**Supporting information for**

# "Synthesis and Anion binding properties of Novel 3,12- and 3,7-bis(4'-nitrophenyl)-azo-Calix[4]pyrrole receptors"

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## General

Melting points were determined on a Capillary melting point apparatus and are uncorrected. The $\nu_{max}$ in IR spectra are expressed in $cm^{-1}$. The $\lambda_{max}$ in electronic spectra are expressed in nanometers. $^1$H (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded at room temperature using TMS as an internal standard. The chemical shifts (δ ppm) are referenced to the respective solvents and splitting patterns are designed as

*s*(singlet), *d*(doublet), *m*(multiplet), *br* (broad) and *bs*(broad singlet). The column chromatography was carried out using silica gel (60-120 mesh) and neutral alumina. The TLC and PTLC analysis was carried out on double coated silica glass plates (20 × 5 cm and 20 × 20 cm). All the solvents and tetrabutylammonium (TBA) salts were used as received.

**UV-vis binding titration method**

The absorption spectroscopic titrations of azo-sensors with different anions (as tetrabutylammonium salts) were carried out in dry DMSO. A sensor solution was titrated by adding a solution of an anion containing the same concentration of a sensor (Each 5.0 × $10^{-5}$ M). The resulting decrease in intensity was fit using eq 1, as described by Connors.[1]

$$\Delta A = (Q_t K \Delta\varepsilon[L])/(1 + K[L]) \quad (1)$$

Where $\Delta A$ = change in the absorbance from the initial value

$Q_t$ = Total concentration of sensor

$K$ = Binding constant

$\Delta\varepsilon$ = Change in the extinction coefficient between the bound and unbound species

$L$ = Concentration of anion titrated.

**$^1$H NMR binding titration method**

For a specific example, the titration of OMCP, **1** with fluoride anion will be described here. A 0.01 M solution of **1** in DMSO-$d_6$ (0.5 ml) was prepared in 5-mm NMR tube. A 0.1 M solution of tetrabutylammonium fluoride in DMSO-$d_6$ (1.0 ml) was prepared in a 1 ml volumetric flask. An initial NMR spectrum of the solution of **1** was taken, and the initial chemical shift of the NH protons was determined. The solution of fluoride was then added in portions and spectra were recorded after each addition. The aliquots were added until no further change in the chemical shifts of the NHs was observed. The association constant ($K_a$) was obtained by using the eq 2 as reported by Kelly and Kim.[2] The temperature of the NMR probe was 20-21 °C.

$$K_{assoc} = \alpha/[(1-\alpha)([G] - \alpha[H] \quad (2)$$

Where $\alpha = (\delta-\delta_0)/(\delta_{max}-\delta_0)$,

$\delta_0$ = Initial chemical shift (host alone)

$\delta$ = Chemical shift at each titration point

$\delta_{max}$ = Chemical shift when receptor is entirely bound

[G] = Concentration of guest at each titration point

[H] = Concentration of host at each titration point

**Continuous variation method (Job's method)**

The stoichiometry of the host-guest Complex was determined by the continuous variation method (Job's Plot). The azo-sensors and tetrabutylammonium salts of anions were dissolved in dry DMSO separately at appropriate concentrations, which were then mixed and diluted with the solvent to control the concentrations. The sum of the total concentration of the host $[H]_T$ and anion $[A^-]_T$ namely $[H]_T + [A^-]_T$ was maintained to be 0.1 mM in DMSO. At the same time, the ratio $[H]_T/[A^-]_T$ was varied from 1:9 to 9:1. After recording the UV-visible spectrum of these solutions, the appropriate absorbance values were plotted against the mole fraction of the anions. The appearance of maximum at 0.5 confirmed the 1:1 stoichiometry between hosts and guests.

**Synthetic experimental**

The 5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole (OMCP) **1** and 5,5,10,10,15,15,20,20-octamethyl-N-confused calix[4]pyrrole (NC-OMCP) **2** were prepared as reported previously by us.[3]

Synthesis of 2-(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole[4,5] **3** and 3-(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl-N-confused calix[4]pyrrole[6] **4** was performed by diazotization of **1** and **2** using 1.1 equiv of aq p-nitrophenyldiazonium chloride under milder basic conditions.[7]

**Synthesis of bisarylazo-calix[4]pyrroles 5 and 6**

A cold solution of 4-nitrophenyldiazonium chloride (2.2 equiv), prepared from 4-nitroaniline (1.28 g, 10 mmol), sodium nitrite (0.69 g, 10 mmol) and conc HCl (1.5 mL) in water (2 mL), was added dropwise to a cold (-10°C) solution of OMCP **1** (2.0 g, 4.68 mmol) and $NaHCO_3$ (0.92 g, 10.1 mmol) in THF (100 mL). A dark red suspension was

immediately formed in the reaction flask. The stirring was continued for further 15 min at low temp. The solution was diluted by water and extracted with ethyl acetate. Organic extracts were washed four times with water (100×4 mL) and dried over anhyd magnesium sulfate. The Solvent was evaporated under reduced pressure and crude was subjected to column chromatography. The elution of column with ethyl acetate: petroleum ether, (0.8:10, v/v) gave 2-(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole **(3)** as orange product. Yield: 54 mg, 2 % (based on OMCP).

Further elution of the column with ethyl acetate: petroleum ether, (1:10, v/v) gave 3,12-bis(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole **5** as red solid. Final elution of column with 15 % ethyl acetate and petroleum ether mixture afforded 3,7-bis(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole **6** as orange solid. The compd **5** and **6** were further purified by PTLC (18 % ethyl acetate in petroleum ether) and dried. The obtained yields of **5** and **6** after chromatographic purification are given in characterization data.

**5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole** (**1**): mp 295$^{o}$C; $R_f$ = 0.8 ($SiO_2$, 3:2 petroleum ether/chloroform); IR (KBr pellet): 3435 (*br*, pyrrole NH), 3023, 2842, 1541, 1187, 752 cm$^{-1}$; $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 1.50 (*s*, 24H, $CH_3$), 5.89 (*d*, *J* = 2.5 Hz, 8H, β-pyrrole CH), 7.00 (*bs*, 4H, Pyrrole NH); $^{1}$H NMR (300 MHz, DMSO-$d_6$): δ = 1.42 (*s*, 24H, $CH_3$), 5.59 (*d*, *J* = 2.1 Hz, 8H, β-pyrrole CH), 9.18 (*s*, 4H, Pyrrole NH); $^{13}$C NMR (75MHz, $CDCl_3$) δ = 29.0 ($CH_3$), 35.1 (*meso* C), 102.7 (β-pyrrole CH), 138.3 (α-pyrrole C); HRMS (ESI-MS) for $C_{28}H_{36}N_4$ $[M-H]^-$ : calcd, 427.2862; found, 427.2860.

**5,5,10,10,15,15,20,20-octamethyl-N-confused calix[4]pyrrole** (**2**): mp 185$^{o}$C; $R_f$ = 0.45 ($SiO_2$, 3:2 petroleum ether/chloroform); IR (KBr pellet): 3430, 2910, 2845, 1521, 1616, 1179, 749 cm$^{-1}$; $^{1}$H NMR (300 MHz, $CDCl_3$) δ = 1.48-1.54 (*m*, 24H, $CH_3$), 5.07 (*bs*, 1H, β-pyrrole CH), 5.87 (*m*, 2H, β-pyrrole CH), 5.89 (*br*, 2H, β-pyrrole CH), 5.90 (*br*, 2H, β-pyrrole CH), 6.51 (*s*, 1H, α-pyrrole CH), 6.97 (*br*, 1H, pyrrole NH), 7.13 (*br*, 1H, pyrrole NH), 7.48 (*br*, 1H, pyrrole NH),7.76 (*br*, 1H, pyrrole NH); $^{1}$H NMR (300 MHz, DMSO-$d_6$): δ = 1.32-1.43 (*m*, 24H, $CH_3$), 5.11 (*bs*, 1H, β-pyrrole CH), 5.45-5.59 (*m*, 6H, β-pyrrole CH), 6.26 (*bs*, 1H, α-pyrrole CH), 8.67 (*bs*, 1H, pyrrole NH), 8.73 (*bs*, 1H,

pyrrole NH), 9.64 (*b*s, 1H, pyrrole NH), 10.05 (*bs*, 1H, pyrrole NH); $^{13}$C NMR (75MHz, $CDCl_3$) δ = 29.0, 29.4, 29.6, 30.3 (4x $CH_3$), 34.6, 35.3, 35.8, 35.9 (4x meso C), 101.6, 101.8, 102.1, 102.8, 103.3, 103.9, 104.2 (7x β-pyrrole CH), 111.6 (α-pyrrole CH), 133.2 (β-pyrrole C), 137.5, 137.8, 138.2, 138.7, 138.8, 139.4, 141.1 (7x α-pyrrole C); HRMS (ESI-MS) for $C_{28}H_{36}N_4$ $[M-H]^-$ : calcd, 427.2862; found, 427.2859.

**2-(4'-nitro phenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole (3)**: mp: 259 $^oC$; $R_f$ = 0.92 ($SiO_2$, 82:18, hexane/ethylacetate); UV-vis (DMSO, $\lambda_{max}$/nm): 412 (0.27); IR (KBr Pellet): 3443 (*br*, pyrrole NH), 3035 (aryl CH), 2942, 2793, 1733, 1601 (-N=N), 1450 (-$NO_2$, antisymmetric), 1357 (-$NO_2$, symmetric), 861, 757, 588, 524 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ = 1.54-1.56 (*m*, 18H, $CH_3$), 1.85 (*s*, 6H, $CH_3$), 5.83 (*s*, 1H, β-pyrrolic CH), 5.89 (*s*, 1H, β-pyrrolic CH ), 5.99-6.02 (*m*, 4H, β-pyrrolic CH), 6.43 (*s*, 1H, β-pyrrolic CH), 6.90 (*s*, 1H, pyrrole NH), 7.17 (*s*, 1H, pyrrole NH), 7.28 (*s*, 2H, pyrrole NH), 7.82 (*d*, *J* = 8.4 Hz, 2H, aryl CH), 8.30 (*d*, *J* = 7.5 Hz, 2H, aryl CH); $^1$H NMR (300 MHz, DMSO-$d_6$): δ = 1.43-1.49 (*m*, 18H, $CH_3$), 1.79 (*s*, 6H, $CH_3$), 5.59 (*br*, 4H, β-pyrrole CH), 5.77 (*s*, 1H, β-pyrrole CH), 5.84 (*s*, 1H, β-pyrrole CH), 6.15 (*s*, 1H, β-pyrrole CH), 7.7 (*d*, *J* = 8.7 Hz, 2H, aryl CH), 8.2 (*d*, *J* = 9.0 Hz, 2H, aryl CH), 9.12 (*bs*, 1H, pyrrole NH), 9.52 (*bs*, 1H, pyrrole NH), 9.64 (*bs*, 1H, pyrrole NH), 9.79 (*bs*, 1H, pyrrole NH); $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ = 28.0, 28.6, 29.4, 30.2 (4x $CH_3$), 34.3, 34.3, 34.8, 37.5 (4x meso C), 92.6, 101.6, 101.8, 102.0, 102.5, 102.7, 103.3 (7x β-pyrrole CH), 122.0, 125.0 (2x aryl CH), 136.4, 136.7, 138.2, 138.7, 138.8, 139.2, 140.1, 141.0 (7x α-pyrrole C), 146.3 (β-pyrrole C), 147.2, 157.1 (2x aryl C); HRMS (ESI-MS) for $C_{34}H_{39}N_7O_2$ : calcd, 577.3165, found, 577.3160; $R_f$ = 0.60 (ethyl acetate-petroleum ether, 1:10 v/v).

**3-(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl-N-confused calix[4]pyrrole (4)**: Dark red solid; mp: 193 $^oC$; $R_f$ = 0.89 ($SiO_2$, 82:18, hexane/ethylacetate); UV-vis (DMSO, $\lambda_{max}$/nm): 465 (0.58); $^1$H NMR (300 MHz, DMSO-$d_6$): 1.50 (*s*, 12H, $CH_3$), 1.54 (*s*, 6H, $CH_3$), 1.71 (*s*, 6H, $CH_3$), 5.06 (*br*, 1H, β -pyrrole CH), 5.66 - 5.70 (*m*, 6H, β-pyrrole CH), 7.7 (*d*, *J* = 8.7 Hz, 2H, aryl CH), 8.2 (*d*, *J* = 9.0 Hz, 2H, aryl CH), 9.13 (*br*, 2H, NH), 9.42 (*br*, 1H, NH), 10.98 (*bs*, 1H, NH);$^{13}$C NMR (75 MHz, $CDCl_3$): 29.3, 29.4,

29.8, 30.3 (4x $CH_3$), 34.6, 35.3, 35.9, 36.0 (4x *meso* C), 101.3, 101.8, 102.5, 102.9, 103.2, 103.8, 104.2 CH (7x β-pyrrole CH), 121.7, 125.0 (2x aryl CH), 133.3 (β-pyrrole C), 137.8, 137.9, 138.3, 138.6, 138.8, 139.4, 140.8, 141.0 (8x α-pyrrole C), 148.1, 157.4 (2x aryl C); HRMS (ESI-MS) for $C_{34}H_{39}N_7O_2$ : calcd, 577.3165, found, 577.3162.

**3,12-bis(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole (5)**: Red solid; mp: 102-104 $^oC$; Yield: 203 mg, 6% (based on OMCP); $R_f$ = 0.84 ($SiO_2$, 82:18, hexane/ethylacetate); UV-vis (DMSO, $\lambda_{max}$/nm): 468 (1.68); $^1H$ NMR (300 MHz, DMSO-$d_6$): δ = 1.22 (*s*, 12H, $CH_3$), 1.68 (*s*, 12H, $CH_3$), 5.72 (*s*, 2H, β-pyrrole CH), 6.04 (*s*, 2H, β-pyrrole CH), 6.93 (*s*, 2H, β-pyrrole CH), 7.8 (*d*, *J* = 8.7 Hz, 4H, aryl CH), 8.3 (*d*, *J* = 8.7 Hz, 4H, aryl CH), 10.1 (*s*, 1H, pyrrole NH), 10.3 (*s*, 1H pyrrole NH), 11.7 (*br*, 2H, pyrrole NH); $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 1.29 (*s*, 12H, $CH_3$), 1.71 (*s*, 12H, $CH_3$), 6.10 (*d*, *J* = 2.7 Hz, 2H, β-pyrrole CH), 6.30 (*d*, *J* = 2.9 Hz, 2H, β-pyrrole CH), 7.01 (*d*, *J* = 2.9 Hz, 2H, β-pyrrole CH), 7.46 (*s*, 1H, pyrrole NH), 7.58 (*br*, 1H, pyrrole NH), 7.76 (*d*, *J* = 9.0 Hz, 4H, aryl CH), 7.89 (*br*, 2H, pyrrole NH), 8.23 (*d*, *J* = 9.0 Hz, 4H, aryl CH); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 28.5, 29.6 (2x $CH_3$), 35.7, 36.0 (2x *meso* C), 103.7, 104.3, 104.7 (3x β-pyrrole CH), 122.1, 124.6 (2x aryl CH), 135.9 C, 136.9, 139.1, 139.2 (4x α-pyrrole C), 145.4 (β-pyrrole C), 147.8, 156.2 (2x aryl C); HRMS (ESI-MS) for $C_{40}H_{42}N_{10}O_4$ : calcd, 726.3391; found, 726.3388.

**3,7-bis(4'-nitrophenyl)-azo-5,5,10,10,15,15,20,20-octamethyl calix[4]pyrrole (6)**: Red solid; mp: 129-131 $^oC$; Yield: 101 mg, 3% (based on OMCP); $R_f$ = 0.46 ($SiO_2$, 82:18, hexane/ethylacetate); UV-vis (DMSO, $\lambda_{max}$/nm): 455 (1.12); $^1H$ NMR (300 MHz, DMSO-$d_6$): δ = 1.49-1.52 (*m*, 18H, $CH_3$), 2.30 (*s*, 6H, $CH_3$), 6.3 (*d*, *J* = 3.6 Hz, 2H, β-pyrrole CH), 6.5 (*d*, *J* = 3.0 Hz, 2H, β-pyrrole CH), 7.00 (*s*, 2H, β-pyrrole CH), 7.8 (*d*, *J* = 8.7 Hz, 4H, aryl CH), 8.3 (*d*, *J* = 8.7 Hz, 4H, aryl CH), 9.99 (*s*, 2H, pyrrole NH), 11.7 (*br*, 2H pyrrole NH); $^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 1.24 (*s*, 6H, $CH_3$), 1.52 (*s*, 12H, $CH_3$), 1.77 (*s*, 6H, $CH_3$), 6.25 (*d*, *J* = 2.7 Hz, 2H, β-pyrrole CH), 6.61 (*d*, *J* = 3.1 Hz, 2H, β-pyrrole CH), 7.06 (*d*, *J* = 2.7 Hz, 2H, β-pyrrole CH), 7.83 (*d*, *J* = 9.0 Hz, 4H, aryl CH), 8.06 (*bs*, 2H pyrrole NH), 8.29 (*d*, *J* = 9.0 Hz, 4H, aryl CH), 8.47 (*br*, 2H pyrrole NH);

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 28.5, 29.4, 29.6 (3x $CH_3$), 35.6, 35.9, 36.1 (3x *meso* C), 104.3, 104.7, 104.9 (3x β-pyrrole CH), 122.1, 124.7 (2x aryl CH), 135.9, 136.9, 139.1, 139.9 (4x α-pyrrole C), 145.4 (β-pyrrole C), 146.9, 156.3 (2x aryl C); HRMS (ESI-MS) for $C_{40}H_{42}N_{10}O_4$: calcd, 726.3391; found, 726.3395.

