SUPPORTING INFORMATION

OHMIC HEATING ASSISTED SYNTHESIS OF COUMARINYLPORPHYRIN DERIVATIVES

Mariana F. do C. Cardoso[1,2], Ana T. P. C. Gomes[1], Vera L. M. Silva[1], Artur M. S. Silva[1], Maria G. P. M. S. Neves[1], Fernando de C. da Silva[2], Vitor F. Ferreira[2] and José A. S. Cavaleiro[1]

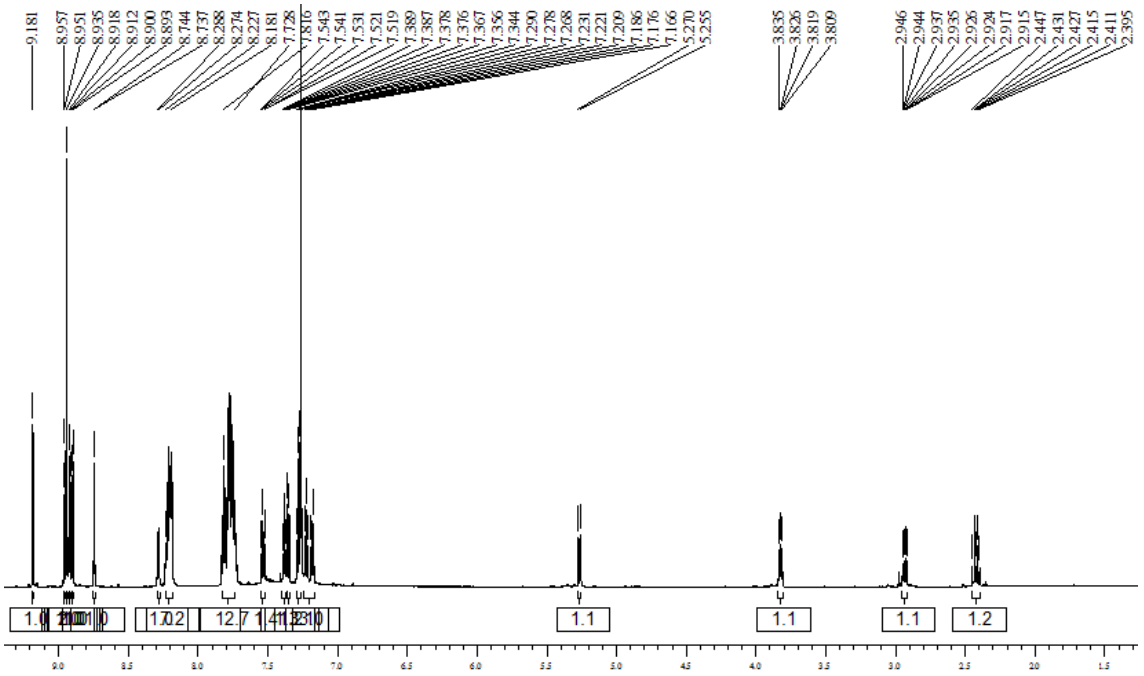
[1]*Department of Chemistry and QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal*

[2]*Universidade Federal Fluminense, Instituto de Química, Departamento de Química Orgânica, Valonguinho, 24020-150, Niterói, RJ*

{2-(4-Phenyl-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6a.1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.42 (dt, *J* 14.5, 11.0 Hz, 1H, H-3'), 2.94 (ddd, *J* 14.5, 6.3, 1.5 Hz, 1H, H-3'), 3.82 (dd, *J* 11.0, 6.3 Hz, 1H, H-4'), 5.26 (br d, *J* 11.0 Hz, 1H, H-2'), 7.17–7.29 (m, 6H, H-2",3",4",5",6", H-9'), 7.34 (dd, *J* 8.0, 0.5 Hz, 1H, H-7'), 7.36-7.38 (m, 1H, *m,p*-Ph-20), 7.53 (ddd, *J* 8.0, 7.0, 1.0 Hz, 1H, H-8'), 7.73-7.81 (m, 12H, 11H *m,p*-Ph, H-10'), 8.18-8.22 (m, 7H, *o*-Ph), 8.27-8.28 (m, 1H, *o*-Ph-20), 8.74 (d, *J* 4.6 Hz, 1H, H_β), 8.89 (d, *J* 4.6 Hz, 1H, H_β), 8.91 (d, *J* 4.6 Hz, 1H, H_β), 8.93 (s, 2H, H-12 and H-13), 8.95 (d, *J* 4.6 Hz, 1H, H_β), 9.18 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.2 (C-4'), 42.3 (C-3'), 76.1 (C-2'), 104.7 (C-4a'), 115.9 (C-10a'), 116.6 (C-7'), 123.0 (C-10'), 123.6, 126.5, 126.6 (C-2",6"), 126.6 (C-9'), 126.6, 126.7, 127.6, 127.7, 128.5, 128.6, 128.7 (C*m,p*-Ph), 131.6, 131.8 (C-8'), 132.3, 132.5, 132.6 (C_β), 134.4, 134.5, 134.6 (C*o*-Ph), 143.4 (C-1), 145.6 (C-1"), 150.3, 150.5, 150.6, 150.9 (C-10, C-11, C-14, C-15), 152.8 (C-6a'), 161.4 (C-10b'), 162.4 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 425 (4.91), 553 (4.55), 595 (4.00) nm. HRMS (ESI^+): *m/z* $[M+H]^+$ calcd. for $C_{62}H_{40}N_4O_3Zn$: 953.2392; found: 953.2394.

RMN ^{1}H: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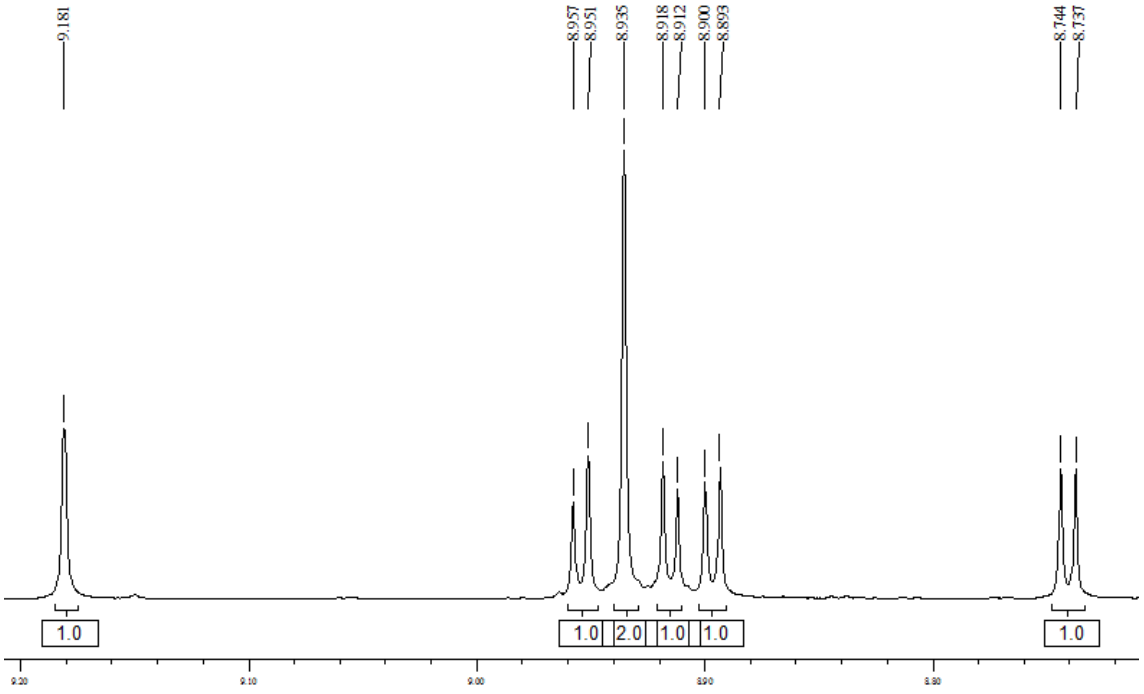
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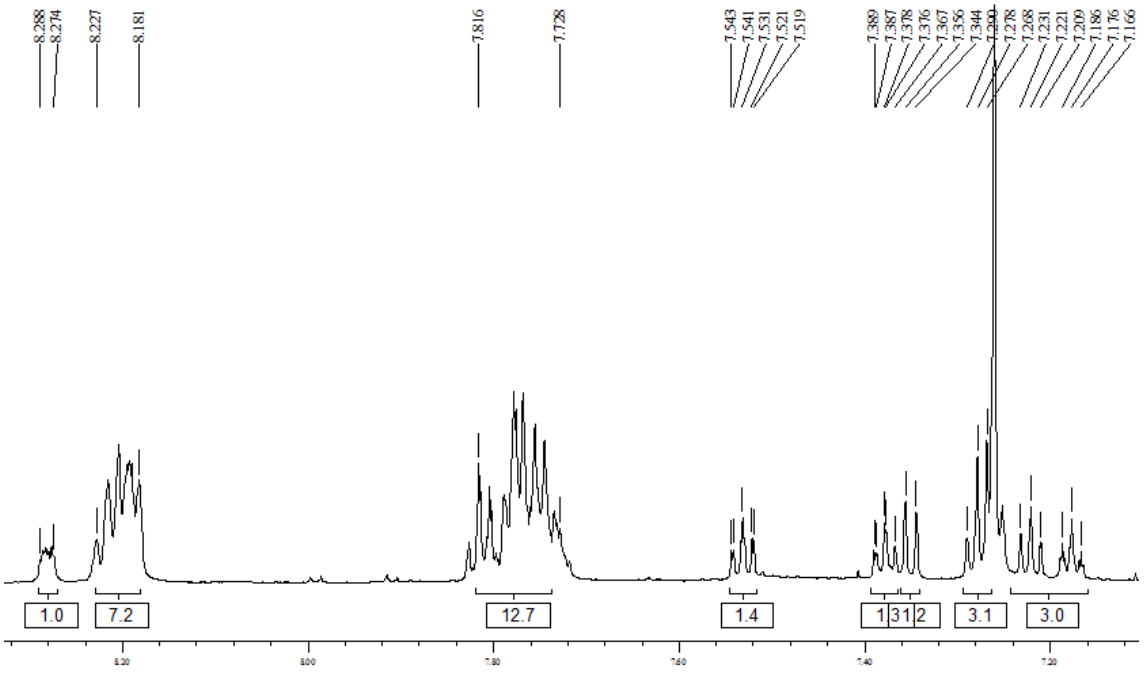
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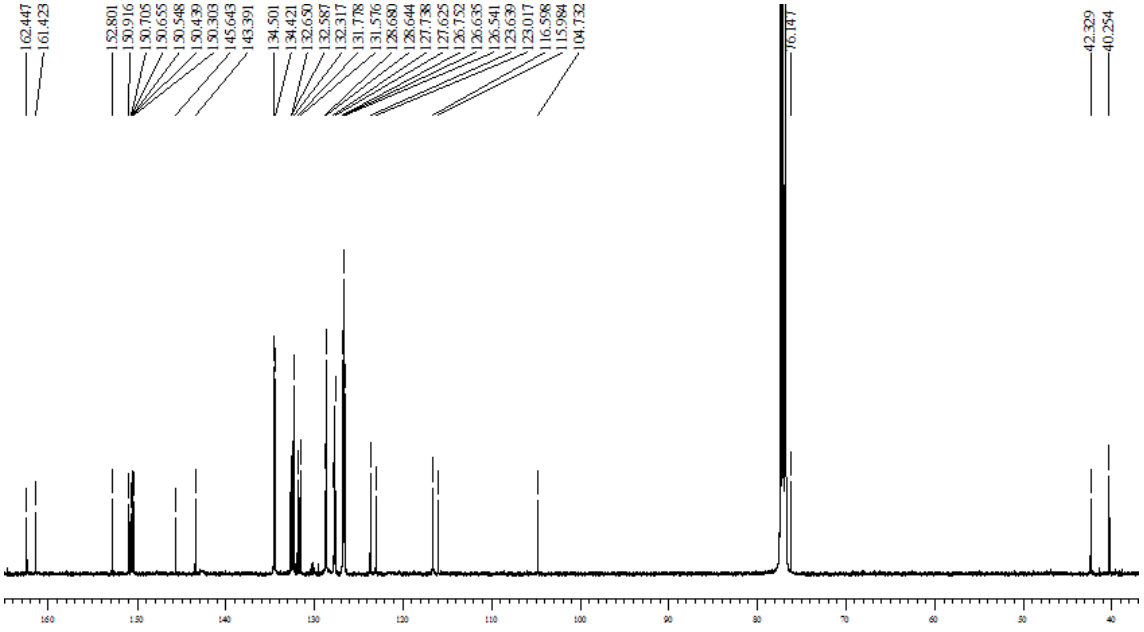
RMN ^{13}C: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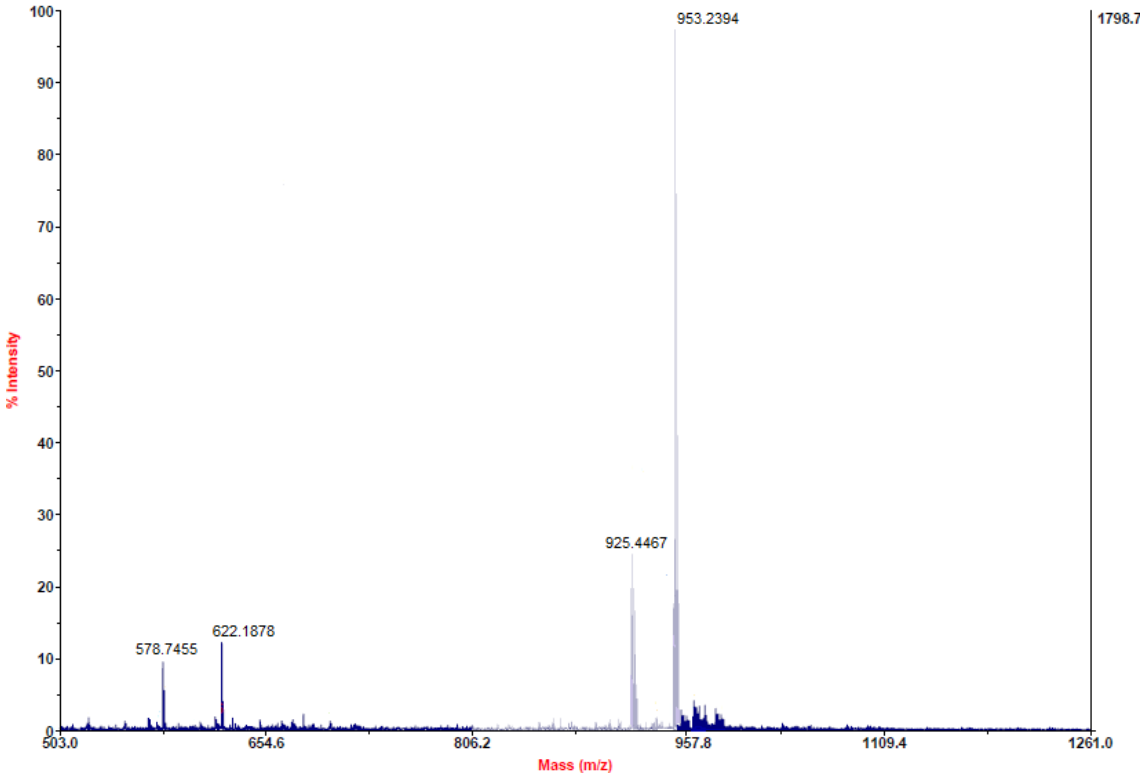
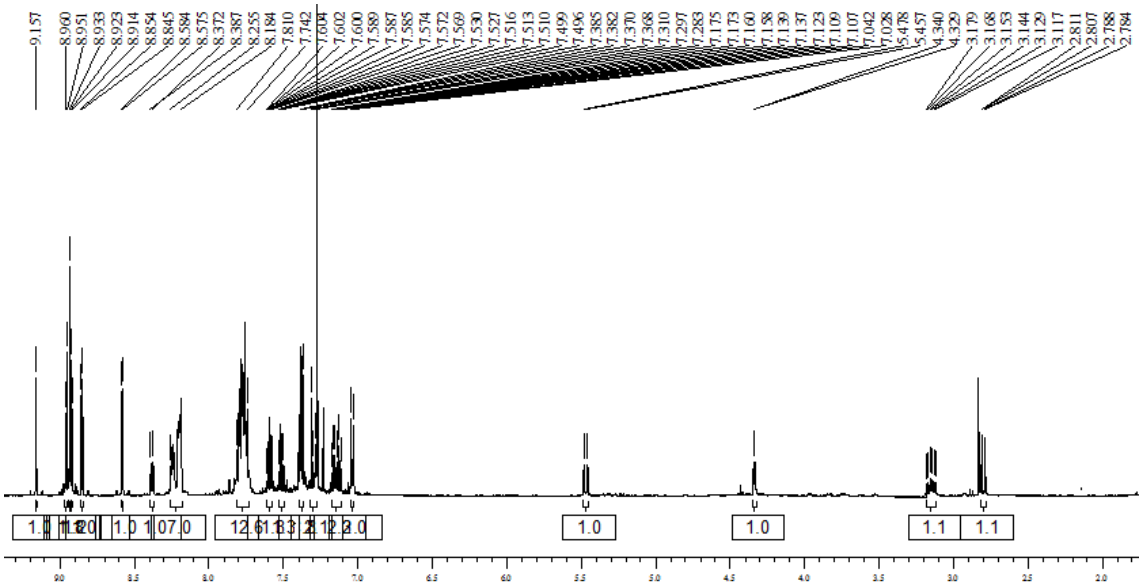
HRMS (ESI$^+$):



{2-(4-Phenyl-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6a.2)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.80 (dd, *J* 14.3, 11.7 Hz, 1H, H-3'), 3.15 (m, 1H, H-3'), 4.33 (d, *J* 5.1 Hz, 1H, H-4'), 5.47 (dd, *J* 11.7, 1.3 Hz, 1H, H-2') 7.03–7.31 (m, 6H, H-2",3",4",5",6", H-9'), 7.38 (dd, *J* 7.5, 1.2 Hz, 1H, H-7'), 7.50-7.53 (m, 1H, *m,p*-Ph-20), 7.59 (td, *J* 7.6, 1.2 Hz, 1H, H-8'), 7.74-7.81 (m, 12H, 11H *m,p*-Ph, H-10'), 8.18-8.25 (m, 7H, *o*-Ph), 8.37-8.39 (m, 1H, *o*-Ph-20), 8.58 (d, *J* 4.7 Hz, 1H, H_β), 8.85 (d, *J* 4.7 Hz, 1H, H_β), 8.92 (d, *J* 4.7 Hz, 1H, H_β), 8.93 (s, 2H, H-12 and H-13), 8.96 (d, *J* 4.7 Hz, 1H, H_β), 9.16 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.8 (C-4'), 36.4 (C-3'), 69.2 (C-2'), 101.9 (C-4a'), 115.6 (C-10a'), 116.7 (C-7'), 123.1, 123.5 (C-10'), 125.4, 126.5, 126.6, 126.7 (C-2",6"), 126.6 (C-9'), 127.6, 127.7, 128.2, 128.3, 128.6 (C*m,p*-Ph), 131.5, 131.6 (C-8'), 132.3, 132.9, 133.0, 133.6 (C_β), 134.4, 134.5, 134.6 (C*o*-Ph), 143.1 (C-1), 146.3 (C-1"), 150.1, 150.5, 150.6, 150.7 (C-10, C-11, C-14, C-15), 152.9 (C-6a'), 161.3 (C-10b'), 162.5 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 425 (4.90), 552 (4.55), 596 (4.00) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{62}H_{40}N_4O_3Zn$: 953.2392; found: 953.2393.

