Supporting Information

Design and synthesis of dichromeno[2,3-*b*; 3',2'-*e*]pyridine-12,14-dione to evaluate its optical properties

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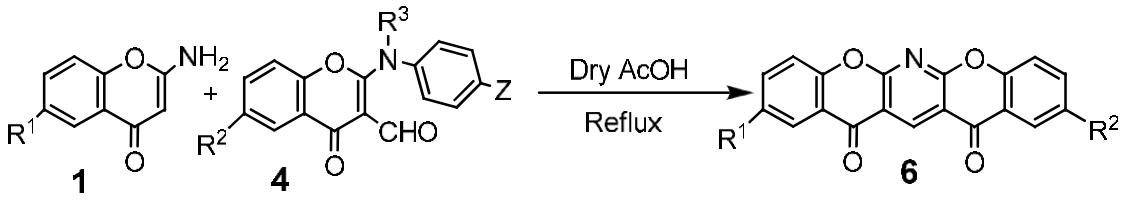
Table of contents

1. Materials and Methods

The recorded mps are uncorrected. IR spectra were recorded in KBr on a Shimadzu FTIR spectrophotometer, IR Affinity-1, ^{1}H NMR / ^{13}C NMR spectra on a bruker 300 MHz / 75 MHz or 400 MHz / 100 MHz spectrometer in $CDCl_3$ unless stated otherwise, all mass spectra on a Qtof micro YA 263 instrument and elemental analysis on a Perkin Elmer 240c elemental analyzer. Light petroleum refers to the fraction with 60-80 ^{o}C. All chemicals used were of commercial grade and were used as such.

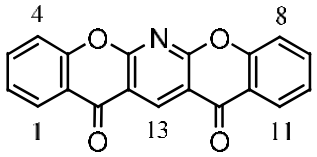
2. General procedure for the synthesis of dichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione 6a-6f:



A mixture of **1** (0.25 mmol) and **4** (0.25 mmol) was dissolved in acetic acid (5 mL) in a 10 mL round-bottom flask and the resultant solution was heated under reflux in an oil bath for 5 h. The solvent from the reaction mixture was removed under reduced pressure and ice-water (10 g) was added to the concentrate. The deposited solid was filtered out, washed with water, dried in air and crystallized from acetic acid to get white solid **6a-f**.

3. Analytical data of Compounds 6a-6f

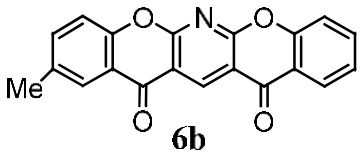
6a: Dichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione



6a

White solid, yield: (55 mg, 70%); m.p. >290 ^{o}C (lit.[17] 303 ^{o}C); $\sqrt{}_{max}$(KBr) 3080, 1670, 1602, 1399 cm^{-1}; δ_H ($CDCl_3$) 9.73 (1H, s, H-13), 8.38 (2H, dd, *J* = 8.0, 1.2 Hz, H-1 and H-11), 7.88-7.84 (2H, m, H-3 and H-9), 7.67 (2H, br d, *J* = 8.4 Hz, H-4 and H-8), 7.55-7.51 (2H, m, H-2 and H-10); δ_C (DMSO-d_6) 175.9, 161.5, 155.1, 138.8, 136.6, 126.3, 125.8, 121.1, 118.7, 115.0; HRMS(ESI): Calculated for $C_{19}H_9NO_4Na$ 338.0429, found 338.0437.

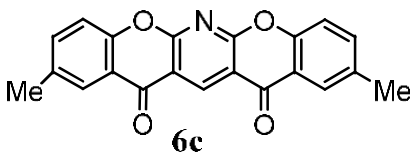
6b: 2-Methyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione



6b

White solid, yield: (55 mg, 67%); m.p. >300 ^{o}C; [Found: C, 73.02; H, 3.32; N, 4.21. $C_{20}H_{11}NO_4$ requires C, 72.95; H, 3.37; N, 4.25%]; $\sqrt{}_{max}$(KBr) 3090, 1666, 1606, 1463, 1400 cm^{-1}; δ_H ($CDCl_3$) 9.70 (1H, s, H-13), 8.35 (1H, dd, *J* = 8.0, 1.6 Hz, H-11), 8.14 (1H, br s, H-1), 7.86-7.81 (1H, m, H-9), 7.66-7.63 (2H, m, H-3 and H-8), 7.54 (1H, d, *J* = 8.8 Hz, H-4), 7.52-7.48 (1H, m, H-10), 2.51 (3H, s, Me); δ_C ($CDCl_3$) 176.2, 176.1, 161.9, 161.8, 155.4, 153.6, 141.2, 137.2, 136.1, 135.7, 127.0, 126.4, 125.6, 121.5, 121.1, 118.5, 118.3, 115.2, 115.0, 20.9; MS: m/z 330 ($M+H^+$), 352 ($M+Na^+$).

