Supporting Information

A Method for Rapid Screening of Photosensitizers by Scanning Electrochemical Microscopy (SECM) and the Synthesis and Testing of a Porphyrin Sensitizer

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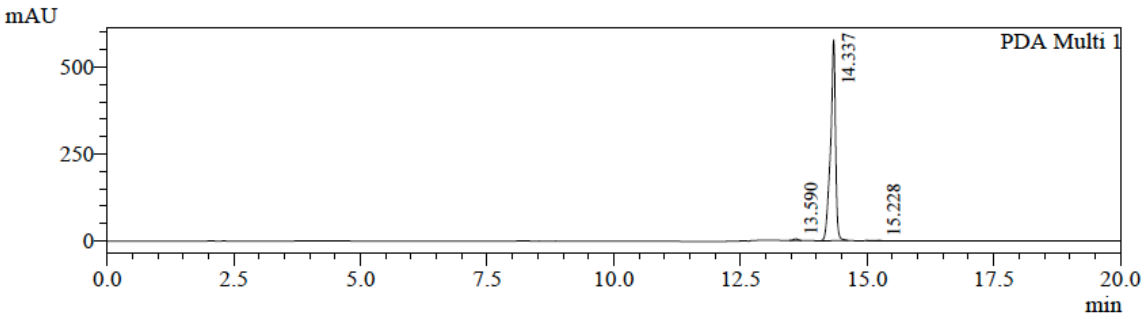
HPLC analysis of 2a.

HPLC analysis of **2a** was carried out on Shimadzu HPLC system: SIL-20AC auto sampler, DGU-20A5 degasser, SPD-M20A diode array detector and LC-6AD liquid chromatograph, equipped with an Agilent eclipse XDB-C18 column (3.5 μm, 2.1 × 150 mm) and water-acetonitrile mixture used as a mobile phase.



1 PDA Multi 1 / 393nm 4nm

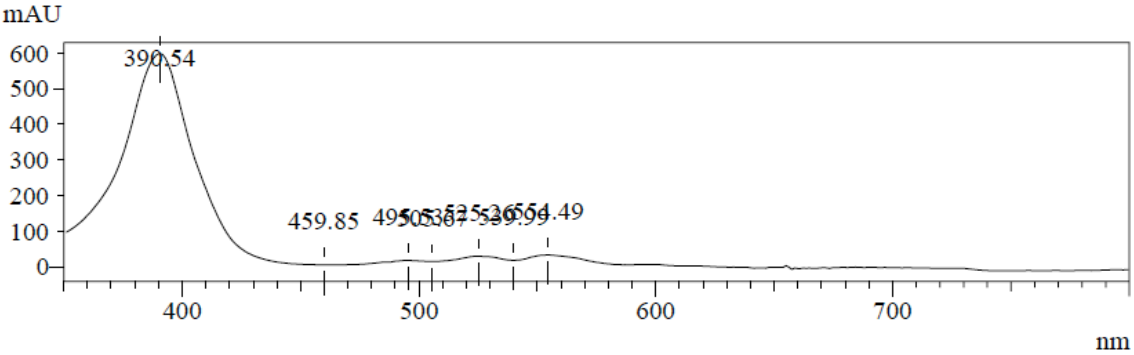
PeakTable

PDA Ch1 393nm 4nm

Peak#	Ret. Time	Area	Area %
1	13.590	24260	0.610
2	14.337	3941124	99.017
3	15.228	14867	0.374
Total		3980251	100.000

Time	Unit	Command	Value
2.00	Pumps	B.Conc	10
5.00	Pumps	B.Conc	10
7.00	Pumps	B.Conc	25
10.00	Pumps	B.Conc	99
17.99	Pumps	B.Conc	99
18.00	Pumps	B.Conc	10
25.00	Controller	Stop	

Peak# : 2
Retention Time : 14.337
Compound Name :
Spectrum Operation : None



Crystallographic analysis of 1.

