Supporting Information Ref: B714612D Chemical Communications.

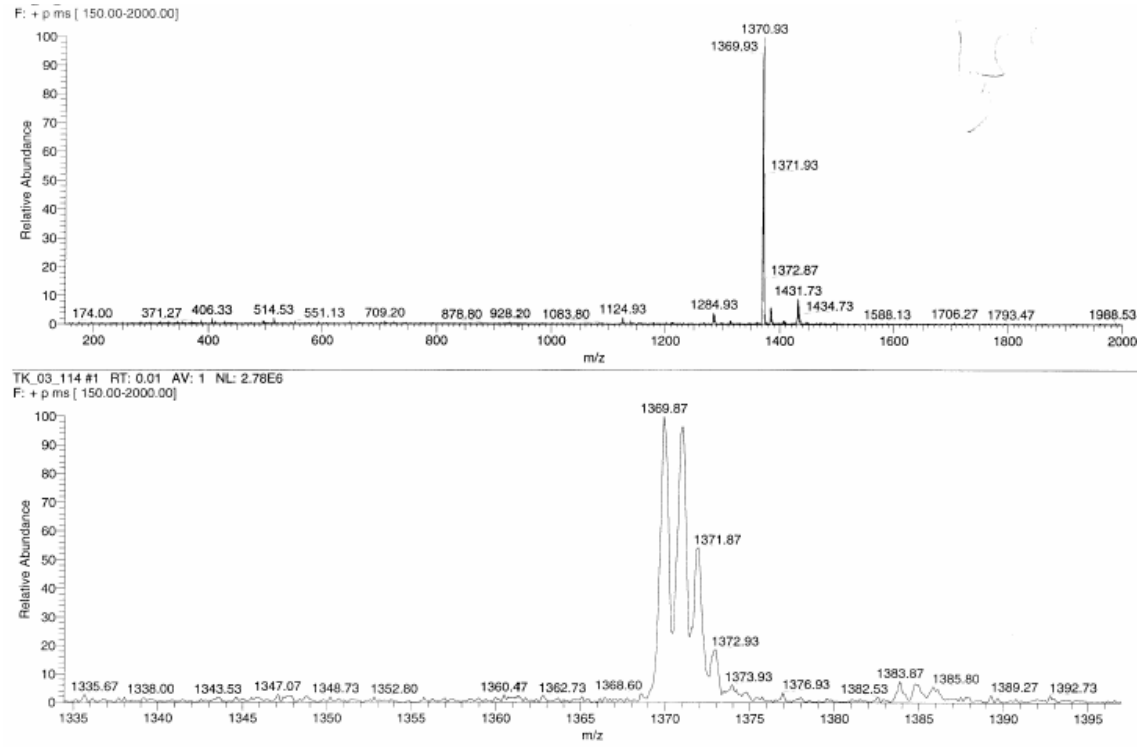
A Strategy for stepwise Ring Annulation of all Four Pyrrolic Rings of a Porphyrin

Tony Khoury and Maxwell Crossley

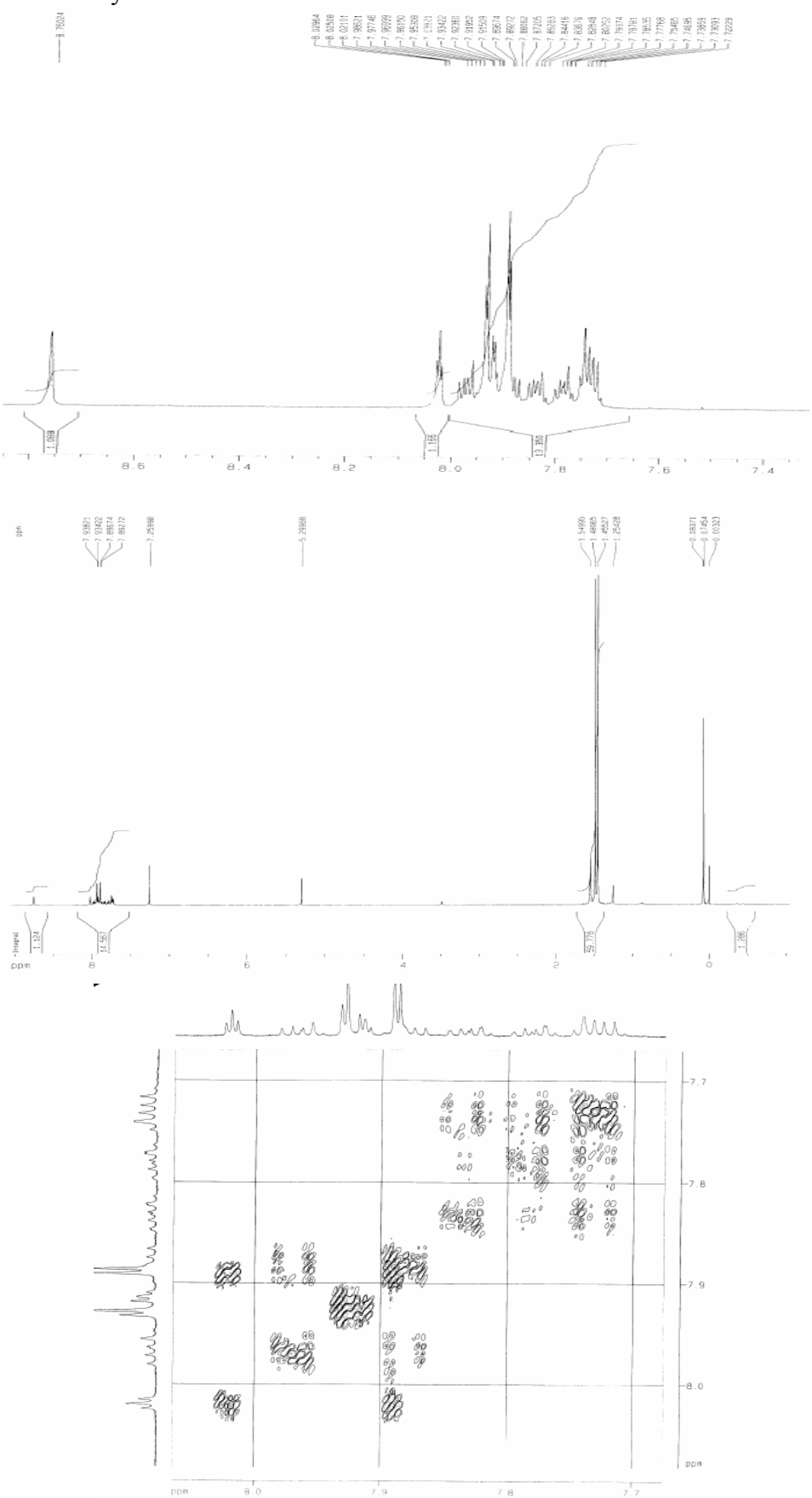
Selected Spectra:

I. Trisquinoxalinoporphyrin 1

ESI

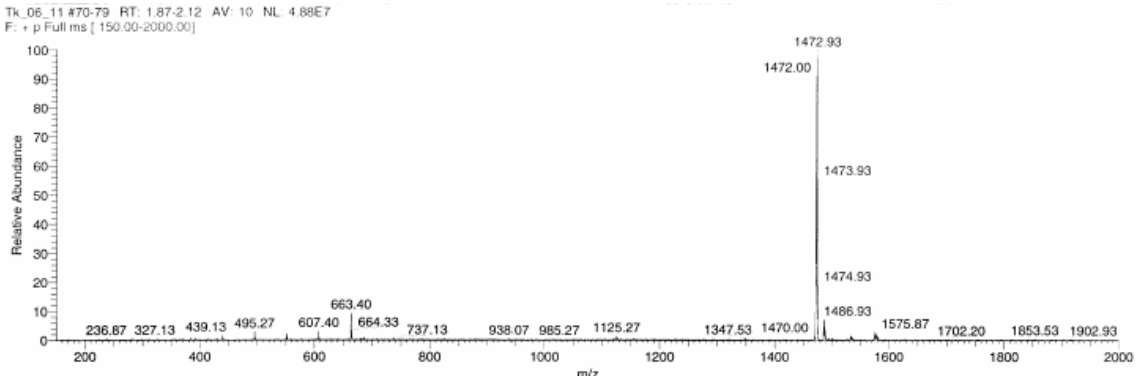


^{1}H NMR and cosy of **1**

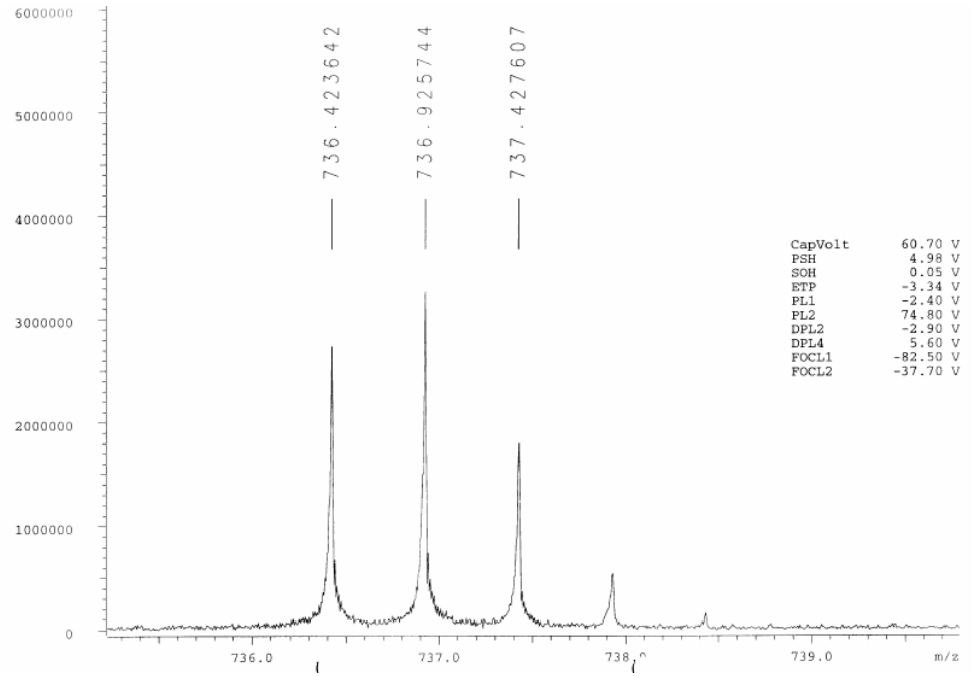


II. Tetrakisquinoxalinoporphyrin 2

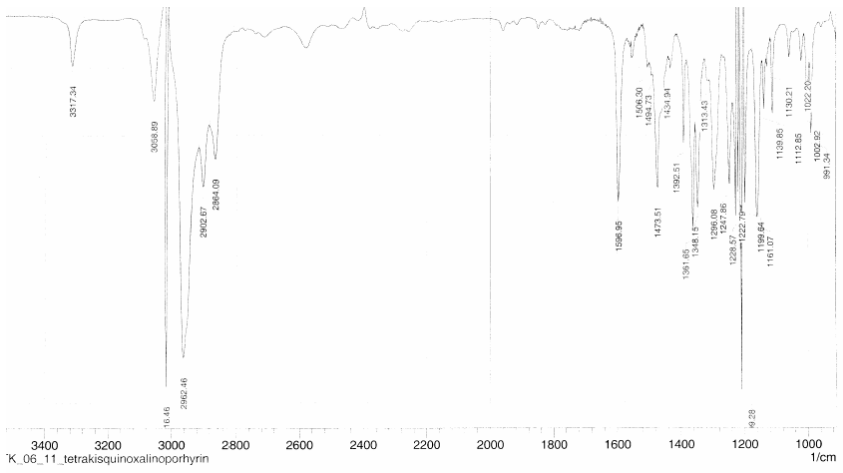
ESI



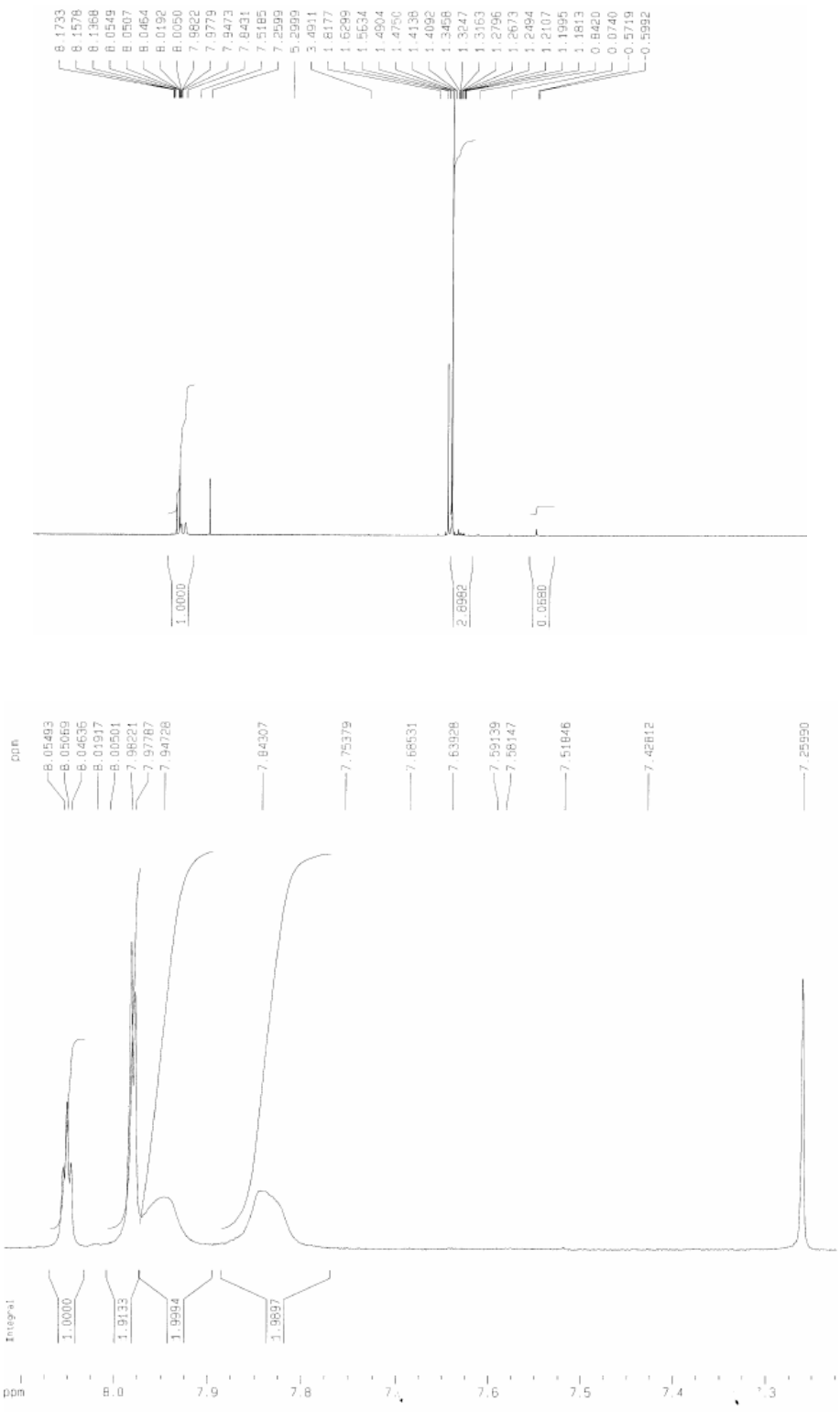
ICR



IR



^{1}H NMR of **2**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8.1368
8.0549
8.0507
8.0464
8.0192
8.0050
7.9822
7.9779
7.9473
7.8431
7.5185
7.2599
5.2999
3.4911
1.8177
1.6299
1.5634
1.4904
1.4750
1.4138
1.4092
1.3458
1.3247
1.3163
1.2796
1.2673
1.2494
1.2107
1.1995
1.1813
0.8420
0.0740
-0.5719
-0.5992
1.0000
2.8982
0.0680
ppm
8.0549
8.0507
8.0464
8.0192
8.0050
7.9822
7.9779
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7.5914
7.5814
7.5184
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7.2599
Integral
1.0000
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1.9994
1.9897
ppm
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7.8
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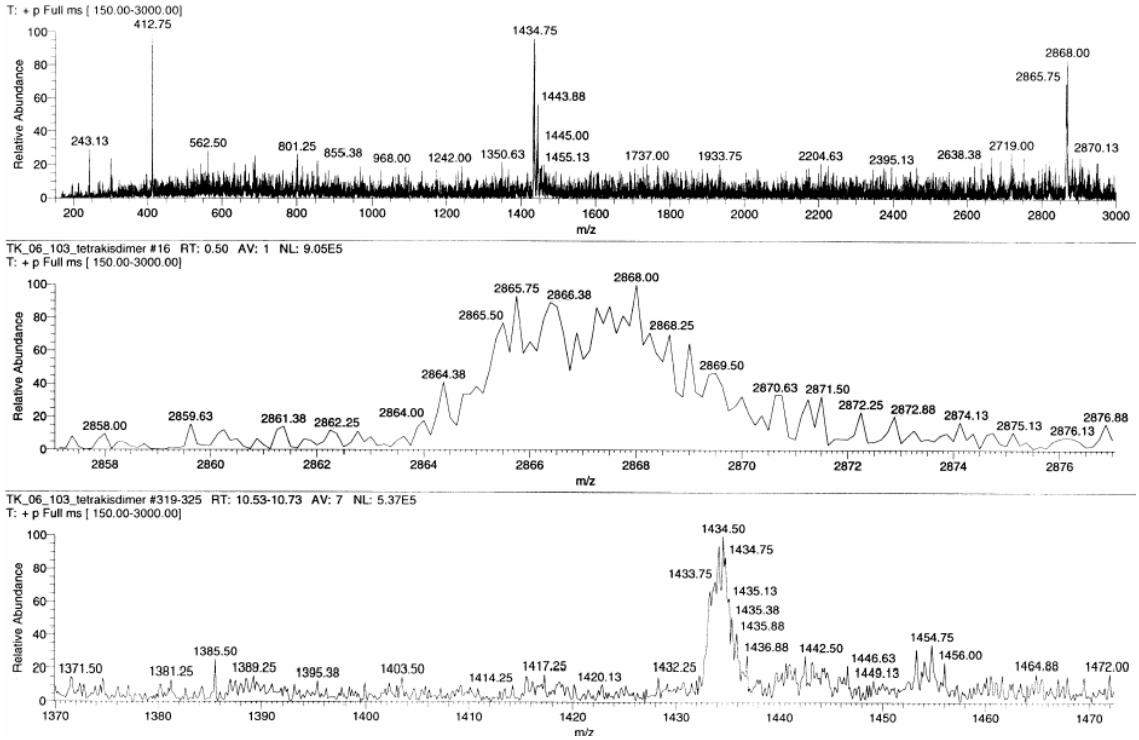
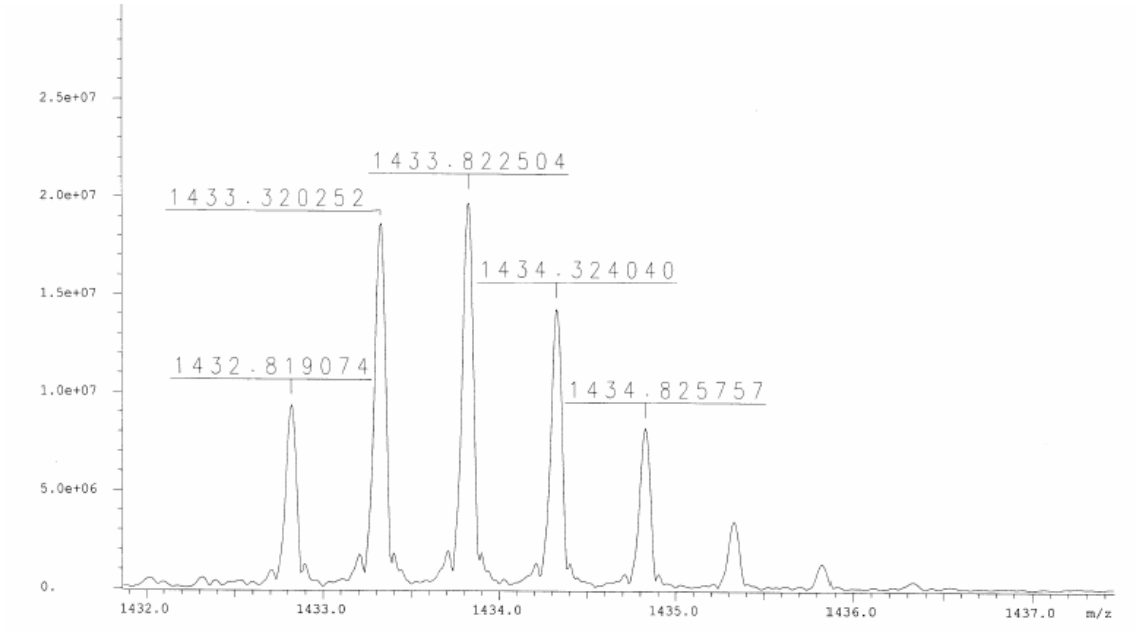
7.6
7.5
7.4
7.3