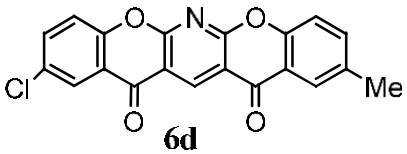
6c: 2,10-Dimethyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione



6c

White solid, yield: (50 mg, 58%); m.p. >300 ^{o}C; [Found: C, 73.38; H, 3.79; N, 4.04. $C_{21}H_{13}NO_4$ requires C, 73.46; H, 3.82; N, 4.08%]; $\sqrt{}_{max}$(KBr) 3040, 1670, 1616, 1599, 1489, 1396 cm^{-1}; δ_H ($CDCl_3$) 9.70 (1H, s, H-13), 8.13 (2H, br s, H-1 and H-11), 7.63 (2H, dd, *J* = 8.4, 1.6 Hz, H-3 and H-9), 7.53 (2H, d, *J* = 8.4 Hz, H-4 and H-8), 2.51 (6H, s, Me-2 and Me-10); δ_C ($CDCl_3$) 176.3, 161.8, 153.6, 141.2, 137.2, 135.6, 126.4, 121.2, 118.3, 115.0, 20.9; MS: m/z 344 ($M+H^+$), 366 ($M+Na^+$).

6d: 2-Chloro-10-Methyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione

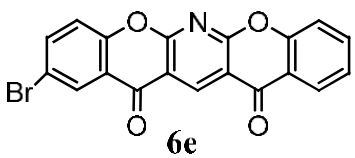


6d

White solid, yield: (65 mg, 72%); m.p. >300 ^{o}C; [Found: C, 65.98; H, 2.73; N, 3.82. $C_{21}H_{17}NO_5$ requires C, 66.04; H, 2.77; N, 3.85%]; $\sqrt{}_{max}$(KBr) 3050, 1670, 1597, 1425, 1398 cm^{-1}; δ_H ($CDCl_3$) 9.70 (1H, s, H-13), 8.32 (1H, d, *J* = 2.4 Hz, H-1), 8.15 (1H, br s, H-11), 7.78 (1H, dd, *J* = 8.8, 2.4 Hz, H-3), 7.66 (1H, br d, *J* = 8.4 Hz, H-9), 7.62 (1H, d, *J* = 8.8 Hz,

H-4), 7.55 (1H, d, *J* = 8.4 Hz, H-8), 2.53 (3H, s, Me); MS: m/z 364 ($M+H^+$), 366 ($M+2+H^+$), 386 ($M+Na^+$), 388 ($M+2+Na^+$).

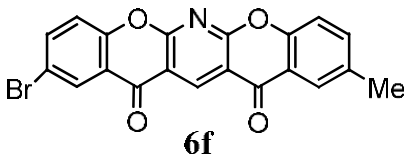
6e: 2-Bromodichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione



6e

White solid, yield: (55 mg, 56%); m.p. >280 ^oC; [Found: C, 57.80; H, 2.02; N, 3.51. $C_{19}H_8BrNO_4$ requires C, 57.89; H, 2.05; N, 3.55%]; $\sqrt{}_{max}$(KBr) 3030, 1670, 1600, 1552, 1404 cm^{-1}; δ_H ($CDCl_3$) 9.72 (1H, s, H-13), 8.49 (1H, d, *J* = 2.4 Hz, H-1), 8.38 (1H, dd, *J* = 8.0, 1.6 Hz, H-11), 7.93 (1H, dd, *J* = 8.8, 2.4 Hz, H-3), 7.89-7.85 (1H, m, H-9), 7.67 (1H, br d, *J* = 8.4 Hz, H-8), 7.57 (1H, d, *J* = 8.8 Hz, H-4), 7.56-7.52 (1H, m, H-10), MS: m/z 394 ($M+H^+$), 396 ($M+2+H^+$), 416 ($M+Na^+$), 418 ($M+2+Na^+$).

6f: 2-Bromo-10-Methyldichromeno[2,3-b; 3',2'-e]pyridine-12,14-dione



6f

White solid, yield: (60 mg, 59%); m.p. >280 ^oC; [Found: C, 55.79; H, 2.43; N, 3.39. $C_{20}H_{10}BrNO_4$ requires C, 55.85; H, 2.47; N, 3.43%]; $\sqrt{}_{max}$(KBr) 3065, 1676, 1602, 1552, 1398 cm^{-1}; δ_H ($CDCl_3$) 9.71 (1H, s, H-13), 8.49 (1H, d, *J* = 2.4 Hz, H-1), 8.15 (1H, d, *J* = 1.5 Hz, H-11), 7.93 (1H, dd, *J* = 8.8, 2.4 Hz, H-3), 7.66 (1H, dd, *J* = 8.4, 1.5 Hz, H-9), 7.57 (1H, d, *J* = 8.8 Hz, H-4), 7.56 (1H, d, *J* = 8.4 Hz, H-8), 2.53 (3H, s, Me); MS: m/z 408 ($M+H^+$), 410 ($M+2+H^+$), 430 ($M+Na^+$), 432 ($M+2+Na^+$).

