Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information

## Synthesis of meso−(4′−cyanophenyl)porphyrins: efficient photocytotoxicity against A549 cancer cells and their DNA interactions

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**General Methods**

The reagents and solvents were procured from commercial sources and used as such unless otherwise mentioned. Tetrahydrofuran (THF) was freshly distilled over sodium wire in presence of benzophenone, dichlormethane (DCM) was kept over anhydrous calcium chloride overnight and distilled over calcium hydride prior to use, diethyl ether was stored over anhydrous calcium chloride overnight and passed over activated basic alumina prior to use. Hexane was distilled prior to use to remove any higher boiling fractions. Silica gel for chromatography and TLC plates (60 F254) was procured from Merck. Fourier transform–infrared (FTIR) spectra were performed on Shimadzu IRPrestige–21 spectrometer. $^1$H NMR spectra were recorded on Bruker Advance II 400 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Spectral 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). Electron Spray Ionization–time of flight MS (MALDI–TOF MS) spectrometry was performed using 2,5-dihyrdoxybenzoic acid (DHB) as the matrix. Steady-state absorption spectra were recorded on a Perkin-Elmer model Lambda25 absorption spectrophotometer. Fluorescence spectra were taken in a Hitachi model FL4500 spectrofluorimeter and all the spectra were corrected for the instrument response function. Quartz cuvettes of 10 mm optical path length received from PerkinElmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively. For fluorescence emission, the sample was excited at 450 nm. In both the cases, 5 nm bandpass was used in the excitation and emission side. The relative experimental error in the measured photophysical parameters was estimated within ±5%.

**Synthesis of 5-(4'-methylcarbonylphenyl)-10,15,20-triphenylporphyrin (1).**[1]

To a refluxing solution of methyl 4-formylbenzoate (10 g, 60.97 mmol) in propionic acid (1200 mL), was added freshly distilled benzaldehyde (17.8 g, 167.9 mmol) and pyrrole (17.2 mL, 244 mmol) simultaneously at the same rates. The reaction mixture was heated under reflux for 1 h. After completion of the reaction, propionic acid was distilled off, cooled the residue and added water (500 mL). It was then basified to pH 8 with sodium carbonate and extracted with chloroform (3 × 500 mL). The organic layers were collected, dried over anhydrous sodium sulphate and then evaporated. The residue was purified by column chromatography on silica gel using chloroform/hexane (70:30 *v/v*) as eluent to afford **1** .

Purple colour solid, 9 % yield; IR (KBr): 3350, 3210, 2922, 1716 (C=O), 1600 (Ar-C=C), 1338, 1280 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.95 – 8.80 (m, 6H), 8.73 (d, $J$ = 4.8 Hz, 2H), 8.34 (d, $J$ = 8.3 Hz, 2H), 8.21 (d, $J$ = 7.4 Hz, 6H), 8.06 (d, $J$ = 8.3 Hz, 2H), 7.83 – 7.68 (m, 8H), -2.80 (s, 2H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 168.3, 150.7, 149.3, 148.8, 144.1, 134.6, 134.5, 132.4, 129.6, 127.1, 126.7, 125.9, 120.6, 118.1, 117.9; MALDI-TOF: *m/z* for $C_{42}H_{29}N_5$ $(M + H)^+$: Calcd:639.743; found: 643.2914.

**5-(4'-methylcarbonylphenyl)-10,15,20-tri(4-pyridyl)porphyrin (2).**[2]

Methyl-4-formylbenzoate (10 g, 66.6 mmol) was stirred in propionic acid (1200 mL) and heated at 110 ˚C, then pyridine-4-carbaldehyde (19.2 mL, 200 mmol) and pyrrole (18.7 mL, 266.4 mmol) were added dropwise at the same rates over a period of 15 min at 110 °C. The reaction mixture was then refluxed for 1 h and then the solvent was distilled under reduced pressure. The crude residue was taken into chloroform (300 mL), washed with saturated sodium carbonate solution (3 × 100 mL) and dried over anhydrous sodium sulphate. After removal of solvent *in vacuo*, the crude product so obtained was adsorbed over silica-gel and chromatographed on a silica column using a mixture of chloroform/ methanol (85:15) as eluent. The fifth fraction gave porphyrin **2.**

Purple colour solid, 7% yield; IR (KBr): 3350, 3210, 2922, 1716 (C=O), 1600 (Ar-C=C), 1338, 1280 $cm^{-1}$. $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.95 – 8.80 (m, 3H), 8.73 (d, $J$ = 4.8 Hz, 1H), 8.34 (d, $J$ = 8.3 Hz, 1H), 8.21 (d, $J$ = 7.4 Hz, 3H), 8.06 (d, $J$ = 8.3 Hz, 1H), 7.83 – 7.68 (m, 4H), -2.80 (s, 1H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 168.3, 150.7, 149.3, 148.8, 144.1, 134.6, 134.5, 132.4, 129.6, 127.1, 126.7, 125.9, 120.6, 118.1, 117.9.

**5-(4'-carboxamidophenyl)-10,15,20-triphenyl-porphyrin (3)**.

Purple colour solid, 85 % yield; Mp. > 300 ˚C; IR (KBr): 3466, 3317, 2922, 1666 , 1220, 1072 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.44-8.40 (m, 8H), 8.13 (d, $J$ = 7.5 Hz, 2H), 7.52 (d, $J$ = 7.2 Hz, 2H), 7.32-7.28 (m, 6H), 7.21 – 7.17 (m, 9H), -2.66 (s, 2H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 169.3, 150.7, 149.3, 148.8, 144.1, 134.6, 134.5, 132.4, 129.6, 127.1, 126.7, 125.9, 120.6, 118.1, 117.9; FAB-MS: *m/z* for $C_{45}H_{32}N_5O$ $(M + H)^+$: Calcd:658.2607; found: 658.2672.

**5-(4'-carboxamidophenyl)-10,15,20-tripyridyl-porphyrin (4)**.

Purple colour solid, 78% yield; IR (KBr): 3470, 3058, 2929, 1669, 1596, 1222 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.44-8.40 (m, 6H), 8.17 (d, $J$ = 8.6 Hz, 2H), 7.78-7.75 (m, 8H), 7.35 (d, $J$ = 8.7 Hz, 2H), -2.76 (s, 2H); ESI-MS: *m/z* for $C_{42}H_{29}N_8O$ $(M + H)^+$: Calcd:661.2664; found: 661.2941.

**5-(4'-thiocarboxamidophenyl)-10,15,20-triphenylporphyrin (5).**[3]

Lawesson's reagent (0.52 g, 1.29 mmol) was added to stirred suspension of **3** (0.5 g, 0.761 mmol) in dry toluene (25 mL) and heated the reaction mixture at 90 ˚C for 1 h. After completion of the reaction, the solvent was evaporated and the crude product was purified by a silica gel column chromatography using a mixture of chloroform:methanol (99:1 *v/v*) as eluent to give porphyrin **5.**

Purple colour solid, 78% yield; Mp. > 300 ˚C; IR (KBr): 3425, 3317, 2922, 1618, 1597, 1350 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.46 – 8.44 (m, 8H), 8.14 (d, $J$ = 7.7 Hz, 2H), 7.68 (d, $J$ = 7.6 Hz, 2H), 7.36-7.33 (m, 6H), 7.32–7.29 (m, 9H), -2.69 (s, 2H); FAB-MS: *m/z* for $C_{42}H_{32}N_5S$ $(M + H)^+$: Calcd:674.2378; found: 674.2394.

**5-(4'-thiocarboxamidophenyl)-10,15,20-tripyridylporphyrin (6).**

Brown solid, 45% yield; Mp. > 300 ˚C; IR (KBr): 3427, 3320, 3048, 1616, 1598, 1474, 1355, 1187 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.88-8.84 (m, 6H), 8.22–8.20 (m, 6H), 8.15 (d, $J$ = 8.9 Hz, 2H), 7.76–7.74 (m, 8H), 7.36 (d, $J$ = 8.6 Hz, 2H, meso), −2.78 (s, 2H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 168.3, 150.7, 149.3, 148.8, 144.1, 134.6, 134.5, 132.4, 129.6, 127.1, 126.7, 125.9, 120.6, 118.1, 117.9; MALDI-TOF: *m/z* for $C_{42}H_{28}N_8S$ $(M + H)^+$: Calcd:667.2236; found: 661.2247.

**5-(4'-cyanophenyl)-10,15,20-triphenyl-porphyrin (7a).**

To solution of porphyrin thioamide **5** (0.350 g, 0.52 mmol) in dry dichloromethane (30 mL) was added iodobenzene diacetate (0.176 g, 0.546 mmol) in one portion while maintaining the

temperature 27 °C. The reaction mixture was stirred at same temperature for 1h. The reaction contents were diluted with 10% sodium bicarbonate solution (15 mL) and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with water (2 × 20 mL), dried over anhydrous sodium sulphate and the solvent was removed *in vacuo*. The solid so obtained was washed with methanol and dried under reduced pressure to afford analytical pure cyanoporphyrin **7a**

Dark brown solid**,** 66% yield; Mp. > 300 ˚C; IR (KBr): 3310, 3053, 3026, 2227, 1595, 1002 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.8 –8.86 (m, 6H), 8.73 (d, $J$ = 4.8 Hz, 2H), 8.35 (d, $J$ = 9.2 Hz, 2H), 8.22-8.20 (m, 6H), 8.07 (d, $J$ = 9.2, 2H), 7.79–7.74 (m, 9H), −2.80 (s, 2H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 155.9, 144.8, 143.8, 134.4, 131.7, 130.9, 120.2, 118.1, 115.2, 114.5, 111.2; ESI-MS: *m/z* for $C_{45}H_{30}N_5$ (M+H) Calcd:640.2993; found: 640.3026; UV–vis $\lambda_{max}$ (nm): 409 ( log $\varepsilon$ = 5.4), 518 (log $\varepsilon$ = 4.4), 553 (log $\varepsilon$ = 4.0), 592 (log $\varepsilon$ = 3.9), 647 (log $\varepsilon$ = 3.7).

**[5-(4'-cyanophenyl)-10,15,20-triphenylporphyrinato]Zn(II) (7b).**

To a stirred solution of cyanoporphyrin **7** (0.050 g, 0.078 mmol) in chloroform:methanol (3:1, 10 mL) was added zinc acetate (0.019 g, 0.0858 mmol) and refluxed the mixture for 1h. After the reaction was complete, the contents were diluted with water (50 mL). The organic layers were separated, dried over anhydrous sodium sulphate and the solvent was evaporated *in vacuo*. The crude solid product was stirred in methanol, filtered and dried under reduced pressure to afford analytically pure cyanoporphyrinate **7b.**

Dark brown solid**,** 94% yield; Mp. > 300 ˚C; IR (KBr): 3010, 2922, 2227,1600, 1335, 1101 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.81–8.72 (m, 8H), 8.38 (d, $J$ = 7.8 Hz, 2H), 8.26 (d, $J$ = 8.3 Hz, 2H), 8.17–8.16 (m, 6H), 7.79–7.78 (m, 9H); ESI-MS: *m/z* for $C_{45}H_{28}N_5Zn$ $(M + H)^+$ Calcd:702.2036; found: 702.2071; UV–vis $\lambda_{max}$ (nm): 425 ( log $\varepsilon$ = 5.5), 560 (log $\varepsilon$ = 4.6), 601 (log $\varepsilon$ = 4.2).

**[5-(4'-cyanophenyl)-10,15,20-triphenyl-porphyrinato]Cu(II) (7c).**

Dark brown solid**,** 96% yield; Mp. > 300 ˚C; IR (KBr): 3012, 2922, 2227,1601,1335, 1101 $cm^{-1}$; ESI-MS: *m/z* for $C_{45}H_{29}CuN_5$ $(M+H)^+$ Calcd: 701.1641; found: 701.2040.

**5-(4'-cyanophenyl)-10,15,20-tripyridyl-porphyrin (8a).**

To a solution of (thiocarboxamidophenyl)porphyrin **6** (0.2 g, 0.29 mmol) in dry dichloromethane (20 mL) was added iodobenzene diacetate (0.098 g, 0.304 mmol) in one portion while maintaining the temperature 27 °C. The reaction mixture was stirred at same temperature for 1h.

The reaction contents were diluted with 10% sodium bicarbonate solution (15 mL) and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with water (2 × 20 mL), dried over anhydrous sodium sulphate and concentrated in vacuo. The solid obtained was washed with a mixture of dichloromethane/hexane and dried under reduced pressure to afford analytical pure cyanoporphyrin **8a.**

Brown solid, 58% yield; Mp. > 300 ˚C; IR (KBr): 3437, 3255, 3027, 2925, 2228, 1598, 1345 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.98–8.97 (m, 6H), 8.57–8.56 (m, 2H), 8.46–8.44 (m, 2H), 8.25–8.24 (m, 6H), 7.79– 7.75 (m, 8H), –2.74 (s, 2H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 150.8, 148.7, 145.6, 144.4, 139.2, 135.0, 129.6, 127.6, 123.2, 122.7, 119.8, 114.9.