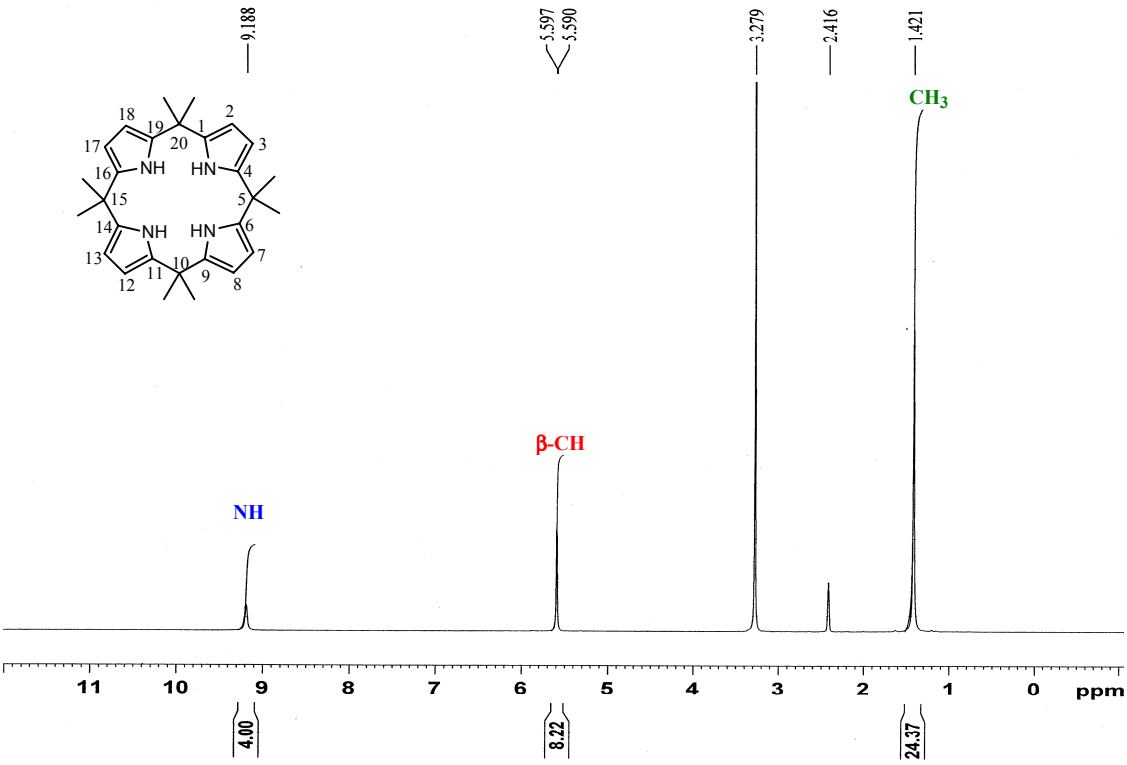



**Figure S1.** $^{1}$H NMR spectra of OMCP (**1**) in DMSO-$d_6$-0.5% water

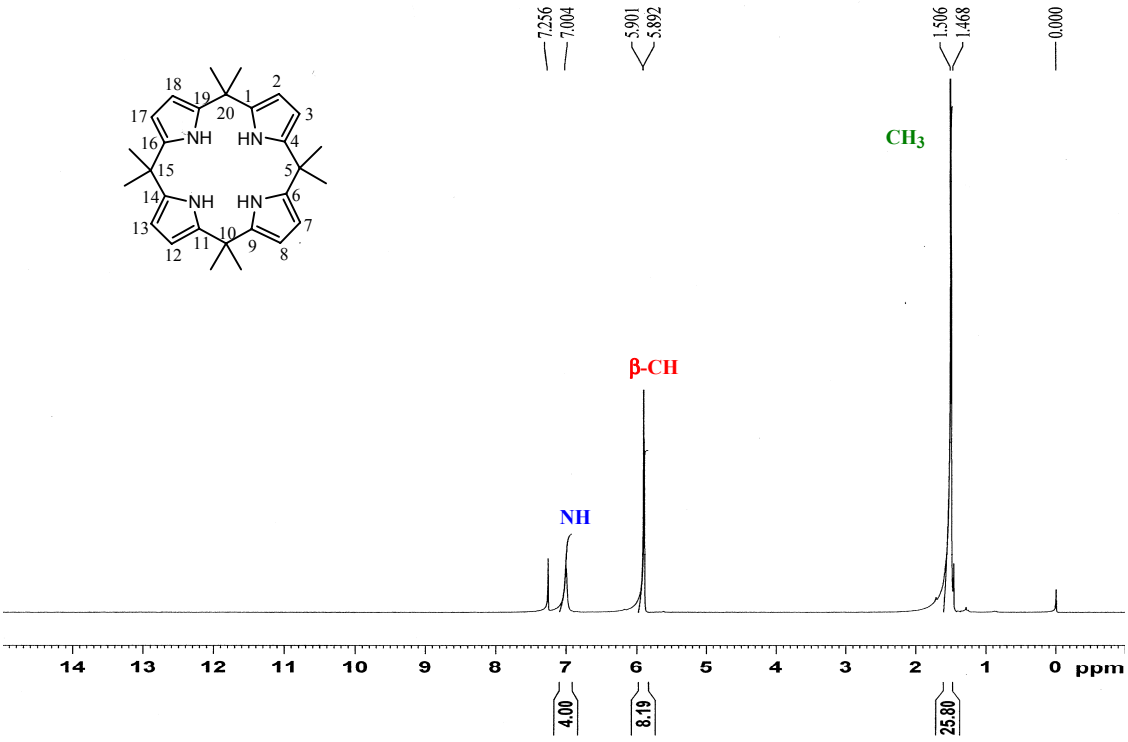



**Figure S2.** $^{1}$H NMR spectra of OMCP (**1**) in $CDCl_3$

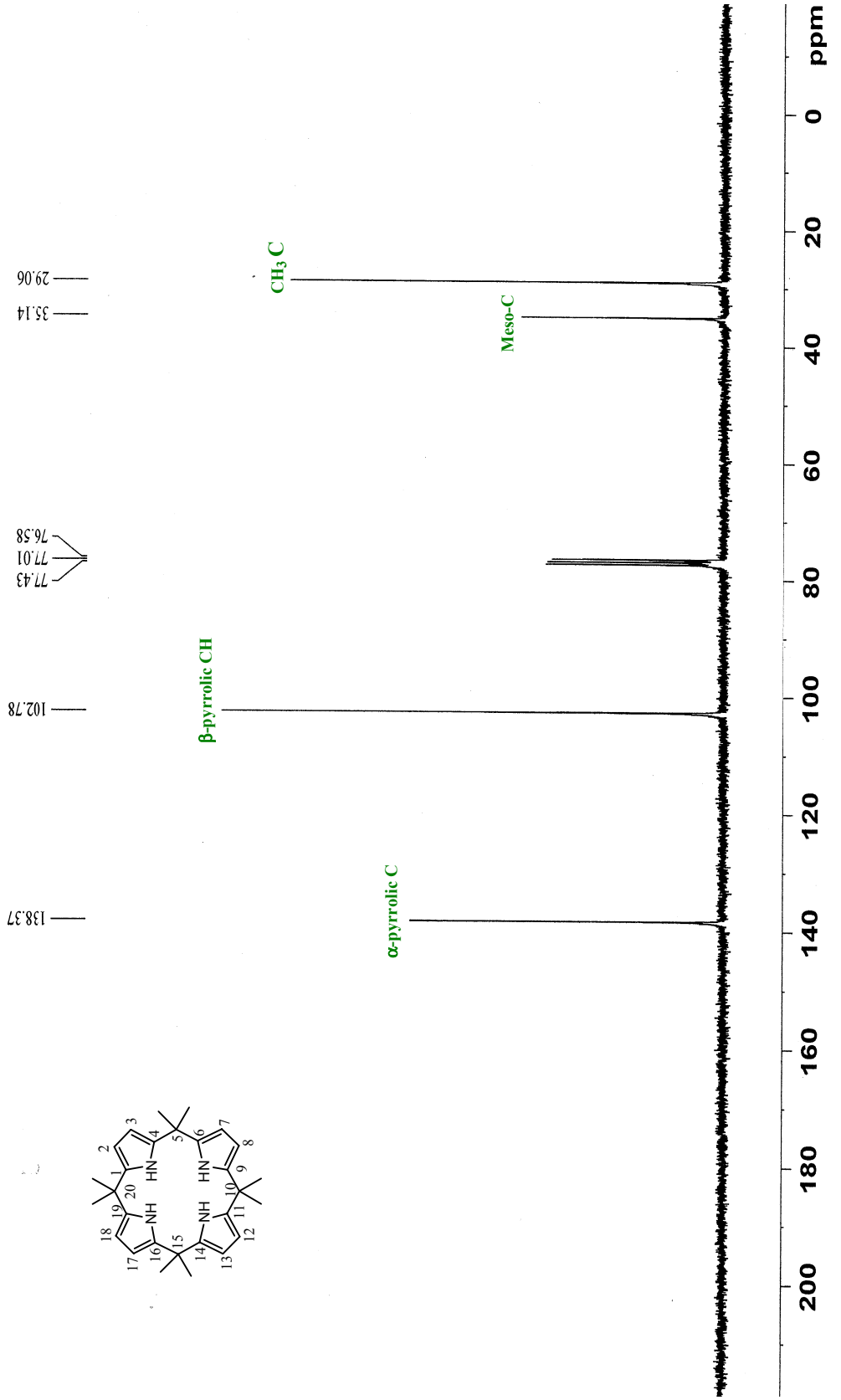



**Figure S3.** $^{13}C$ NMR spectra of OMCP (**1**) in $CDCl_3$

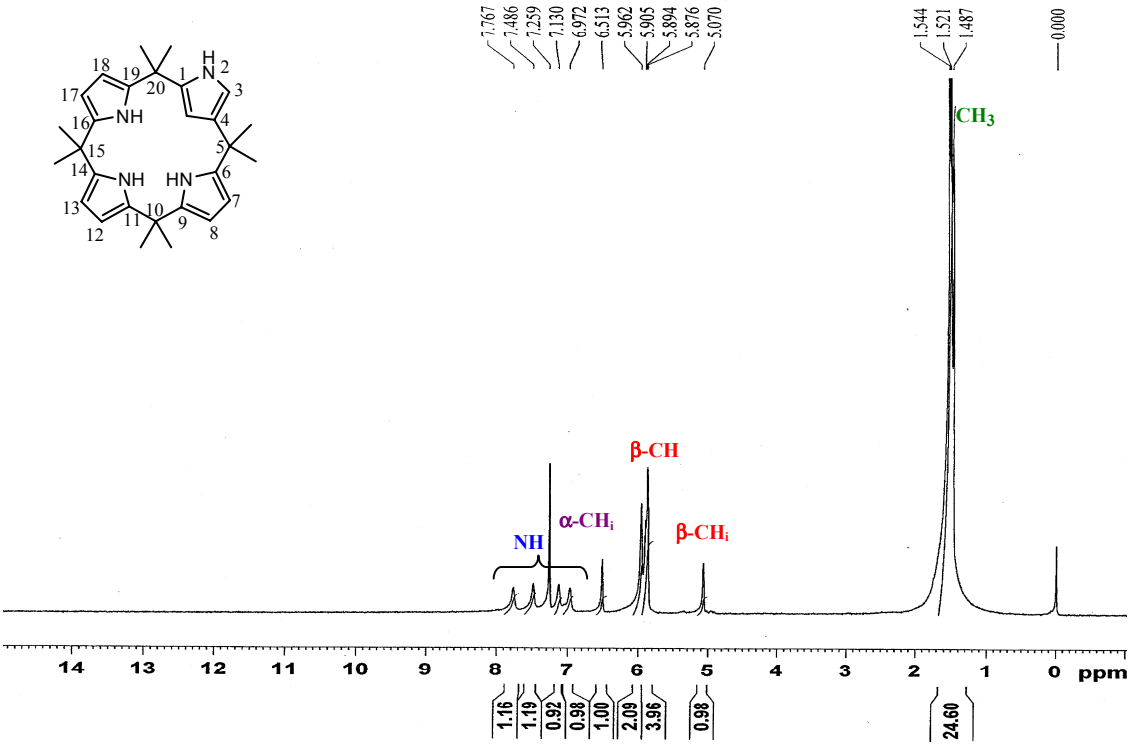



**Figure S4.** $^{1}$H NMR spectra of NC-OMCP (**2**) in $CDCl_3$

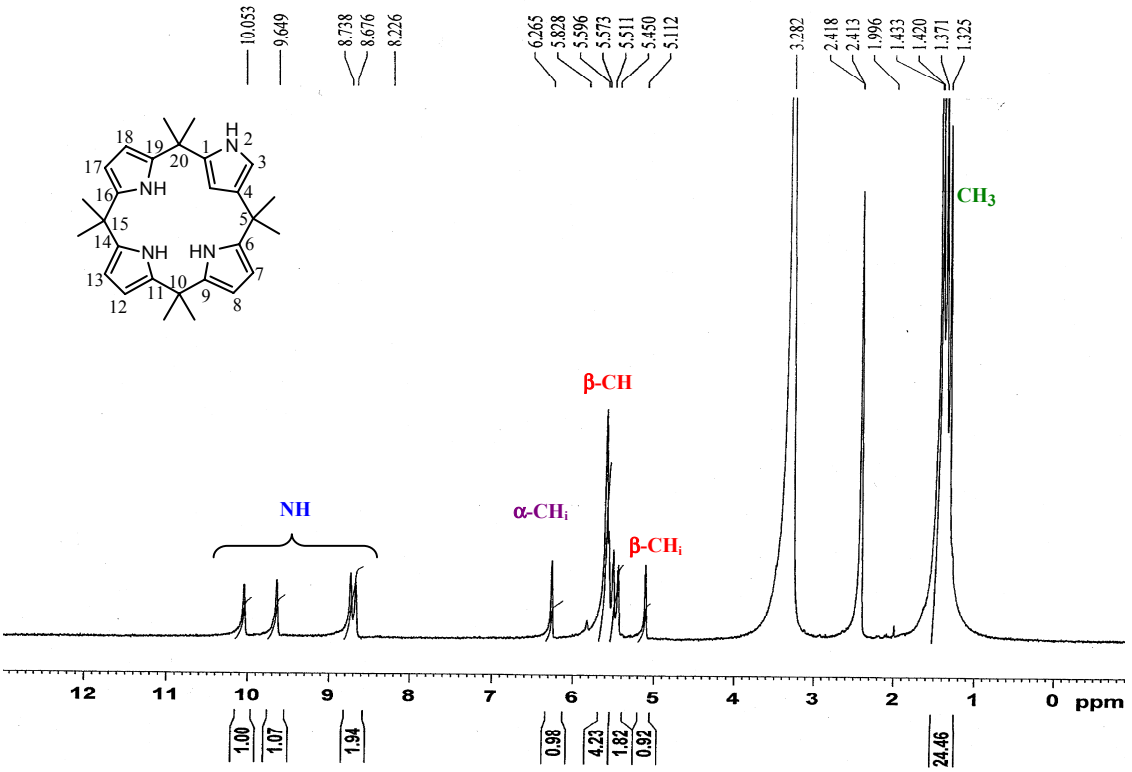



**Figure S5.** $^{1}$H NMR spectra of NC-OMCP (**2**) in DMSO-$d_6$-0.5% water

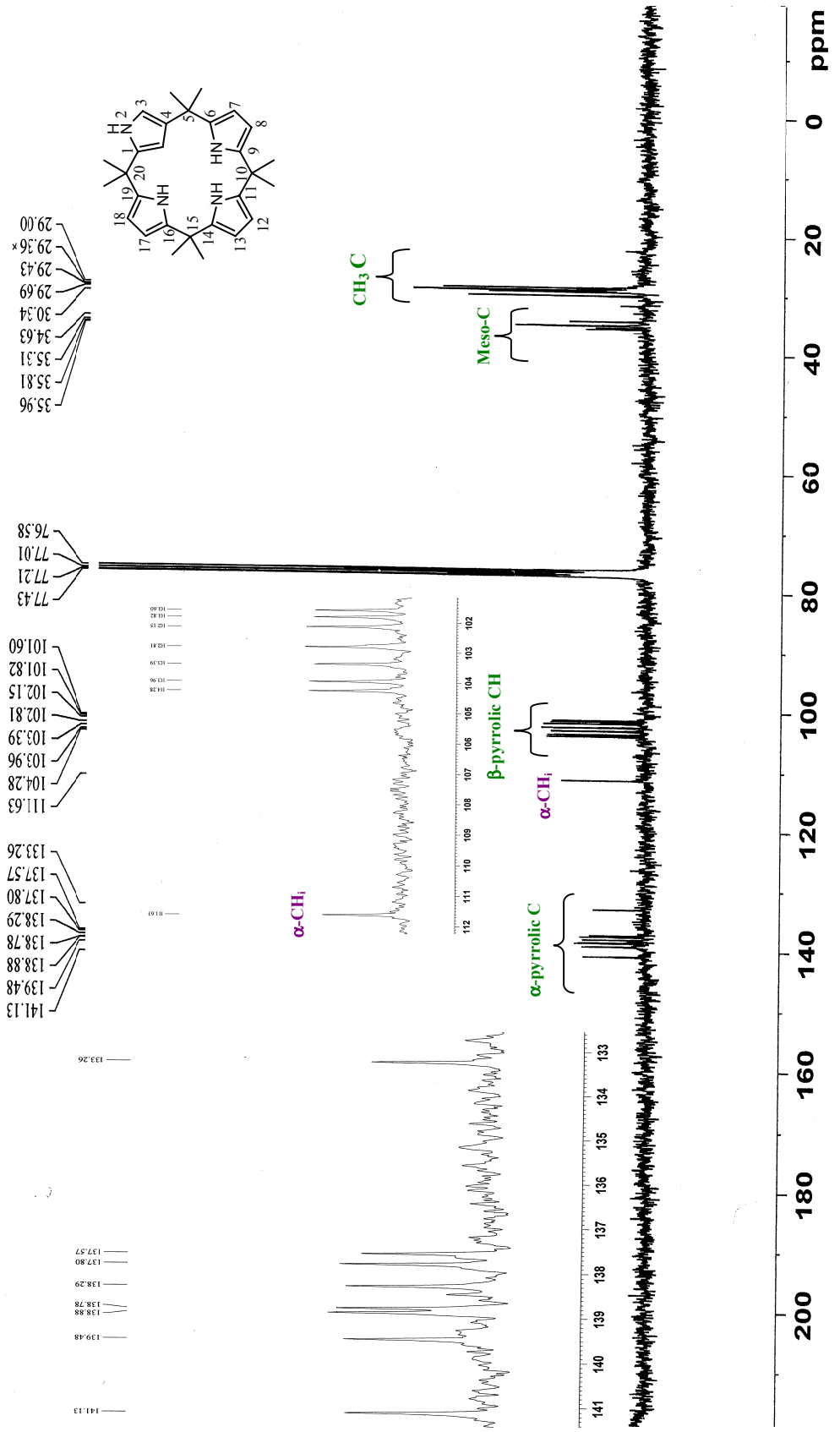



**Figure S6.** $^{13}C$ NMR spectra of NC-OMCP (**2**) in $CDCl_3$

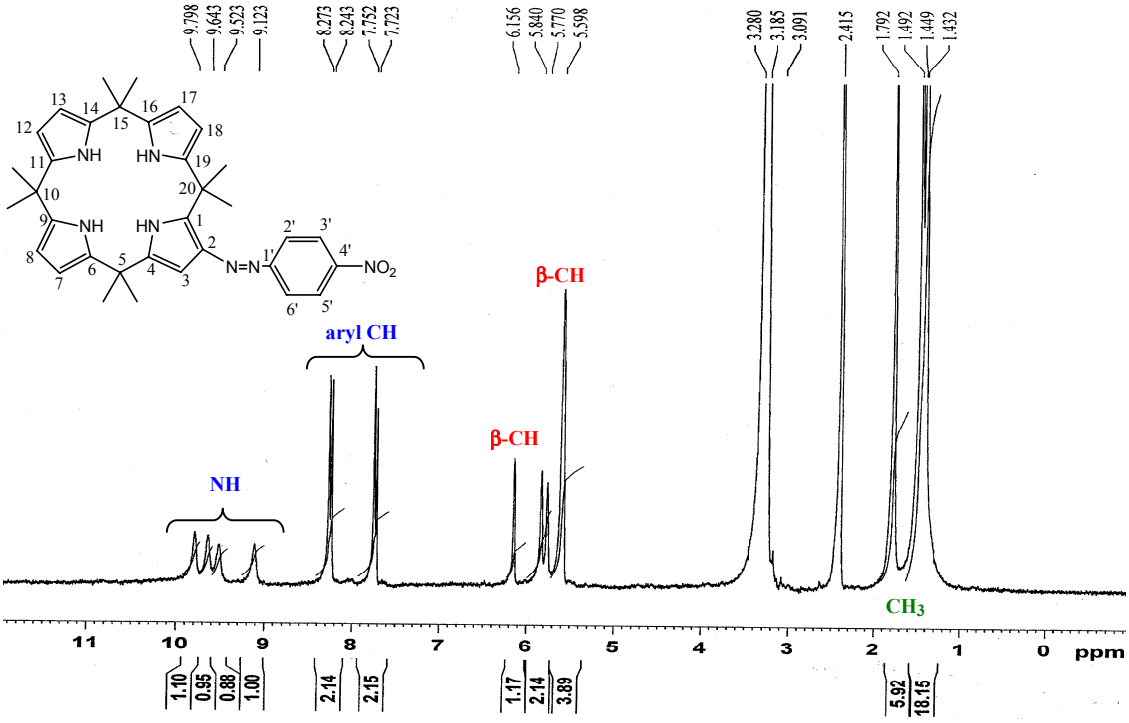



**Figure S7.** $^{1}$H NMR spectra of 2-(4'-nitrophenyl)-azo-OMCP (**3**) in DMSO-$d_6$-0.5% water

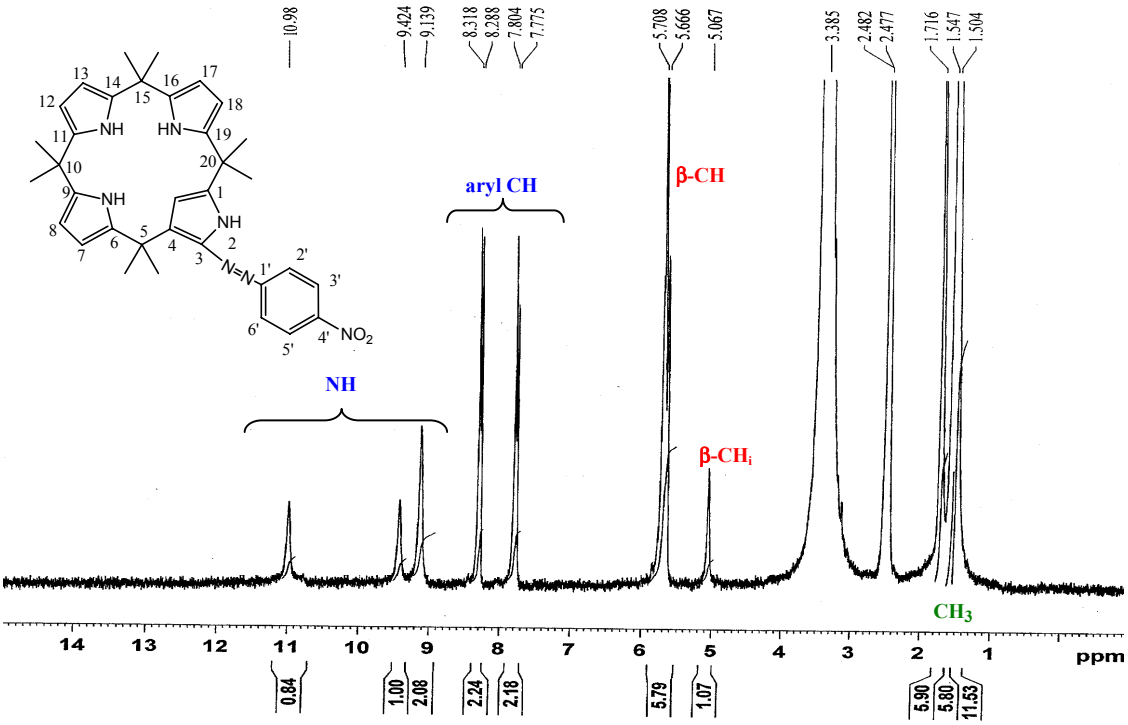