III- Bis-porphyrin 3

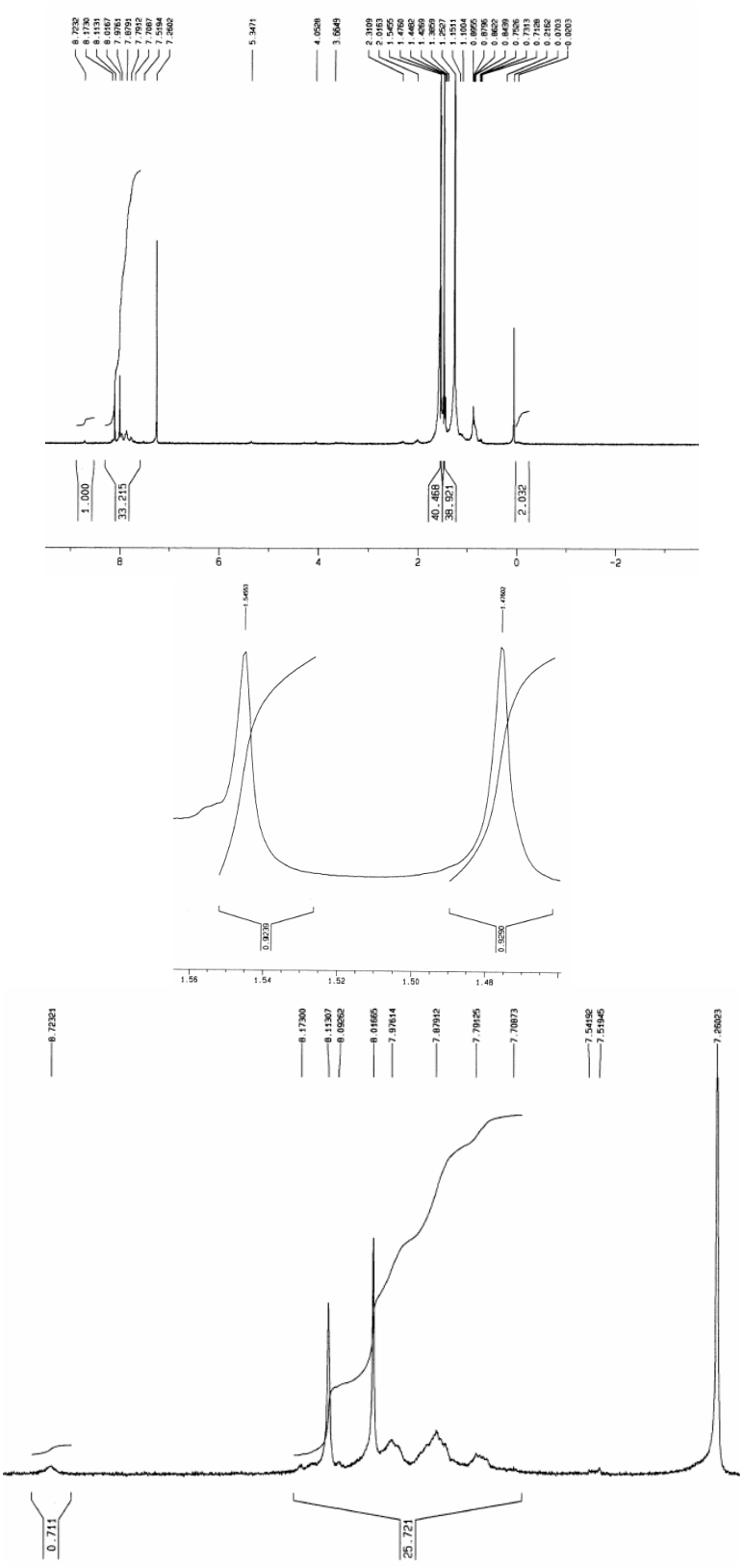
ESI



ICR

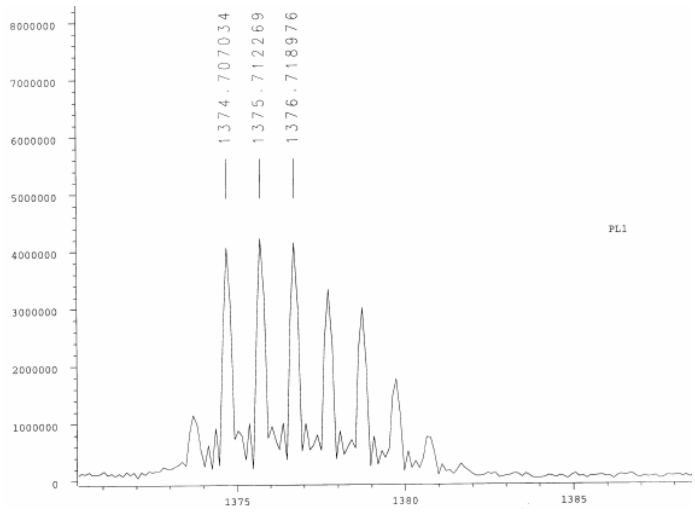


^{1}H NMR of **3**

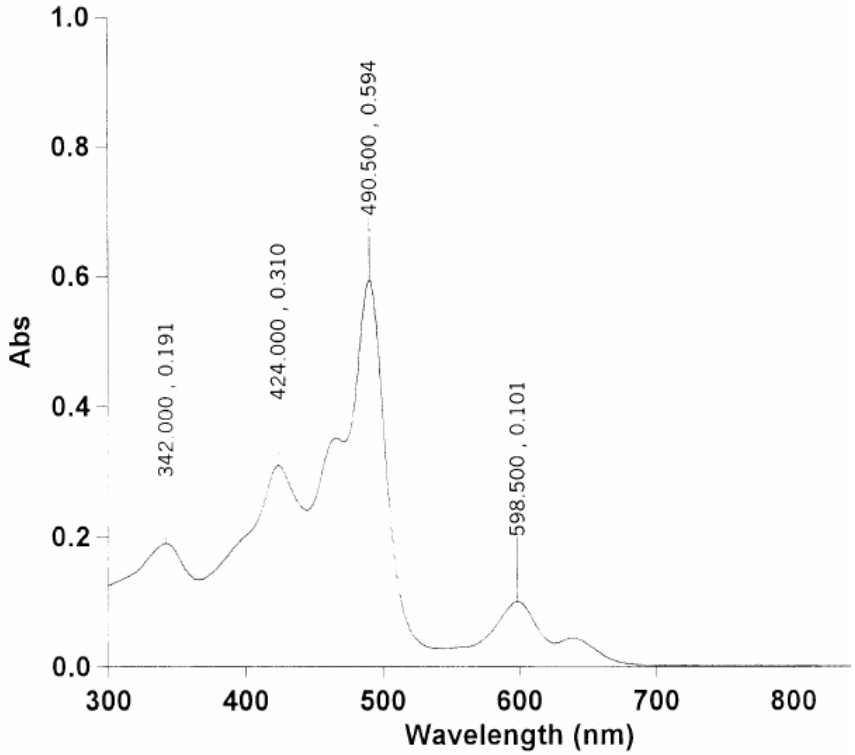


Compound corner zinc(II) nitro-bisquinoxalinoporphyrins 6

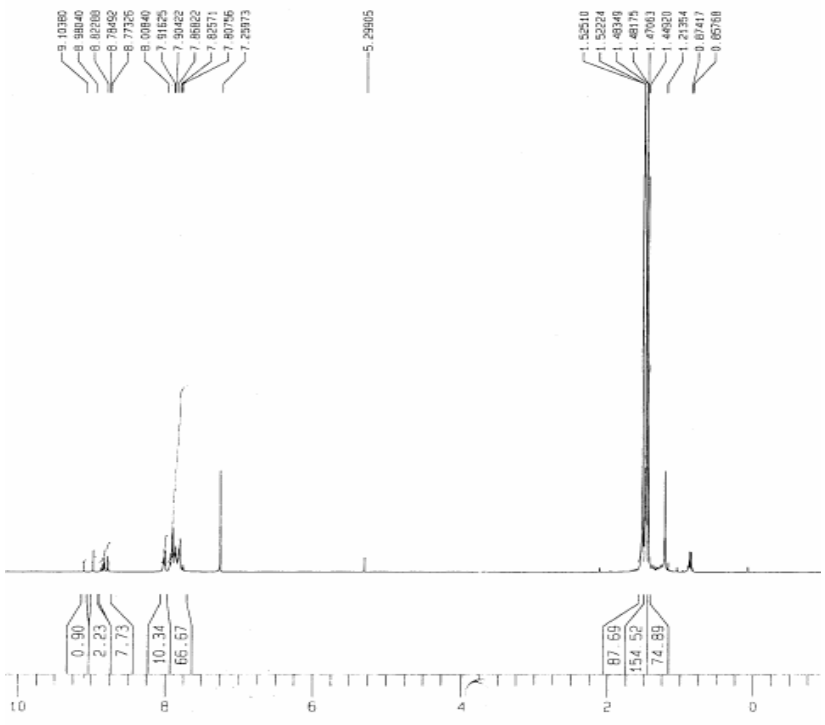
ICR



UV-Visible



^{1}H NMR of **6**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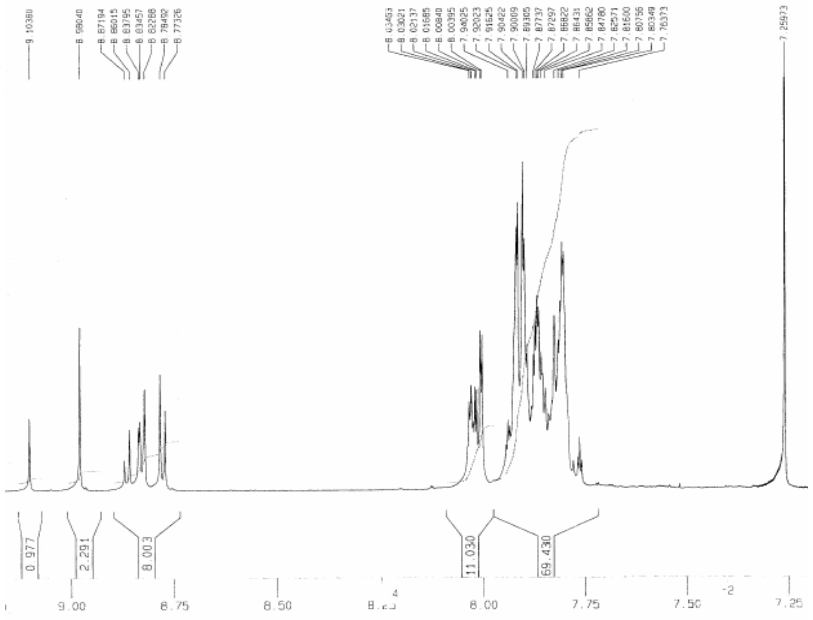
9.98840
8.82280
8.78492
8.77326
8.00840
7.91625
7.90462
7.86822
7.80571
7.80756
7.25973
5.29805
1.52510
1.53224
1.48349
1.48175
1.47063
1.44920
1.21354
0.87417
0.85768
0.90
2.23
7.73
10.34
66.67
87.69
154.52
74.89
10
8
6
4
2
0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8.99846
8.87194
8.86015
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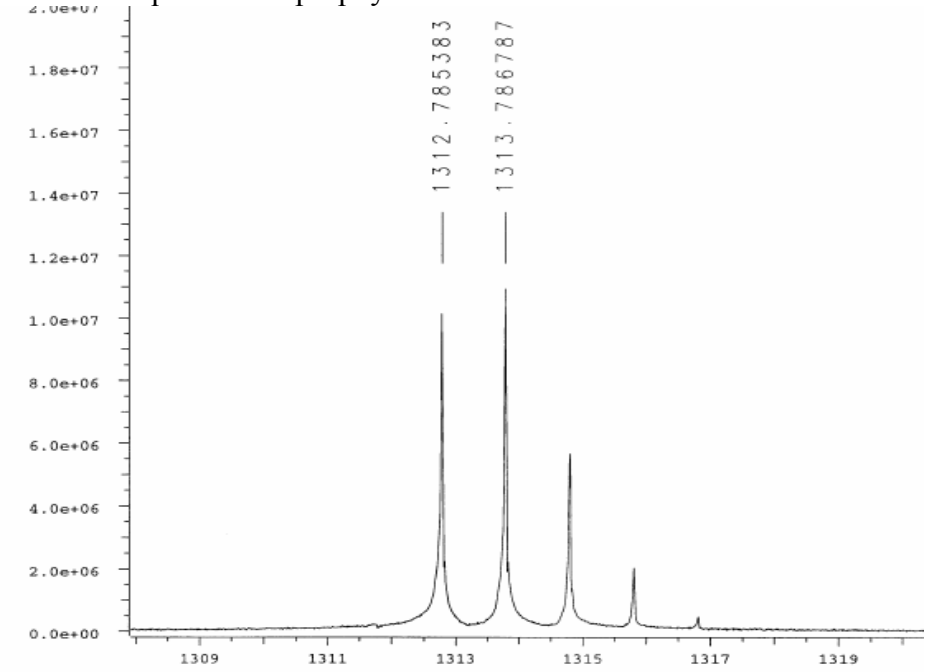
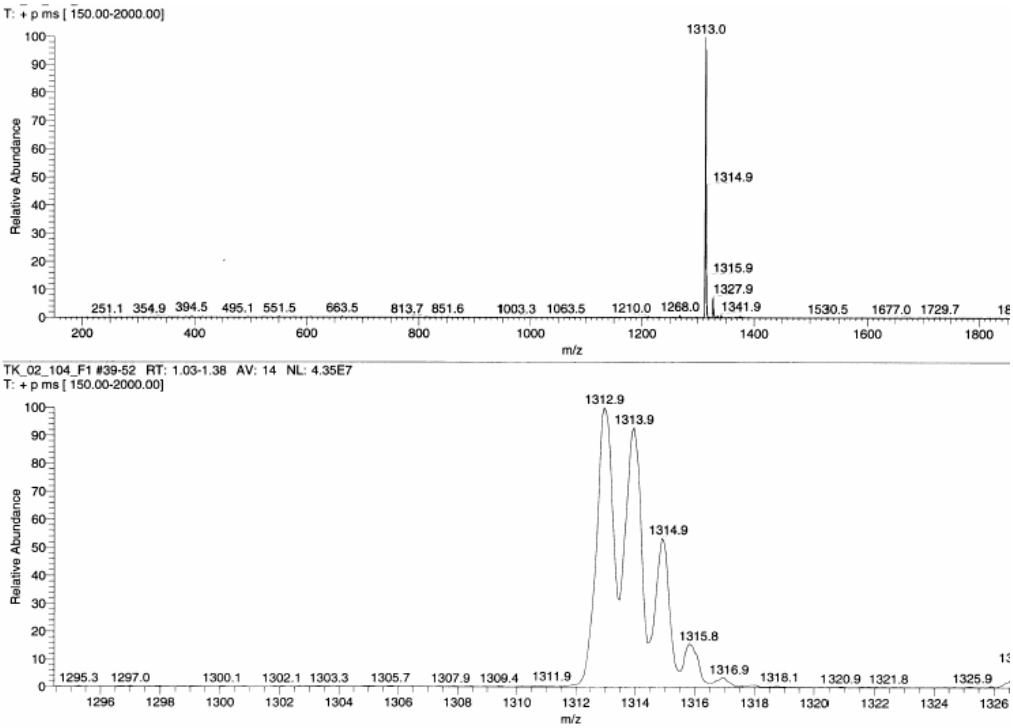
8.77326
8.03453
8.02931
8.02311
8.01585
8.00848
8.00395
7.94025
7.92023
7.91625
7.90462
7.90069
7.88765
7.87737
7.87297
7.86822
7.86431
7.85862
7.84780
7.82571
7.81600
7.80756
7.80348
7.76373
7.25973
0.977
2.291
8.003
11.030
69.430
9.00
8.75
8.50
8.00
7.75
7.50
7.25

V. Corner 12- and 13-Nitro-bisquinoxalinoporphyrins 7 {two isomers 7a and 7b)

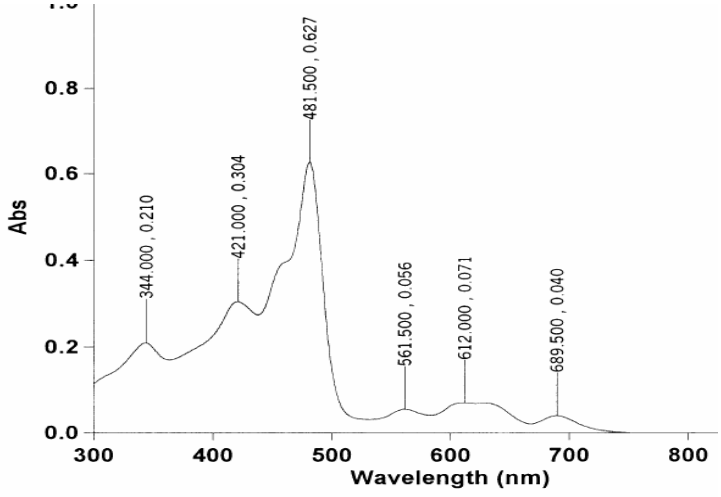
ICR of 13-nitro-bisquinoxalinoporphyrin **7b**



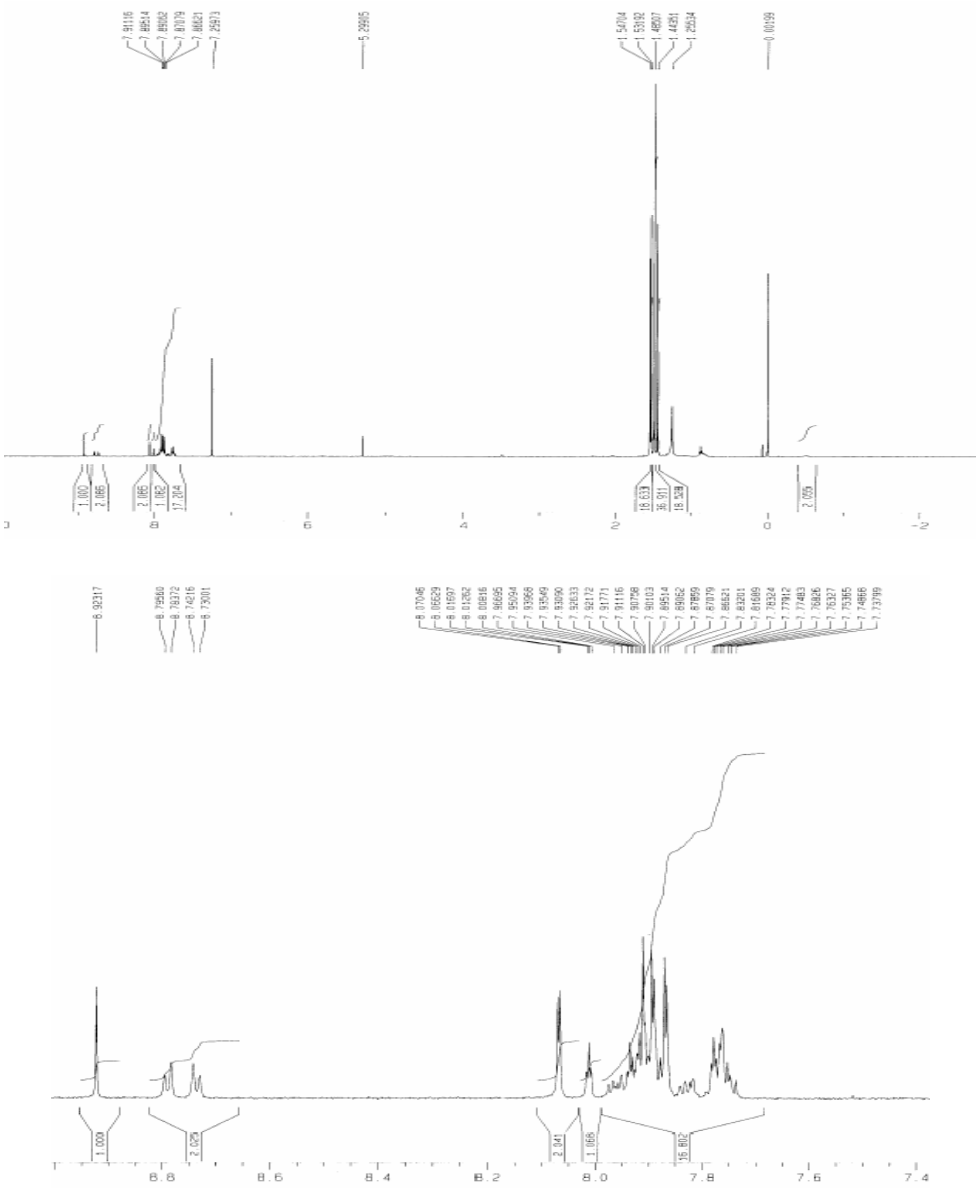
ESI



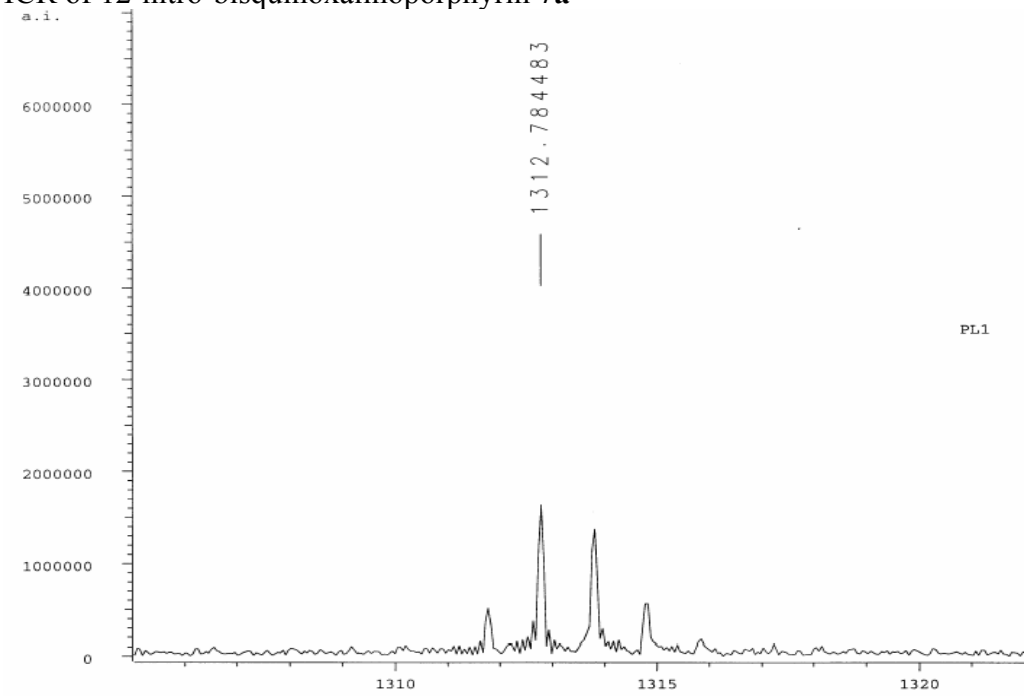
UV-visible of **7b**



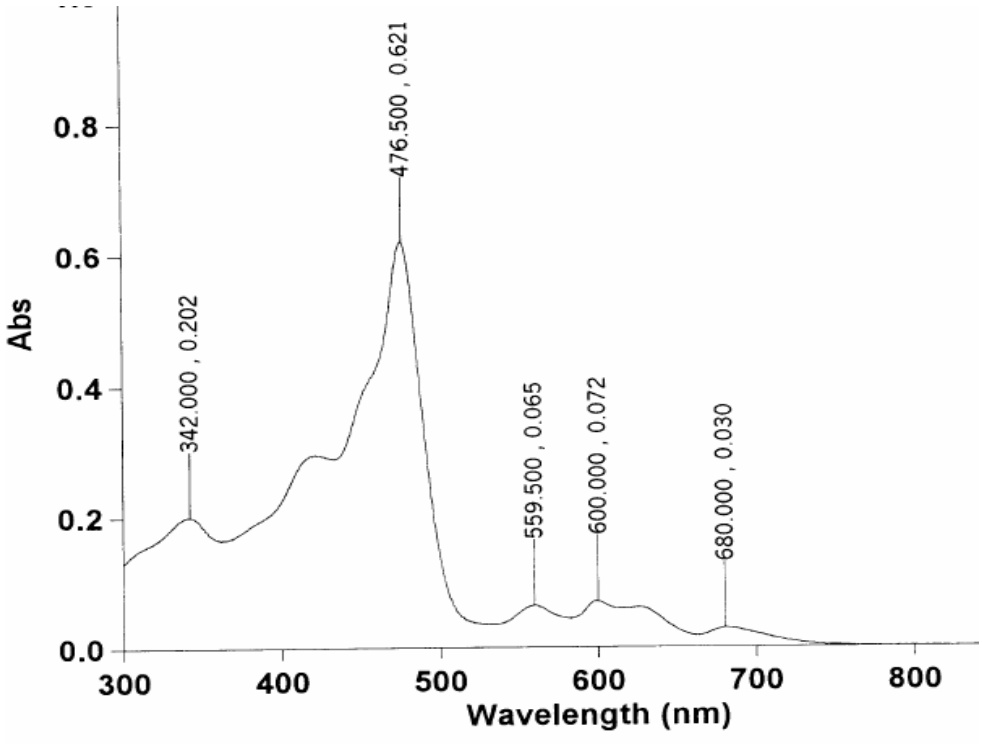
^{1}H NMR **7b**



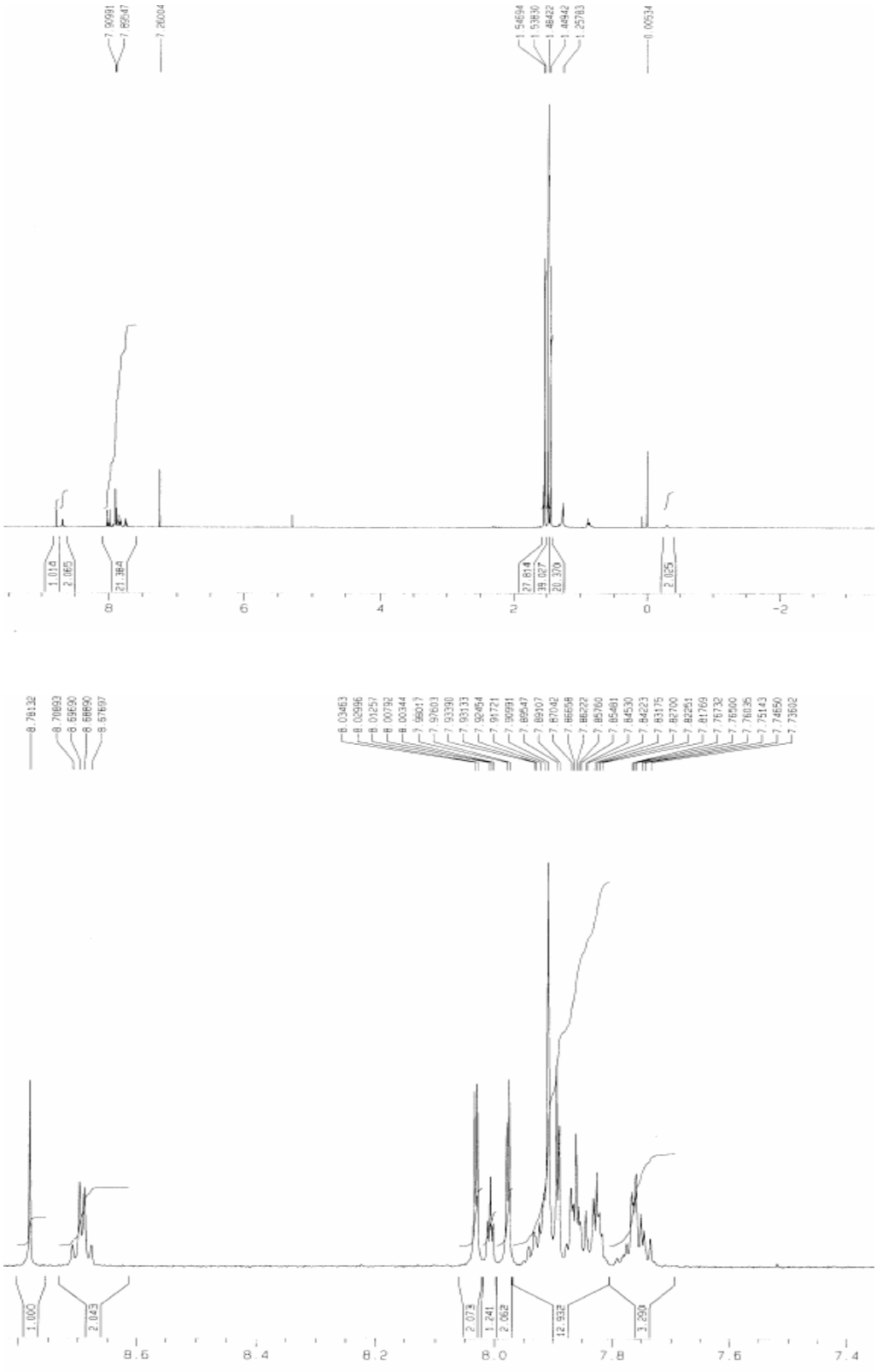
ICR of 12-nitro-bisquinoxalinoporphyrin **7a**