**[5-(4'-cyanophenyl)-10,15,20-tripyridylporphyrinato]Zn(II) (8b).** Dark brown solid**,** Mp. > 300 ˚C; IR (KBr): 3436, 3254, 3010, 2922, 2227,1600, 1335, 1101 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.81–8.72 (m, 8H), 8.38 (d, $J$ = 7.8 Hz, 2H), 8.26 (d, $J$ = 8.3 Hz, 2H), 8.17–8.16 (m, 6H), 7.79–7.78 (m, 9H); ESI-MS: *m/z* for $C_{45}H_{28}N_5Zn$ $(M + H)^+$ Calcd:702.2036; found:702.2071; UV–vis $\lambda_{max}$ (nm): 427 ( log $\varepsilon$ = 5.5), 560 (log $\varepsilon$ = 4.6), 601 (log $\varepsilon$ = 4.2).

**5-(4'-cyanophenyl)-10,15,20-tri-(4-*N* methylpyridiniumyl) porphyrin (9a**).

To a stirred solution of 5-(4'-cyanophenyl)-10,15,20-tripyridylporphyrin **8a** (50 mg, 0.078 mmol) in dry chloroform (10 mL) and DMF (1.0 mL) in a two-necked flask equipped with a condenser and a rubber septum was added a large excess of iodomethane (0.50 mL, 7.78 mmol) via syringe. The reaction mixture was stirred at 65 °C for 72 h. After cooling to room temperature, the solvents were evaporated in vacuo. The residue was precipitated with dry diethyl ether and methanol (1:1) and then thoroughly washed with the same mixture of solvents to obtain porphyrin **9a**.

Brown solid, 95% yield; Mp. > 300 ˚C; IR (KBr): 3417, 3085, 2925, 2229 1593 ,1352 $cm^{-1}$; $^1H$ NMR (500 MHz, DMSO-$d_6$) $\delta$ 9.51–9.50 (m, 6H), 9.22–9.14 (m, 6H), 9.02 (s, 8H,), 8.47–8.37 (m, 4H), 4.75 (s, 9H, H), -3.03 (s, 2H); $^{13}C$ NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 156.8, 145.7, 144.8, 135.4, 132.7, 131.7, 121.1, 119.4, 116.1, 115, 48.4; ESI-MS: *m/z* for $C_{45}H_{36}N_8$ $(M^+)$ Calcd: 687.2968; found: 687.3010; UV–vis $\lambda_{max}$ (nm): 420 ( log $\varepsilon$ = 5.3), 518 (log $\varepsilon$ = 4.1), 583 (log $\varepsilon$ = 3.7), 599 (log $\varepsilon$ = 3.5), 640 (log $\varepsilon$ = 3.2).

**[5-(4'-cyanophenyl)-10,15,20-tri-(4-*N*-methylpyridiniumyl) porphyrinato]Zn(II) (9b)**.

Dark brown solid, 94%. Yield; Mp. > 300 ˚C; IR (KBr): 3126, 3024, 2976, 2229, 1591, 1276, 1066 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.41–9.39 (m, 6H), 9.05–8.89 (m, 10H), 8.38–7.93

(m, 8H), 4.69 (s, 9H); $^{13}$C NMR (100.5 MHz, DMSO-$d_6$) $\delta$ 158.5, 150.1, 148.9, 144.1, 135.5, 133.6, 133.2, 133.1, 131.4, 116.4 ,48.4); ESI-MS: m/z for $C_{45}H_{33}N_8Zn$ ($M^+$) Calcd: 749.2362; found: 749.2377; UV–vis $\lambda_{max}$ (nm): 434 ( log $\varepsilon$ = 4.8), 562 (log $\varepsilon$ = 3.7), 604 (log $\varepsilon$ = 3.3).

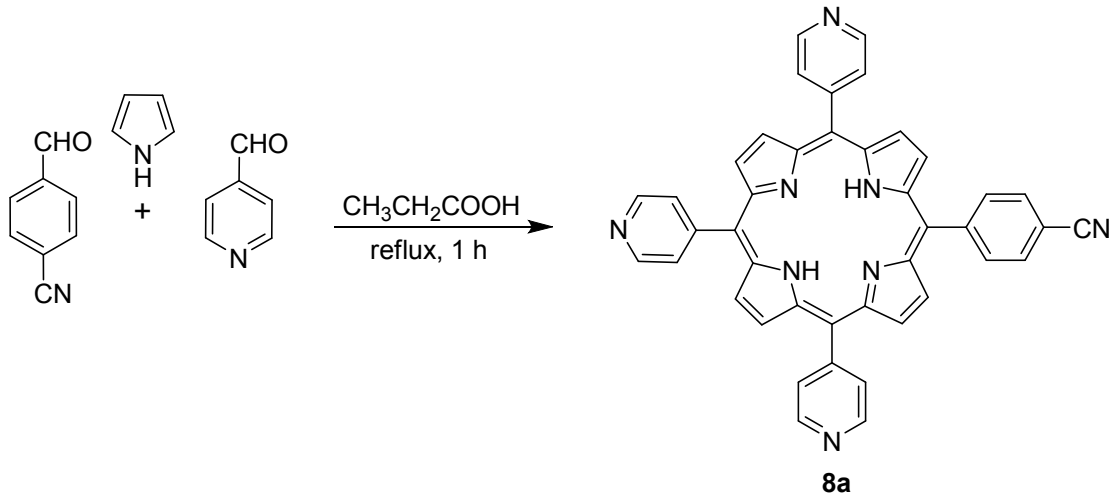
**DNA Cleavage Assay**

Photoirradiation was carried out using a high pressure Xe-arc through a band-path filter (UTVAF-36U, Sigma-Koki, Tokyo, Japan) ($\lambda$ = 300-390 nm, 4 mWcm$^{-2}$, UV-A) or a white LED light source (ISL-150×150-WW, CCS, Kyoto, Japan) ($\lambda$ = 400-800 nm, 2 mWcm$^{-2}$, visible). Because excitaion with the Ze-arc at around 400 nm resulted in too efficient DNA fragmentation, a band-path filter (UTVAF-36U, Sigma-Koki, Tokyo, Japan) ($\lambda$ = 300-390 nm, 4 mWcm$^{-2}$, UV-A) was used for the UV irradiation. Irradiance from the light sources were measured at the positions of the samples (4 cm from the lamp house (UV-A); 2 cm from the surface of LED light source (vis)) with a UVX Radiometer (UVP). Photointensity from the light sources were measured with 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 (1-0.5 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 ($\lambda_{ex}$ = 312 nm, ETX-35.M, Vilber-Lourmat, France).

**Assessment of cytotoxicity toward A549 cells**

A549 cells were cultured in Dulbecco's modified Eagle's medium (DMEM) containing 10% fetal bovine serum (FBS). The cells were seeded into 96-well plates (2000 cells/well) and cultured at 37 °C in a well-humidified incubator with 5% $CO_2$ and 95% air for 24 h. The cells were then incubated with various concentrations of porphyrins for 24 h, and then washed with PBS. Cells were exposed to UV-A or visible light for 10 min, and then the medium was replaced to DMEM. After further incubation for 24 h, cell viability was determined using a Cell Counting kit-8 (WST-8, DOJINDO, Japan) and a microplate spectrophotometer (xMark, BIO-RAD). Cell vaiability after UV- or vis-light exposure in the absence of porphyrins are 76.5% and 97.5%, respectively.

**Preparation of porphyrin 8a by an alternate method.**[4, 5]




**Scheme S1** Synthesis of 5-(4-cyanophenyl)-10,15,20-tri(4-pyridyl)porphyrin **8a**.

To a refluxing solution of 4-cyanobenzaldehyde (1 g, 7.63 mmol) in propionic acid (120 mL), was added freshly distilled 4-pyridine carboxaldehyde (2.16 mL, 22.89 mmol) and pyrrole (2.15 mL, 30.52 mmol) simultaneously at the same rates. The reaction mixture was heated under reflux for 1 h. After completion of the reaction, propionic acid was distilled off, cooled the residue and added water (100 mL). It was then basified to pH 8 with sodium carbonate and extracted with chloroform (3 × 150 mL). The organic layers were collected, dried over anhydrous sodium sulphate and then evaporated. The residue was purified by column chromatography on silica gel using chloroform/methanol (99:1 *v/v*) as eluent to afford **8a** (0.37 g, Yield: 7.5 %), m.p. >300 °C. IR (KBr): 3439, 3256, 3027, 2925, 2229, 1598, 1346 $cm^{-1}$.

## Absorption Spectra for porphyrins 7b-c

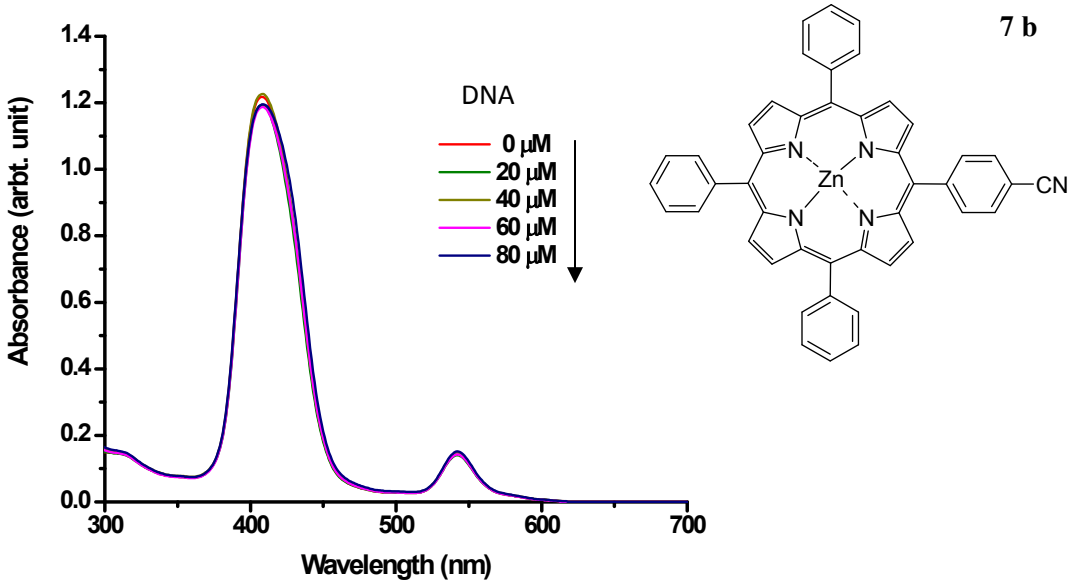



**Fig. S1** Absorption spectra for **7b**

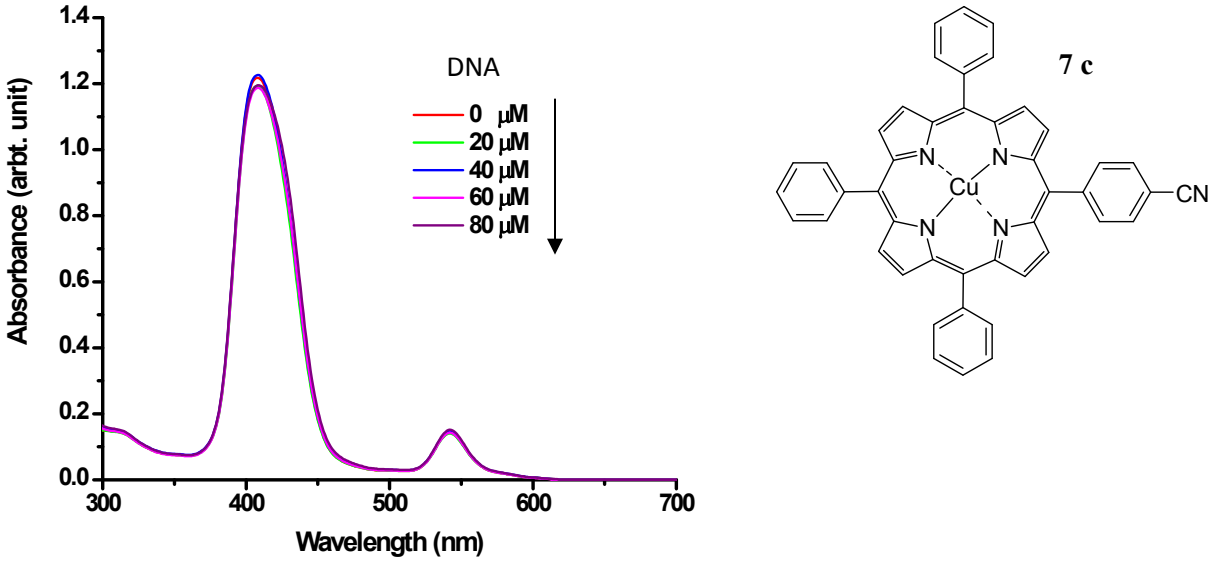



**Fig. S2** Absorption spectra for **7c**

## DNA photocleavage assay and cell viability plots

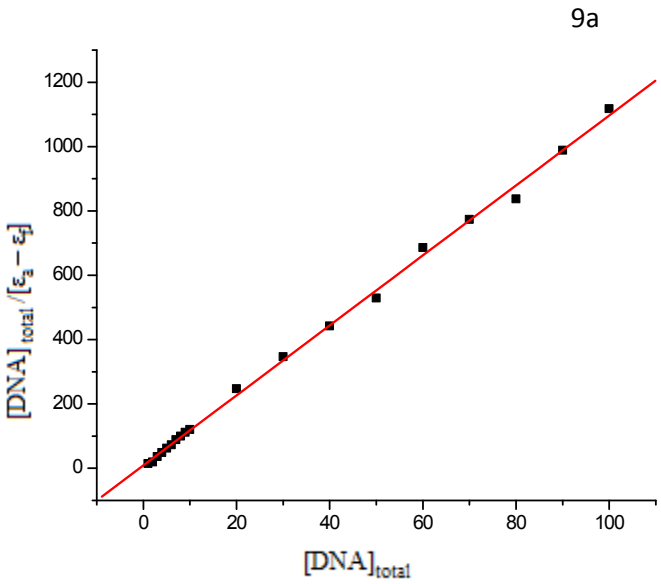



**Fig. S3** Plot of $[DNA]_{total}/[\varepsilon_a - \varepsilon_f]$ versus $[DNA]_{total}$ derived for calculating $K_{app}$