**Figure S8.** $^{1}$H NMR spectra of 3-(4'-nitrophenyl)-azo-NC-OMCP (**4**) in DMSO-$d_6$-0.5% water

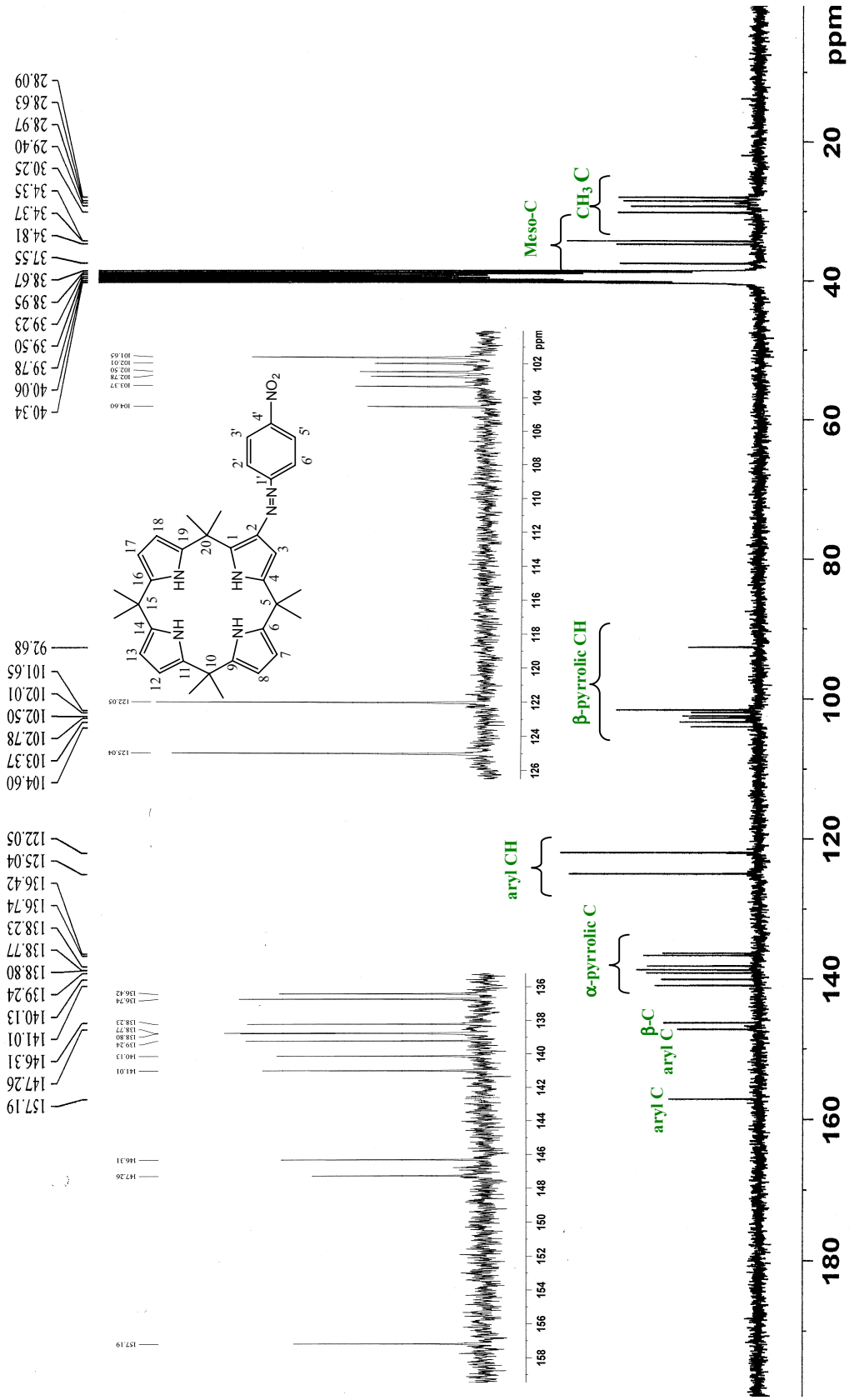



**Figure S9.** $^{13}C$ NMR spectra of 2-(4'-nitrophenyl)-azo-OMCP (**3**) in DMSO-$d_6$-0.5% water

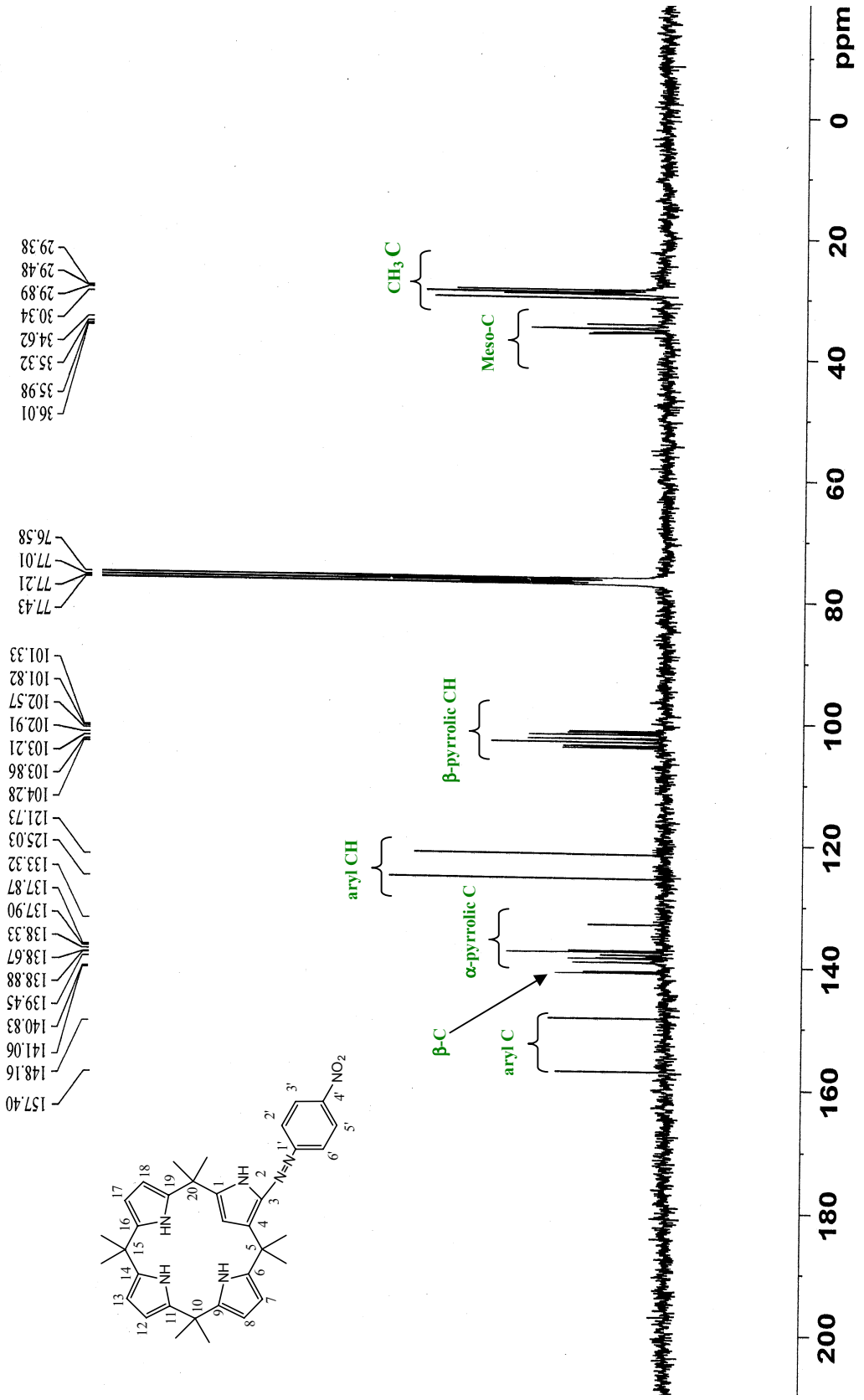



**Figure S10.** $^{13}$C NMR spectra of 3-(4'-nitrophenyl)-azo-NC-OMCP (**4**) in $CDCl_3$

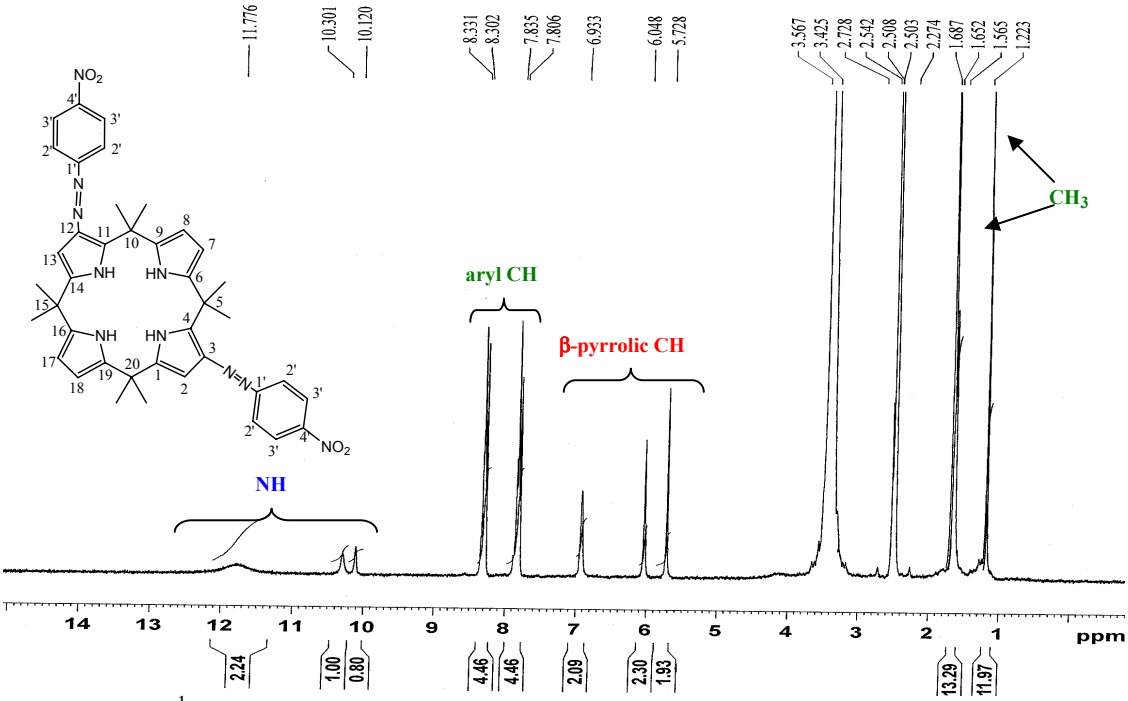



**Figure S11.** $^{1}$H NMR spectra of 3,12-bis-(4'-nitrophenyl)-azo-OMCP (**5**) in DMSO-$d_6$-0.5% water

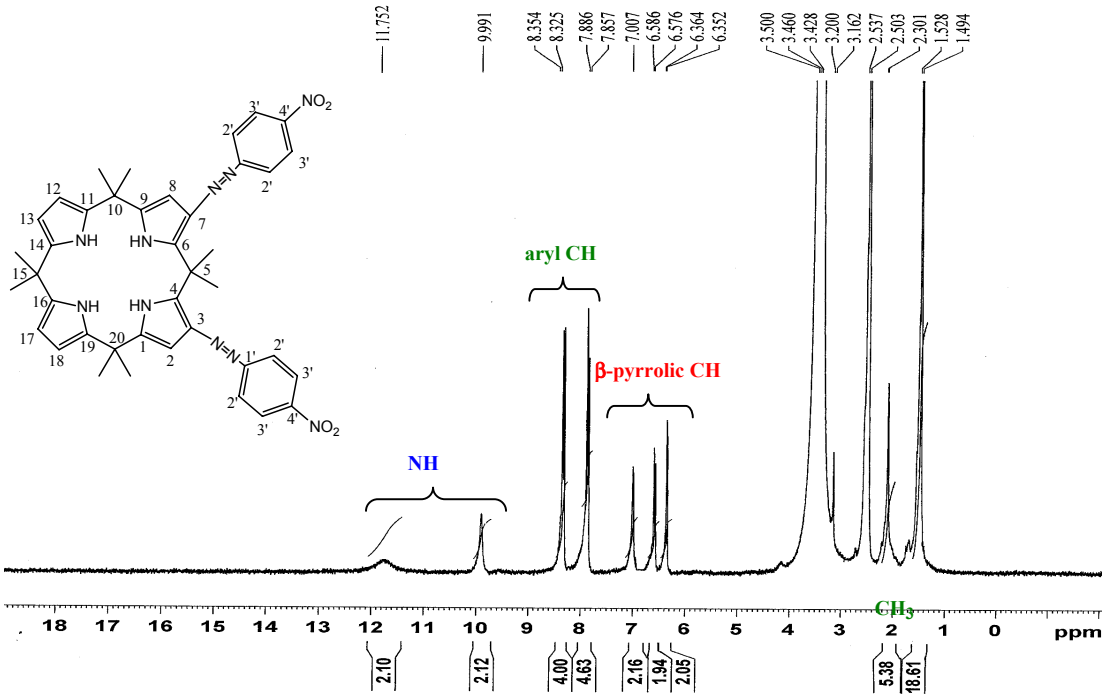



**Figure S12.** $^{1}$H NMR spectra of 3,7-bis-(4'-nitrophenyl)-azo-OMCP (**6**) in DMSO-$d_6$-0.5% water

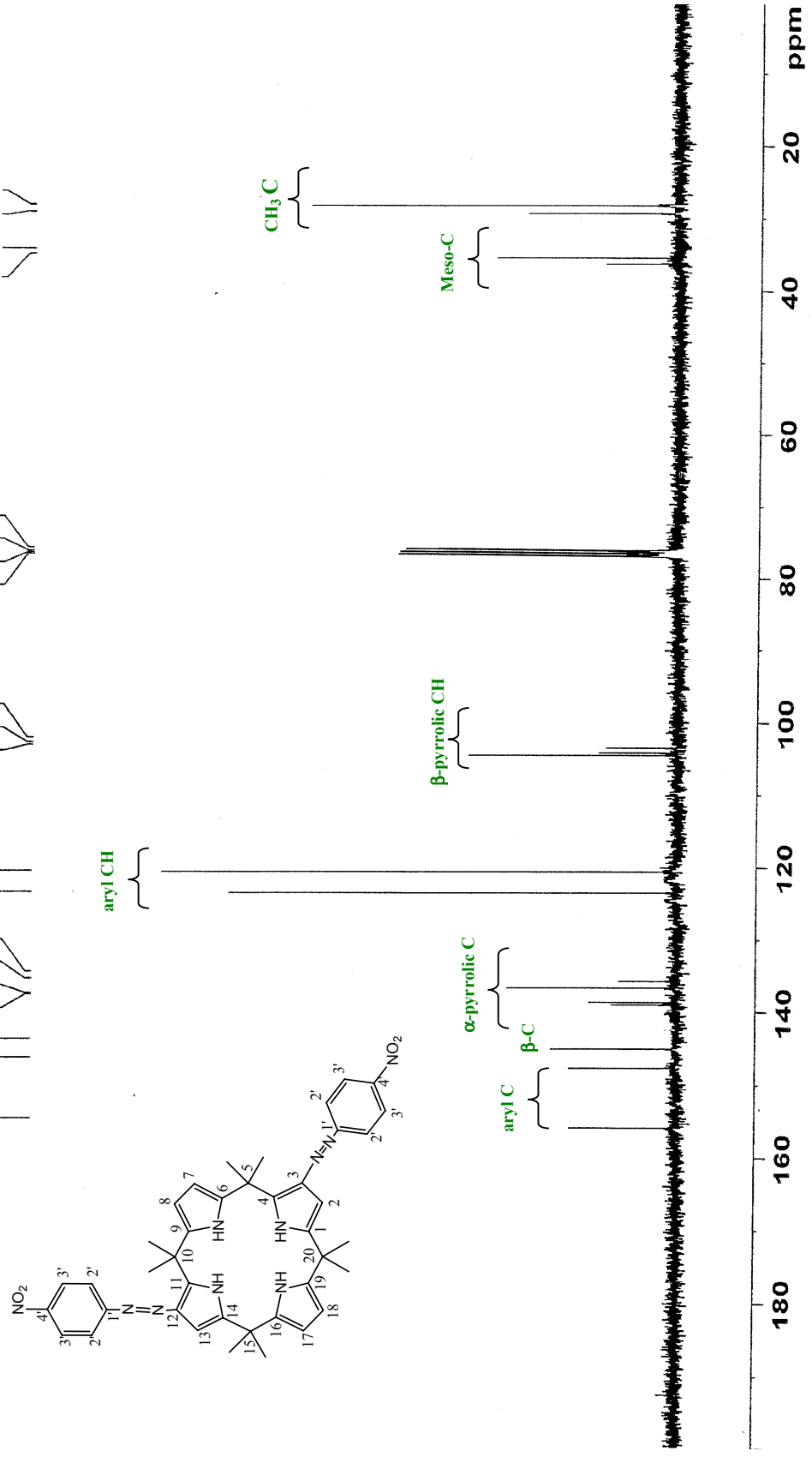



**Figure S13.** $^{13}$C NMR spectra of 3,12-bis(4'-nitrophenyl)-azo-OMCP (**5**) in $CDCl_3$

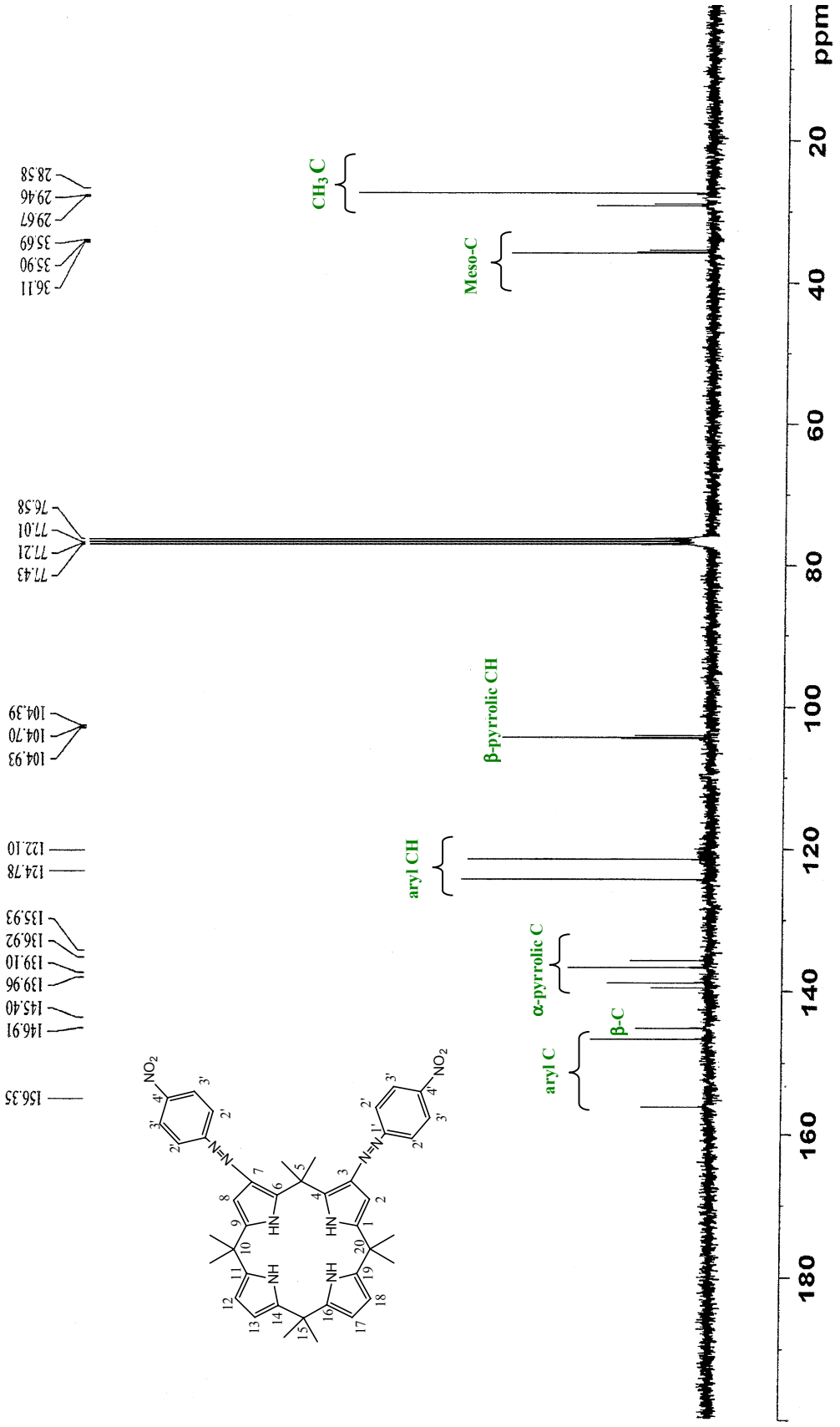
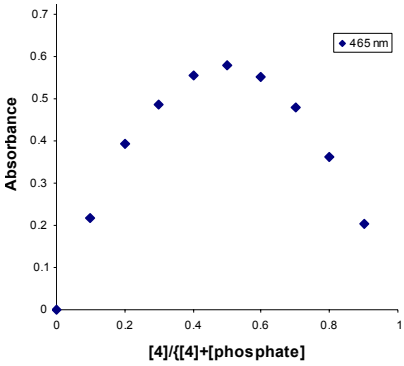


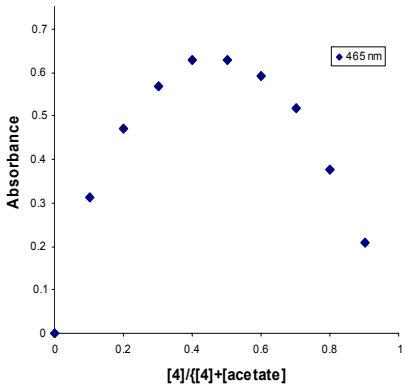