X-ray experimental for $C_{50}H_{46}N_4O_4S_4$: Crystals grew as red plates by slow diffusion of methanol into the dichloromethane solution. The crystal had the following approximate dimensions: 0.52 mm × 0.40 mm × 0.10 mm. The data was collected using a Nonius Kappa CCD diffractometer coupled with a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 477 frames of data were collected using ω-scans

with a scan range of 1.4° and a counting time of 163 s per frame. The data was collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction was performed using a DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

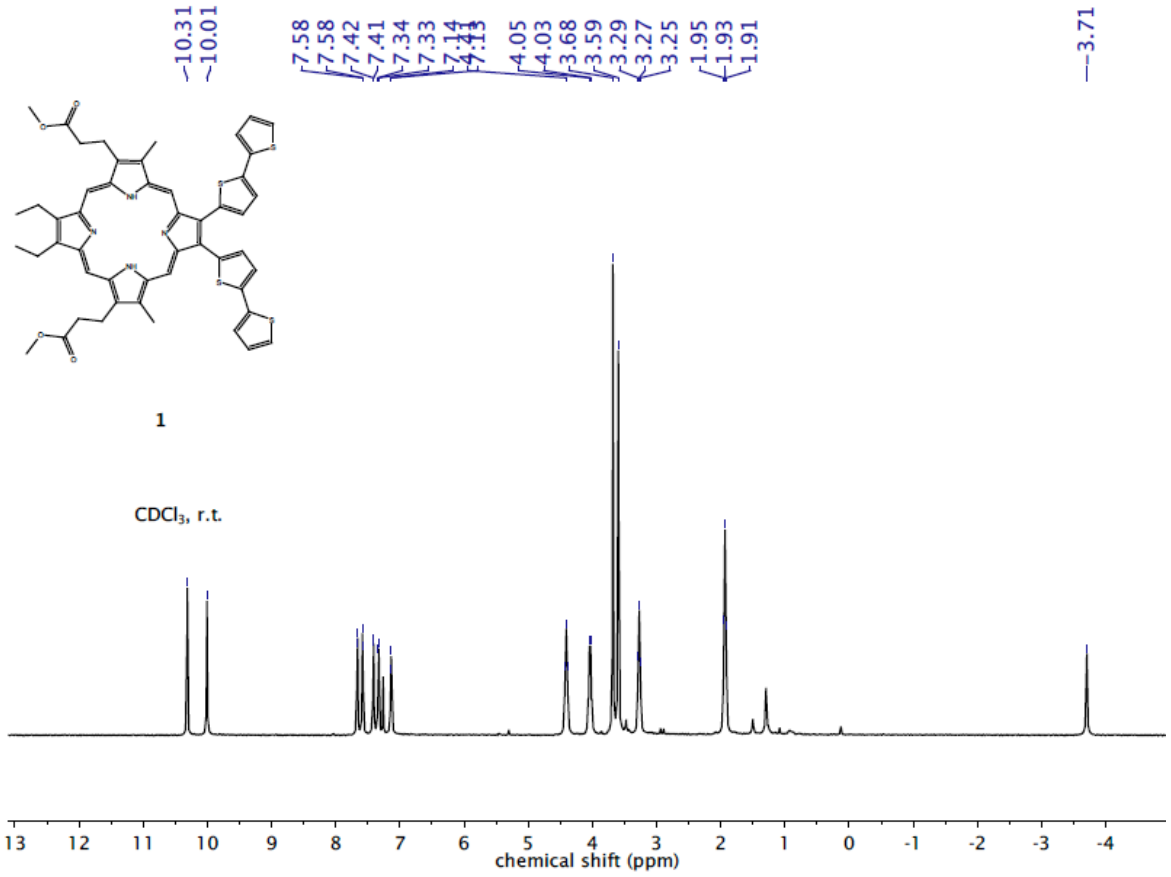
One of the ethyl methyl ester groups and two of the thiophene rings were disordered. The disorder was modeled in the same manner for each group. The variable x was assigned to the site occupancy factor for one component of the disordered group, while (1-x) was assigned to the alternate component. A common isotropic displacement parameter was refined while refining x. Geometric restraints were applied throughout the refinement process. Bond length and angle constraints were applied to the ethyl methyl ester groups. All non-H atoms were refined anisotropically but were restrained to be approximately isotropic. All H atoms were calculated in idealized positions.