4. Copies of ^1H NMR and ^{13}C NMR spectra of compound **6a**-**6f**


1.00
2.18
2.31
2.24
2.30
1.26
9.728
8.390
8.387
8.370
8.367
7.880
7.876
7.858
7.841
7.837
7.680
7.659
7.546
7.527
7.508
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2.297
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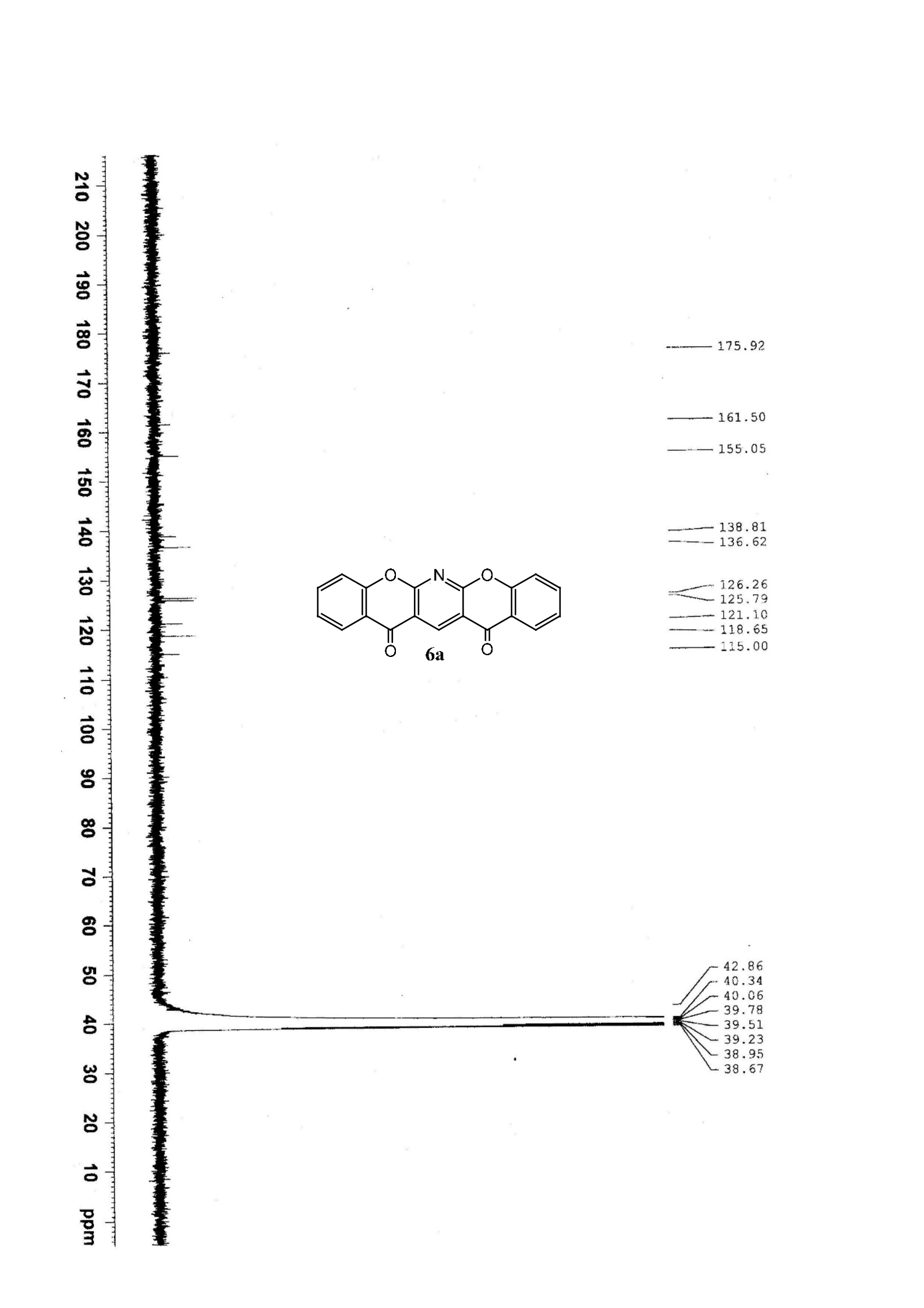
N
O
O
O
6a
ppm
ppm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126.26
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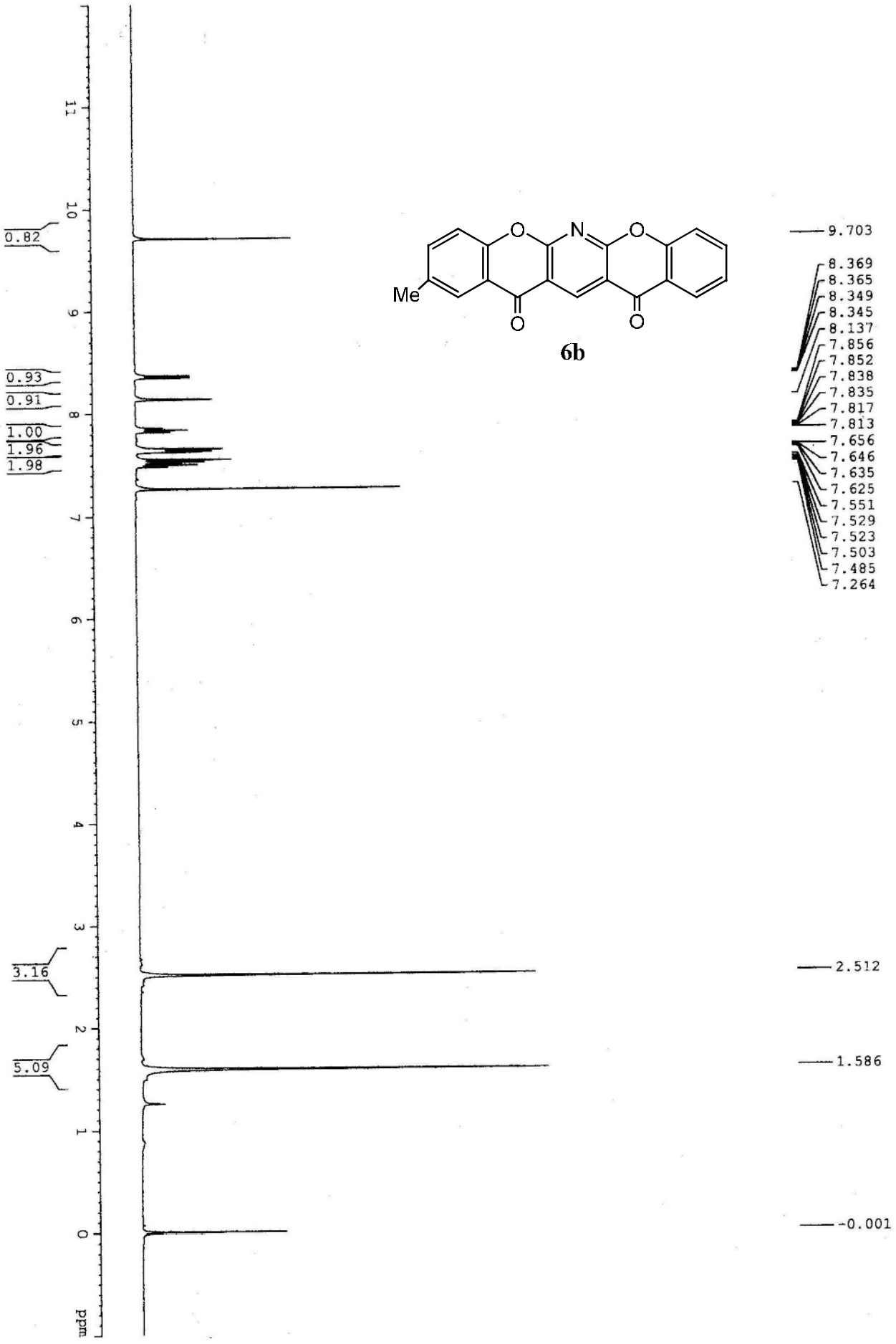
118.65
115.00
42.86
40.34
40.06
39.78
39.51
39.23
38.95
38.67