**Figure S14.** $^{13}$C NMR spectra of 3,7-bis(4'-nitrophenyl)-azo-OMCP (**6**) in $CDCl_3$

## Job plots for complexation of sensors and anions

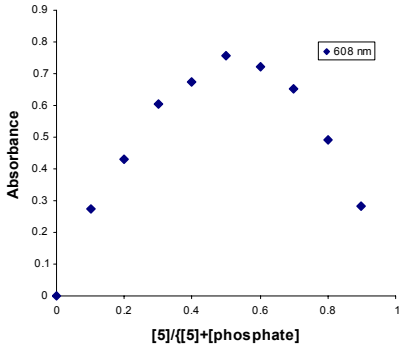
**Figure S15** job plots for sensors **4**, **5** and **6** titrated with anions in DMSO

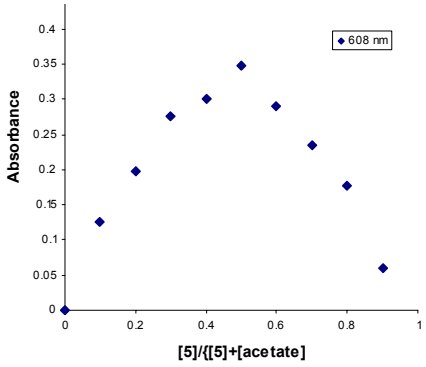
Sensor **4** titrated with $H_2PO_4^-$ and $AcO^-$. ([**4**] + [Anion] = $1.0 \times 10^{-4}$ M)



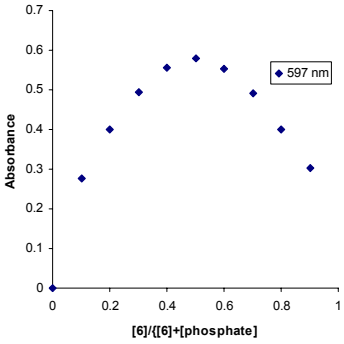




Sensor **5** titrated with $H_2PO_4^-$ and $AcO^-$. ([**5**] + [Anion] = $1.0 \times 10^{-4}$ M)




Sensor **6** titrated with $H_2PO_4^-$ and $AcO^-$. ([**6**] + [Anion] = $1.0 \times 10^{-4}$ M)



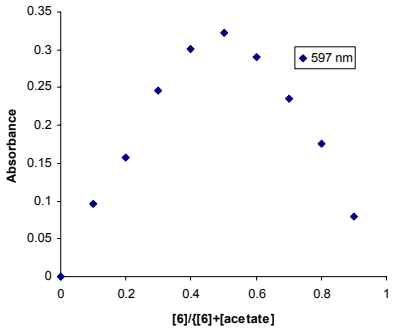



**Figure S16.** Color changes of compd **3** (5 x $10^{-5}$ M) in DMSO upon the addition of anions (10 equiv).

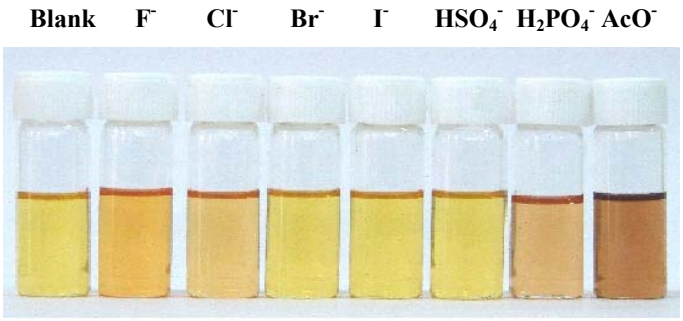
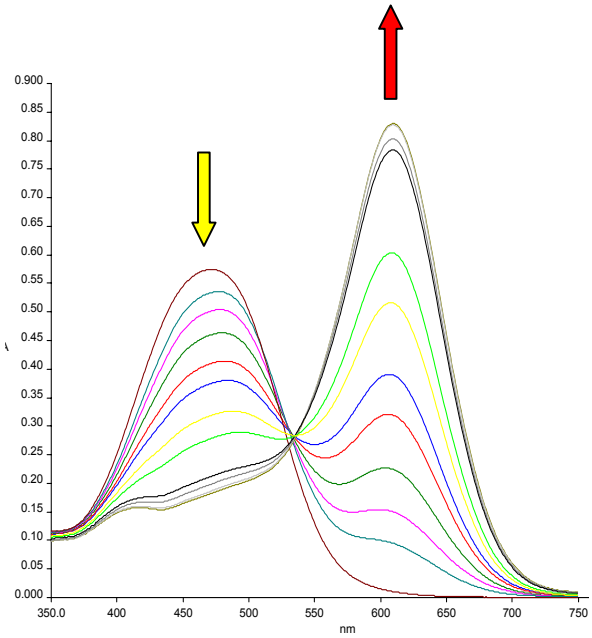
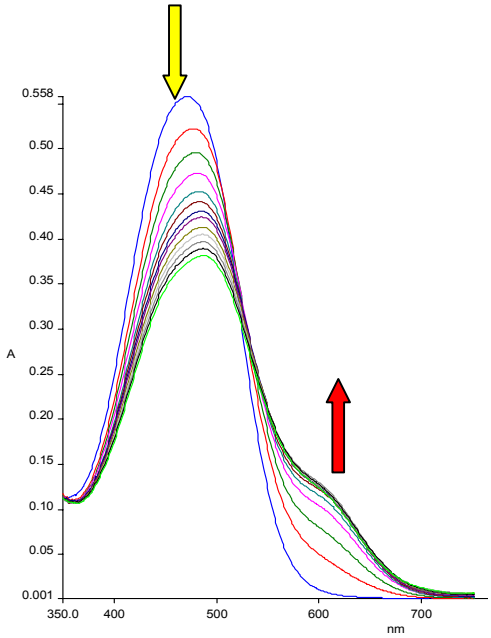


