Supplementary Information

for

Unsymmetrically Functionalized Benzoporphyrins

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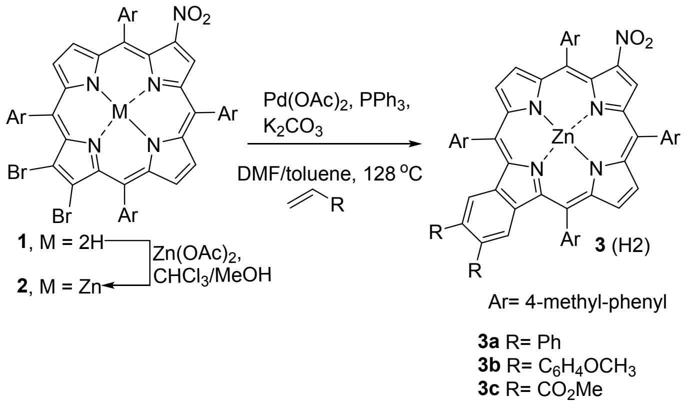
I. General

All solvents were Analytical Reagent grade obtained either from Sigma-Aldrich or ACROS and used without further purification unless otherwise noted. Analytical TLC's were performed on Silicycle UltraPure Silica Gel 60 F254 TLC plates. Preparative column chromatography was performed on silica gel (40–60 □m), which was purchased from Silicycle.

^{1}H and ^{13}C NMR experiments were conducted on a Bruker Avance 500 spectrometer. All samples were prepared in $CDCl_3$ or C_6D_6 and chemical shifts were referenced to $CHCl_3$ at 7.26 ppm, to C_6H_6 at 7.15 for ^{1}H NMR and referenced to the $CDCl_3$ at 77.0 ppm, to C_6D_6 at 128.6 for ^{13}C NMR. Mass spectra were obtained on Bruker MALDI-TOF mass spectrometer. UV-Visible spectra were recorded on an Agilent 8453 UV-Visible spectrometer in CH_2Cl_2 or $CHCl_3$.

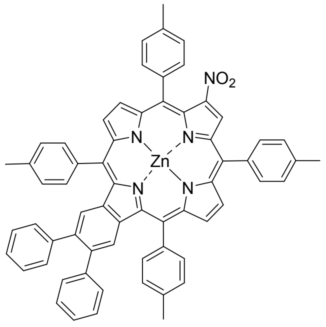
II. Synthetic Procedures

General procedure for the synthesis of substituted monobenzoporphyrins 3

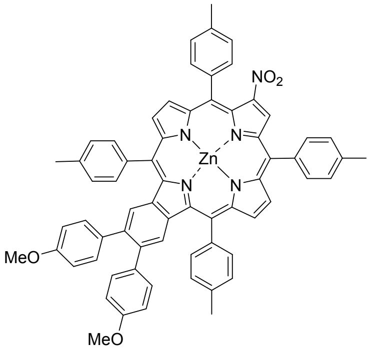


Zinc inserted dibromoporphyrin **2** was prepared according to published procedures.[1] Substituted monobenzoporphyrin **3** was synthesized based on a concise and versatile method developed in our laboratory for the synthesis of benzoporphyrins. [2,3]

Dibromoarylporphyrin **2** (0.045 mmol), palladium acetate (0.011 mmol), triphenylphosphine (0.030 mmol) and K_2CO_3 (0.10 mmol) were added to a schlenk tube and dried under vacuum. The vacuum was released under argon to allow the addition of dry DMF (10 mL) and dry Toluene (10 mL) and vinyl precursor (20-fold excess). The mixture was then degassed via four freeze-pump-thaw cycles before the vessel was purged with argon again. The schlenk flask was sealed and heated to reflux for 48h. After 48 h, the mixture was diluted with EtOAc and washed with water for 3 times. The organic layer was removed under vacuum. The residue was subjected to silica column chromatography. The bands containing the desired porphyrins were collected and recrystallized from $CHCl_3$/MeOH.

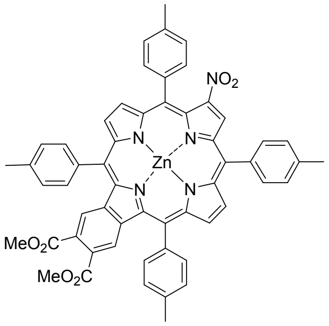


3a: Yield (65%). mp > 320 °C. UV-Vis λ_{max} ($CHCl_3$)/nm 454 (log ε = 5.29), 575 (4.27), 621 (3.89); ^{1}H NMR (500 MHz, $CDCl_3$) □ 9.01 (1 H, br. s), 8.93 (2 H, m), 8.82 (2 H, br. s.), 8.05 (8 H, m), 7.55 (10 H, m), 7.23 (4 H, d, *J*=6.41 Hz), 7.08 - 7.18 (6 H, m), 2.63 - 2.81 (12 H, m). Calculated Mass, 979.286, Found MS (MALDI-TOF), m/z 980.856 (M+H). Due to low solubility of the compound **3.2** demetalation was done to obtain the ^{13}C NMR. Dematalated compound ^{1}H NMR (500 MHz, $CDCl_3$) □ 9.00 (1 H, s), 8.97 (1 H, d, *J*=4.89 Hz), 8.93 (1 H, d, *J*=4.89 Hz), 8.81 - 8.87 (2 H, m), 8.05 - 8.22 (8 H, m), 7.52 - 7.67 (8 H, m), 7.23 - 7.28 (6 H, m), 7.07 - 7.13 (4 H, m), 7.05 (2 H, m), 2.67 - 2.76 (12 H, m), -2.25 (2 H, m). ^{13}C NMR (126 MHz, $CDCl_3$) □ 152.25, 145.68, 142.38, 141.73, 141.46, 141.34, 139.26, 138.82, 138.77, 138.62, 138.37, 138.29, 138.09, 137.67, 137.15, 135.30, 134.78, 133.67, 133.40, 131.22, 130.16, 129.76, 129.19, 128.82, 128.31, 128.05, 127.83, 127.75, 127.67, 127.48, 126.44, 124.17, 120.95, 117.67, 117.28, 26.94, 21.65, 21.55.



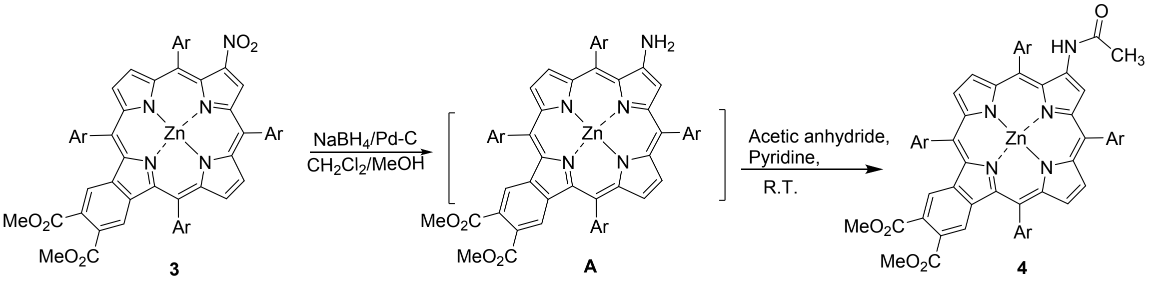
3b: Yield (42%). mp > 320 °C. UV-Vis λ_{max} ($CHCl_3$)/nm 456 (log ε = 5.33), 576 (4.34), 621 (3.99); ^{1}H NMR (500 MHz, $CDCl_3$) □ 9.09 (1 H, s), 8.94 (1 H, d, *J*=4.58 Hz), 8.90 (1 H, d, *J*=4.58 Hz), 8.81 (2 H, m), 8.08 (4 H, d, *J*=7.79 Hz), 8.03 (4 H, d, *J*=7.79 Hz), 7.63 (4 H, d, *J*=7.79 Hz), 7.58 (2 H, d, *J*=7.79 Hz), 7.51 (2 H, d, *J*=7.79 Hz), 7.16 - 7.23 (2 H, m), 7.06 (4 H, d, *J*=8.25

Hz), 6.83 (4 H, d, *J*=8.25 Hz), 3.87 (6 H, s), 2.66 - 2.79 (12 H, m). ^{13}C NMR (126 MHz, $CDCl_3$) □ 158.34, 153.89, 150.13, 149.90, 148.73, 148.65, 148.17, 141.93, 140.00, 139.26, 139.20, 138.71, 138.43, 138.36, 138.21, 138.16, 137.92, 137.84, 137.57, 134.59, 134.33, 134.20, 133.92, 133.16, 133.11, 133.04, 131.53, 131.27, 128.72, 127.70, 127.62, 127.58, 124.91, 122.01, 118.01, 117.73, 113.31, 55.25, 21.63, 21.60, 21.52; Calculated Mass, 1039.307, Found MS (MALDI-TOF), m/z 1040.972 (M+H).



3c: Yield (60%). mp > 320 °C. UV-Vis λmax (CH_2Cl_2)/nm 446 (log ε = 5.59), 569 (4.81), 625 (4.74); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05-8.73 (5 H, m), 8.01-7.93 (8 H, m), 7.60-7.44 (8 H, m), 7.39 (2 H, s), 3.77 (6 H, m), 2.74-2.63 (12 H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.61, 29,71, 52.44, 118.08, 118.53, 121.28, 124.42, 125.88, 127.90, 128.75, 129.31, 129.62, 129.89, 131.58, 133.87, 134.88, 135.39, 137.69, 138.33, 138.86, 139.20, 141.26, 142.98, 143.15, 146.35, 150.58, 150.98, 152.77, 168.06; Calculated Mass, 943.235, Found MS (MALDI-TOF), m/z 898.014 (M-NO_2).

General procedure for the synthesis of porphyrin 4

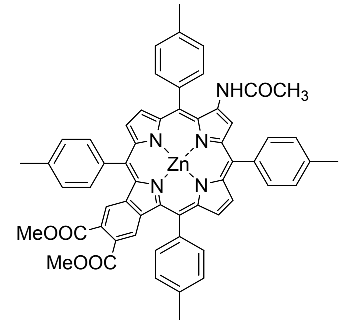


i. General procedure for the synthesis of 2-aminoporphyrin A

This procedure was based upon the literature protocol for similar compound. In a two-neck round-bottom flask porphyrin **3** (50 mg, 0.053 mmol), dry dichloromethane (12 mL), and dry methanol (12 mL) was taken. Palladium (10% on carbon, 44 mg) was added to the solution and the solution was purged with argon and stirred at room temperature for 1 h, and then placed into the ice-bath. Over a 10 min period Sodium borohydride (48 mg, 1.28 mmol) was added to the solution in small portions. Progress of the reaction was monitored by UV-Visble spectroscopy, which shows shift in a soret band at 442 nm and also by TLC using DCM/Cyclohexane (1:1) as eluent. Complete consumption of starting material was observed after 1.2 h of the reaction. Solvent was removed by using rotary evaporator, and the residue was passed through a plug of Celite using dichloromethane as eluent in the dark. The crude product was concentrated in vacuum, and was directly used for the next reaction without further purification due to the unstability against photo-oxidation.