O
N
O
O
O
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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N
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O
O
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8.345
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7.835
7.817
7.813
7.656
7.646
7.635
7.625
7.551
7.529
7.523
7.503
7.485
7.264
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0.91
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5.09
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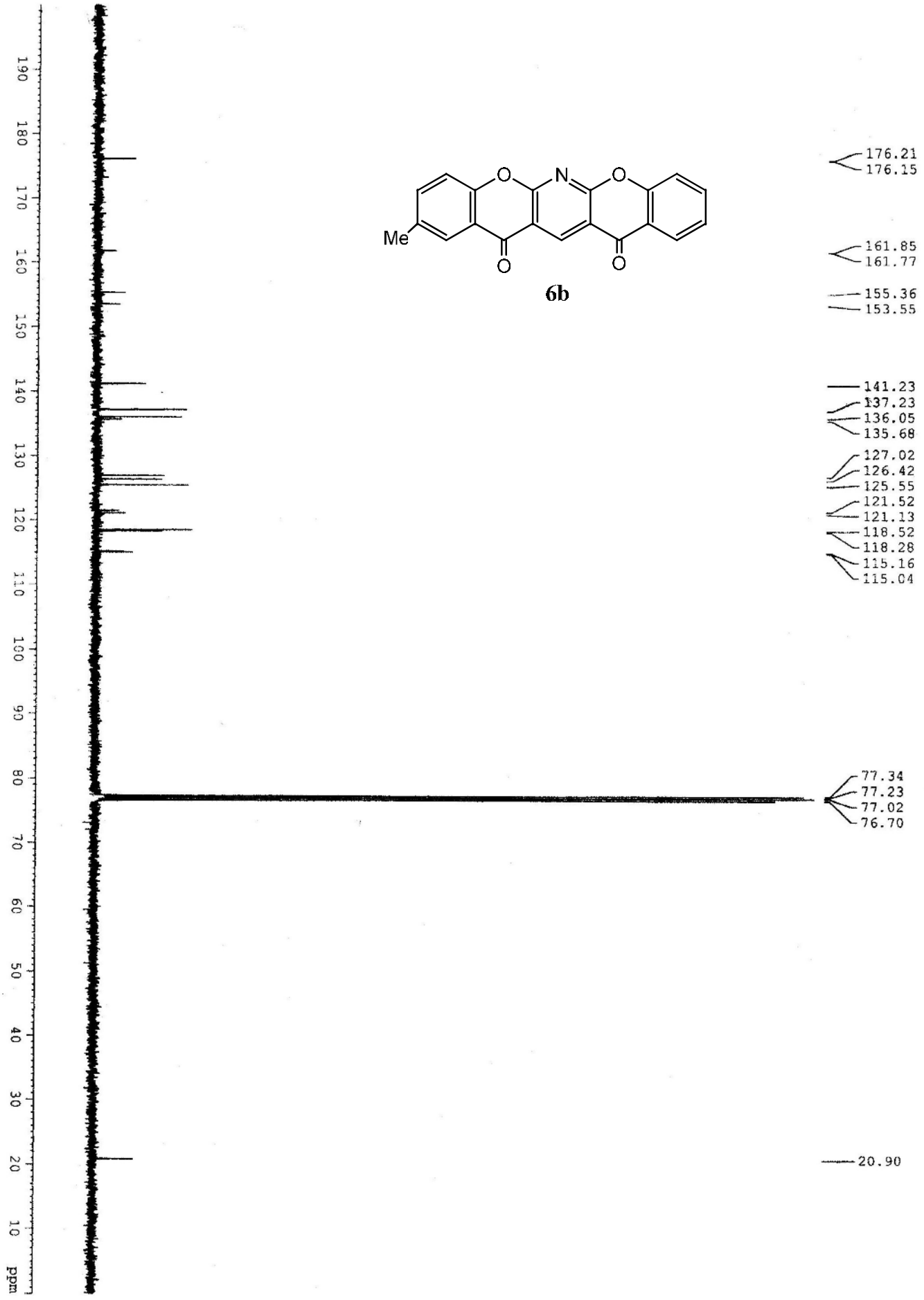
ppm