**Figure S17** UV-vis spectroscopic titrations of compd **4** (5 x $10^{-5}$ M) with different anions (5 x $10^{-5}$ M).

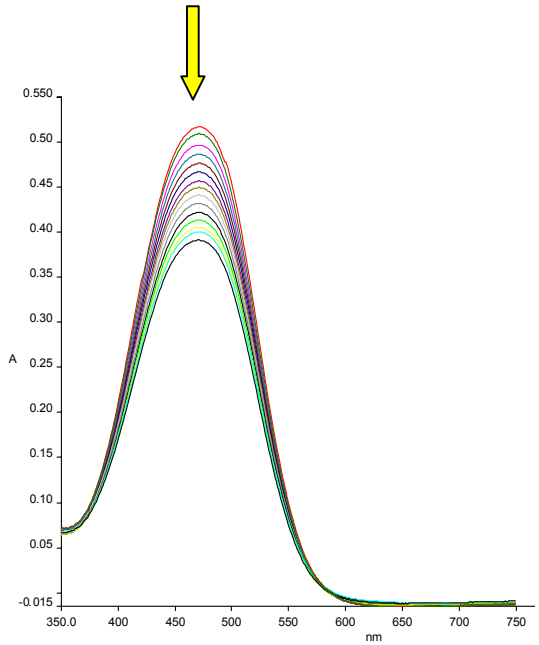
1) **4** / $F^-$



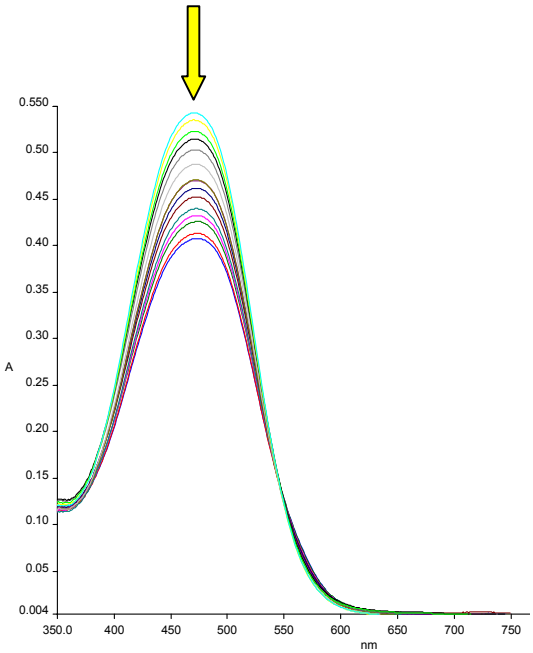

2) **4** / $H_2PO_4^-$



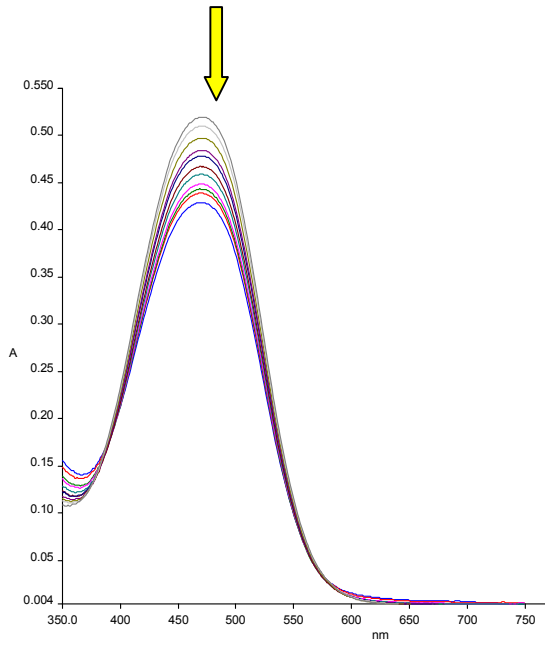

3) **4** / $HSO_4^-$



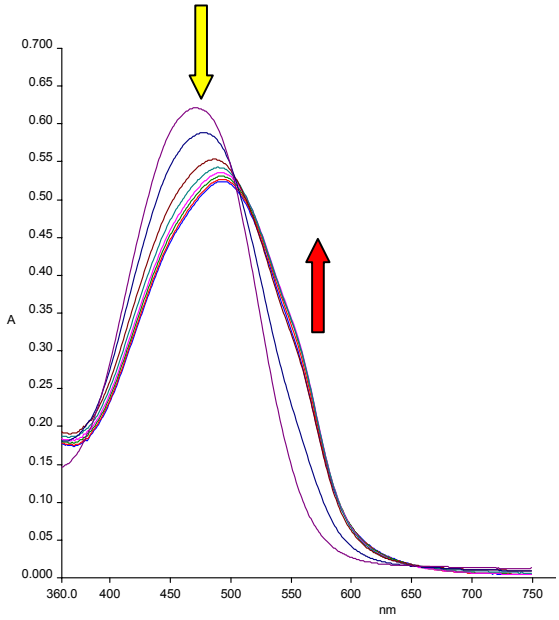

4) **4** / $Br^-$



5) **4** / $Cl^-$




6) **4** / $CH_3COO^-$




7) **4** / $I^-$

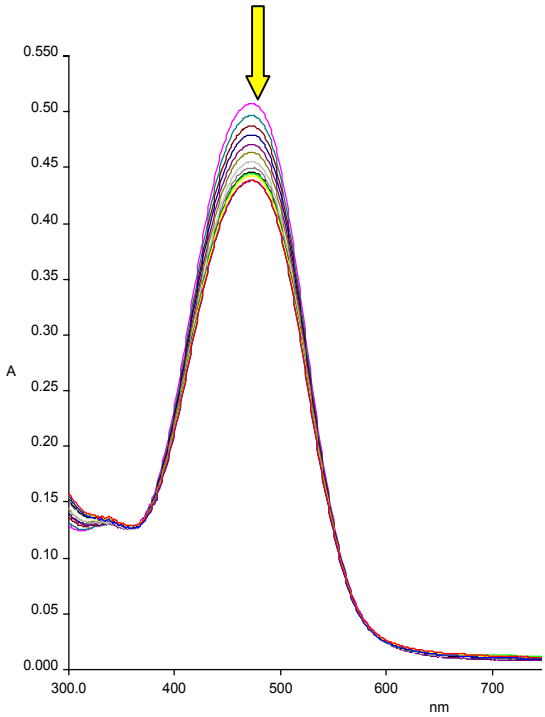


**Figure S18.** Color changes of compd **4** (5 x $10^{-5}$ M) in DMSO upon the addition of anions (10 equiv).

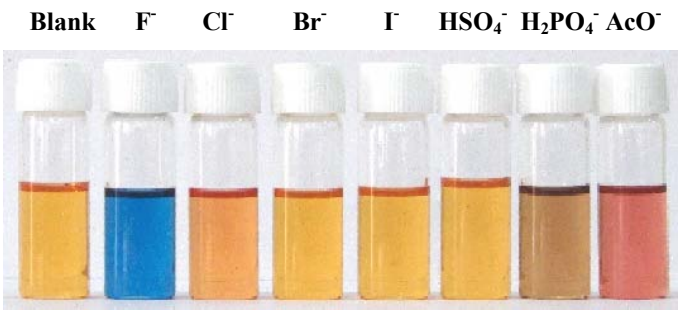
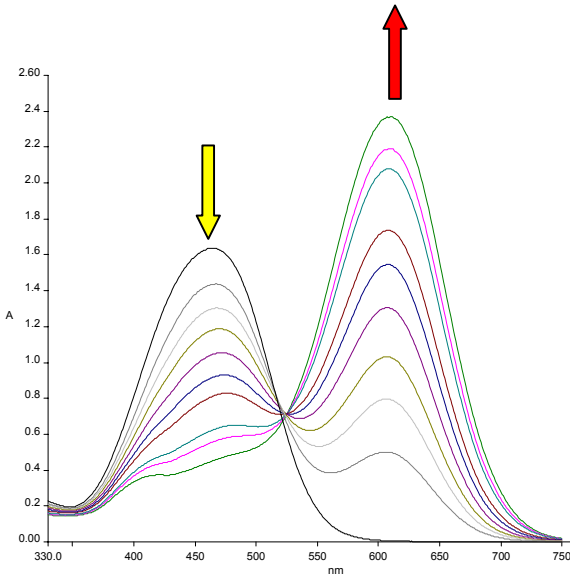
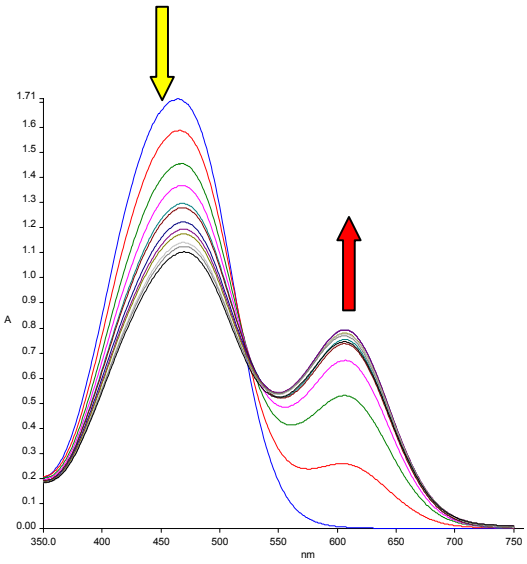


**Figure S19** Absorption spectroscopic titrations of compd **5** (5 x $10^{-5}$ M) in DMSO with different anions (5 x $10^{-5}$ M).

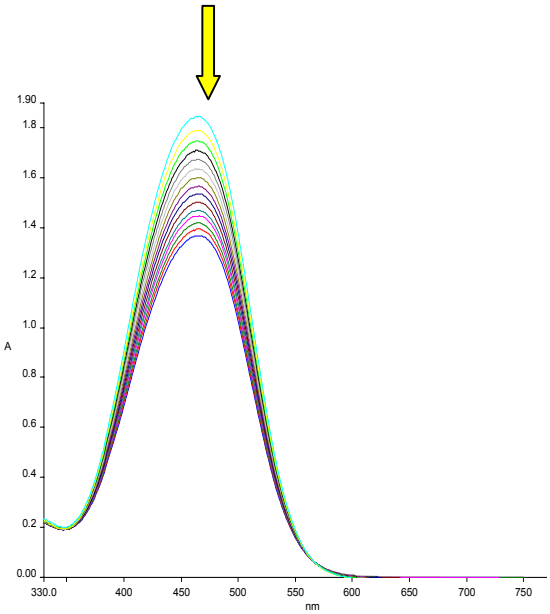
1) **5** / $F^-$



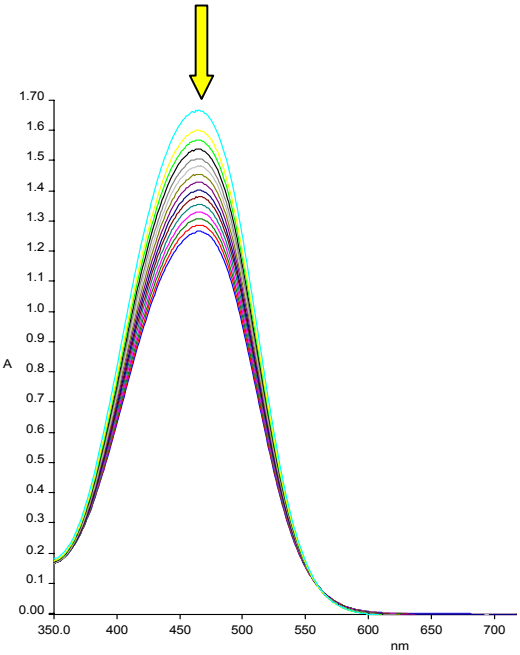

2) **5** / $H_2PO_4^-$



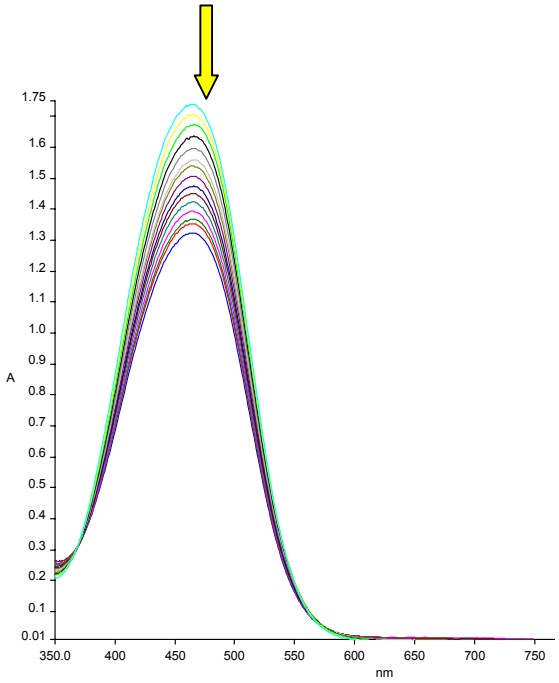

3) **5** / $Br^-$



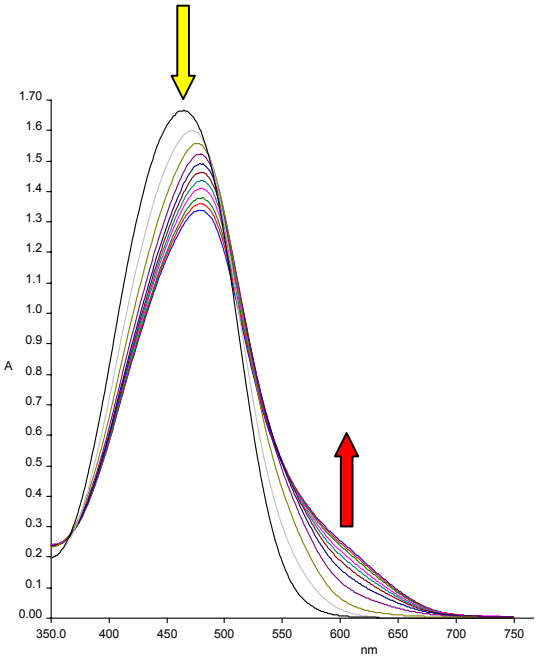

4) **5** / $Cl^-$



5) **5** / $HSO_4^-$




6) **5** / $CH_3COO^-$




7) **5** / $I^-$

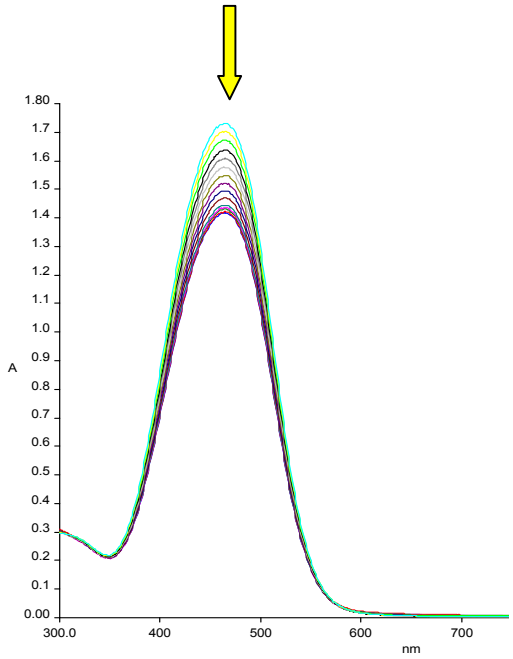


**Figure S20.** Color changes of compd **5** (5 x $10^{-5}$ M) in DMSO upon the addition of anions (10 equiv).

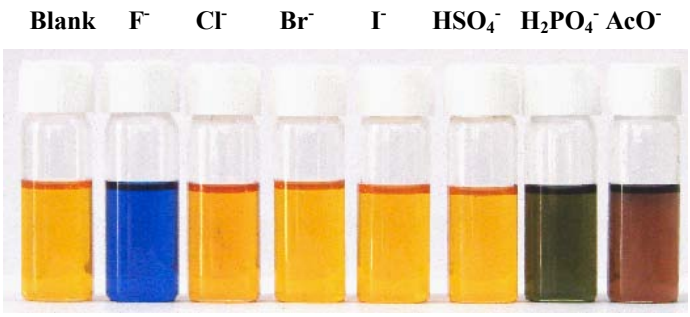
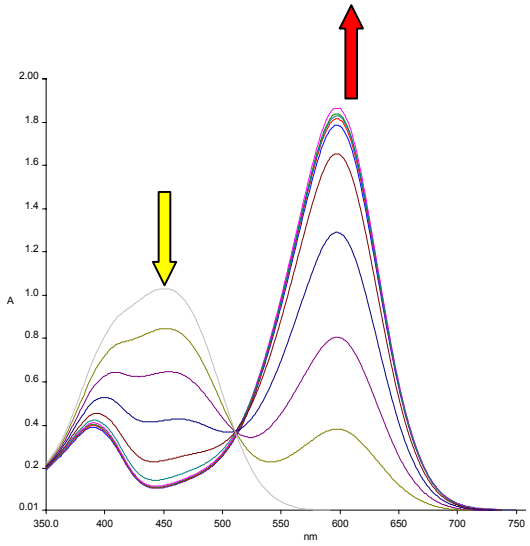
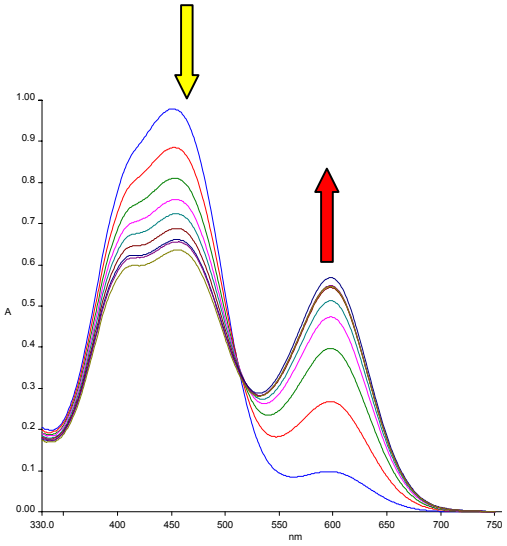


**Figure S21** Absorption spectroscopic titrations of compd **6** (5 x $10^{-5}$ M) with different anions (5 x $10^{-5}$ M).

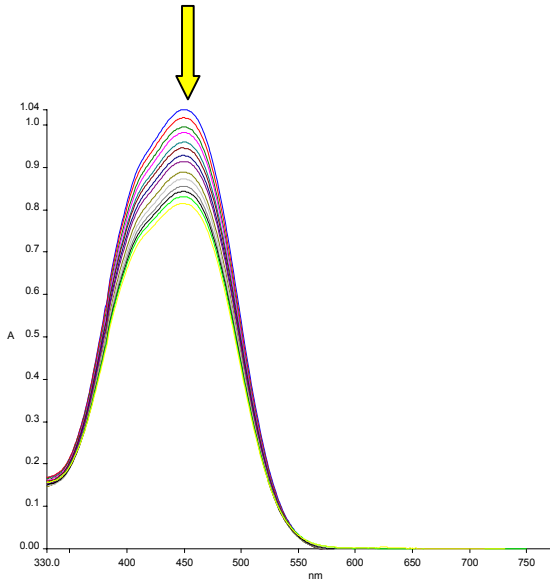
1) **6**/ $F^-$



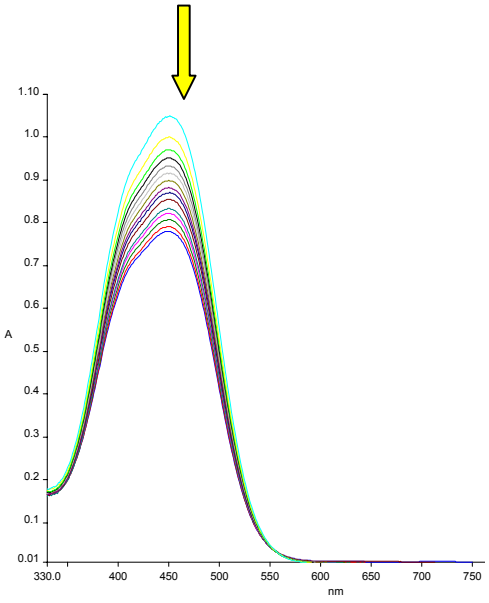

2) **6**/ $H_2PO_4^-$




3) **6**/ $Br^-$




4) **6**/ $Cl^-$



5) **6**/ $HSO4^-$ 6) **6**/ $Br^-$

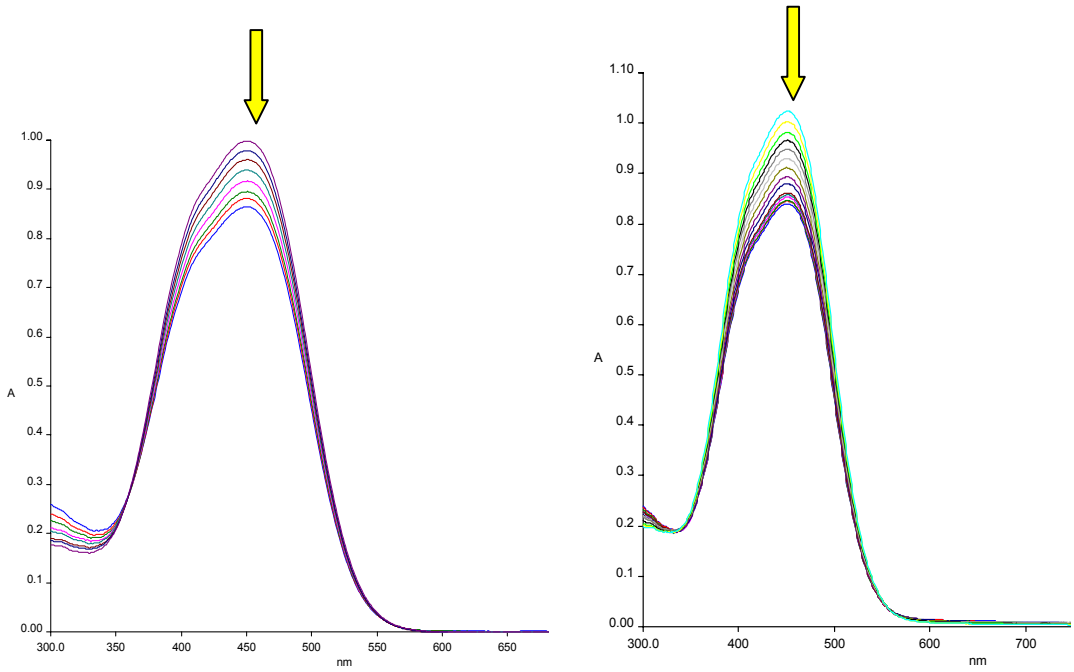



**Figure S22.** Color changes of compound **6** ($5 \times 10^{-5}$ M) in DMSO upon the addition of anions (10 equiv).

**Blank** **$F^-$** **$Cl^-$** **$Br^-$** **$I^-$** **$HSO_4^-$** **$H_2PO_4^-$** **$AcO^-$**

**Figure S23** UV-vis spectral changes of compd **5** (left) and compd **6** (right) in DMSO in the presence of different anions. Labeling has been done only with most basic anions, tested.

