Electronic Supporting Information

Geometric Deconstruction of Core and Electron Activation of π-System in Deformed Porphyrin Series: Mimics of Heme

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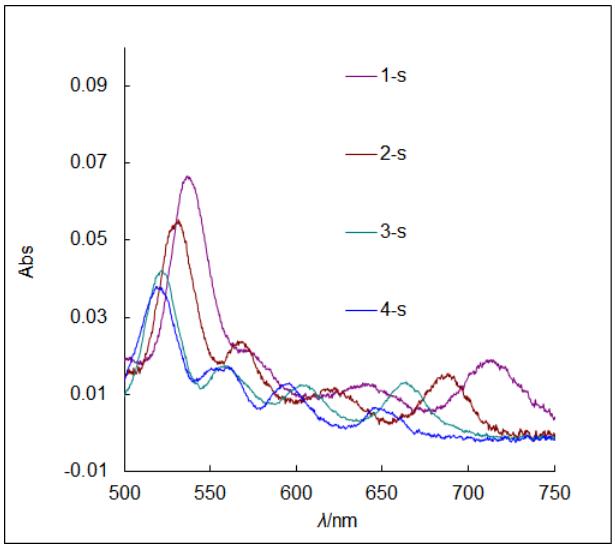
Contents

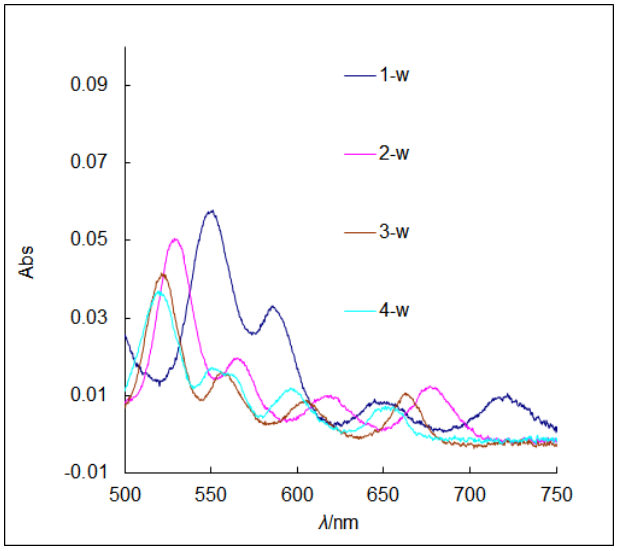
1. UV/Vis spectral data

Table S1. UV/Vis spectral data, λ_{max} [nm] (logε) of all mimics in $CHCl_3$ at 293 K

Compound	Soret region	Q region			
1-*s*	446 (5.30)	537 (4.13)	573 (3.64)	630 (2.78)	711 (3.58)
2-*s*	438 (5.46)	532 (4.20)	568 (3.82)	611 (2.94)	689 (3.64)
3-*s*	428 (5.63)	522 (4.24)	558 (3.86)	593 (3.11)	663 (3.74)
4-*s*	425 (5.68)	519 (4.24)	552 (3.91)	585 (3.16)	646 (3.53)
1-*w*	457 (5.19) [a]	551 (3.95)	586 (3.71)	645 (3.14)	722 (3.45)
2-*w*	436 (5.56)	529 (4.24)	565 (3.86)	610 (3.04)	678 (3.64)
3-*w*	428 (5.66)	522 (4.28)	557 (3.86)	592 (3.14)	663 (3.70)
4-*w*	426 (5.69)	520 (4.27)	551 (3.92)	585 (3.17)	656 (3.54)
1-*r*	447 (5.33)	546 (4.02)	588 (3.81)	622 (3.62)	682 (3.19)
2-*r*	440 (5.44)	538 (4.08)	578 (3.92)	613 (3.74)	672 (3.41)
3-*r*	431 (5.57)	527 (4.18)	563 (3.87)	612 (3.73)	660 (3.31)
4-*r*	423 (5.71)	516 (4.31)	550 (4.09)	593 (3.84)	649 (3.72)

[a]: Sample **1**-*w* show a maximal spectral red-shift, the shift is up to 39 nm compared with that of regular porphyrin TPP (λ_{max} = 418 nm).





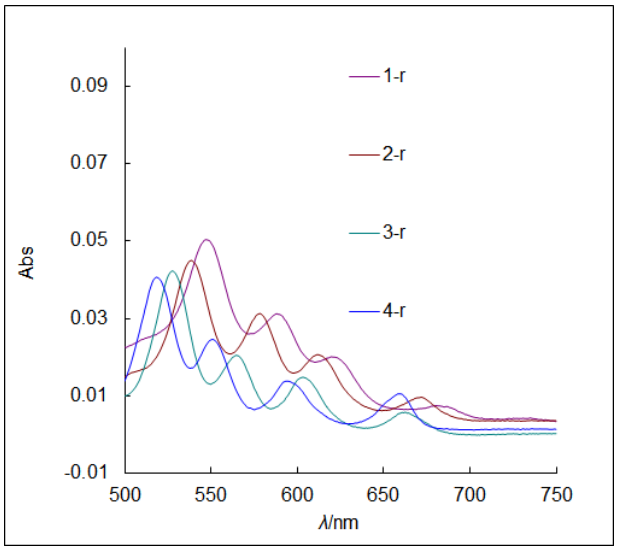


Figure S1. Q-band comparison

2. The fluorescent comparison

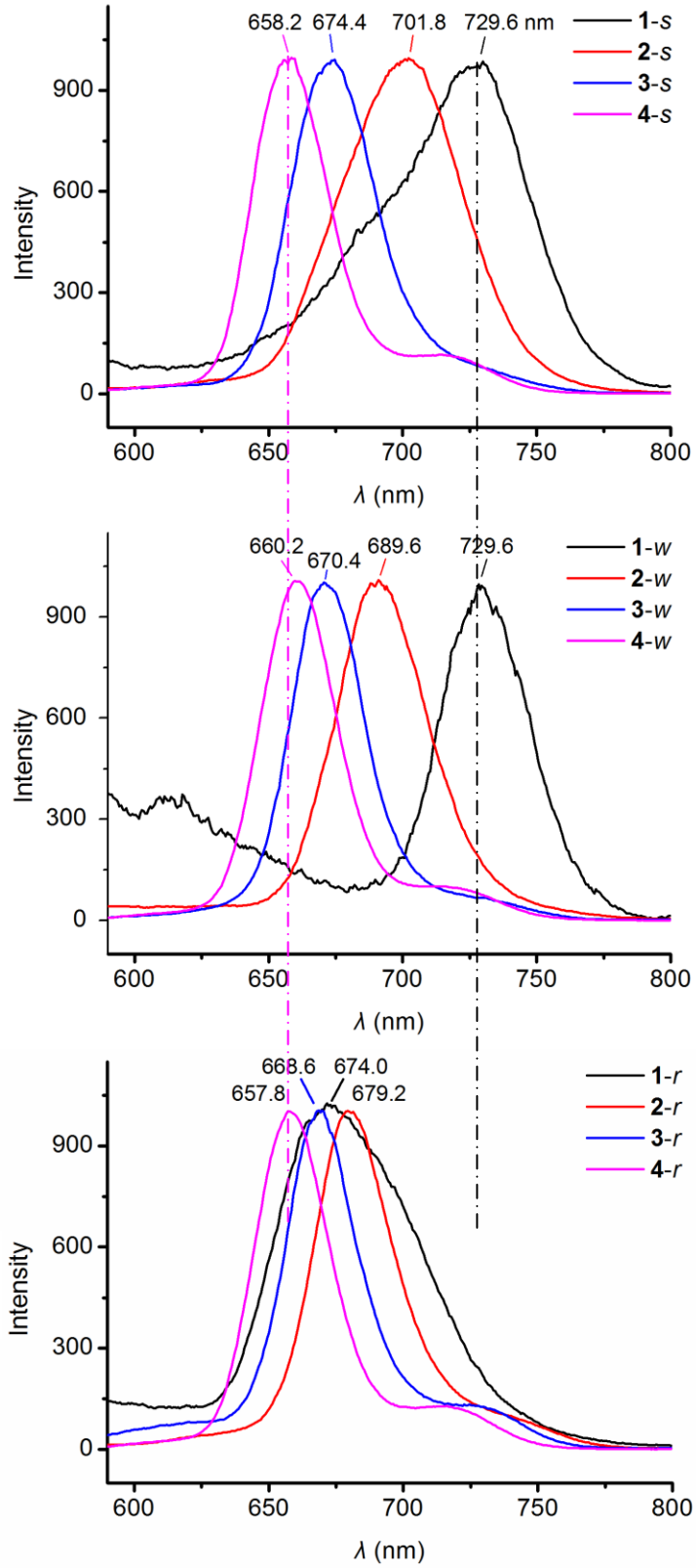


Figure S2. Fluorescent comparison

3. The computation results

Table S2 HOMO and LUMO energy level of deformed porphyrins **1**-*s*, **1**-*w* and **1**-*r*

Energy Level / material	*E*(HOMO)		*E*(LUMO)		*ΔE*(LUMO-HOMO)	
	(a.u.)	(eV)	(a.u.)	(eV)	(a.u.)	(eV)
1-*s*	-0.1781	-4.85	-0.0874	-2.38	0.0908	2.47
1-*w*	-0.1737	-4.73	-0.0825	-2.24	0.0912	2.48
1-*r*	-0.1835	-5.03	-0.0895	-2.45	0.0899	2.58
TPP	-0.1897	-5.16	-0.0913	-2.48	0.0985	2.68

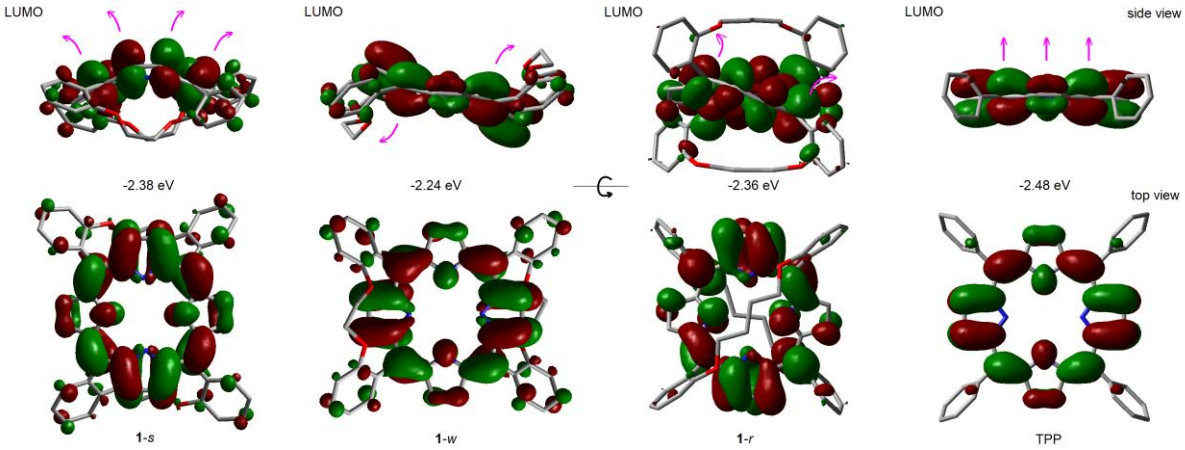


Figure S3. LUMO orbitals of materials **1**-*s*, **1**-*w*, **1**-*r* and TPP.