Me
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O
O
O
6b
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176.15
161.85
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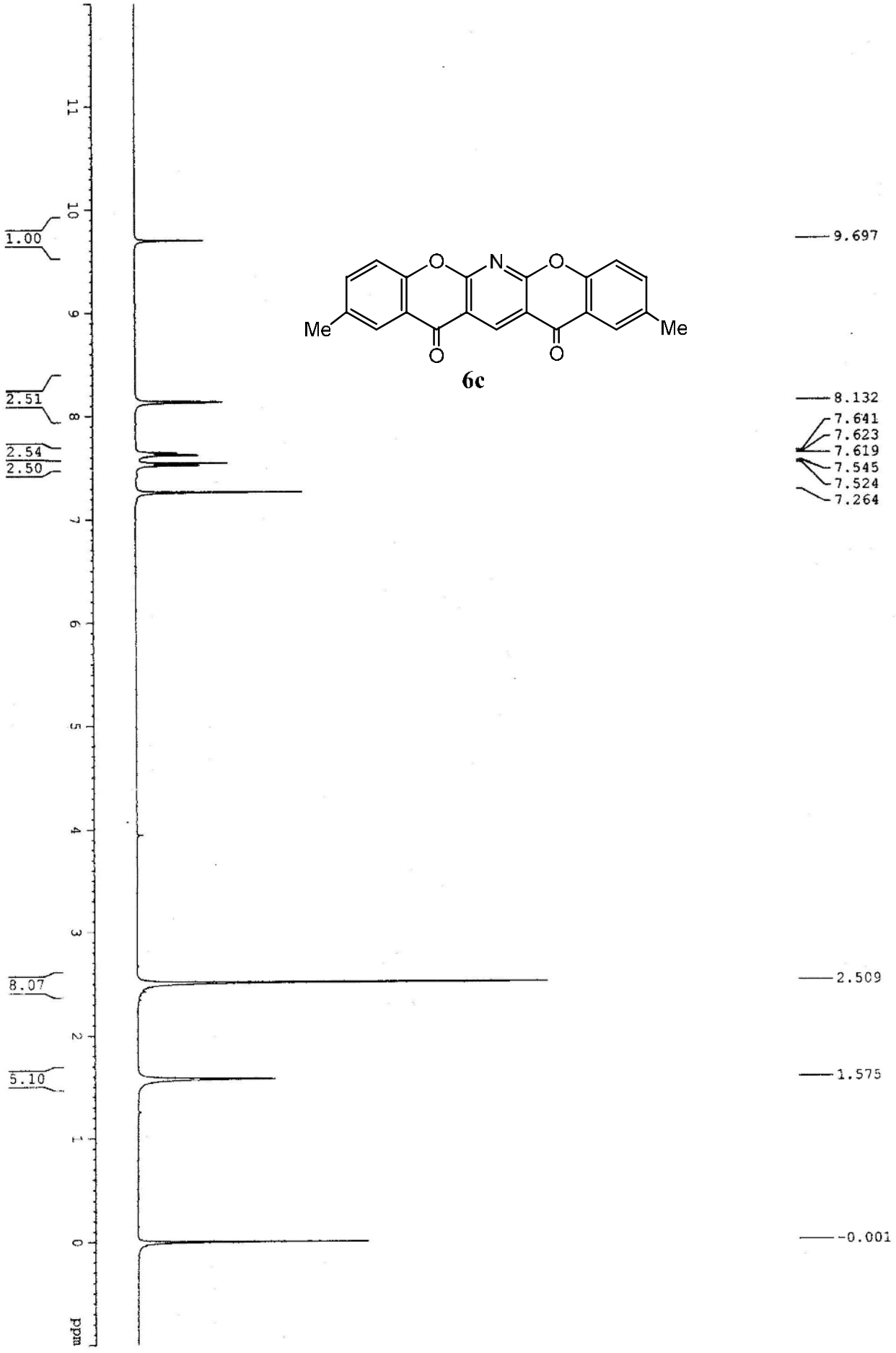
155.36
153.55
141.23
137.23
136.05
135.68
127.02
126.42
125.55
121.52
