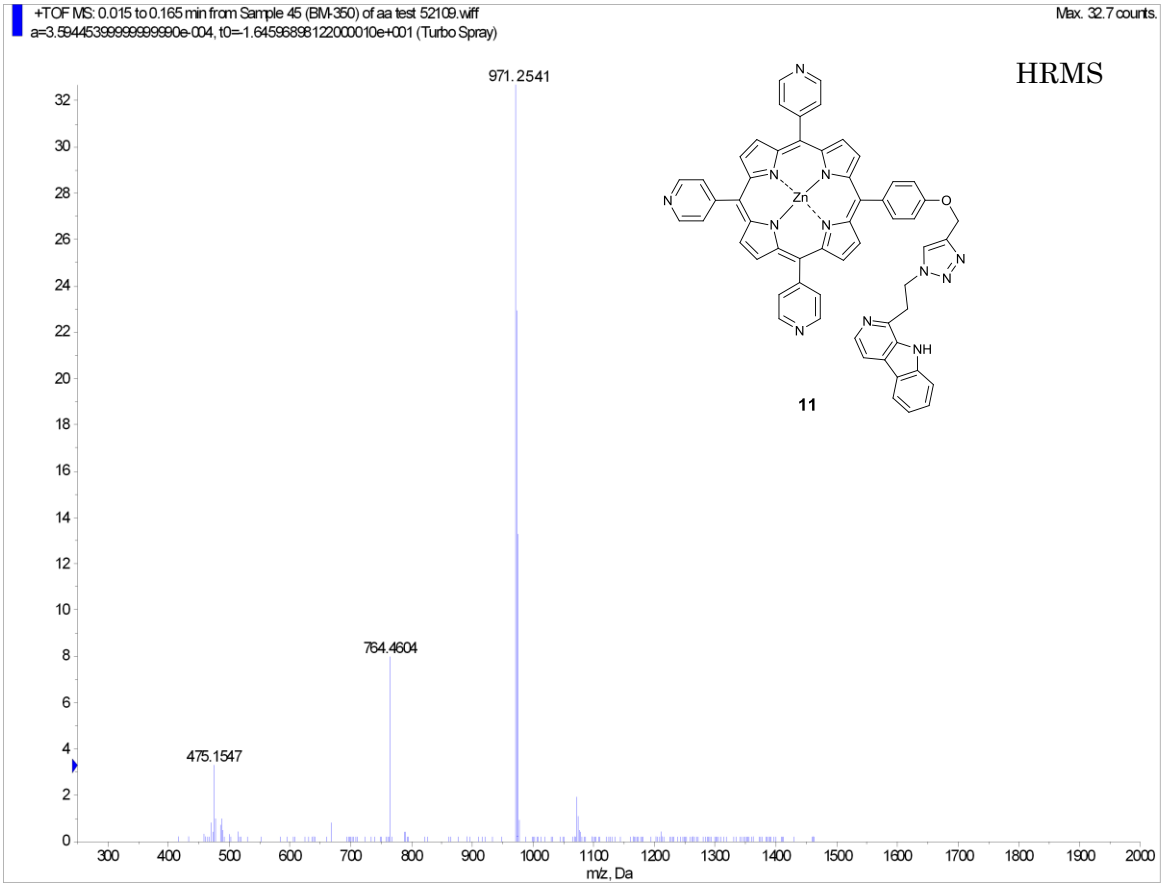
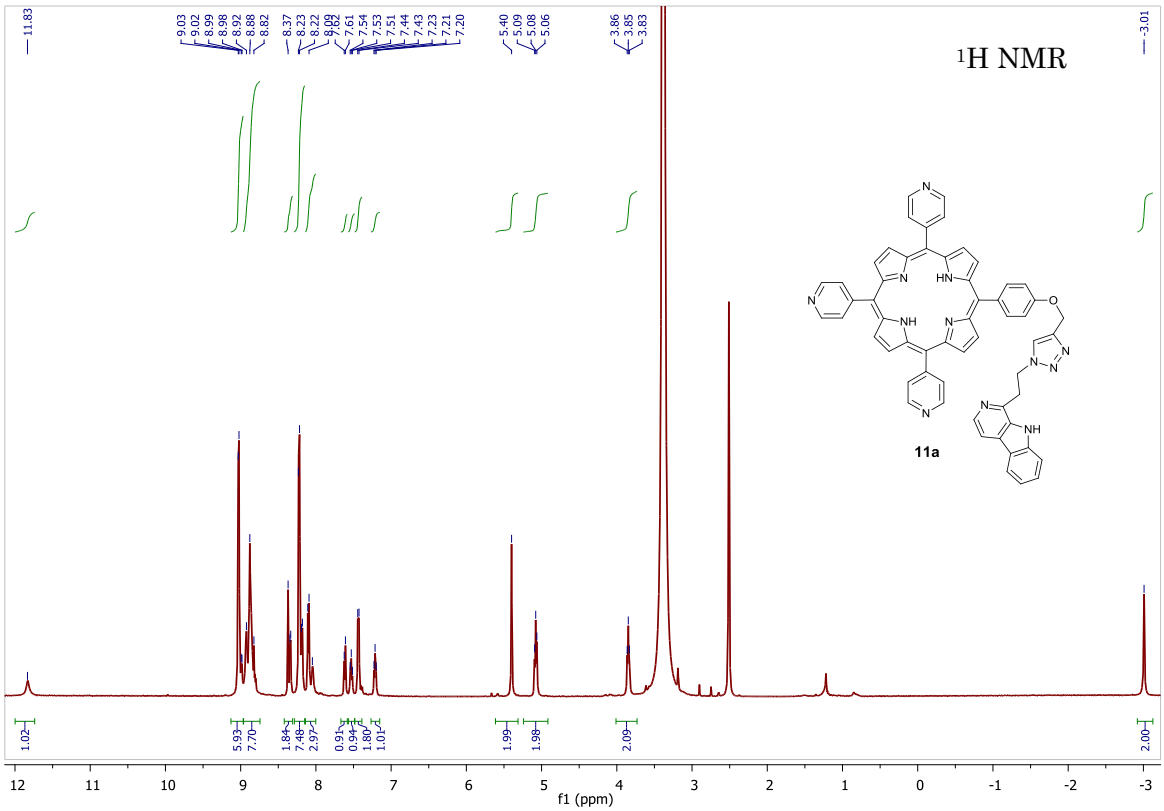
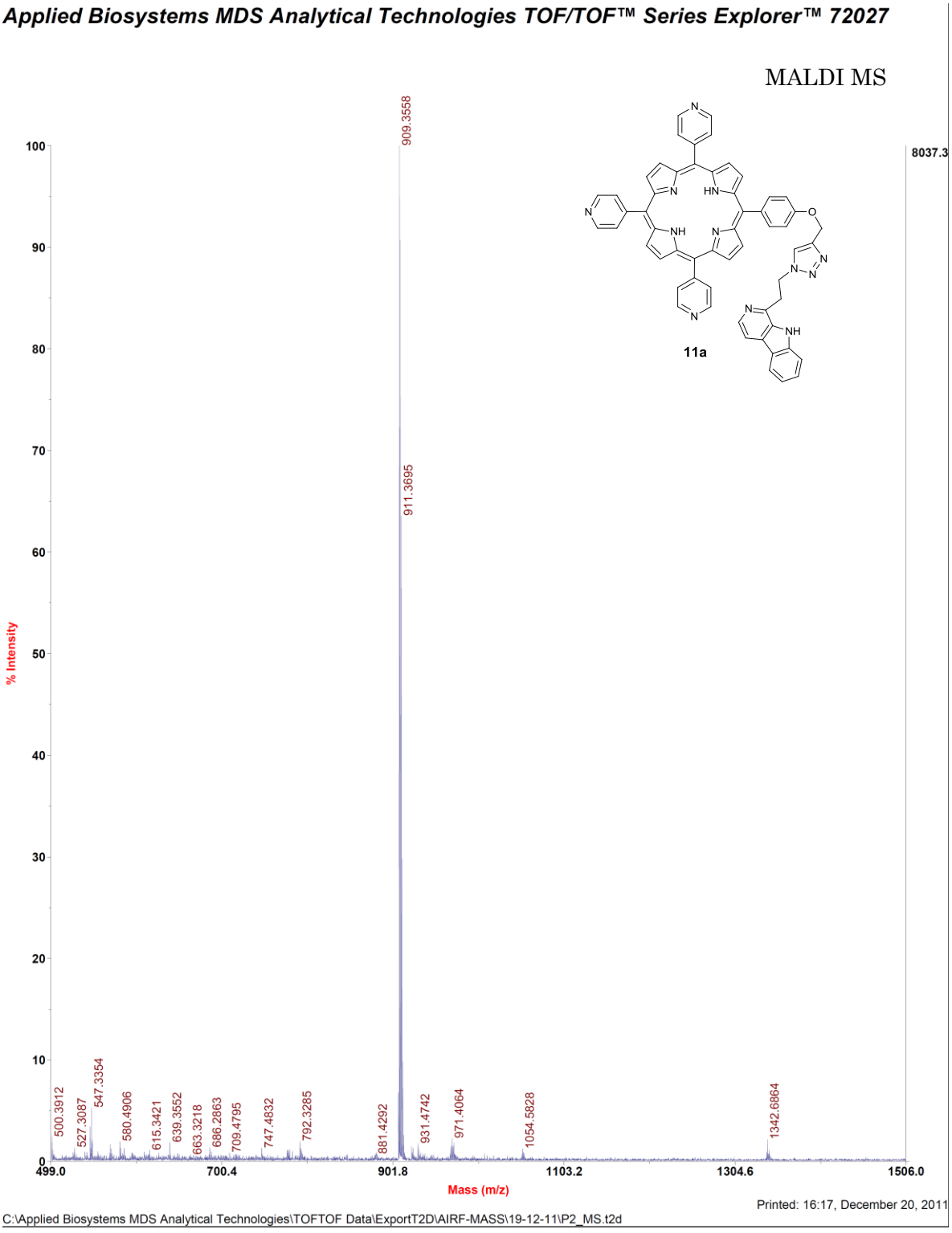

^{1}H NMR
11
f1 (ppm)


+TOF MS: 0.015 to 0.165 min from Sample 45 (BM-350) of aa test 52109.wiff
a=3.59445399999999990e-004, t0=-1.64596898122000010e+001 (Turbo Spray)
Max. 32.7 counts.
HRMS
971.2541
