Supporting Information

for

Synthesis and self-assembly of DNA-chromophore hybrid amphiphiles

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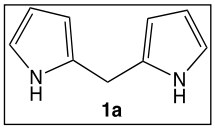
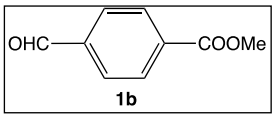
Synthesis of 1

Synthesis of 1a:[S1] A solution of paraformaldehyde (2.0 g, 66.6 mmol) suspended in 115.6 mL of freshly distilled pyrrole (1.66 mol) was degassed for 5 min. Then TFA (0.5 mL, 6.66 mmol) was added and stirred up to 10 min. After the completion of reaction triethylamine, was added to quench the reaction mixture and then excess pyrrole was removed by vacuum distillation. Then the product was purified by column chromatography using DCM as eluent to obtain desired product as colourless solid. M.P. 68.9 °C; TLC (DCM), R_f = 0.72; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm : 3.91 (s, 2H), 5.96 (s, 2H), 6.07 (s, 2H), 6.59 (s, 2H), 7.82 (bs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm : 28.69, 105.33, 107.40, 116.20, 128.01; HR-MS (*m/z*): $[M]^{\cdot+}$ calcd. for $[C_9H_{10}N_2]^{\cdot+}$: 146.0844, found 146.0761.



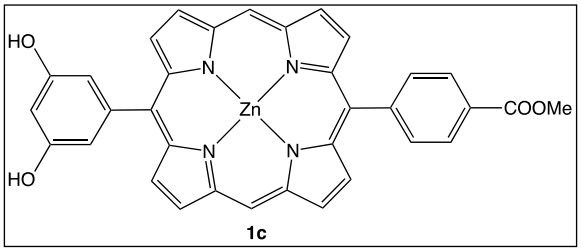
1a

Synthesis of 1b:[S2] A mixture of of 4-Formylbenzoic acid (5.0 g, 33.304 mmol) and anhydrous MeOH (100 mL) was cooled to 0 °C and then $SOCl_2$ (20 mL) was added drop wise under stirring. The mixture was stirred for 1 h at room temperature. After that the reaction mixture was poured into ice cold water (500 mL) and extracted with DCM and dried on sodium sulphate. Then the crude product was purified through column chromatography using pet-ether and DCM (1:1) as eluent to obtain desired product as colourless solid. M.P. 61 °C; TLC (petroleum ether:DCM, 1:1), R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm : 3.89 (s, 3H), 7.88 (d, *J* = 8.35 Hz, 2H), 8.12 (d, *J* = 8.25 Hz, 2H), 10.03 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm : 51.55, 128.49, 129.18, 134.09, 138.15, 165.04, 190.59; HR-MS (*m/z*): $[M+H]^+$ calcd. for $[C_9H_9O_3]^+$: 165.0473; found: 165.0390.



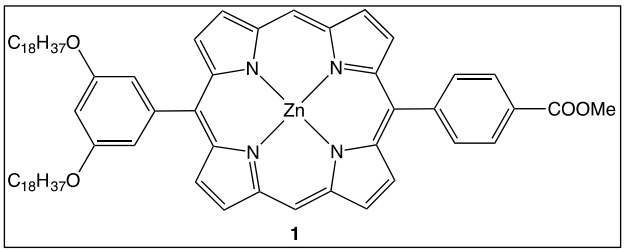
1b

Synthesis of 1c:[S3] To a mixture of 3, 5-dihydroxybenzaldehyde (0.2 g, 1.4479 mmol), 4-formylmethylbenzoate (**1b**) (0.237 g, 1.4479 mmol) and dipyrromethane (0.423 g, 2.895 mmol) in DCM/MeOH (20:5, 140 mL) was stirred in the presence of $BF_3.OEt_2$ (0.33 mL) under nitrogen at room temperature and in dark for 12 h. After stirring, DDQ (0.956 g, 4.2133 mmol),was added and the reaction mixture was stirred for an additional 12 hr at room temperature. After that the reaction mixture was concentrated to volume 50 mL and then separated by column chromatography using DCM:MeOH (97:3) as eluent. Without further purification, the product was dissolved in 10% MeOH/DCM containing $Zn(OAc)_2$ (1.303 g, 5.936 mmol) and then stirred for 12 h at room temperature. Then remove the solvent by rotary vapour, the reaction mixture was purified by column chromatography with 3% MeOH/DCM, to obtain reddish purple solid (15%). M.P. >300 °C; TLC (4% MeOH/DCM), R_f = 0.41; ^{1}H NMR (500 MHz, CD_3OD) δ ppm : 4.01 (s, 3H), 6.65 (t, *J* = 2.2 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 2H), 8.24 (d, *J* = 8.10 Hz, 2H), 8.35 (d, *J* = 8.10, 2H), 8.85 (d, *J* = 4.4 Hz, 2H), 9.07 (d, *J* = *4*.07 Hz, 2H), 9.29-9.30 (m, 4H), 10.15 (s, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ ppm: 51.48, 101.30, 105.40, 113.27, 114.62, 117.42, 119.80, 127.25, 128.83, 130.87, 131.10, 131.40, 131.79, 134.54, 138.75, 145.06, 149.18, 149.47, 149.75, 149.90, 156.15, 167.56; HR-MS (*m/z*): $[M+H]^+$ calcd. for $[C_{34}H_{23}N_4O_4Zn]^+$: 615.0933; found: 615.0991.



1c

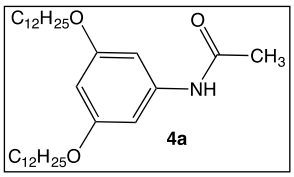
Synthesis of 1: In dry THF (5 mL) mixture of 1-bromooctadecane (1.0 mL, 2.93 mmol), **1c** (0.09 g, 0.1465 mmol), anhydrous K_2CO_3 (0.201 g, 1.456 mmol) and 18-crown-6-ether (0.0077 g, 0.0293 mmol) were refluxed under nitrogen for 24 h and subsequently evaporated, product was extracted with DCM, washed with water and dried on sodium sulphate evaporated. The residue was purified by column chromatography on silica gel and pet-ether/DCM (1:1), to obtain bright red colour solid (70%). M.P. 86 ^oC; TLC (pet-ether/DCM), R_f = 0.205; ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 0.76 (t, *J* = 7.5 Hz, 6H), 1.12 -1.40 (m, 58H), 1. 75 -1.81 (m, 4H), 4.02 (s, 3H), 4.05 (t, *J* = 6.50 Hz, 4H), 6.82 (t, *J* = 2.00 Hz, 1H), 7.32 (d, *J* = 2.50 Hz, 2H), 8.22 (d, *J* = 8.00 Hz, 2H), 8.35 (d, *J* = 8.00 Hz, 2H), 8.95 (d, *J* = 4.50 Hz, 2H), 9.16 (d, *J* = 4.50 Hz, 2H), 9.32 (d, *J* = 4.00 Hz, 4H), 10.19 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 13.04, 21.63, 25.11, 28.30, 28.41, 28.43, 28.56, 28.57, 28.60, 28.64, 30.88, 51.65, 67.44, 100.02, 105.30, 113.57, 117.49, 119.34, 126.81, 128.30, 130.77, 130.92, 131.77, 133.61, 143.18, 146.56, 148.39, 148.41, 148.67, 149.08, 157.36, 166.40; HR-MS (*m/z*): $[M+H]^+$ calcd. for $[C_{70}H_{95}N_4O_4Zn]^+$: 1119.6567; found: 1119.6618.



1

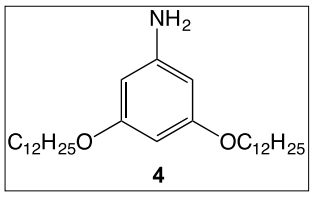
Synthesis of 4

Synthesis of 4a: To a solution of N-(3,5-dihydroxyphenyl)acetamide (3a) (7.0 g, 41.88 mmol) in 60 ml of DMF, K_2CO_3 (57.87 g, 418.8 mmol) was added and stirred at rt for 30 min. To this bromododecane (62.62 g, 251.28 mmol) was added, reaction mixture was stirred at 60 °C for 7 h, compound was extracted with dichloromethane and purified by column chromatography using dichloromethane as eluent (94.72 %). M.P = 83 °C, R_f = 0.32 ; ^1H NMR (500 MHz, $CDCl_3$), δ (ppm) = 0.81 (t, *J* = 7, 6H), 1.18-1.30 (m, 40H), 1.66-1.69 (m, 4H), 2.07 (s, 3H), 3.84 (t, *J* = 6.5, 4H), 6.15 (s, 1H), 6.63 (s, 2H), 6.96 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 13.08, 21.67, 25.02, 28.21, 28.33, 28.37, 28.56, 28.59, 28.62, 28.65, 30.91, 67.14, 96.65, 97.52, 138.48, 159.58, 167.13; HR-MS (*m/z*): $[M+H]^+$ calcd. for $[C_{32}H_{58}NO_3]^+$: 504.4388; found: 504.4296.