UV-visible

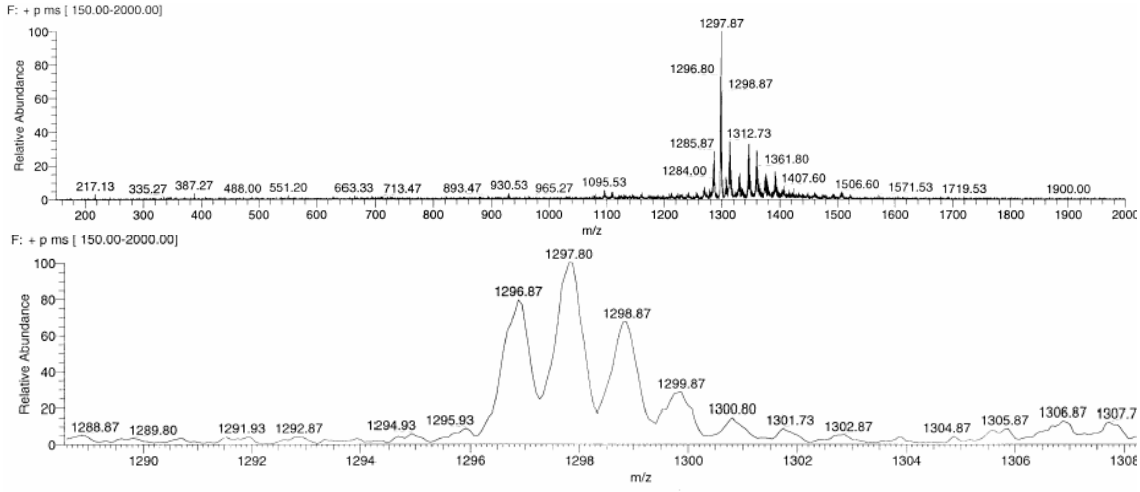


^{1}H NMR of **7a**

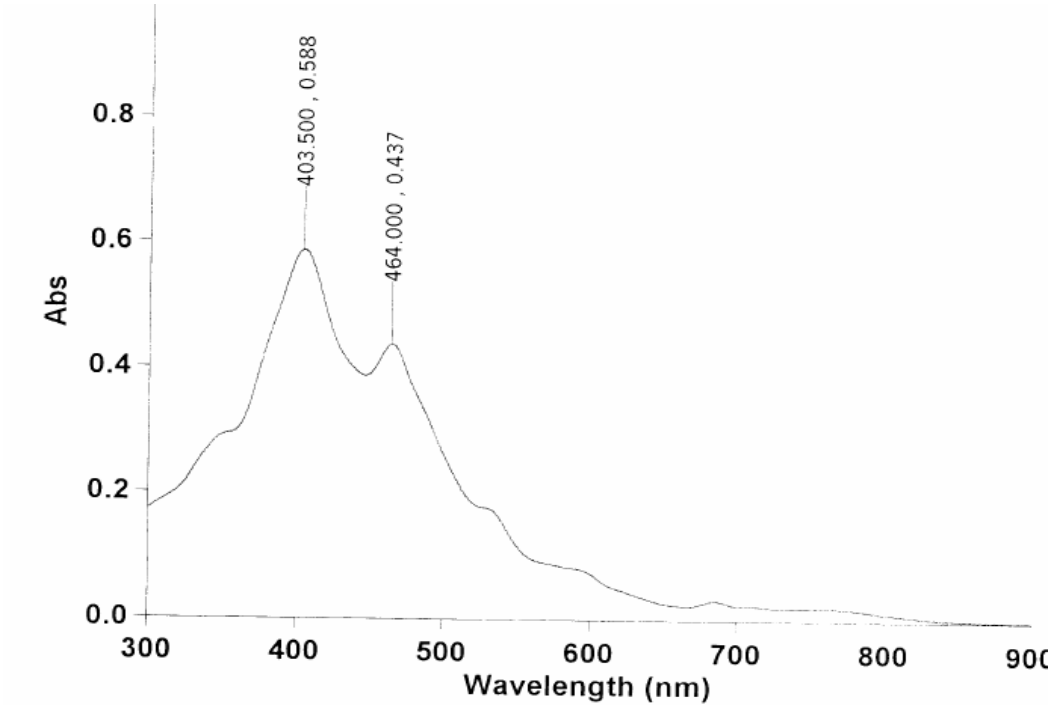


Corner bisquinoxalinoporphyrin-dione 9

ESI



UV-visible



HR ESI

```
LIST:  tk03116-c1                                10-Dec-03   Elapse:   00:25.6        1
Samp:  tk # ELE: c88 h97 n8 o2 na #                          Start :   09:48:43       8
Mode:  ESI +VE +HMR  ESCAN (EXP) UP HR NRM
Oper:  gm                                                    Inlet :
Limt: (     0 )     .     .     .     .     .
    : ( 133 ) C88.H97.13C.Na.O2.N8
Peak:  1000.00  mmu     R+D:  -2.0 > 60.0
Data:  CMASS : converted

                 112                          (ppm)
    Mass  Intensity      %RA   Flags Delta  R+D  Composition
1297.772        3631     6.48    #       1.5 44.5  C88.H97.O2.N8
                                            -2.0 45.0  C87.H96.13C.O2.N8
                                            -3.8 42.5  C85.H97.13C.Na.O2.N8
1298.776        4000     7.14    #       0.4 44.5  C87.H97.13C.O2.N8
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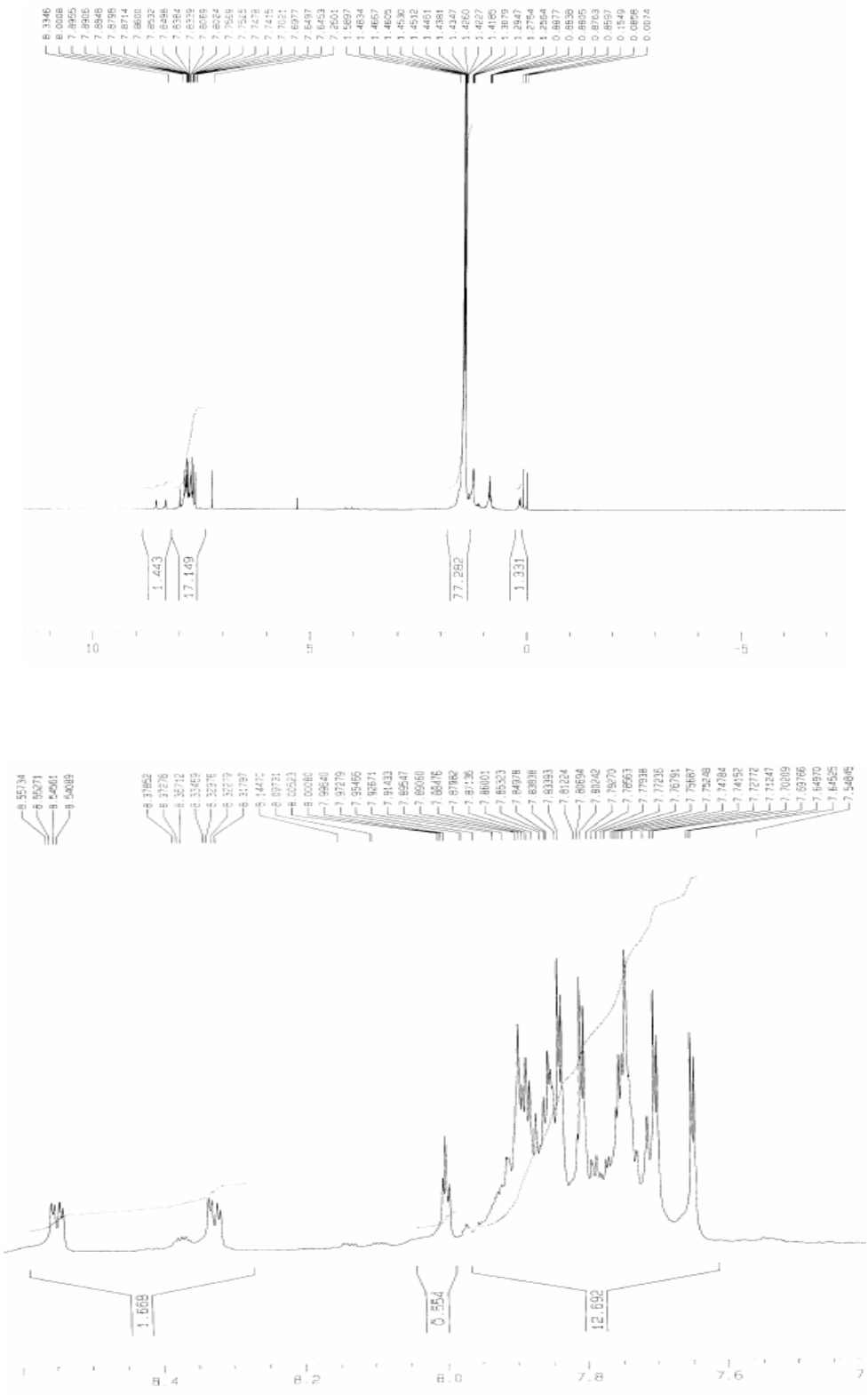