4. Additional Electrochemical and spectroelectrochemical results

4.1 Electrochemical results

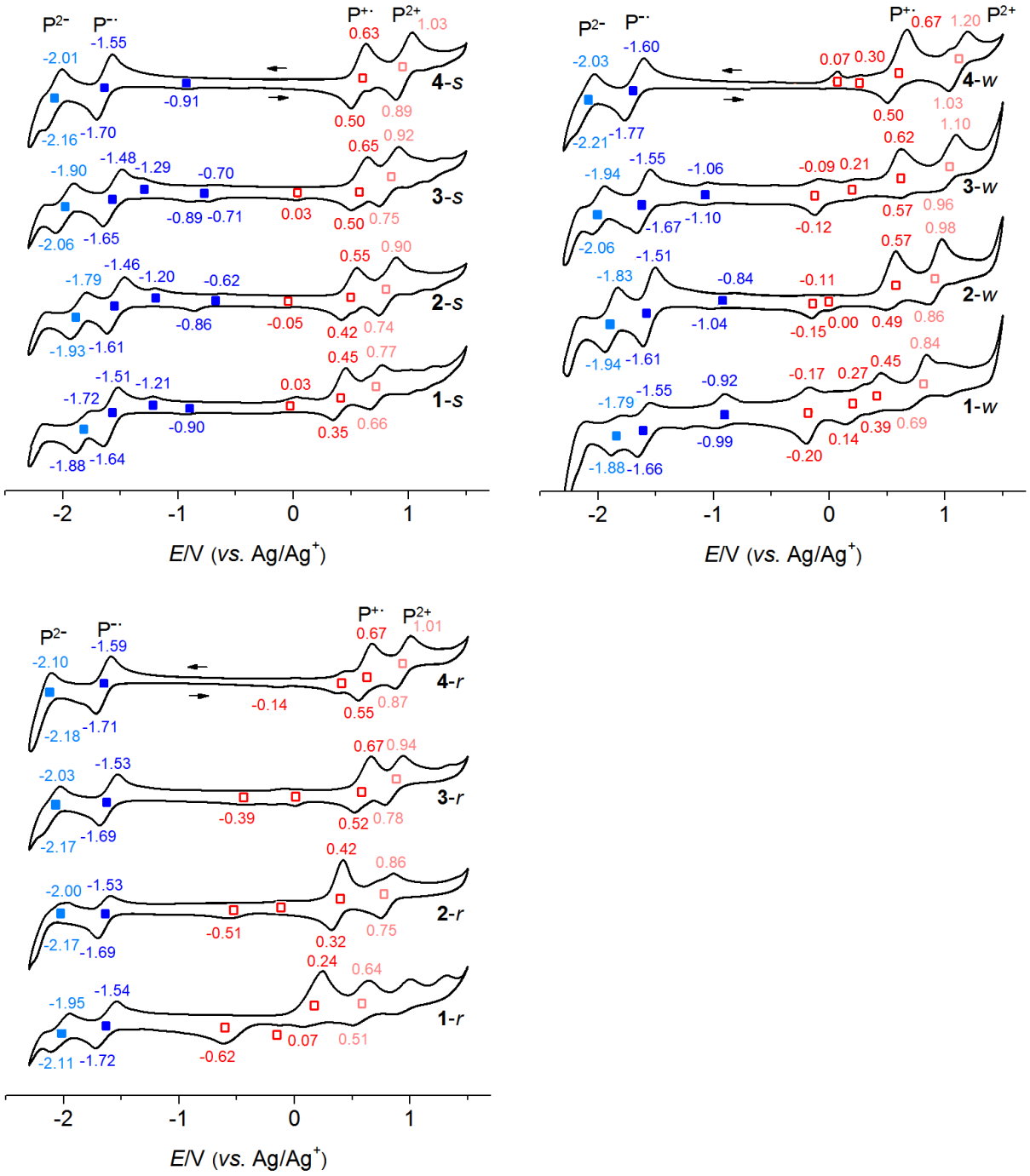
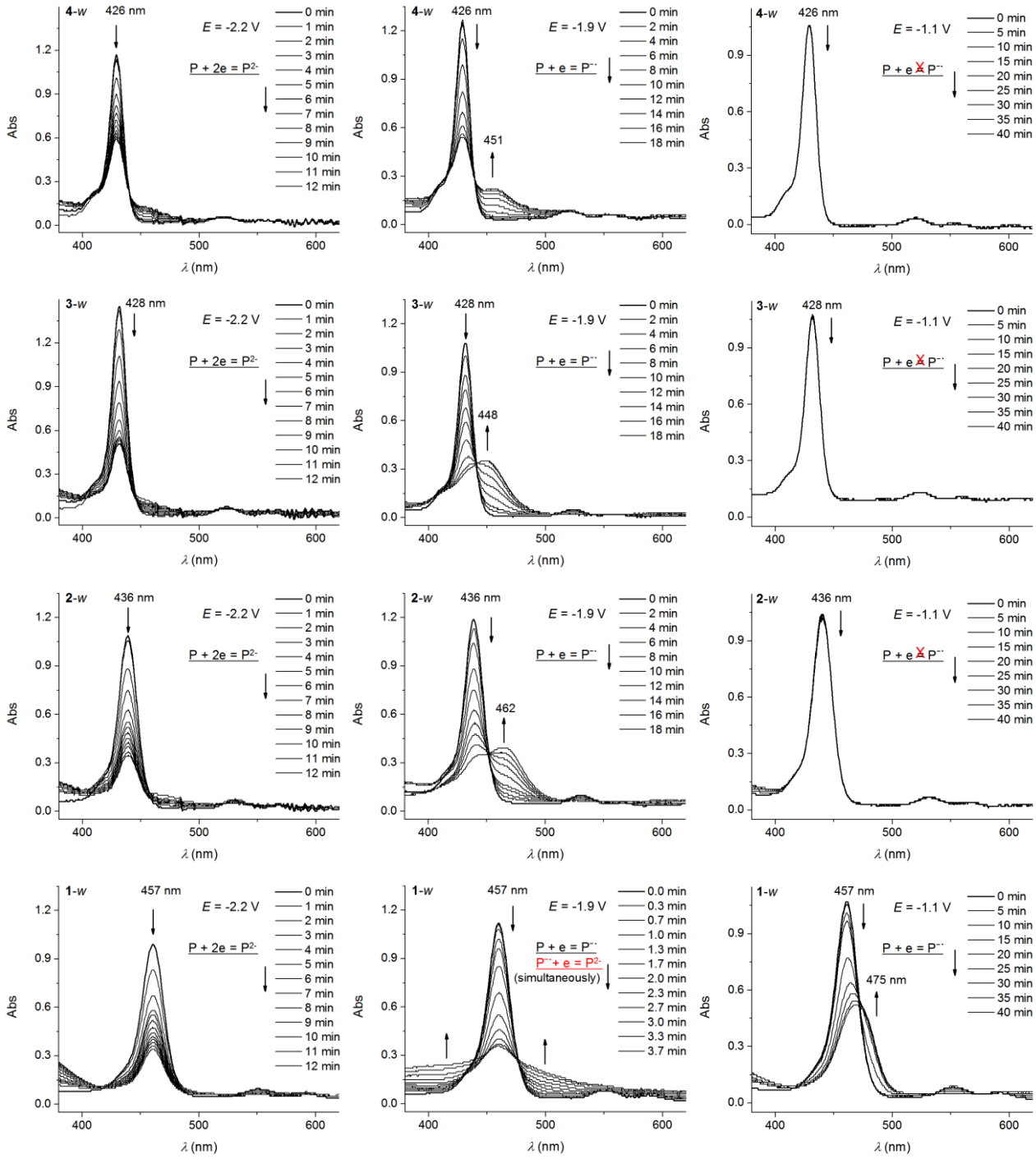


Figure S4. All V_{ap} and V_{cp} values

Note: V_{ap} and V_{cp} denote peak potentials of reduction and oxidation, respectively.

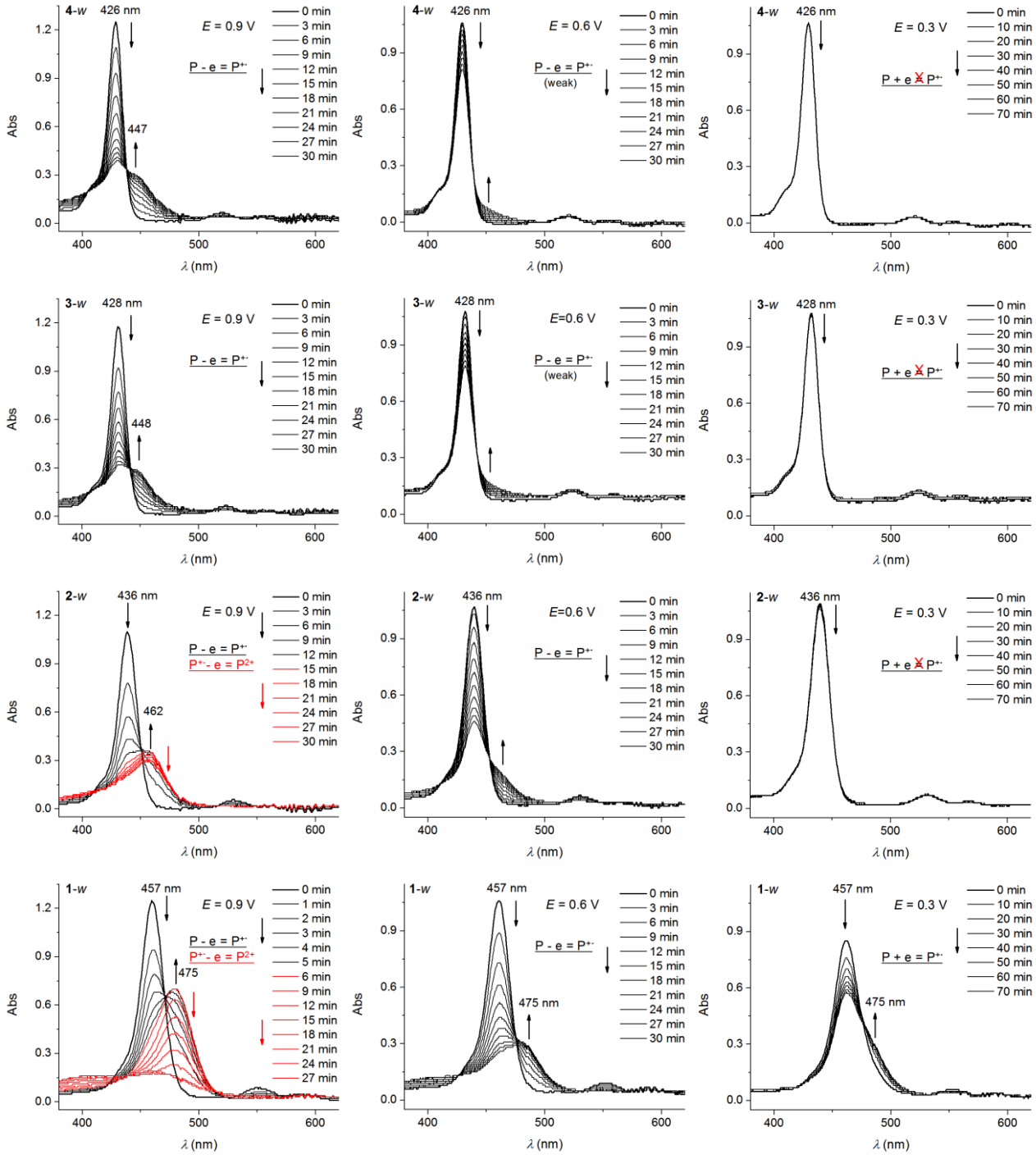
4.2 spectroelectrochemical results



(a) (b) (c)

Figure S5. Spectroelectrochemical changes upon the macrocycle-centered reductions.