764.4604
475.1547
11
m/z, Da


^{1}H NMR
11a
f1 (ppm)


Applied Biosystems MDS Analytical Technologies TOF/TOF™ Series Explorer™ 72027
MALDI MS
909.3558
911.3695
8037.3
11a
% Intensity
Mass (m/z)
500.3912
527.3087
547.3354
580.4906
615.3421
639.3552
663.3218
686.2863
709.4795
747.4832
792.3285
881.4292
931.4742
971.4064
1054.5828
1342.6864
Printed: 16:17, December 20, 2011
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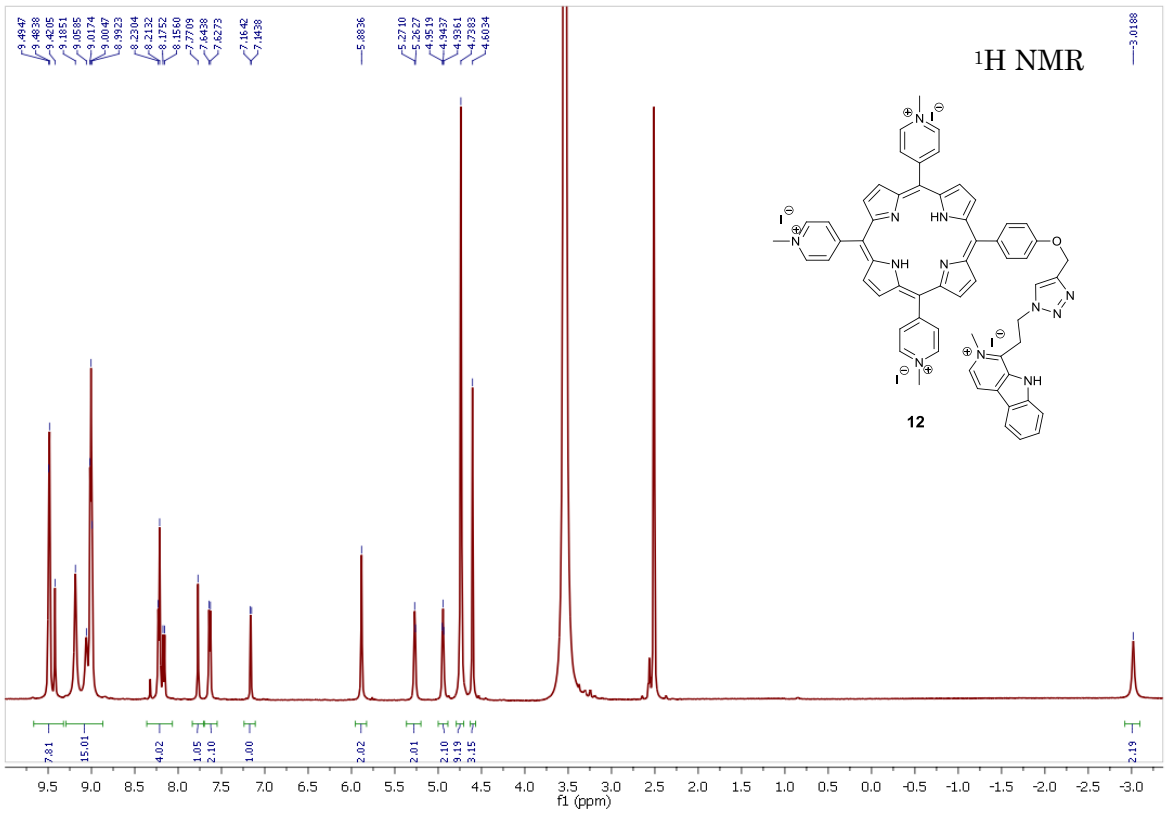
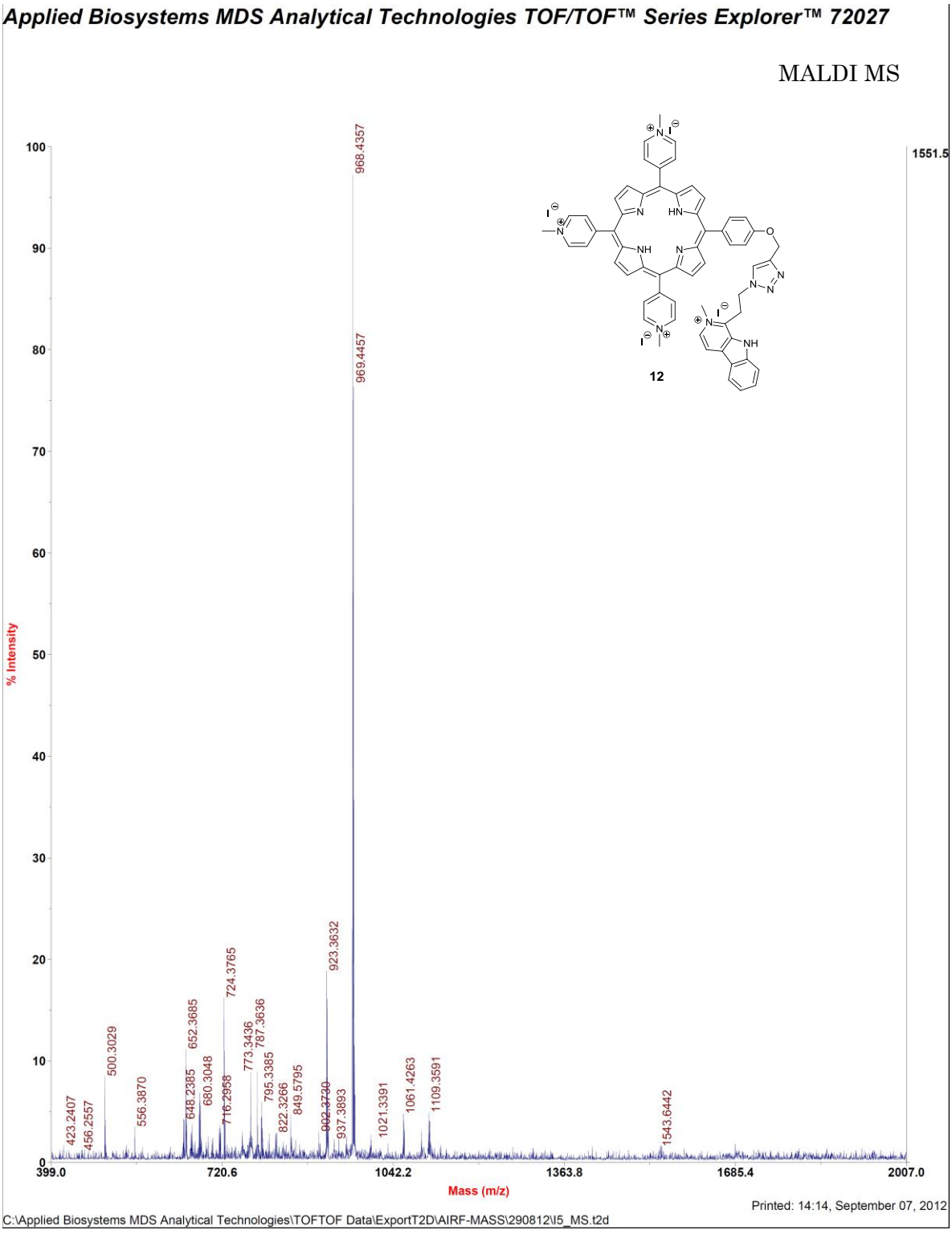

^{1}H NMR
12
f1 (ppm)


Applied Biosystems MDS Analytical Technologies TOF/TOF™ Series Explorer™ 72027
MALDI MS
12
968.4357
969.4457
1551.5