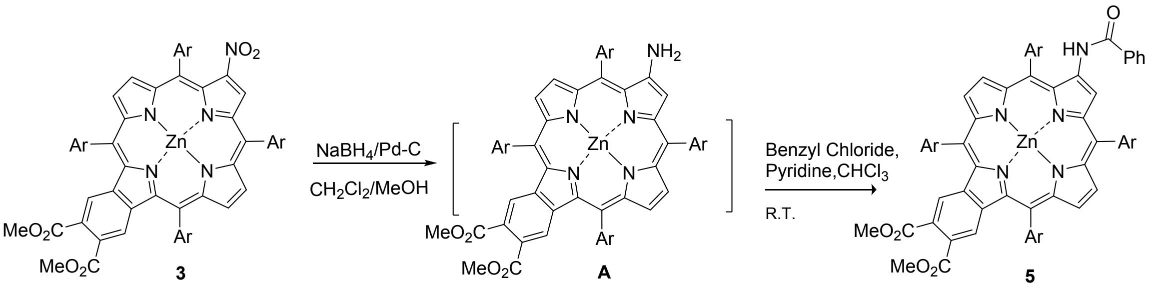
ii. General procedure for acetylation of porphyrin 4

This procedure was based upon the literature protocol for similar compound. Pyridine (0.4 mL) and acetic anhydride (4 mL) was added to Porphyrin **A** (40 mg, 0.044 mmol). Solution was stirred overnight at room temperature. The reaction mass was poured into water and stirred for another 15 minutes and was extracted with chloroform. TLC was carried out using DCM/cyclohexane (20:1) as eluent which shows formation Porphyrin **4** which were separated by column chromatography.

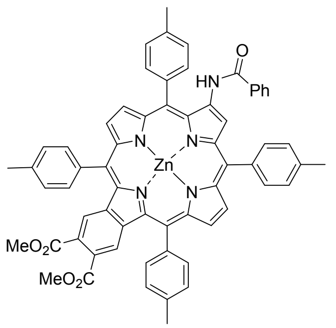


4: Yield **(**66%). UV-Vis λ_{max} (CH_2Cl_2)/nm 441 (log ε = 5.89), 566 (5.04), 607 (4.82); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.25 (1 H, s), 8.88-8.66 (5 H, m), 8.01-7.97 (8 H, m), 7.66-7.47 (10 H, m), 3.90 (6 H, s), 2.76-2.66 (12 H, m), 1.73 (3 H, s), ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.45, 21.59, 29.68, 52.43, 114.19, 118.42, 118.53, 119.16, 119.77, 121.96, 122.36, 126.28, 127.90, 128.75, 129.31, 129.62, 129.89, 131.58, 133.87, 134.88, 135.39, 137.69, 138.33, 138.86, 139.20, 141.26, 142.98, 143.15, 146.35,149.39, 149.47, 150.06, 150.59, 151.39, 167.06, 168.06 Calculated Mass, 955.103, Found MS (MALDI-TOF), m/z 955.216.

General procedure for the synthesis of porphyrin 5

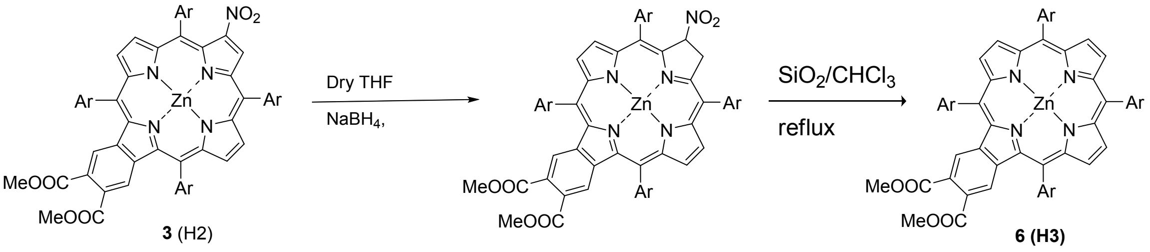


Porphyrin **A** (40 mg, 0.044 mmol) was dissolved in chloroform (10ml) and pyridine (0.016 mL) and benzoyl chloride (0.010 mL) was added to it. Solution was stirred for 8 hours at room temperature. The reaction mass was poured into water and stirred for another 15 minutes and was extracted with chloroform. TLC was carried out using DCM/Cyclohexane (15:1) which shows new spot. Using short plug of silica porphyrin **5** was collected.



5: Yield (33%). mp > 320 °C. UV-Vis λ_{max} (CH_2Cl_2)/nm 444 (log ε 6.30), 569 (5.22), 608 (4.77); ^{1}H NMR (500 MHz, C_6D_6) δ 10.47 (1 H, s), 9.08 (2 H, d, *J* = 5.0 Hz), 9.07 (2 H, dd, *J* = 5.0, 12.0 Hz), 8.68 (1 H, d, *J* = 5.0 Hz), 8.31 (2 H, d, *J* = 7.5 Hz), 8.09-8.06 (4 H, m), 8.00 (2 H, d, *J* = 12.5 Hz), 7.93 (2 H, d, *J* = 7.5 Hz), 7.55 (2 H, d, *J* = 7.5 Hz), 7.47-7.44 (4 H, m), 7.40 (2 H, d, *J* = 7.5 Hz), 7.15-7.11 (5 H, m), 3.65 (6H, s), 2.57 (3H, s), 2.56 (3H, s), 2.42 (3H, s), 2.28 (3H, s). ^{13}C NMR (126 MHz, $CDCl_3$) □ ppm 21.63, 21.66, 52.54, 117.34, 117.67, 118.73, 120.25, 121.20, 121.36, 125.81, 127.02, 127.79, 128.03, 128.39, 128.53, 128.58, 128.95, 129.01, 129.59, 131.70, 133.58, 133.62, 133.70, 134.40, 134.48, 137.36, 137.68, 138.54, 138.76, 139.04, 139.08, 139.68, 140.93, 142.83, 142.94, 164.60, 168.48, 168.53. Calculated Mass, 1017.287, Found MS (MALDI-TOF), m/z 1017.181.

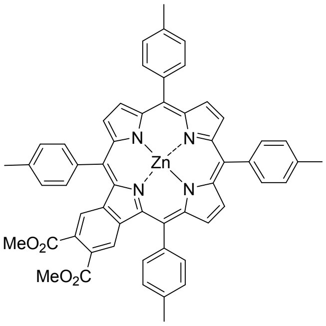
General procedure for the synthesis of porphyrin 6



Denitration of porphyrin **3** was carried out using literature reported procedure by Smith et al.[1] Porphyrin **3** (50 mg, 0.053 mmol) and $NaBH_4$, (4 mg, 0.106 mmol) was added to a cold solution (ice/NaCl) of dried THF (10 mL) under argon. The resulting reaction mixture was stirred for 2 h but the ice bath was removed after one hour. Progress of the reaction was monitored by UV-Visble spectroscopy, which shows shift in a soret band from 448 to 441 nm. Dichloromethane (100 mL) was then added to the reaction mixture and solution was poured into water. The organic phase was collected and evaporated to dryness. The residue was redissolved in dichloromethane and passed through a short alumina plug. Solvent was evaporated and crude product was used for the next step.

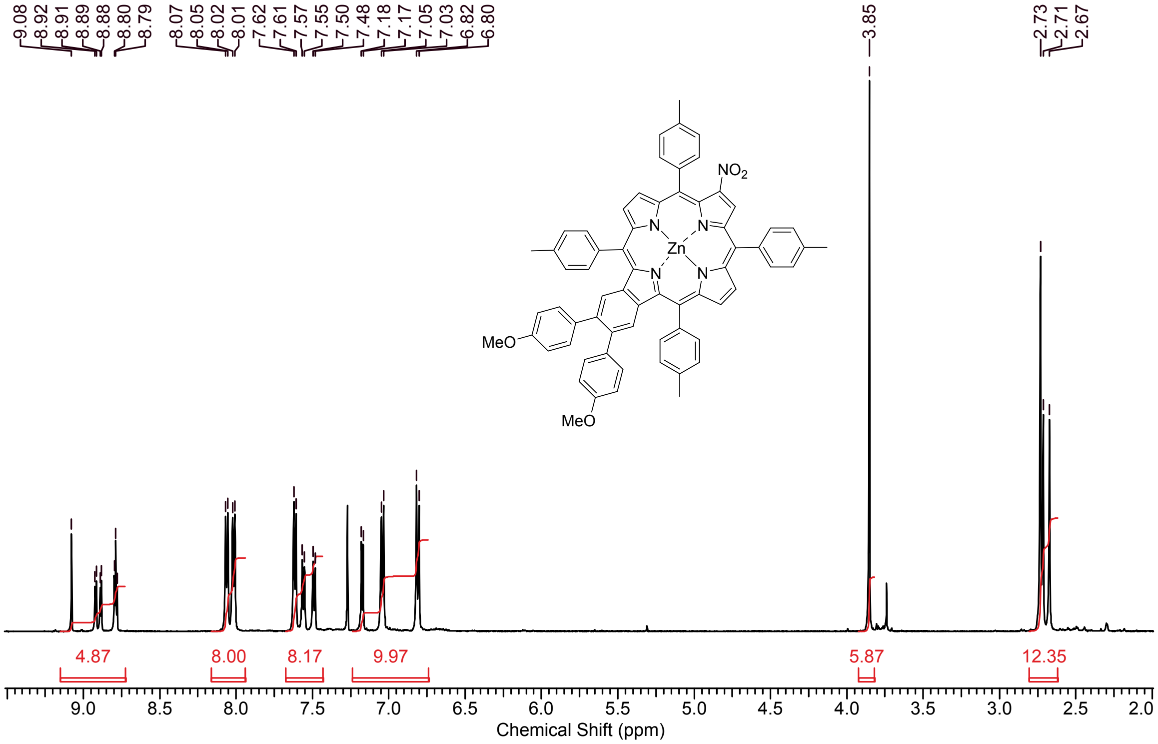
Crude product was dissolved in chloroform (40 mL) and silica gel (2 g) was added to it, the reaction mixture was refluxed for 1 d under argon. The reaction mixture was cooled to room temperature and filtered to remove silica gel and washed thoroughly with dichloromethane. Solvent was evaporated and TLC was carried out using DCM as eluent shows formation of a new spot which was purified by column chromatography.

6: Yield (33%). mp > 320 °C. UV-Vis λ_{max} (CH_2Cl_2)/nm 437 (log ε = 5.62), 562 (4.74), 626 (4.59); ^1H NMR (500 MHz, $CDCl_3$) δ 8.93-8.86 (6 H, m), 8.07-7.99 (8 H, m), 7.64-7.52 (10 H, m), 3.90 (6H, s), 2.77 (12 H, m), ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.65, 29.72, 52.49, 118.48, 122.81, 126.39, 127.36, 128.40, 131.37, 131.68, 132.19, 133.17, 134.24, 137.25, 138.15, 139.61, 139.88, 140.82, 144.48, 149.38, 150.20, 151.60, 168.45; Calculated Mass, 898.182, Found MS (MALDI-TOF), m/z 898.141.