RMN ^{1}H: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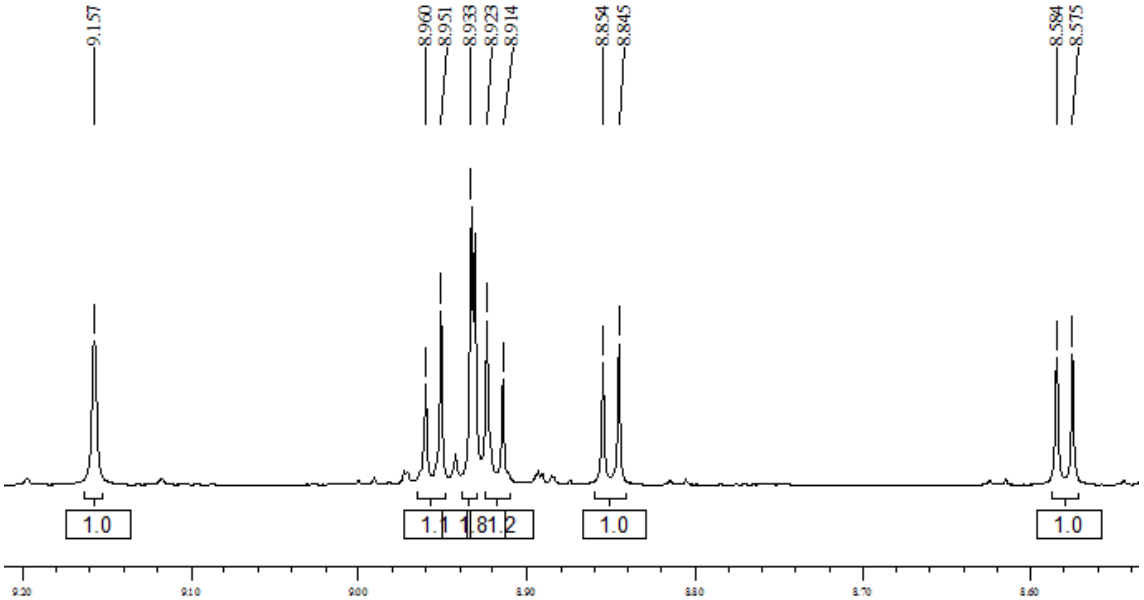
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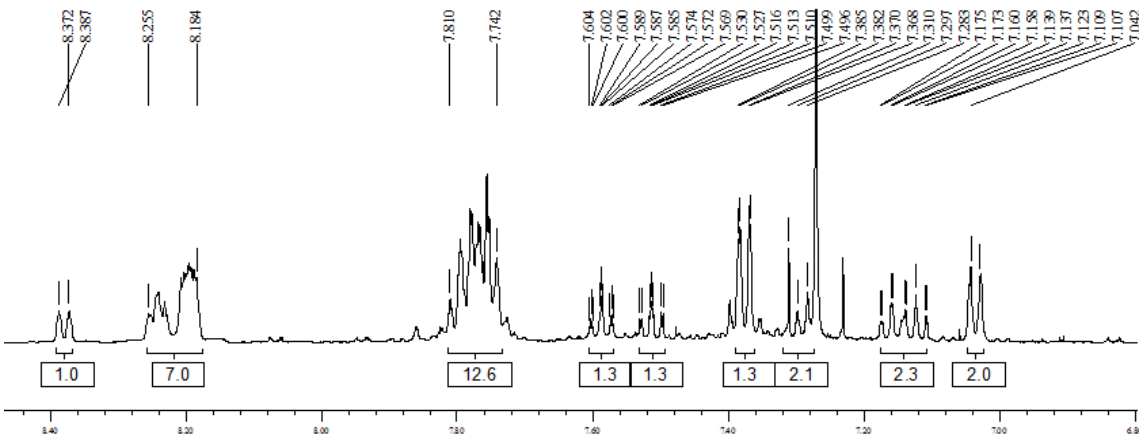
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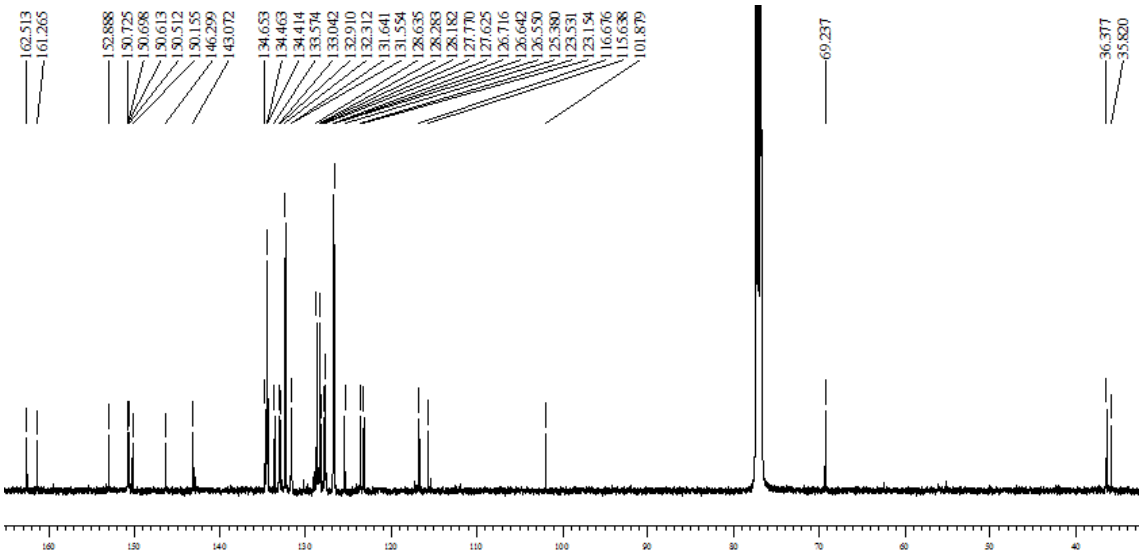
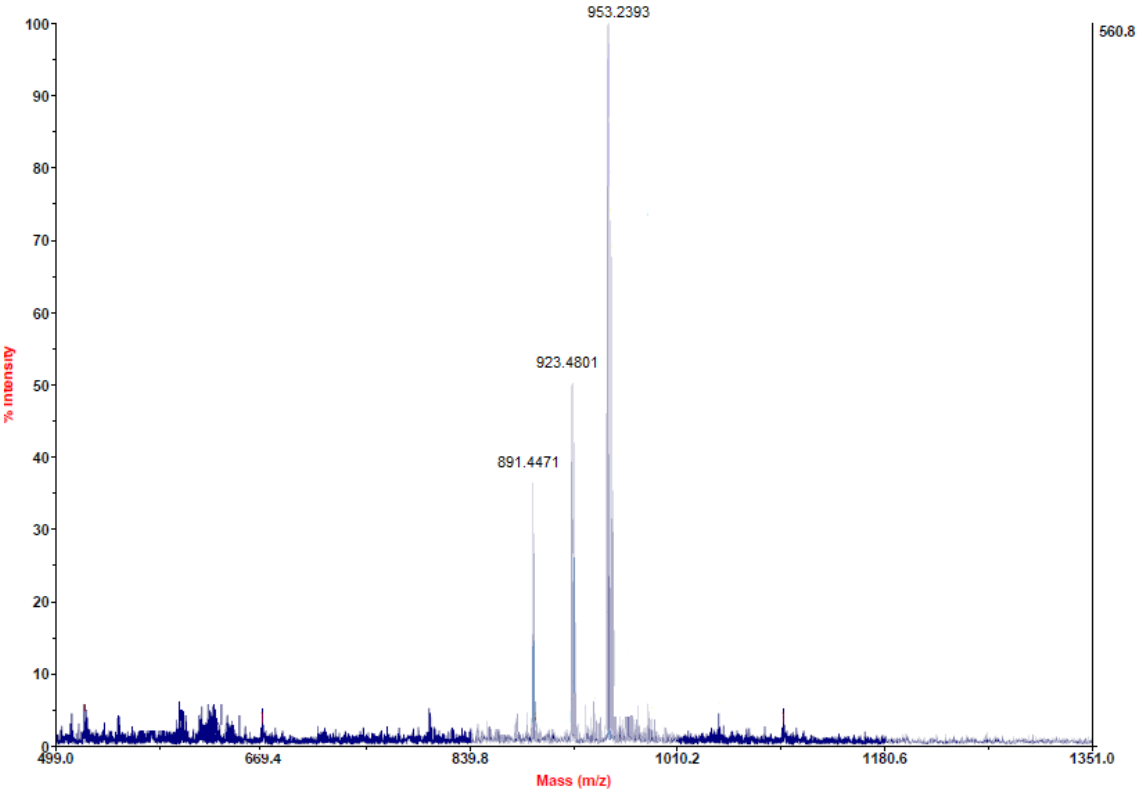
RMN ^{13}C:



HRMS (ESI$^+$):

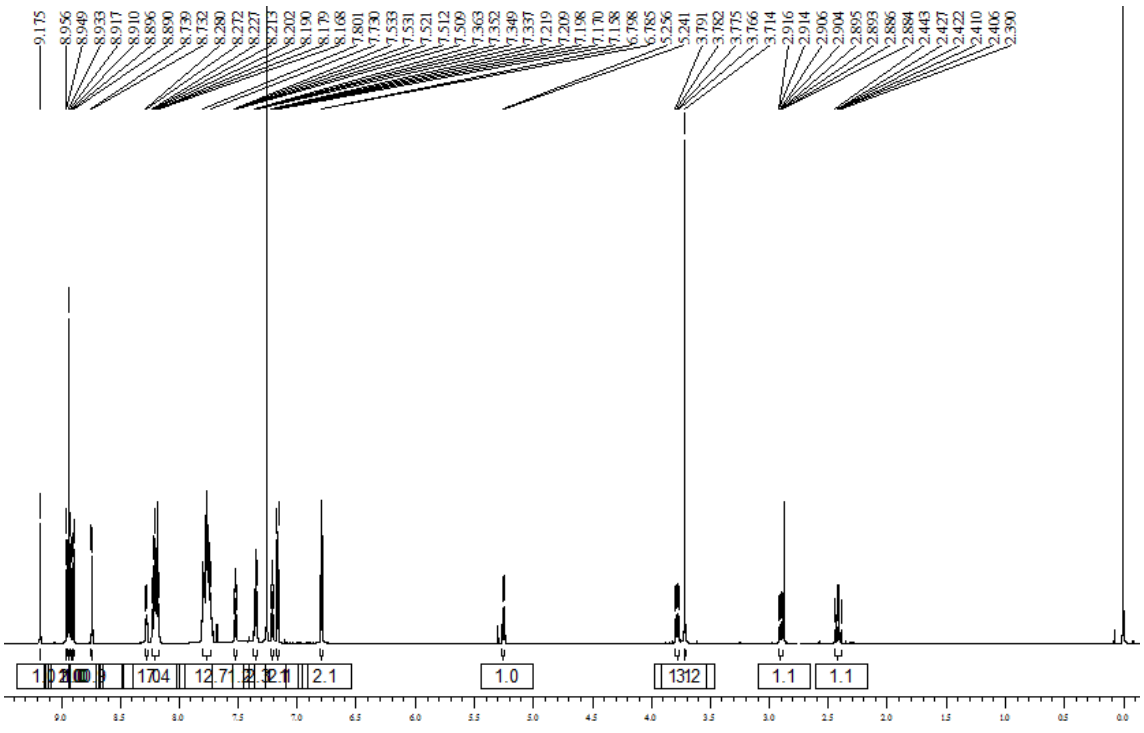


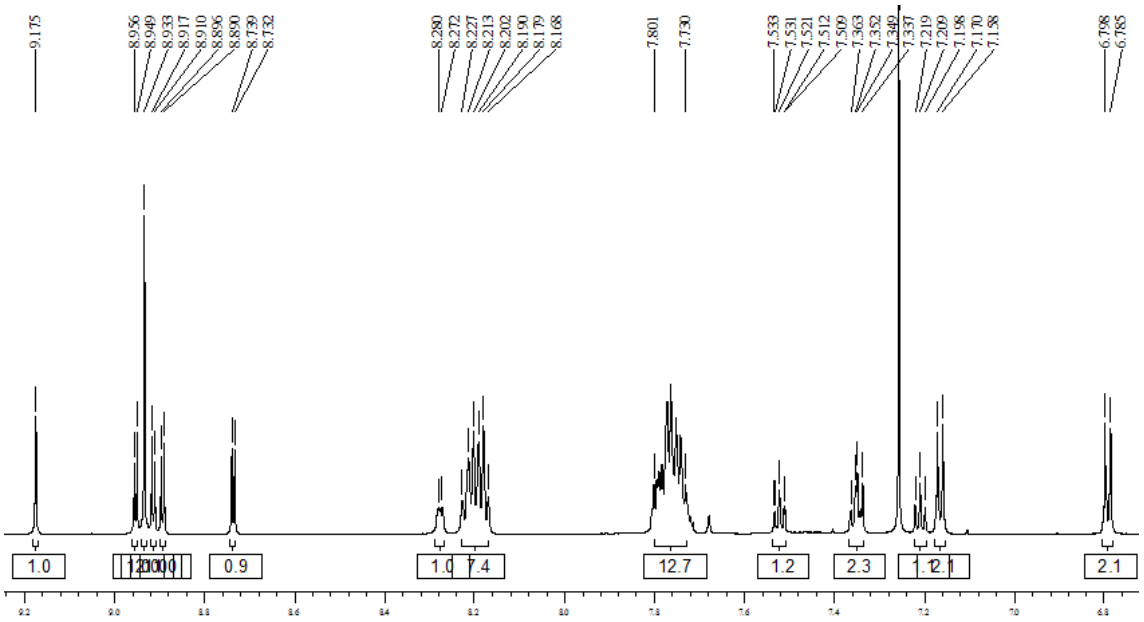
{2-(4-(4-Methoxyphenyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6b.1)

^1H NMR (500 MHz, $CDCl_3$): δ = 2.42 (dt, *J* 14.2, 11.1 Hz, 1H, H-3'), 2.90 (ddd, *J* 14.2, 6.5, 1.3 Hz, 1H, H-3'), 3.71 (s, 3H, OCH_3), 3.78 (dd, *J* 11.1, 6.5 Hz, 1H, H-4'), 5.25 (br

d, *J* 11.1 Hz, 1H, H-2'), 6.79 (d, *J* 8.9 Hz, 2H, H-3",5"), 7.16 (dd, *J* 8.9, 1.8 Hz, 2H, H-2",6"), 7.21 (dt, *J* 8.5, 2.0 Hz, 1H, H-9'), 7.34-7.30 (m, 2H, *m,p*-Ph-20, H-7'), 7.52 (ddd, *J* 8.5, 7.2, 1.5 Hz, 1H, H-8'), 7.73-7.80 (m, 12H, 11H *m,p*-Ph and H-10'), 8.17-8.23 (m, 7H *o*-Ph), 8.27-8.28 (m, 1H, *o*-Ph-20), 8.74 (d, *J* 4.6 Hz, 1H, H_β), 8.89 (d, *J* 4.6 Hz, 1H, H_β), 8.91 (d, *J* 4.6 Hz, 1H, H_β), 8.93 (s, 2H, H-12 and H-13), 8.95 (d, *J* 4.6 Hz, 1H, H_β), 9.17 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.4 (C-4'), 42.3 (C-3'), 55.2 ($O\underline{C}H_3$), 76.1 (C-2'), 104.9 (C-4a'), 114.0 (C-10a'), 116.0, 116.6 (C-3",5"), 120.4 (C-7'), 121.1, 121.4, 121.6 (C-2",6"), 123.0, 123.6 (C-10'), 126.5, 126.6, 126.7, 127.6, 127.7 (C*m,p*-Ph), 128.7 (C-9'), 131.5 (C-8'), 132.3, 132.6, 132.7 (C_β), 133.6, 133.7, 134.4, 134.5, 135.3 (C*o*-Ph), 142.4 (C-2), 142.6, 142.7, 142.8 (C-1), 145.7 (C-1"), 150.3, 150.4, 150.5, 150.6, 150.7, 150.9 (C-10, C-11, C-14, C-15), 152.8 (C-6a'), 156.1 (C-4"), 161.4 (C-10b'), 162.3 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 424 (4.93), 555 (4.57), 595 (4.55) nm. HRMS (ESI^+): *m/z* $[M+H]^+$ calcd. for $C_{63}H_{42}N_4O_4Zn$: 983.2498; found: 983.2495.

RMN ^{1}H:

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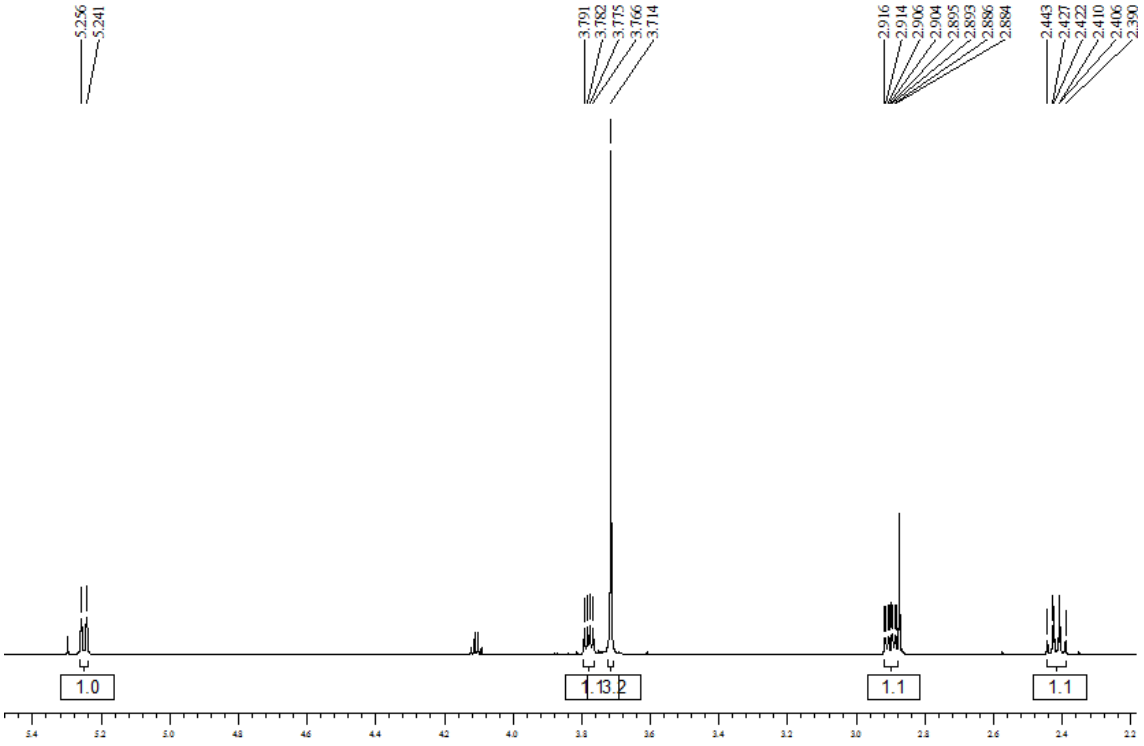
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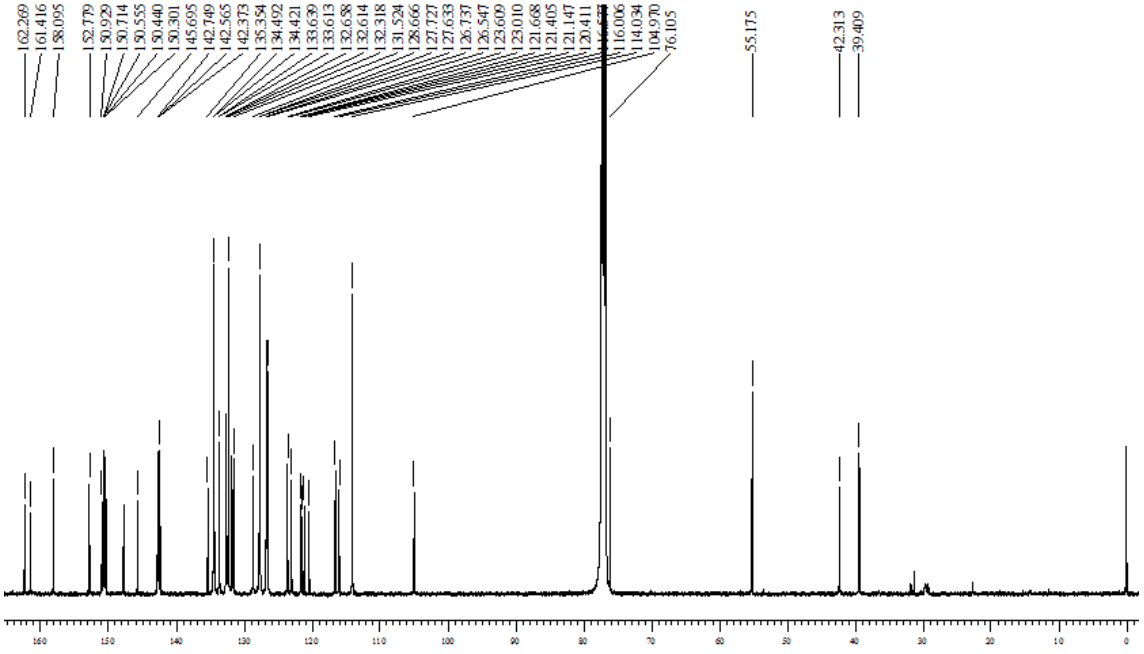
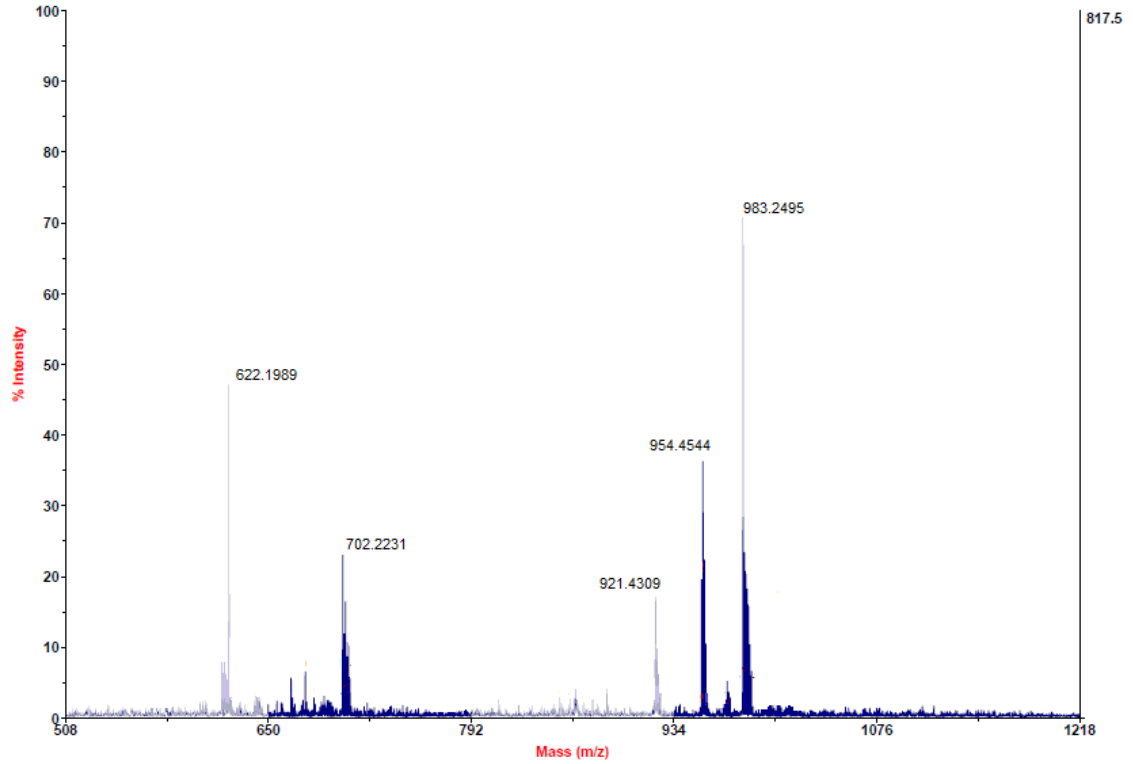
RMN ^{13}C:



HRMS (ESI$^+$):

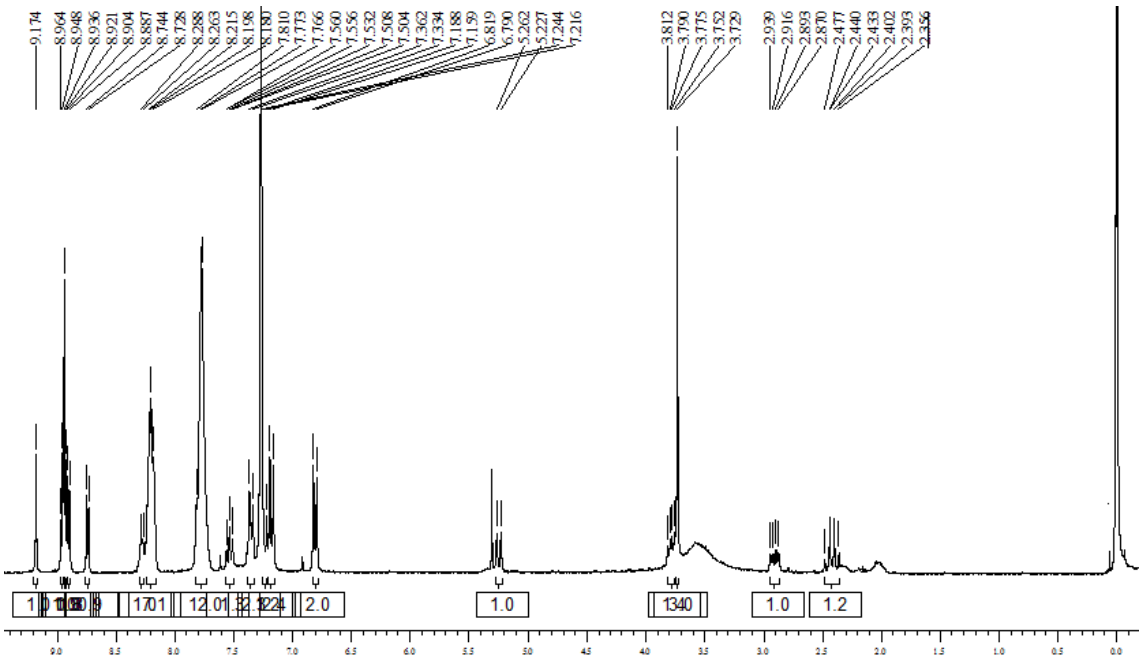


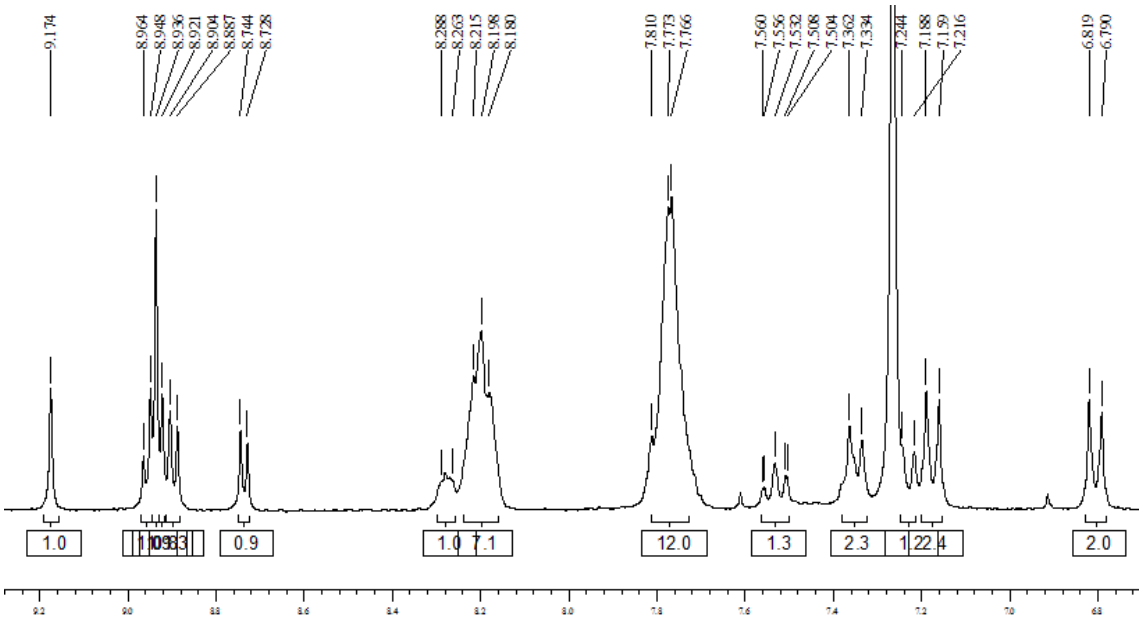
{2-(4-(4-Methoxyphenyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6b.2)

^1H NMR (500 MHz, $CDCl_3$): δ = 2.42 (dt, *J* 14.4, 11.0 Hz, 1 H, H-3'), 2.91 (m, 1H, H-3'), 3.73 (s, 3H, OCH_3), 3.78 (d, *J* 5.4 Hz, 1H, H-4'), 5.24 (br d, *J* 11.0 Hz, 1H, H-2'), 6.80 (d, *J* 8.6 Hz, 2H, H-3",5"), 7.18 (d, *J* 8.6 Hz, 2H, H-2",6"), 7.22 (d, *J* 7.2 Hz, 1H,

H-9'), 7.33-7.36 (m, 2H, *m,p*-Ph-20, H-7'), 7.53 (td, *J* 7.2, 1.3 Hz, 1H, H-8'), 7.77-7.81 (m, 12H, 11H *m,p*-Ph and H-10'), 8.18-8.21 (m, 7H *o*-Ph), 8.26-8.29 (m, 1H, *o*-Ph-20), 8.74 (d, *J* 4.7 Hz, 1H, H_β), 8.90 (d, *J* 4.7 Hz, 1H, H_β), 8.92 (d, *J* 4.7 Hz, 1H, H_β), 8.94 (s, 2H, H_β, H-12 and H-13), 8.96 (d, *J* 4.7 Hz, 1H, H_β), 9.17 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.9 (C-4'), 38.7 (C-3'), 51.8 ($O\underline{C}H_3$), 68.1 (C-2'), 101.5 (C-4a'), 114.0 (C-10a'), 116.0, 116.5 (C-3",5"), 120.5 (C-7'), 121.1, 121.3, 122.5 (C-2",6"), 123.6 (C-10'), 126.4, 126.5, 126.6, 126.7 (C*m,p*-Ph), 127.6, 127.7 (C-9'), 131.2 (C-8'), 132.2, 132.3, 132.4, 132.6 (C_β), 133.5, 134.4, 134.5 (C*o*-Ph), 142.3 (C-2), 142.5, 142.7, 142.8 (C-1), 145.6 (C-1"), 150.2, 150.4, 150.5, 150.6, 150.7, 150.9 (C-10, C-11, C-14, C-15), 152.4 (C-6a'), 157.5 (C-4"), 163.3 (C-10b'), 167.7 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 423 (4.93), 554 (4.58), 595 (4.55) nm. HRMS (ESI^+): *m/z* $[M+H]^+$ calcd. for $C_{63}H_{42}N_4O_4Zn$: 983.2498; found: 983.2497.

RMN ^{1}H:

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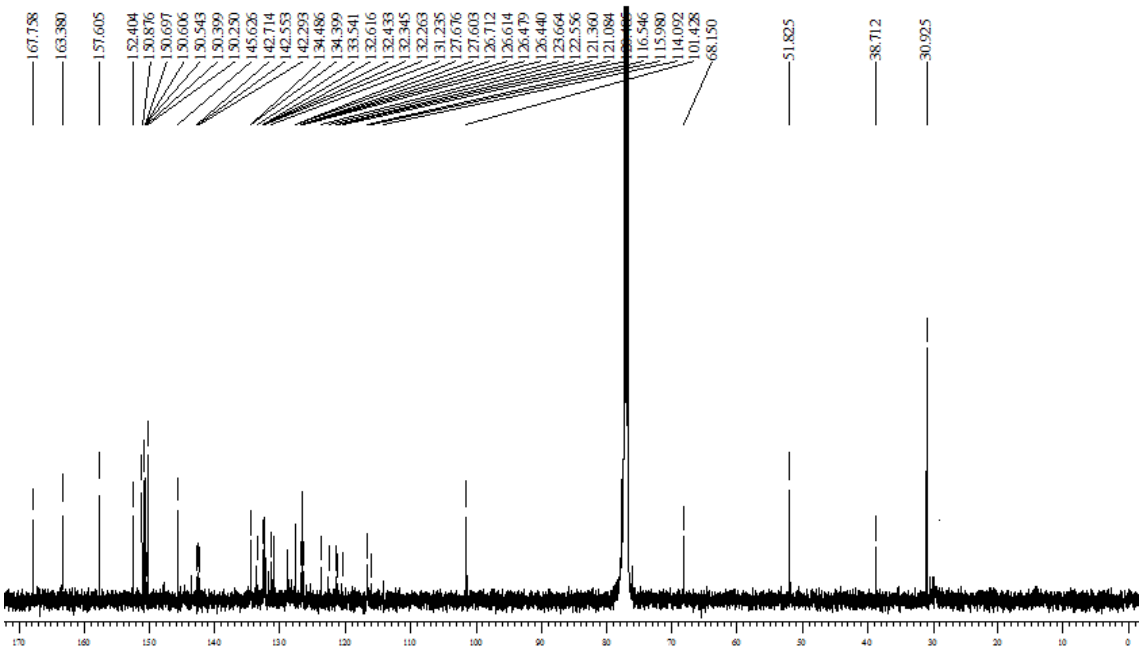
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131.235
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127.603
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126.614
126.479
126.440
123.664
122.556
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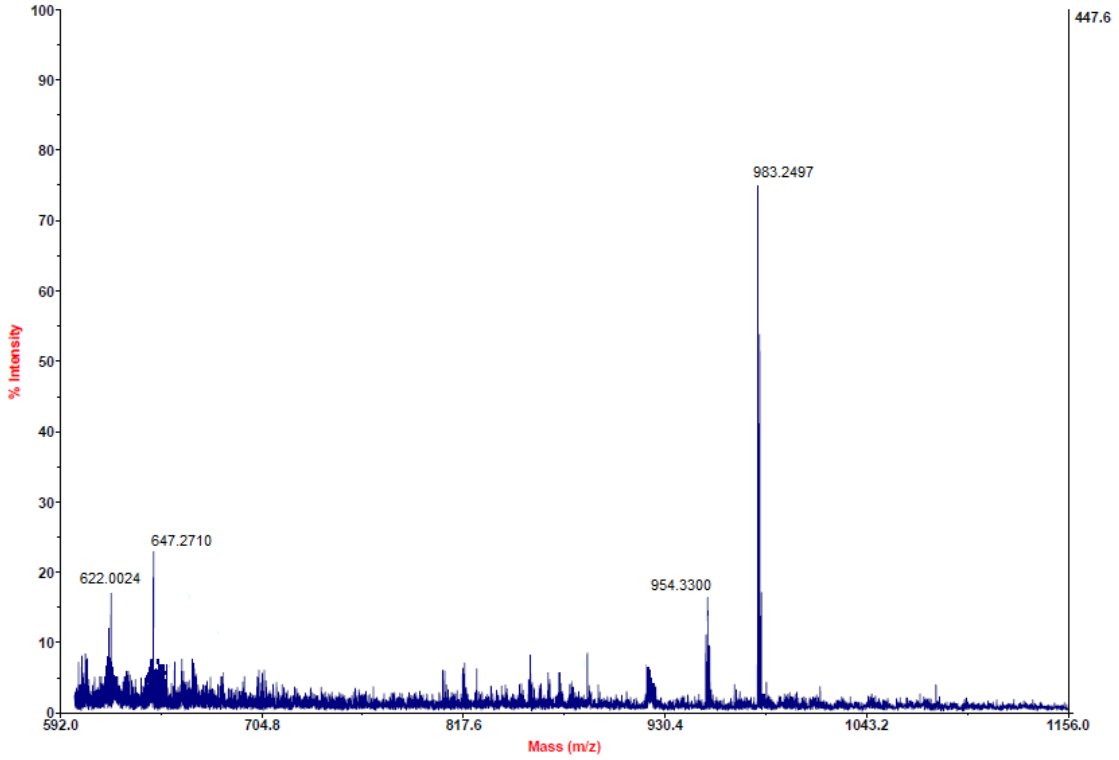
121.084
116.546
115.980
114.092
101.428
68.150
51.825
38.712
30.925

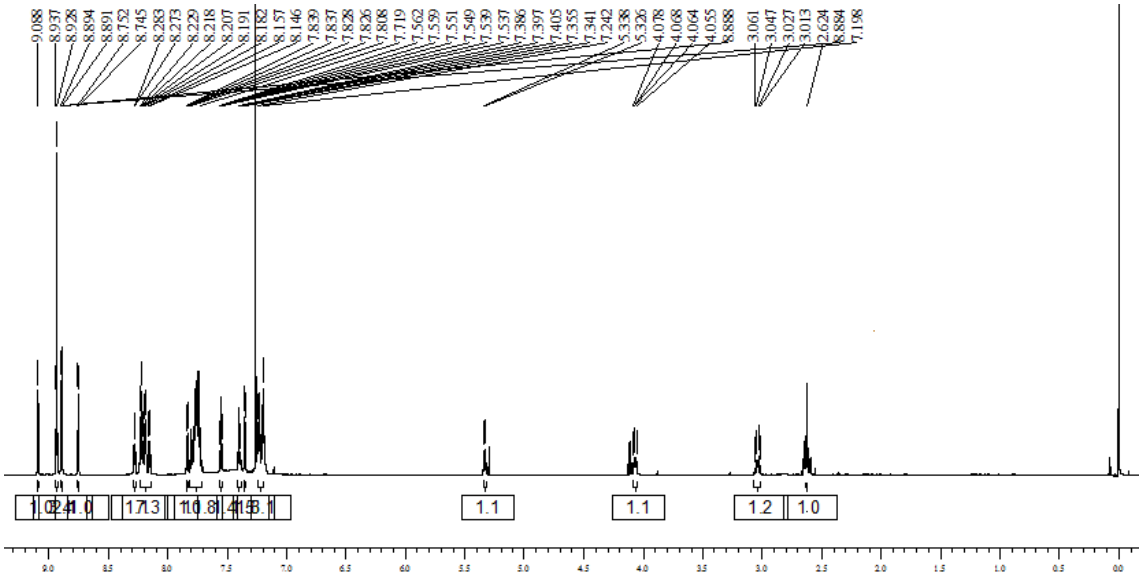
HRMS (ESI$^+$):



{2-(4-(2-Chlorophenyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6c.1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.61 (dt, *J* 14.4, 11.7 Hz, 1H, H-3'), 3.04 (dd, *J* 14.5, 6.4 Hz, 1 H, H-3'), 4.07 (dd, *J* 11.5, 6.6 Hz, 1H, H-4'), 5.33 (br d, *J* 11.7 Hz, 1H, H-2'), 7.19–7.24 (m, 5H, H-3",4",5",6", H-9'), 7.35 (dd, *J* 8.5, 0.6 Hz, 1H, H-7'), 7.39-7.41 (m, 1H, *m,p*-Ph-20), 7.55 (ddd, *J* 8.5, 7.2, 1.5 Hz, 1H, H-8'), 7.72-7.81 (m, 11H, *m,p*-Ph), 7.83 (dd, *J* 8.0, 1.4 Hz, 1H, H-10'), 8.15-8.23 (m, 7H, *o*-Ph), 8.28 (d, *J* 7.2 Hz, 1H, *o*-Ph-20), 8.75 (d, *J* 4.6 Hz, 1H, H_β), 8.87 (d, *J* 4.6 Hz, 1H, H_β), 8.89 (d, *J* 4.6 Hz, 1H, H_β), 8.93 (s, 2H, H-12 and H-13), 8.94 (d, *J* 4.6 Hz, 1H, H_β), 9.09 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.4 (C-4'), 37.8 (C-3'), 75.8 (C-2'), 102.7 (C-4a'), 115.9 (C-10a'), 119.7, 120.0 (C-5"), 120.3 (C-7'), 121.0, 121.3, 121.6 (C-3" and C-6"), 123.1, 123.8 (C-10'), 126.4, 126.5, 126.6, 127.8 (C*m,p*-Ph), 127.6, 127.7 (C-4"), 128.6 (C-9'), 131.7, 131.8 (C-8'), 132.3, 132.6, 133.0 (C_β), 133.7, 133.8, 134.3, 134.4, 134.6 (C*o*-Ph), 136.7 (C-2"), 142.2 (C-2), 142.5, 142.6, 142.7 (C-1), 145.6 (C-1"), 150.2, 150.4, 150.5, 150.6, 150.7, 150.9 (C-10, C-11, C-14, C-15), 152.7 (C-6a'), 161.8 (C-10b'), 162.4 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 422 (5.75), 548 (4.60), 593 (4.51) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{62}H_{39}ClN_4O_3Zn$: 987.2002; found: 987.2006.