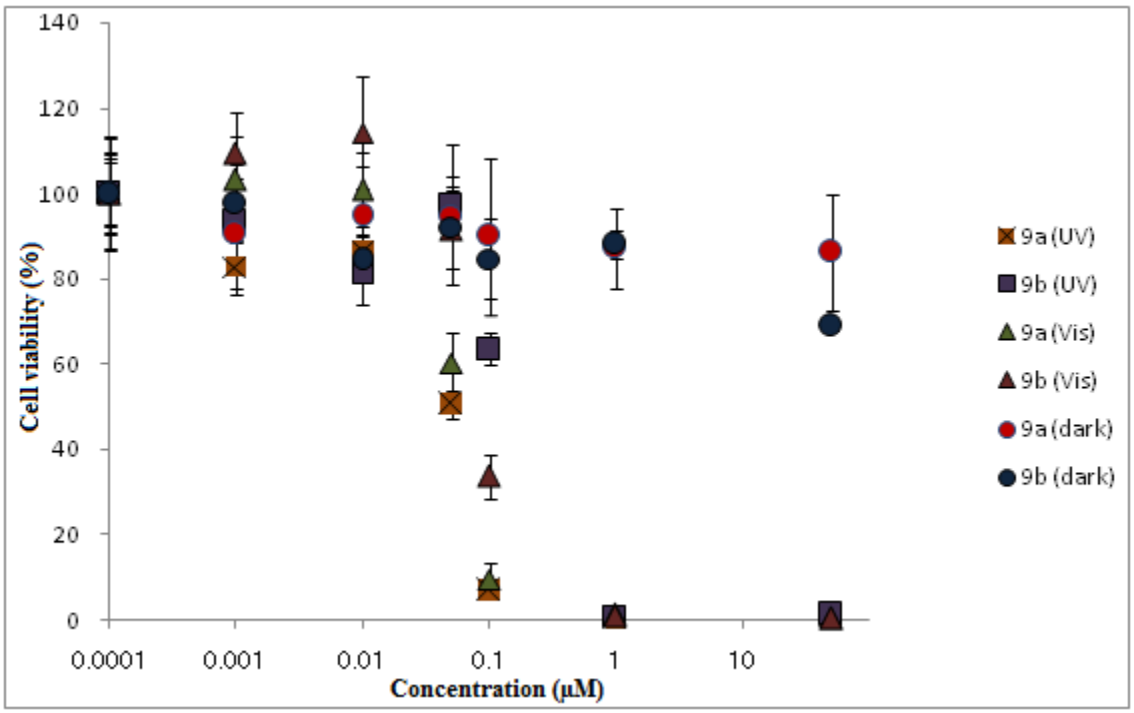
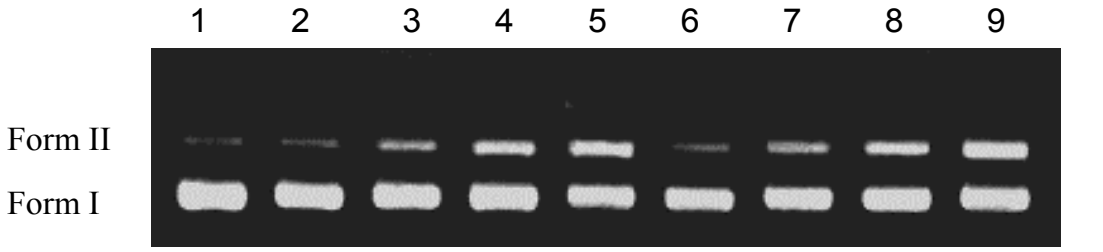



**Fig. S4** Cell viability plots for 5-(4′-cyanophenyl)porphyrins **9** in presence/absence of light




| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Form II(%) | 3 | 5 | 17 | 30 | 38 | 7 | 22 | 32 | 41 |
| Form I (%) | 97 | 95 | 83 | 70 | 62 | 93 | 78 | 68 | 59 |

**Fig. S5** Photoinduced DNA cleavage by $H_2$TMPyP. ΦX174 supercoiled DNA (1.0 μg) was incubated with $H_2$TMPyP (1 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 UV-A light (lanes 2-5) or to visible light (>400 nm) (lanes 6-9) for the indicated periods. Lane 1: DNA alone.

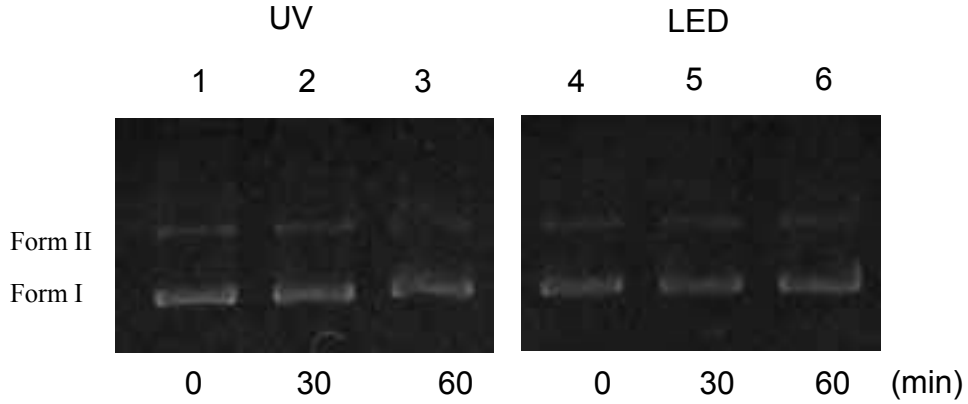



**Fig. S6** Control experiments (without Porphyrin) for the DNA cleavage assay. FX174 supercoiled DNA (1.0 mg) was incubated in 20 ml of Tris-HCl (20 mM, pH 7.2) containing NaCl (20 mM), DMSO (2.5 vol%) at ambient temperature in the dark for 30 min, and then exposed to (lanes 1-3) UV-light (310~390 nm) or (lanes 4-6) visible light (>400 nm) for the indicated periods.

## DNA photocleavage assay for compounds 7a and 7b

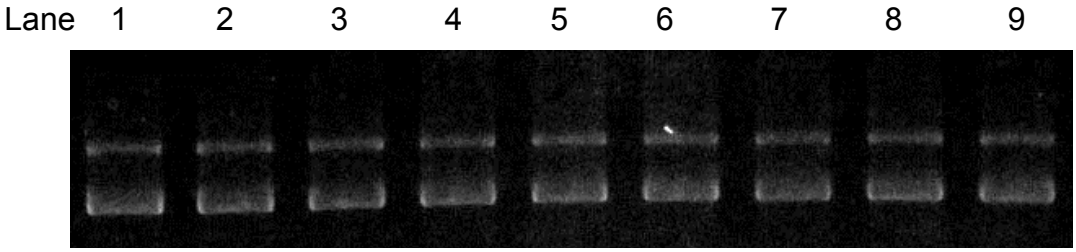



**Fig. S7** Photoinduced DNA cleavage by **7a**. FX174 supercoiled DNA (1 mg) was incubated with **7a** (1 mM) in 20 mL of Tris-HCl (20 mM, pH 7.2) containing NaCl (20 mM), DMSO (2.5 vol%) at ambient temperature in the dark for 30 min, and then exposed to (lanes 3-5) UV-A or (lanes 7-9) visible light. Lanes 2 and 6, DNA + **7a**; lanes 3 and 7, DNA + **7a** + hn 15 min; lanes 4 and 8, DNA + **7a** + hn 30 min; lanes 5 and 9, DNA + **7a** + hn 60 min; lane 1, DNA alone.

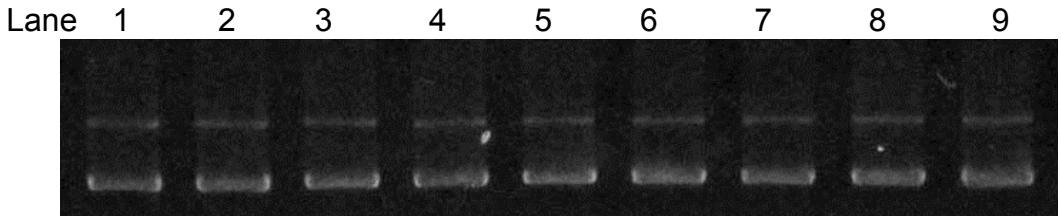
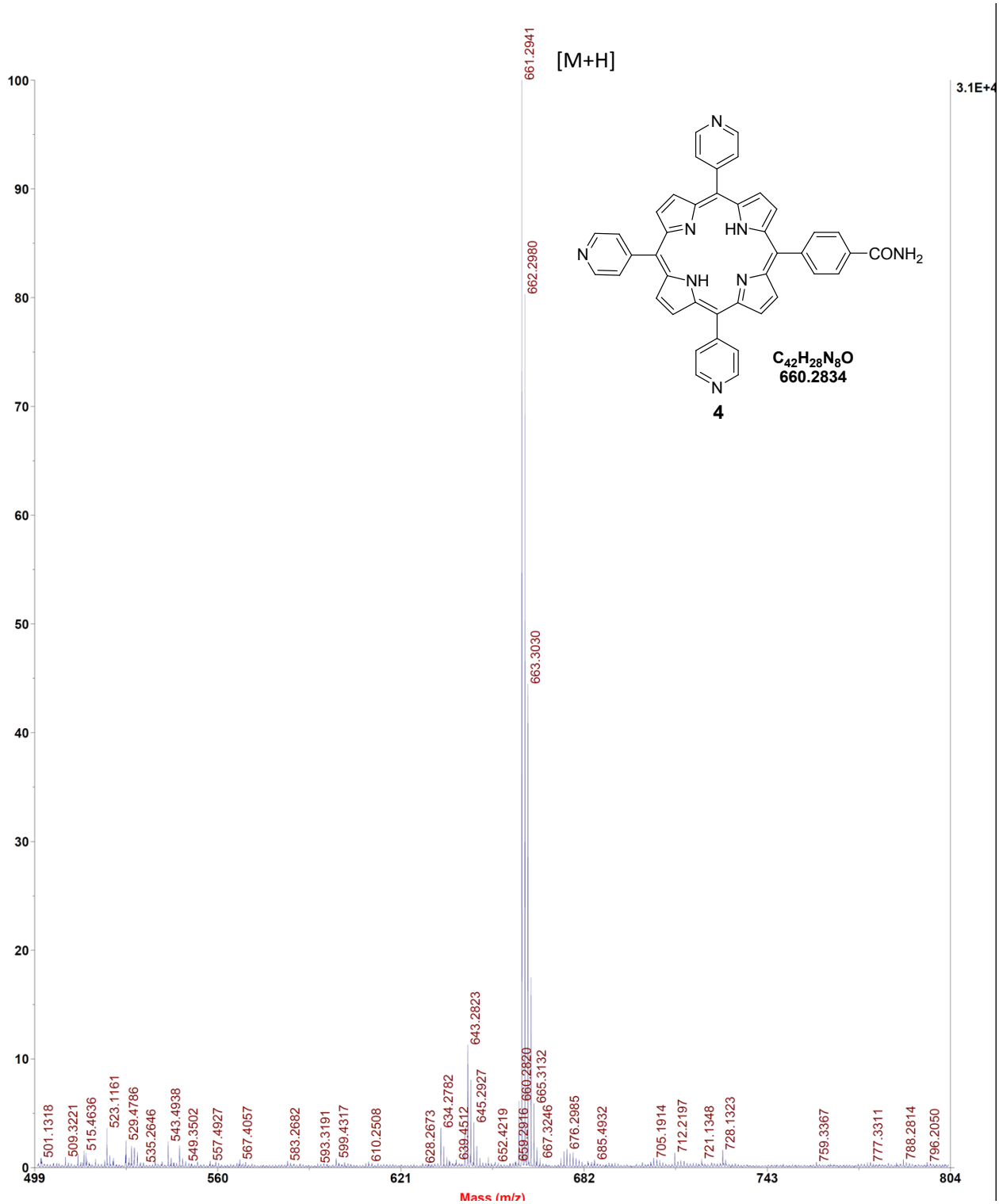