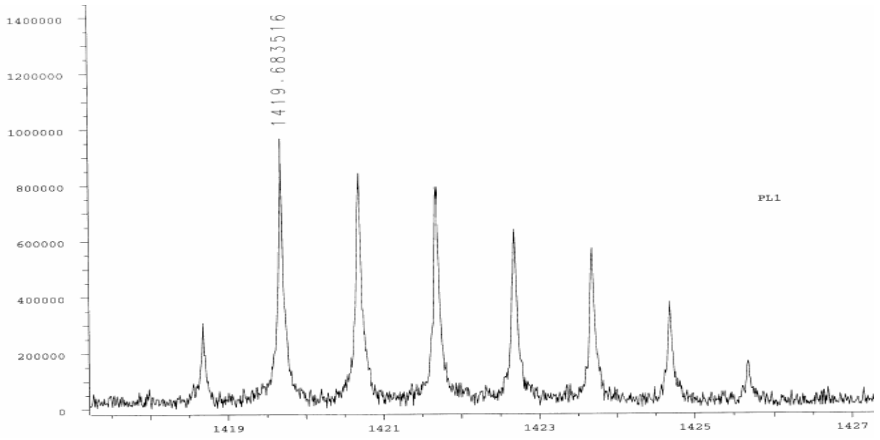
^{1}H NMR of **9**

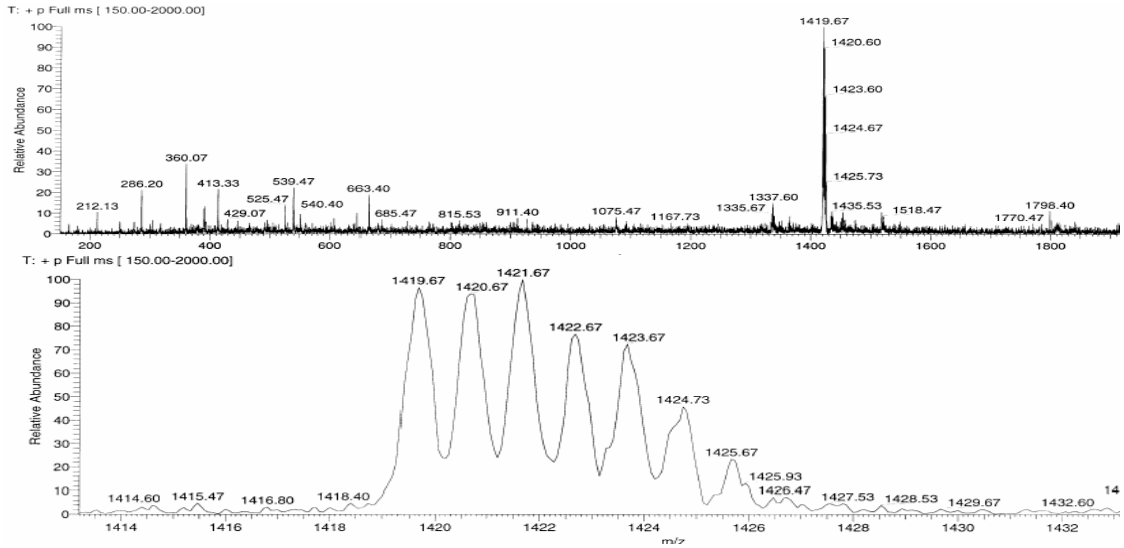


Corner Zinc(II) dinitro-bisquinoxalinoporphyrin 11

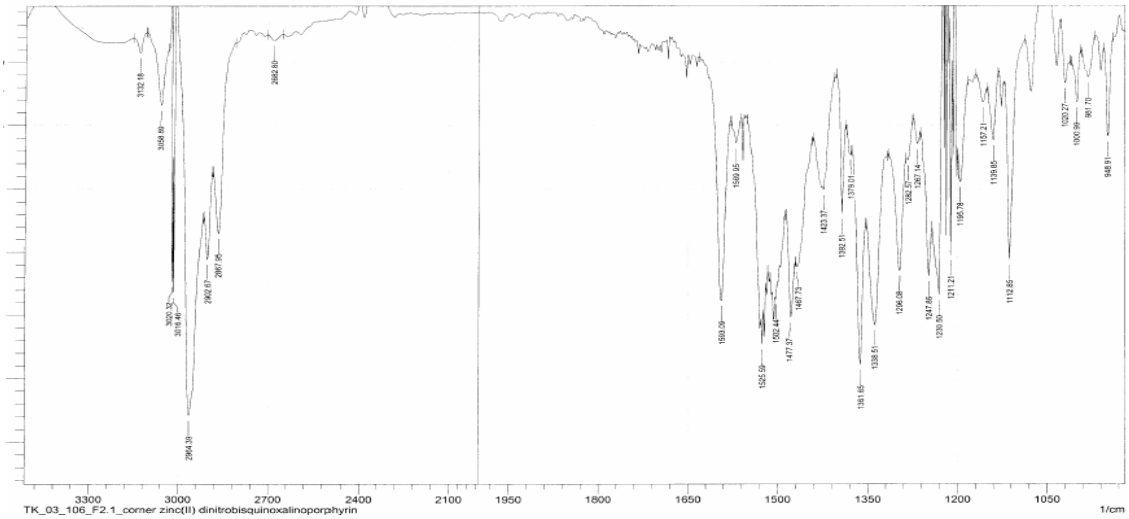
ICR



ESI

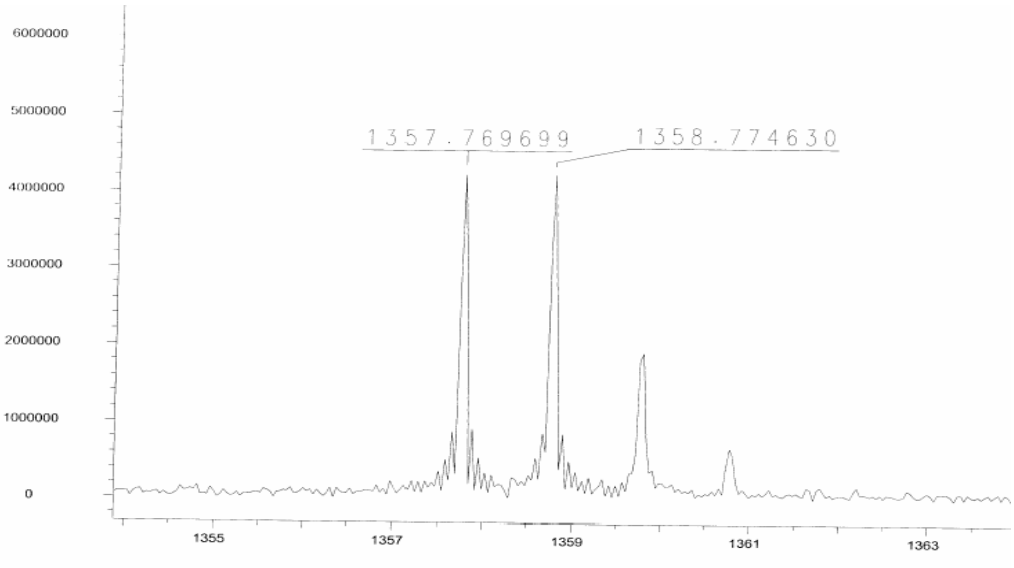


IR

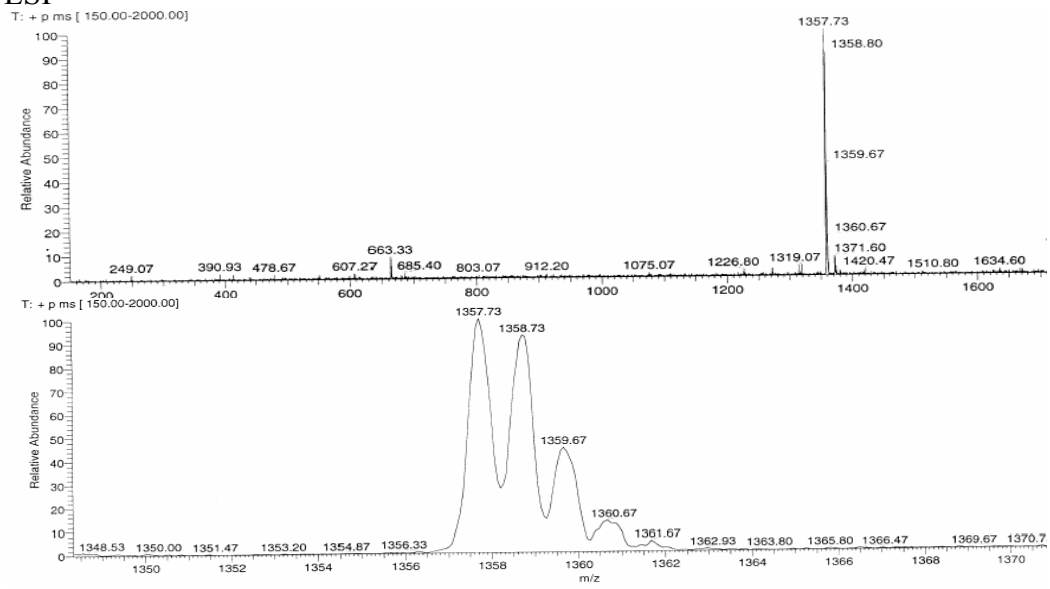


Corner dinitro-bisquinoxalinoporphyrin 12

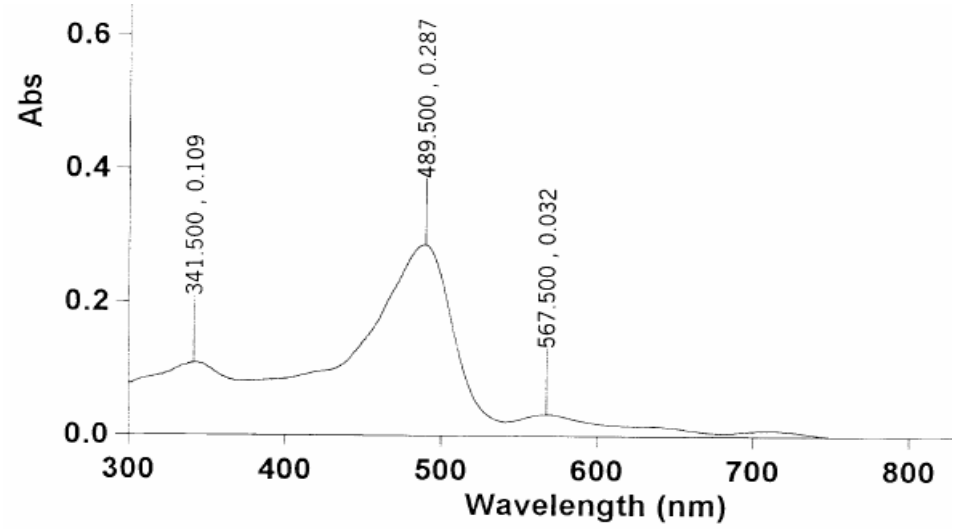
ICR



ESI

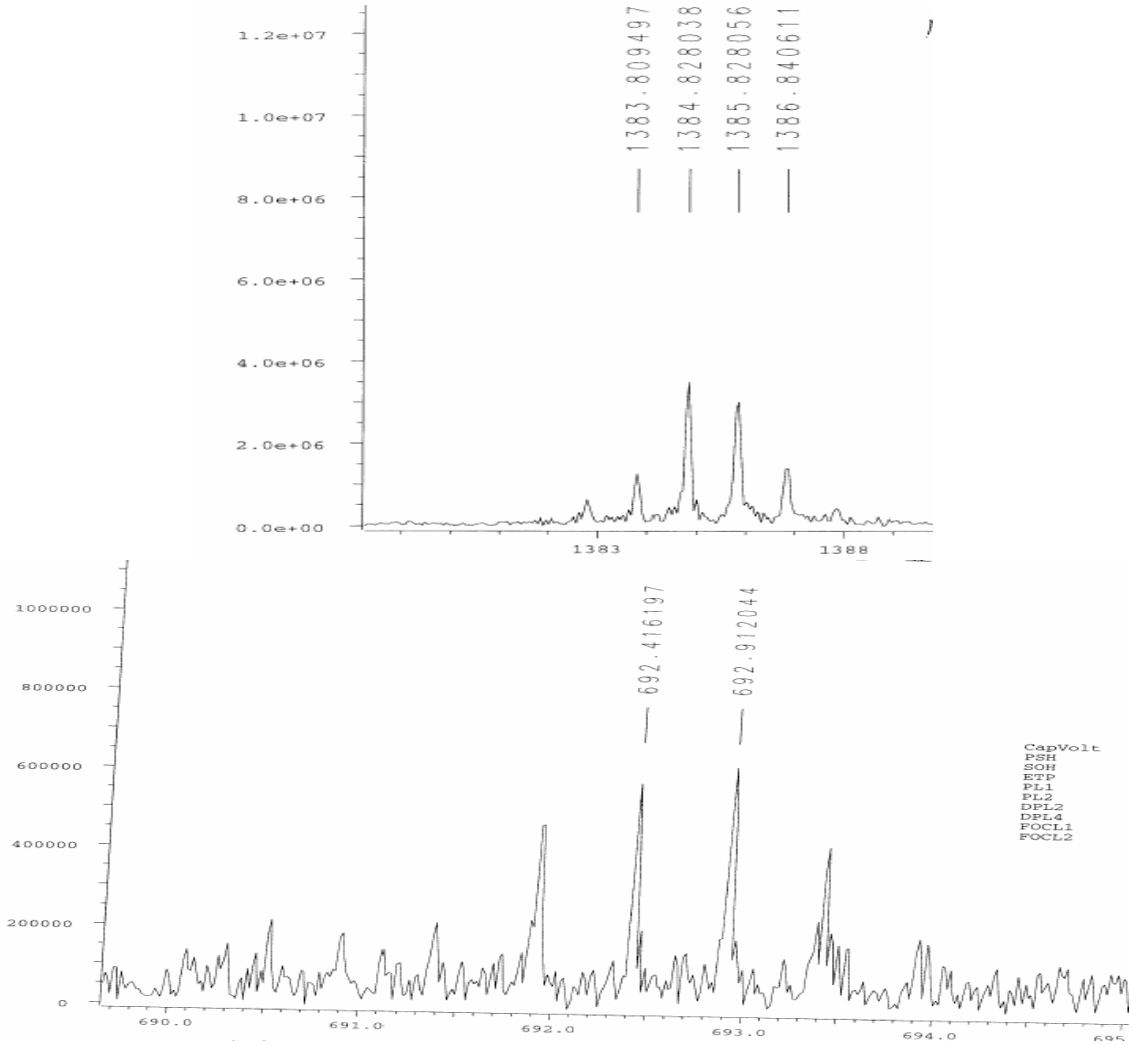


UV-Visible

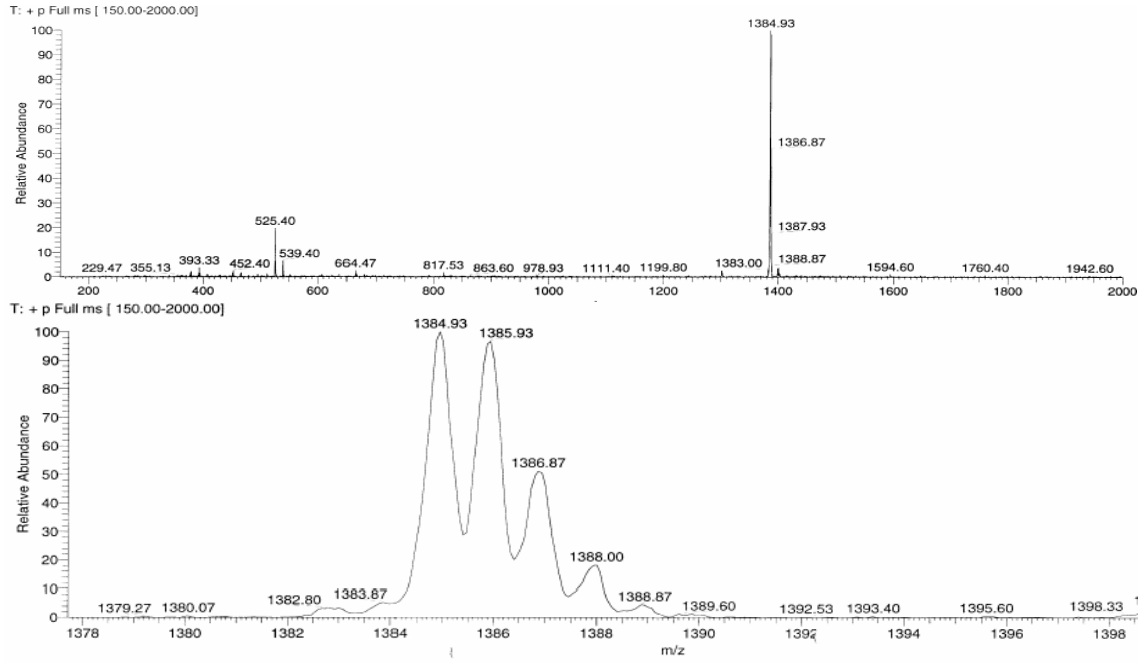


Amino-trisquinoxalinoporphyrin 15

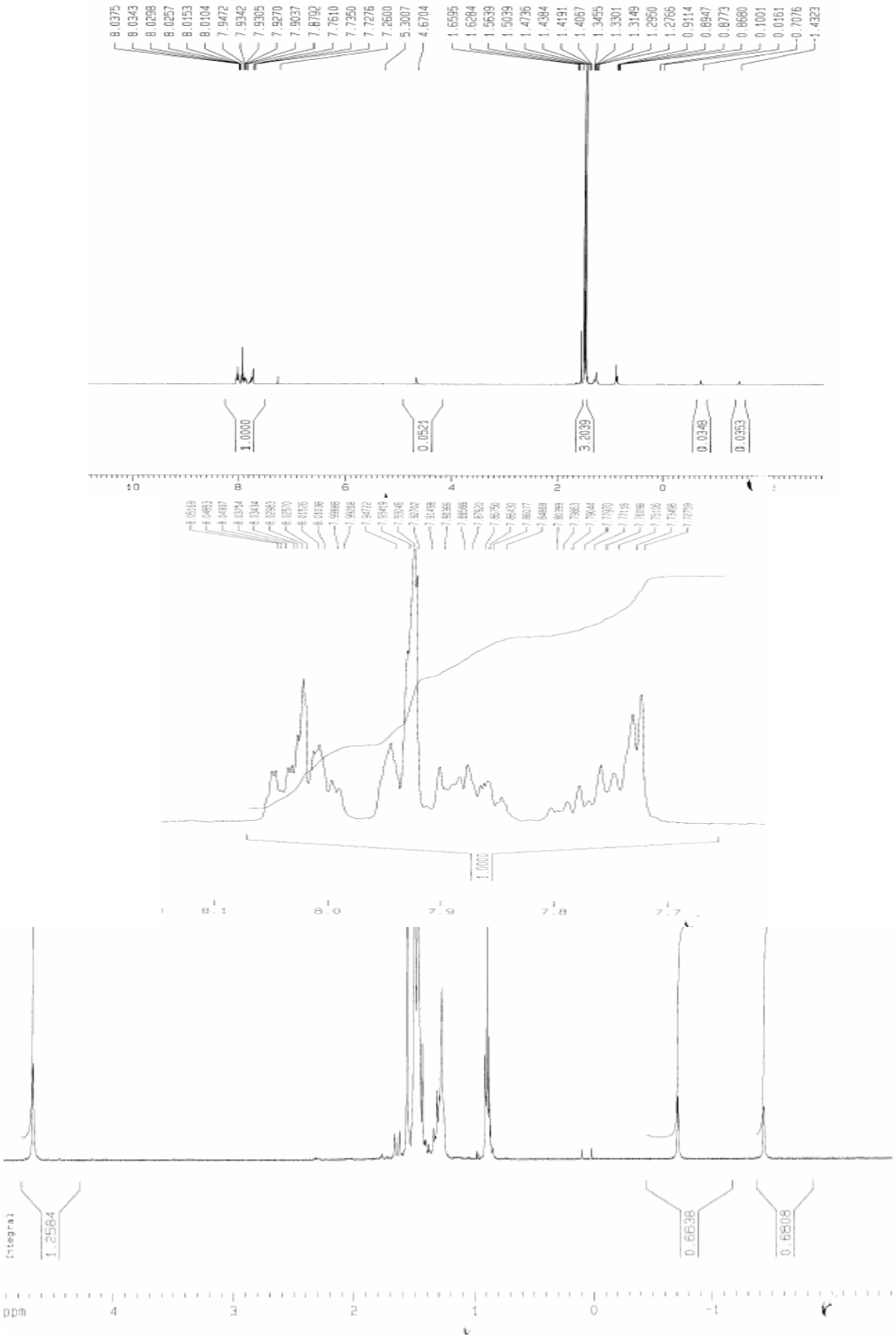
ICR



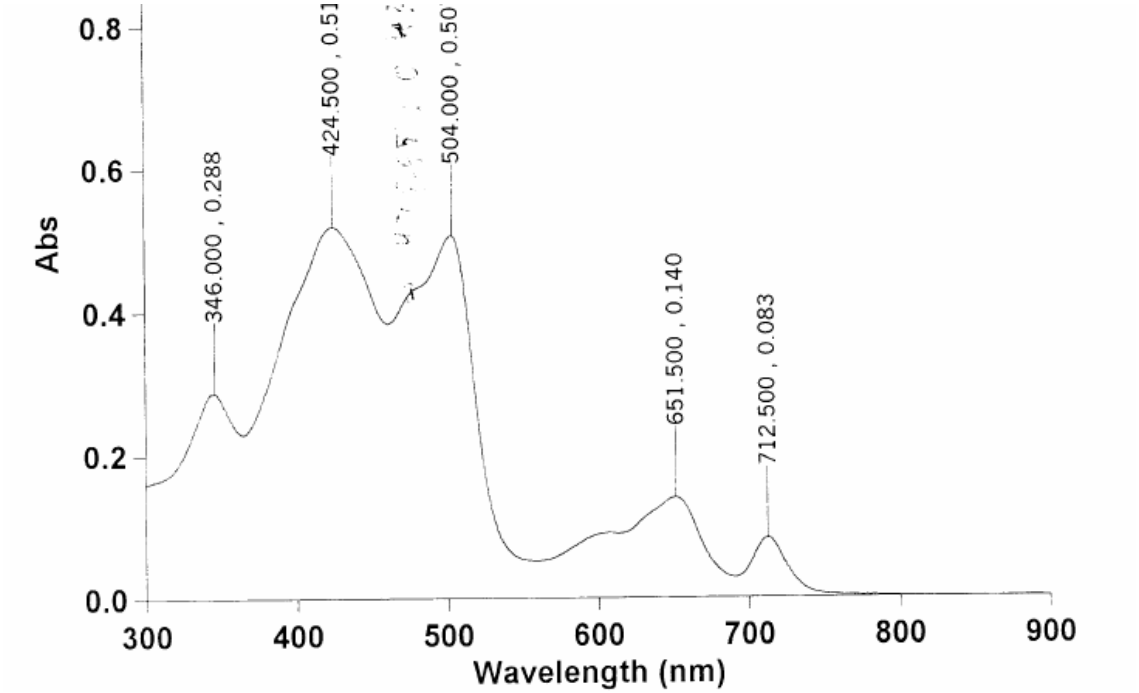
ESI



^{1}H NMR of **15**



UV-visible of **15**



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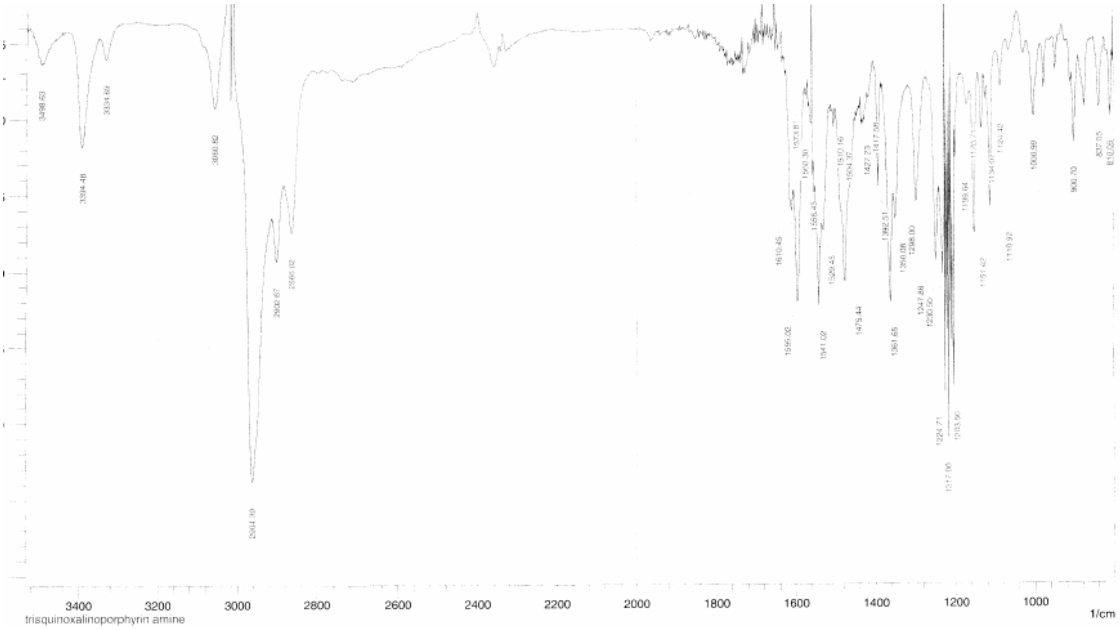
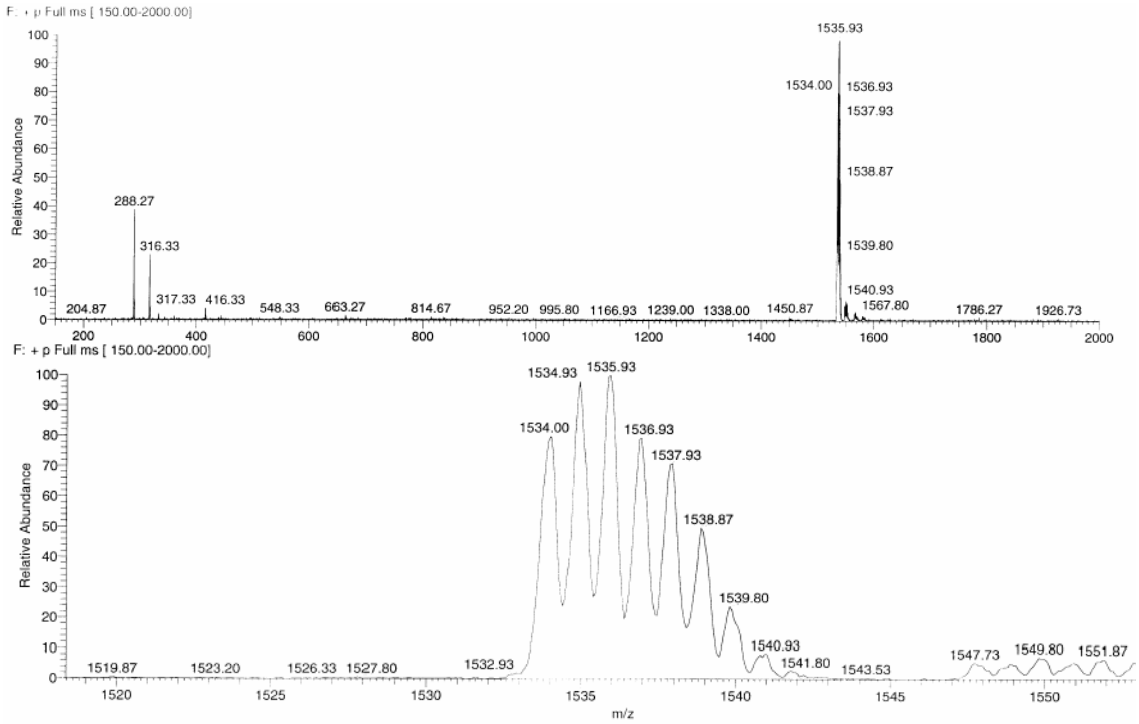
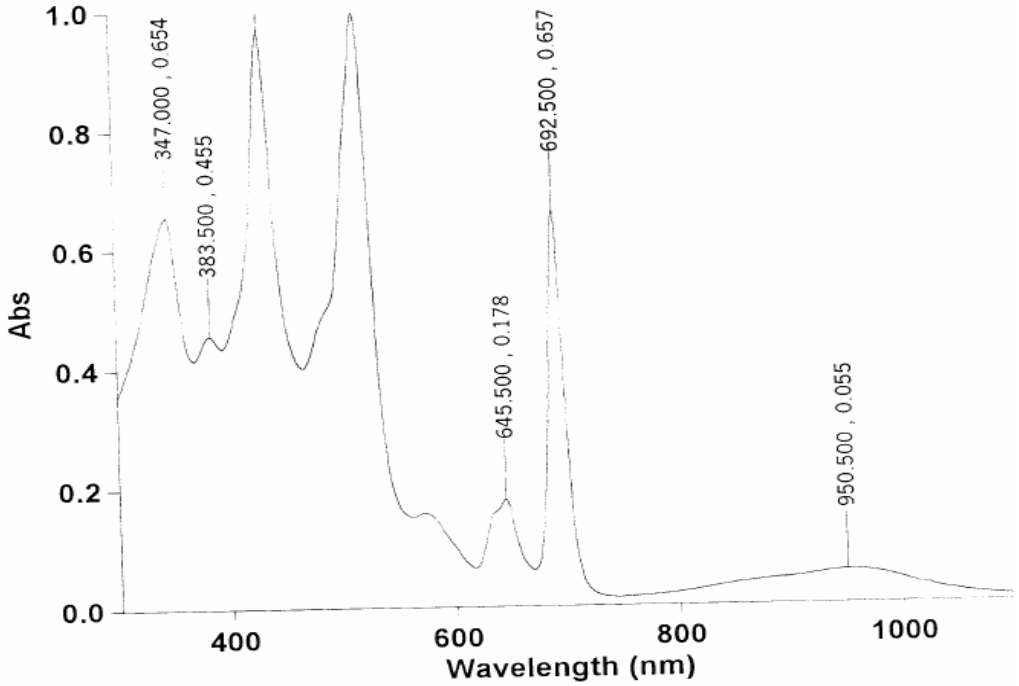


Zinc(II) Tetrakisquinoxalinoporphyrin 18

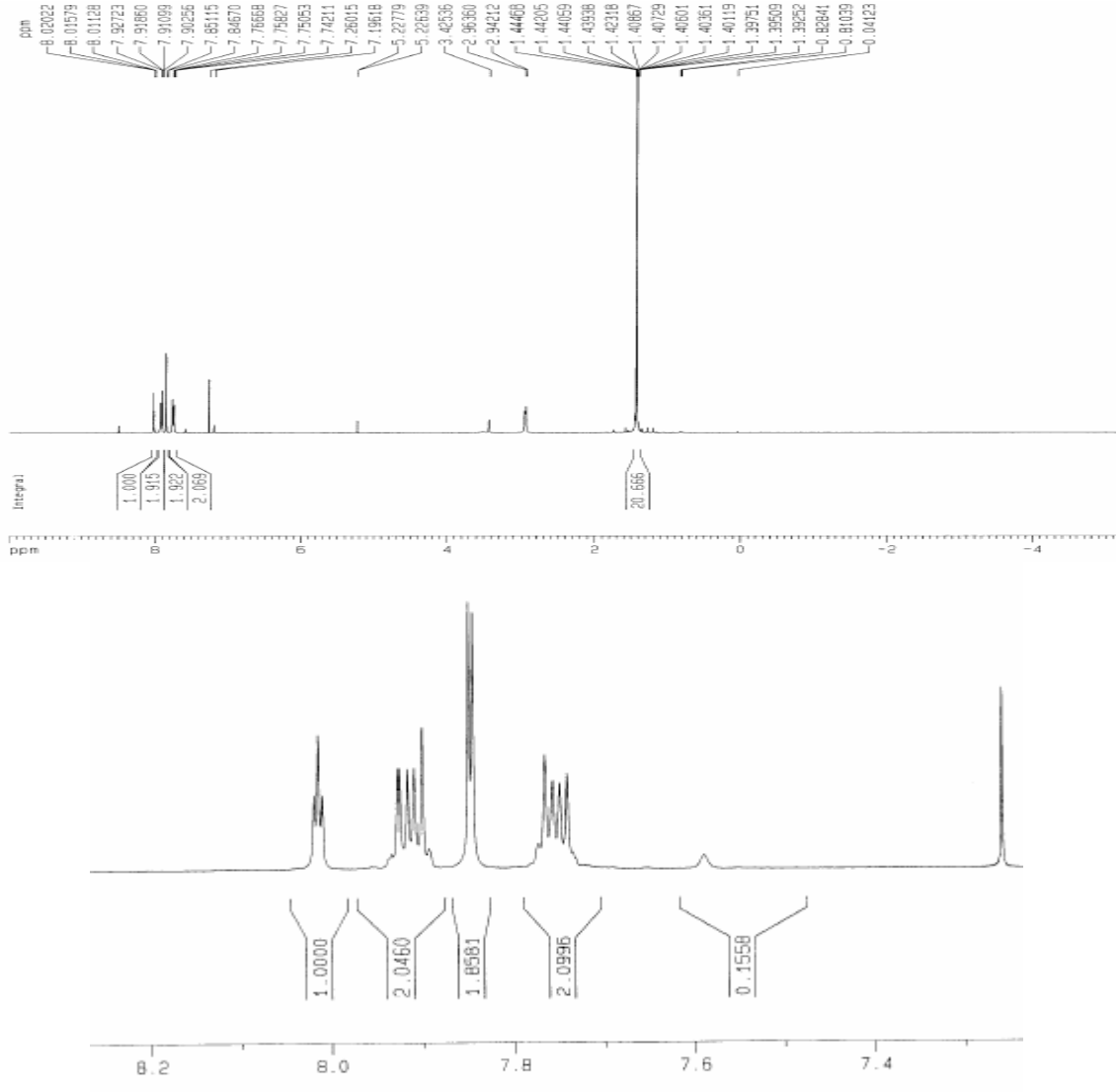
ESI



UV-visible



H NMR of **18**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8.01128
7.92723
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7.85115
7.84670
7.76668
7.75827
7.75053