RMN ^{1}H: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8.157
8.146
7.839
7.837
7.828
7.826
7.808
7.719
7.562
7.559
7.551
7.549
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7.537
7.386
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7.355
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7.242
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5.326
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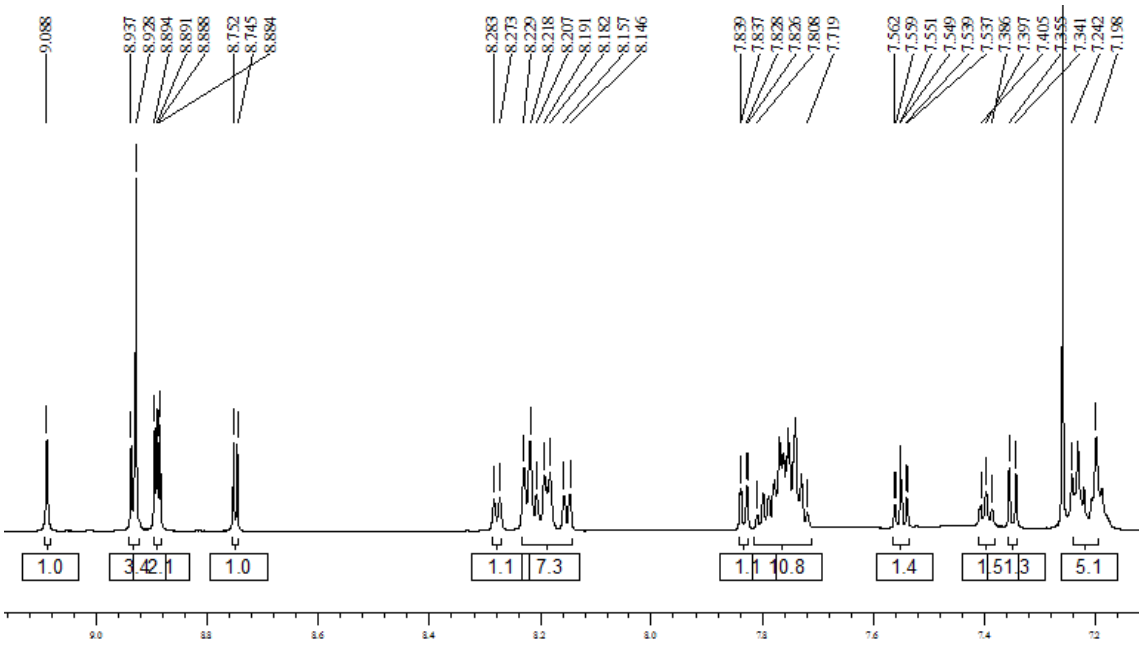
9.088
8.937
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8.157
8.146
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7.386
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7.341
7.242
7.198
1.0
3.4
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7.3
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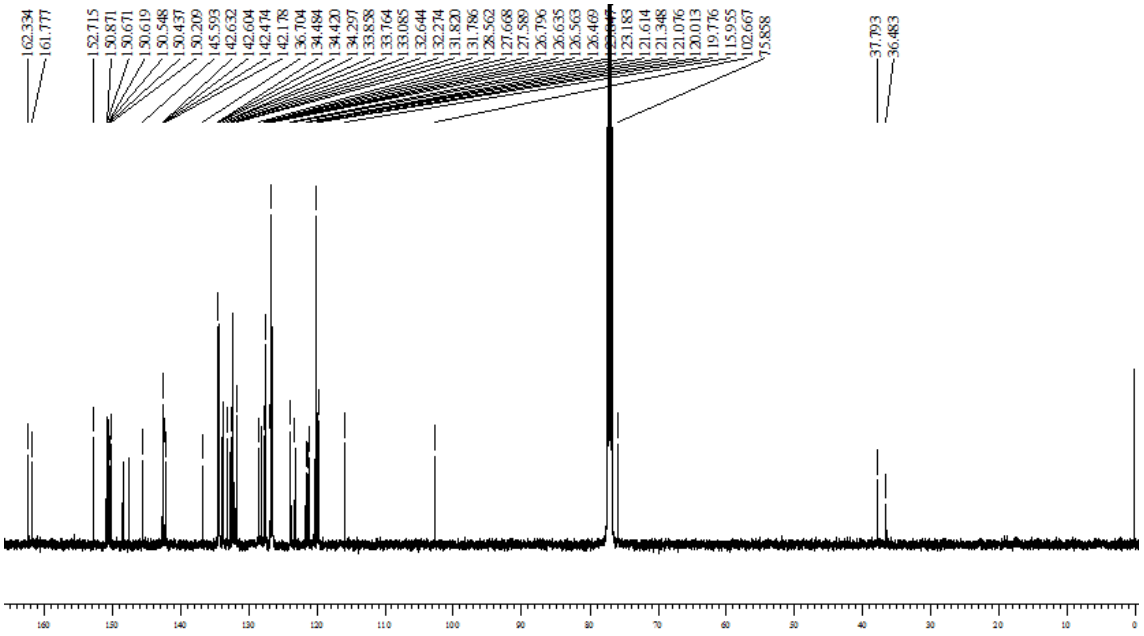
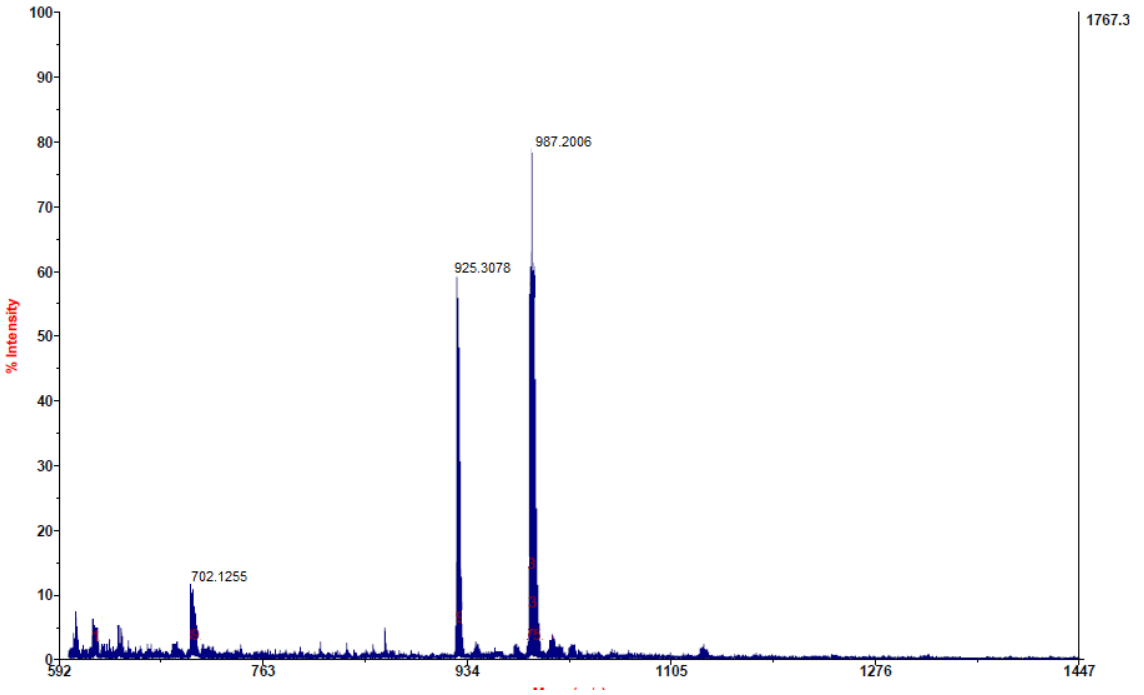
1.4
1.5
1.3
5.1

RMN ^{13}C:



HRMS (ESI^+):

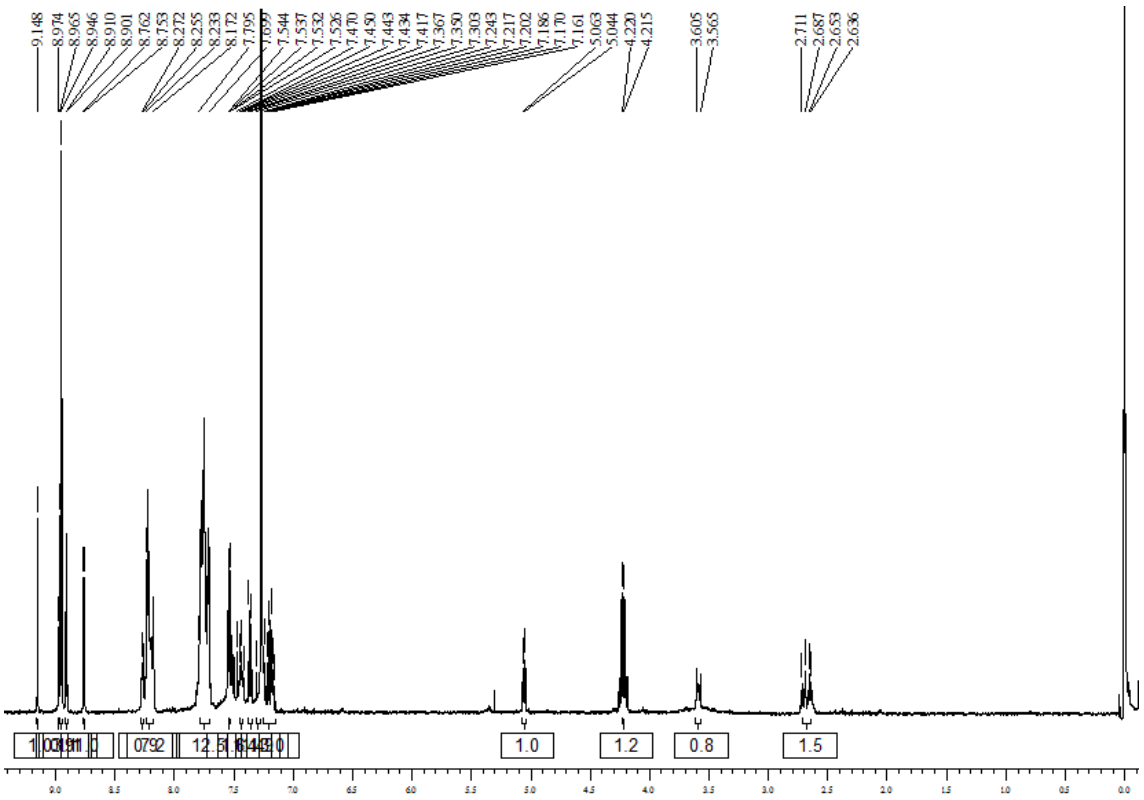


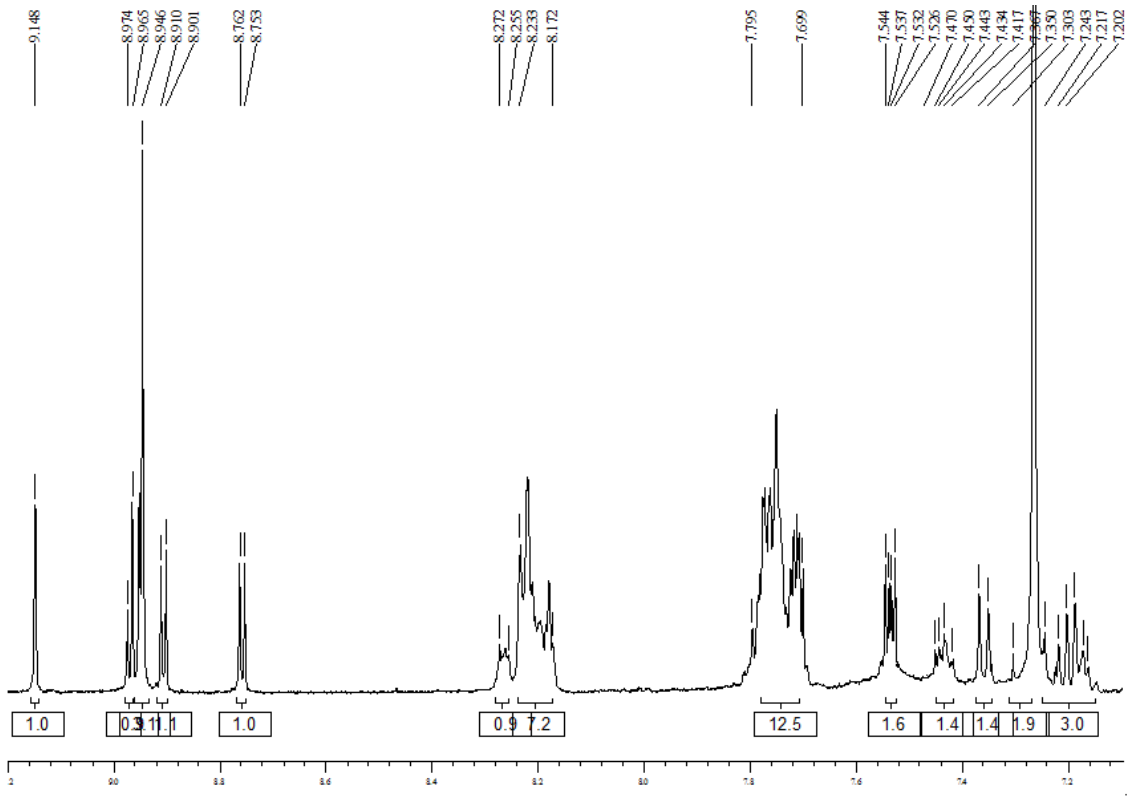
{2-(4-(2-Chlorophenyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6c.2)

^1H NMR (500 MHz, $CDCl_3$): δ = 2.67 (dd, *J* 14.4, 11.1 Hz, 1H, H-3'), 3.56-3.61 (m, 1H, H-3'), 4.22 (d, *J* 5.9 Hz, 1H, H-4'), 5.05 (br d, *J* 11.1 Hz, 1H, H-2'), 7.16–7.30 (m, 5H, H-3",4",5",6", H-9'), 7.36 (d, *J* 8.3 Hz, 1H, H-7'), 7.41-7.47 (m, 1H, *p*-Ph-20), 7.53 (ddd, *J* 8.3, 7.0, 1.5 Hz, 1H, H-8'), 7.70-7.80 (m, 12H, 11H-*m,p*-Ph, H-10'), 8.16-8.25

(m, 7H, *o*-Ph), 8.25-8.28 (m, 1H, *o*-Ph-20), 8.76 (d, *J* 4.7 Hz, 1H, H_β), 8.91 (d, *J* 4.7 Hz, 1H, H_β), 8.95 (s, 3H, H_β, H-12 and H-13), 8.97 (d, *J* 4.7 Hz, 1H, H_β), 9.15 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.9 (C-4'), 36.5 (C-3'), 76.4 (C-2'), 101.0 (C-4a'), 116.5 (C-10a'), 119.4 (C-5"), 120.2 (C-7'), 121.3, 121.4 (C-3" and C-6"), 123.3 (C-10'), 126.3, 126.4, 126.5 (C*m*,*p*-Ph), 127.2, 127.4 (C-4"), 128.4 (C-9'), 130.6, 130.7 (C-8'), 132.3, 132.4, 132.5 (C_β), 134.4, 134.5, 134.6, 134.8 (C*o*-Ph), 136.0 (C-2"), 141.4 (C-2), 142.6, 142.7 (C-1), 145.1 (C-1"), 150.0, 150.1, 150.4, 150.5, (C-10, C-11, C-14, C-15), 151.2 (C-6a'), 161.3 (C-10b'), 162.6 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 421 (5.73), 547 (4.60), 591 (4.50) nm. HRMS (ESI^+): *m/z* $[M+H]^+$ calcd. for $C_{62}H_{39}ClN_4O_3Zn$: 987.2002; found: 987.2004.

RMN ^{1}H:

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8.255
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7.699
7.544
7.537
7.532
7.526
7.470
7.450
7.443
7.434
7.417
7.330
7.303
7.243
7.217
7.202
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0.9
7.2
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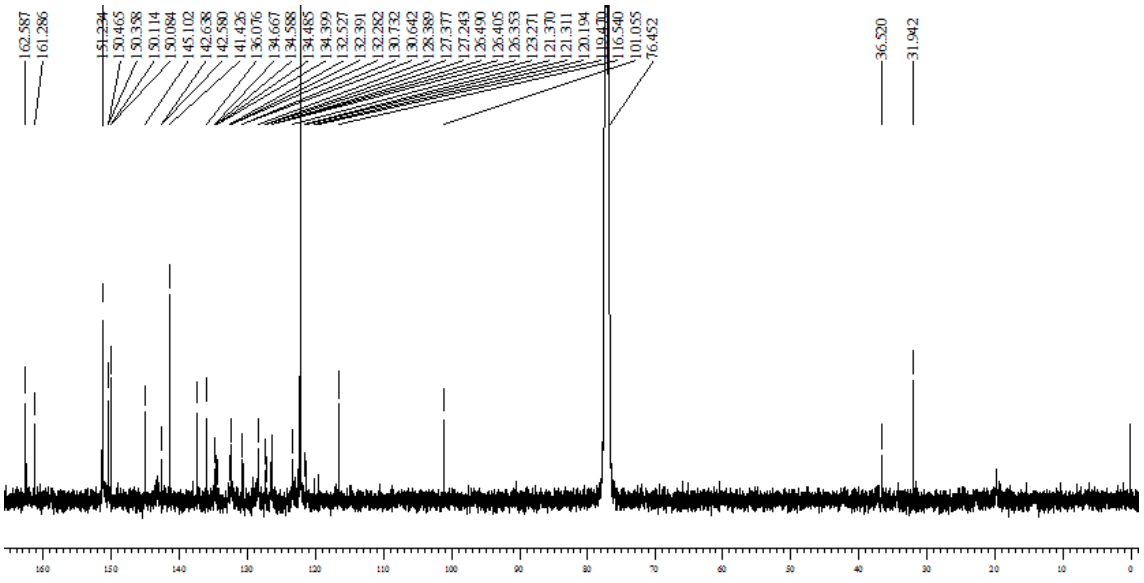
1.6
1.4
1.4
1.9
3.0

RMN ^{13}C: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150.114
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142.580
141.426
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134.588
134.485
134.399
132.527
132.391
132.282
130.732
130.642
128.389
127.377
127.243
126.490
126.405
126.353
123.271
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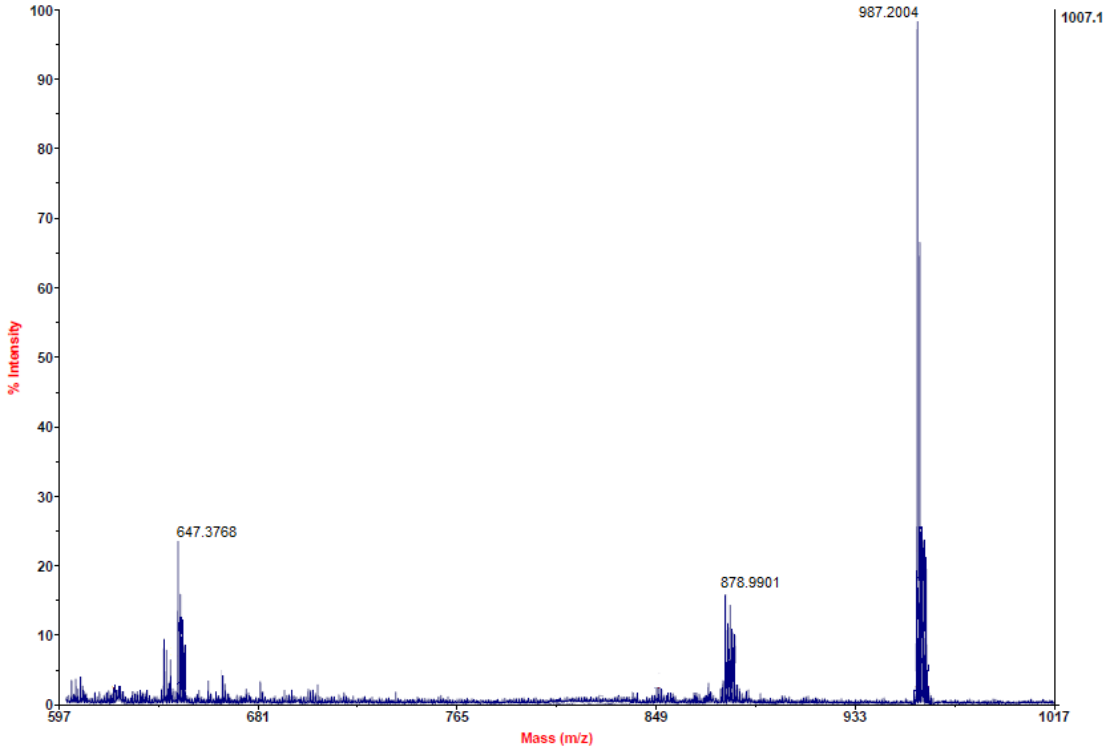
101.055
76.452
36.520
31.942