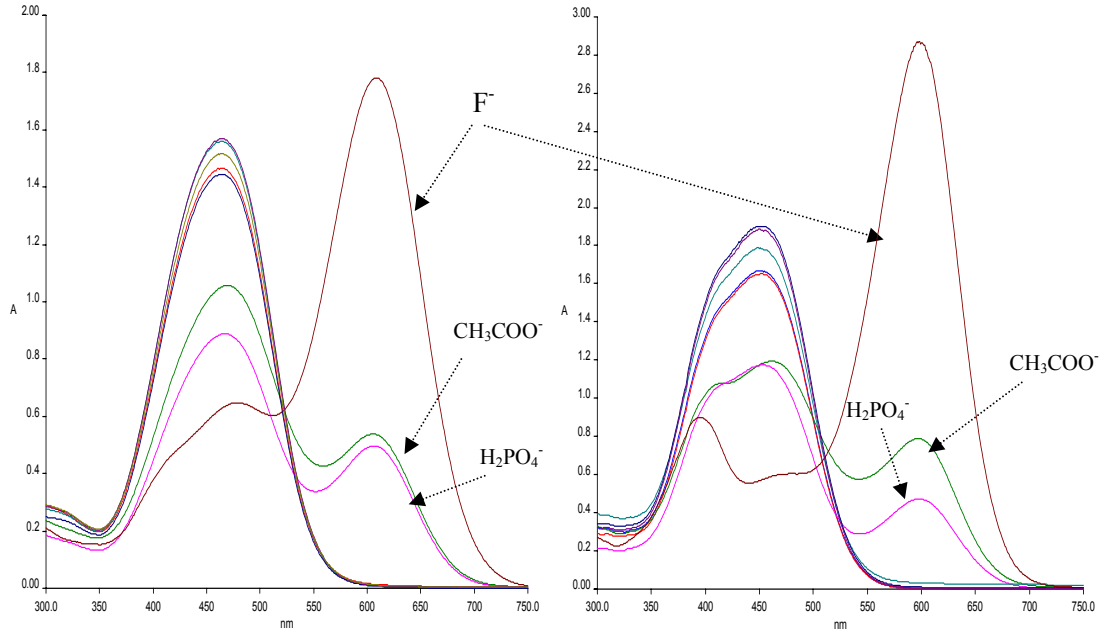


**Figure S24 (a).** UV-vis spectral changes of compd **5** (left) and compd **6** (right) recorded in different solvents at a concentration of ~$10^{-5}$M.

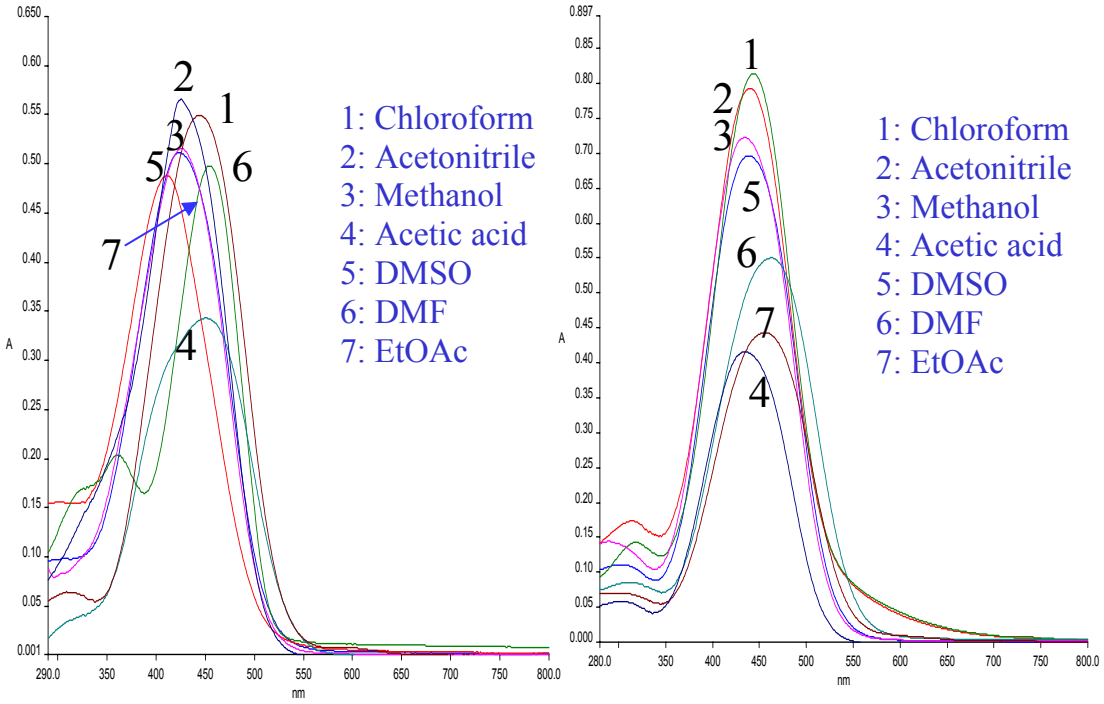
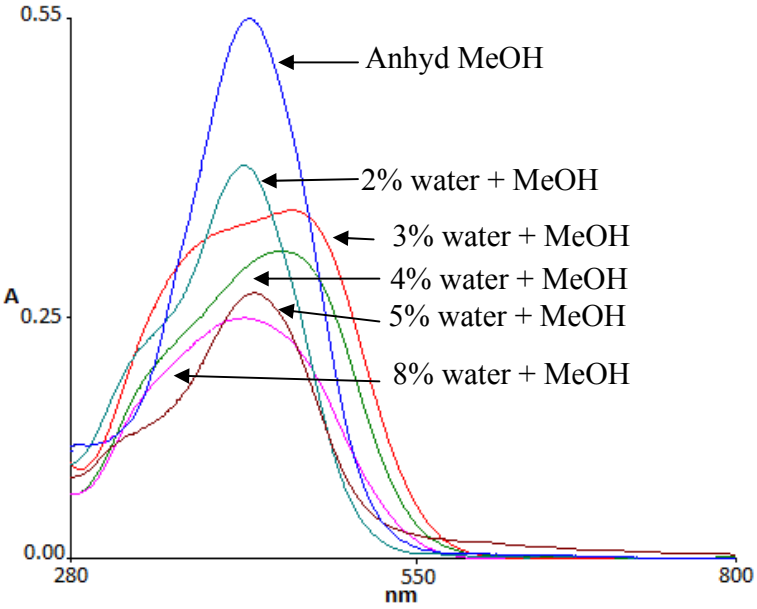



**Figure S24 (b).** UV-vis spectral changes of compd **5** recorded in aq solution (MeOH + water) at a concentration of ~$10^{-5}$M.



## $^1$H NMR spectroscopic titrations

**Figure S25.** $^1$H NMR titrations of compd **1** (1.0 x $10^{-2}$ M) with $F^-$ in DMSO-$d_6$-0.5% water.

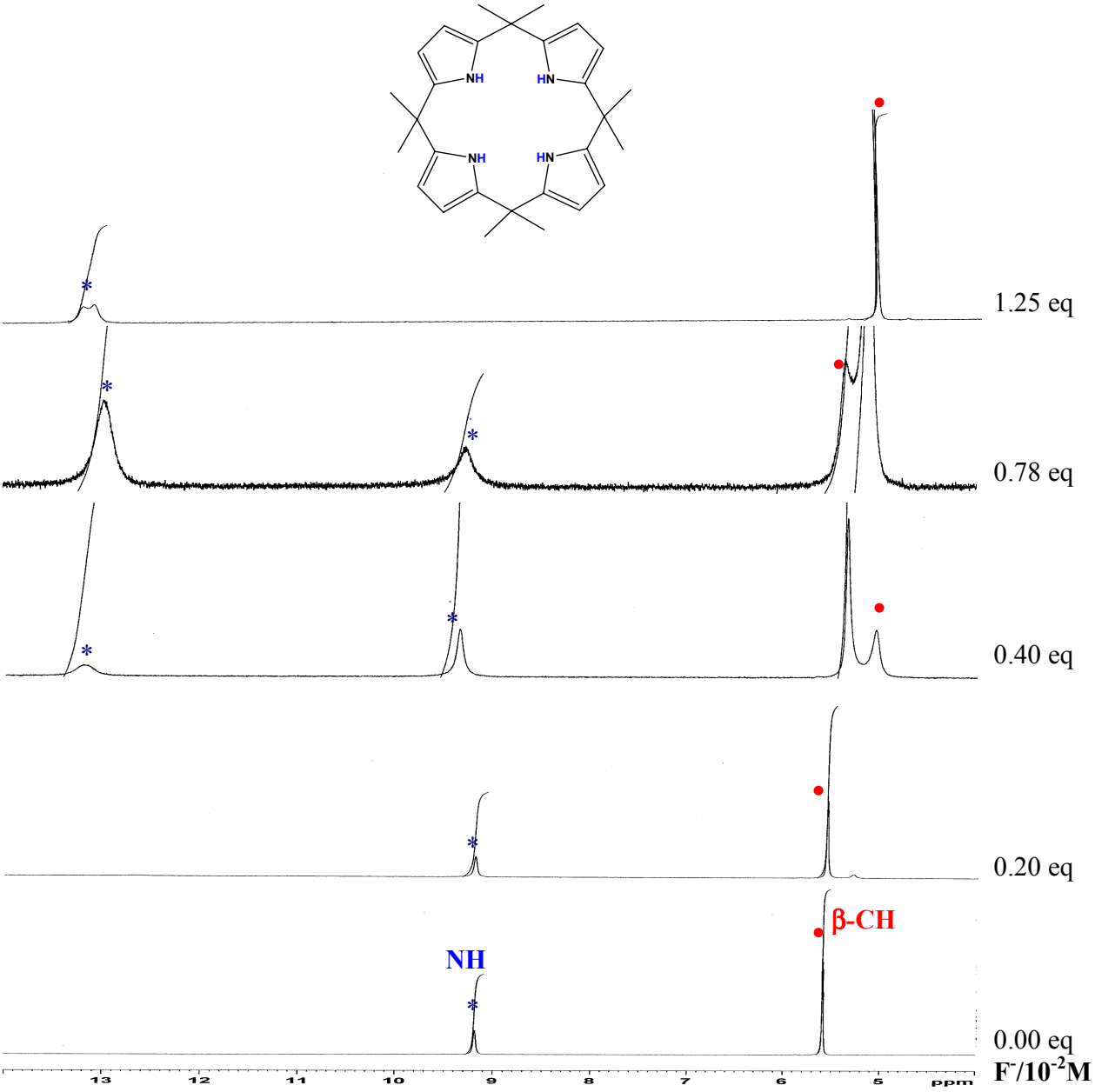


**Figure S26.** $^{1}$H NMR titrations of compd **2** (1.0 x $10^{-2}$ M) with $F^-$ in DMSO-$d_6$-0.5% water. The inverted pyrrole $^{1}$H resonances in **2** are labeled as follows: pyrrole $NH_i$ ● (red), α-$CH_i$ # (green), β-$CH_i$ @ (violet)