Materials: **1**-*w* to **4**-*w*, under experimental voltages of -2.2, -1.9, -1.1 V (a→c) in benzonitrile, 0.1 M $TBAPF_6$. The inserted equations denote the electrochemical reactions.

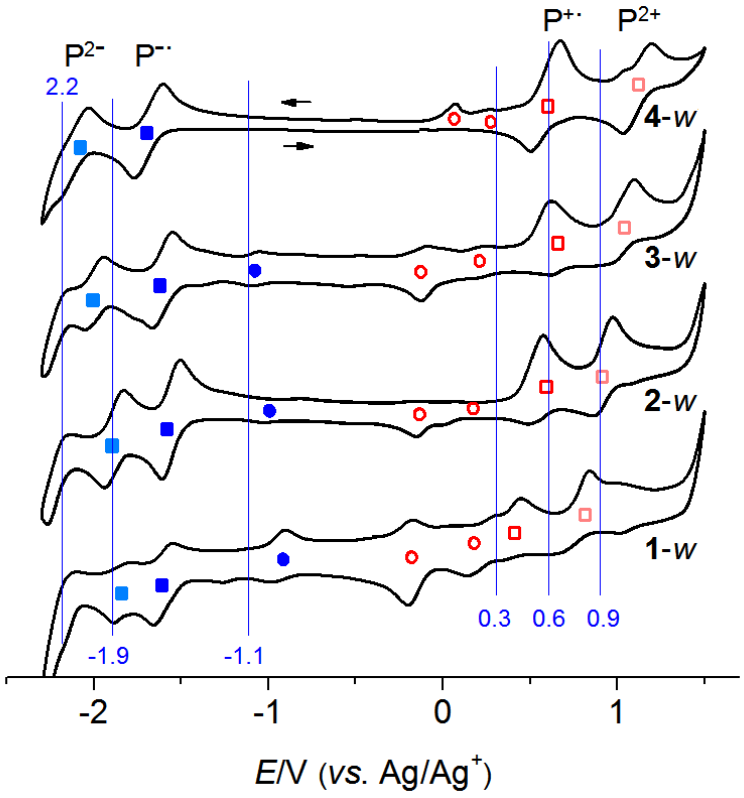


(d) (e) (f)

Figure S6. Spectroelectrochemical changes upon the macrocycle-centered oxidations

Materials: **1**-*w* to **4**-*w*, under experimental voltages of +0.9, +0.6 and +0.3 V (d→f) in benzonitrile, 0.1 M $TBAPF_6$. The inserted equations denote the electrochemical reactions.

4.3 Setting of experimental voltages



Take the waved porphyrins as examples.

Figure S7. Setting of experimental voltages in spectroelectrochemical measurements.

The large macrocyclic distortion facilitates not only the electronic transition of the center metal, as manifested in our previous reports, [Inorg. Chem. 2018, 57, 277] but also the electron transfer of the macrocycle itself.

4.4 Absorbance changes

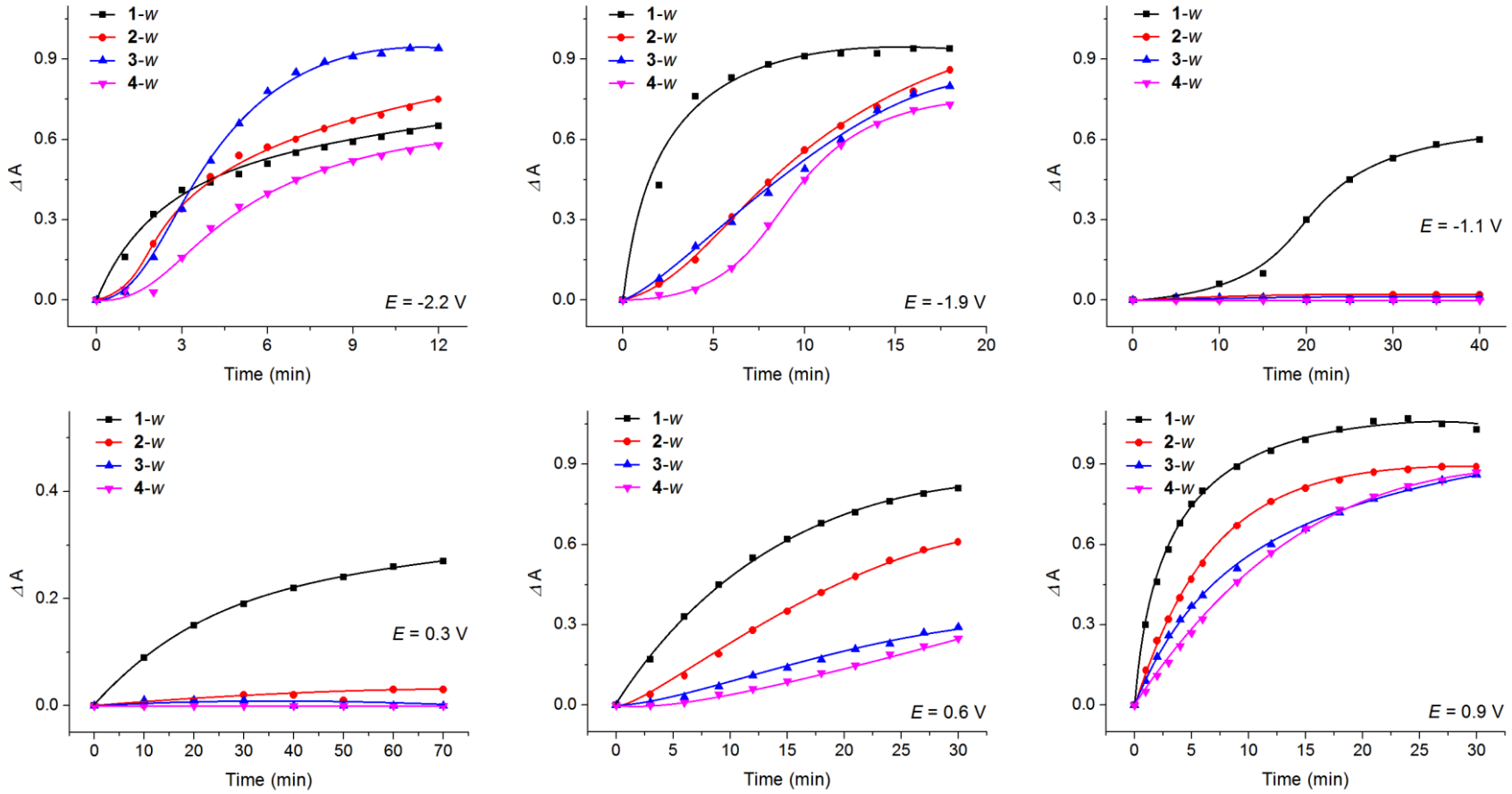
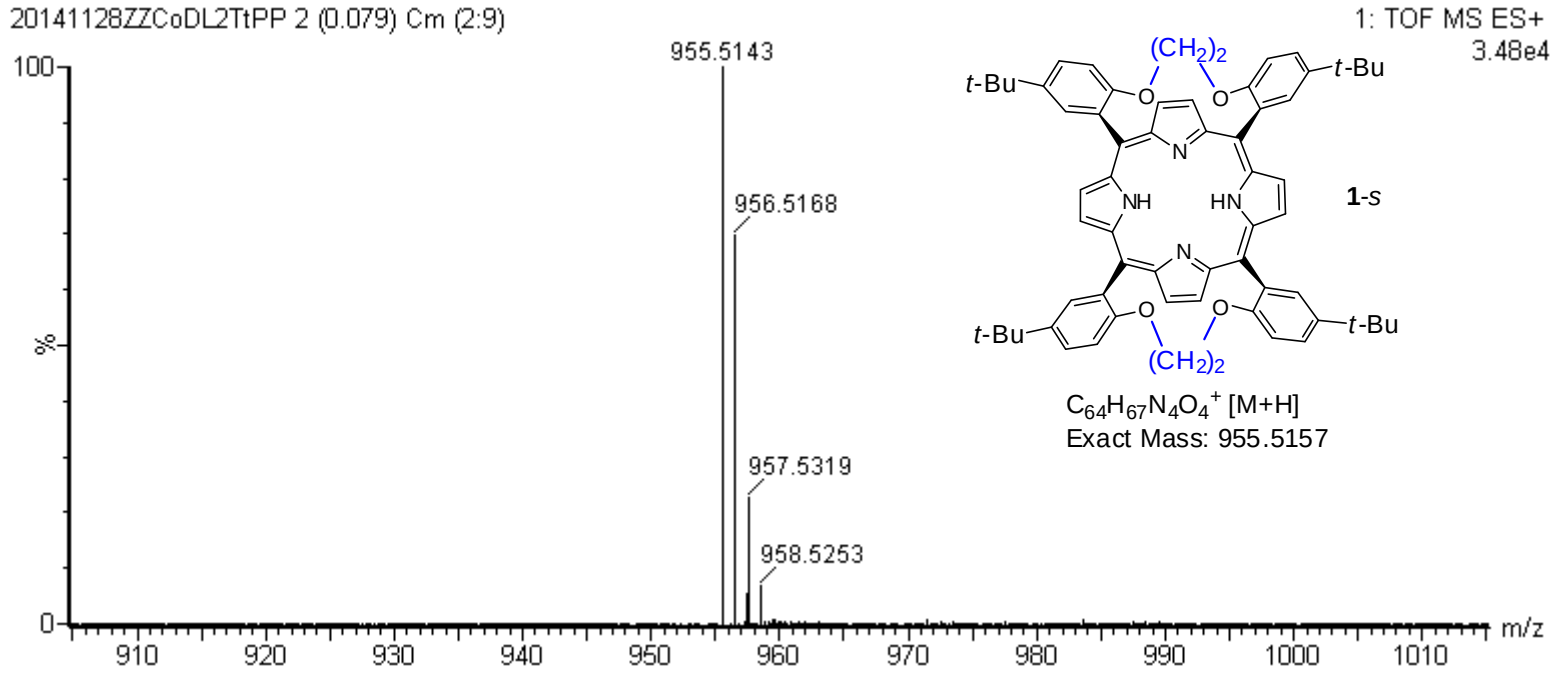


Figure S8. Absorbance changes (Δ*A*) over time at voltage of -2.2, -1.9, -1.1, 0.3, 0.6 and 0.9 V.