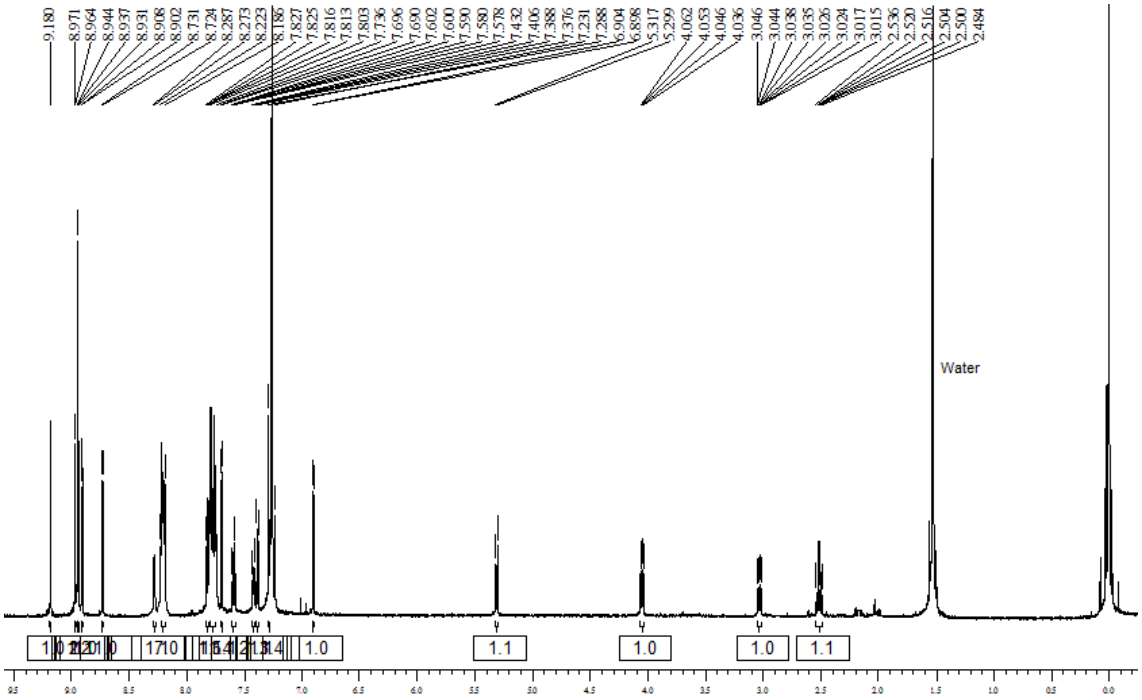
HRMS (ESI$^+$):

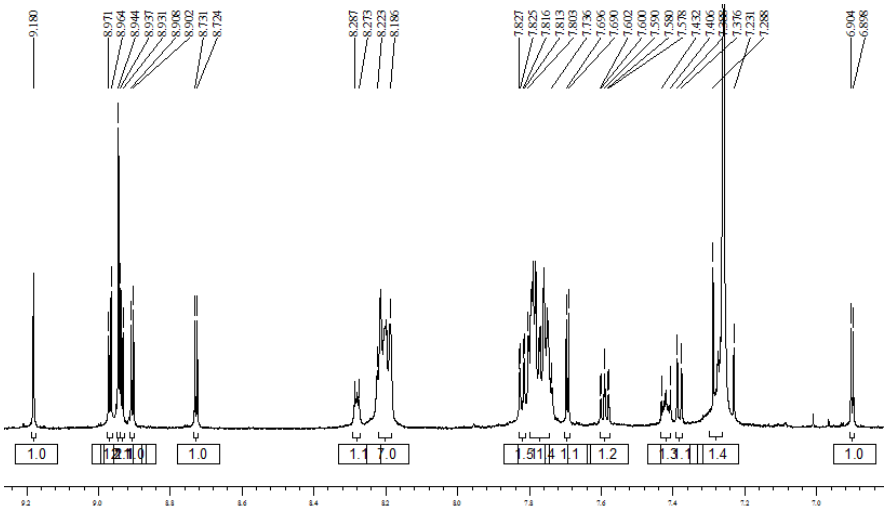


{2-(4-(5-Nitrothiophen-2-yl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6d.1)

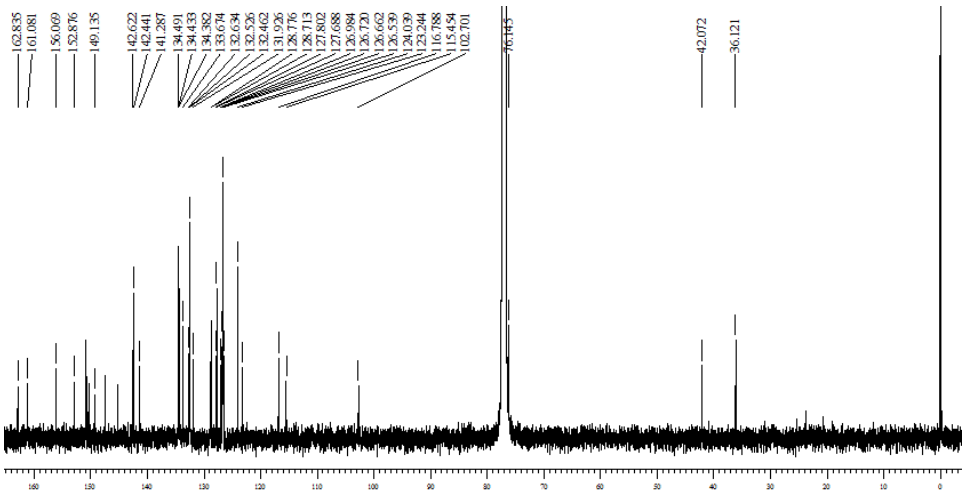
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.51 (dt, *J* 13.6, 11.2 Hz, 1 H, H-3'), 3.03 (ddd, *J* 13.6, 6.4, 1.5 Hz, 1 H, H-3'), 4.05 (dd, *J* 11.2, 6.4 Hz, 1H, H-4'), 5.31 (br d, *J* 13.6 Hz, 1H, H-2'), 6.90 (d, *J* 4.3 Hz, 1H, H-2"), 7.23–7.28 (m, 1H, H-9'), 7.38 (d, *J* 8.5 Hz, 1H, H-7'), 7.41-7.43 (m, 1H, *m,p*-Ph-20), 7.58 (ddd, *J* 8.5, 7.2, 1.5 Hz, 1H, H-8'), 7.69 (d, *J* 4.3 Hz, 1H, H-3"), 7.73-7.81 (m, 11H, *m,p*-Ph), 7.82 (dd, *J* 8.1, 1.5 Hz, 1H, H-10'), 8.17-8.23 (m, 7H, *o*-Ph), 8.27-8.29 (m, 1H, *o*-Ph), 8.73 (d, *J* 4.6 Hz, 1H, H_β), 8.90 (d, *J* 4.6 Hz, 1H, H_β), 8.93 (d, *J* 4.6 Hz, 1H, H_β), 8.94 (s, 2H, H-12 and H-13), 8.97 (d, *J* 4.6 Hz, 1H, H_β), 9.18 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.1 (C-4'), 42.1 (C-3'), 76.1 (C-2'), 102.7 (C-4a'), 115.4 (C-10a'), 116.8 (C-7'), 123.2 (C-10'), 124.0 (C-2"), 126.5, 126.6, 126.7, 127.7, 127.8 (C*m,p*-Ph), 127.0 (C-9'), 128.7, 128.8 (C-3"), 131.9, 132.4, 132.5, 132.6 (C-8', C_β), 133.7, 134.3, 134.4, 134.5 (C*o*-Ph), 141.3 (C-2), 142.4, 142.6 (C-1), 149.1 (C-1"), 152.9 (C-6a'), 156.1 (C-4"), 161.1 (C-10b'), 162.8 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 420 (5.72), 547 (4.59), 596 (4.50) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{60}H_{37}N_5O_5SZn$: 1004.1807; found: 1004.1801.

RMN ^{1}H:

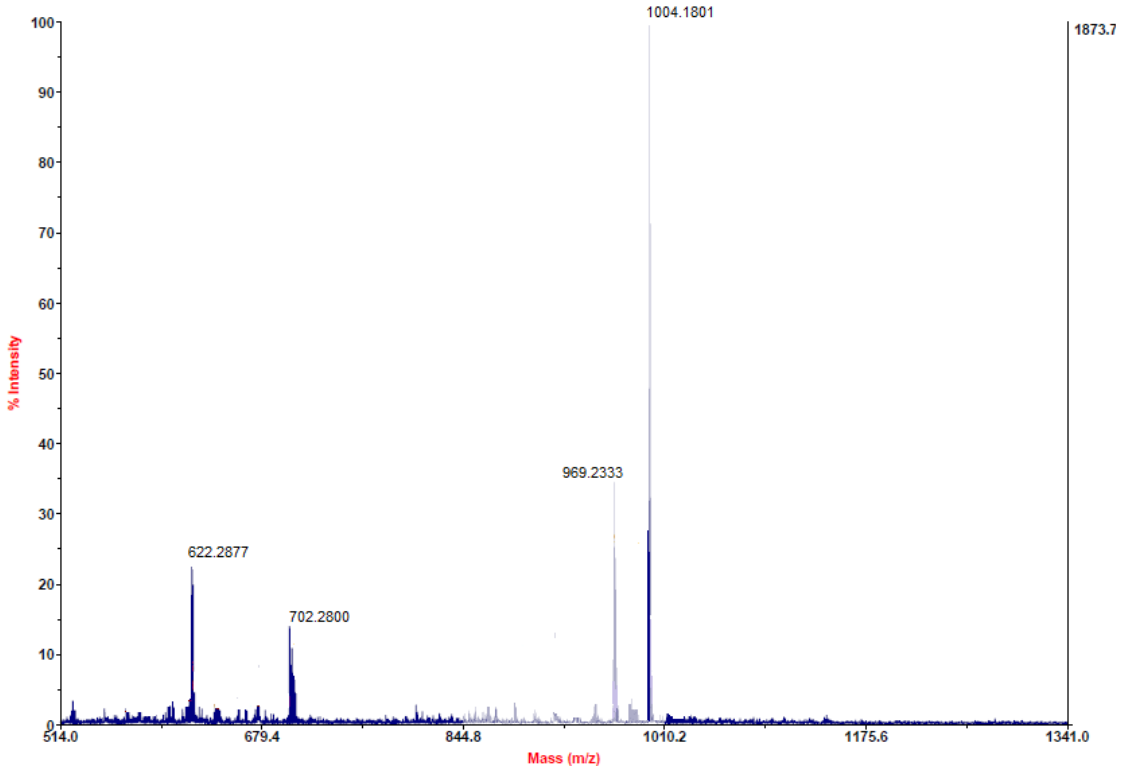




RMN ^{13}C:



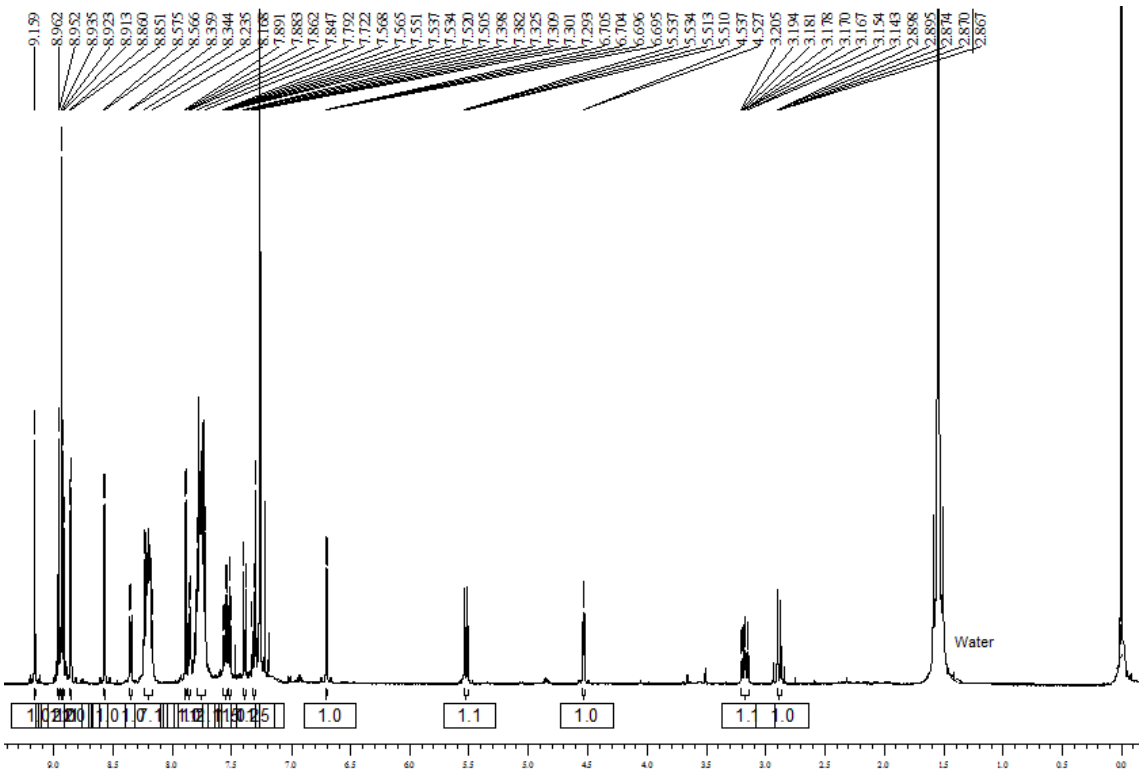
HRMS (ESI$^+$):

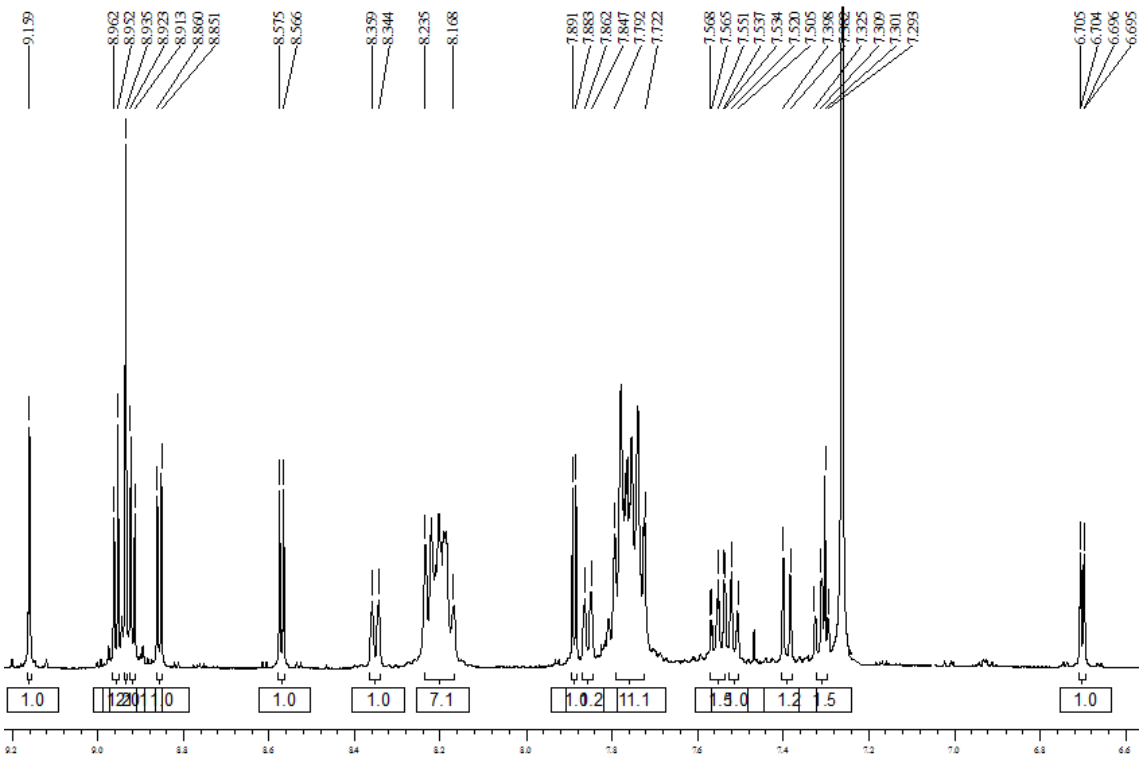


{2-(4-(5-Nitrothiophen-2-yl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6d.2)

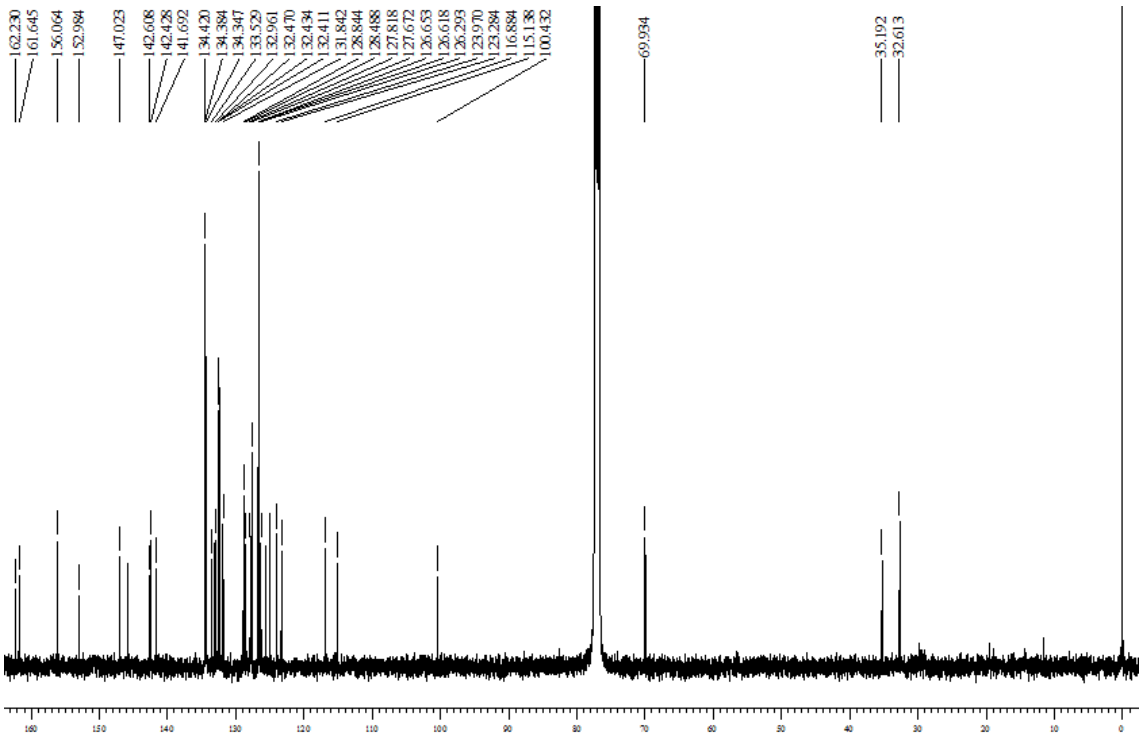
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.88 (dt, *J* 14.0, 11.8 Hz, 1 H, H-3'), 3.17-3.21 (m, 1 H, H-3'), 4.53 (d, *J* 5.3 Hz, 1H, H-4'), 5.31 (dd, *J* 11.8, 1.5 Hz, 1H, H-2'), 6.70 (dd, *J* 4.2, 0.7 Hz, 1H, H-2"), 7.29–7.32 (m, 1H, H-9'), 7.39 (dd, *J* 8.3, 0.5 Hz, 1H, H-7'), 7.51-7.52 (m, 1H, *m,p*-Ph-20), 7.54 (ddd, *J* 8.3, 7.1, 1.4 Hz, 1H, H-8'), 7.72-7.79 (m, 11H, *m,p*-Ph), 7.85 (d, *J* 7.5 Hz, 1H, H-10'), 7.89 (d, *J* 4.2 Hz, 1H, H-3"), 8.17-8.23 (m, 7H, *o*-Ph), 8.34-8.36 (m, 1H, *o*-Ph), 8.57 (d, *J* 4.7 Hz, 1H, H_β), 8.86 (d, *J* 4.7 Hz, 1H, H_β), 8.92 (d, *J* 4.7 Hz, 1H, H_β), 8.93 (s, 2H, H-12 and H-13), 8.96 (d, *J* 4.7 Hz, 1H, H_β), 9.16 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.7 (C-4'), 35.2 (C-3'), 69.9 (C-2'), 100.4 (C-4a'), 115.1 (C-10a'), 116.9 (C-7'), 123.3 (C-10'), 123.9 (C-2"), 126.3, 126.6, 127.7, 127.8 (C*m,p*-Ph), 126.5 (C-9'), 128.5, 128.8 (C-3"), 131.8, 132.4, 132.5, 132.9 (C-8', C_β), 133.5, 134.3, 134.4 (C*o*-Ph), 141.7 (C-2), 142.4, 142.7 (C-1), 147.0 (C-1"), 152.9 (C-6a'), 156.0 (C-4"), 161.6 (C-10b'), 162.2 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 422 (5.71), 547 (4.60), 595 (4.50) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{60}H_{37}N_5O_5SZn$: 1004.1807; found: 1004.1804.