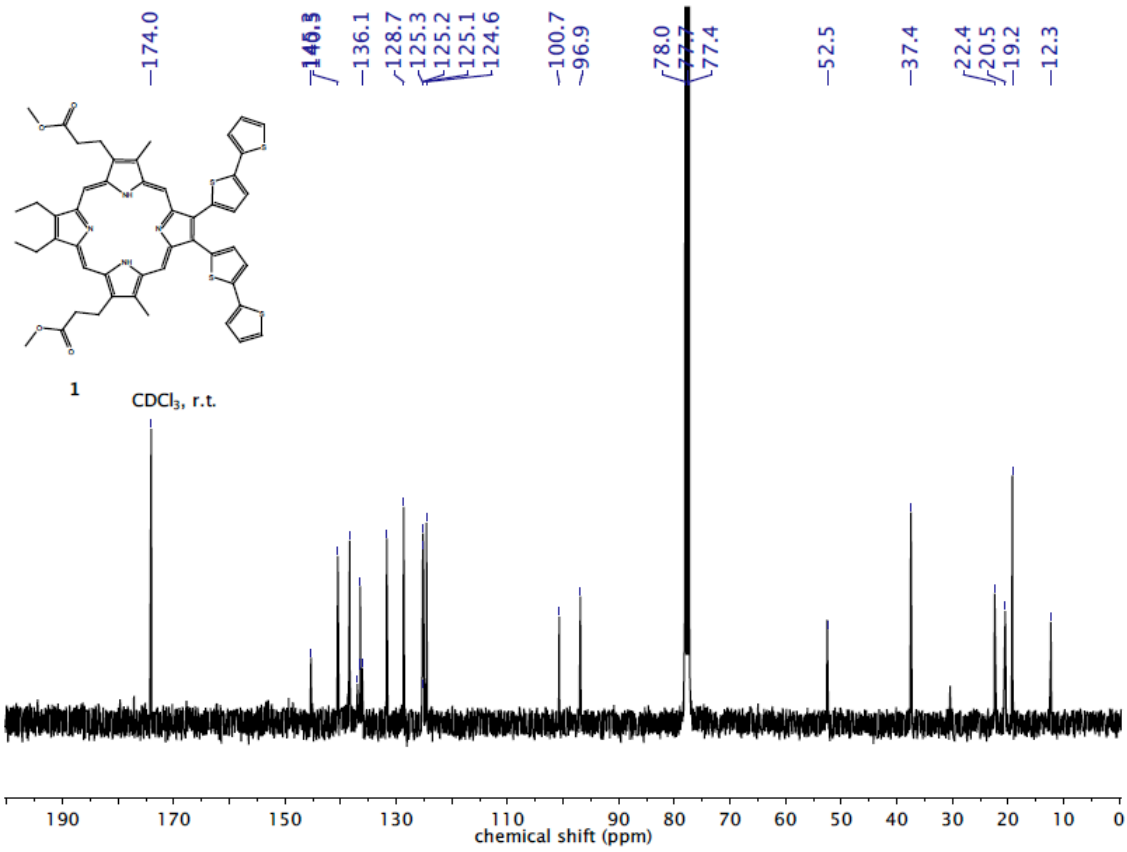
The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.1*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.318, with R(F) equal to 0.104 and a goodness of fit, S, = 2.38. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[4] Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere. Further details of the crystallography may be obtained from the Cambridge Crystallographic Data Centre by quoting reference no. 795817.