Spectroelectrochemistry can well distinguish the reaction rate, the reaction progress, and the difference between the oxidation and reduction of each compound.

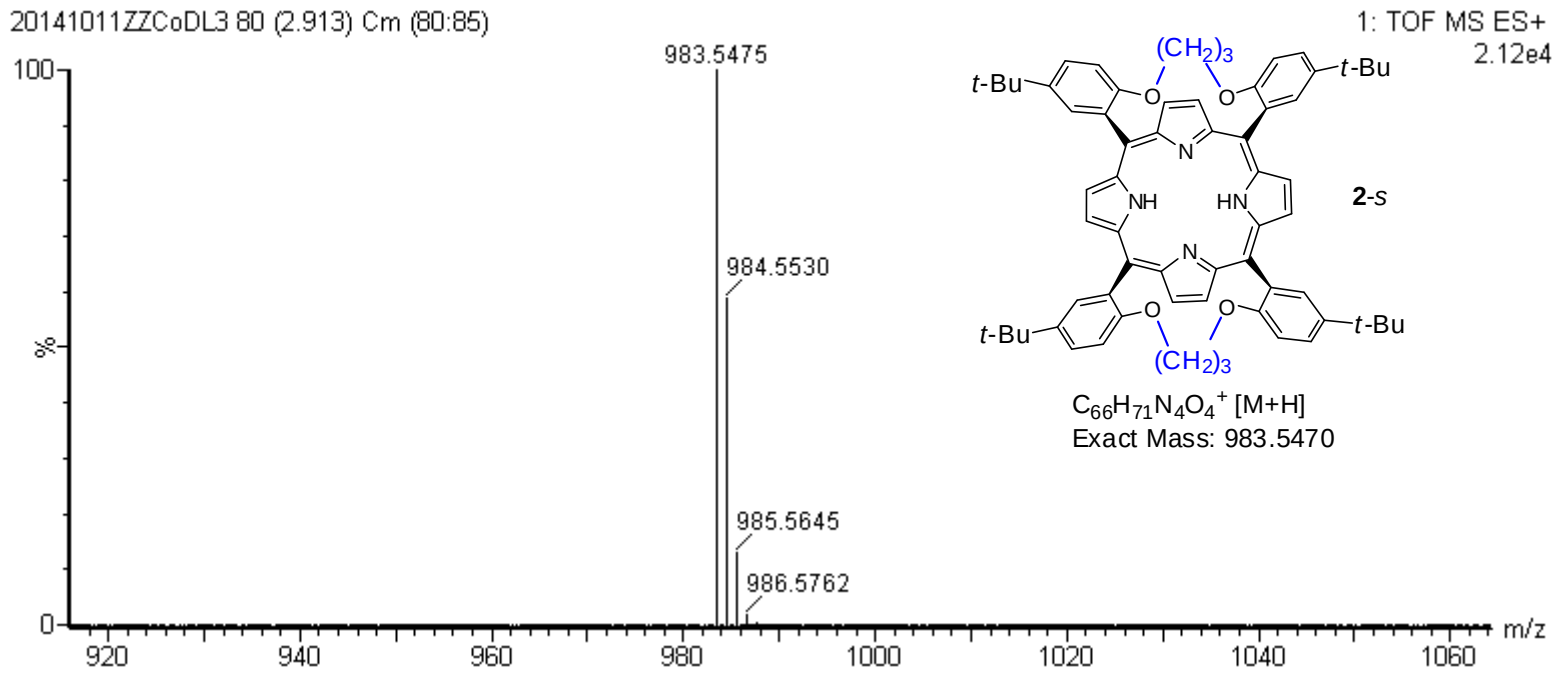
5. HR-MS of new compounds

5.1 HR-MS of **1**-*s*

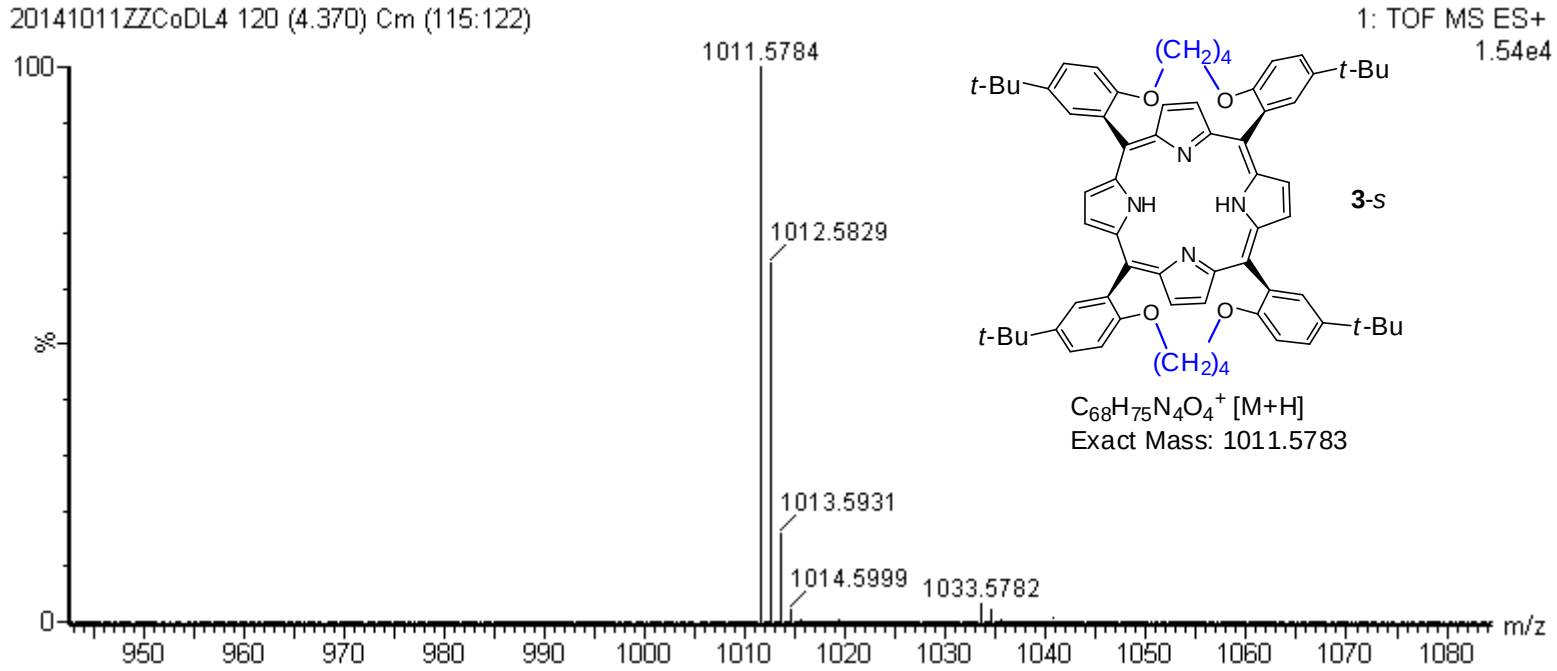


All MS are obtained from ESI source.

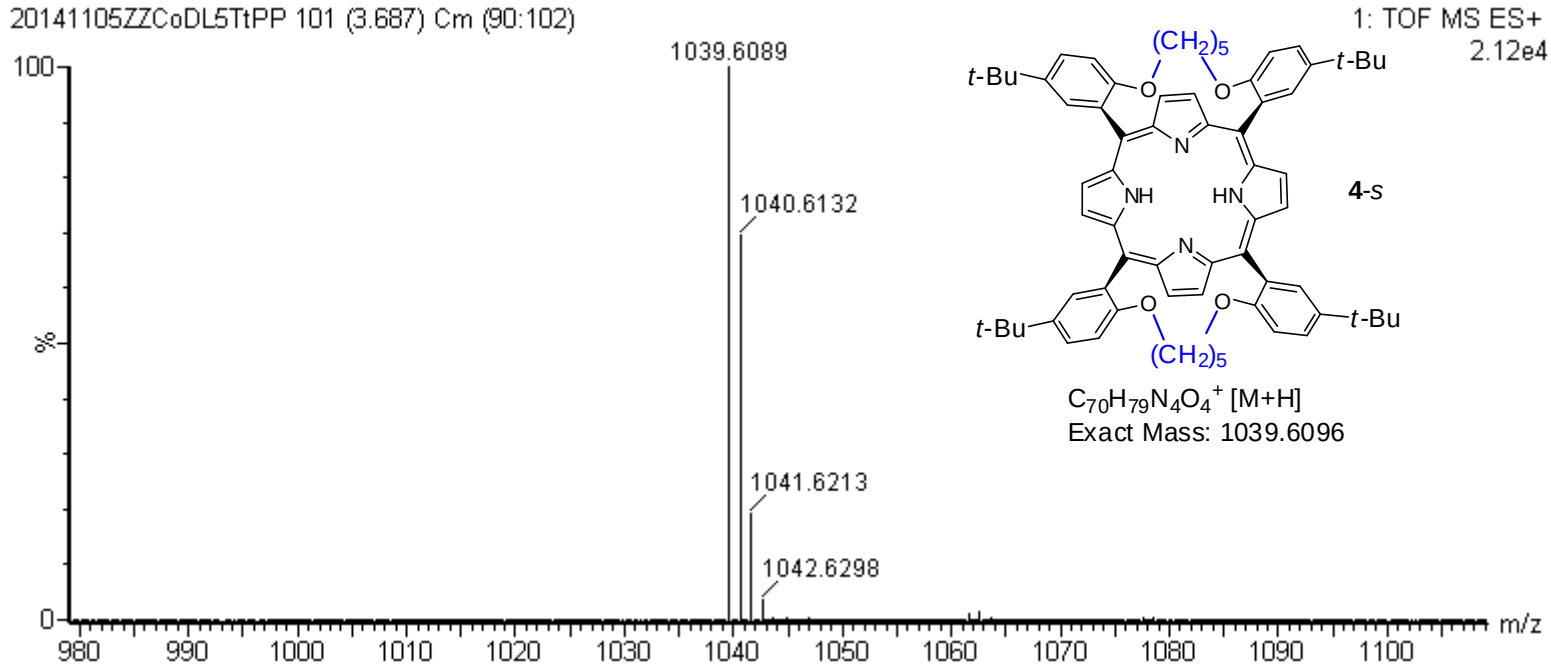
5.2 HR-MS of **2**-*s*


20141011ZZCoDL3 80 (2.913) Cm (80:85)
1: TOF MS ES+
2.12e4
100
%
0
983.5475
984.5530
985.5645
986.5762
920
940
960
980
1000
1020
1040
1060
m/z
t-Bu
t-Bu
t-Bu
t-Bu
(CH2)3
(CH2)3
O
O
O
O
N
NH
HN
N
2-s
C66H71N4O4+ [M+H]
Exact Mass: 983.5470