% Intensity
Mass (m/z)
399.0
720.6
1042.2
1363.8
1685.4
2007.0
423.2407
456.2557
500.3029
556.3870
648.2385
652.3685
680.3048
716.2958
724.3765
773.3436
787.3636
795.3385
822.3266
849.5795
923.3632
937.3693
1021.3391
1061.4263
1109.3591
1543.6442
Printed: 14:14, September 07, 2012
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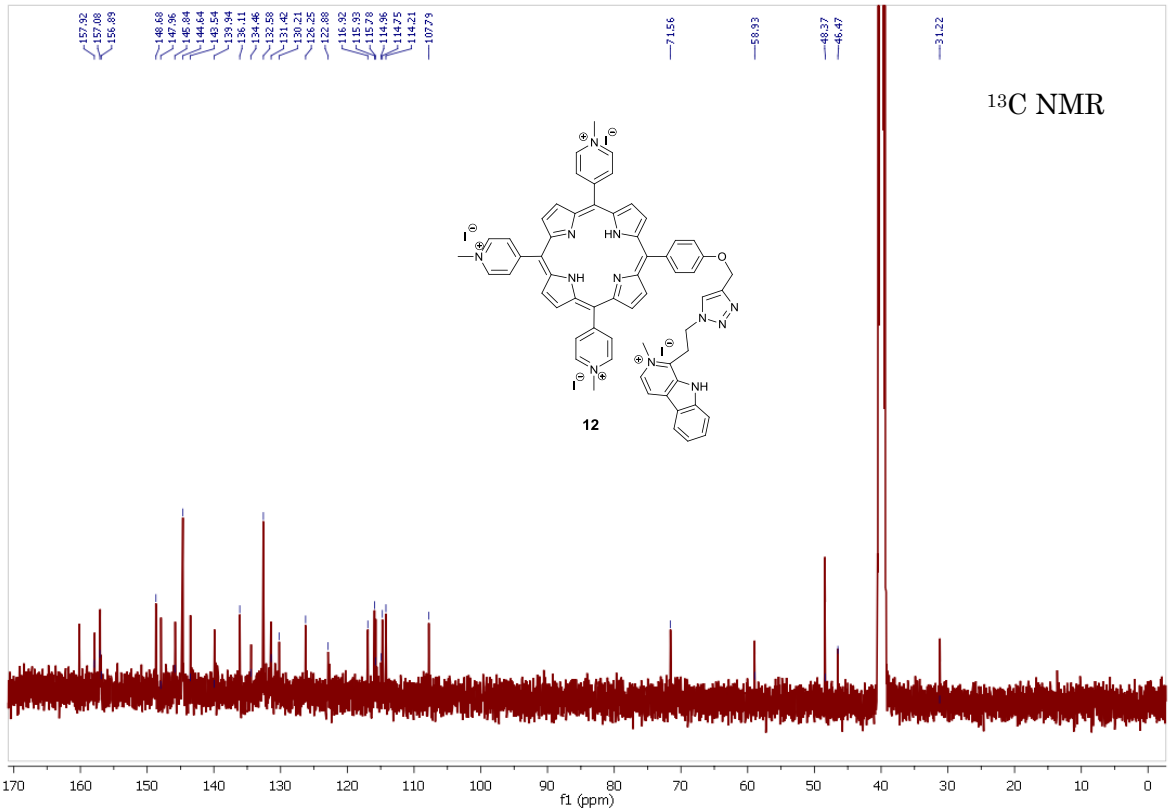