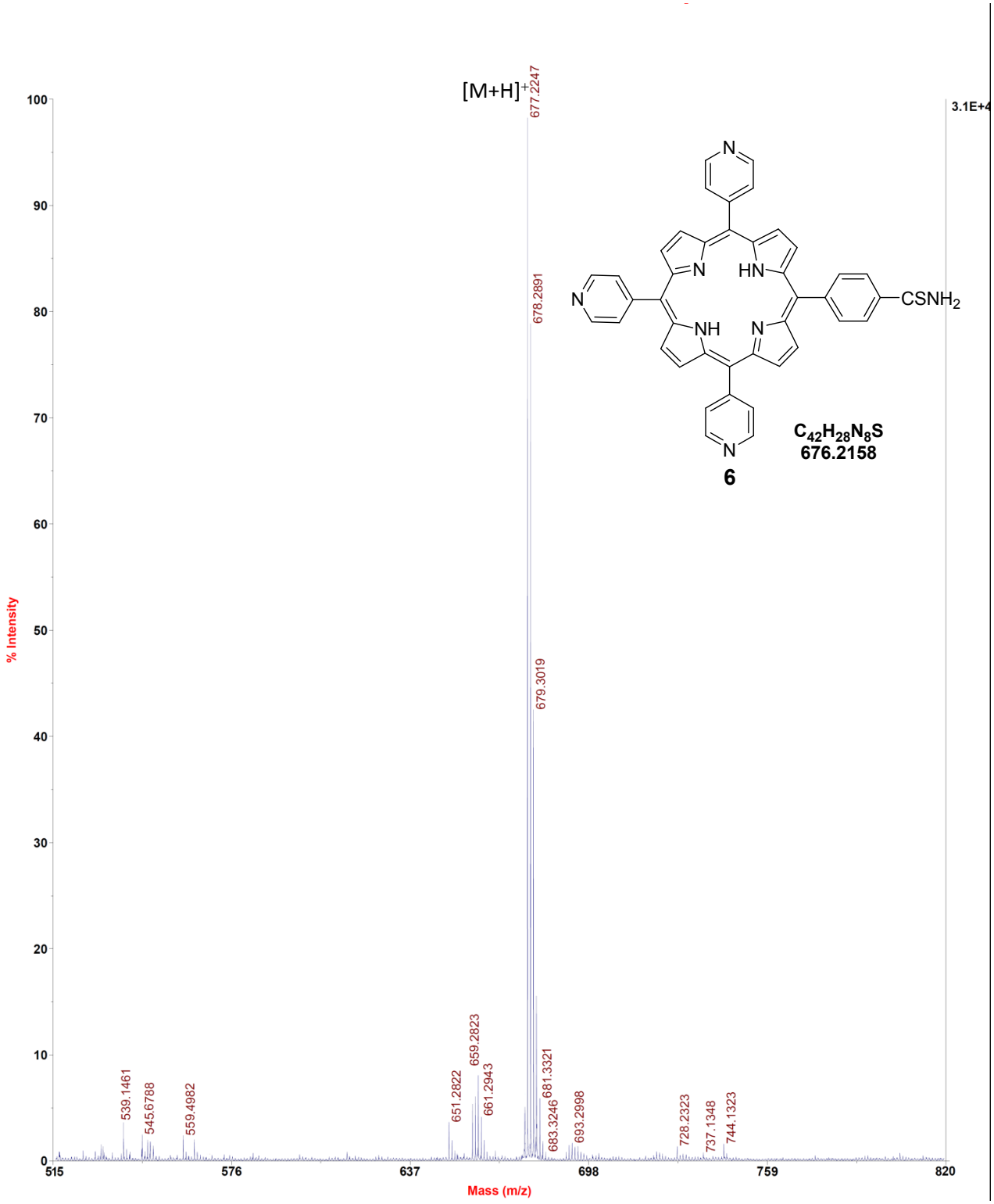

**Fig. S8** Photoinduced DNA cleavage by **7b**. FX174 supercoiled DNA (1 mg) was incubated with **7b** (1 mM) in 20 mL of Tris-HCl (20 mM, pH 7.2) containing NaCl (20 mM), DMSO (2.5 vol%) at ambient temperature in the dark for 30 min, and then exposed to (lanes 3-5) UV-A or (lanes 7-9) visible light. Lanes 2 and 6, DNA + **7b**; lanes 3 and 7, DNA + **7b** + hn 15 min; lanes 4 and 8, DNA + **7b** + hn 30 min; lanes 5 and 9, DNA + **7b** + hn 60 min; lane 1, DNA alone.

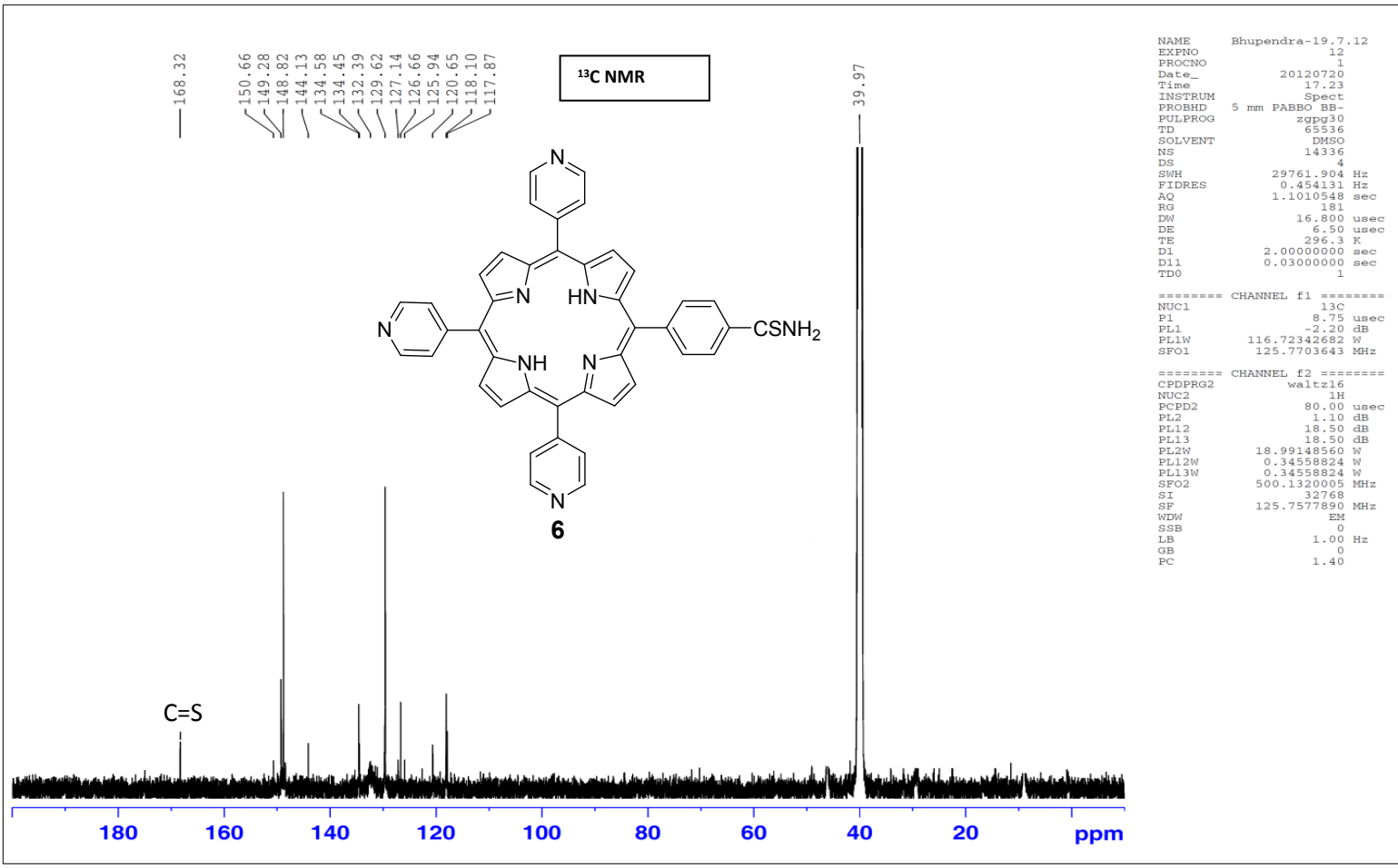
**Table S1** Cell viability data for cationic 5-(4′-cyanophenyl)porphyrins **9**

| **Dose** (μM) | **9a** (UV) | **9a** (UV,S.D) | **9b** (UV) | **9b** (UV,S.D) | **9a** (Vis) | **9a** (Vis, S.D.) | **9b** (Vis) | **9b** (S.D.) | **9a** Dark | **9a** (SD) | **9b** Dark | **9b** (SD) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 100 | 13.21 | 100 | 7.30 | 100 | 9.78 | 100 | 12.81 | 100 | 7.98 | 100 | 9.29 |
| 0.001 | 83 | 6.30 | 93 | 2.91 | 103 | 10.15 | 109 | 9.67 | 91 | 12.73 | 98 | 9.34 |
| 0.01 | 86 | 4.09 | 81 | 7.17 | 101 | 8.64 | 114 | 13.14 | 95 | 11.59 | 84 | 5.43 |
| 0.05 | 51 | 3.32 | 98 | 6.04 | 60 | 7.14 | 91 | 9.12 | 95 | 16.38 | 92 | 9.57 |
| 0.1 | 7 | 0.70 | 63 | 3.78 | 9 | 3.90 | 34 | 5.30 | 90 | 18.31 | 85 | 9.42 |
| 1 | 1 | 0.15 | 1 | 0.18 | 1 | 0.55 | 1 | 0.30 | 87 | 9.38 | 88 | 3.25 |
| 50 | 1 | 0.31 | 1 | 0.18 | 0 | 0.71 | 1 | 0.15 | 86 | 13.60 | 69 | 0.87 |

*SD = standard deviation


[M+H]
661.2941
662.2980
663.3030
3.1E+4
100
90
80
70
60
50
40
30
20
10
0
499
560
621
682
743
804
Mass (m/z)
501.1318
509.3221
515.4636
523.1161
529.4786
535.2646
543.4938
549.3502
557.4927
567.4057
583.2682
593.3191
599.4317
610.2508
628.2673
634.2782
639.4512
643.2823
645.2927
652.4219
659.2916
660.2820
665.3132
667.3246
676.2985
685.4932
705.1914
712.2197
721.1348
728.1323
759.3367
777.3311
788.2814
796.2050
N
HN
NH
N
CONH2
C42H28N8O
660.2834
4


[M+H]+
677.2247
3.1E+4
100
90
80
70
60
50
40
30
20
10
0
% Intensity
678.2891
679.3019
539.1461
545.6788
559.4982
651.2822
659.2823
661.2943
681.3321
683.3246
693.2998
728.2323
737.1348
744.1323
515
576
637
698
759
820
Mass (m/z)
N
HN
NH
N
N
N
CSNH2
C42H28N8S
676.2158
6