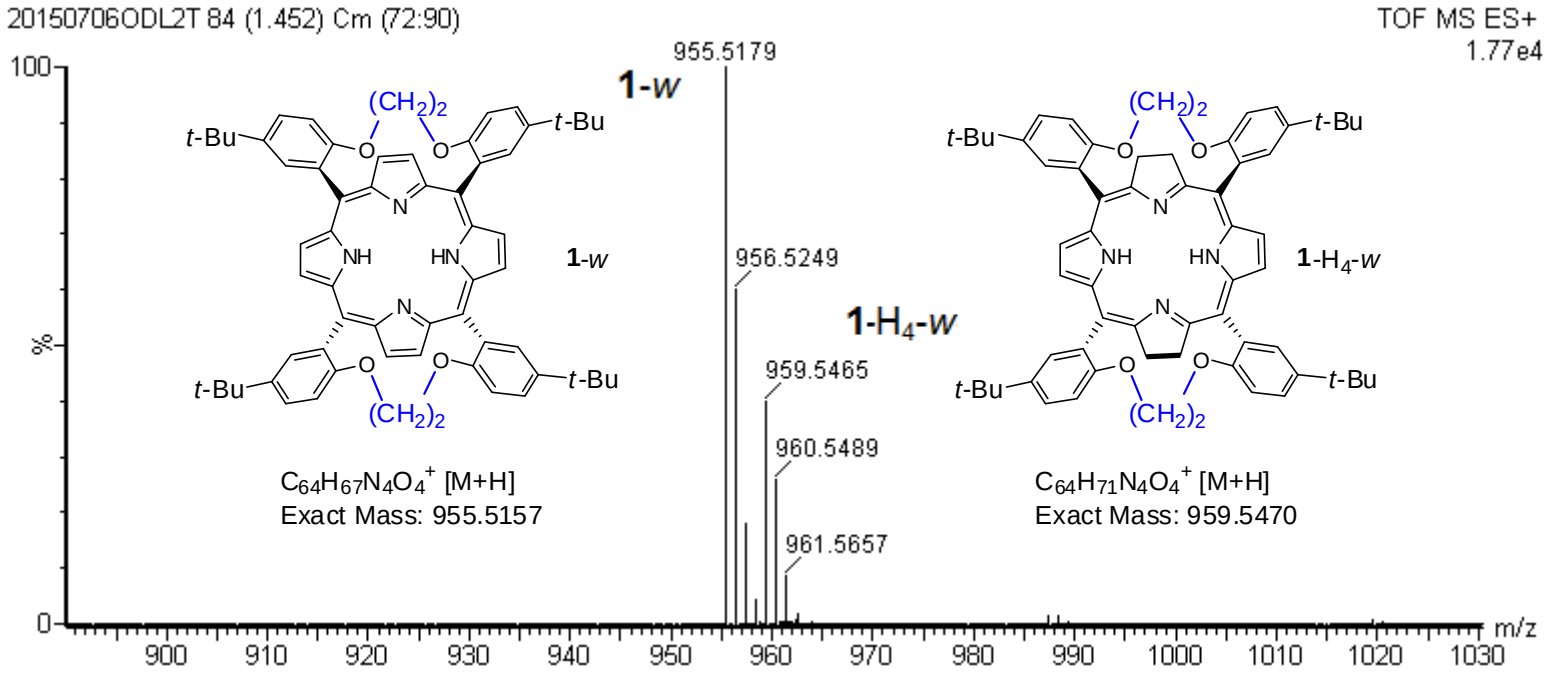
5.3 HR-MS of **3**-*s*


20141011ZZCoDL4 120 (4.370) Cm (115:122)
1: TOF MS ES+
1.54e4
100
%
0
1011.5784
1012.5829
1013.5931
1014.5999
1033.5782
950
960
970
980
990
1000
1010
1020
1030
1040
1050
1060
1070
1080
m/z
(CH2)4
t-Bu
O
N
NH
HN
3-s
C68H75N4O4+ [M+H]
Exact Mass: 1011.5783

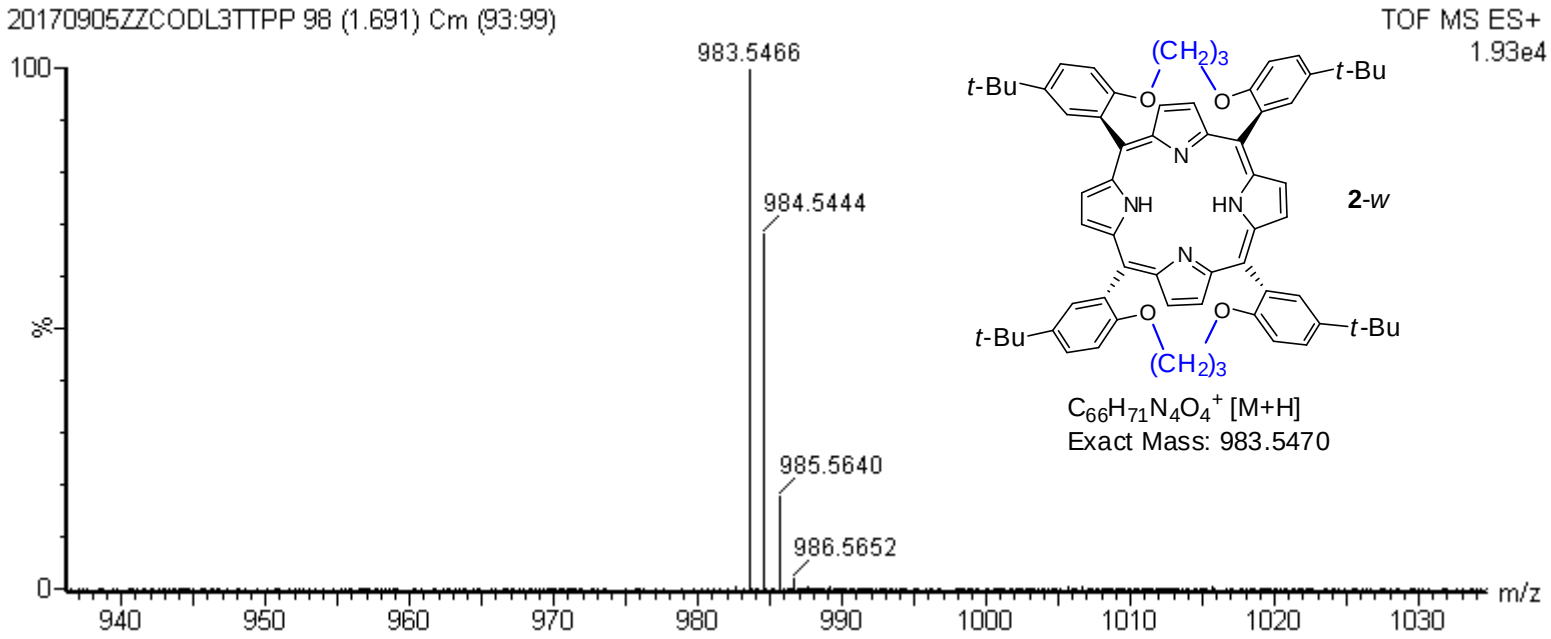
5.4 HR-MS of **4**-*s*


20141105ZZCoDL5TtPP 101 (3.687) Cm (90:102)
1: TOF MS ES+
2.12e4
1039.6089
1040.6132
1041.6213
1042.6298
100
%
0
980
990
1000
1010
1020
1030
1040
1050
1060
1070
1080
1090
1100
m/z
(CH2)5
t-Bu
O
N
NH
HN
4-s
C70H79N4O4+ [M+H]
Exact Mass: 1039.6096

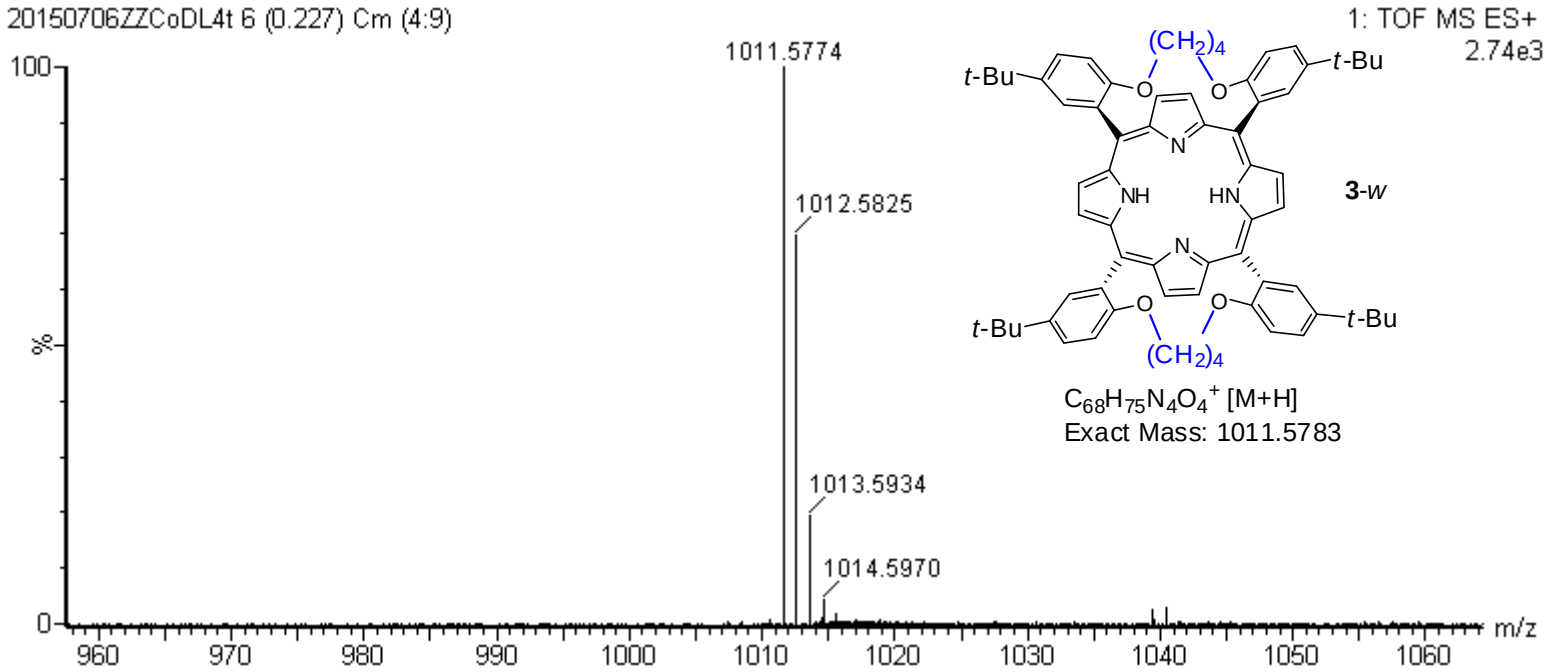
5.5 HR-MS of **1**-*w*


20150706ODL2T 84 (1.452) Cm (72:90)
TOF MS ES+
1.77e4
955.5179
1-w
956.5249
959.5465
960.5489
961.5657
1-H4-w
1-w
1-H4-w
C64H67N4O4+ [M+H]
Exact Mass: 955.5157
C64H71N4O4+ [M+H]
Exact Mass: 959.5470
100
%
0
m/z
900
910
920
930
940
950
960
970
980
990
1000
1010
1020
1030