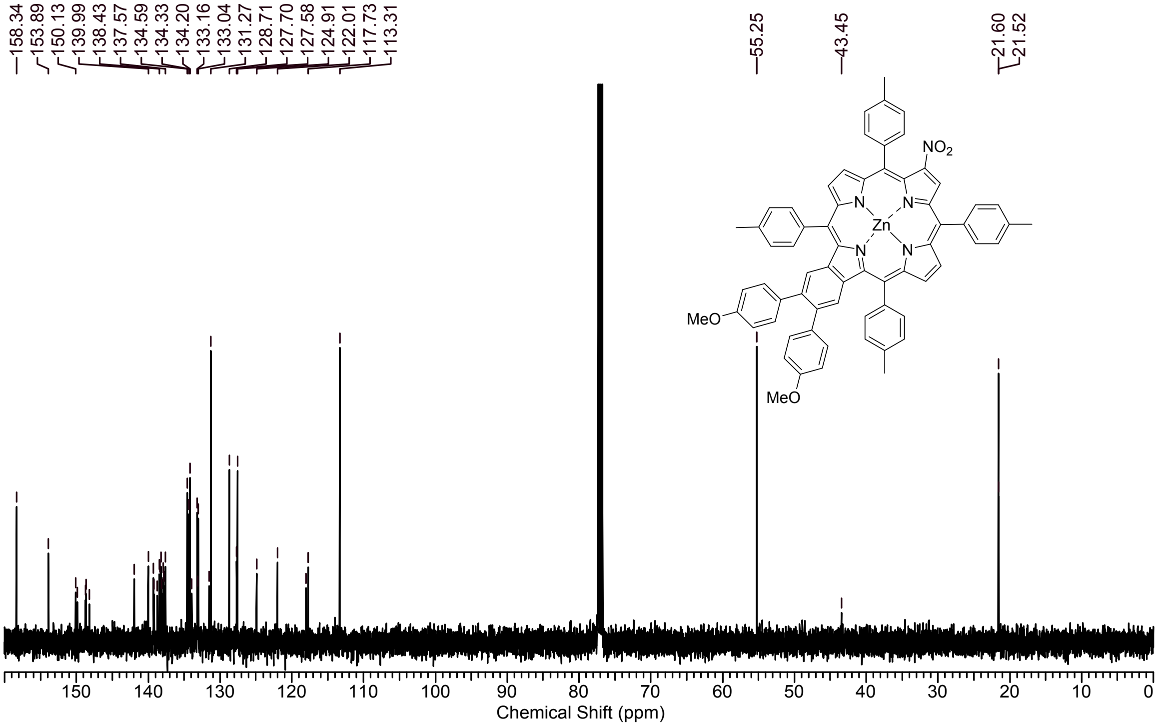


III Spectroscopic data

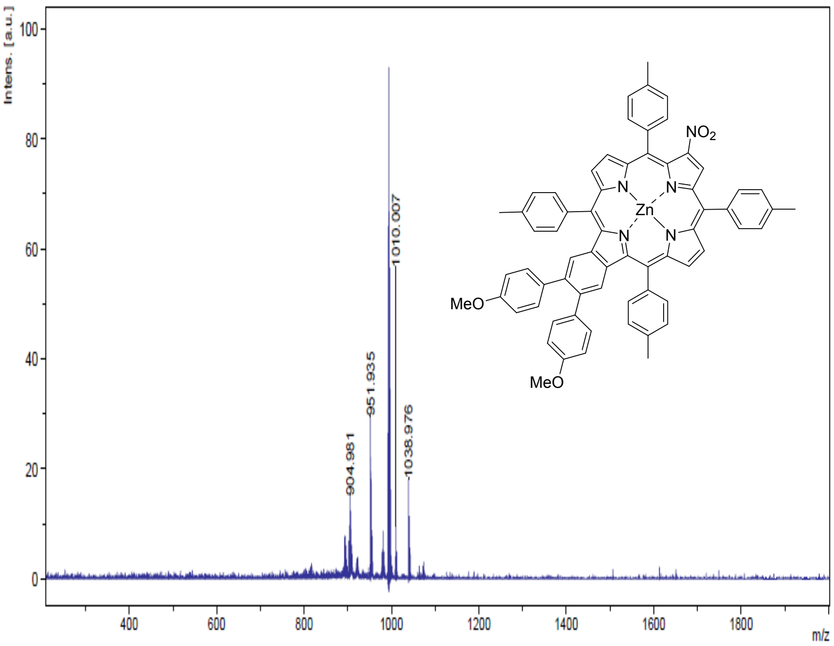
^{1}H NMR spectrum of **3b** in $CDCl_3$ at 500 MHz

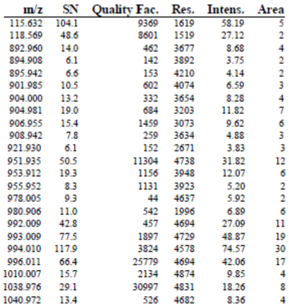


^{13}C NMR spectrum of **3b** in $CDCl_3$ at 126 MHz



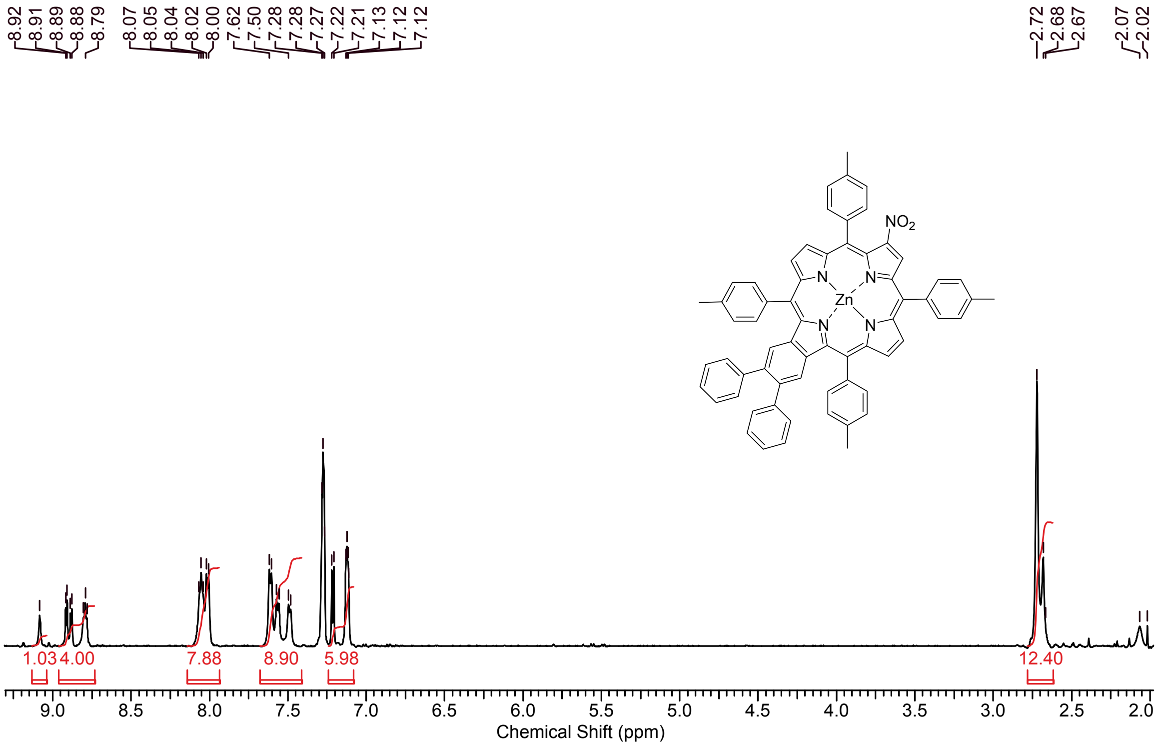
MALDI-TOF spectra for compound **3b**



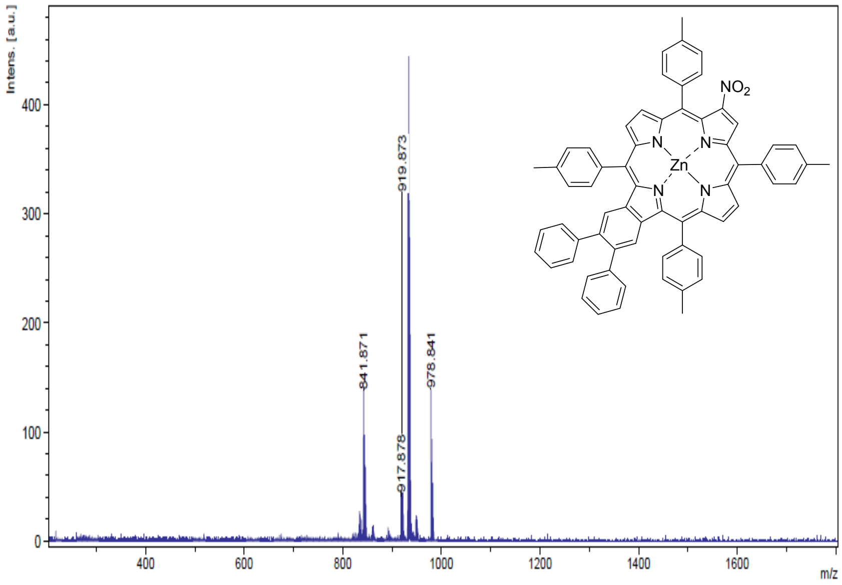


m/z	SN	Quality Fac.	Res.	Intens.	Area
115.632	104.1	9369	1619	58.19	5
118.569	48.6	8601	1519	27.12	2
892.960	14.0	462	3677	8.68	4
894.908	6.1	142	3892	3.75	2
895.942	6.6	153	4210	4.14	2
901.985	10.5	602	4074	6.59	3
904.000	13.2	332	3654	8.28	4
904.981	19.0	684	3203	11.82	7
906.955	15.4	1459	3073	9.62	6
908.942	7.8	259	3634	4.88	3
921.930	6.1	152	2671	3.83	3
951.935	50.5	11304	4738	31.82	12
953.912	19.3	1156	3948	12.07	6
955.952	8.3	1131	3923	5.20	2
978.005	9.3	44	4637	5.92	2
980.906	11.0	542	1996	6.89	6
992.009	42.8	457	4694	27.09	11
993.009	77.5	1897	4729	48.87	19
994.010	117.9	3824	4578	74.57	30
996.011	66.4	25779	4694	42.06	17
1010.007	15.7	2134	4874	9.85	4
1038.976	29.1	30997	4831	18.26	8
1040.972	13.4	526	4682	8.36	4