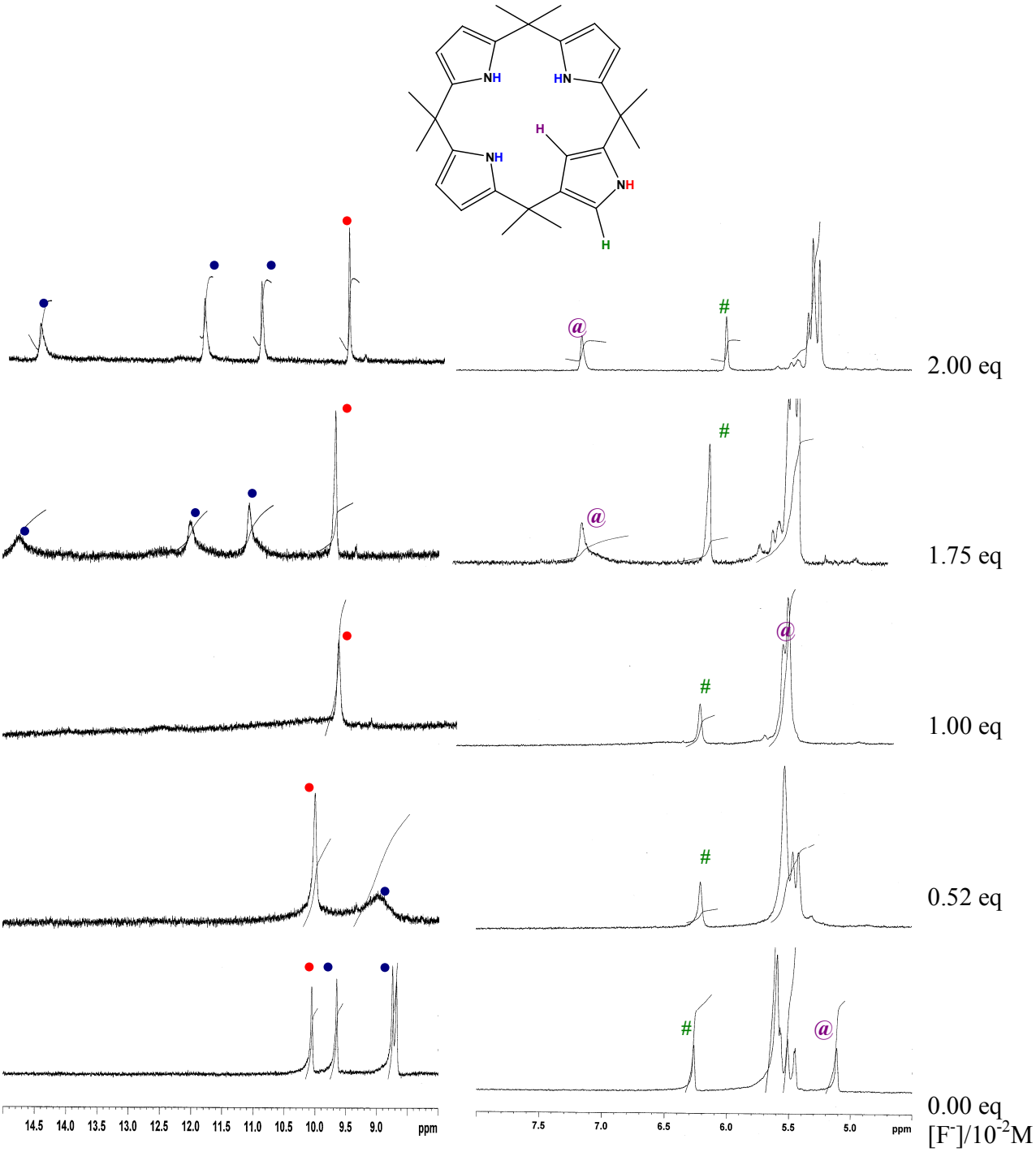


**Figure S27.** $^{1}$H NMR titrations of compd **3** (1.0 x $10^{-2}$ M) with $F^-$ in DMSO-$d_6$-0.5% water.

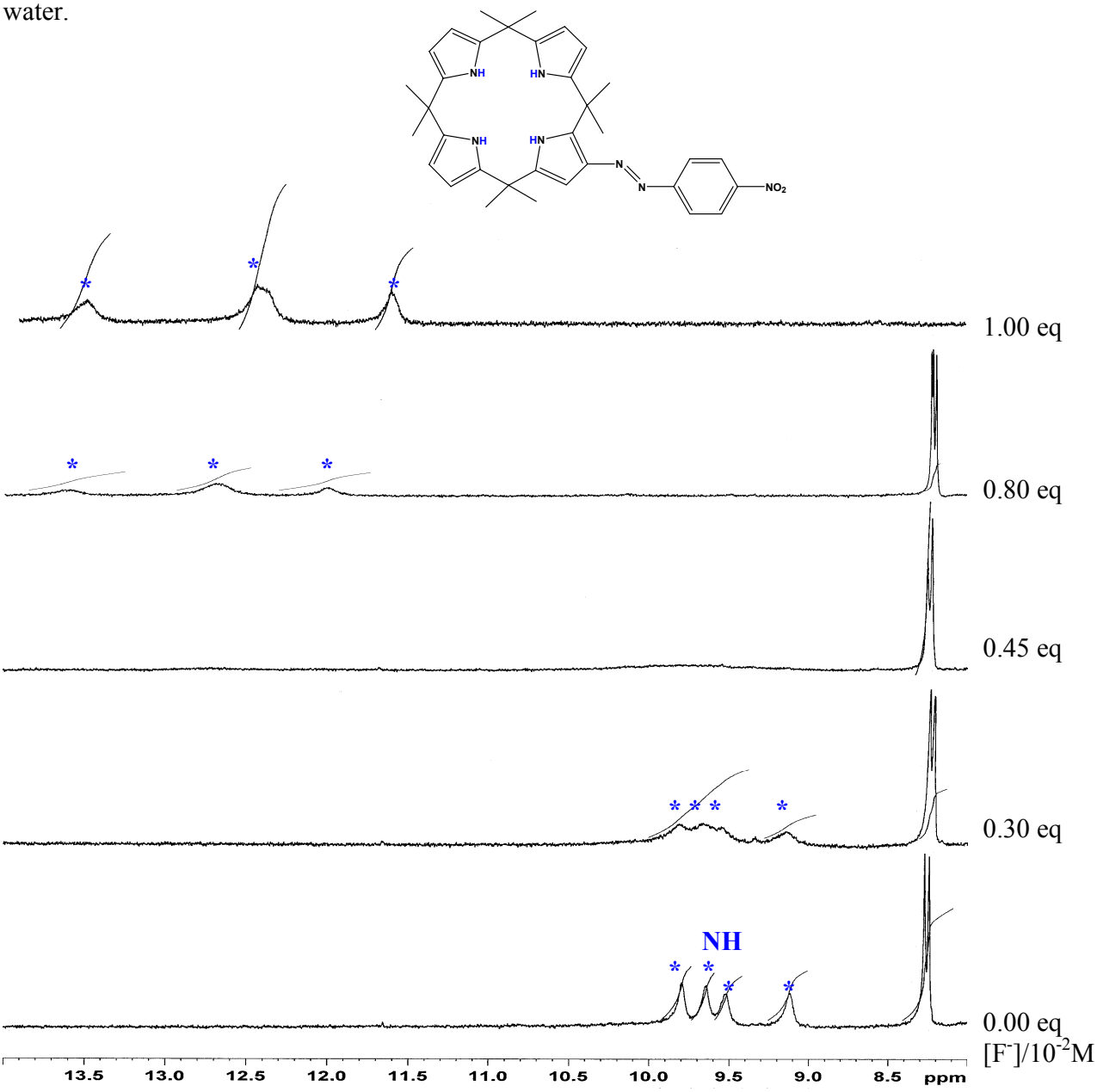


**Figure S28.** $^{1}$H NMR titrations of compd **3** (1.0 x $10^{-2}$ M) with $F^-$ in $CDCl_3$

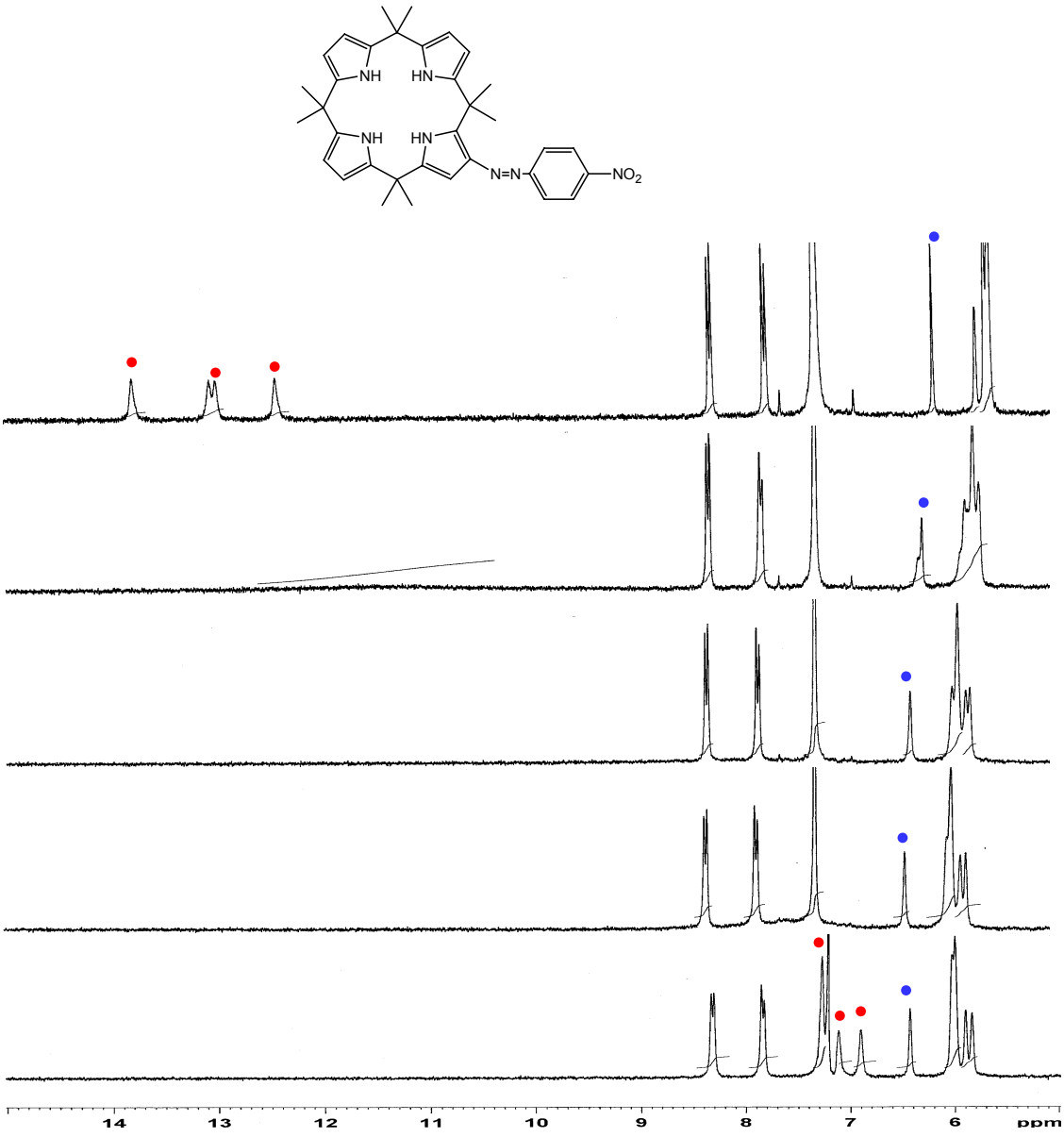


**Figure S29.** $^{1}$H NMR titrations of compd **3** (1.0 x $10^{-2}$ M) with $Cl^-$ in DMSO-$d_6$-0.5% water.

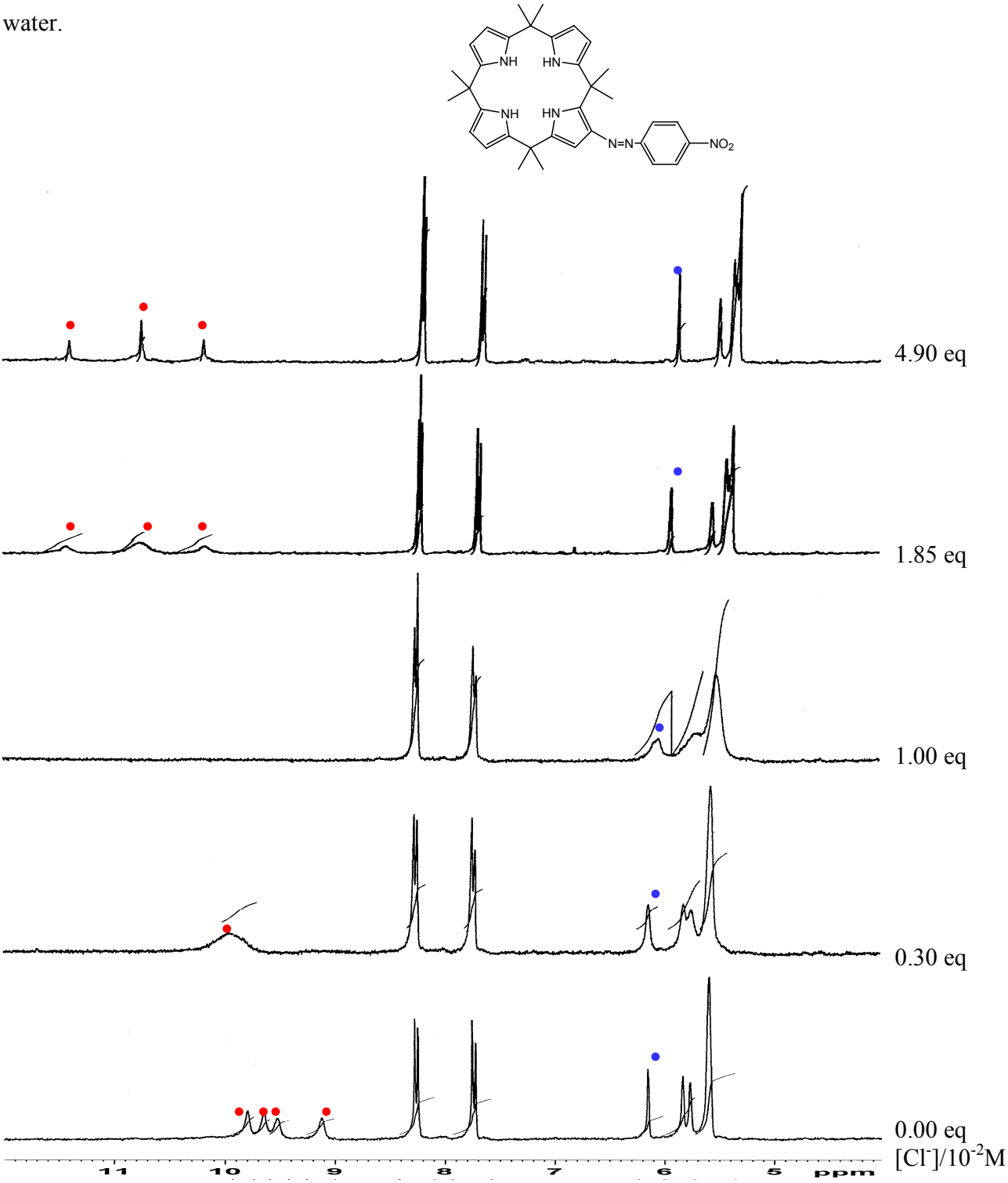
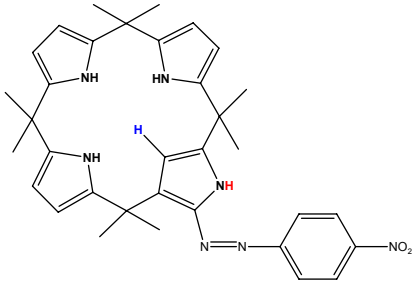


**Figure S30.** $^{1}$H NMR titrations of compd **4** (1.0 x $10^{-2}$ M) with $F^-$ in DMSO-$d_6$-0.5% water. The inverted pyrrole $^{1}$H resonances in **4** are labeled as follows: pyrrole $NH_i$ ● (red), and β-$CH_i$ ● (blue)



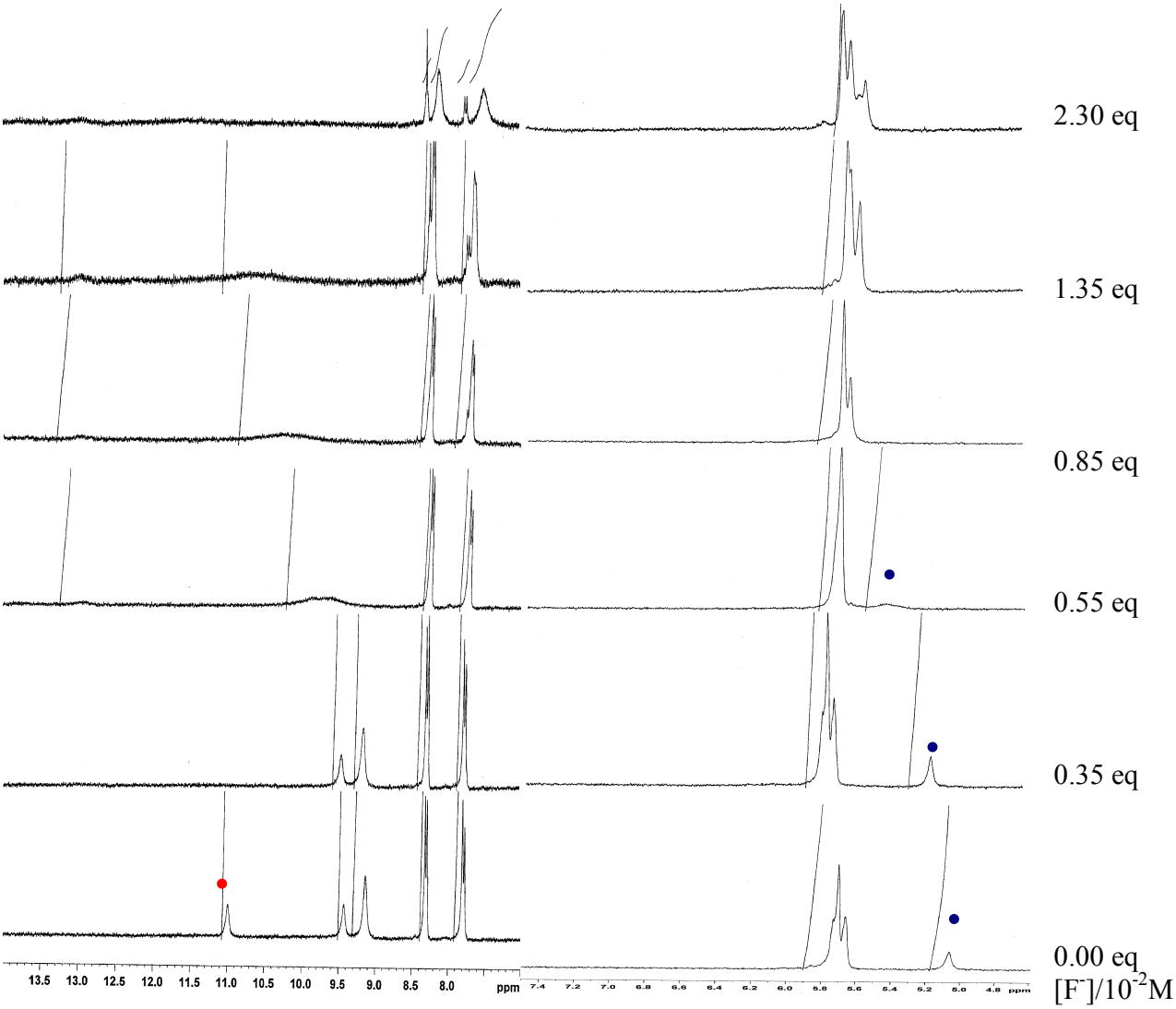



**Figure S31.** $^{1}$H NMR titrations of compd **4** (1.0 x $10^{-2}$ M) with $Cl^-$ in DMSO-$d_6$-0.5% water. The inverted pyrrole $^{1}$H resonances in **4** are labeled as follows: pyrrole $NH_i$ ● (red), and β-$CH_i$ ● (blue)