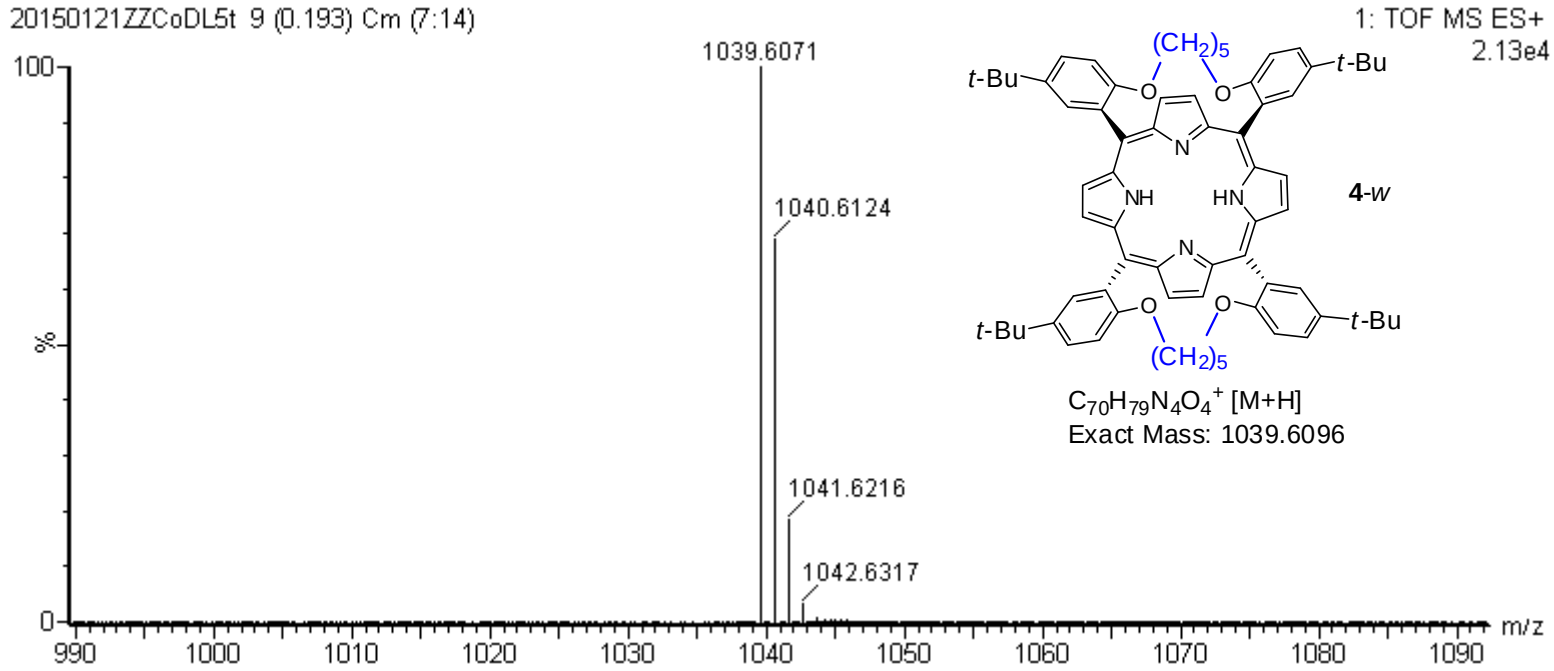
5.6 HR-MS of **2**-*w*


20170905ZZCODL3TTPP 98 (1.691) Cm (93:99)
TOF MS ES+
1.93e4
983.5466
984.5444
985.5640
986.5652
100
%
0
940
950
960
970
980
990
1000
1010
1020
1030
m/z
(CH2)3
t-Bu
O
N
NH
HN
2-w
C66H71N4O4+ [M+H]
Exact Mass: 983.5470

5.7 HR-MS of **3**-*w*


20150706ZZCoDL4t 6 (0.227) Cm (4:9)
1: TOF MS ES+
2.74e3
1011.5774
1012.5825
1013.5934
1014.5970
100
%
0
960
970
980
990
1000
1010
1020
1030
1040
1050
1060
m/z
t-Bu
(CH2)4
O
N
NH
HN
3-w
C68H75N4O4+ [M+H]
Exact Mass: 1011.5783

5.8 HR-MS of **4**-*w*

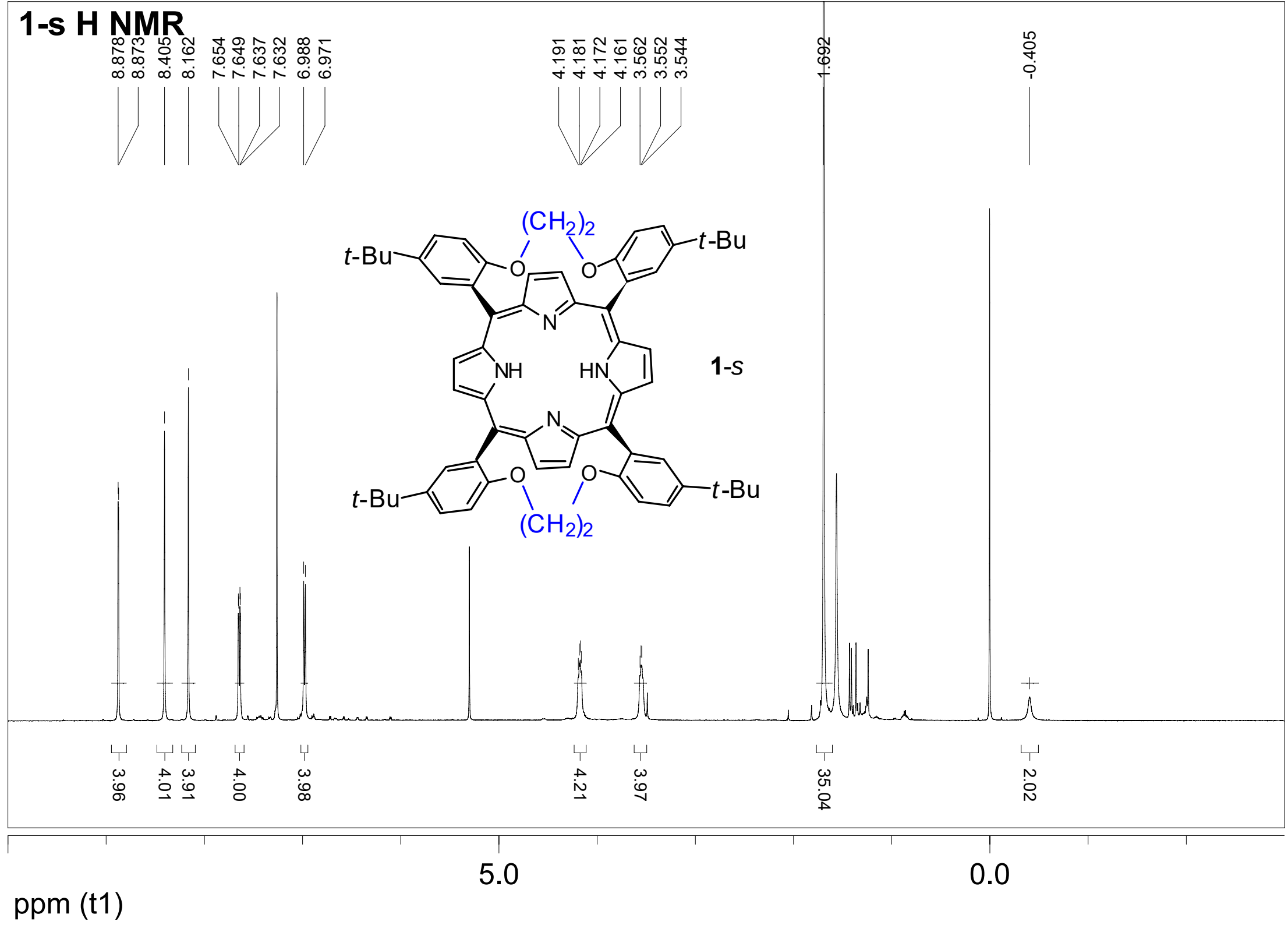

20150121ZZCoDL5t 9 (0.193) Cm (7:14)
1: TOF MS ES+
2.13e4
1039.6071
1040.6124
1041.6216
1042.6317
100
%
0
990
1000
1010
1020
1030
1040
1050
1060
1070
1080
1090
m/z
(CH2)5
t-Bu
t-Bu
O
O
N
NH
HN
N
O
O
t-Bu
t-Bu
(CH2)5
4-w
C70H79N4O4+ [M+H]
Exact Mass: 1039.6096