^{1}H NMR spectrum of **3a** in CDCl$_3$ at 500 MHz



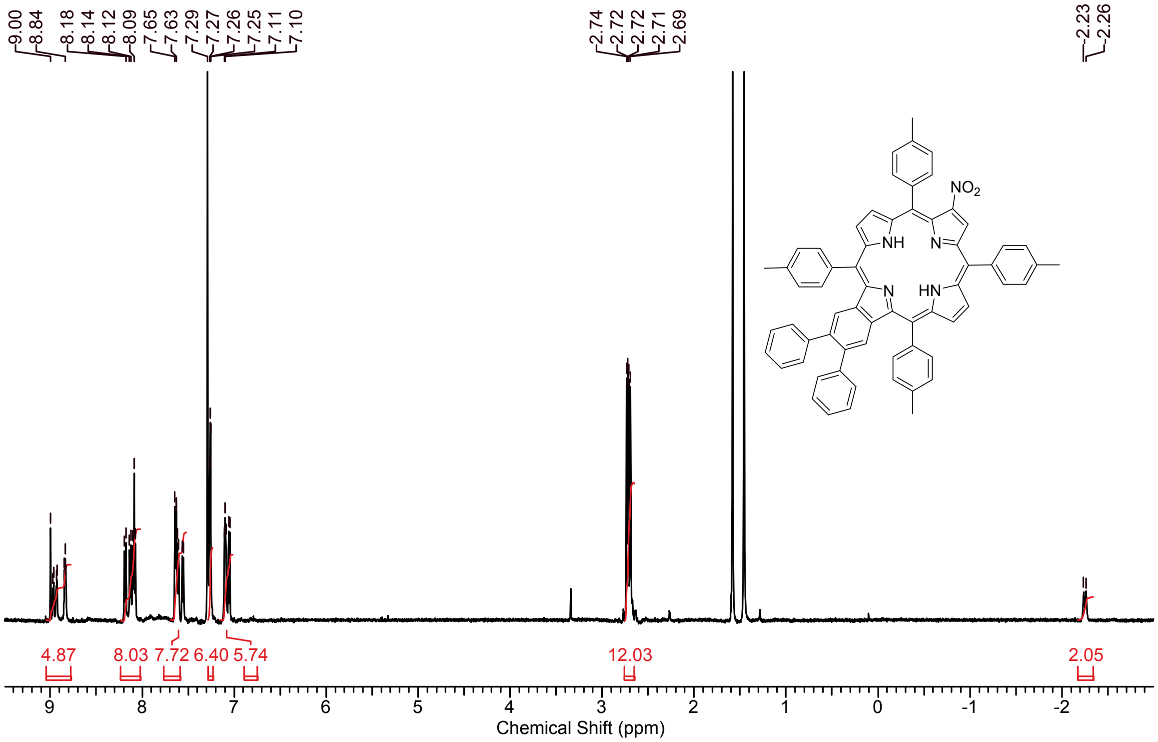
MALDI-TOF spectra for compound **3a**



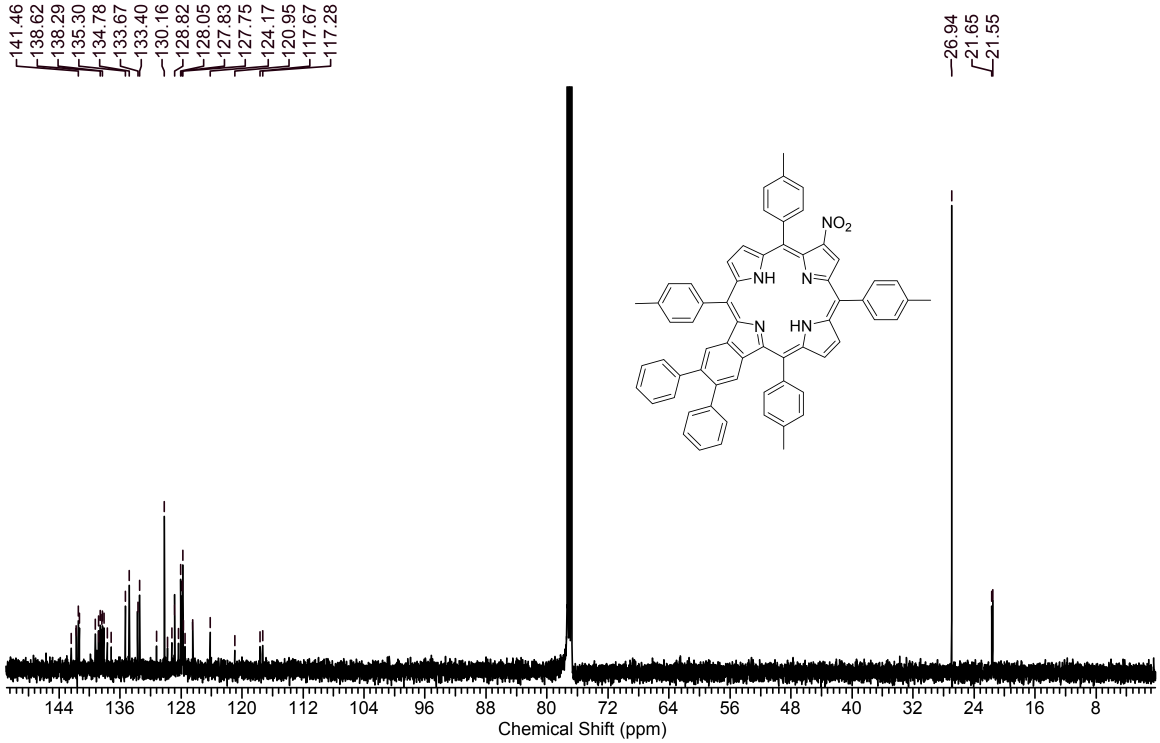
m/z	SN	Quality Fac.	Res.	Intens.	Area
833.857	7.0	52	5571	33.31	9
841.871	28.2	2063	6009	137.00	34
843.872	17.8	594	6265	85.45	21
845.877	11.4	493	6979	55.02	11
917.878	8.7	167	6028	43.49	12
919.873	8.5	135	5348	42.30	13
921.880	7.3	340	6090	36.55	10
931.894	62.4	6026	5417	315.10	103
932.897	35.1	2125	4901	175.40	63
933.886	49.5	1207	3978	248.80	114
934.894	23.4	1654	5375	118.01	38
935.908	33.1	5830	5946	168.64	50
936.895	13.0	270	9758	67.64	12
978.841	26.4	8437	5162	132.21	49
980.856	14.0	770	4765	69.92	27
982.844	6.6	444	5635	32.86	11

^{1}H NMR spectrum of demetalated **3a** in CDCl$_3$ at 500 MHz

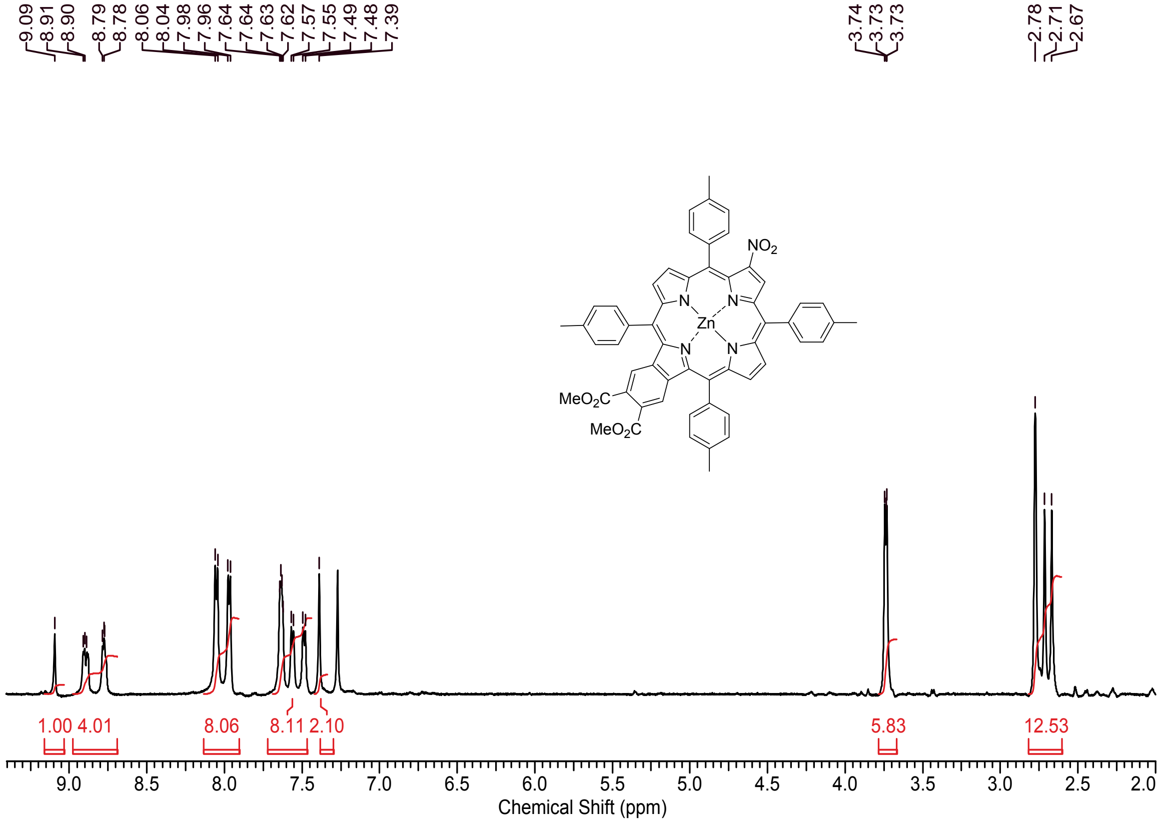
Demetalation of 3a was done to obtain better NMR spectra



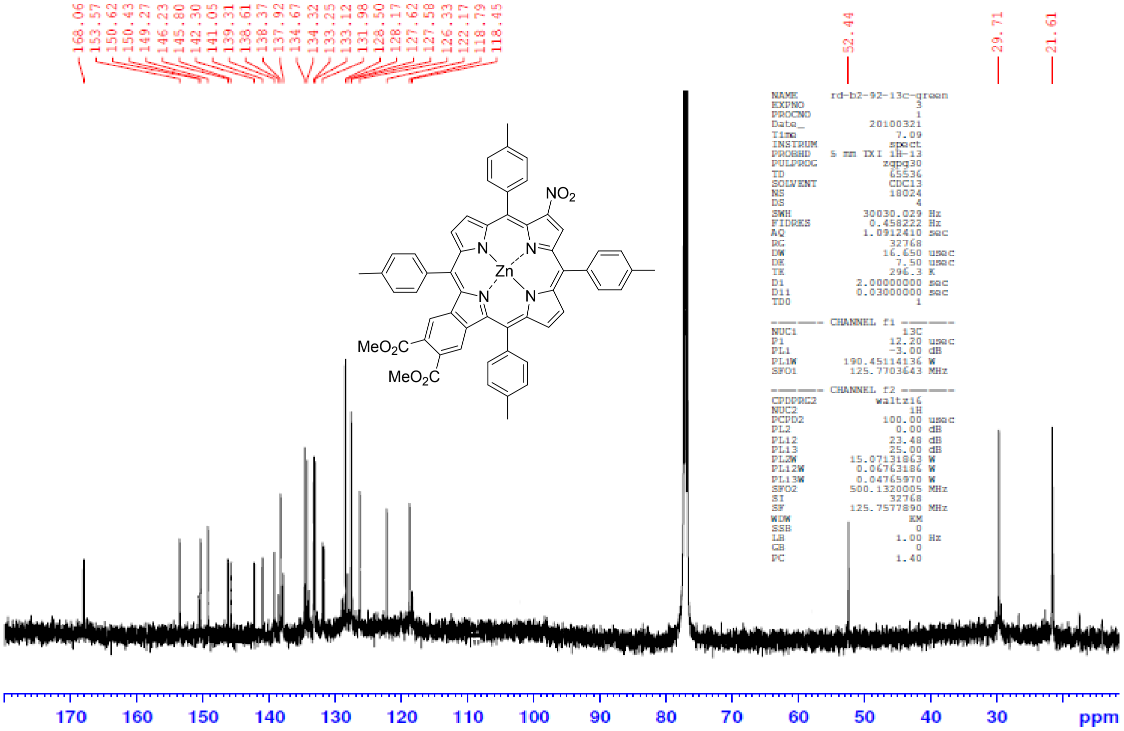
^{13}C NMR spectrum of demetalated **3a** in CDCl$_3$ at 126 MHz