121.13
118.52
118.28
115.16
115.04
77.34
77.23
77.02
76.70
20.90
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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ppm
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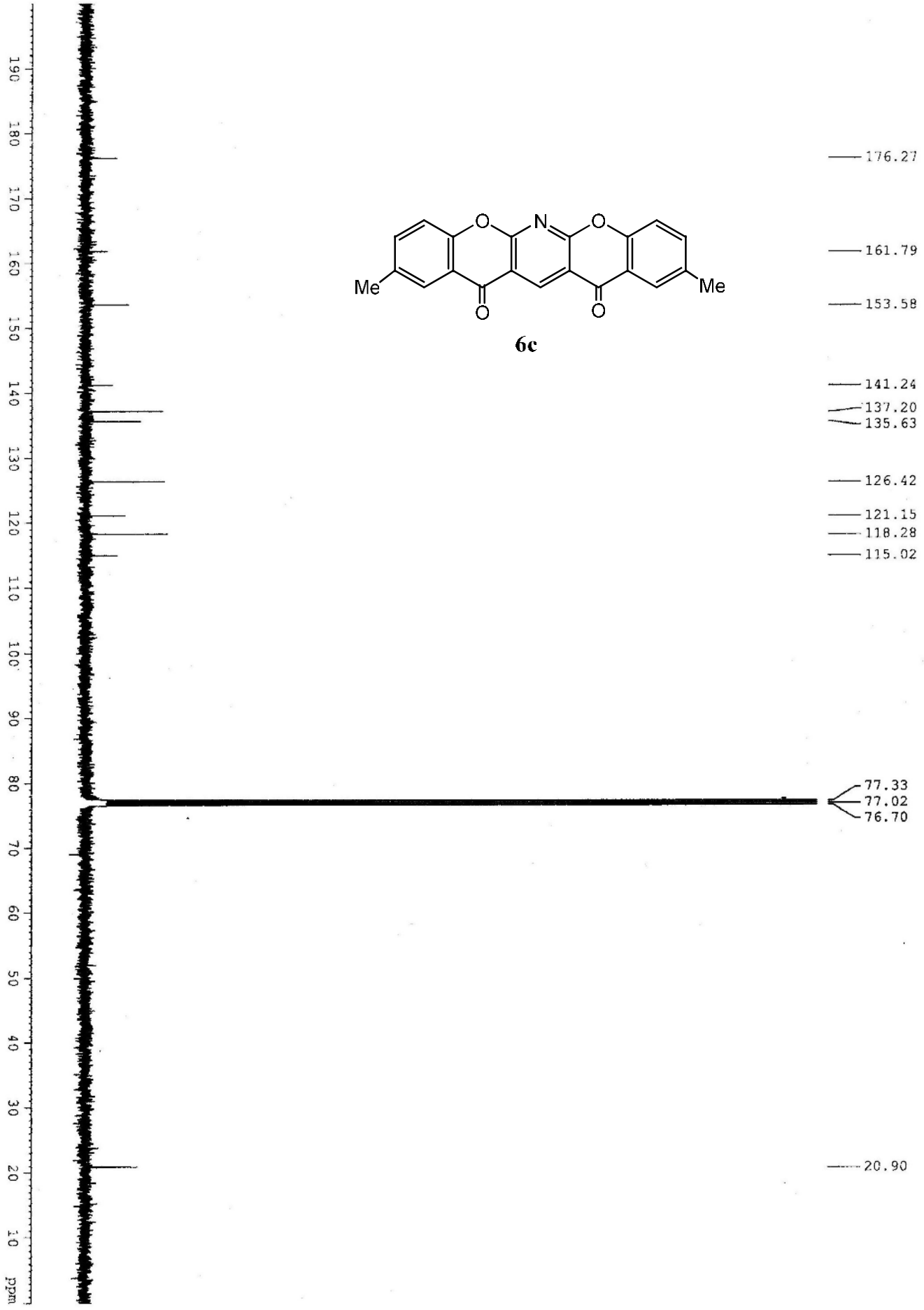
7.524
7.264
2.509
1.575
-0.001