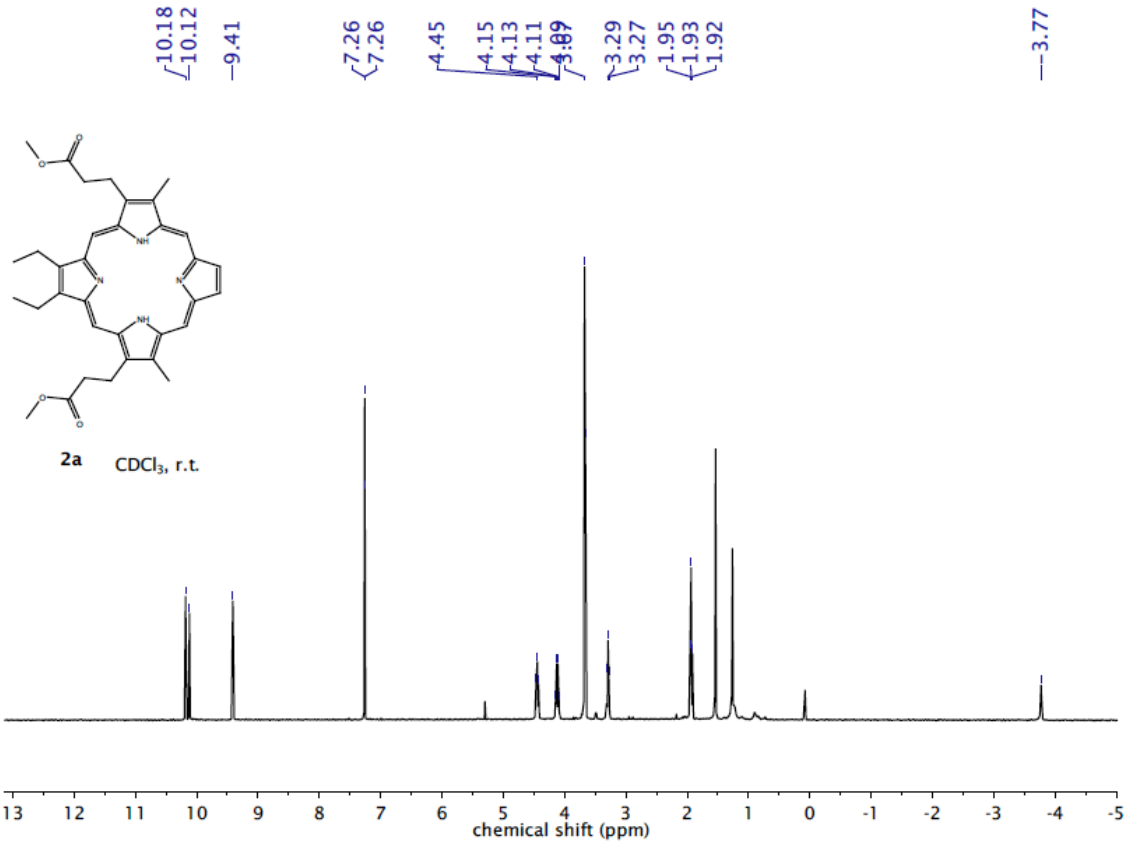
Table S1. Crystal data and structure refinement for **1**.