4a

Synthesis of 4: To a solution of N-(3,5(dodecyloxy)phenyl)acetamide (18 g, 35 mmol) was in 340 ml of ethanol, 80 ml of con. HCl was added and it was stirred at 90 °C for 7 h, compound was extracted using dichloromethane, solvent was removed under reduced pressure and compound was purified by column chromatography using petroleum ether : dichloromethane (81 %). M.P = 53 °C R_f = 0.38; ^1H NMR (500 MHz, $CDCl_3$), δ (ppm) = 0.81 (t, *J* = 7.0 Hz, 6H), 1.19-1.22 (m, 32H), 1.29-1.34 (m, 4H), 1.67-1.69 (m, 4H), 3.53 (s, 2H), 3.80 (t, *J* = 6.5 Hz, 4H), 5.77 (s, 2H), 5.84 (t, *J* = 2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm) = 14.08, 22.67, 26.07, 29.33, 29.39, 29.60, 29.62, 29.65, 31.91, 67.90, 92.21, 92.41, 148.20, 161.27; HR-MS (*m/z*): $[M+H]^+$ calcd. for $[C_{30}H_{56}O_2N]^+$: 462.4233; found: 462.4317.



4

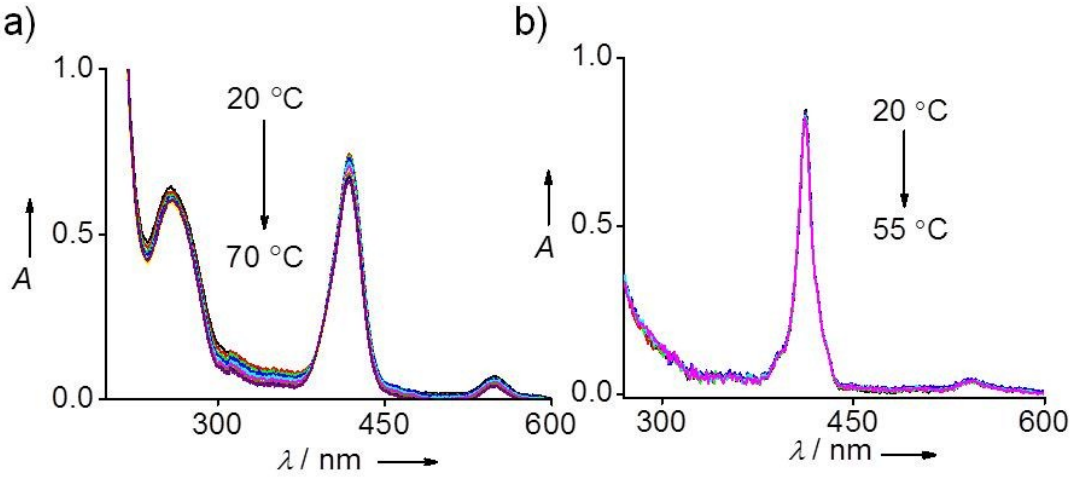


Figure S1. Comparison of temperature dependent absorption spectral changes of (a) **DNA1** in 50 mM Tris buffer (c = 1 μM) and (b) **3** in THF (c = 1 μM). It is to be noted that **DNA1**-aggregates and **3** show similar spectral changes with temperature. This indicates that observed changes in the absorption spectrum of **DNA1** with temperature could be the mere effect of temperature on the photophysical properties of the aggregates, and not due to the disassembly of the aggregates.

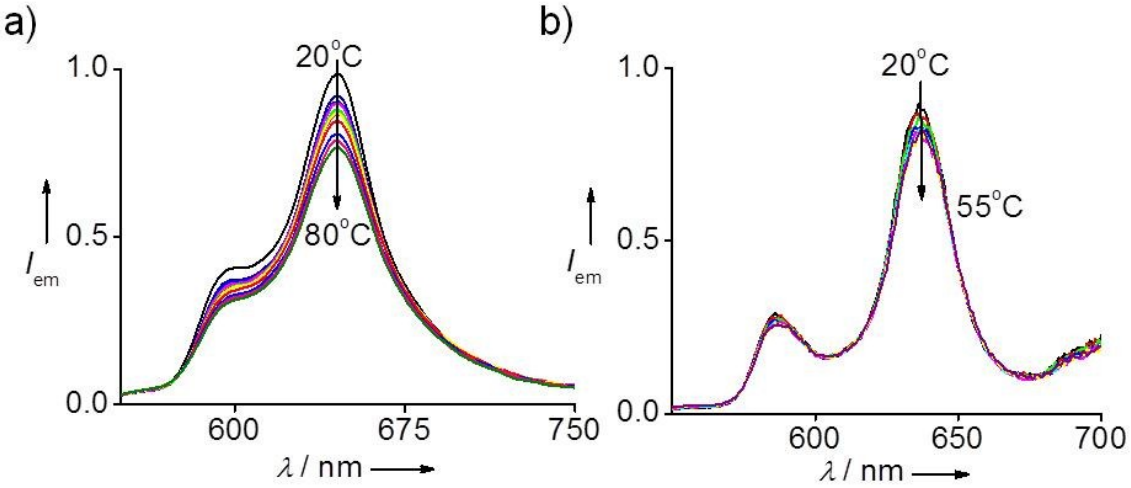


Figure S2. Comparison of temperature dependent emission spectral changes of (a) **DNA1** in in 50 mM Tris buffer (c = 1 μM) and (b) **3** in THF (c = 1 μM). In accordance with the absorption spectral changes, **DNA1**-aggregates (λ_{ex} = 420 nm) and **3** (λ_{ex} = 410 nm) show similar emission changes with temperature. This indicates that observed changes in the emission spectrum of **DNA1** could be the mere effect of temperature on the photophysical properties of the aggregates, and not due to the disassembly of the aggregates with temperature.

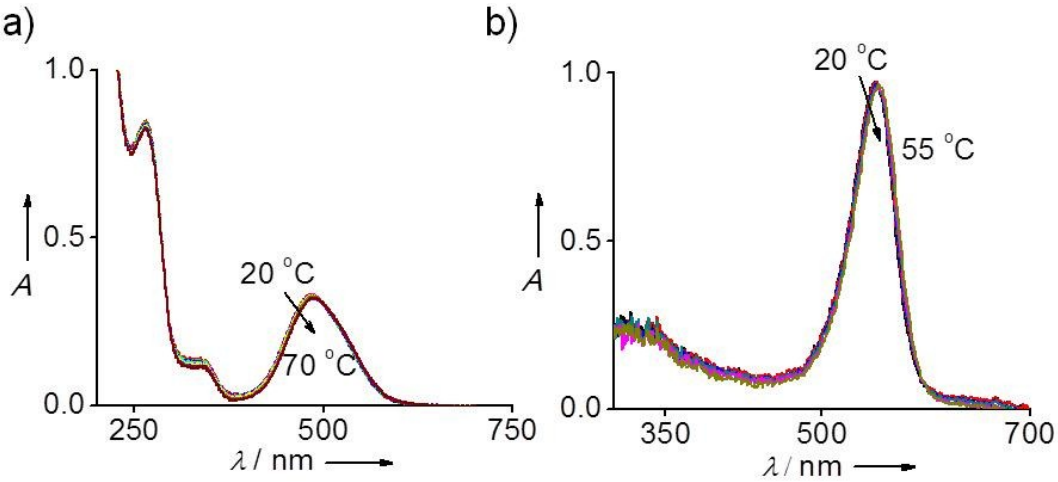


Figure S3. Comparison of temperature dependent absorption spectral changes of (a) **DNA2** in 50 mM Tris buffer (c = 1 μM) and (b) **10** in THF (c = 1 μM). In this case also, **DNA2**-aggregates and **10** show similar spectral changes with temperature. This indicates that, as in the case of **DNA1**-aggregates, observed changes in the absorption spectrum of **DNA2**-aggregates could be the mere effect of temperature on the photophysical properties of the aggregates, and not due to the disassembly of the aggregates.

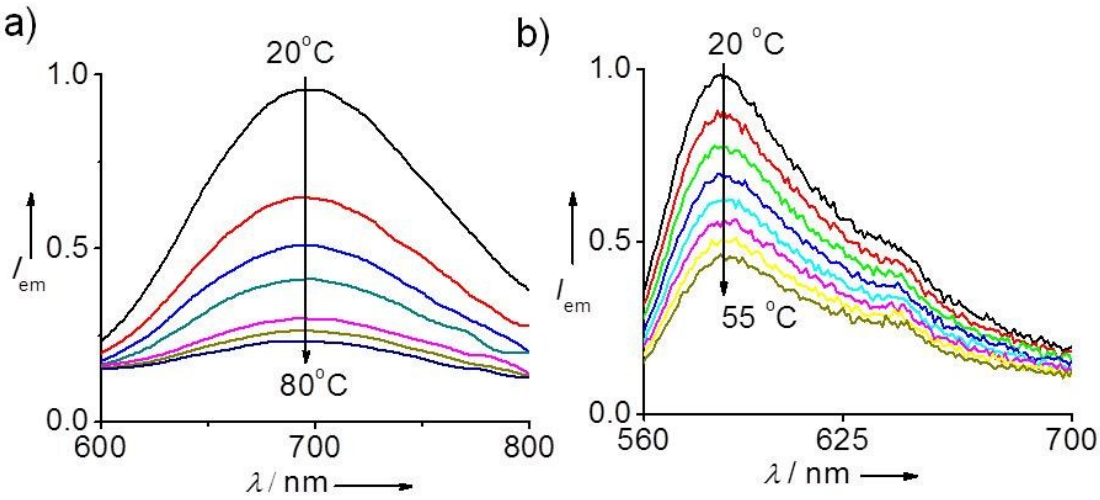


Figure S4. Comparison of temperature dependent emission spectral changes of (a) **DNA2** in 50 mM Tris buffer (c = 1 μM) and (b) **10** in THF (c = 1 μM). In accordance with the absorption spectral changes, **DNA2**-aggregates (λ_{ex} = 480 nm) and **10** (λ_{ex} = 540 nm) show similar emission changes with temperature. This indicates that observed changes in the emission spectrum of **DNA2** could be the mere effect of temperature on the photophysical properties of the aggregates, and not due to the disassembly of the aggregates.