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PROCNO                      1
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Time                    17.23
INSTRUM                 Spect
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                  DMSO
NS                      14336
DS                          4
SWH                 29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010548 sec
RG                        181
DW                     16.800 usec
DE                      6.50 usec
TE                     296.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       8.75 usec
PL1                     -2.20 dB
PL1W               116.72342682 W
SFO1                125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      1.10 dB
PL12                    18.50 dB
PL13                    18.50 dB
PL2W               18.99148560 W
PL12W               0.34558824 W
PL13W               0.34558824 W
SFO2                500.1320005 MHz
SI                        32768
SF                 125.7577890 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
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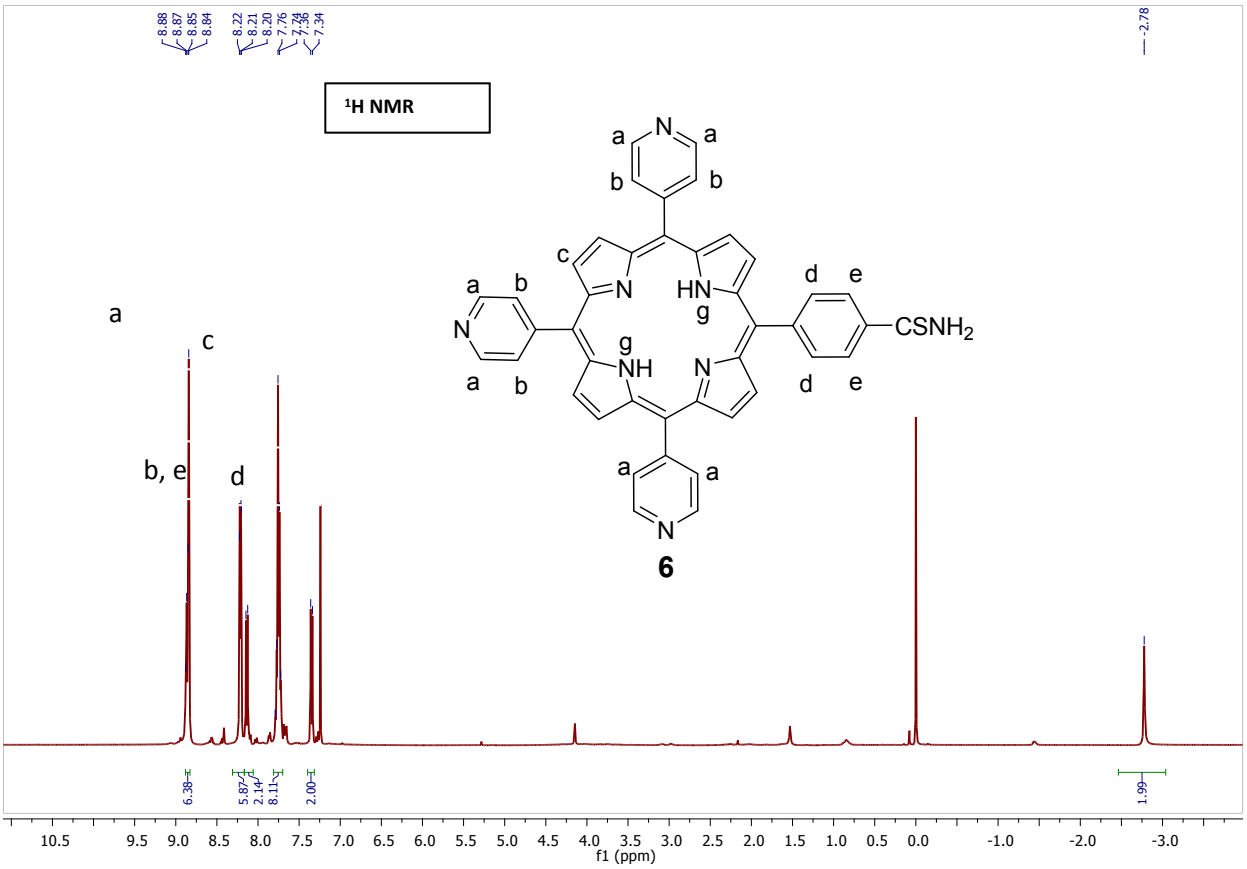
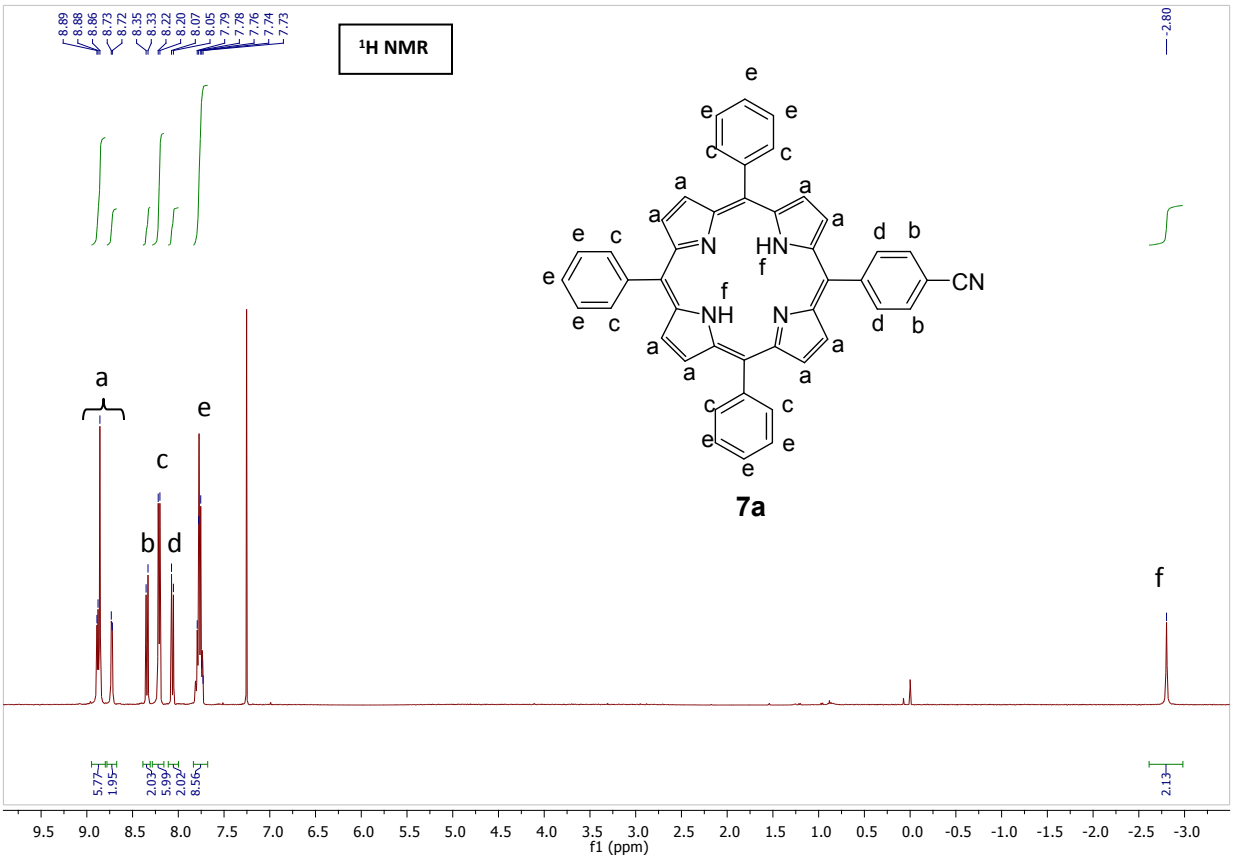

8.88
8.87
8.85
8.84
8.22
8.21
8.20
7.76
7.34
7.34
-2.78
¹H NMR
a
c
b, e
d
a
b
c
d
e
g
CSNH2
6
6.38
5.87
2.14
8.11
2.00
1.99
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
f1 (ppm)

g


¹H NMR
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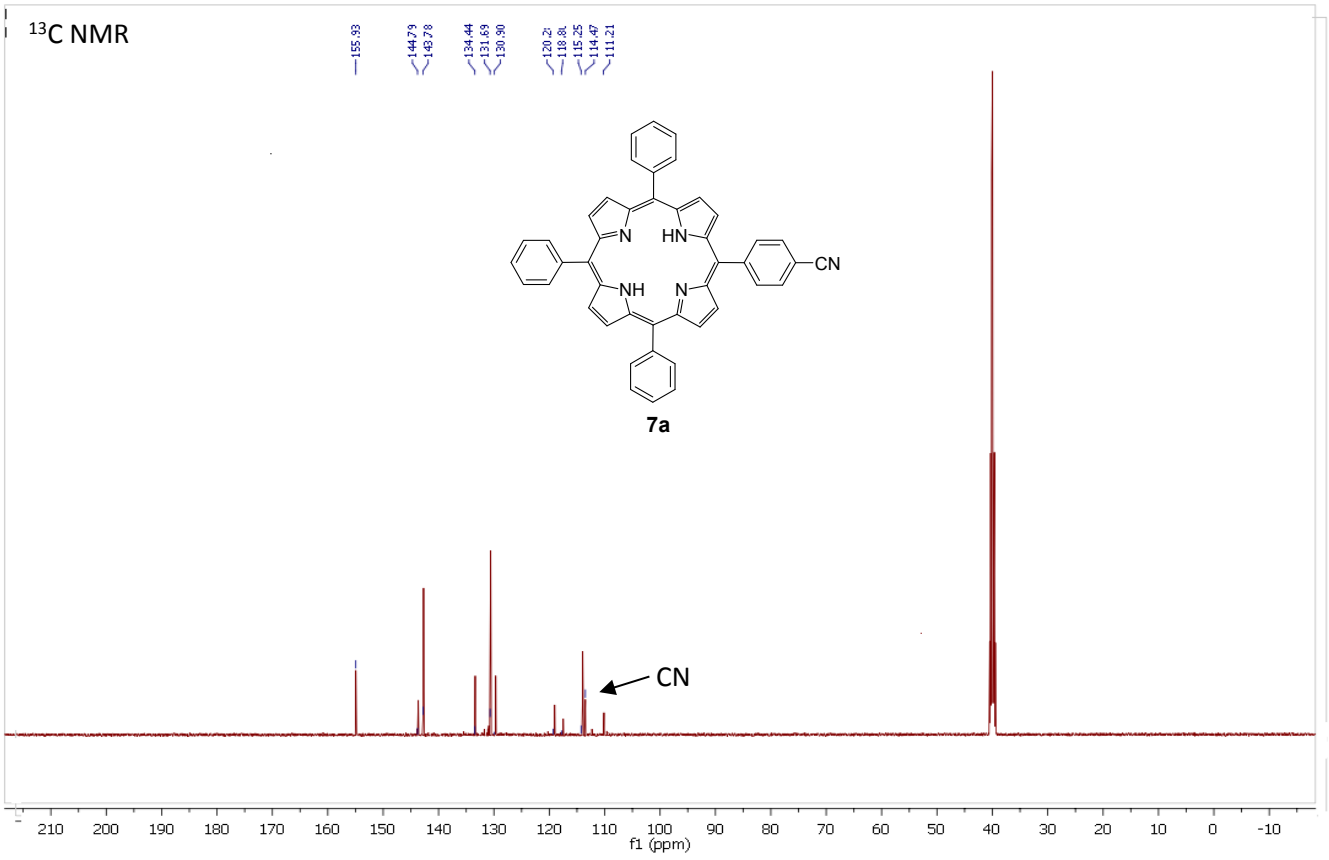
8.88
8.86
8.73
8.72
8.35
8.33
8.22
8.20
8.07
8.05
7.79
7.78
7.76
7.74
7.73
-2.80
a
e
c
b
d
f
CN
HN
NH
N
7a
5.77
1.95
2.03
5.99
2.02
8.56
2.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0
f1 (ppm)

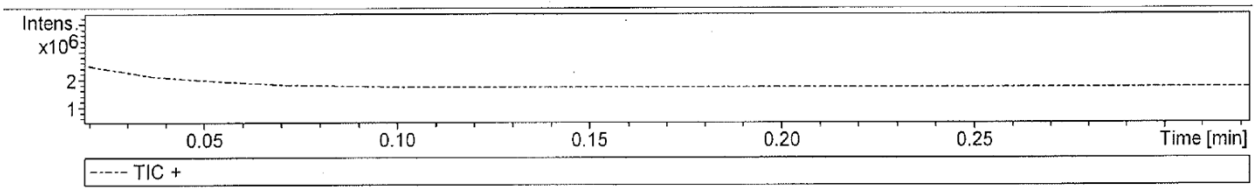
$^{13}$C NMR

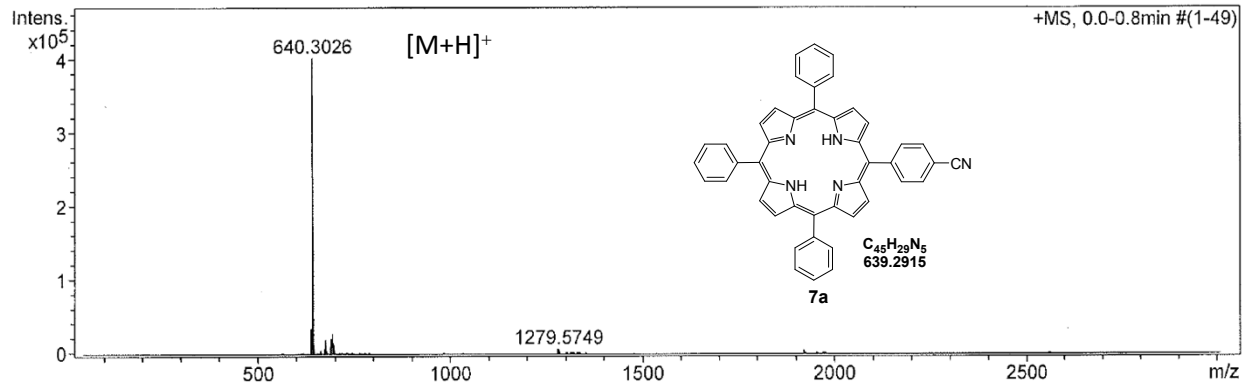

155.93
144.79
143.78
134.44
131.63
130.90
120.21
118.81
115.25
114.47
111.21
N
HN
NH
N
CN
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**7a**