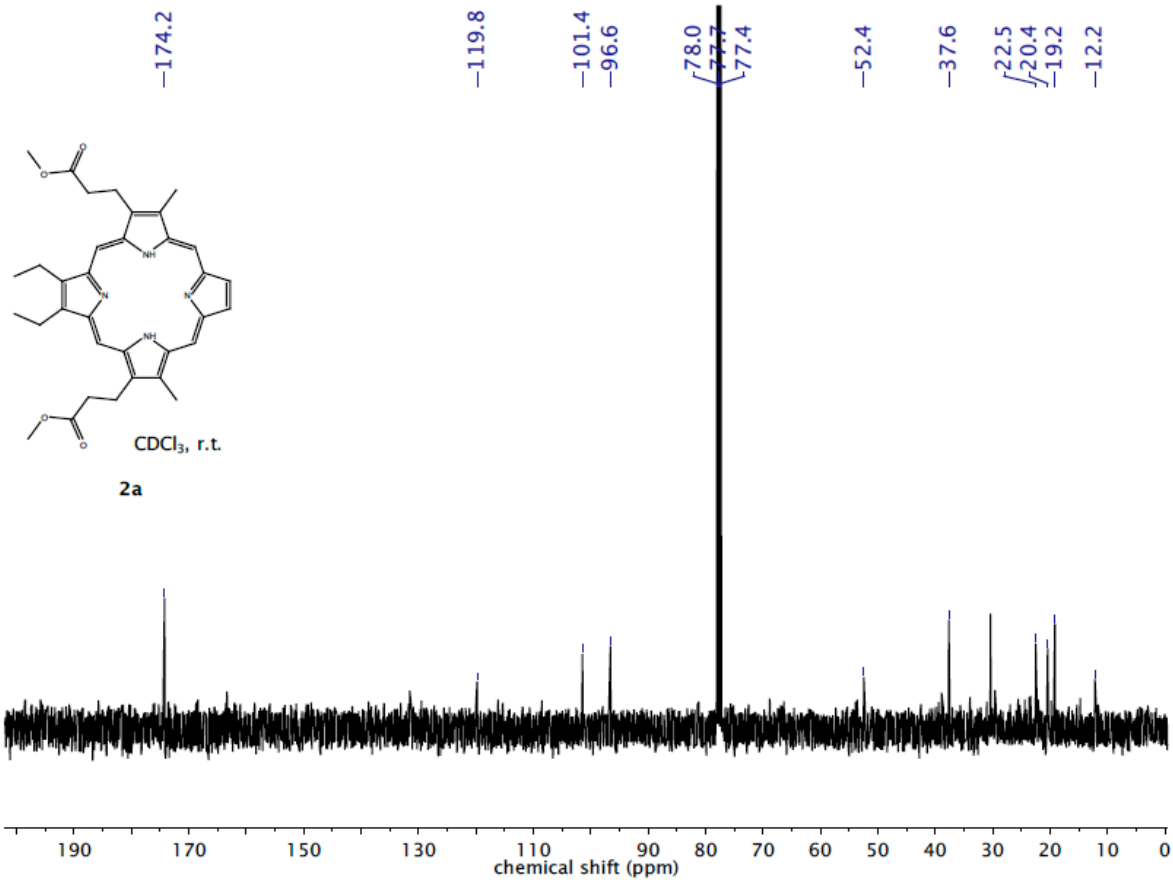
Empirical formula	C50 H46 N4 O4 S4	
Formula weight	895.15	
Temperature	153(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 17.7560(10) Å	α= 90°.
	b = 21.9782(12) Å	β= 100.667(4)°.
	c = 11.5593(7) Å	γ = 90°.
Volume	4433.0(4) $Å^3$	
Z	4	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	0.265 mm^{-1}	
F(000)	1880	
Crystal size	0.52 x 0.40 x 0.10 mm	
Theta range for data collection	2.96 to 25.00°.	
Index ranges	-21<=h<=21, -26<=k<=25, -13<=l<=13	
Reflections collected	15074	
Independent reflections	7778 [R(int) = 0.0265]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.85	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7778 / 917 / 722	
Goodness-of-fit on F^2	2.192	
Final R indices [I>2sigma(I)]	R1 = 0.1037, wR2 = 0.2969	
R indices (all data)	R1 = 0.1420, wR2 = 0.3177	
Largest diff. peak and hole	1.344 and -0.895 $e.Å^{-3}$	