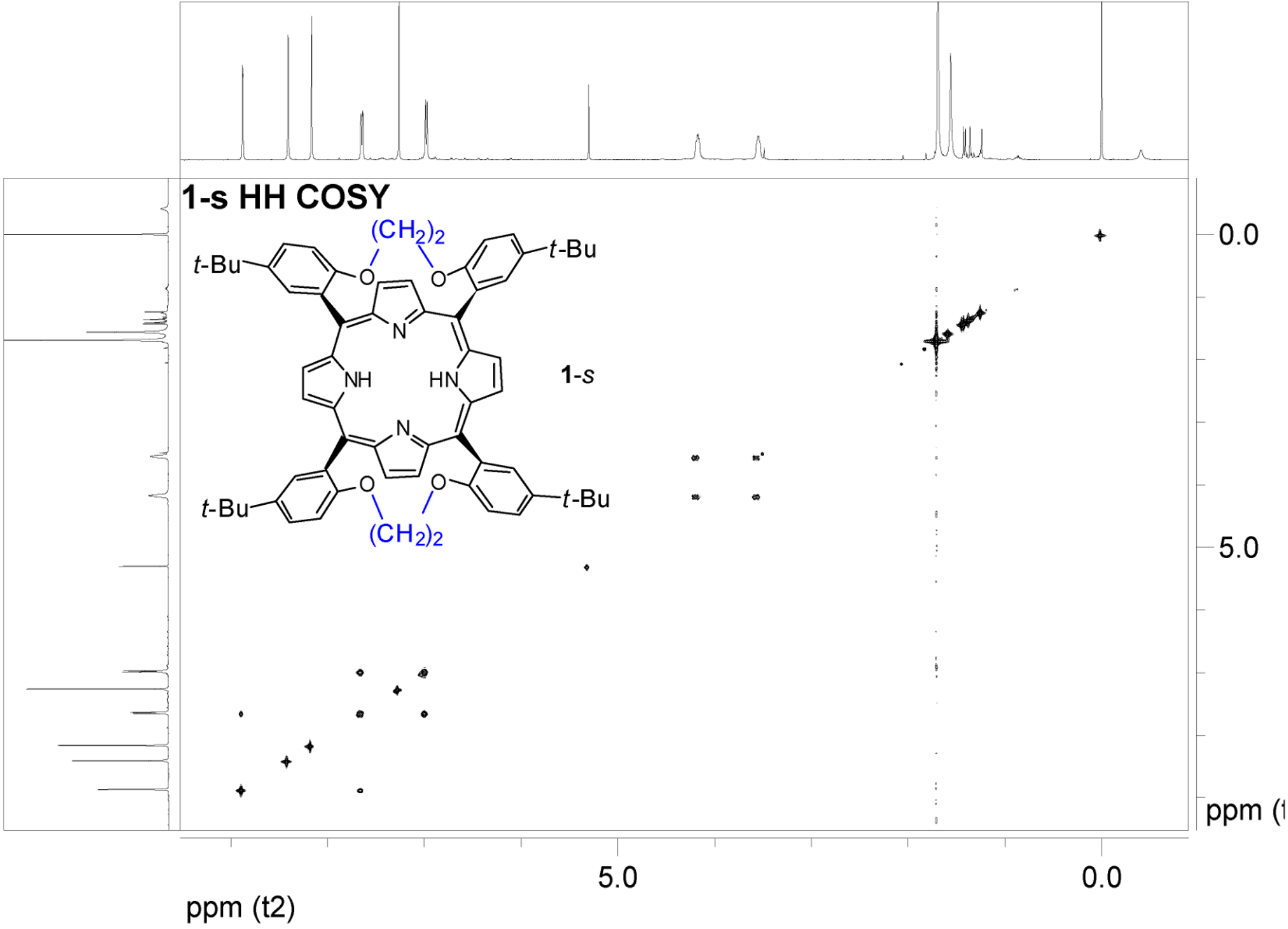
6. NMR of new compounds

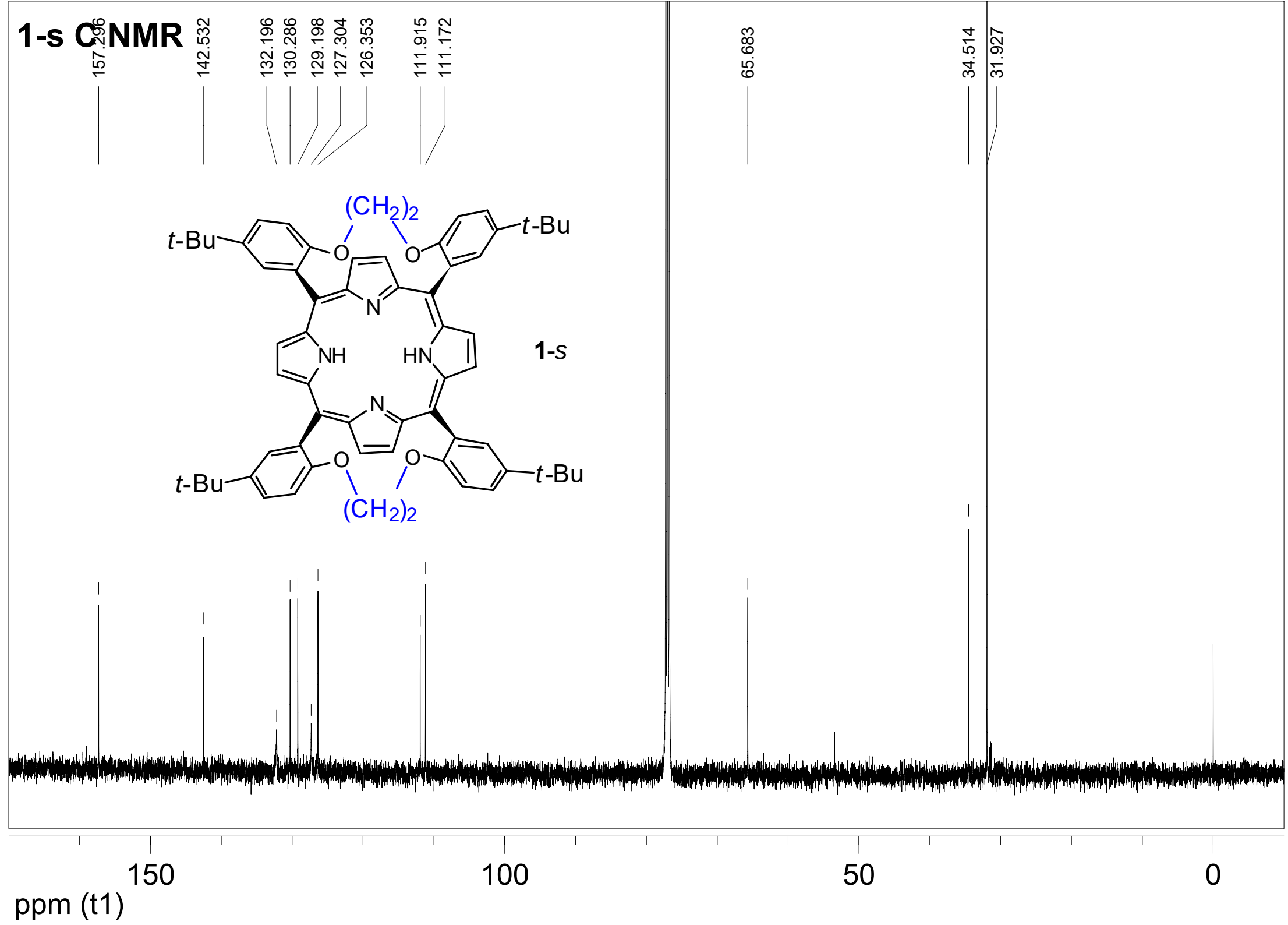
^{1}H NMR, HH COSY and ^{13}C NMR of **1**-*s* to **4**-*s*;

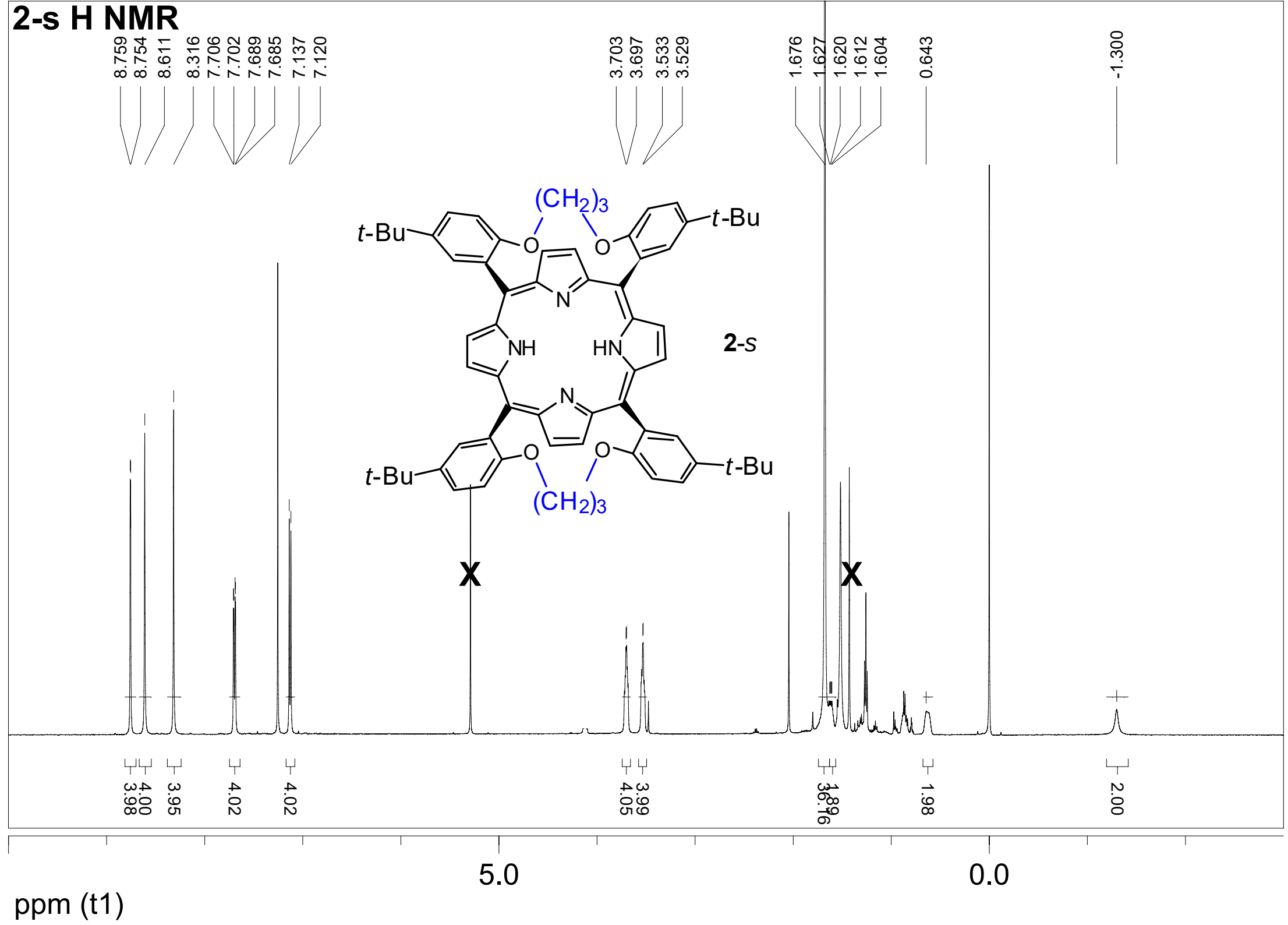
^{1}H NMR, HH COSY and ^{13}C NMR of **1**-*w* to **4**-*w*;