7.74211
7.26015
7.19618
5.22779
5.22639
3.42536
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1.44205
1.44059
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1.42318
1.40867
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1.40601
1.40361
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0.82841
0.81039
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Integral
1.000
1.915
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2.069
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-2
-4
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2.0995
0.1558
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8.0
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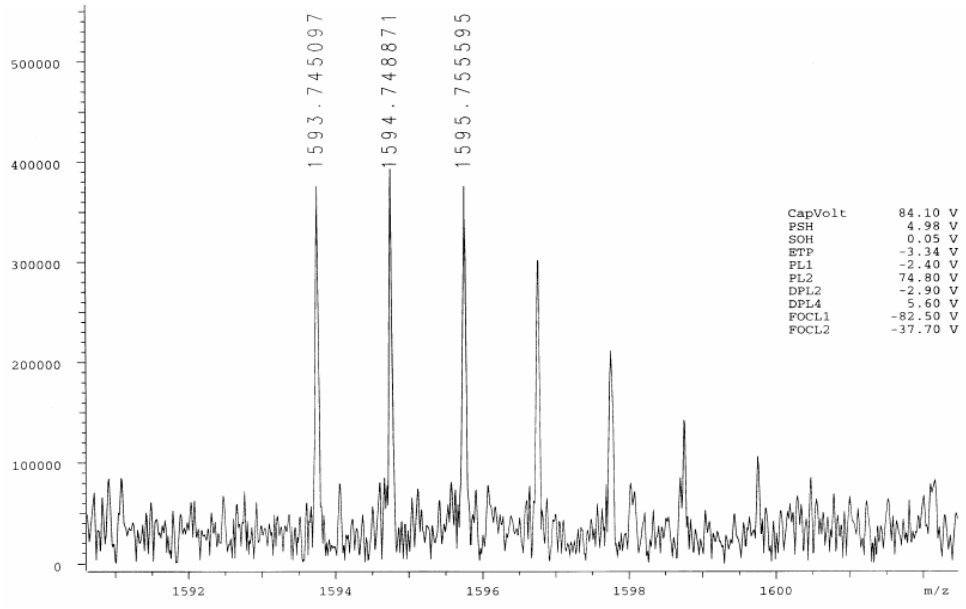
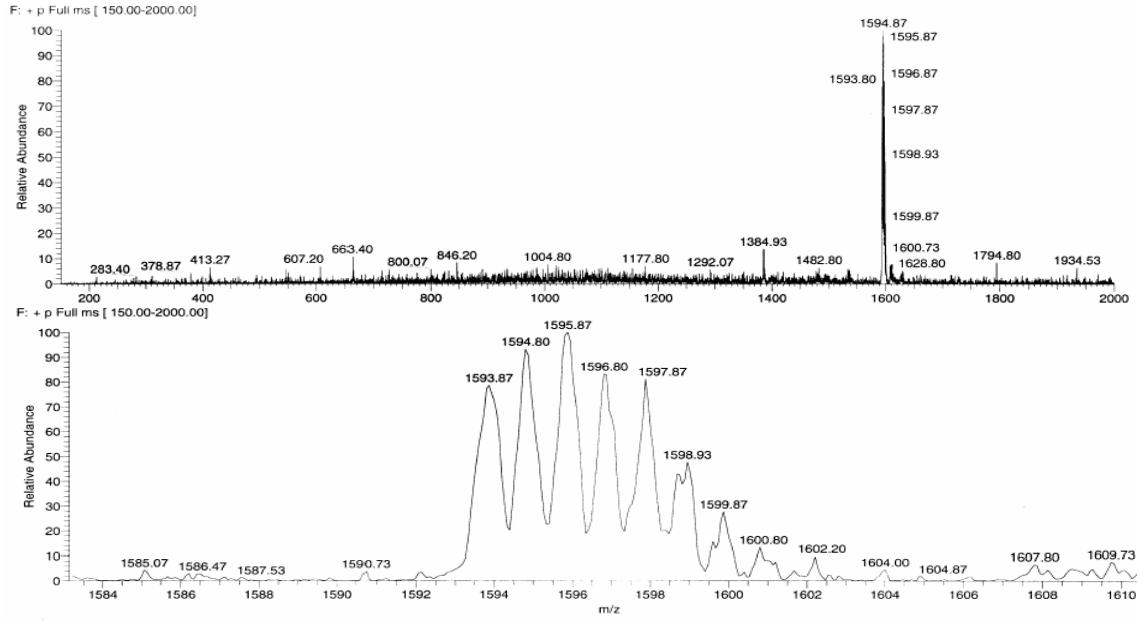
7.6
7.4

Zinc(II) amino-nitro-tetrakisquinoxalinoporphyrin 19

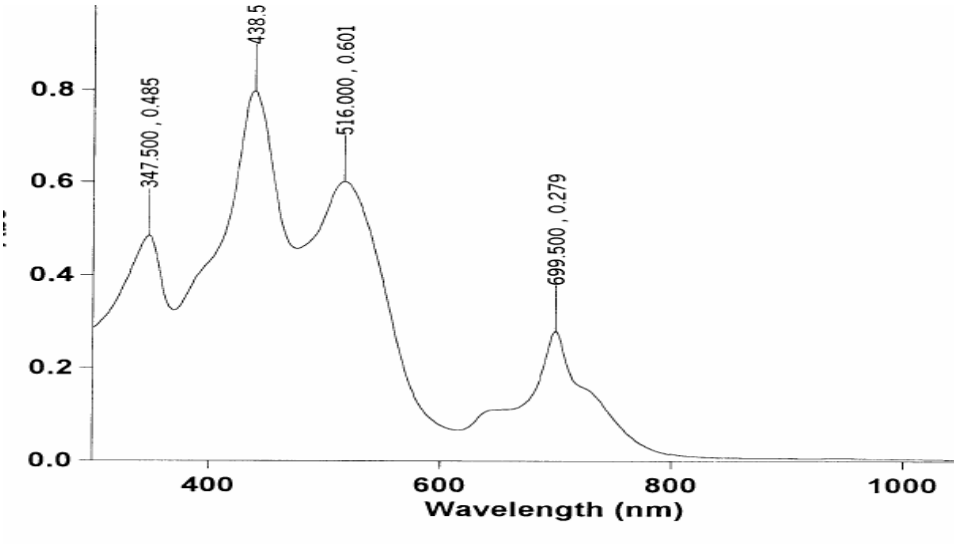
ICR



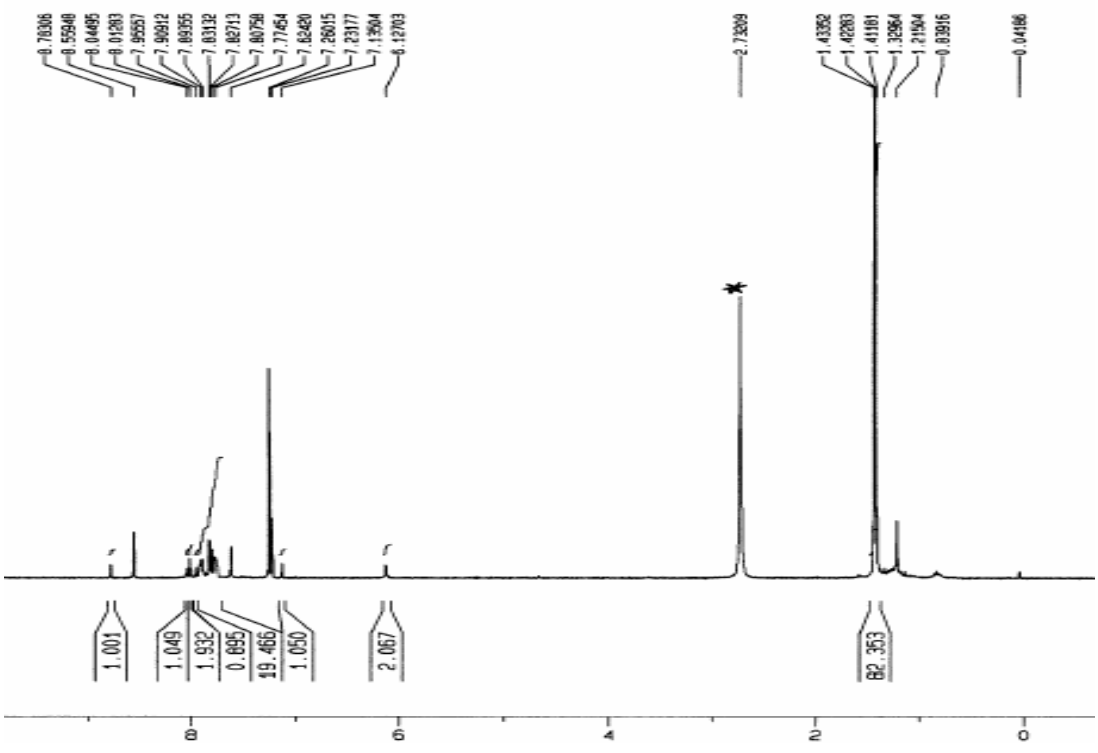
ESI of **19**

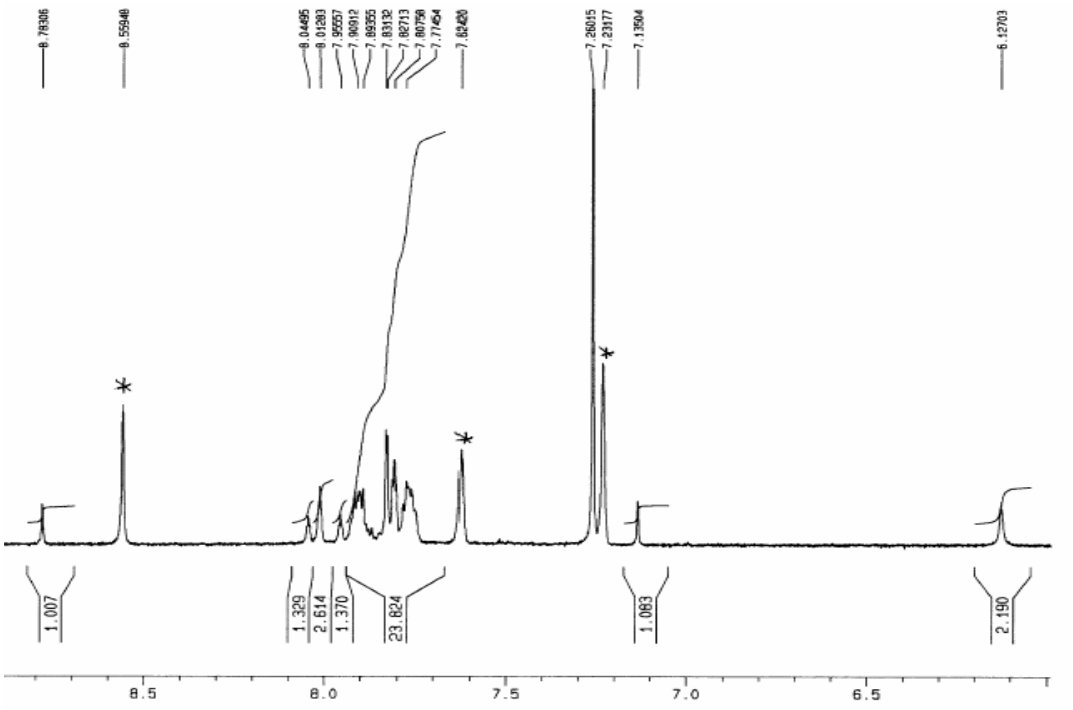


UV-Visible of **19**



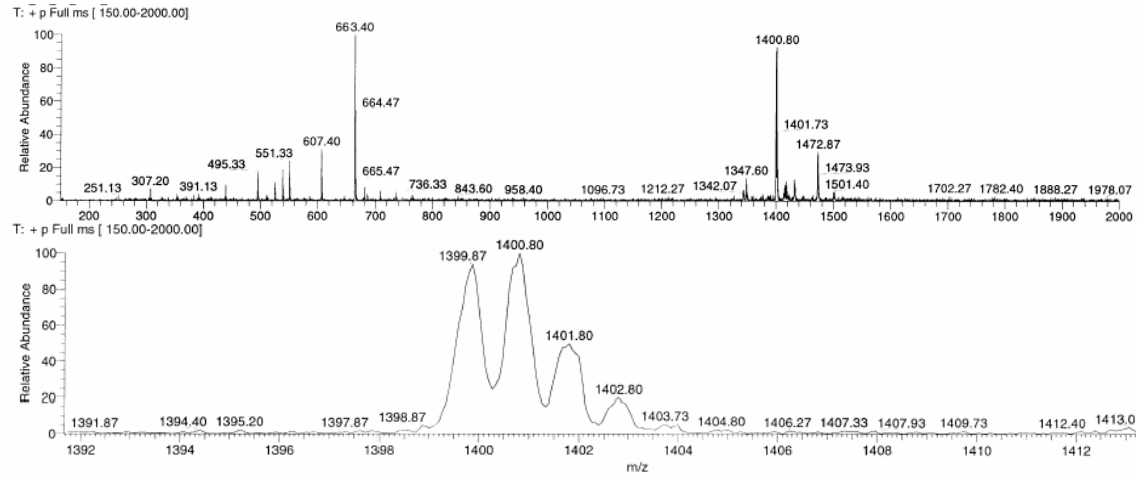
^{1}H NMR of **19**



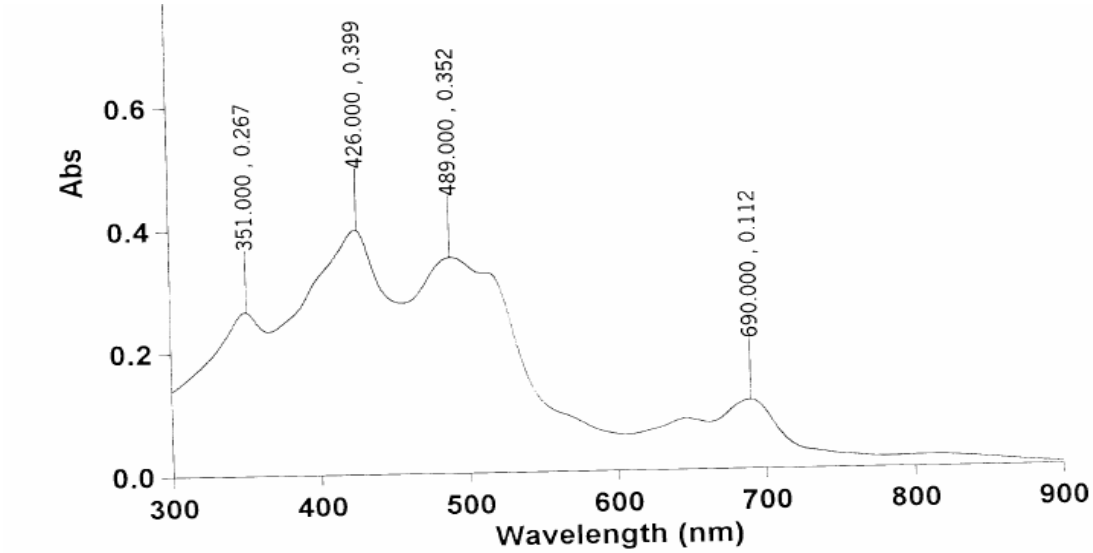

8.78306
8.55940