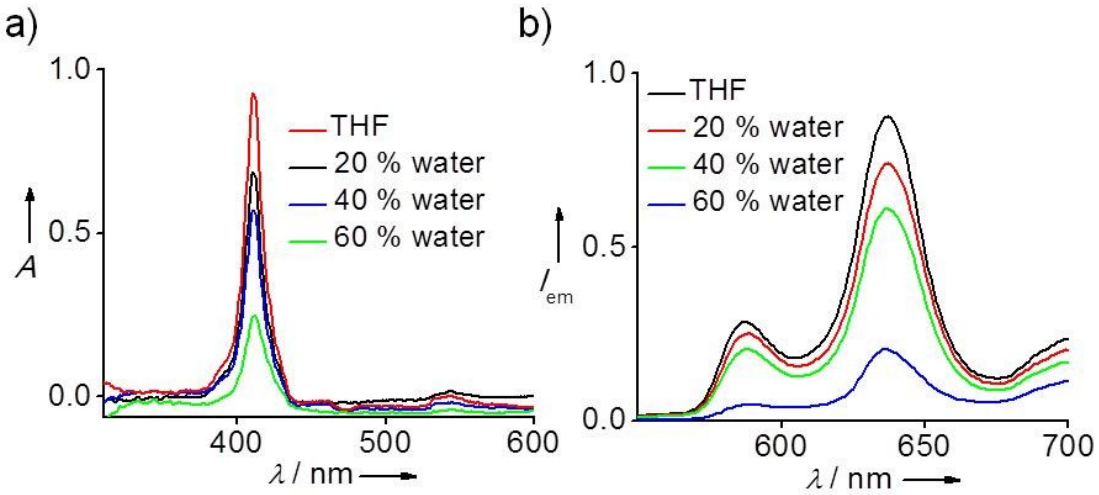


Figure S5. (a) Absorption and (b) emission spectral changes of **3** (λ_{ex} = 410 nm) in THF with the addition of water. In the case of **3**, addition of water into the THF solution shows a decrease in absorbance and quenching of fluorescence without noticeable shift in the absorption and emission maxima. Since the corresponding amphiphile, **DNA1** is not dissociating into the monomeric species either with the increase in temperature or upon dilution, it was not possible to compare their photophysical properties.

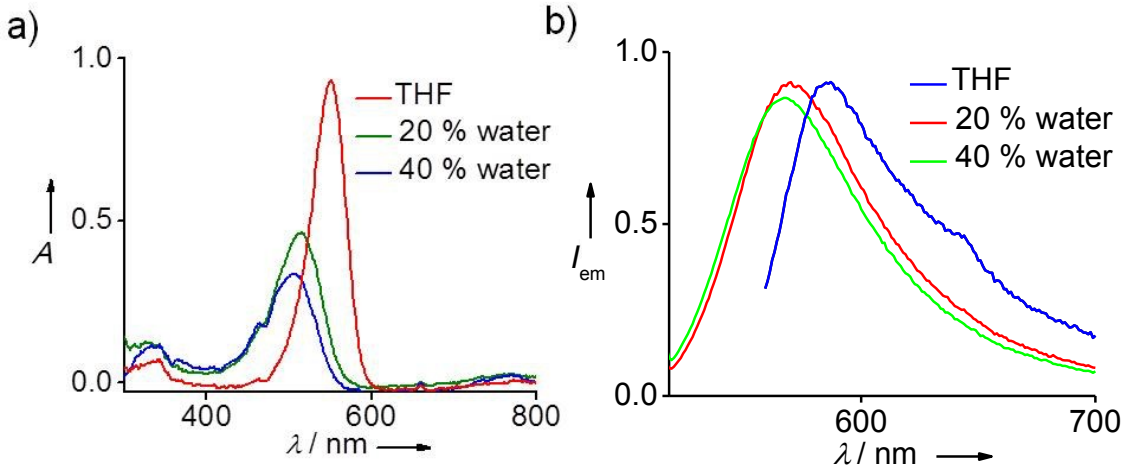


Figure S6. (a) Absorption and (b) emission (normalised) spectral changes of **10** (λ_{ex} = 540 nm, 500 nm for THF and THF-water mixture, respectively) in THF with the addition of water. Addition of water into THF solution of **10** shows a decrease in absorbance with a blue-shift of 43 nm in the absorption maximum from 550 nm to 507 nm. Similarly, emission spectrum also shows a blue-shift in the emission maximum from 585 nm to 568 nm with the addition of water into the THF solution of **10**. In this case also, since the aggregates of **DNA2** are not dissociating into the corresponding monomeric species either with the increase in temperature or with dilution, it was not possible to compare their optical properties with the aggregates of **10**.

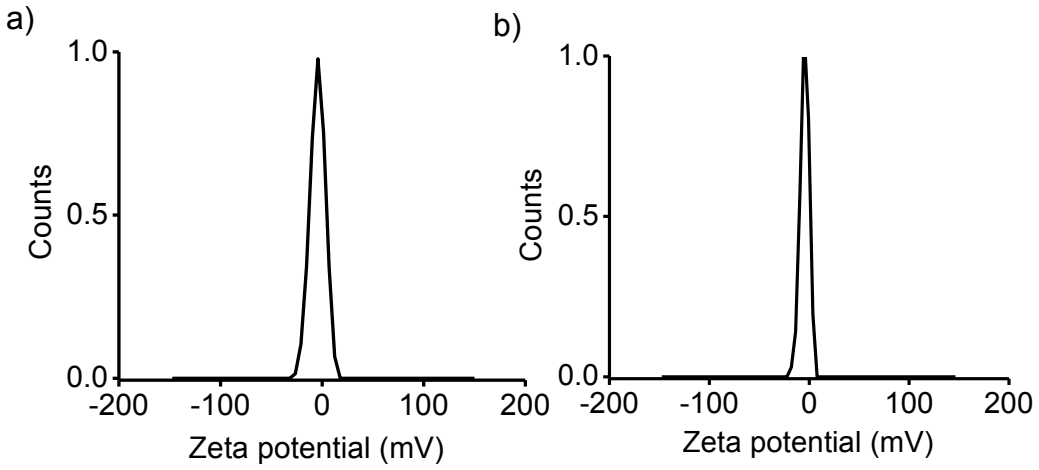


Figure S7. Surface zeta potential graph showing negative zeta potential value (a) for **DNA1** and (b) **DNA2**.

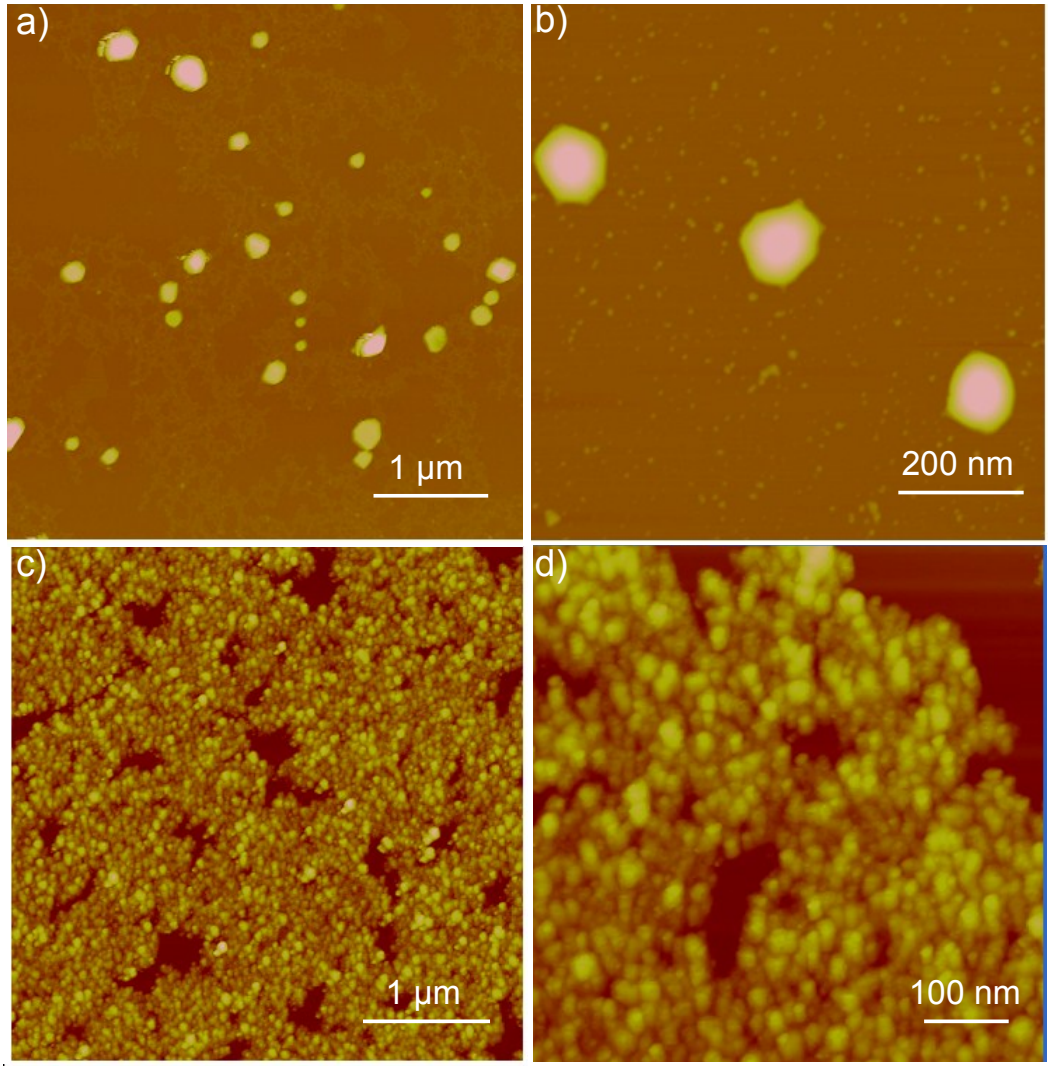


Figure S8. AFM images of **DNA1** vesicle (top row) and **DNA2** micelle (bottom row) after hybridization with the complementary DNA, suggesting that the morphology remains the same even after their hybridization with the complementary DNA strand.