**Acquisition Parameter**

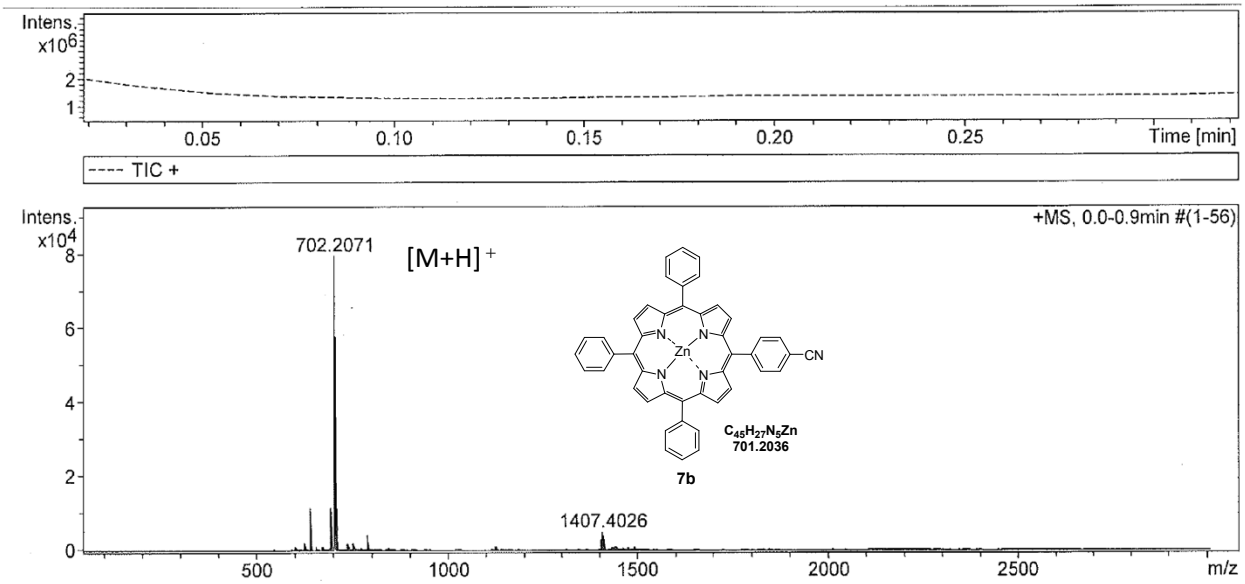
| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Source |



**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Source |



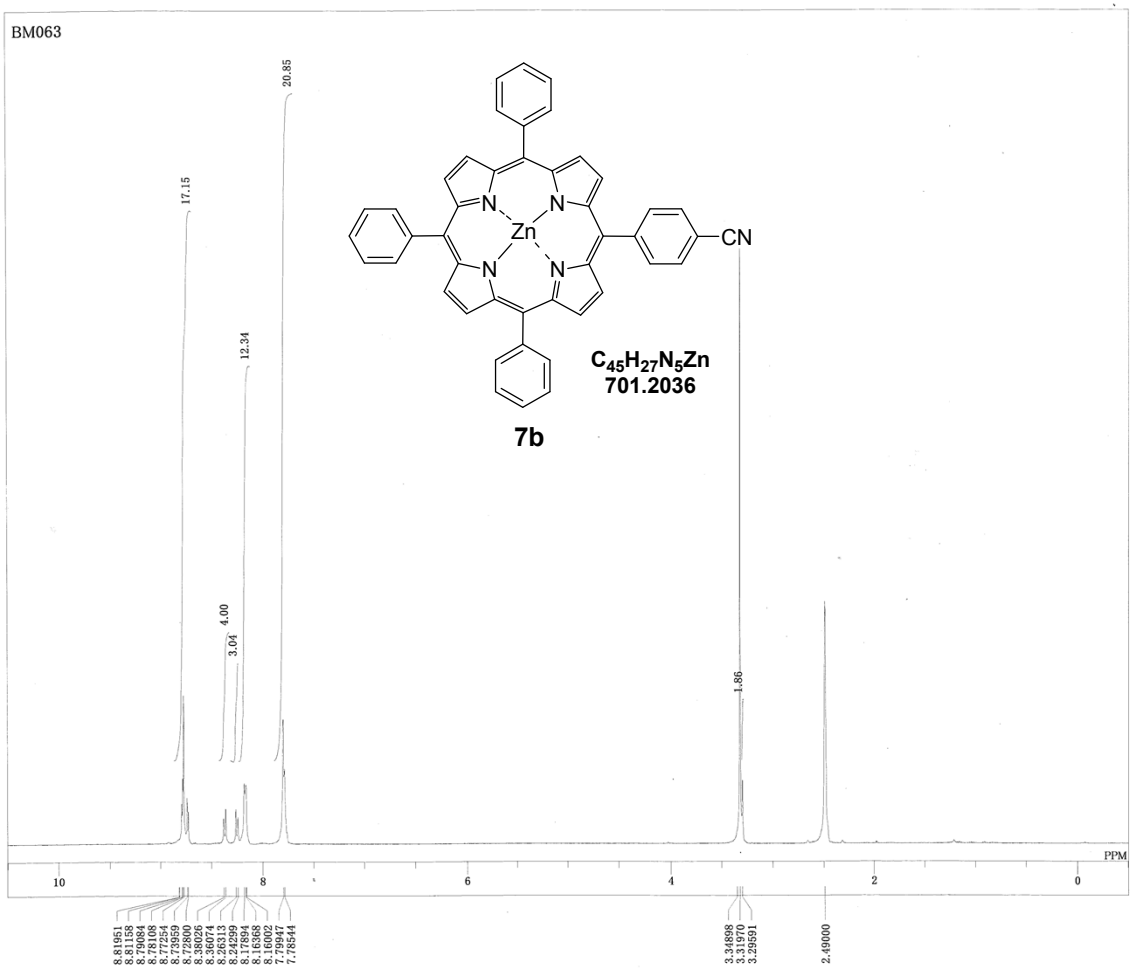







$C_{45}H_{27}N_5Zn$
701.2036

**7b**

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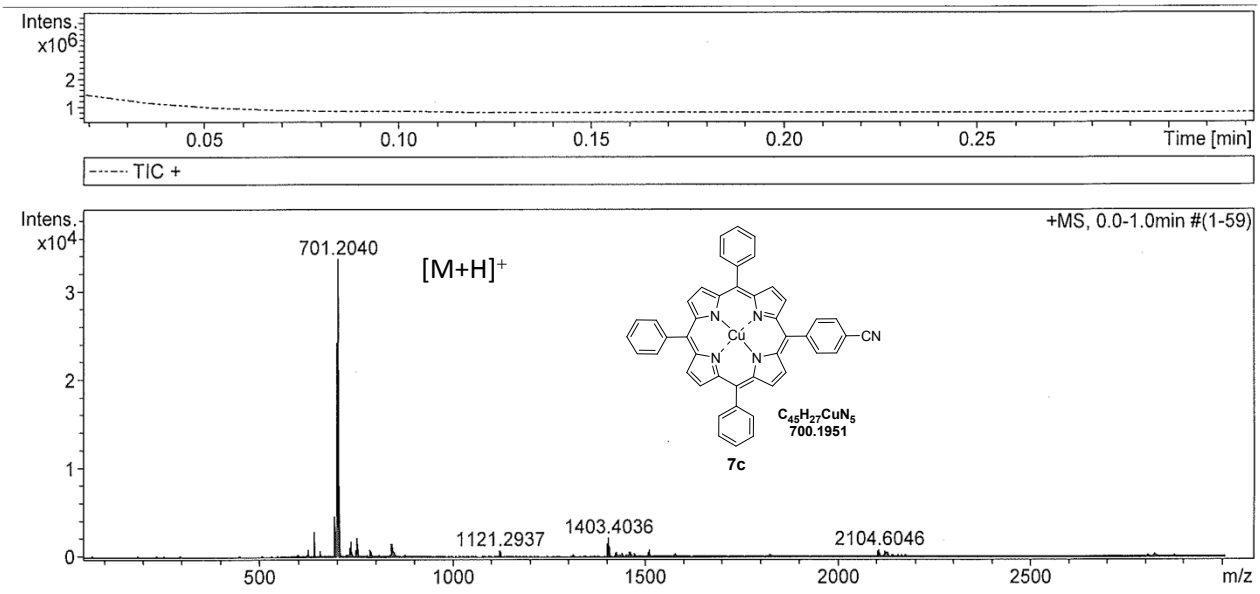
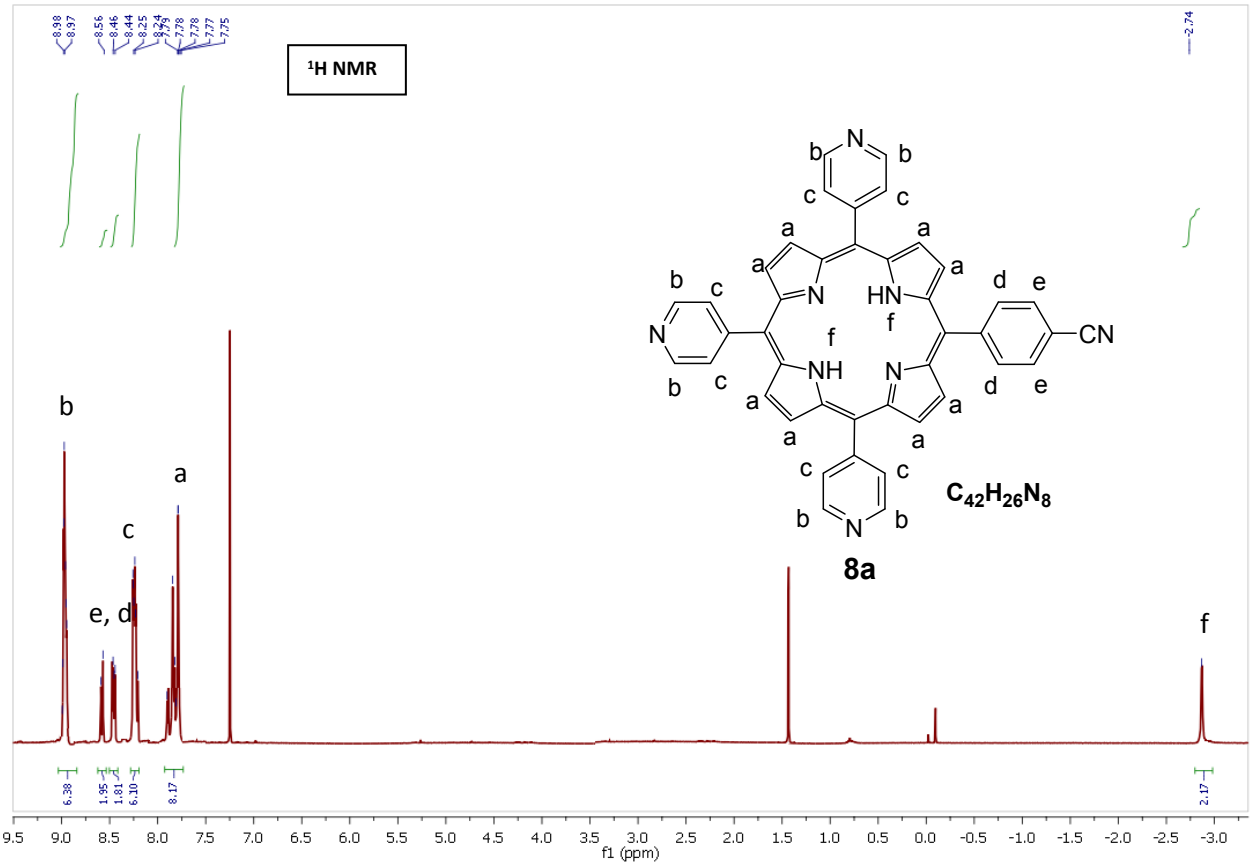
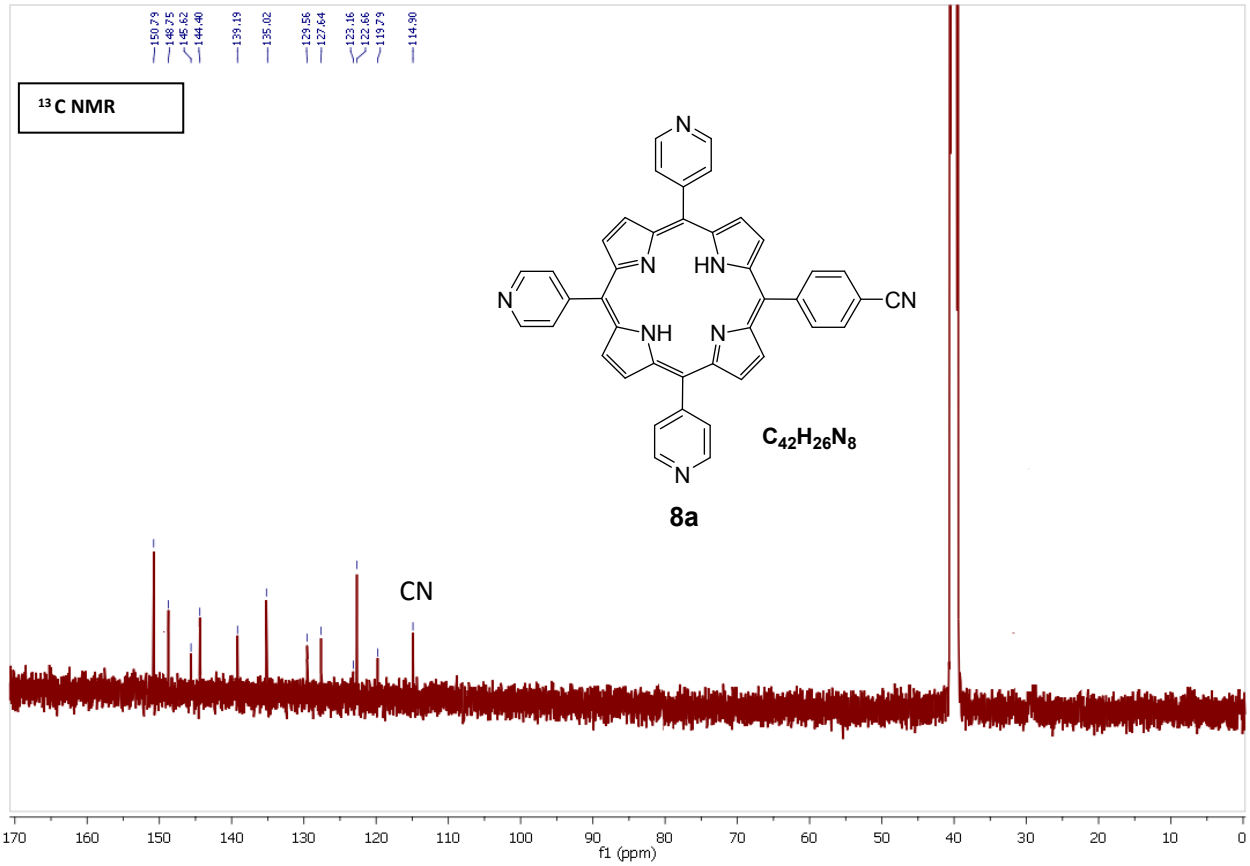
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 51
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 7.20 usec
IRNUC 1H
CTEMP 25.1 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.10 Hz
RGAIN 20