O
N
O
Me
Me
O
O

6c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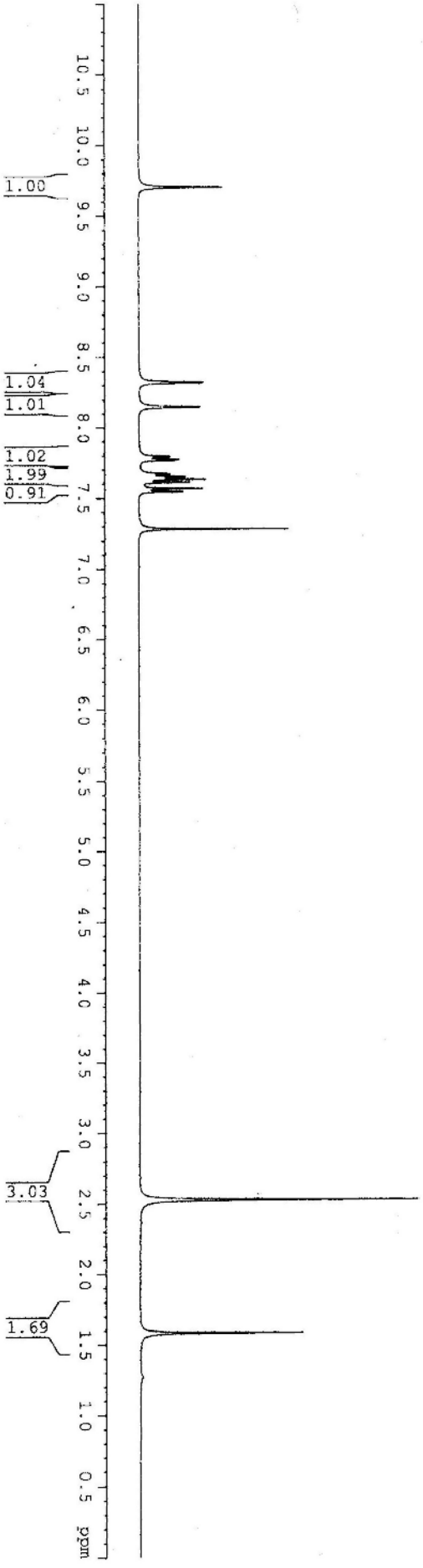
20.90
O
N
O
Me
Me
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

6c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8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
2.5
2.0
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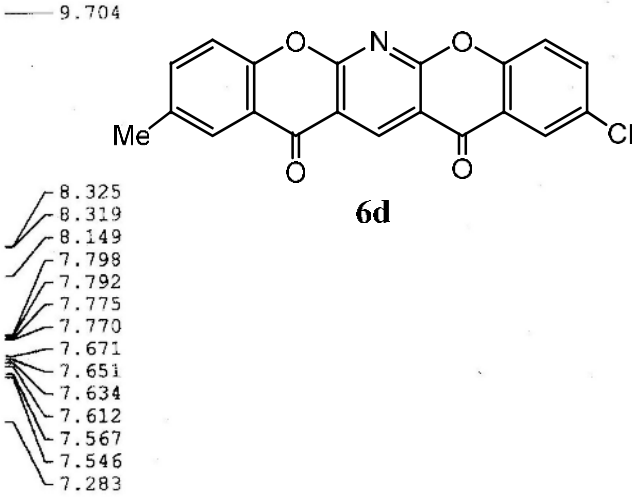
1.0
0.5
ppm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7.546
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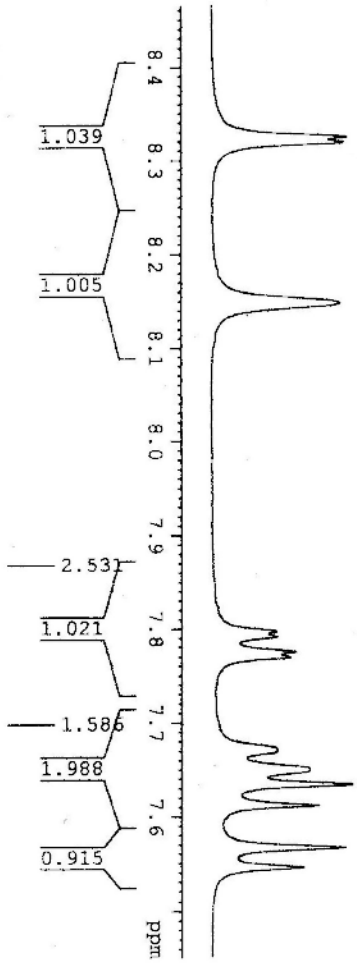
O
N
O
Me
Cl
O
O

6d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7.8
7.7
7.6
ppm


8.325
8.319
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7.651
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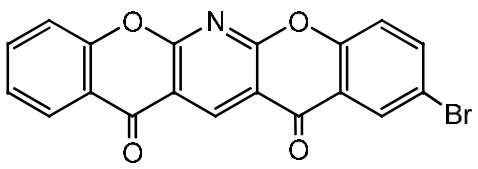
7.612
7.567
7.546


O
N
O
Br
O
O

6e

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1.03
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8.494
8.488
8.391
8.387
8.371
8.368
7.947
7.941
7.925
7.919
7.891
7.887
7.873
7.870
7.852
7.848
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7.663
7.582
7.560
7.537
7.519
7.284
1.595
ppm


1.00
1.00
1.00
1.02
1.04
1.99
3.10
5.24
9.710
8.490
8.484
8.155
8.152
7.940
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7.912
7.679
7.674
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7.653
7.575
7.553
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Br
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N
O
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O
ppm