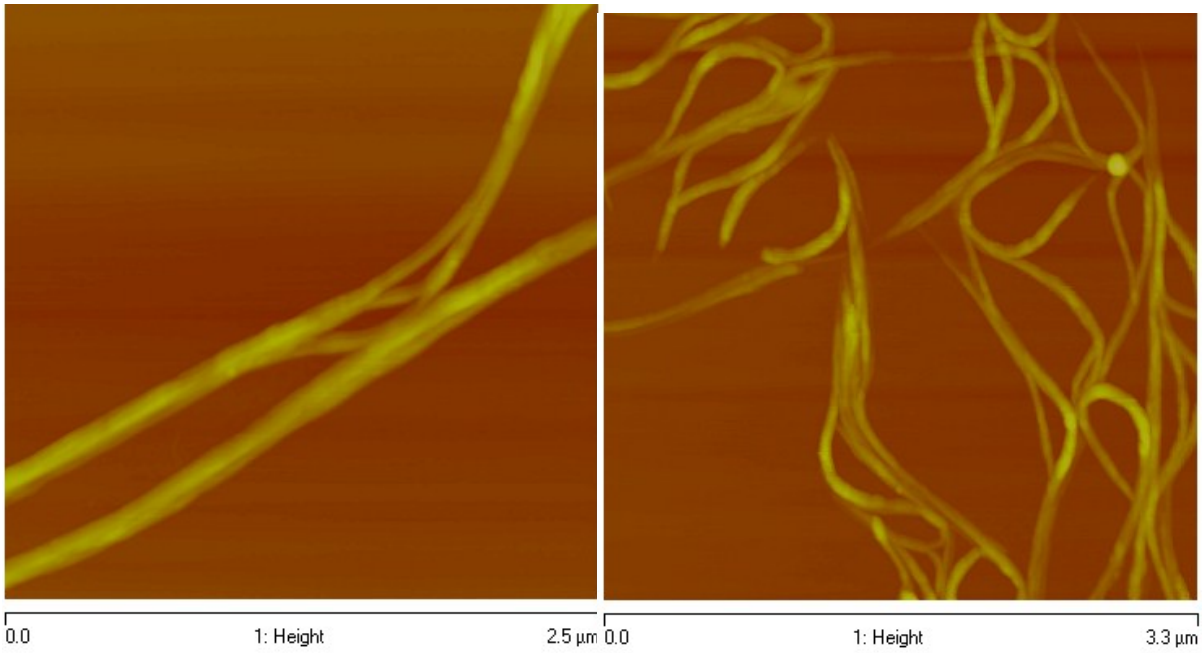


Figure S9. AFM height images of aggregates of **3** (precursor-chromophore for **DNA1**) obtained with the addition of water into THF solution of **3** (40 % water). AFM analysis clearly reveals that aggregates of precursor-chromophore **3** show fibrous morphology, whereas **DNA1** show vesicular morphology. These results indicate that chromophore packing in the aggregates of **3** and **DNA1** are different, and hence, they display dissimilar optical properties as described above.

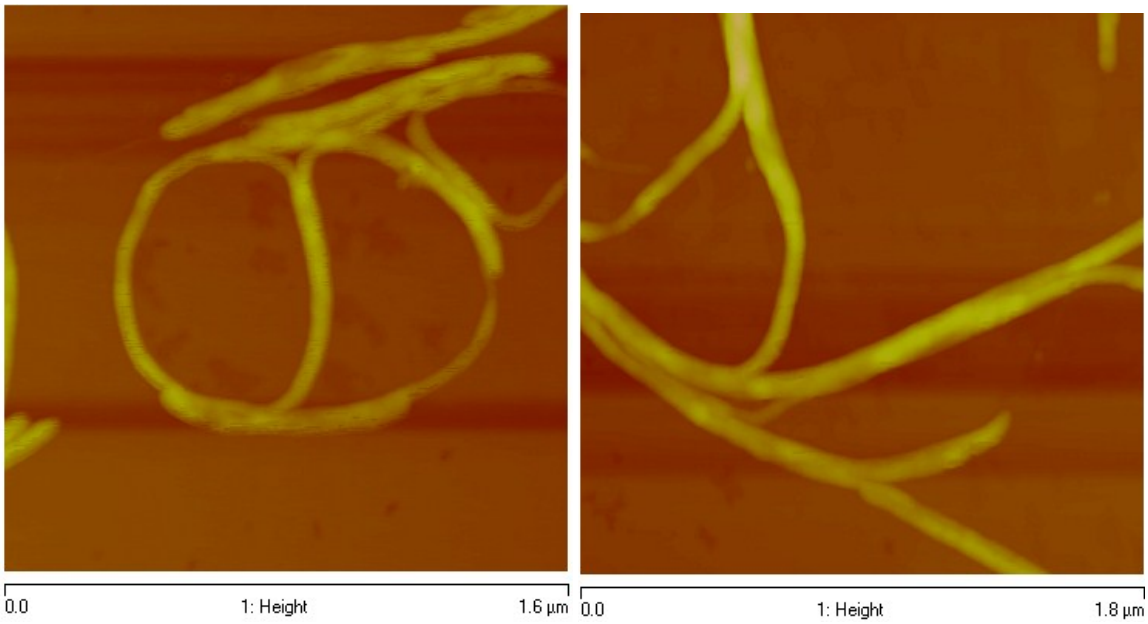


Figure S10. AFM height images of aggregates of **10** (precursor-chromophore for **DNA2**) obtained with the addition of water into THF solution of **10** (40 % water). AFM analysis clearly reveals that aggregates of precursor-chromophore **10** show fibrous morphology, whereas **DNA2** show micellar morphology. As in the case of other systems, these results indicate that chromophore packing in aggregates of **10** and **DNA2** are different, accordingly, they exhibit dissimilar optical properties as described above.