^{1}H NMR spectrum of **3c** in CDCl$_3$ at 500 MHz



^{13}C NMR spectrum of **3c** in CDCl$_3$ at 126 MHz



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PROCNO                       1
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Time                      7.09
INSTRUM                  spect
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PULPROG                zgpg30
TD                       65536
SOLVENT                  CDC13
NS                       18024
DS                           4
SWH                  30030.029 Hz
FIDRES                0.458222 Hz
AQ                   1.0912410 sec
RG                       32768
DW                      16.650 usec
DE                        7.50 usec
TE                       296.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                       12.20 usec
PL1                      -3.00 dB
PL1W              190.45114136 W
SFO1               125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                   100.00 usec
PL2                       0.00 dB
PL12                     23.48 dB
PL13                     25.00 dB
PL2W               15.07131863 W
PL12W               0.06763186 W
PL13W               0.04765970 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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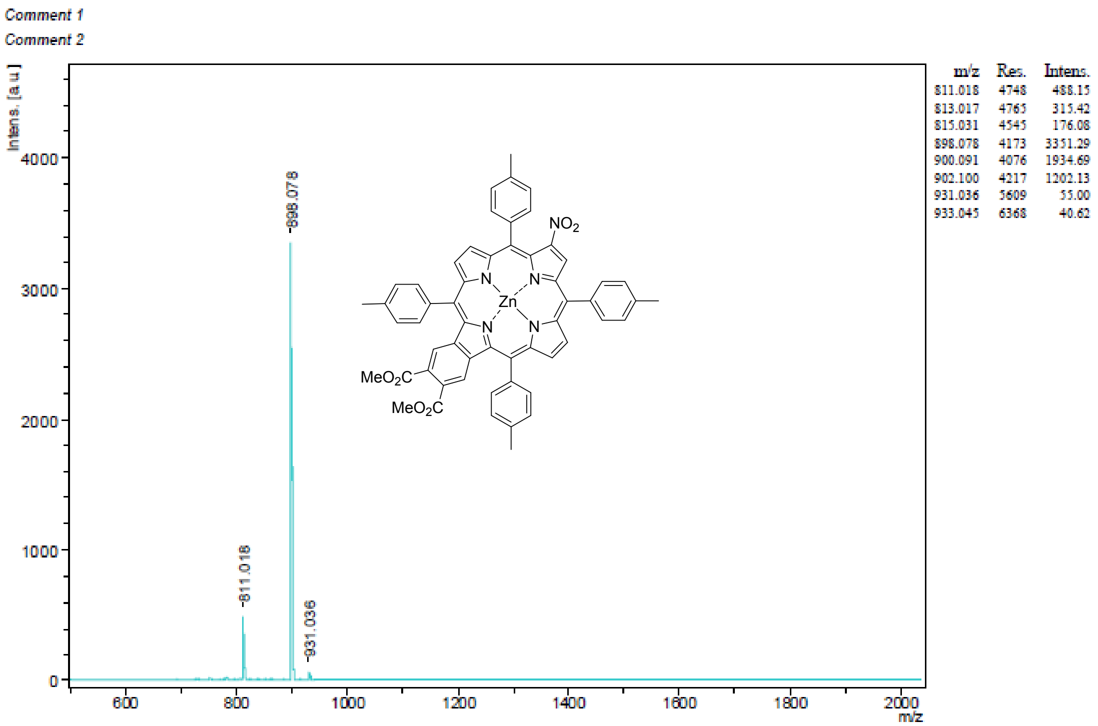
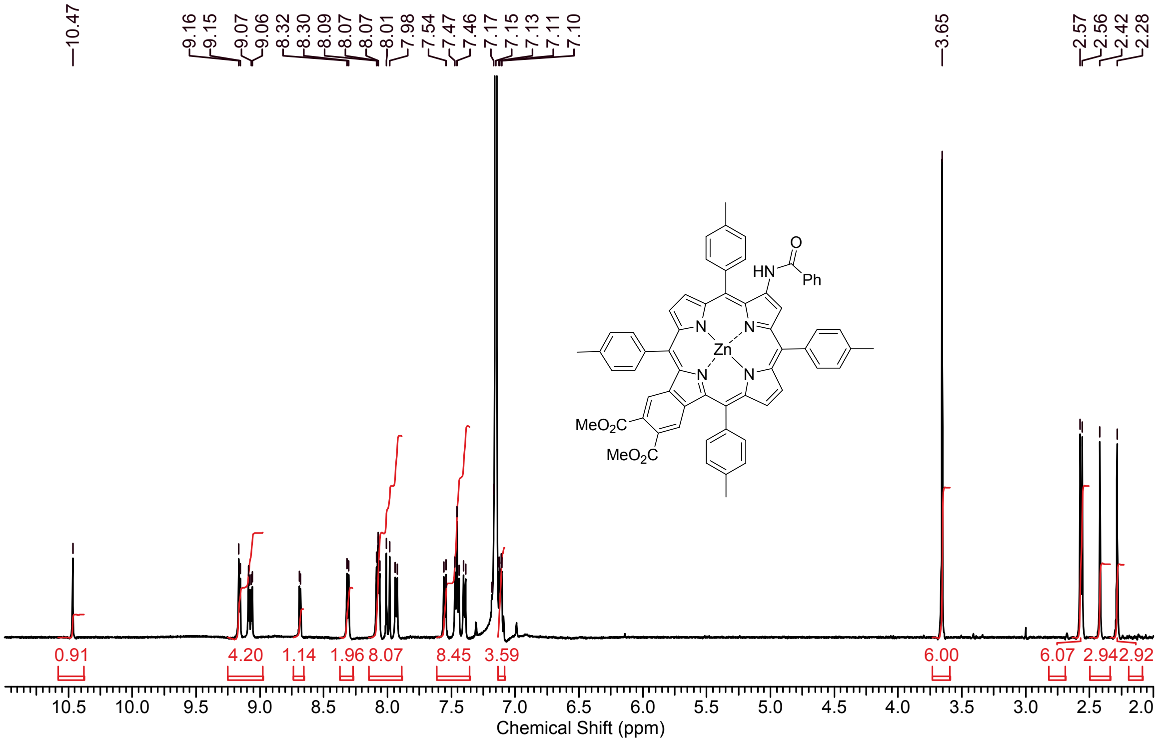
MALDI-TOF spectra for compound **3c**

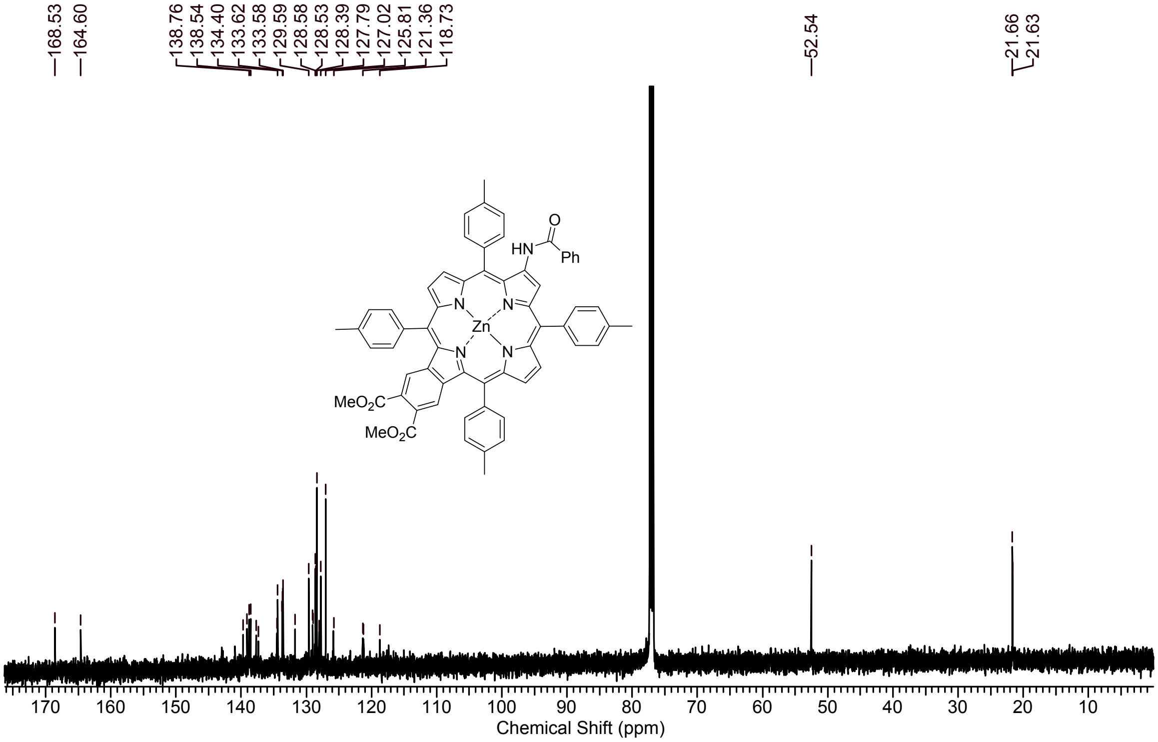


m/z	Res.	Intens.
811.018	4748	488.15
813.017	4765	315.42
815.031	4545	176.08
898.078	4173	3351.29
900.091	4076	1934.69
902.100	4217	1202.13
931.036	5609	55.00
933.045	6368	40.62

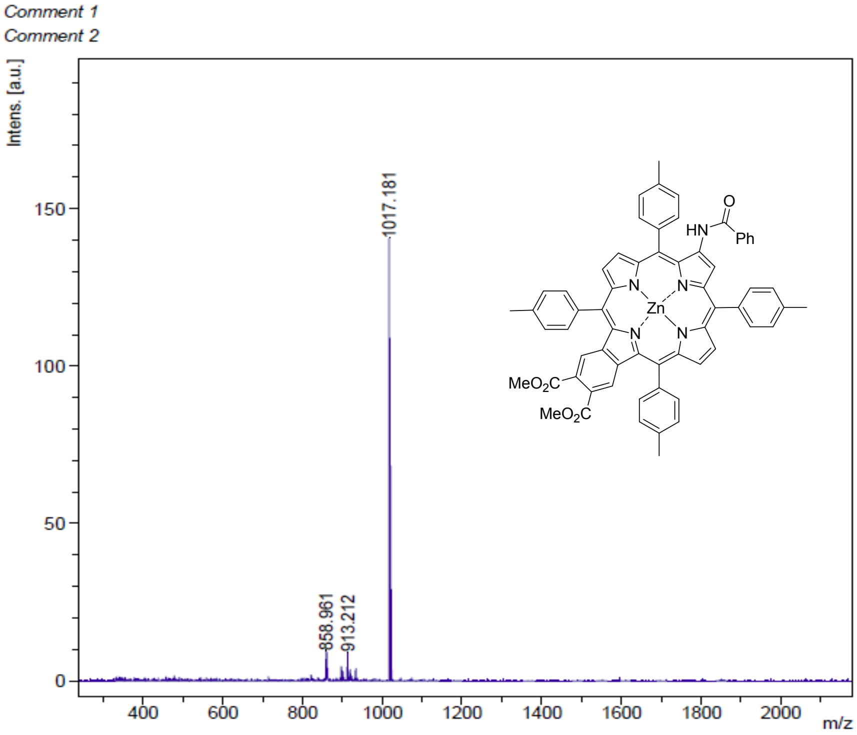
^{1}H NMR spectrum of **5** in $CDCl_3$ at 500 MHz



^{13}C NMR spectrum of **5** in $CDCl_3$ at 126 MHz

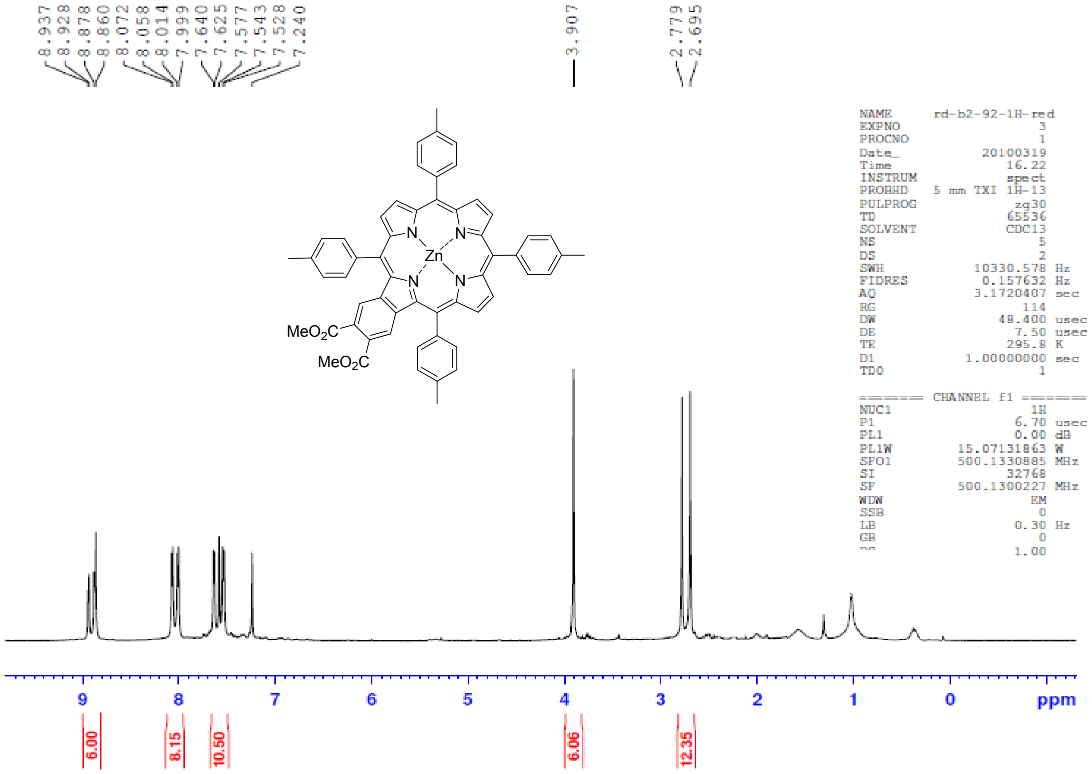


MALDI-TOF spectra for compound **5**



m/z	Res.	Intens.
858.961	1912	8.02
860.908	2112	6.76
897.197	3642	5.44
911.177	4000	5.08
913.212	4141	8.11
932.137	3508	3.78
1017.181	3985	151.70
1019.186	3969	85.32
1021.181	4063	51.21