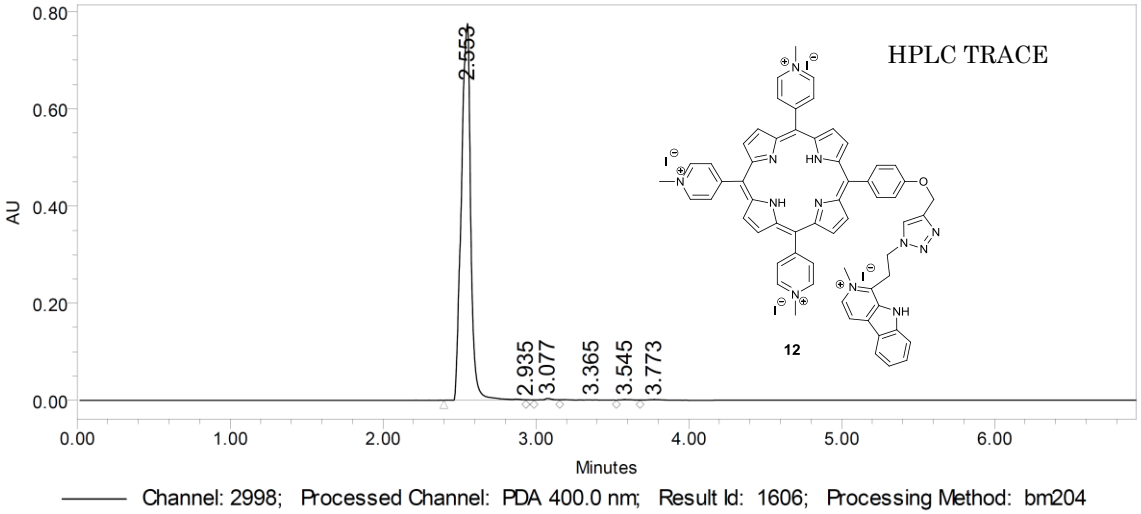

157.92
157.08
156.89
148.68
147.96
145.84
144.64
143.54
139.94
136.11
134.46
132.58
131.42
130.21
126.25
122.88
116.32
115.93
115.78
114.96
114.75
114.21
107.79
71.56
58.93
48.37
46.47
31.22
^{13}C NMR
12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Processed Channel Descr.: PDA 400.0 nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	PDA 400.0 nm	2.553	3303471	99.24	775786
2	PDA 400.0 nm	2.935	3132	0.09	1132
3	PDA 400.0 nm	3.077	17513	0.50	3765
4	PDA 400.0 nm	3.365	2584	0.08	1001
5	PDA 400.0 nm	3.545	1758	0.05	654
6	PDA 400.0 nm	3.773	1406	0.04	513