RMN ^{1}H:

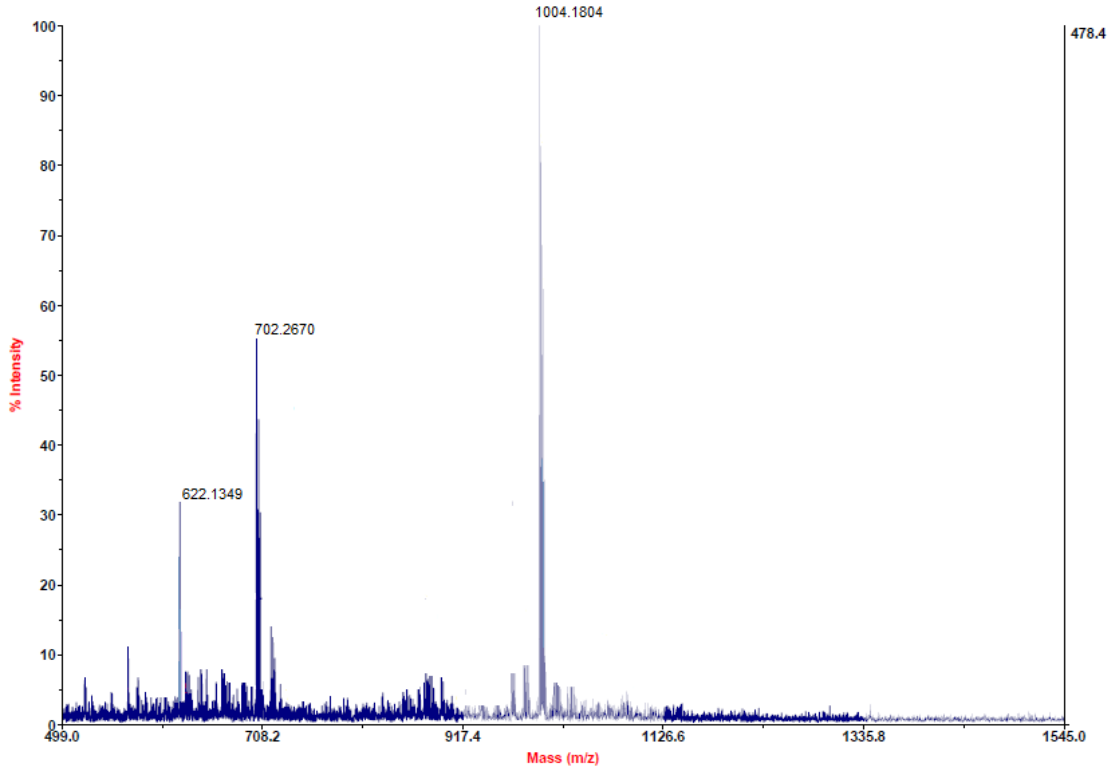




RMN ^{13}C:



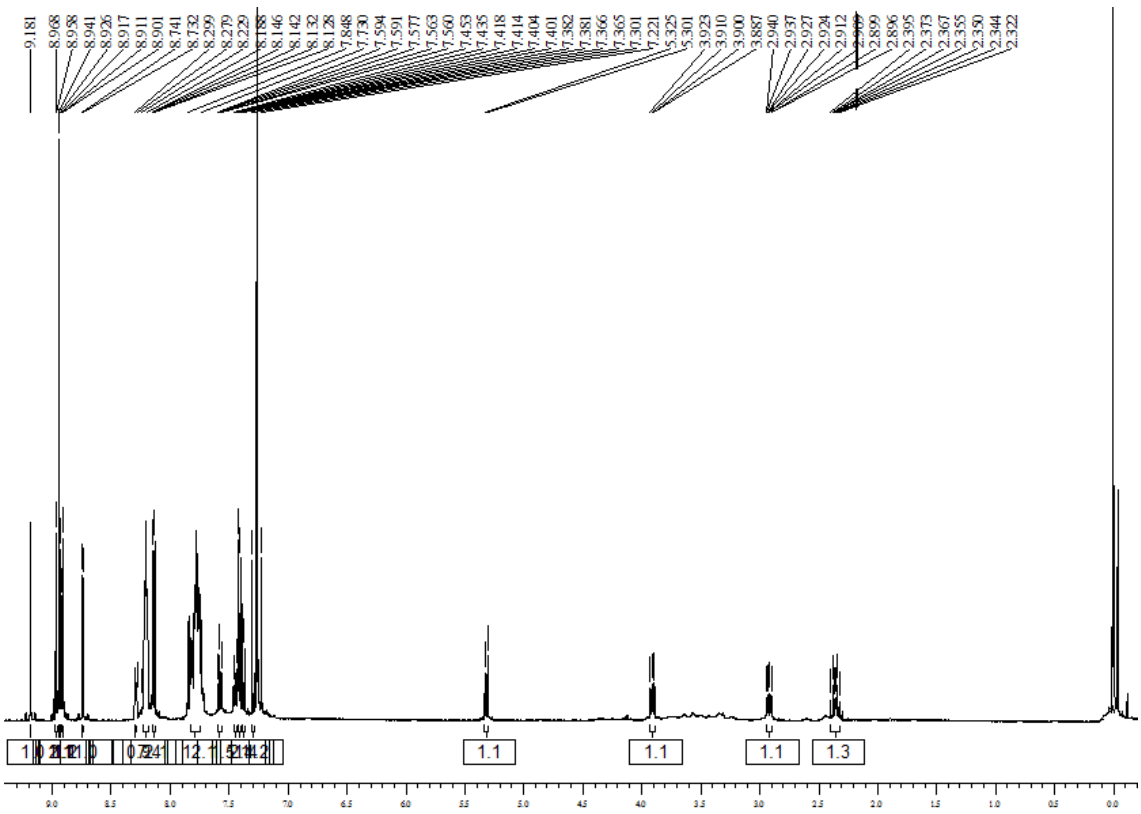
HRMS (ESI$^+$):

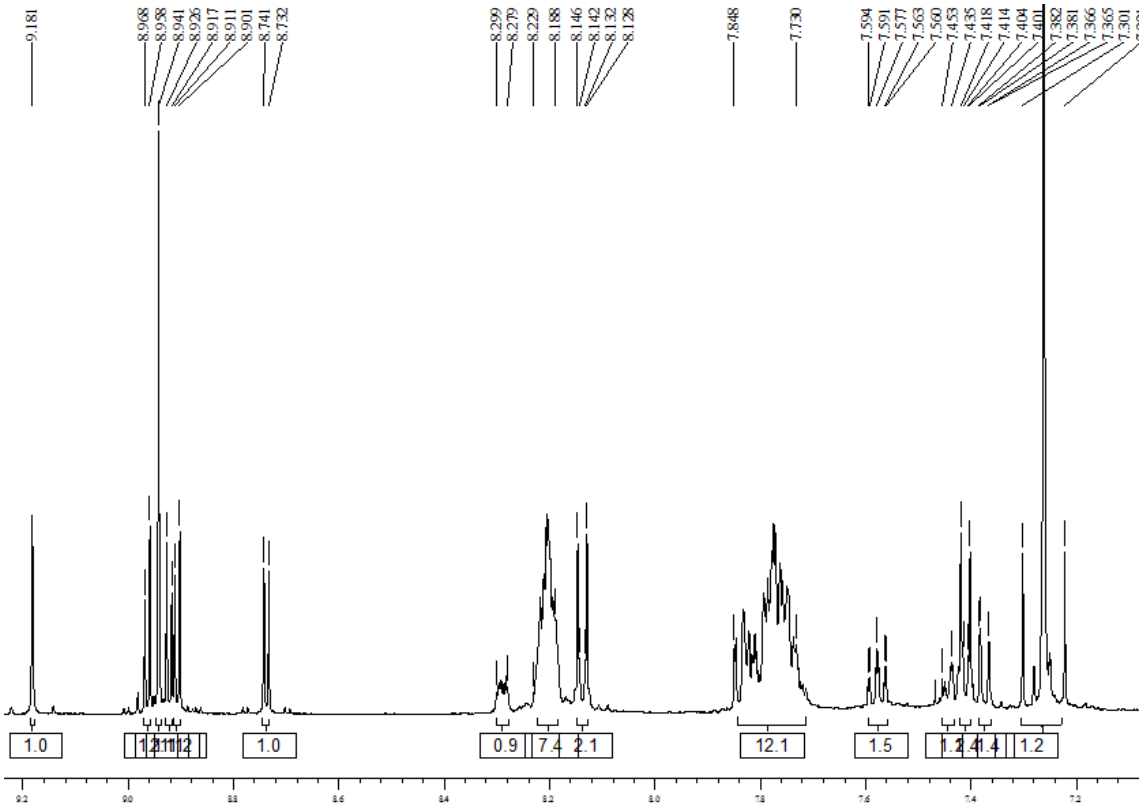


{2-(4-(4-Pyridinyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl) 5,10,15,20-tetraphenylporphyrinato}zinc(II) (6e.1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.36 (dt, *J* 14.2, 11.6 Hz, 1H, H-3'), 2.92 (ddd, *J* 14.2, 6.4, 1.4 Hz, 1H, H-3'), 3.91 (dd, *J* 11.6, 6.4 Hz, 1H, H-4'), 5.31 (br d, *J* 11.6 Hz, 1H, H-2'), 7.22–7.30 (m, 1H, H-9'), 7.37 (dd, *J* 8.4, 0.6 Hz, 1H, H-7'), 7.42 (dd, *J* 8.9, 1.9 Hz, 2H, H-2",6"), 7.43-7.45 (m, 1H, *p*-Ph-20), 7.58 (ddd, *J* 8.4, 7.3, 1.6 Hz, 1H, H-8'), 7.73-7.85 (m, 12H, 11H *m,p*-Ph, H-10'), 8.14 (dd, *J* 8.9, 1.9 Hz, 2H, H-3",5"), 8.18-8.23 (m, 7H, *o*-Ph), 8.27-8.31 (m, 1H, *o*-Ph), 8.74 (d, *J* 4.7 Hz, 1H, H_β), 8.91 (d, *J* 4.7 Hz, 1H, H_β), 8.92 (d, *J* 4.7 Hz, 1H, H_β), 8.94 (s, 2H, H-12 and H-13), 8.96 (d, *J* 4.7 Hz, 1H, H_β), 9.18 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.1 (C-4'), 41.6 (C-3'), 76.2 (C-2'), 103.3 (C-4a'), 115.6 (C-10a'), 120.1 (C-7'), 121.2, 121.5, 121.8 (C-2",6"), 123.9, 124.1 (C-10'), 126.5, 126.6, 126.7, 126.9, 127.6, 127.7 (C*m,p*-Ph), 128.7 (C-9'), 131.8, 132.1 (C-8'), 132.3, 132.4, 132.5, 132.6 (C_β), 134.3, 134.4, 134.5 (C*o*-Ph), 142.4 (C-2), 142.7 (C-1), 145.3 (C-1"), 150.3, 150.5, 150.6, 150.7, 150.8, 150.9 (C-10, C-11, C-14, C-15), 151.2 (C-3",5"), 152.8 (C-6a'), 161.4 (C-10b'), 163.0 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 422 (4.95), 544 (4.56) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{61}H_{39}N_5O_3Zn$: 954.2344; found: 954.2349.

RMN ^{1}H:

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7.418
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7.404
7.401
7.382
7.381
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7.365
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7.4
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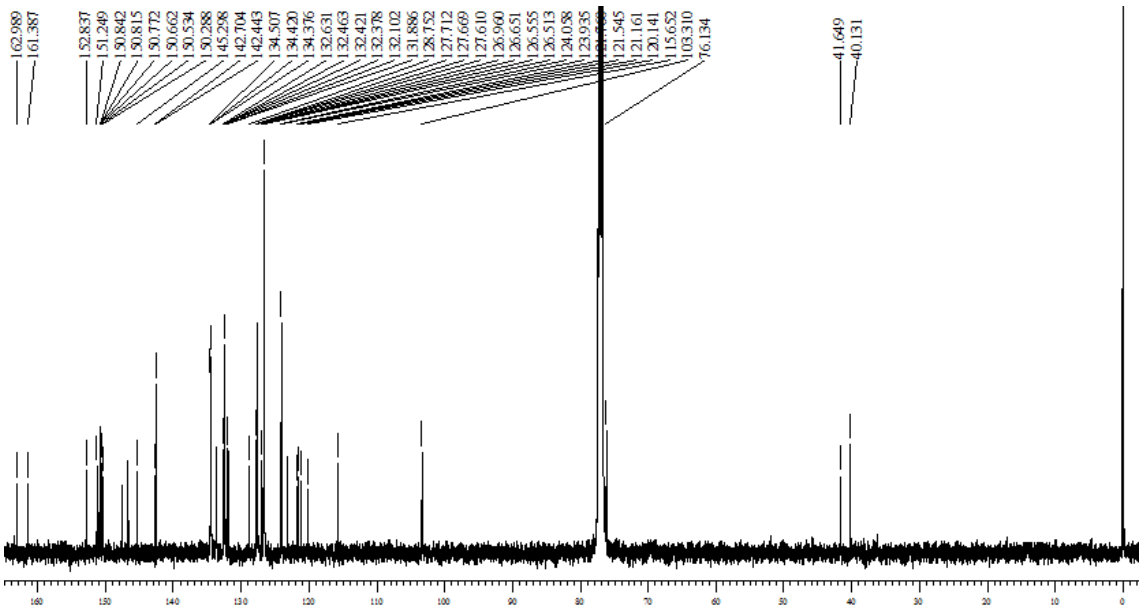
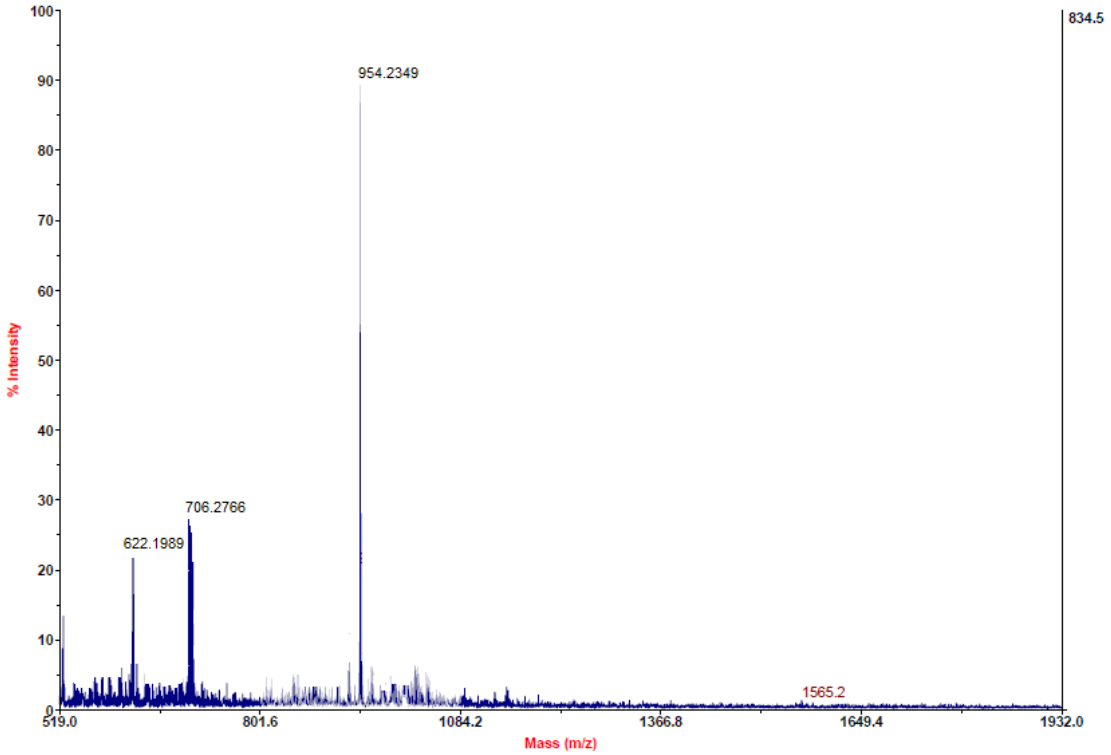
1.5
1.2
1.4
1.2

RMN ^{13}C:


162.980
161.387
152.837
151.249
150.842
150.815
150.772
150.662
150.534
150.288
145.298
142.704
142.443
134.507
134.420
134.376
132.631
132.463
132.421
132.378
132.102
131.886
128.752
127.712
127.669
127.610
126.960
126.651
126.555
126.513
124.058
123.935
121.545
121.161
120.141
115.652
103.310
76.134
41.649
40.131

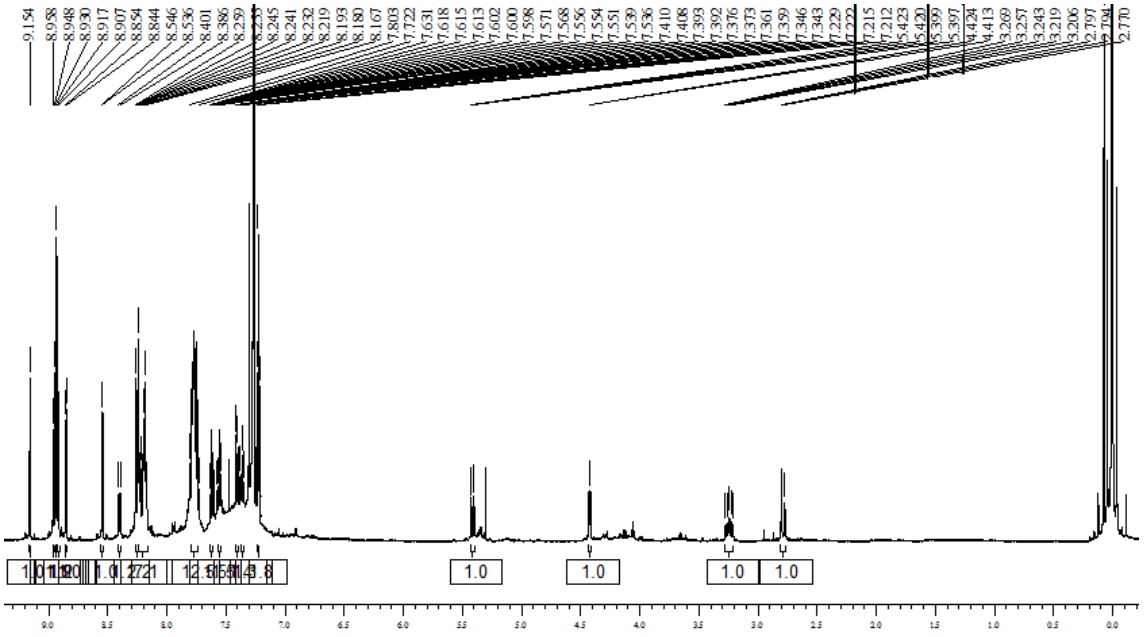
HRMS (ESI$^+$):

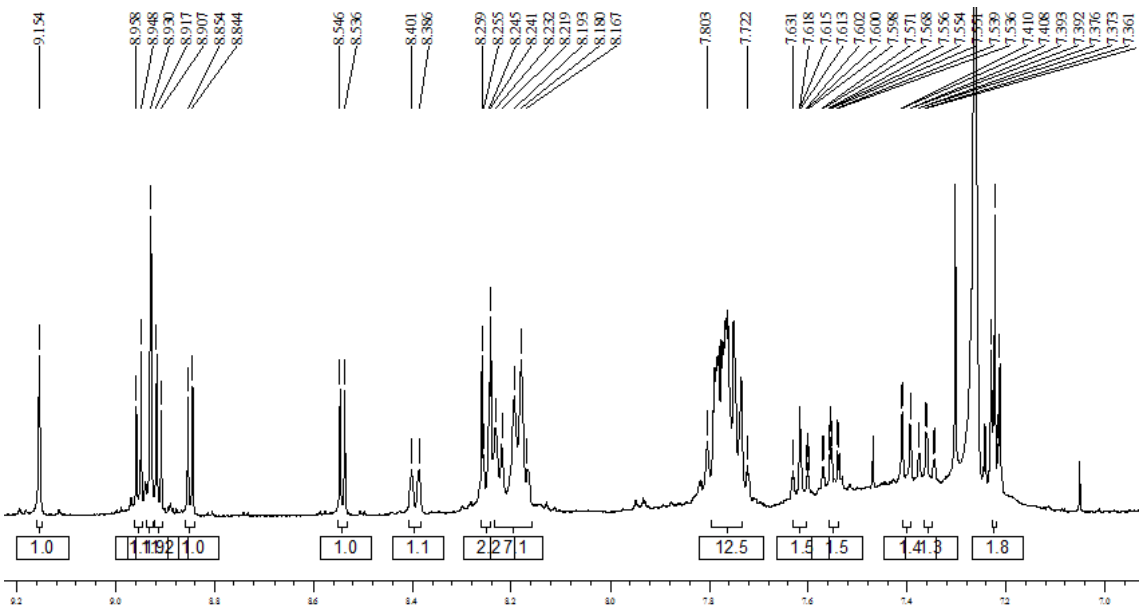


{2-(4-(4-Pyridinyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl) 5,10,15,20-tetraphenylporphyrinato}zinc(II) (6e.2)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.78 (dd, *J* 14.5, 11.0 Hz, 1H, H-3'), 3.24 (m, 1H, H-3'), 4.42 (d, *J* 5.4 Hz, 1H, H-4'), 5.41 (dd, *J* 11.0, 1.5 Hz, 1H, H-2'), 7.22 (dd, *J* 8.7, 1.8 Hz, 2H, H-2",6"), 7.34–7.38 (m, 1H, H-9'), 7.40 (dd, *J* 8.4, 0.8 Hz, 1H, H-7'), 7.53-7.57 (m, 1H, *m,p*-Ph-20), 7.62 (ddd, *J* 8.4, 7.1, 1.3 Hz, 1H, H-8'), 7.72-7.80 (m, 12H, 11H *m,p*-Ph and H-10'), 8.17-8.23 (m, 7H, *o*-Ph), 8.25 (dd, *J* 8.7, 1.8 Hz, 2H, H-3",5"), 8.38-8.41 (m, 1H, *o*-Ph), 8.54 (d, *J* 4.7 Hz, 1H, H_β), 8.85 (d, *J* 4.7 Hz, 1H, H_β), 8.91 (d, *J* 4.7 Hz, 1H, H_β), 8.93 (s, 2H, H-12 and H-13), 8.95 (d, *J* 4.7 Hz, 1H, H_β), 9.15 (s, 1H, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (C-4'), 30.9 (C-3'), 69.2 (C-2'), 100.6 (C-4a'), 115.3 (C-10a'), 116.8 (C-7'), 121.3, 121.5, 121.7 (C-2",6"), 123.8, 123.9 (C-10'), 126.5, 126.6, 126.7, 127.7, 127.8 (C*m,p*-Ph), 129.0 (C-9'), 131.8, 132.1 (C-8'), 132.3, 132.4, 132.9, 133.1, 133.4 (C_β), 134.3, 134.4, 134.7 (C*o*-Ph), 142.4 (C-2), 142.6 (C-1), 145.9 (C-1"), 150.1, 150.6, 150.7, 150.8 (C-10, C-11, C-14, C-15), 151.3 (C-3",5"), 152.9 (C-6a'), 161.9 (C-10b'), 162.3 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 423 (4.95), 545 (4.55) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{61}H_{39}N_5O_3Zn$: 954.2344; found: 954.2345.