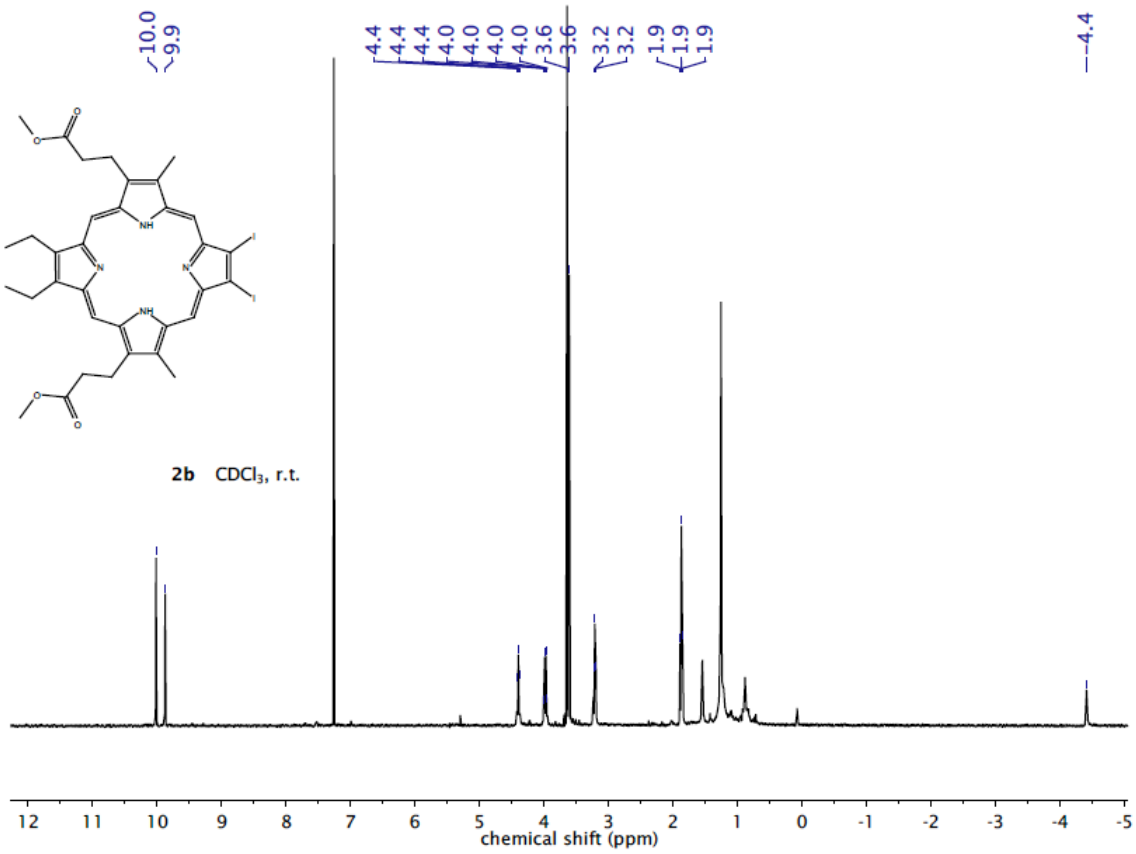
Selected NMR spectra.