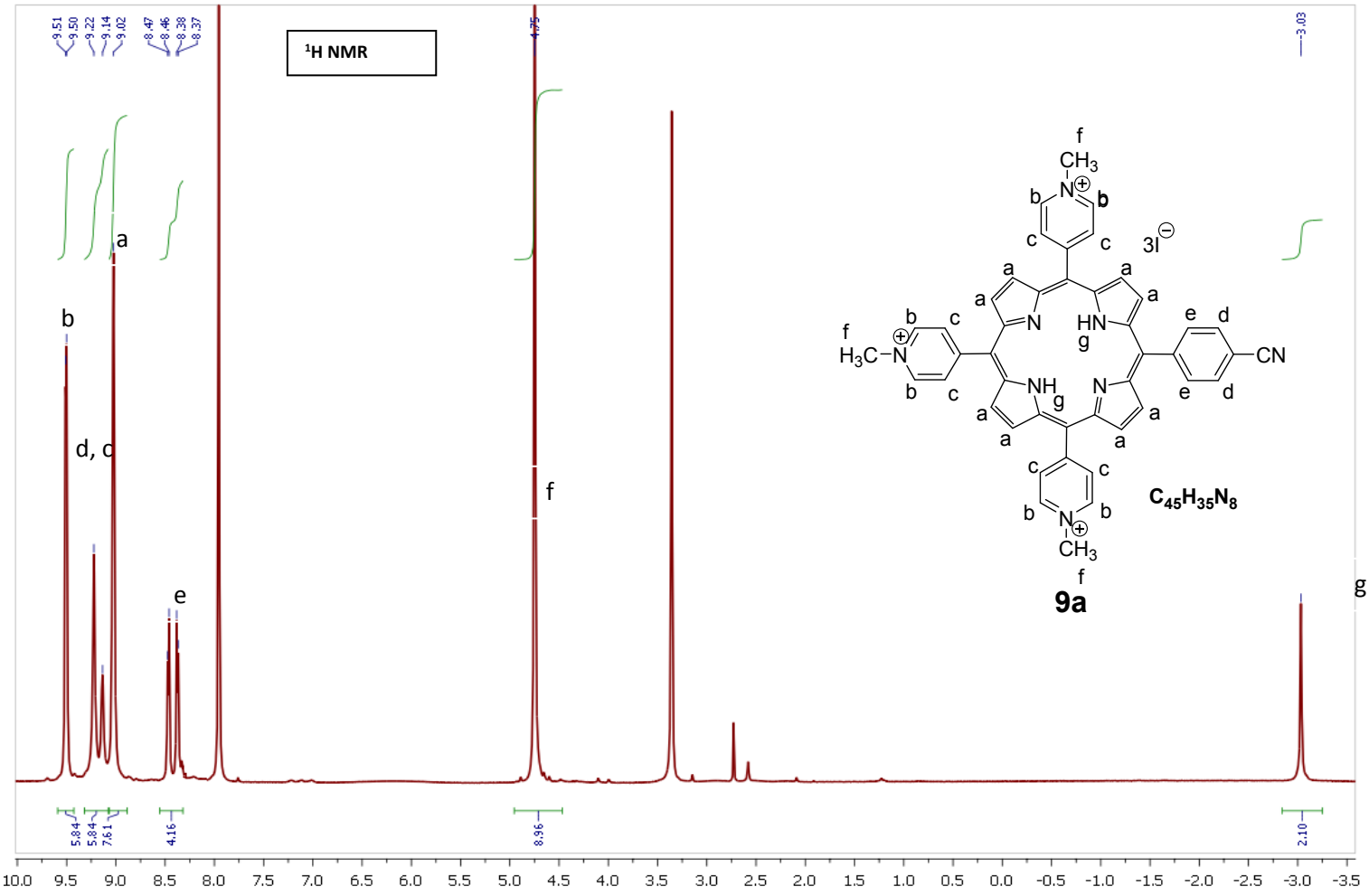
**Acquisition Parameter**

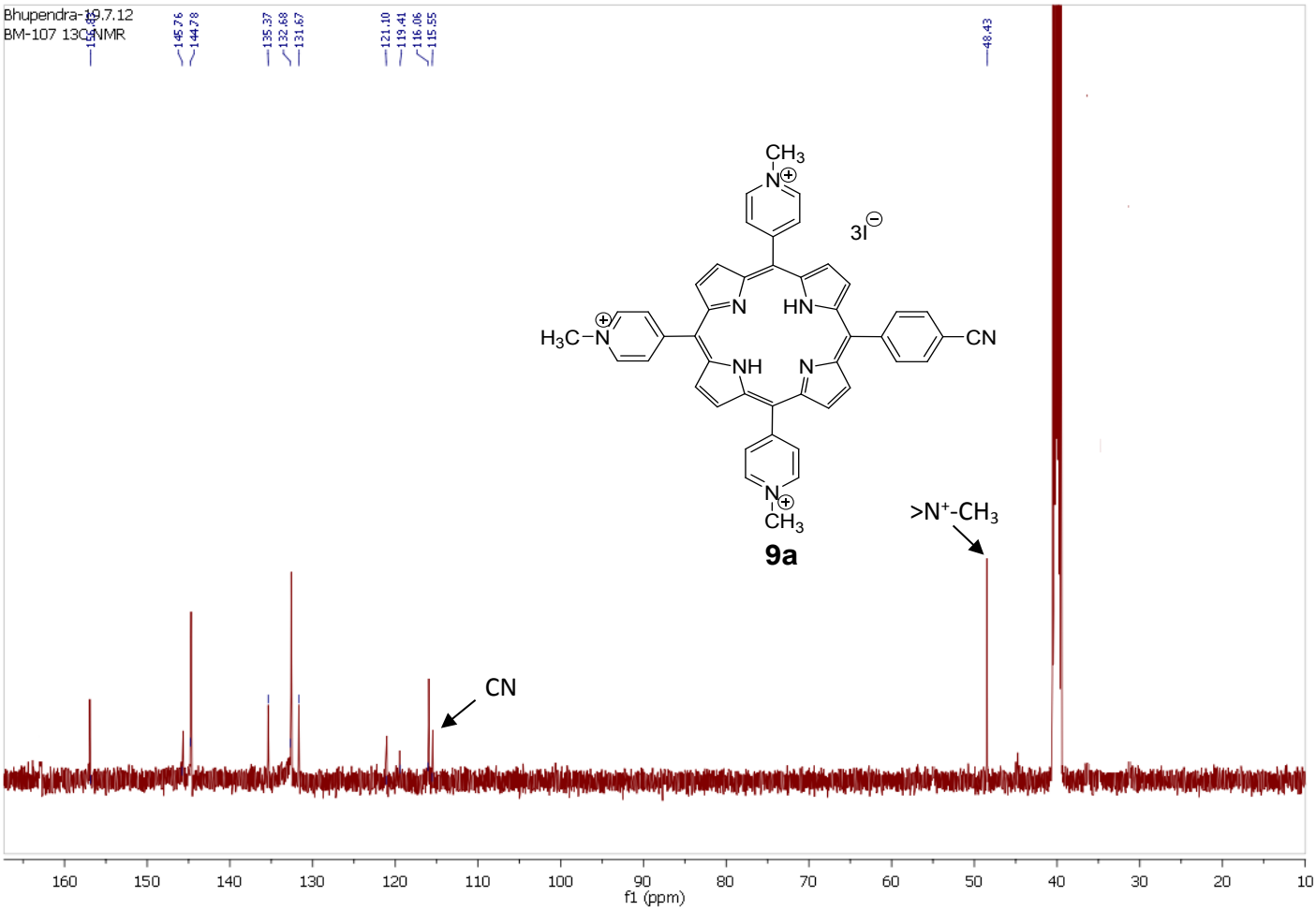
| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Source |




¹H NMR
b
a
c
e, d
f
f1 (ppm)
C42H26N8
8a

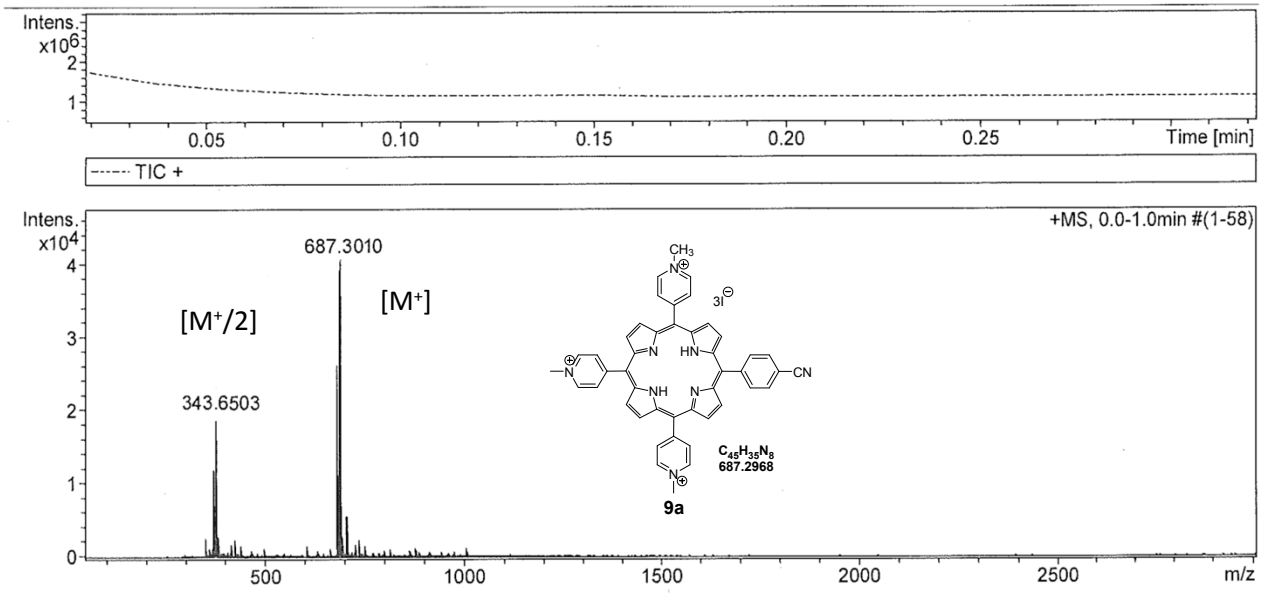

150.79
148.75
145.62
144.40
139.19
135.02
129.56
127.64
123.16
122.66
119.79
114.90
13C NMR
N
HN
N
CN
NH
N
N
C42H26N8
8a
CN
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