^{1}H NMR spectrum of **6** in $CDCl_3$ at 500 MHz



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EXPNO                    3
PROCNO                   1
Date_             20100319
Time                 16.22
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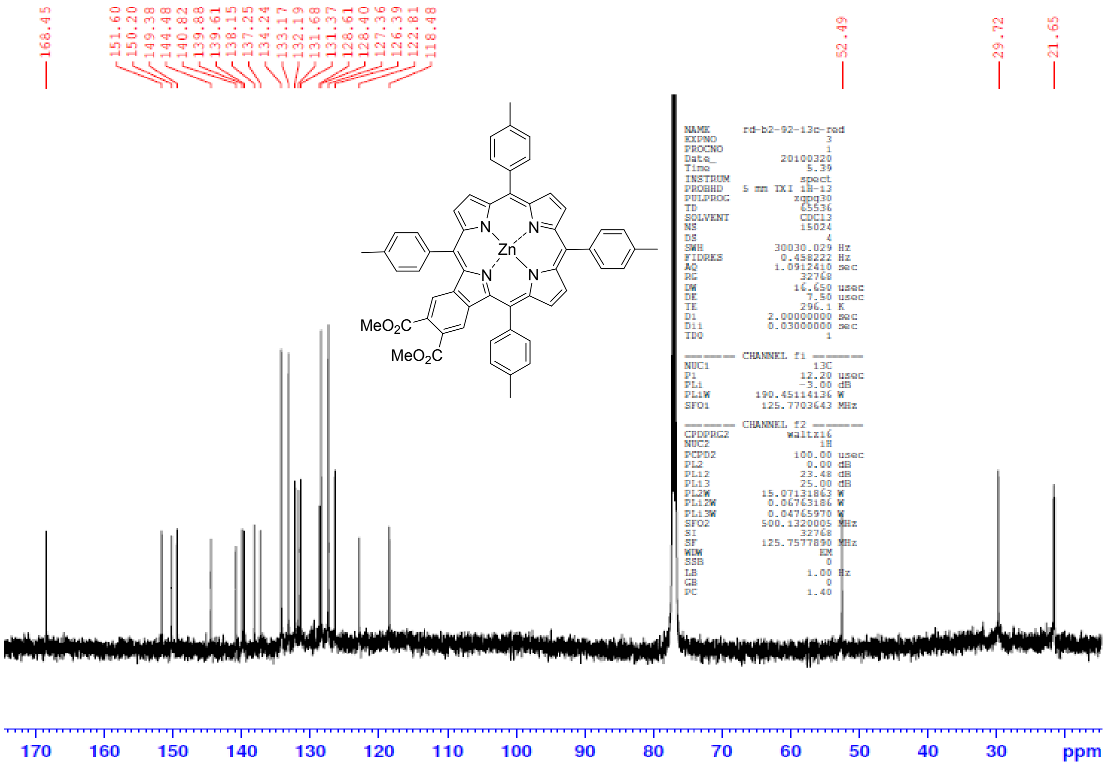
PROBHD     5 mm TXI 1H-13
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       5
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                     114
DW                  48.400 usec
DE                    7.50 usec
TE                   295.8 K
D1              1.00000000 sec
TD0                      1