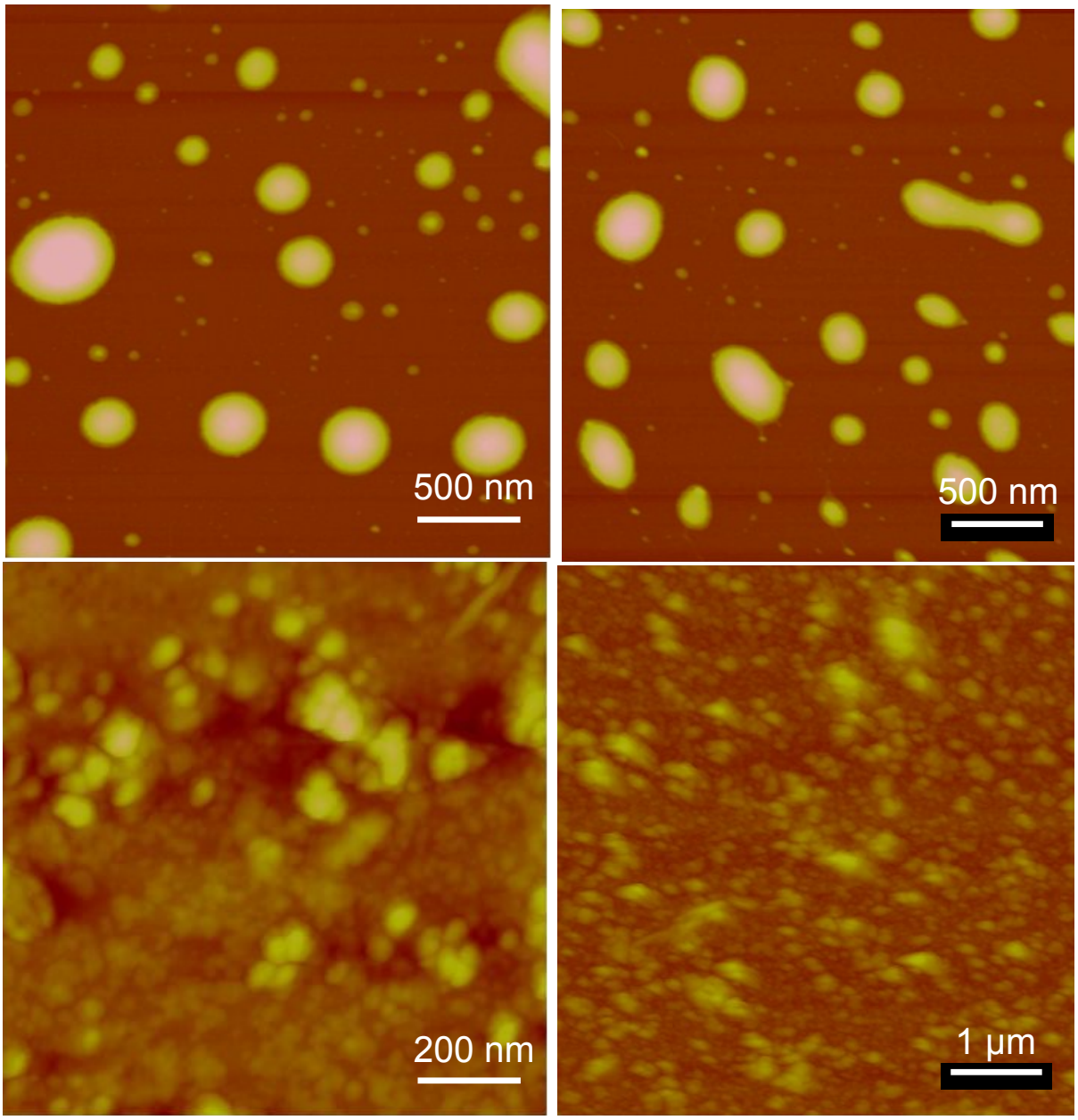


Figure S11: Additional AFM images for **DNA1** (upper row) and **DNA2** (bottom row).

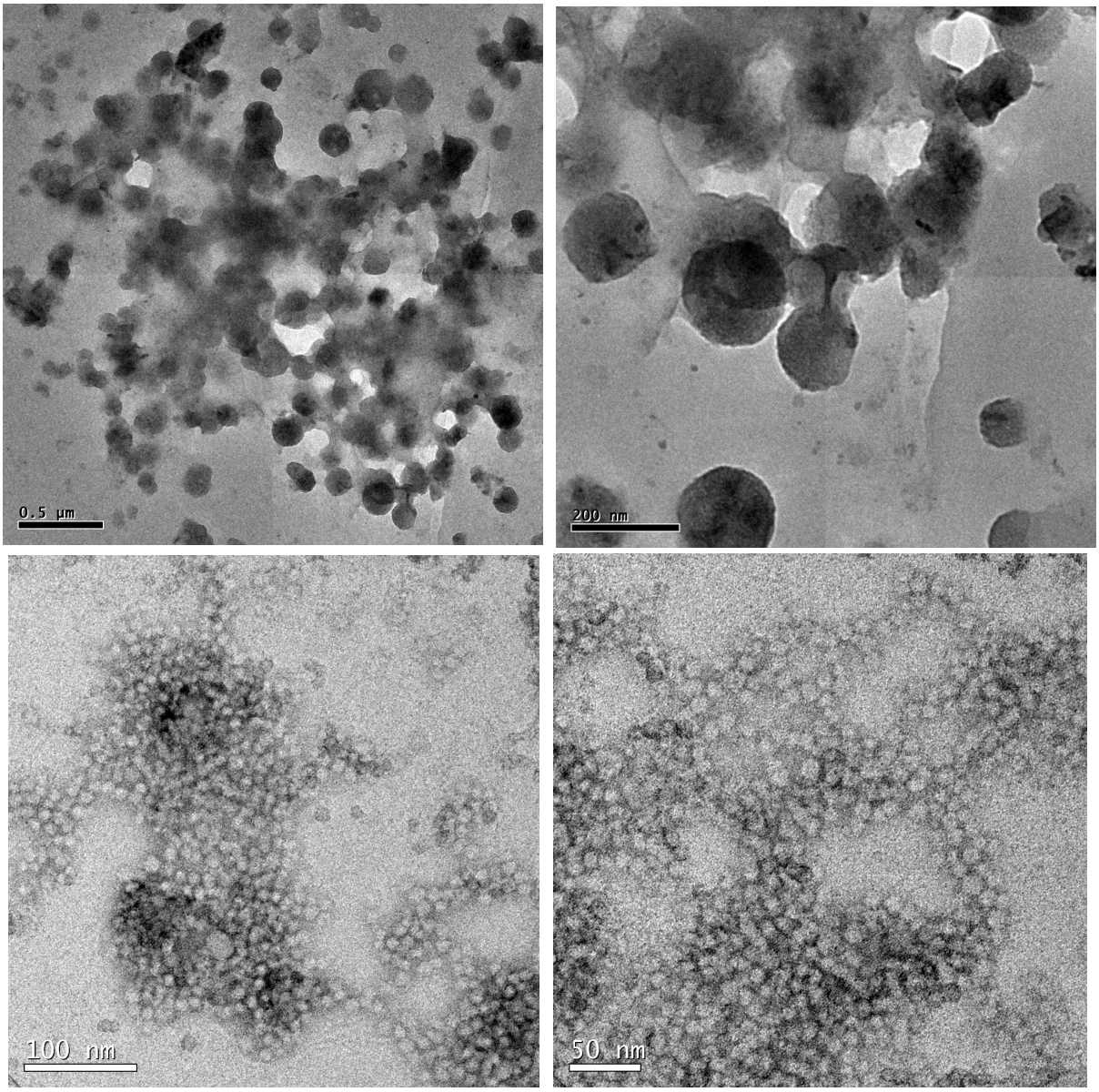


Figure S12: Additional TEM images for **DNA1** (upper row) and **DNA2** (bottom row).

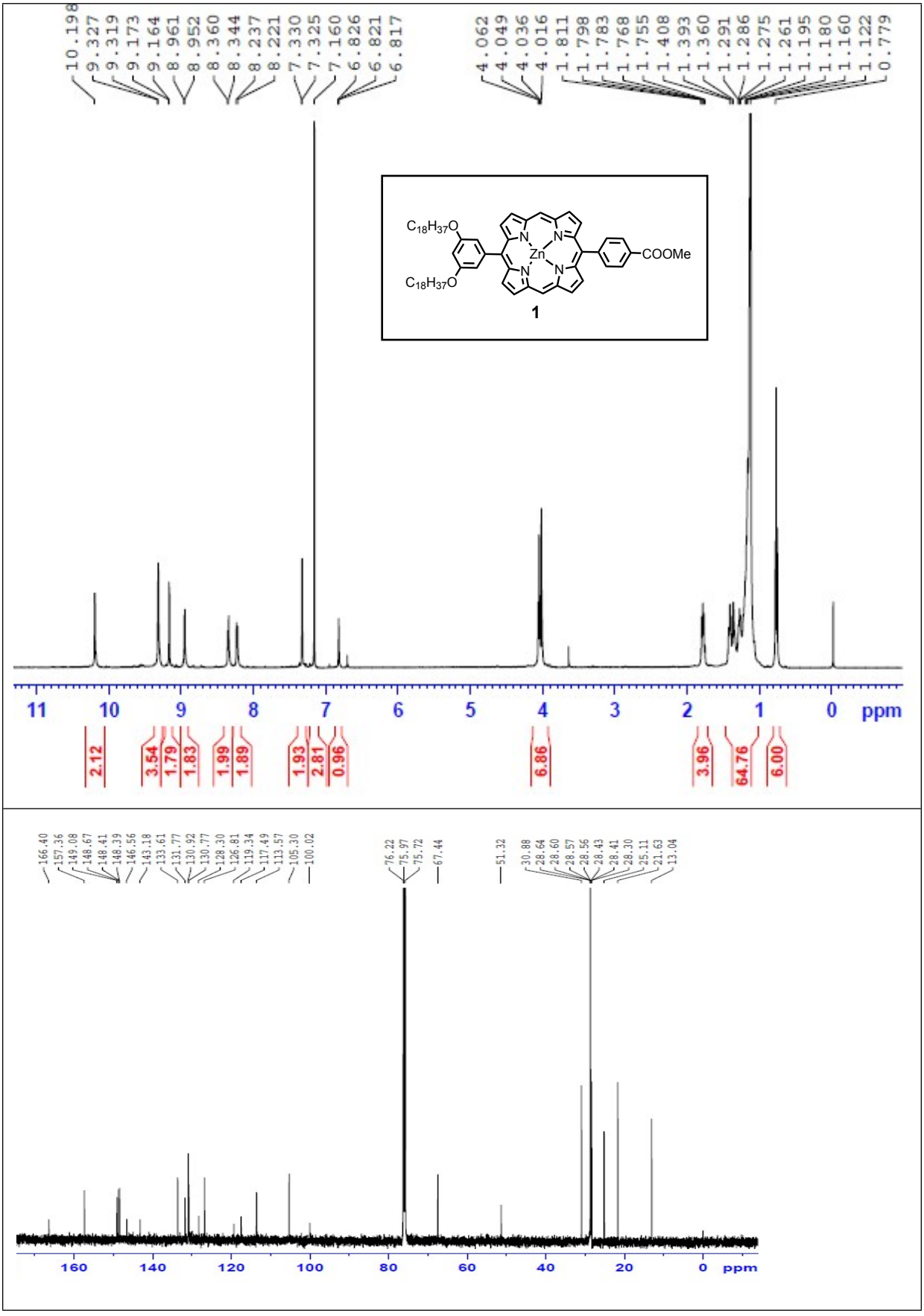


Figure S13: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **1**.