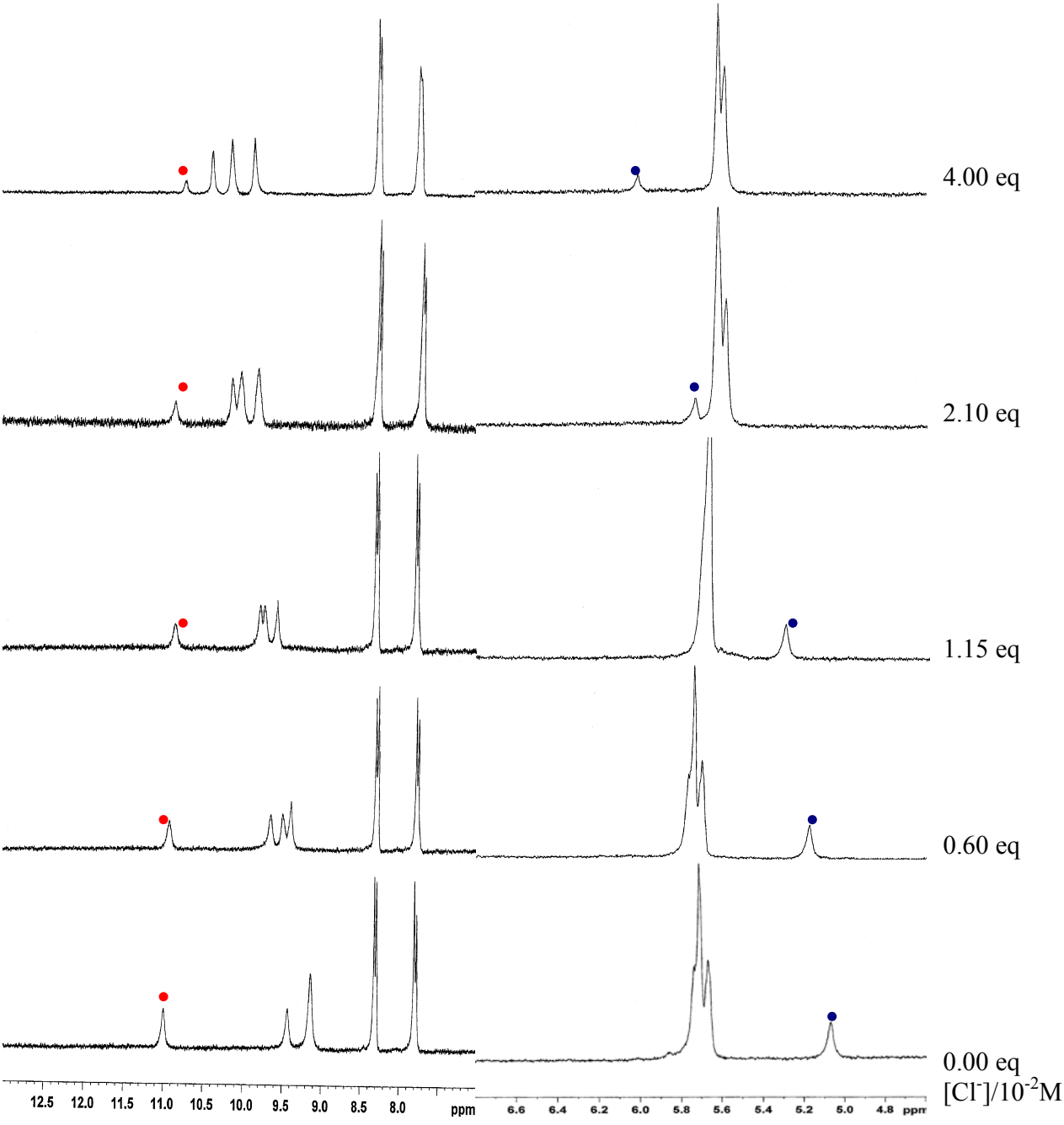


**Figure S32.** $^{1}$H NMR titrations of compd **5** (1.0 x $10^{-2}$ M) with $AcO^{-}$ in DMSO-$d_6$-0.5% water.

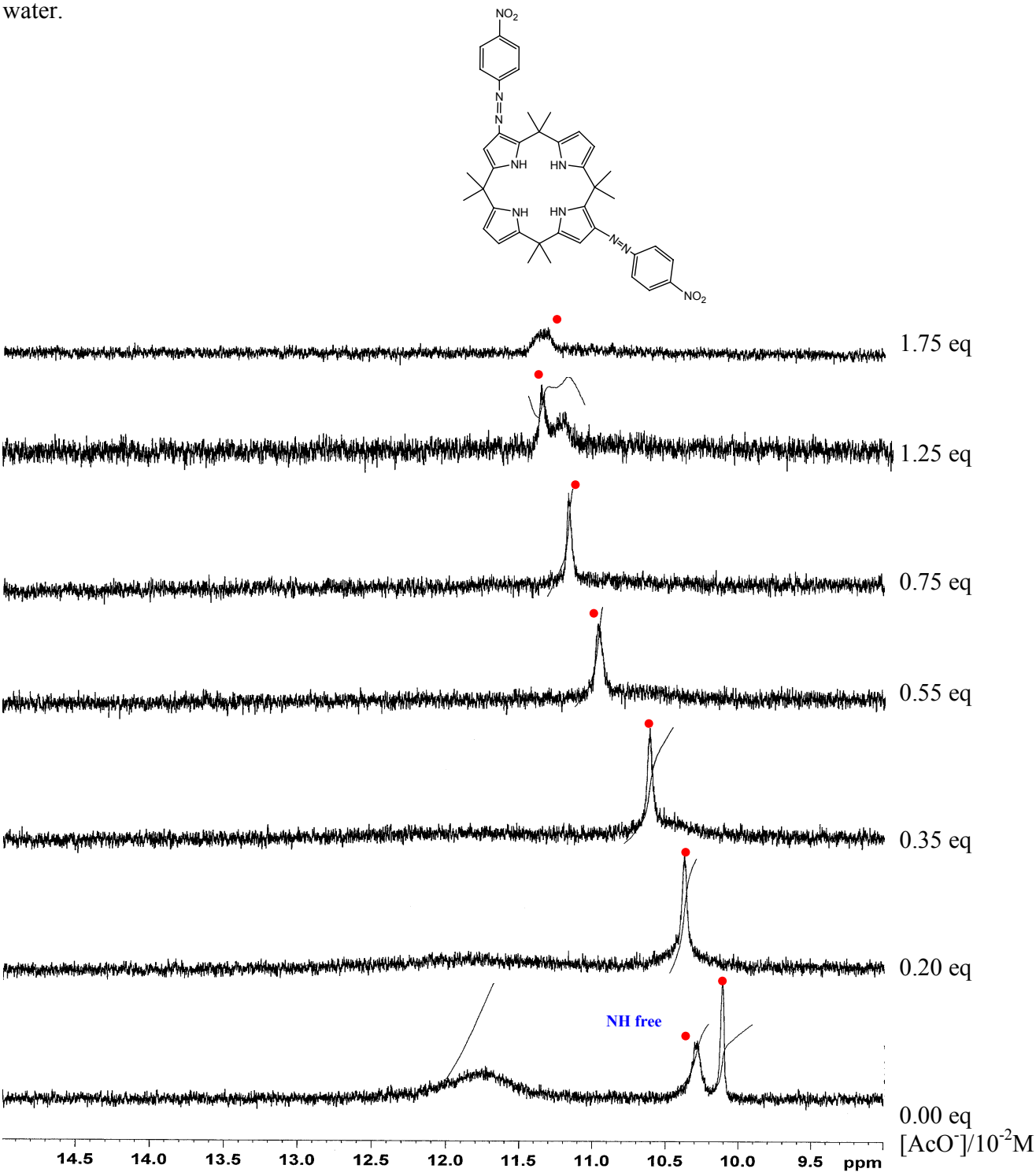


**Figure S33.** $^{1}$H NMR titrations of compd **5** (1.0 x $10^{-2}$ M) with $H_2PO_4^-$ in DMSO-$d_6$-0.5% water.

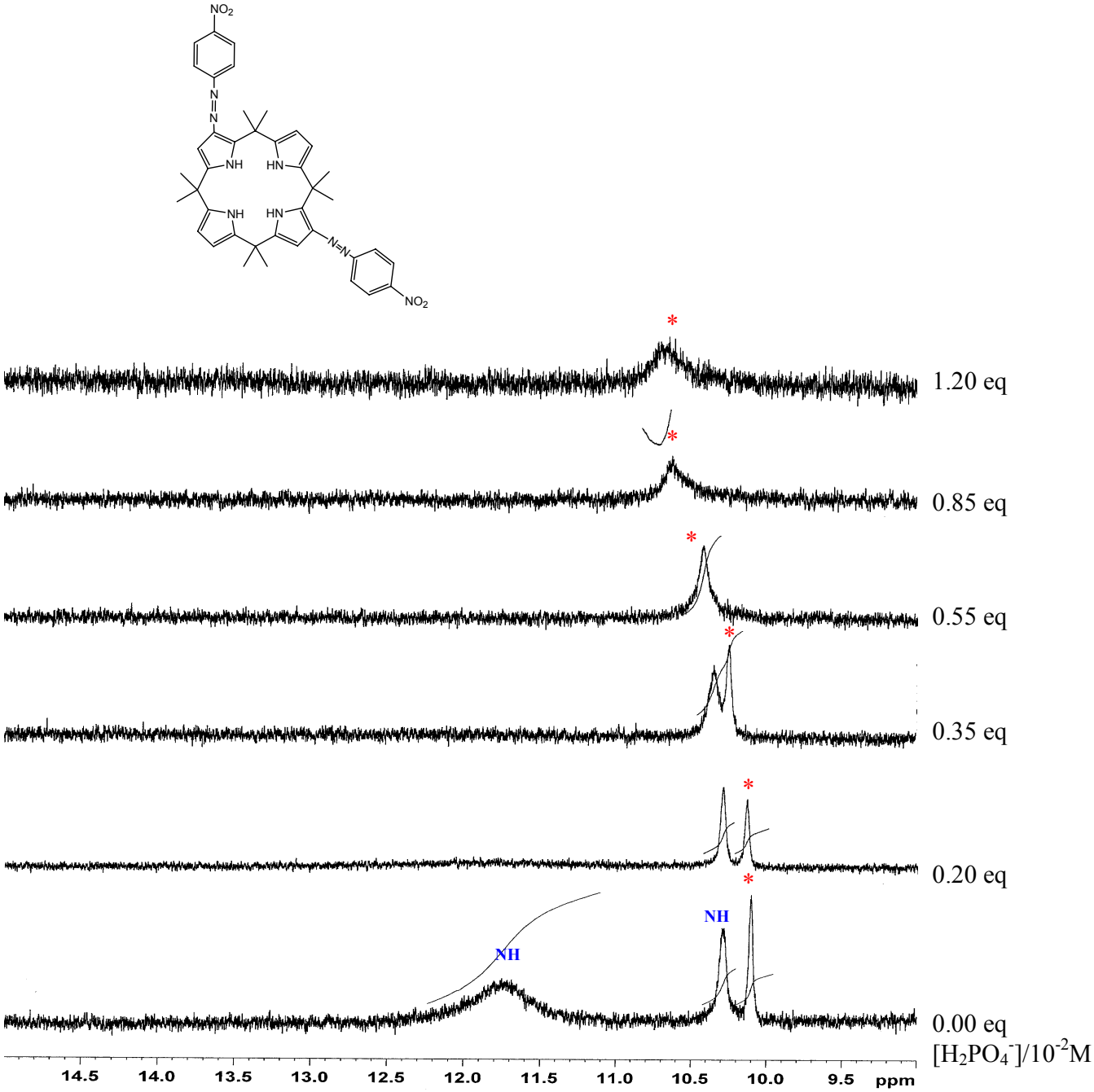


**Figure S34** $^{1}$H NMR titrations of compd **5** (1.0 x $10^{-2}$ M) with $AcO^-$ in $CD_2Cl_2$.

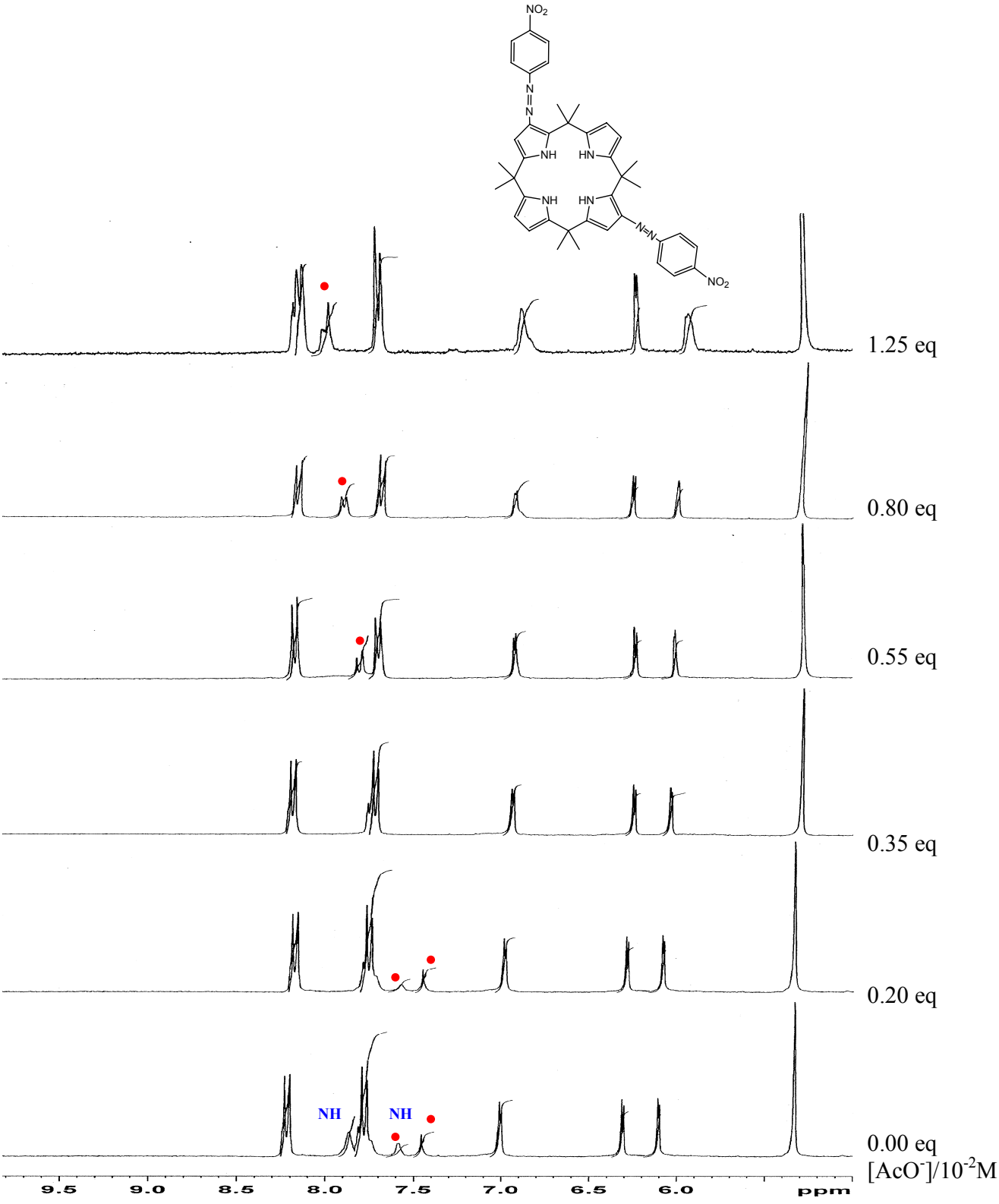


**Figure S35** $^{1}$H NMR titrations of compd **6** (1.0 x $10^{-2}$ M) with $AcO^-$ in $CD_2Cl_2$.

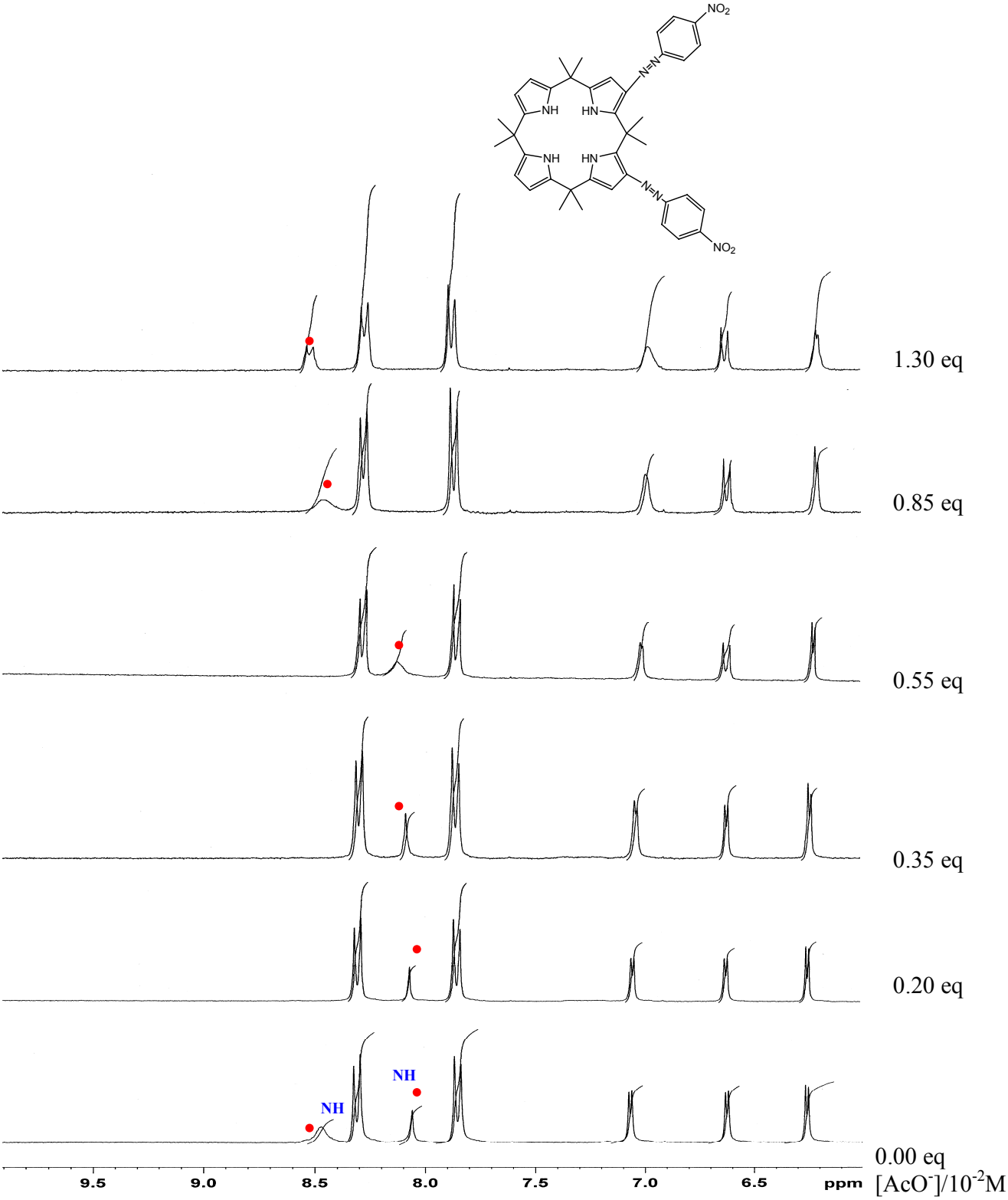


**Figure S36.** $^{1}$H NMR titrations of compd **5** (1.0 x $10^{-2}$ M) with $F^-$ in DMSO-$d_6$-0.5% water.

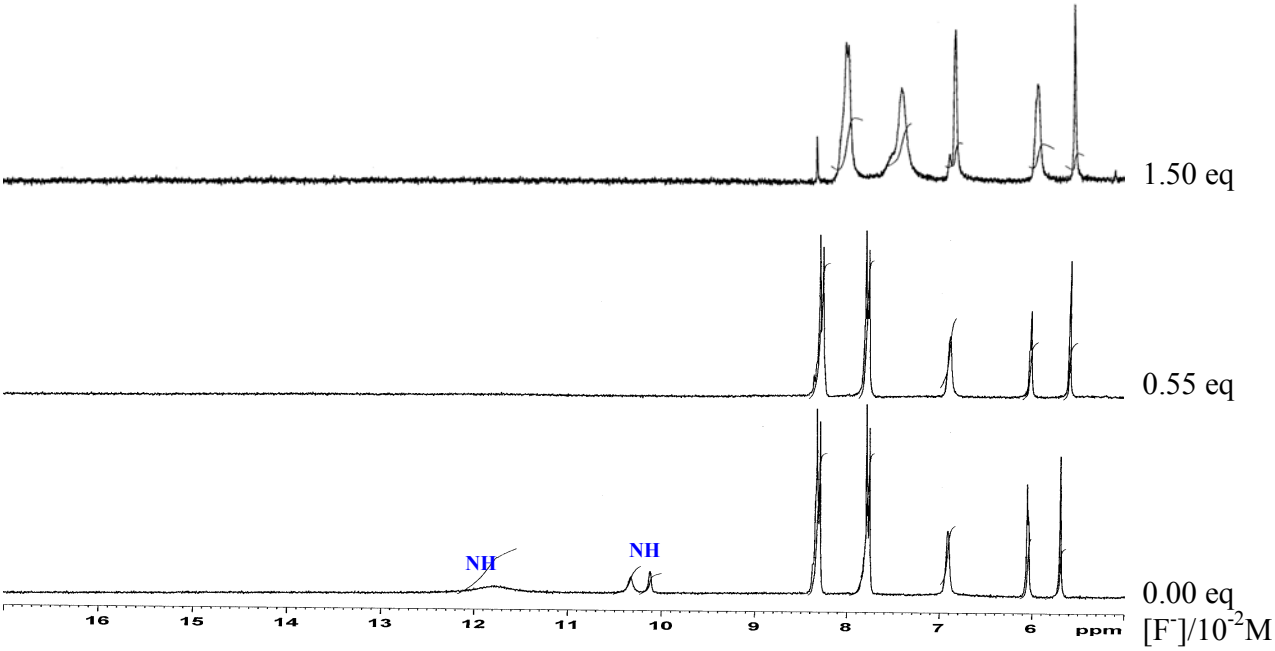
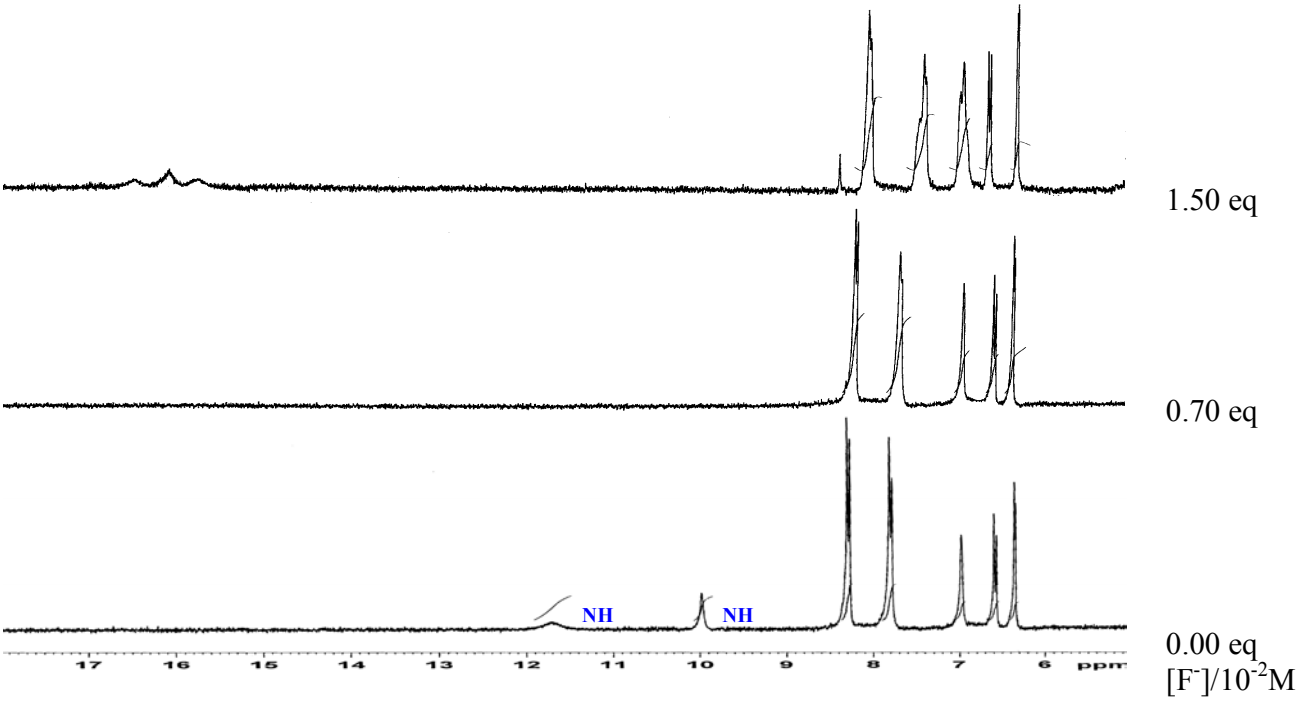



**Figure S37.** $^{1}$H NMR titrations of compd **6** (1.0 x $10^{-2}$ M) with $F^-$ in DMSO-$d_6$-0.5% water.



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