======= CHANNEL f1 =======
NUC1                    1H
P1                    6.70 usec
PL1                   0.00 dB
PL1W           15.07131863 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300227 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
                      1.00
```

^{13}C NMR spectrum of **6** in $CDCl_3$ at 126 MHz



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PROCNO                    1
Date_              20100320
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INSTRUM               spect
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PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                    15024
DS                        4
SWH               30030.029 Hz
FIDRES             0.458222 Hz
AQ                1.0912410 sec
RG                    32768
DW                   16.650 usec
DE                     7.50 usec
TE                    296.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.20 usec
PL1                   -3.00 dB
PL1W           190.45114136 W
SFO1            125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                100.00 usec
PL2                    0.00 dB
PL12                  23.48 dB
PL13                  25.00 dB
PL2W            15.07131863 W
PL12W            0.06763186 W
PL13W            0.04765970 W
SFO2            500.1320005 MHz
SI                    32768
SF              125.7577890 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```
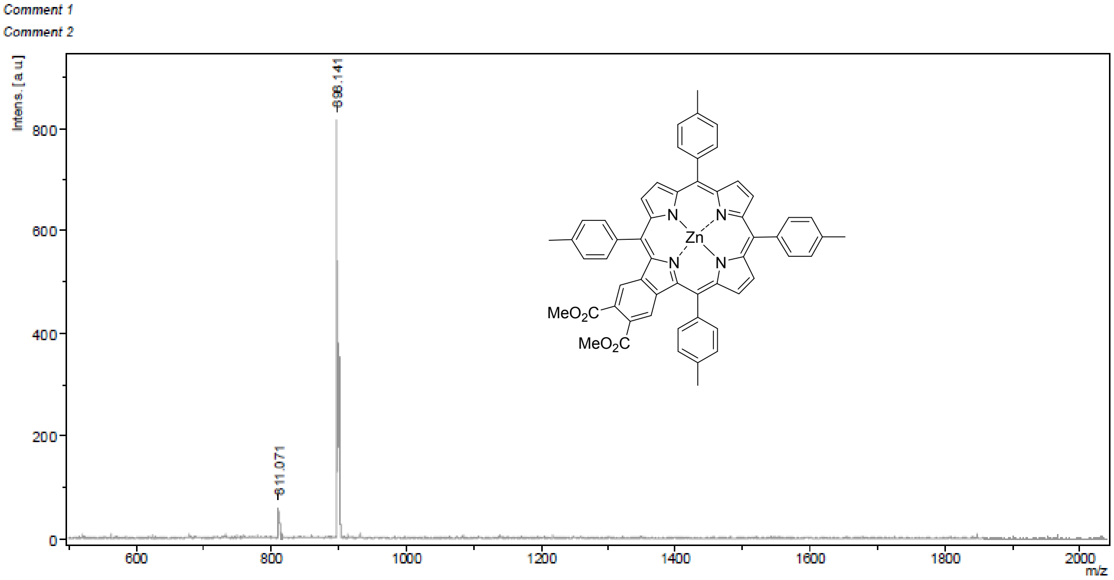
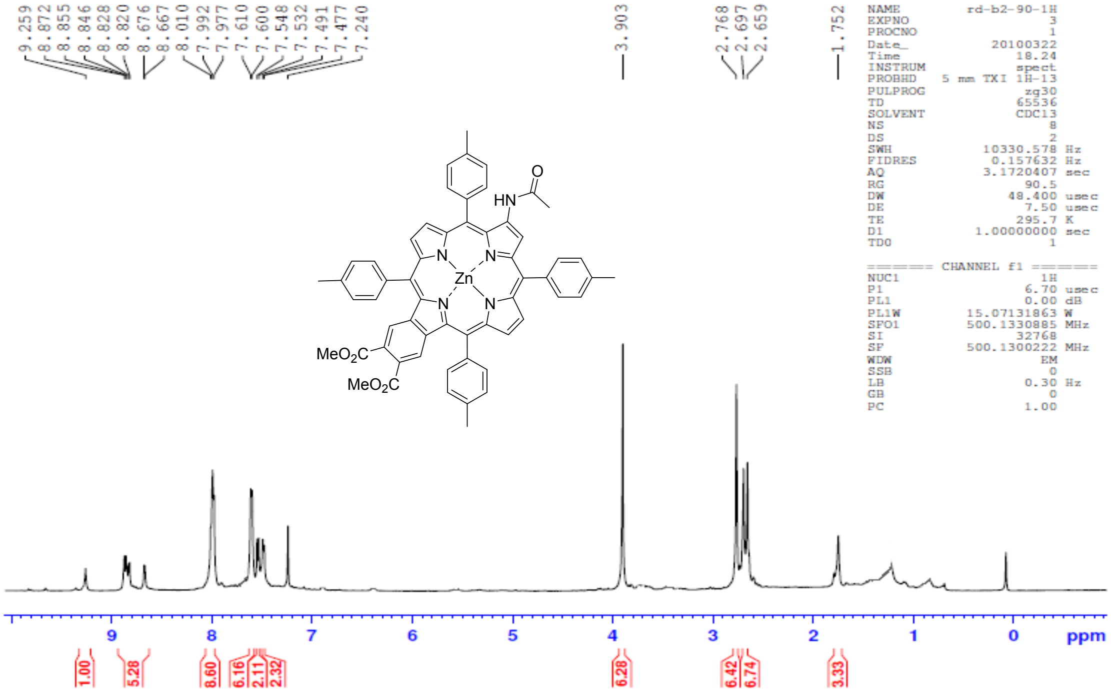

MALDI-TOF spectra for compound **6**



m/z	S/N	Quality Fac.	Res.	Intens.	Area
811.071	11.6	316	5250	55.07	15
813.102	10.4	121	5292	49.33	13
898.141	178.6	4503	4684	850.35	299

^{1}H NMR spectrum of **4** in $CDCl_3$ at 500 MHz

Signal peak broadening in ^{1}H NMR spectrum due to self-aggregation of molecules



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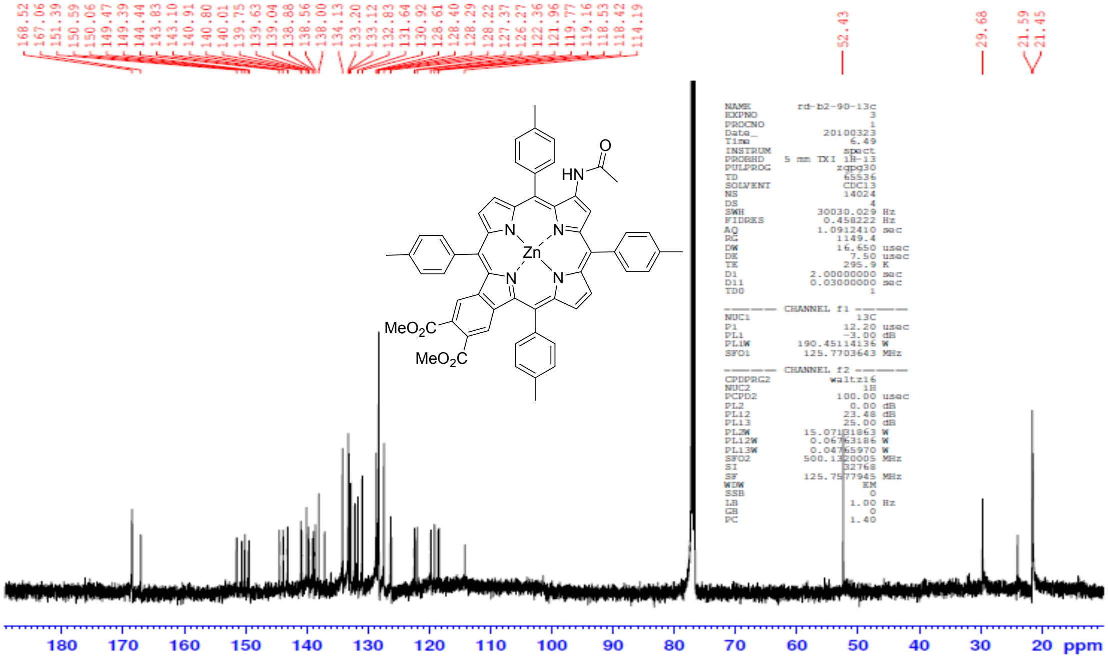
EXPNO                   3
PROCNO                  1
Date_            20100322
Time                18.24
INSTRUM             spect
PROBHD    5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                   90.5
DW                 48.400 usec
DE                   7.50 usec
TE                  295.7 K
D1            1.00000000 sec
TD0                     1

======= CHANNEL f1 =======
NUC1                   1H
P1                   6.70 usec
PL1                  0.00 dB
PL1W          15.07131863 W
SFO1          500.1330885 MHz
SI                  32768
SF            500.1300222 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{13}C NMR spectrum of **4** in $CDCl_3$ at 126 MHz



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NAME         rd-b2-90-13c
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PROCNO                  1
Date_            20100323
Time                 6.49
INSTRUM             spect
PROBHD    5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                  14024