6f

5. Excitation spectra of compounds 6a, 6c, 6d and 6f

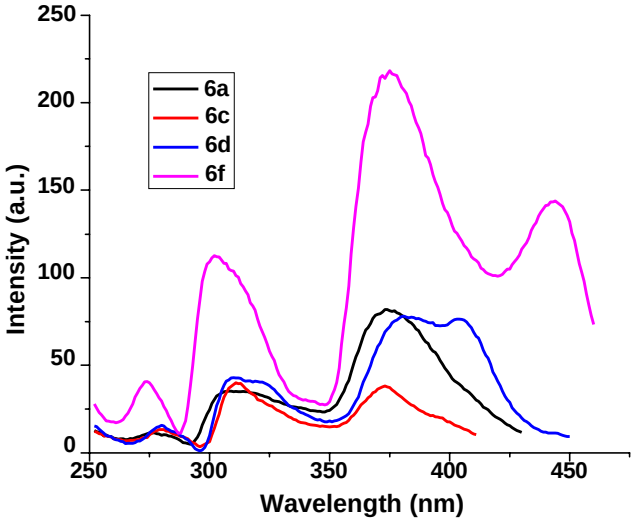

Fig. A. Excitation spectra of compounds **6a-f** in THF

6. Absorption spectra of compound 6f in three different solvents

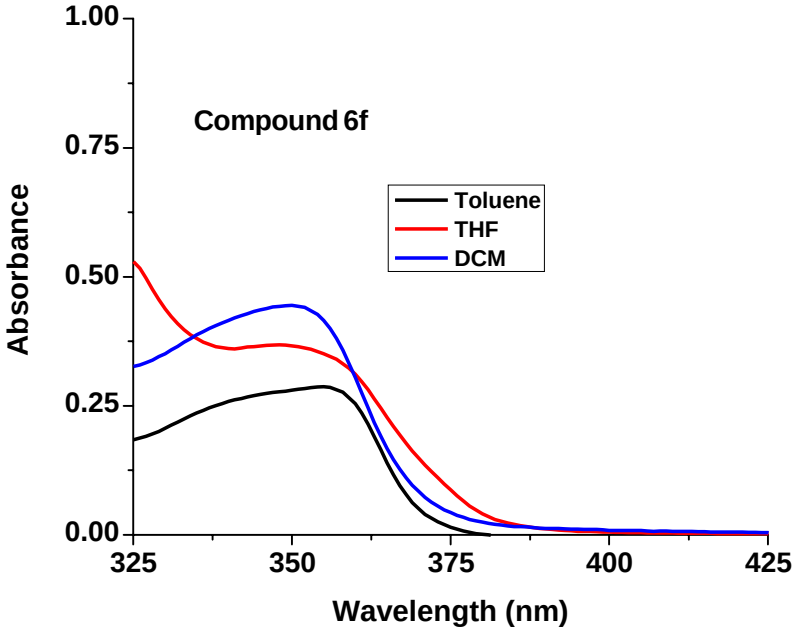

Fig. B. Absorption spectrum of compound **6f** in three different solvents

7. Emission spectra of compound 6f in three different solvents.

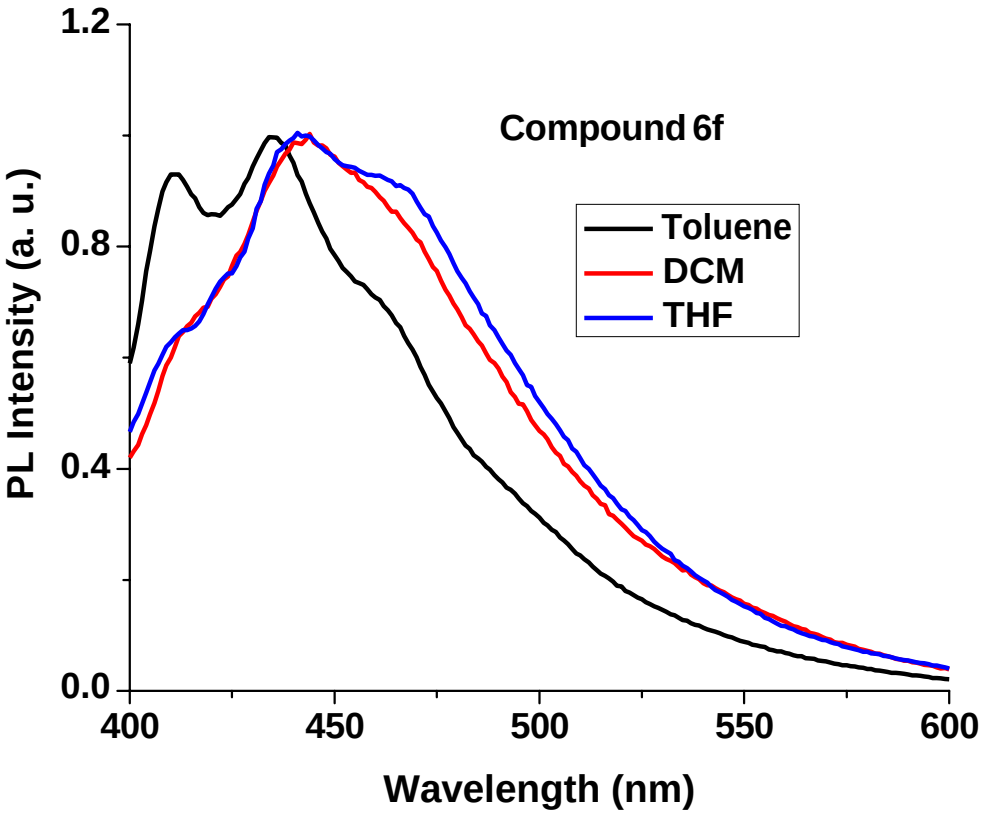

Fig. C. Normalized emission spectra of compound **6f** in three different solvents.