¹H NMR
9.51
9.50
9.22
9.14
9.02
8.47
8.46
8.38
8.37
4.75
3.03
a
b
d, c
e
f
g
5.84
5.84
7.61
4.16
8.96
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5
CH3
3I
HN
NH
N
CN
H3C
C45H35N8
9a


Bhupendra-19.7.12
BM-107 13C-NMR
145.76
144.78
135.37
132.68
131.67
121.10
119.41
116.06
115.55
48.43
CH3
N
3I
N
HN
H3C–N
CN
NH
N
N
CH3
9a
>N+-CH3
CN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Source |

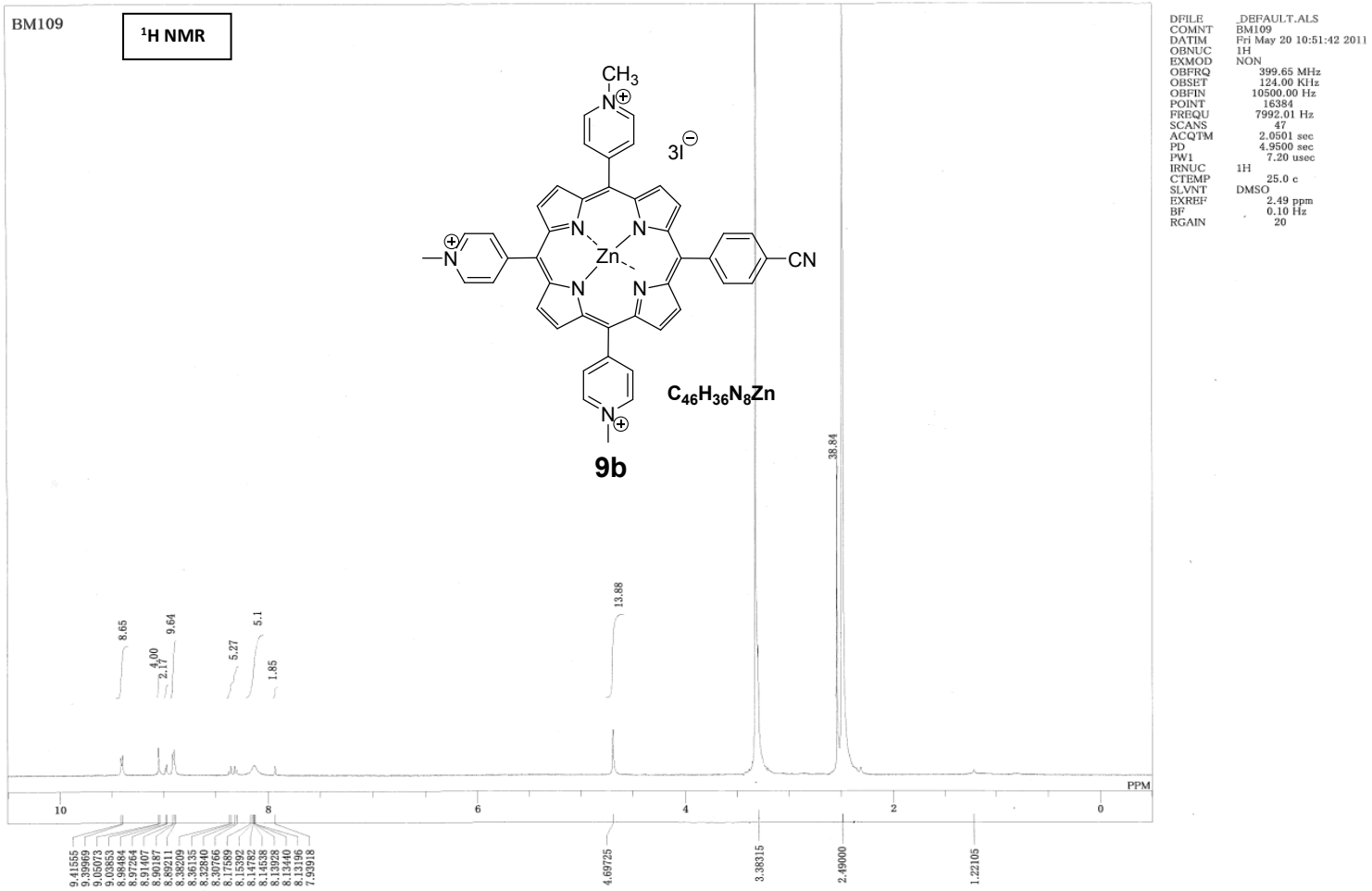









**9a**


BM109
¹H NMR
CH3
3I
Zn
CN
C46H36N8Zn
9b
38.84
13.88
8.65
4.00
2.17
9.64
5.27
5.1
1.85
PPM
10
8
6
4
2
0
9.41555
9.39969
9.05073
9.03853
8.98484
8.97264
8.91187
8.89967
8.89211
8.38209
8.36135
8.32840
8.30766
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8.13928
8.13196
7.93918
4.69725
3.38315
2.49000
1.22105
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EXMOD NON
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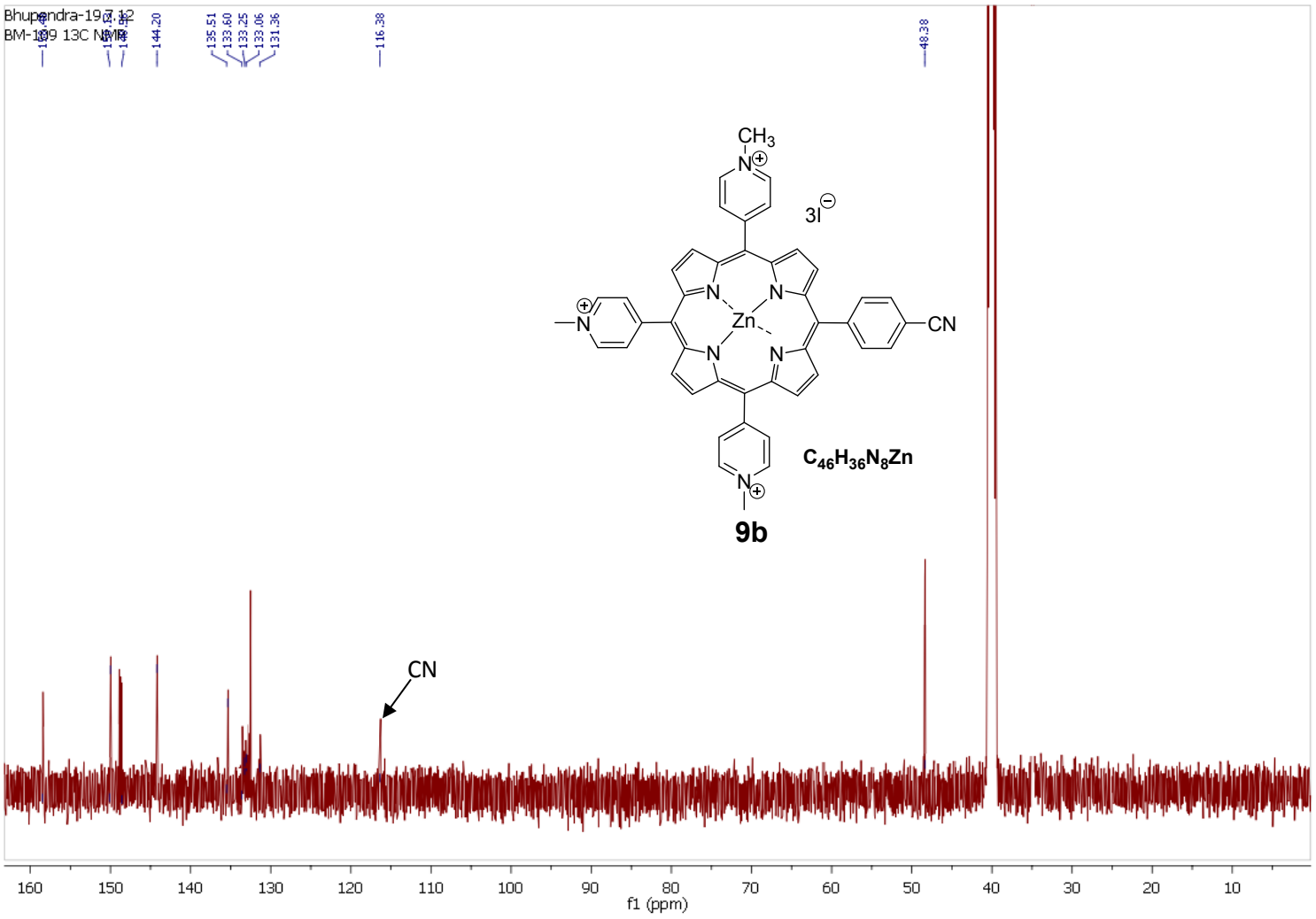
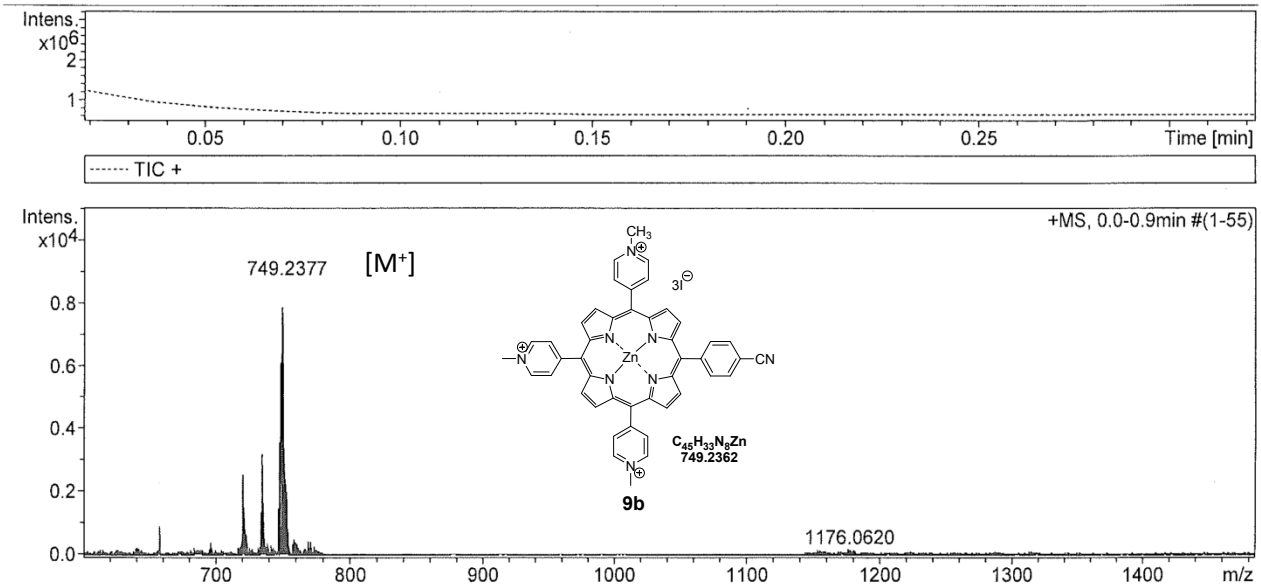
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 47
ACQTM 2.0501 sec
PD 4.9500 sec
PW1 7.20 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.10 Hz
RGAIN 20


Bhupendra-19.7.12
BM-199 13C NMR
144.20
135.51
133.60
133.25
133.06
131.36
116.38
48.38
CH3
3I
CN
Zn
C46H36N8Zn
9b
CN
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Active | | | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set Capillary | 4500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set End Plate Offset | -500 V | Set Divert Valve | Source |



## References


1. K. Suda, T. Kikkawa, S.-I. Nakajima and T. Takanami, *J Am Chem Soc*, 2004, **126**, 9554.
2. D. Kumar, B. A. Mishra, K. C. Shekar, A. Kumar, K. Akamatsu, E. Kusaka and T. Ito, . *Chem. Commun.*, 2013, **49**, 683.
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5. B. Steiger and F. C. Anson, *Inorg. Chem*, 1994, **33**, 5767.