DS                      4
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                 1149.4
DW                 16.650 usec
DE                   7.50 usec
TE                  295.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  12.20 usec
PL1                 -3.00 dB
PL1W         190.45114136 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                  0.00 dB
PL12                23.48 dB
PL13                25.00 dB
PL2W          15.07131863 W
PL12W          0.06763186 W
PL13W          0.04765970 W
SFO2          500.1320005 MHz
SI                  32768
SF            125.7577945 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```
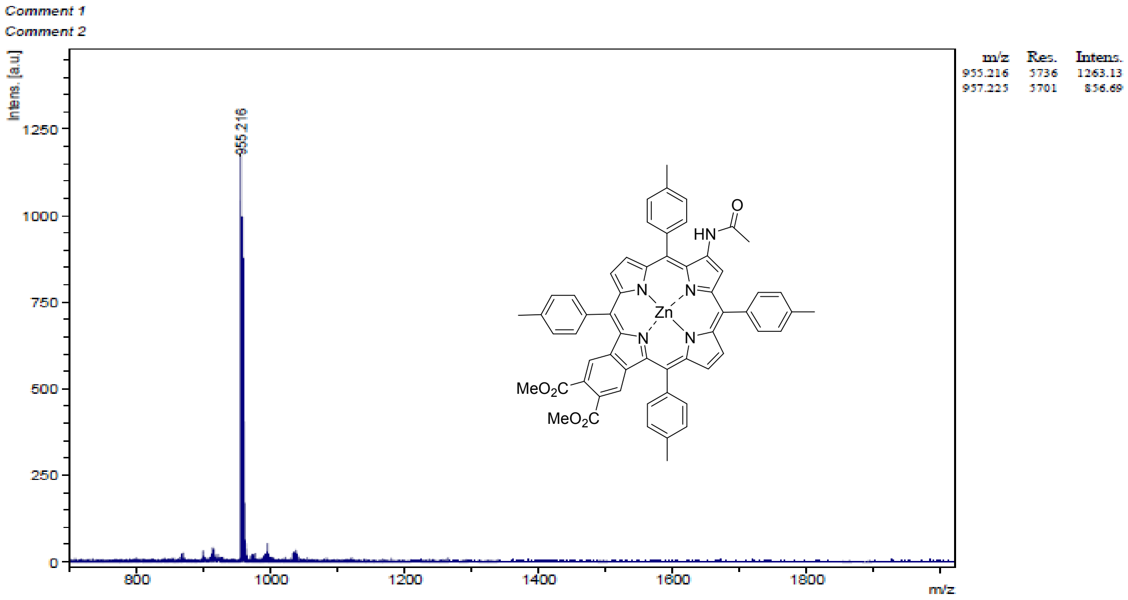

MALDI-TOF spectra for compound **4**



m/z	Res.	Intens.
955.216	5736	1263.13
957.225	5701	856.69

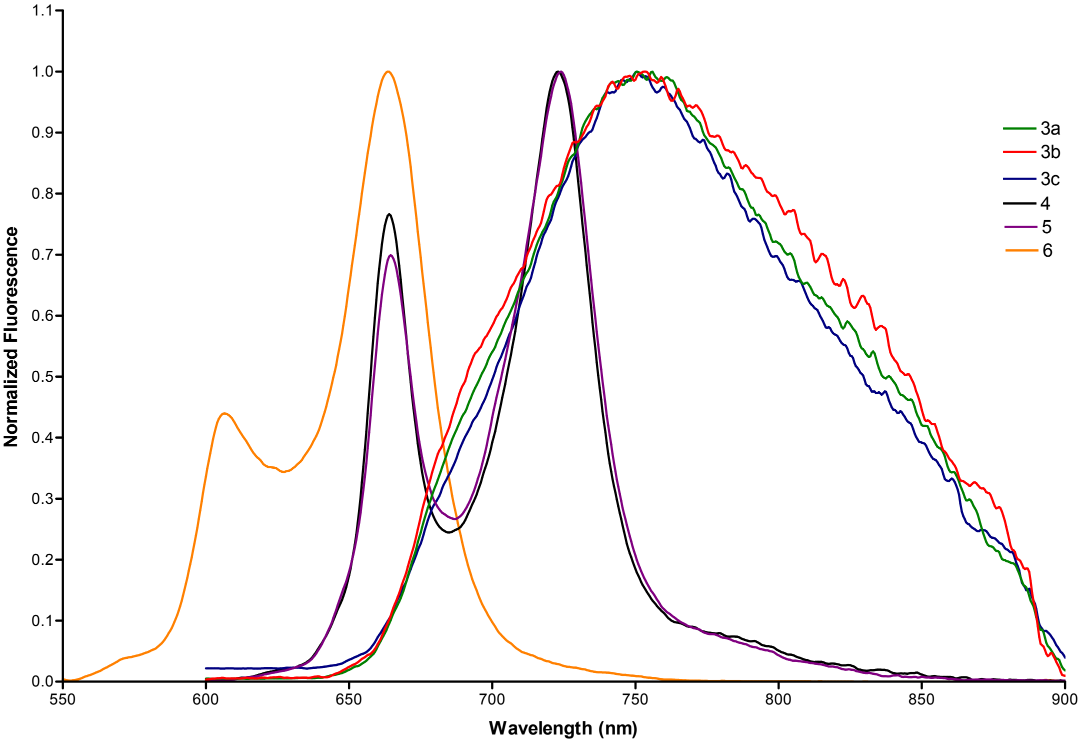


Fig S1: Normalized fluorescence spectra of **3a-6** with excitation of 446 nm in CH_2Cl_2

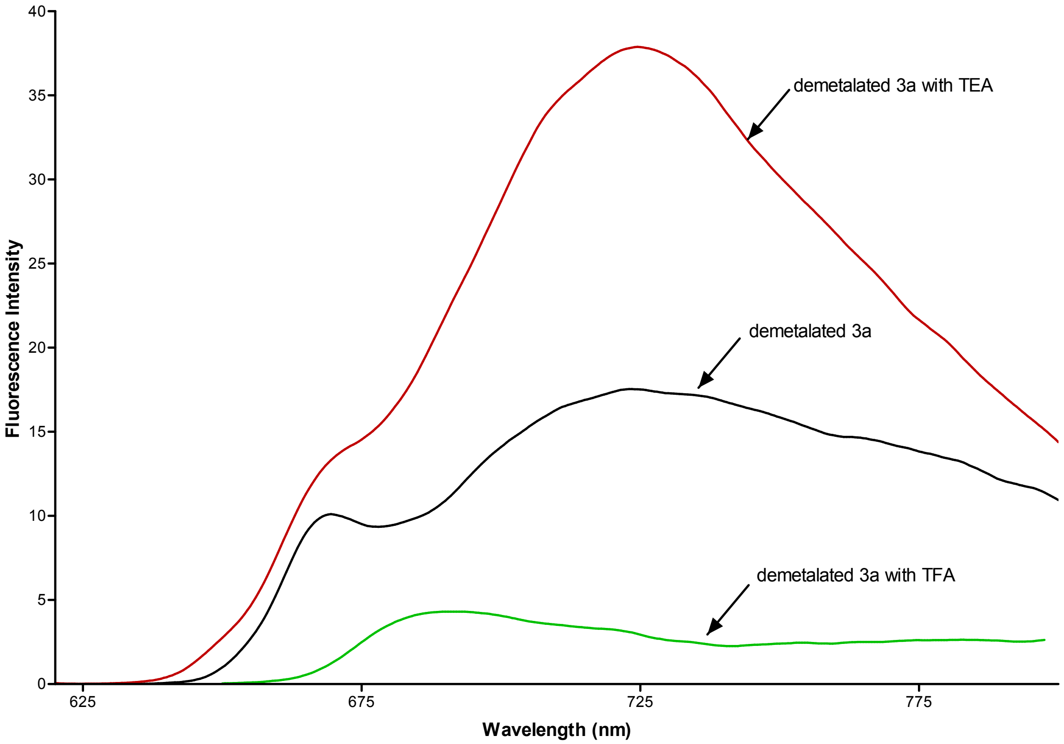


Fig S2: Fluorescence spectra of demetalated **3a** with TEA and TFA excitation at 440 nm in CH_2Cl_2

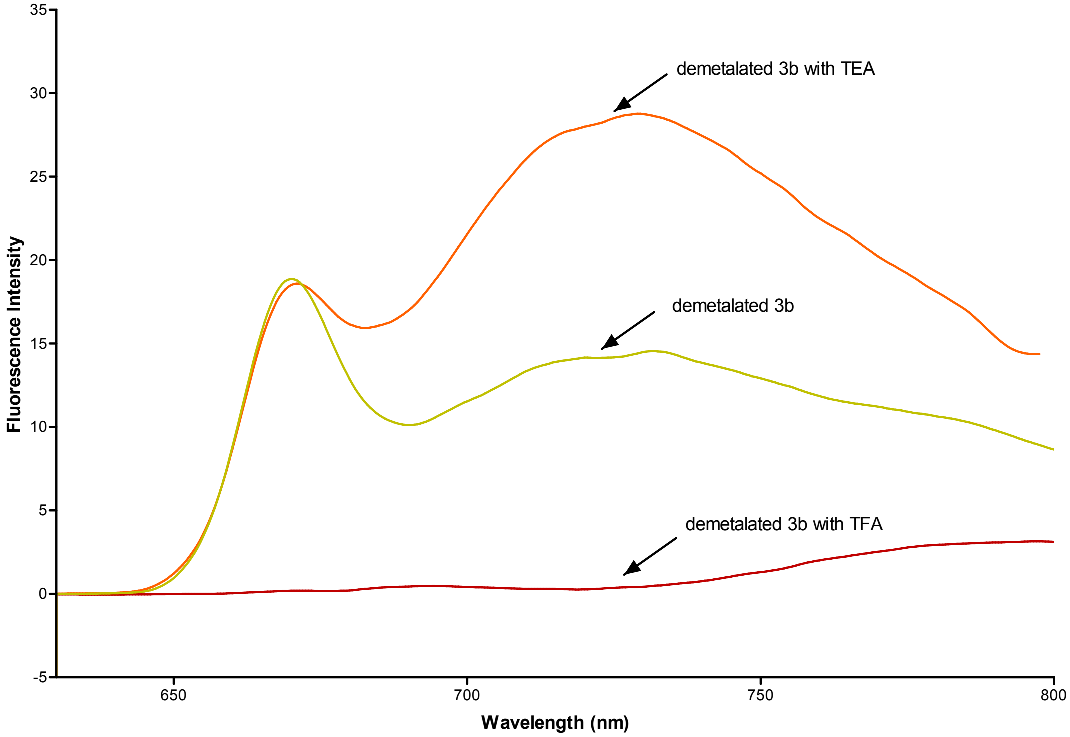


Fig S3: Fluorescence spectra of demetalated **3b** with TEA and TFA excitation at 440 nm in CH_2Cl_2

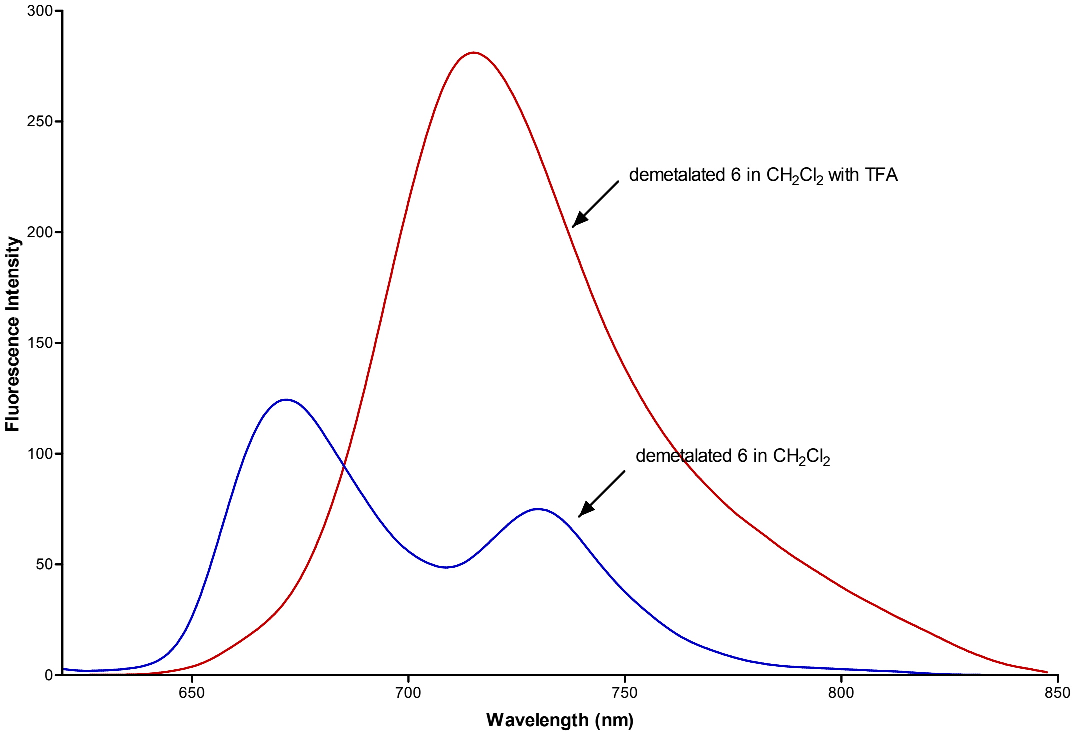


Fig S4: Fluorescent emission spectra of demetalated **6** with and without TFA excitation at 440 nm in CH_2Cl_2.

Table S1. Half-wave potential (V vs SCE) of investigated compounds in pyridine, 0.1 M TBAP.

Cpds	Oxidation (CH_2Cl_2)				Reduction (Pyridine)			H-L gap
	HOMO-1	HOMO			LUMO	LUMO+1		
	2nd	1st	Δ*E*(mV)		1st	2nd	Δ*E*(mV)	
(TPP)Zn	1.09	0.79	300		-1.40	-1.88	480	2.19
3a	1.02	0.79	230		-1.08	-1.43	350	1.87
3b	1.00	0.79	210		-1.08	-1.44	360	1.87
3c	1.06	0.84	220		-1.00	-1.30	300	1.84
4	0.94	0.76	180		-1.32	-1.76	440	2.08
5	0.94	0.76	180		-1.32	-1.73	410	2.08
6	0.97	0.75	220		-1.34	-1.78	440	2.09

IV Computational Information

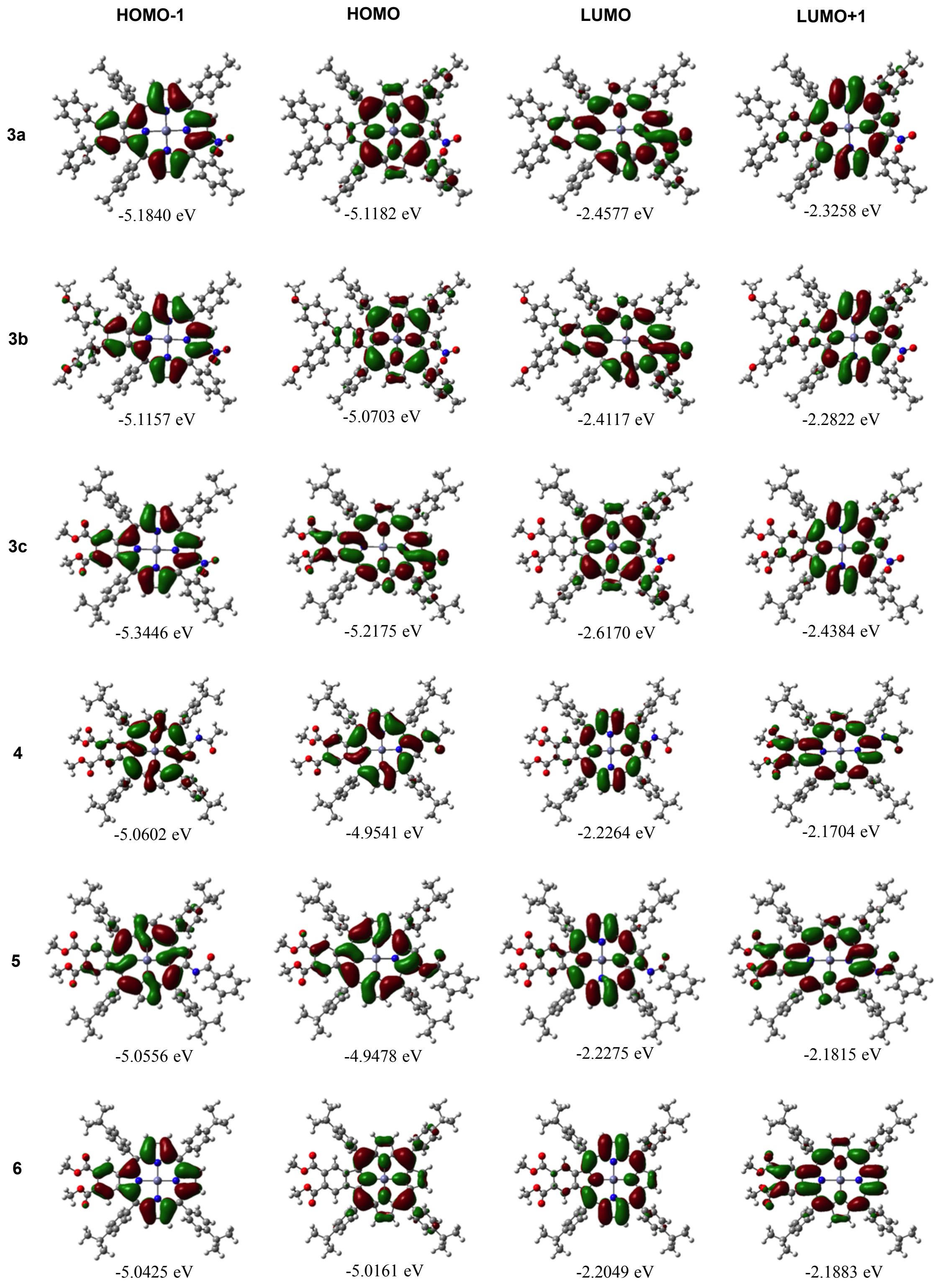


Fig S5: Calculated HOMOs and LUMOs and energy levels for **3a-3c** and **4-6 (**B3LYP/6-31G(d)).

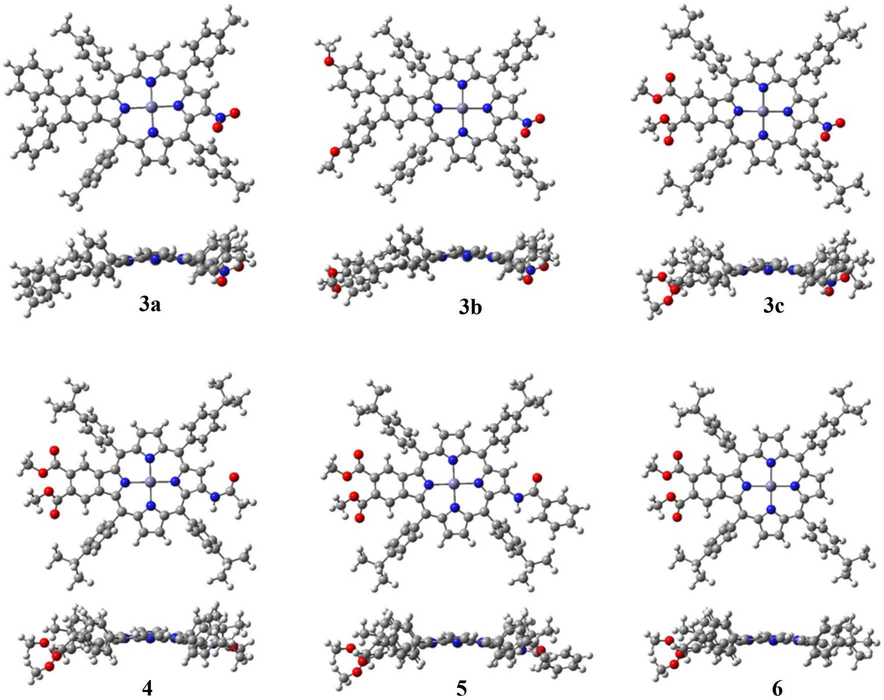


Fig S6: Molecular geometry of **3a**-**3c**, and **4**-**6** calculated at the B3LYP/6-31G(d) level of theory.

Table S2: Calculated molecular orbital energy levels for porphyrin **3a**-**3c**, and **4**-**6***

	HOMO (eV)	**LUMO (eV)**	**ΔE (eV)**
3a	-5.12	-2.46	2.66
3b	-5.07	-2.41	2.66
3c	-5.22	-2.62	2.60
4	-4.95	-2.23	2.72
5	-4.95	-2.23	2.72
6	-5.02	-2.20	2.82

*Orbital energy levels were calculated by DFT calculations with B3LYP/6-31G(d).

V Reference

(1) Jaquinod, L.; Khoury, R. G.; Shea, K. M.; Smith, K. M. *Tetrahedron* **1999**, *55*, 13151.

(2) Deshpande, R.; Jiang, L.; Schmidt, G.; Rakovan, J.; Wang, X. P.; Wheeler, K.; Wang, H. *Org Lett* **2009**, *11*, 4251.

(3) Jiang, L.; Engle, J. T.; Sirk, L.; Hartley, C. S.; Ziegler, C. J.; Wang, H. *Org Lett* **2011**, *13*, 3020.