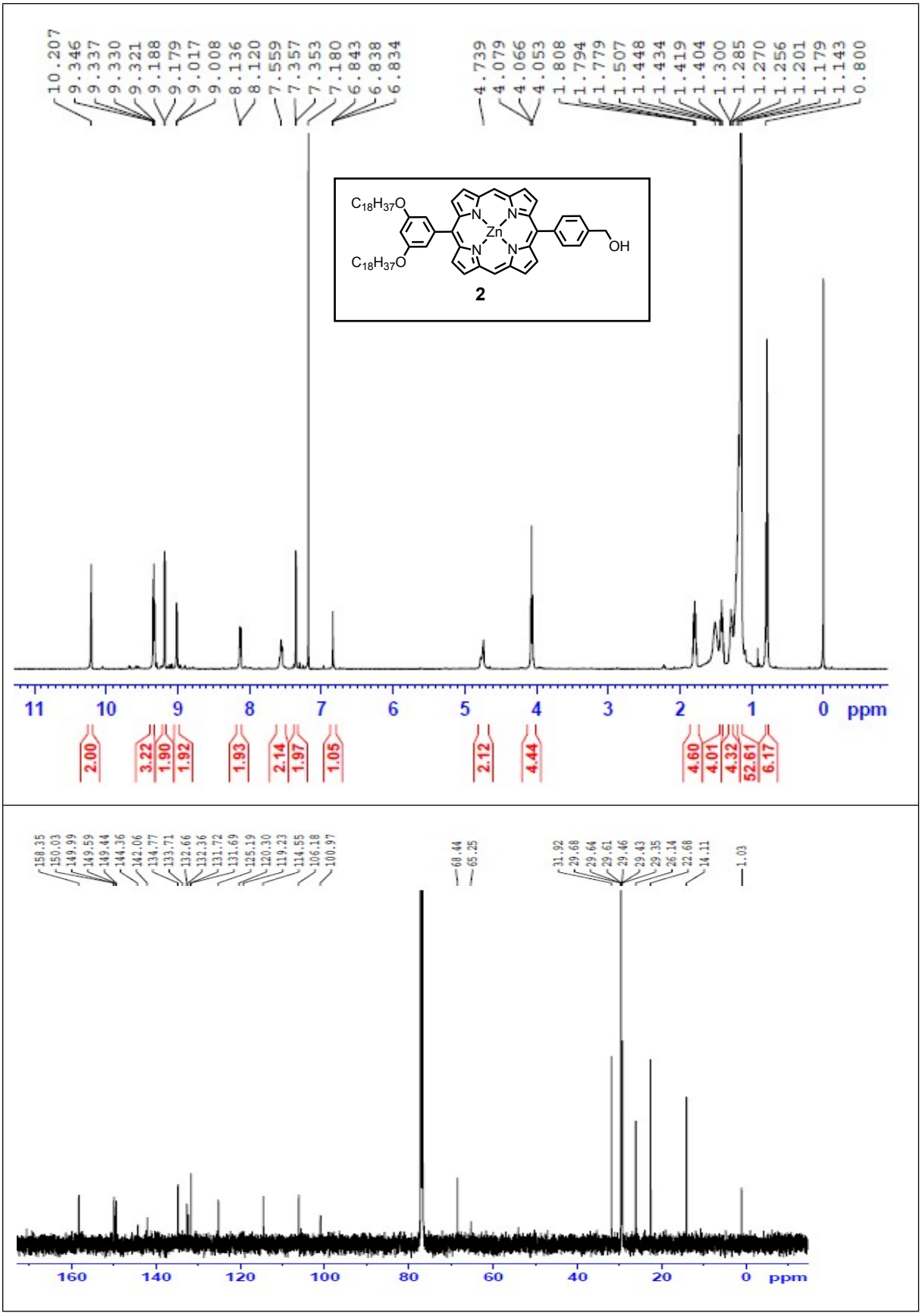


Figure S14: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **2**.

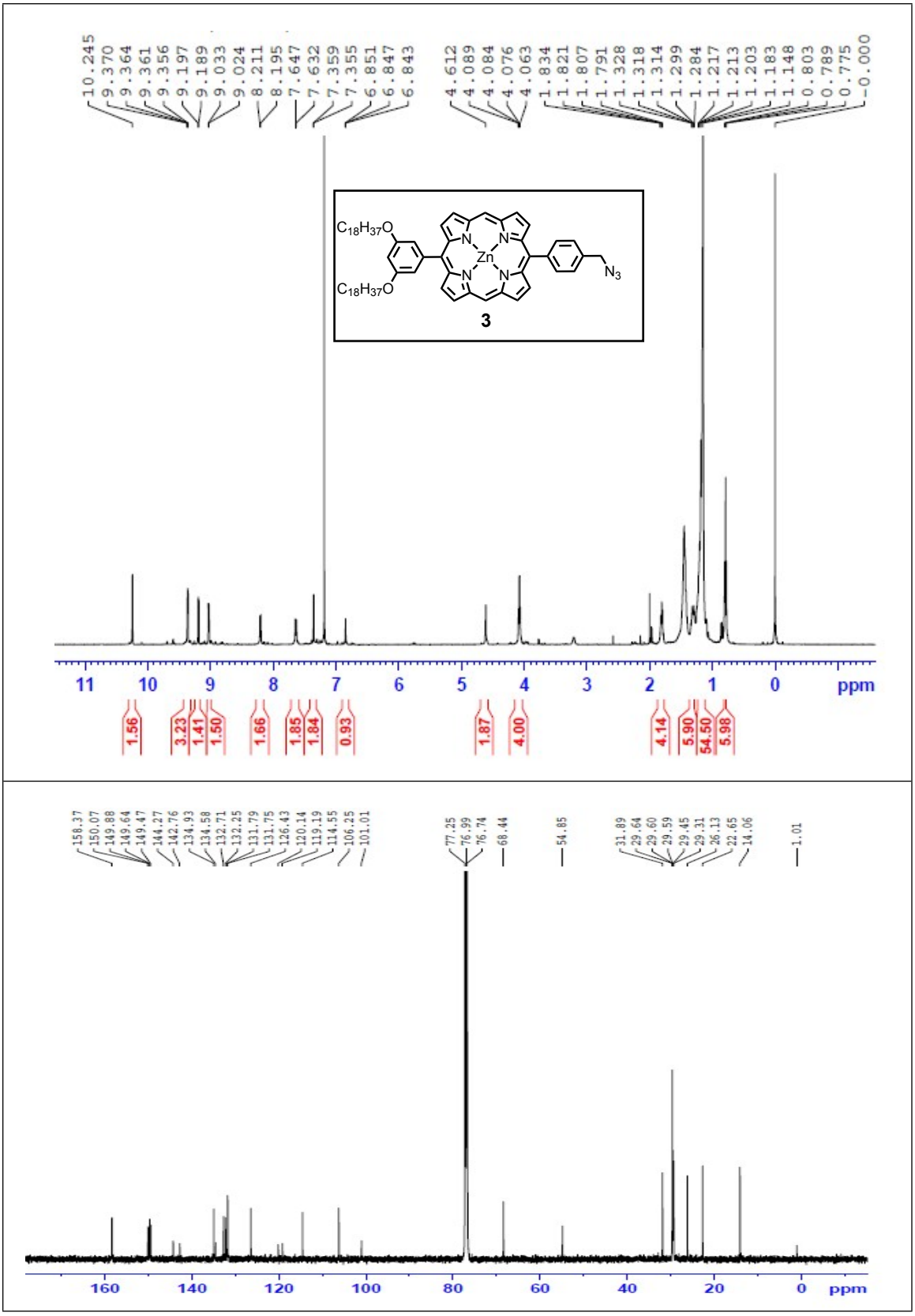


Figure S15: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **3**.