8.04495
8.01283
7.95557
7.90912
7.89355
7.83132
7.82713
7.80798
7.77454
7.62420
7.26015
7.23177
7.13504
6.12703
1.007
1.329
2.614
1.370
23.824
1.083
2.190
8.5
8.0
7.5
7.0
6.5

Trisquinoxalinoporphyrin-dione 21

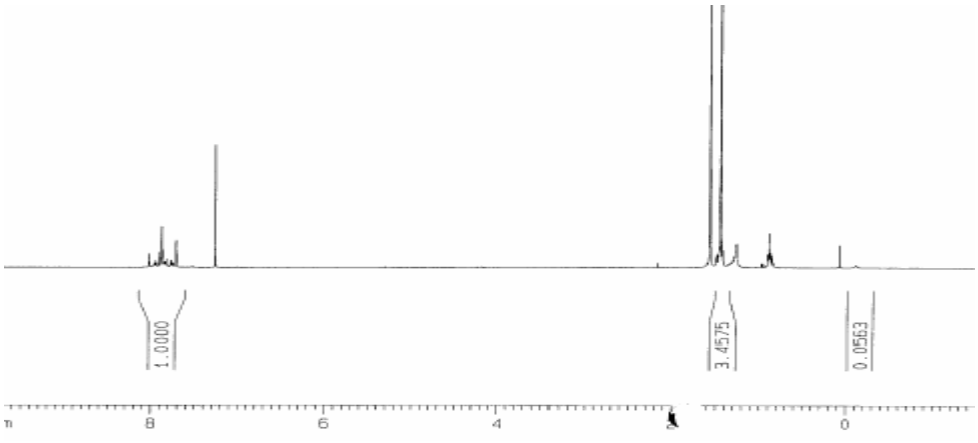
ESI



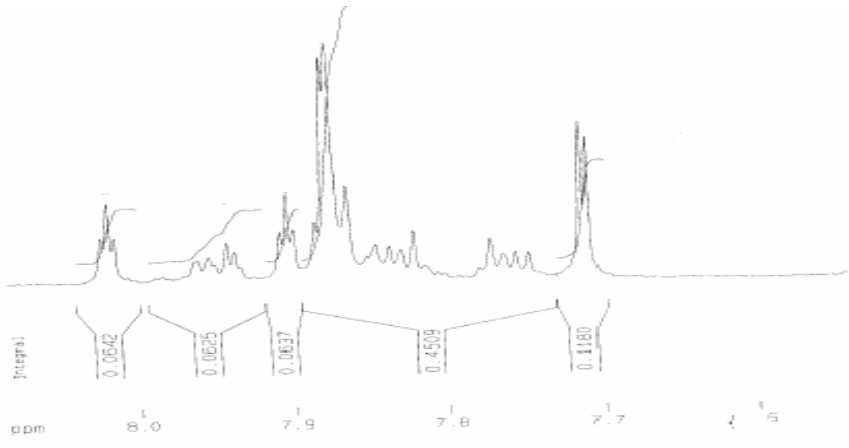
UV-Visible



H NMR of **21**

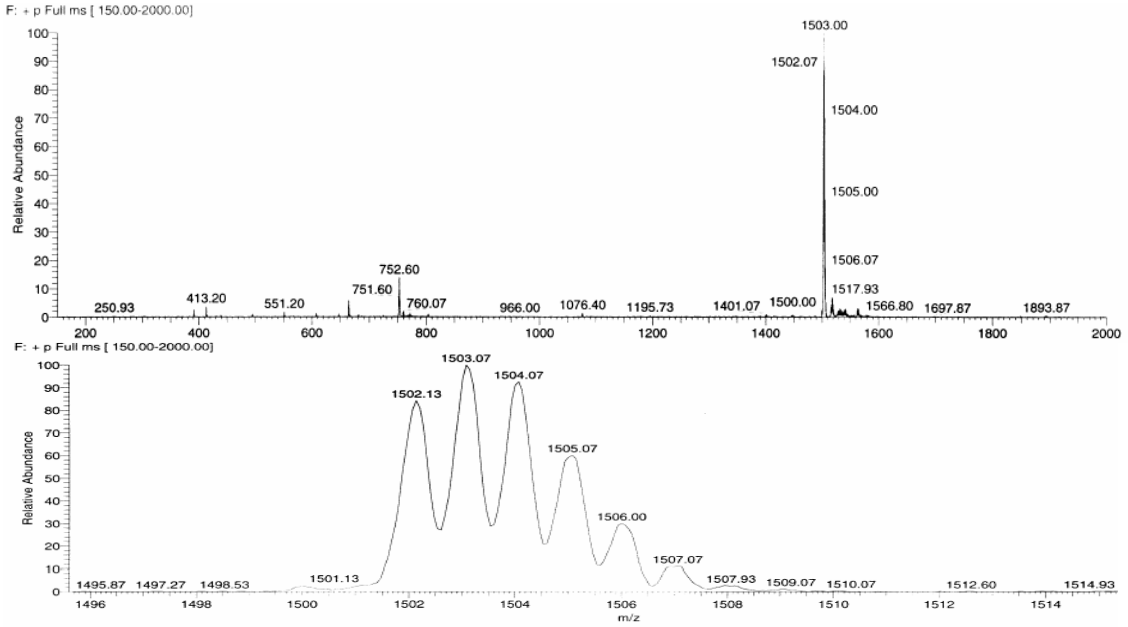


H NMR of **21**

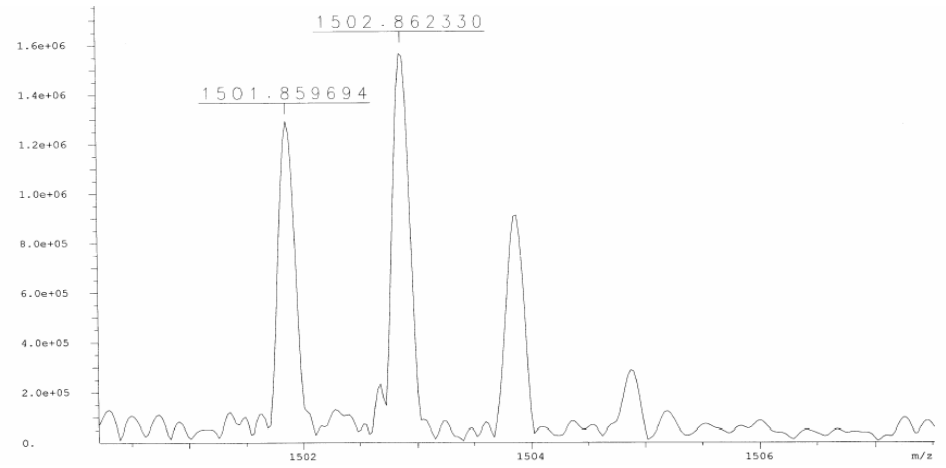


Diamino-Tetrakisquinoxalinoporphyrin 20

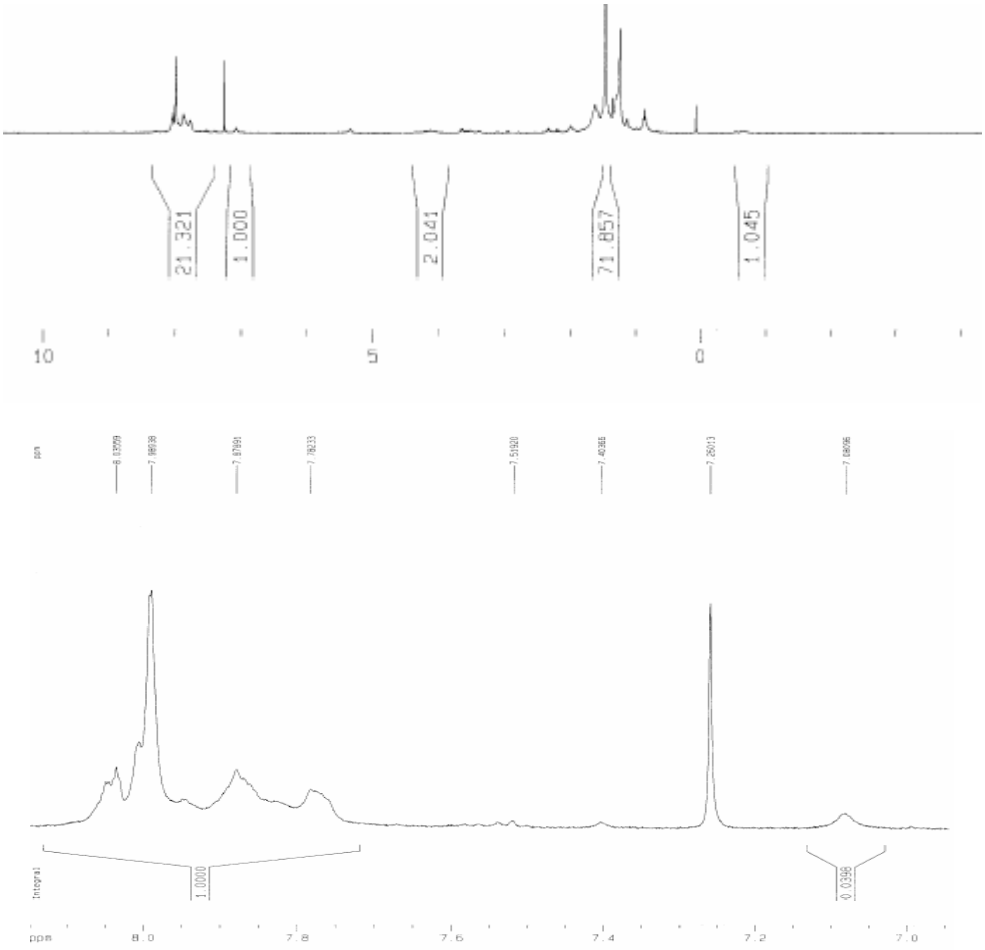
ESI



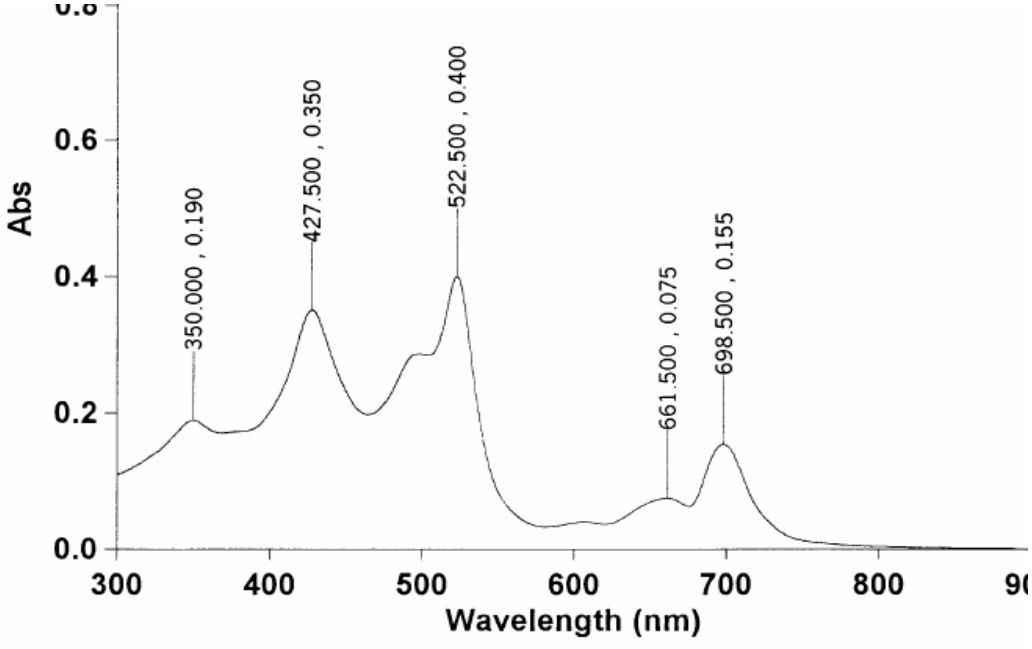
ICR



H NMR of **20**



UV-Visible of **20**



Data for Trisquinoxalinoporphyrin-Trisquinoxalinoporphyrin (Dimer) - (PQ_3)TA(PQ_3) 3

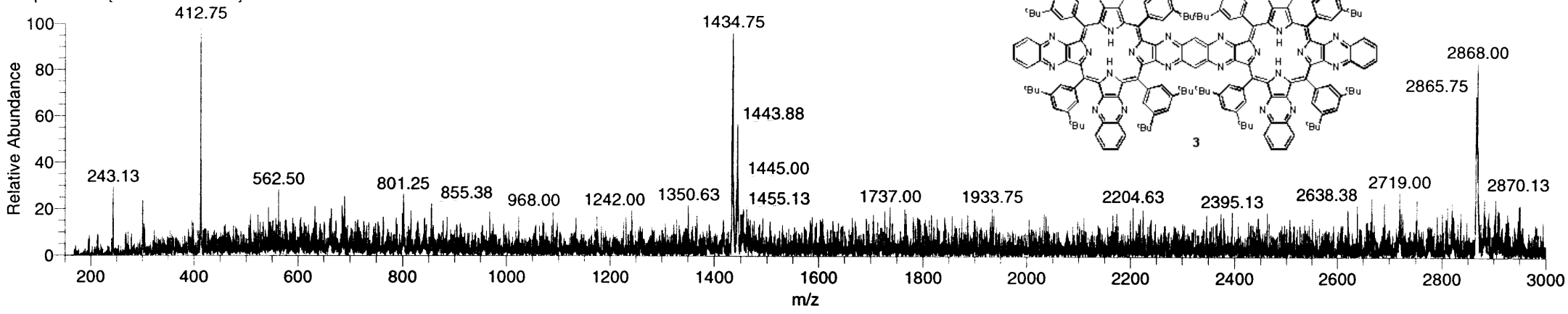
(HR-ESI-FT/ICR Found: $[M + 2 H]^{2+}$ 1433.8225. $C_{194}H_{198}N_{24}$ requires 1433.8219). ν_{max} ($CHCl_3$): 3323 w, 3061 w, 2961 s, 2926 s, 2854 s, 1597 m, 1483 w, 1470 m, 1462 m, 1454 w, 1393 w, 1362 m, 1348 w, 1296 w, 1261 w, 1248 w, 1161 m, 1097 w, 1082 w, 1022 w, 1003 w, 989 w cm^{-1}. λ_{max} ($CHCl_3$) (log ε): 347 (4.65), 440 (4.92), 508 (4.83), 579sh (4.35), 670sh (4.25), 710sh (4.41), 735 (4.64), 823sh (3.60) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ -0.02 (4 H, br s, inner NH); 1.48 (72 H, s, *t*-butyl H); 1.55 (72 H, s, *t*-butyl H); 7.71-8.17 (48 H, m, quinoxaline H, H_o, H_p); 8.72 (2 H, br s, bridging H). Mass spectrum (ESI) (*m/z*): 1433.8 ($[M + 2 H]^{2+}$ requires 1433.9); 2865.8 (M^+ requires 2865.8).

The ESI spectrum and the high resolution ESI-FT-ICR spectrum are attached.

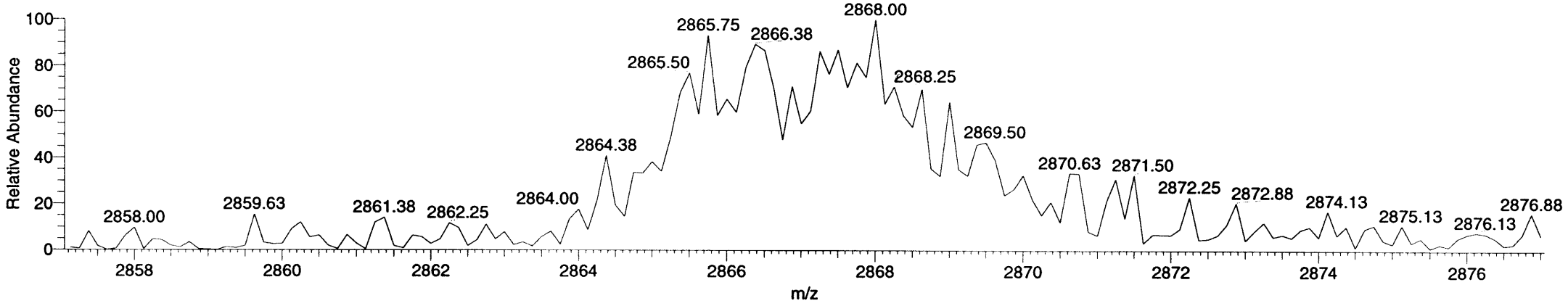
D:\Crossley\TK_06_103_tetrakisdimer
25/03/05 12:04:44 TK_06_103

TK-06_103_tetrakisquinoxalinoporphyrin dimer

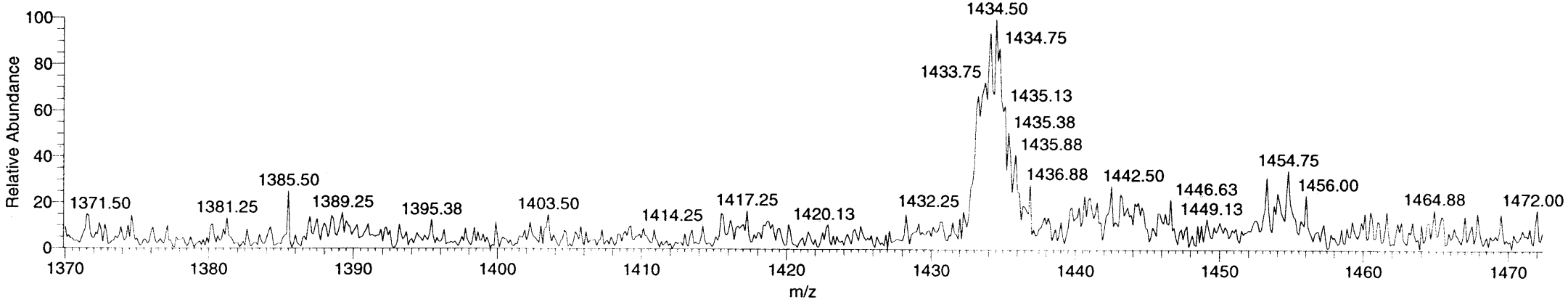
TK_06_103_tetrakisdimer #18-26 RT: 0.57-0.83 AV: 9 NL: 1.05E6
T: + p Full ms [150.00-3000.00]



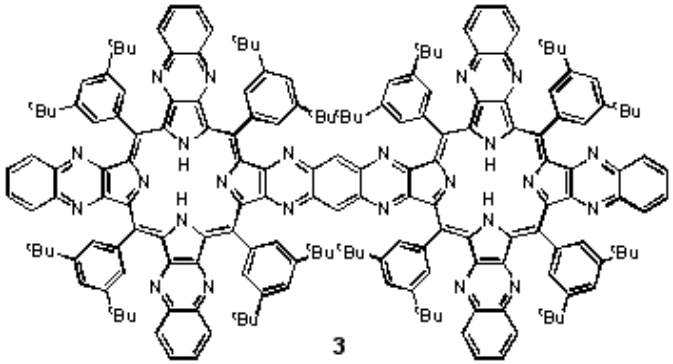
TK_06_103_tetrakisdimer #16 RT: 0.50 AV: 1 NL: 9.05E5
T: + p Full ms [150.00-3000.00]



TK_06_103_tetrakisdimer #319-325 RT: 10.53-10.73 AV: 7 NL: 5.37E5
T: + p Full ms [150.00-3000.00]



TK-08-103



ICR High resolution mass spectrum of two plus ion of M plus two protons (HR-ESI-FT/ICR Found: [M + 2 H]2+ 1433.8225. C194H198N24 requires 1433.8219).