RMN ^{1}H:


9.154
8.958
8.948
8.930
8.917
8.907
8.854
8.844
8.546
8.536
8.401
8.386
8.299
8.255
8.245
8.241
8.232
8.219
8.193
8.180
8.167
7.803
7.722
7.631
7.618
7.615
7.613
7.602
7.600
7.598
7.571
7.568
7.556
7.554
7.551
7.539
7.536
7.410
7.408
7.393
7.392
7.376
7.373
7.361
7.339
7.346
7.343
7.229
7.222
7.215
7.212
5.423
5.420
5.399
5.397
4.424
4.413
3.269
3.257
3.243
3.219
3.206
2.797
2.794
2.770
1.0
1.0
1.0
1.0


9.154
8.958
8.948
8.930
8.917
8.907
8.854
8.844
8.546
8.536
8.401
8.386
8.259
8.255
8.245
8.241
8.232
8.219
8.193
8.180
8.167
7.803
7.722
7.631
7.618
7.615
7.613
7.602
7.600
7.598
7.571
7.568
7.556
7.554
7.539
7.536
7.410
7.408
7.393
7.392
7.376
7.373
7.361
1.0
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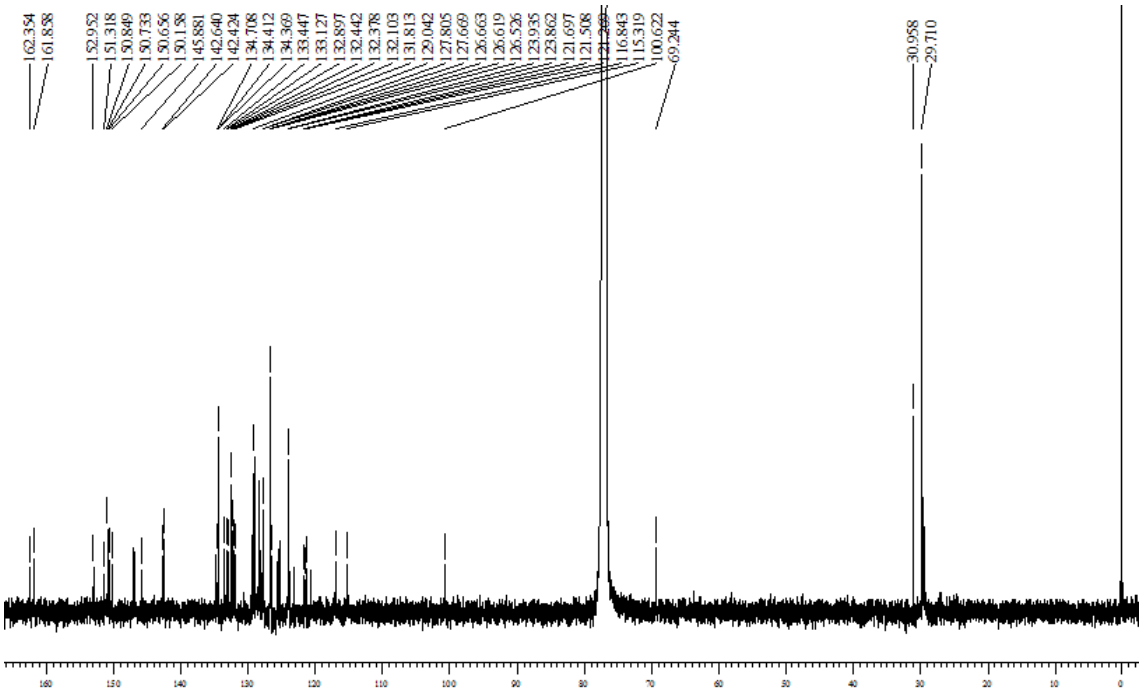
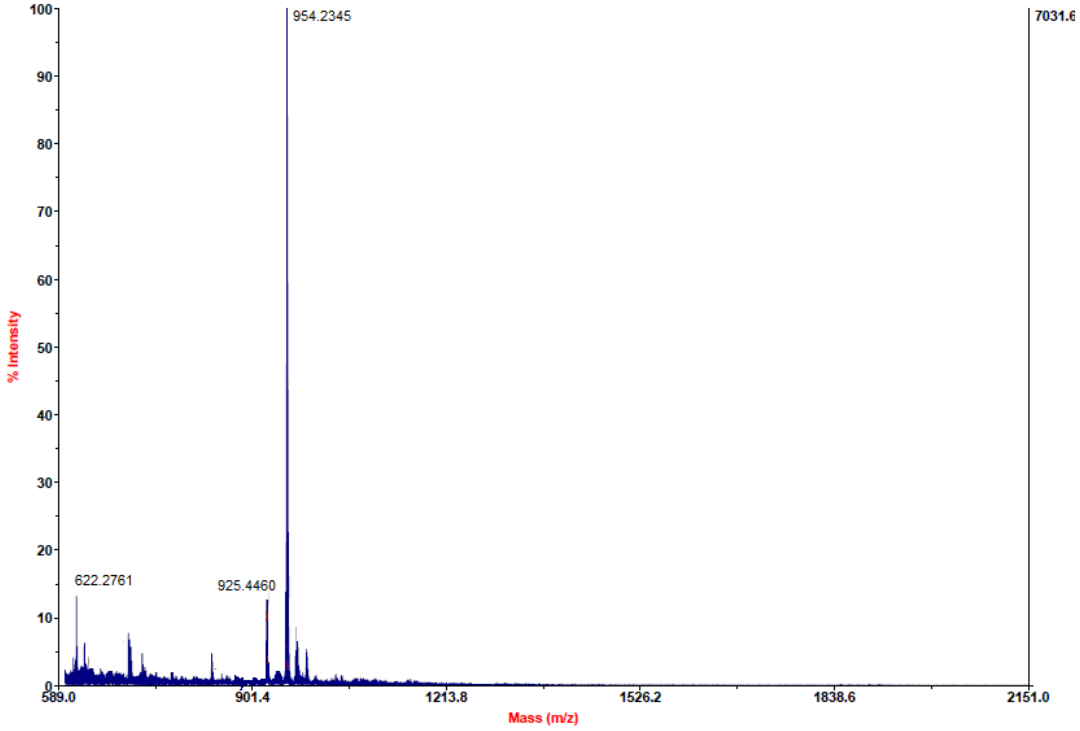
1.0
1.1
2.2
7.1
12.5
1.5
1.5
1.4
1.3
1.8

RMN 13C:



HRMS (ESI$^+$):

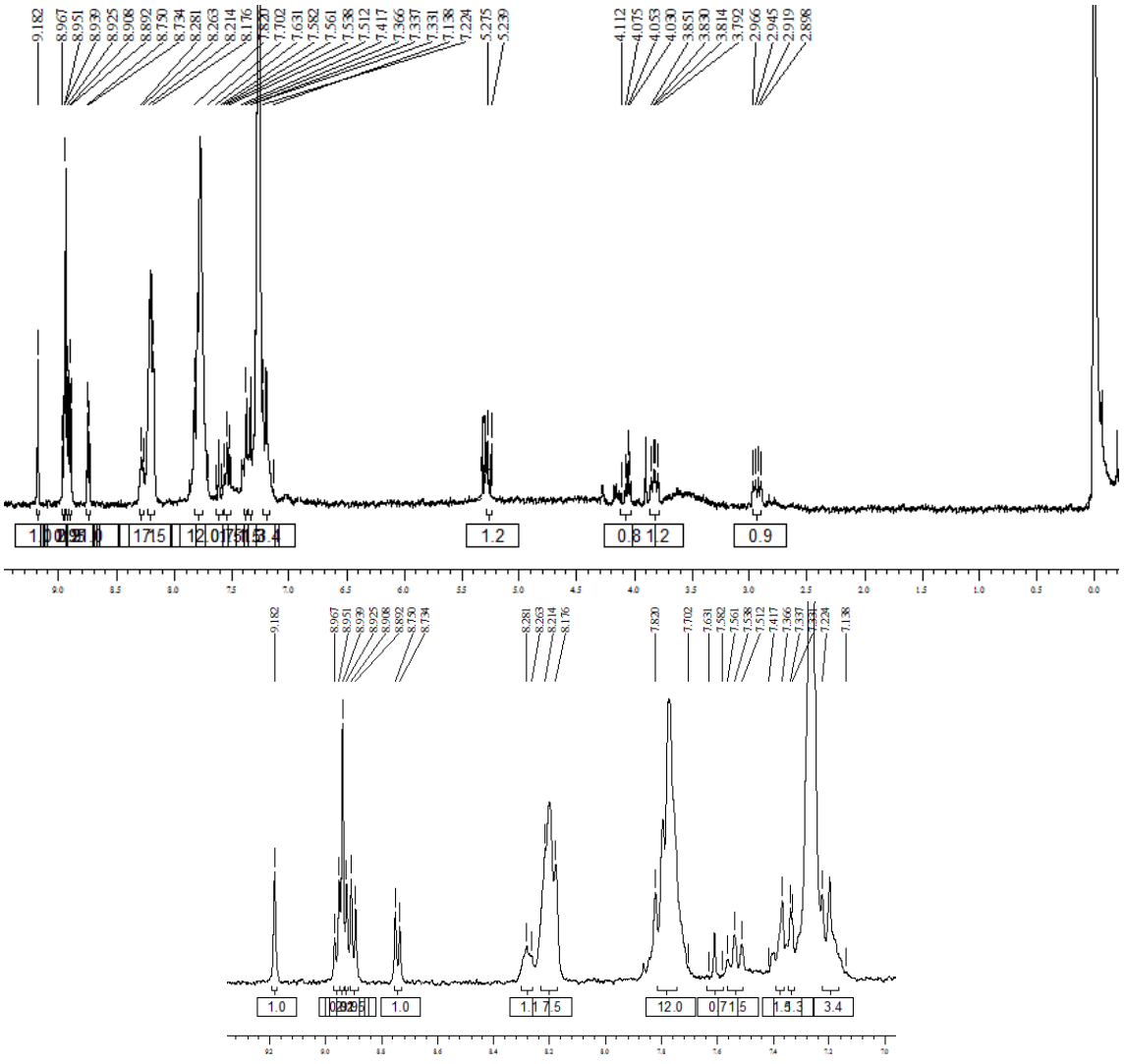


{2-(4-(3-Bromophenyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6f.1)

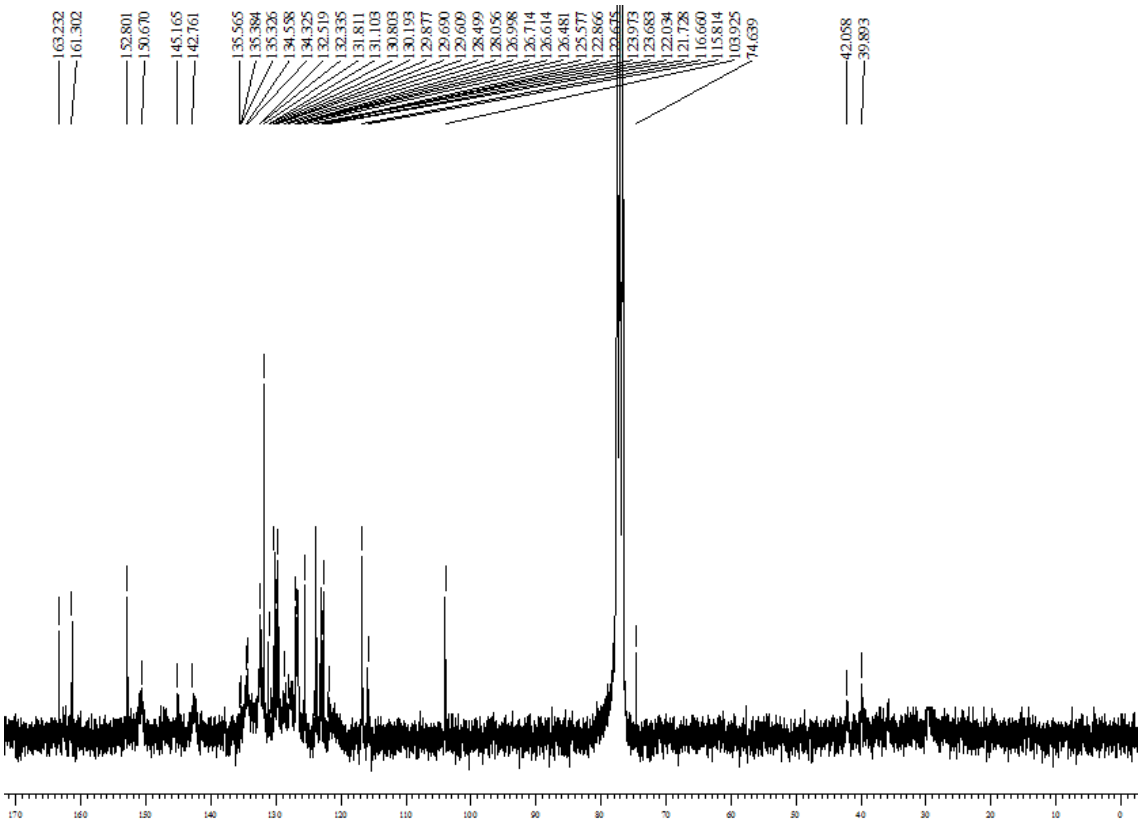
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.93 (dd, *J* 14.3, 11.5 Hz, 1 H, H-3'), 3.82 (dd, *J* 14.3, 6.5 Hz, 1 H, H-3'), 4.00-4.10 (m, 1H, H-4'), 5.24 (br d, *J* 11.5 Hz, 1H, H-2'), 7.14–7.23

(m, 3H, H-5”, H-6” and H-9’), 7.35 (d, *J* 8.1 Hz, 1H, H-7’), 7.38-7.42 (m, 1H, *m,p*-Ph-20), 7.54 (t, *J* 8.1 Hz, 1H, H-8’), 7.59-7.63 (m, 2H, H-2” and H-4”), 7.71-7.83 (m, 12H, 11H *m,p*-Ph and H-10’), 8.15-8.25 (m, 7H, *o*-Ph), 8.25-8.31 (m, 1H, *o*-Ph), 8.74 (d, *J* 4.7 Hz, 1H, H_β), 8.90 (d, *J* 4.7 Hz, 1H, H_β), 8.92 (d, *J* 4.7 Hz, 1H, H_β), 8.94 (s, 2H, H-12 and H-13), 8.96 (d, *J* 4.7 Hz, 1H, H_β), 9.18 (s, 1H_β, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.9 (C-4’), 42.0 (C-3’), 74.6 (C-2’), 103.7 (C-4a’), 115.4 (C-10a’), 116.7 (C-7’), 121.7, 122.0, 123.7, 123.9 (C-2” and C-6”), 122.7, 122.9 (C-10’), 125.3 (C-4”), 126.5, 126.6, 126.8, 127.0 (C*m,p*-Ph), 128.0, 128.2 (C-9’), 129.6, 129.7, 129.9, 130.2 (C-5”), 130.9, 131.1, 131.8, 132.3, 132.5 (C-8’, C_β), 134.5, 134.6, 135.3, 135.5 (C*o*-Ph), 142.7 (C-1), 145.2 (C-2), 150.7 (C-1”), 152.8 (C-6a’), 161.3 (C-10b’), 163.2 (C-5’). UV/vis ($CHCl_3$): λ_{max} (log ε): 420 (4.98), 544 (4.58) nm. HRMS (ESI^+): *m/z* $[M+H]^+$ calcd. for $C_{62}H_{39}BrN_4O_3Zn$: 1031.1497; found: 1031.1494.