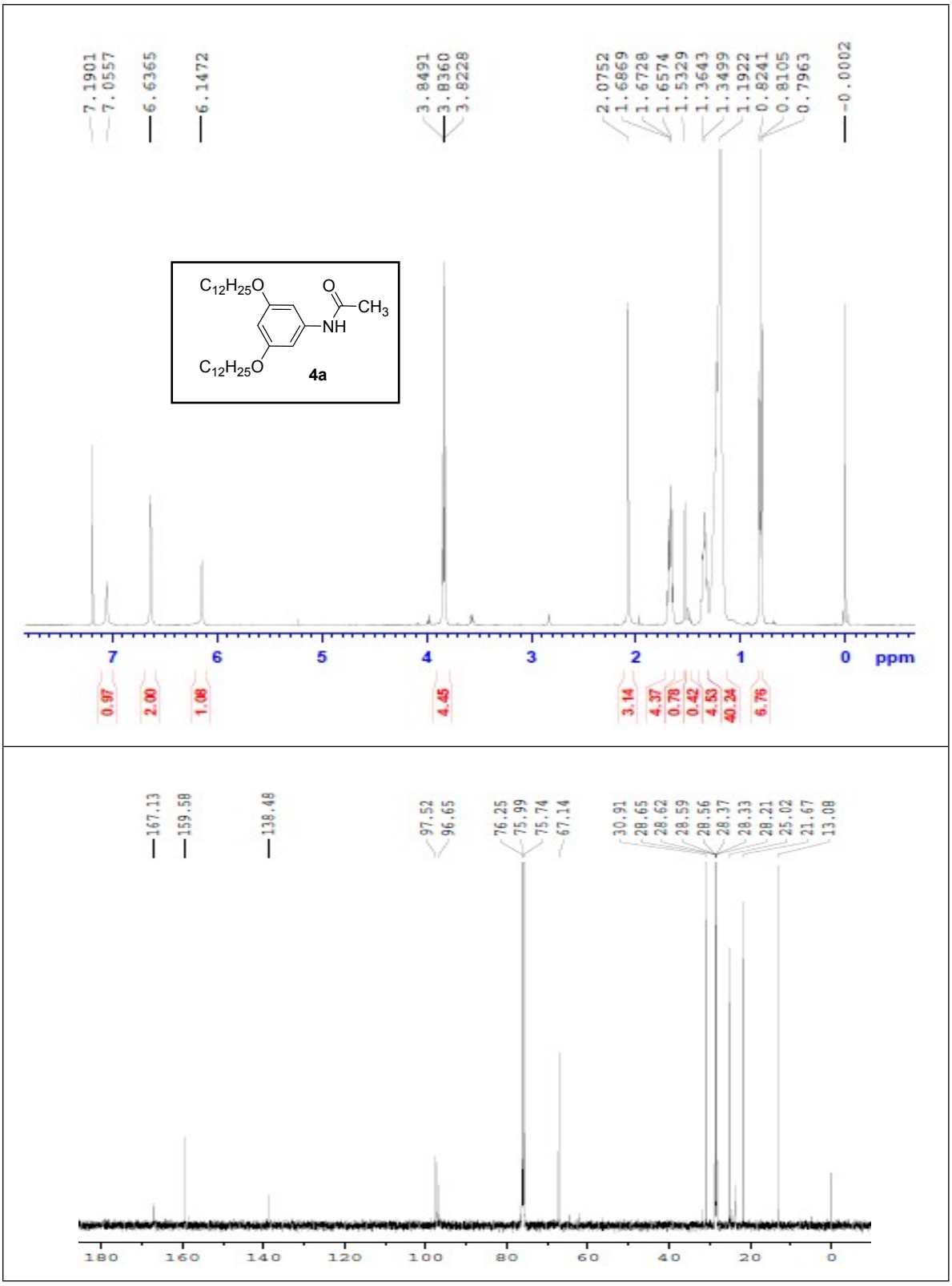


Figure S16: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **4a.**

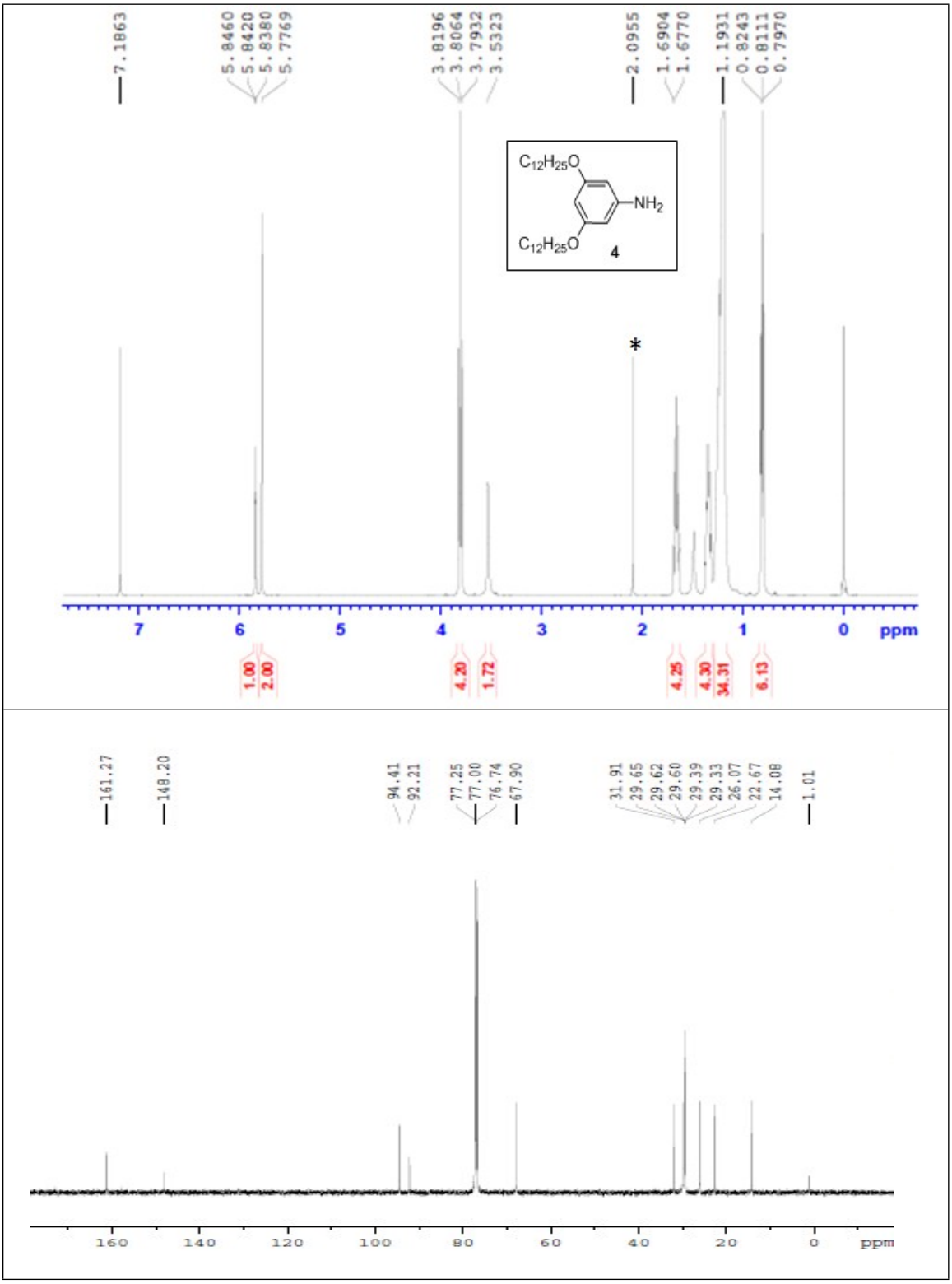


Figure S17: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **4.**

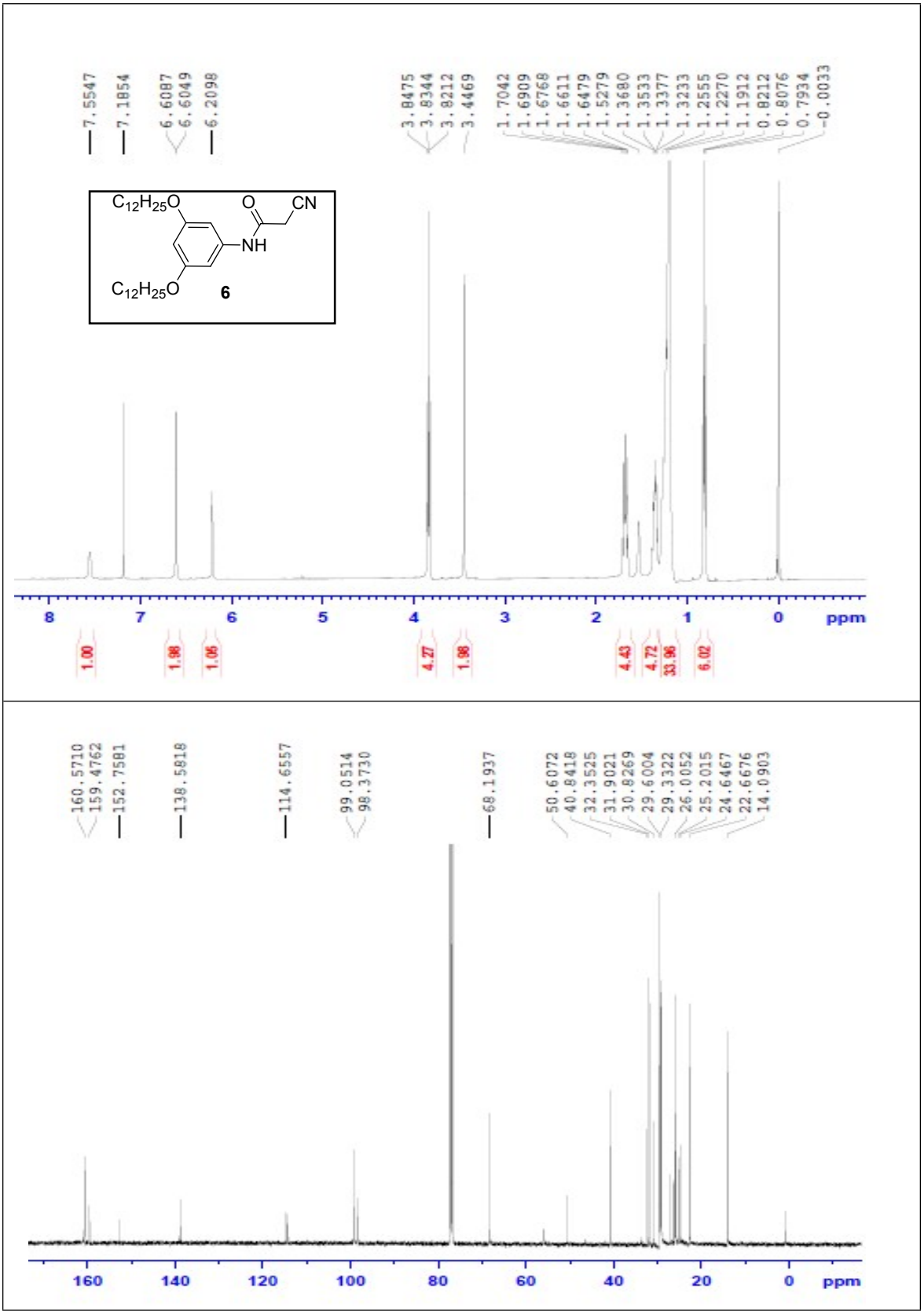


Figure S18: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **6.**

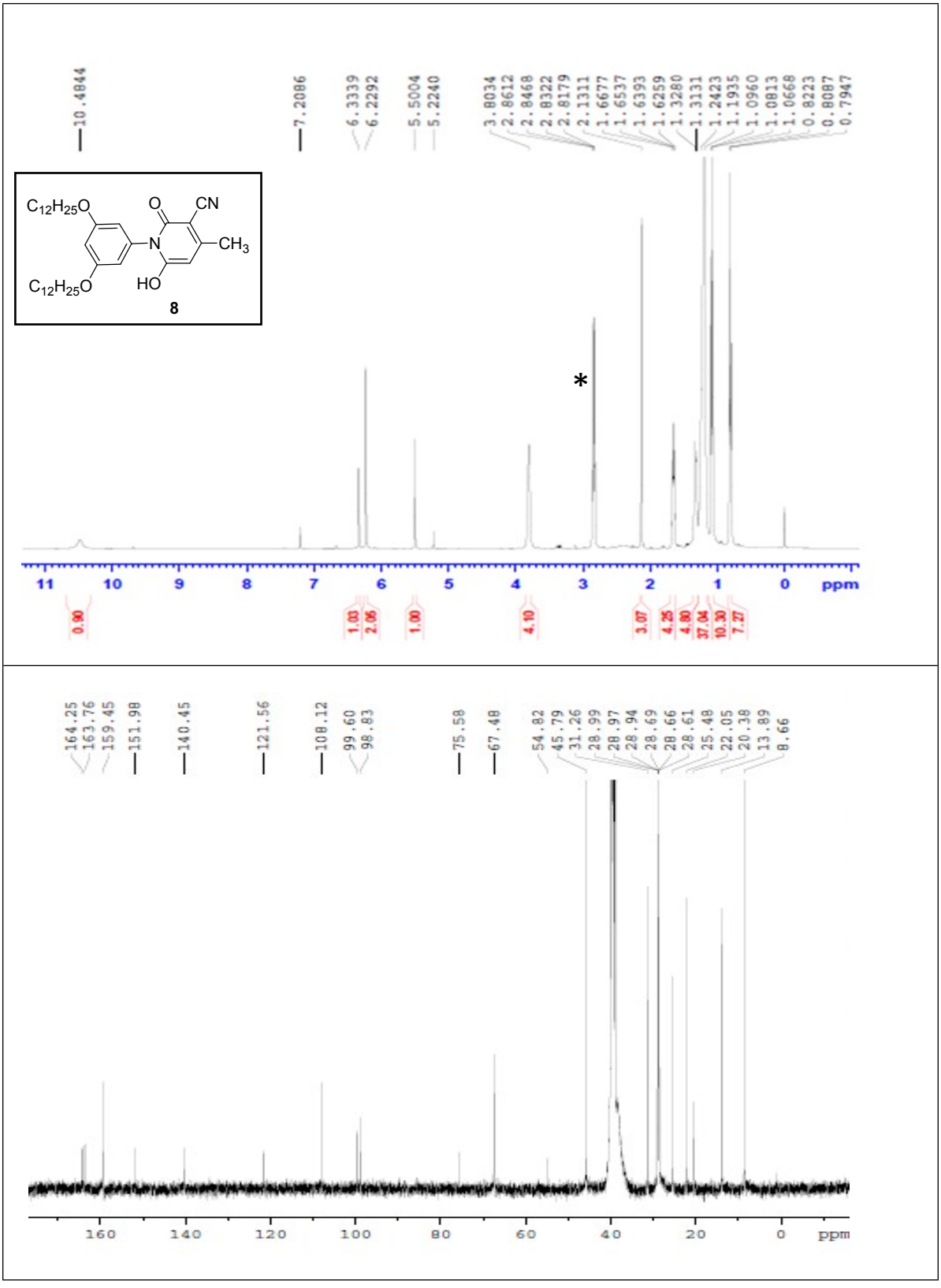


Figure S19: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **8.**

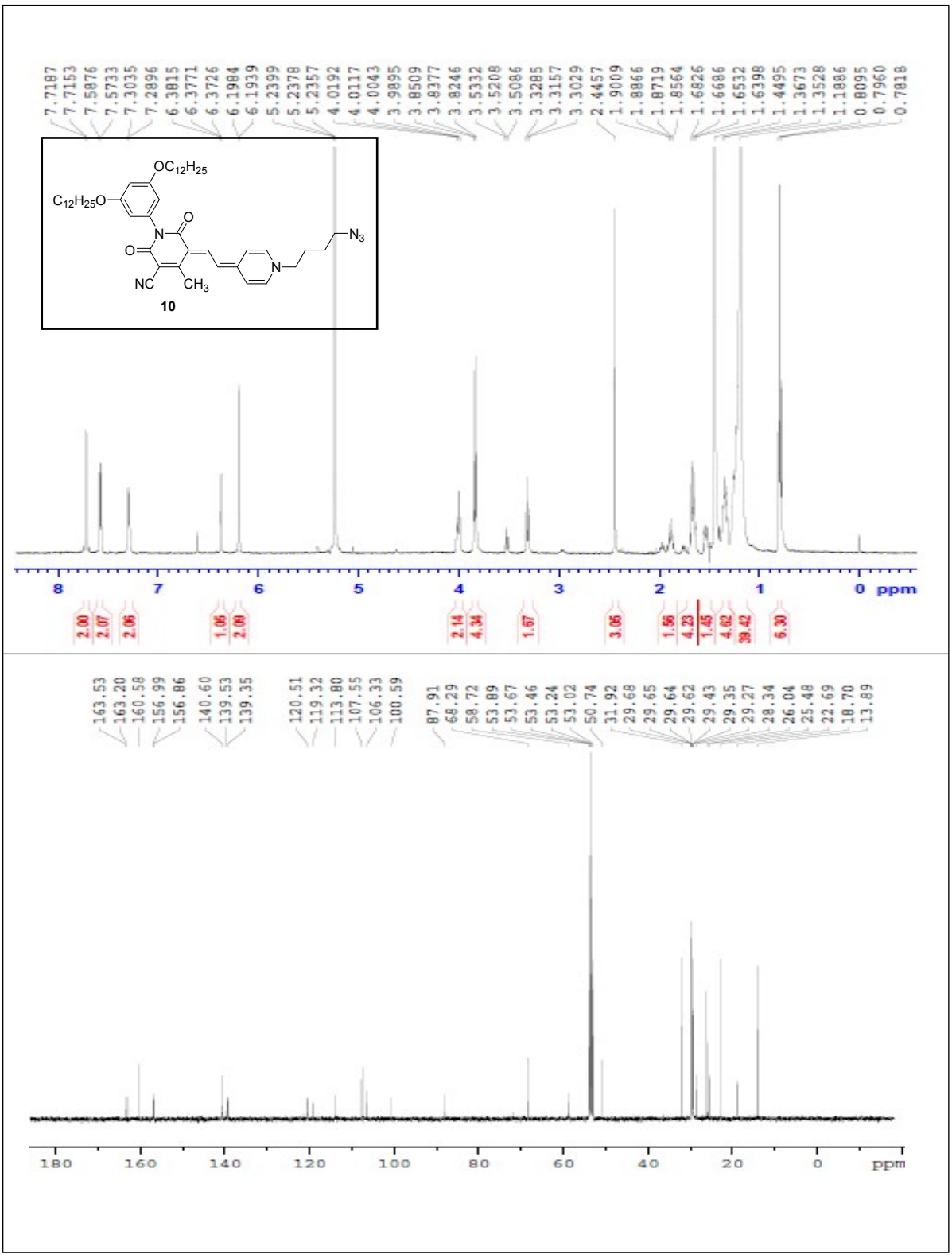


Figure S20: ^{1}H (top) and ^{13}C-NMR (bottom) spectra of **10.**

References:

S1. A. J. F. N. Sobral, N. G. C. L. Rebanda, M. da Silva, S. H. Lampreia, M. R. Silva, A. M. Beja, J. A. Paixao and A. M. d. A. Rocha Gonsalves, *Tetrahedron Lett*., 2003, **44**, 3971-3973.

S2. Majher I. Sarker, T. Shashrin, Mark G. Steinmetz and Quadir K. Timerghazin, *Photochem. Photobiol. Sci.,* 2013, **12**, 309-322.

S3. D. Kim, J. Heo, S. Ham, H. Yoo, C. H. Lee, H. Yoon, D. Ryu, D. Kim, and W. D. Jang, *Chem. Comm.*, 2011, **47**, 2405-2407.