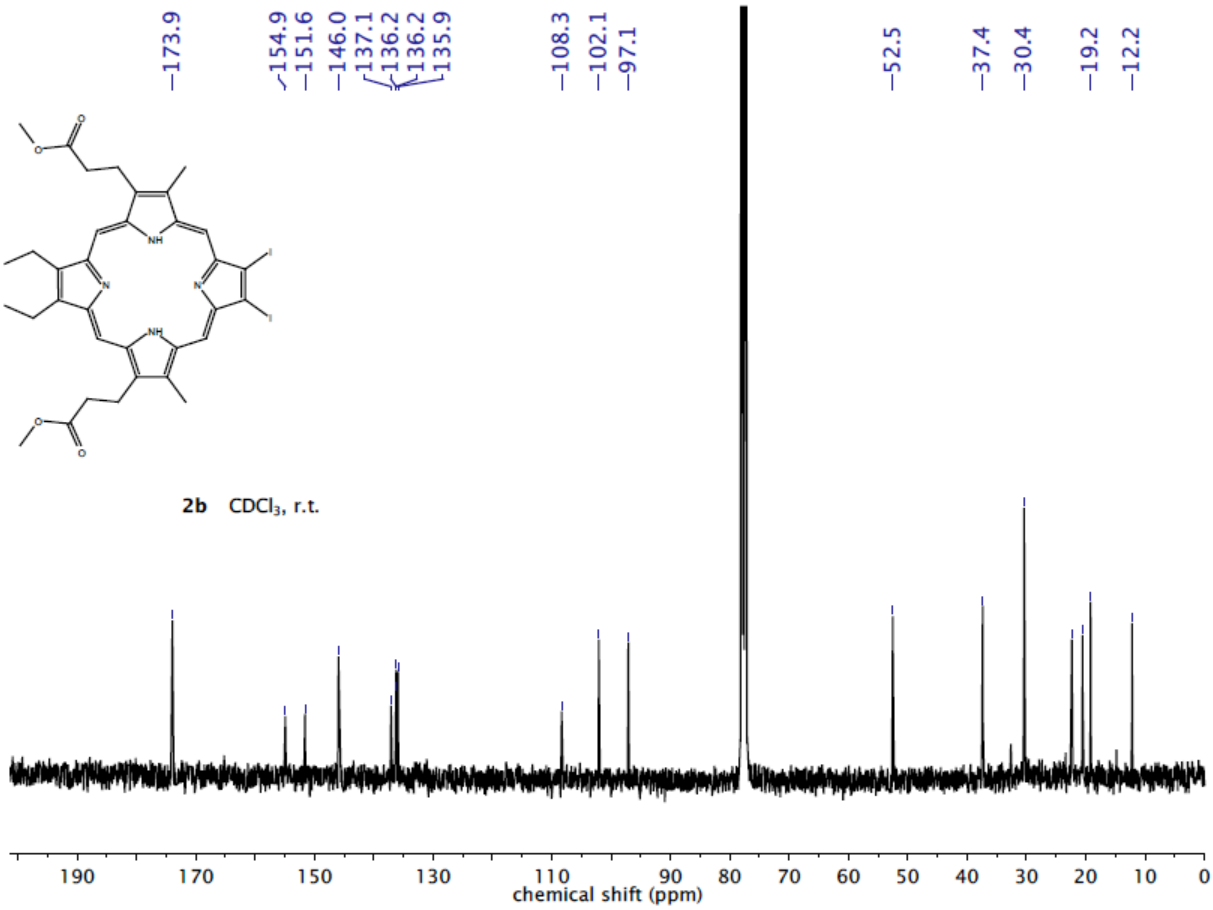



174.0
146.3
145.8
136.1
128.7
125.3
125.2
125.1
124.6
100.7
96.9
78.0
77.7
77.4
52.5
37.4
22.4
20.5
19.2
12.3
1
CDCl3, r.t.
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
chemical shift (ppm)


10.18
10.12
9.41
7.26
7.26
4.45
4.15
4.13
4.11
3.29
3.27
1.95
1.93
1.92
3.77
2a
CDCl3, r.t.
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
chemical shift (ppm)


174.2
119.8
101.4
96.6
78.0
77.7
77.4
52.4
37.6
22.5
20.4
19.2
12.2
CDCl3, r.t.
2a
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
chemical shift (ppm)


10.0
9.9
4.4
4.4
4.4
4.0
4.0
4.0
4.0
3.6
3.6
3.2
3.2
1.9
1.9
1.9
4.4
2b CDCl3, r.t.
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
chemical shift (ppm)


173.9
154.9
151.6
146.0
137.1
136.2
136.2
135.9
108.3
102.1
97.1
52.5
37.4
30.4
19.2
12.2
2b CDCl3, r.t.
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
chemical shift (ppm)

References

1) DENZO-SMN. (1997). Otwinowski Z. and Minor W., Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. Carter Jr. W. and Sweets R. M., Editors, Academic Press.

2) SIR97. Altomare A., Burla M. C., Camalli M., Cascarano G. L., Giacovazzo C., Guagliardi A., Moliterni A. G. G., Polidori G., Spagna R., A program for crystal structure solution. *J. Appl. Cryst.* **1999,** *32*, 115-119.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, Wilson A. J. C. Editor, Boston: Kluwer Academic Press.

6) Sheldrick G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.