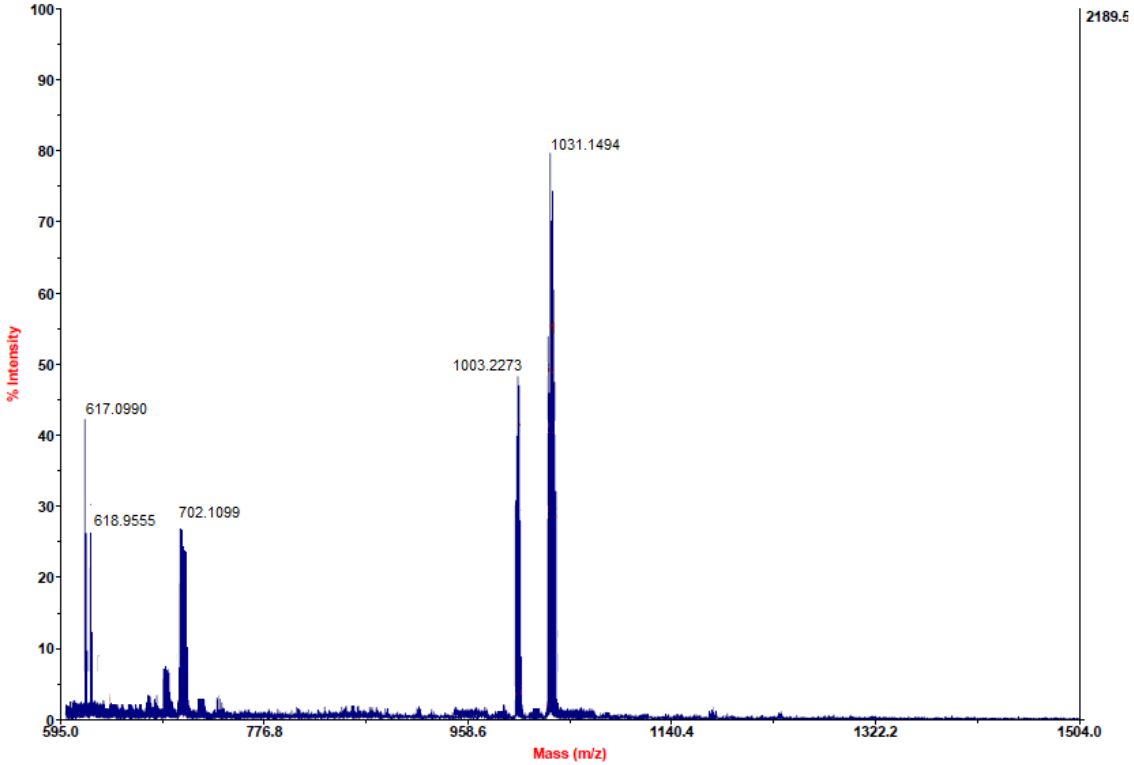
RMN ^{1}H:



RMN ^{13}C:



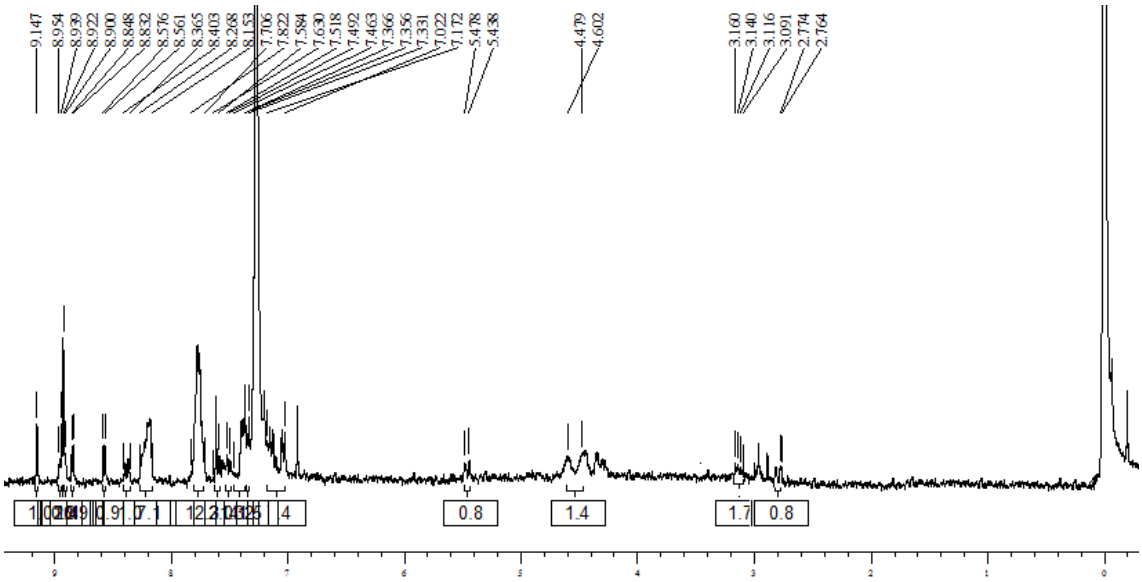
HRMS (ESI^{+}):



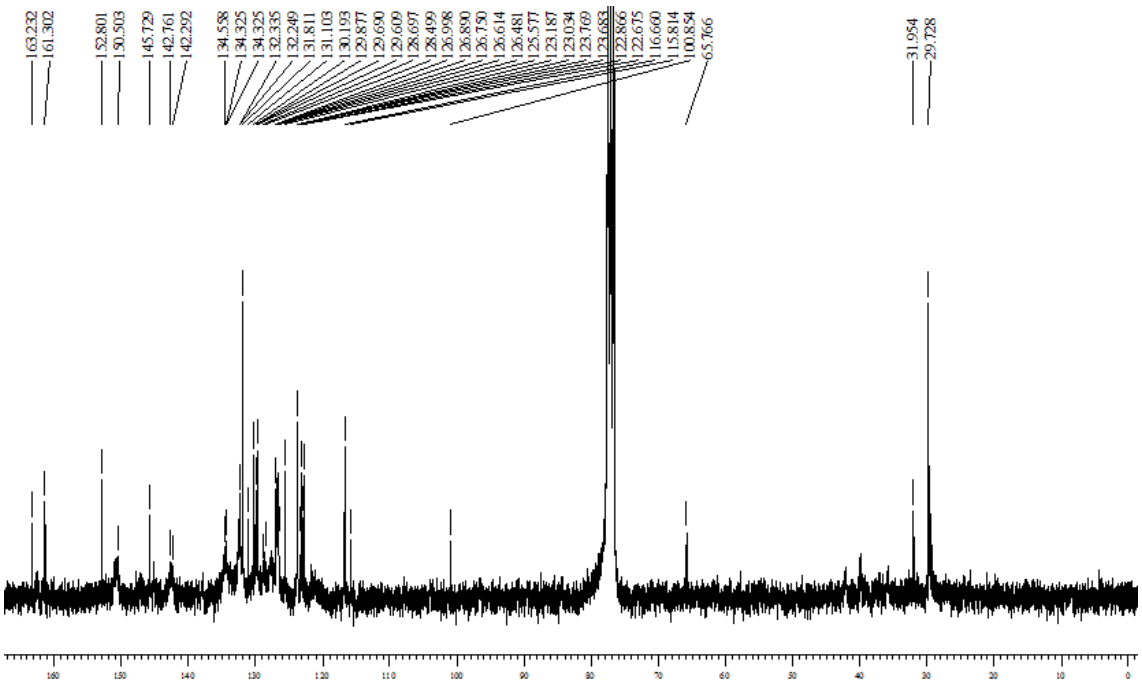
{2-(4-(3-Bromophenyl)-5-oxo-2,3,4,5-tetrahydro-2*H*-pyrano[3,2-*c*]chromen-2-yl)-5,10,15,20-tetraphenylporphyrinato}zinc(II) (6f.2)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.77 (dd, *J* 14.6, 11.3 Hz, 1H, H-3'), 3.11 (dd, *J* 14.3, 5.9 Hz, 1 H, H-3'), 4.53 (d, *J* 5.9 Hz, 1H, H-4'), 5.47 (br d, *J* 11.3 Hz, 1H, H-2'), 7.00–7.17 (m, 3H, H-5", H-6" and H-9'), 7.35 (d, *J* 8.3, 0.8 Hz, 1H, H-7'), 7.37-7.46 (m, 1H, *m,p*-Ph-20), 7.51 (dd, *J* 8.3, 7.9 Hz, 1H, H-8'), 7.57-7.63 (m, 2H, H-2" and H-4"), 7.70-7.83 (m, 12H, 11H *m,p*-Ph and H-10'), 8.14-8.27 (m, 7H, *o*-Ph), 8.34-8.41 (m, 1H, *o*-Ph), 8.57 (d, *J* 4.7 Hz, 1H, H_β), 8.84 (d, *J* 4.7 Hz, 1H, H_β), 8.89 (d, *J* 4.7 Hz, 1H, H_β), 8.92 (s, 2H, H-12 and H-13), 8.95 (d, *J* 4.7 Hz, 1H, H_β), 9.15 (s, 1H_β, H-3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (C-4'), 31.9 (C-3'), 65.7 (C-2'), 100.7 (C-4a'), 115.8 (C-10a'), 116.7 (C-7'), 122.7, 122.9, 123.7, 123.8 (C-2" and C-6"), 123.0, 123.2 (C-10'), 125.6 (C-4"), 126.5, 126.6, 126.7, 126.9, 127.0 (C*m,p*-Ph), 128.5, 128.6 (C-9'), 129.6, 129.7, 129.9 (C-5"), 130.2, 131.1, 131.8, 132.3, 132.4 (C-8', C_β), 133.7, 134.3, 134.4, 134.5 (C*o*-Ph), 142.3, 142.7 (C-1), 145.7 (C-2), 150.5 (C-1"), 152.8 (C-6a'), 161.3 (C-10b'), 162.4 (C-5'). UV/vis ($CHCl_3$): λ_{max} (log ε): 420 (4.97), 546 (4.58) nm. HRMS (ESI$^+$): *m/z* $[M+H]^+$ calcd. for $C_{62}H_{39}BrN_4O_3Zn$: 1031.1497; found: 1031.1490.

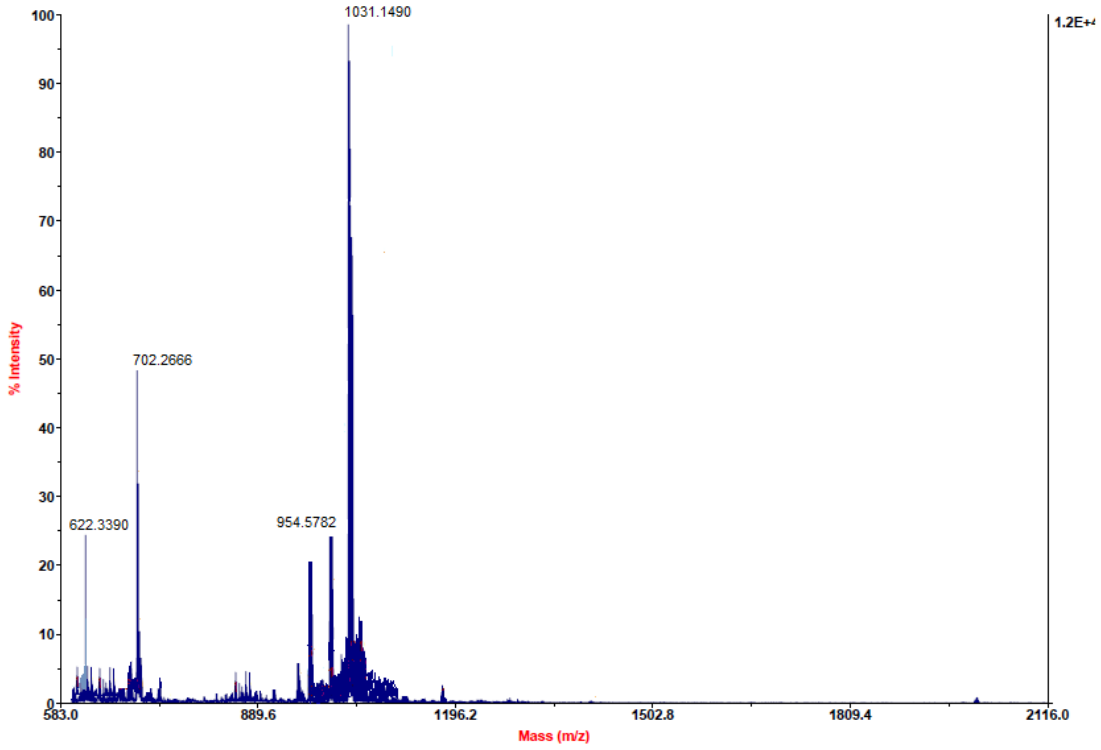
RMN ^{1}H:



RMN ^{13}C:



HRMS (ESI^{+}):



The ohmic heating reactor prototype

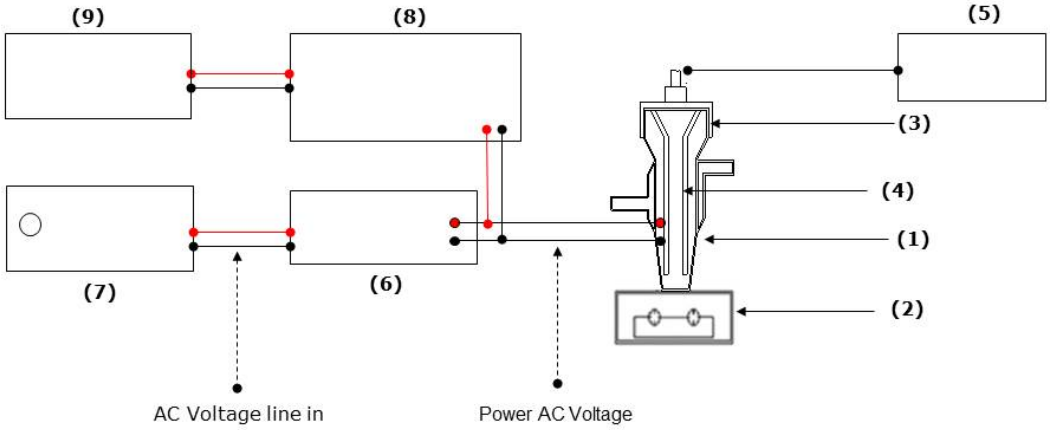


Figure 1. Schematic representation of the ohmic heating reactor **(Portuguese Patent nº 105908)**

1- 10 mL Glass reactor.

2- Magnetic stirring plate and cylindrical magnetic stirrer.

3- Reactor cover (PEEK, polyether ether ketone).

4- Stainless steel (type 316) cylindrical electrodes, arranged in parallel rods (4 mm of diameter); distance between the electrodes: 10 mm.

5- Type J sheathed thermocouple.

6- Power amplifier.

7- Signal function generator.

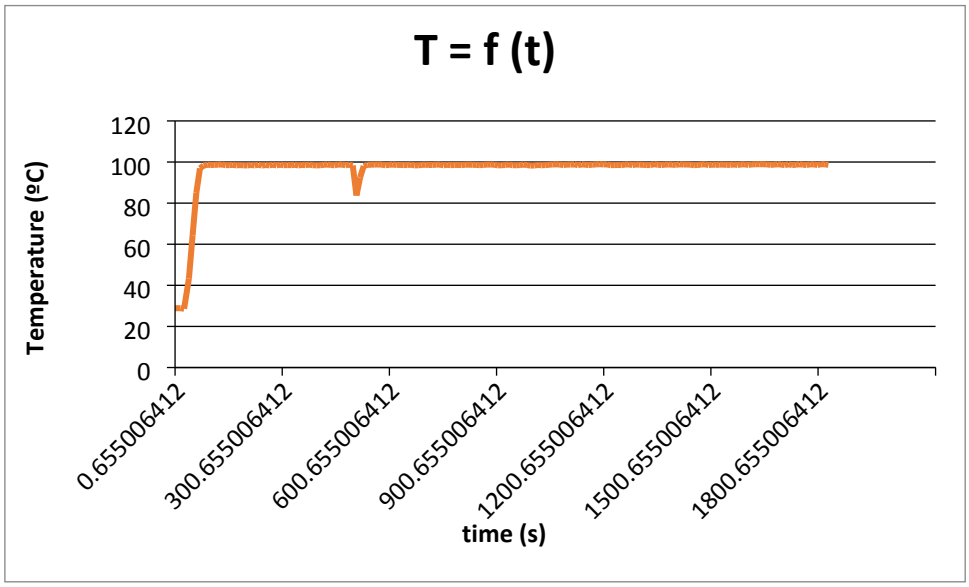
8- Data acquisition / data logger switch unit (data acquisition of temperature, voltage, frequency, electric current and power in the reactor is done using a software application developed in Agilent VEE).

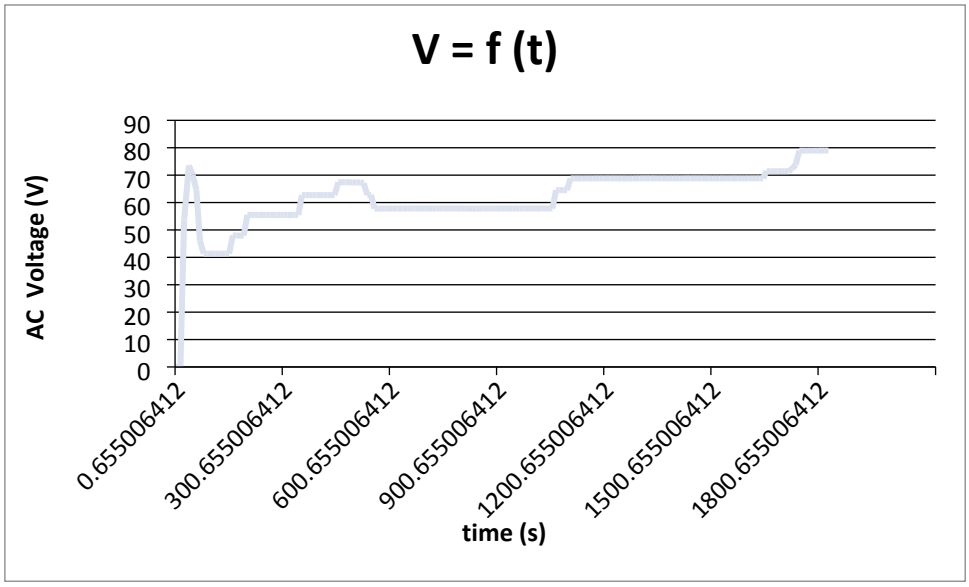
9- Computer.

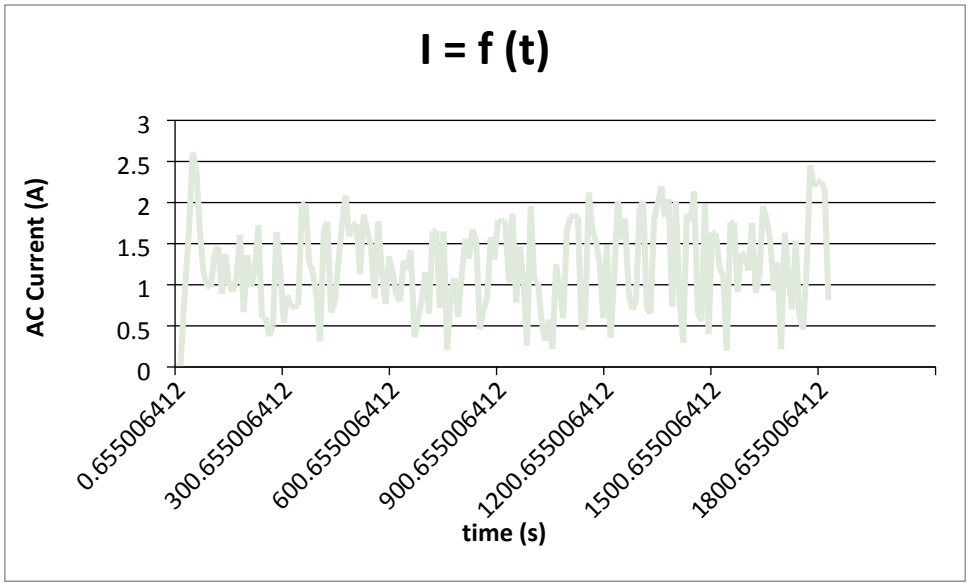
In ohmic heating, the heating process depends on the electrical impedance, more precisely the AC resistance of the medium and the applied voltage. On the other hand the applied voltage depends on the input power from the amplifier, which also depends on the AC resistance of the medium. As the distance between the electrodes is fixed (10

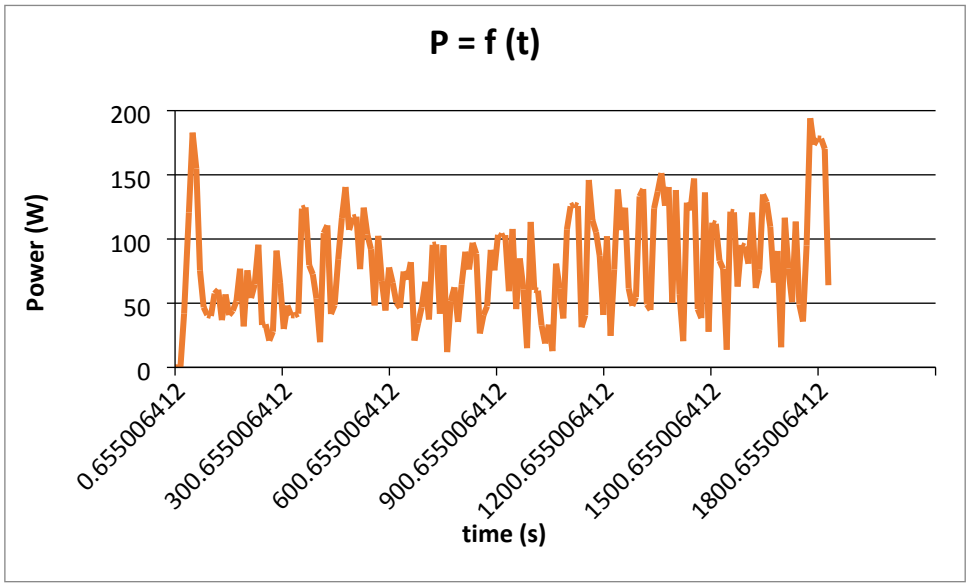
mm), the field strength applied will vary from experiment to experiment. The frequency used in this work was fixed at 25 KHz.

As an example, herein we present the data of temperature, voltage, electric current and power recorded during one experiment (entry 1 of table 1).






I = f (t)
AC Current (A)
3
2.5
2
1.5
1
0.5
0
0.655006412
300.655006412
600.655006412
900.655006412
1200.655006412
1500.655006412
1800.655006412
time (s)


P = f (t)
Power (W)
200
150
100
50
0
0.655006412
300.655006412
600.655006412
900.655006412
1200.655006412
1500.655006412
1800.655006412
time (s)