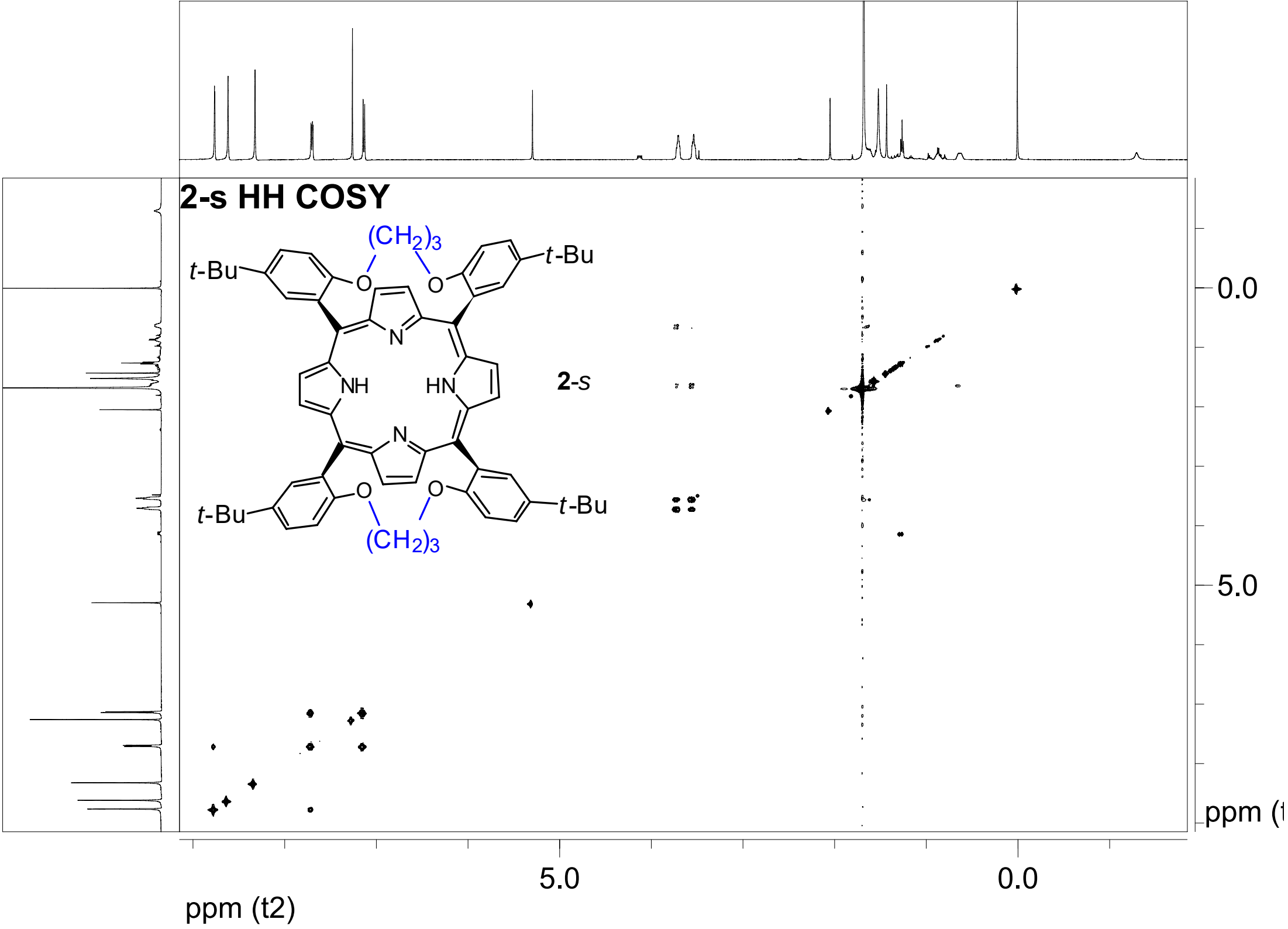
Note: NMR characterization of **1**-*r* to **4**-*r* can be reproduced from previous report.

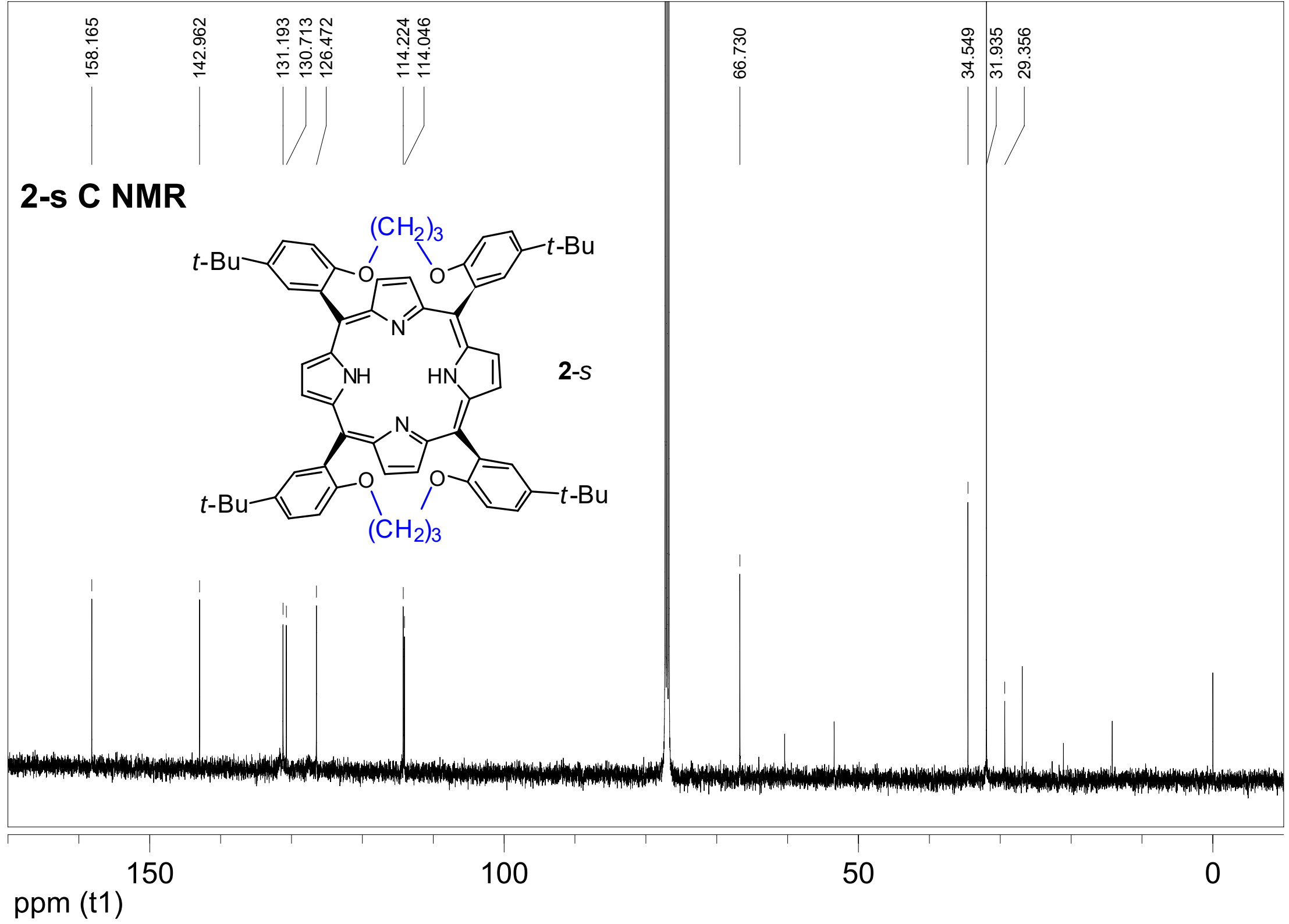

1-s H NMR
8.878
8.873
8.405
8.162
7.654
7.649
7.637
7.632
6.988
6.971
4.191
4.181
4.172
4.161
3.562
3.552
3.544
1.692
-0.405
(CH2)2
t-Bu
t-Bu
O
O
N
NH
HN
N
1-s
t-Bu
t-Bu
O
O
(CH2)2
3.96
4.01
3.91
4.00
3.98
4.21
3.97
35.04
2.02
5.0
0.0
ppm (t1)

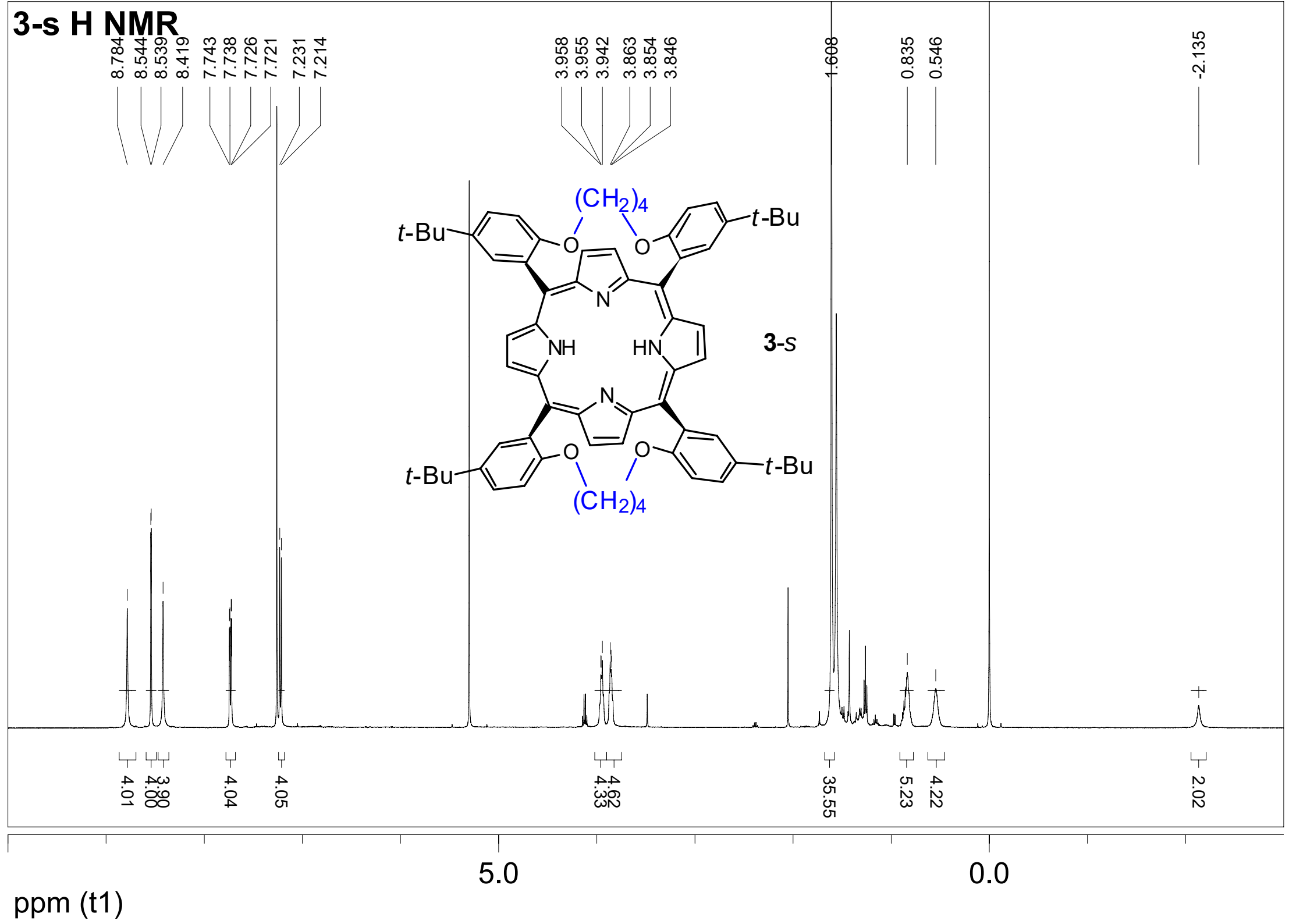

1-s HH COSY
(CH2)2
t-Bu
t-Bu
O
O
N
NH
HN
N
1-s
O
O
t-Bu
t-Bu
(CH2)2
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)

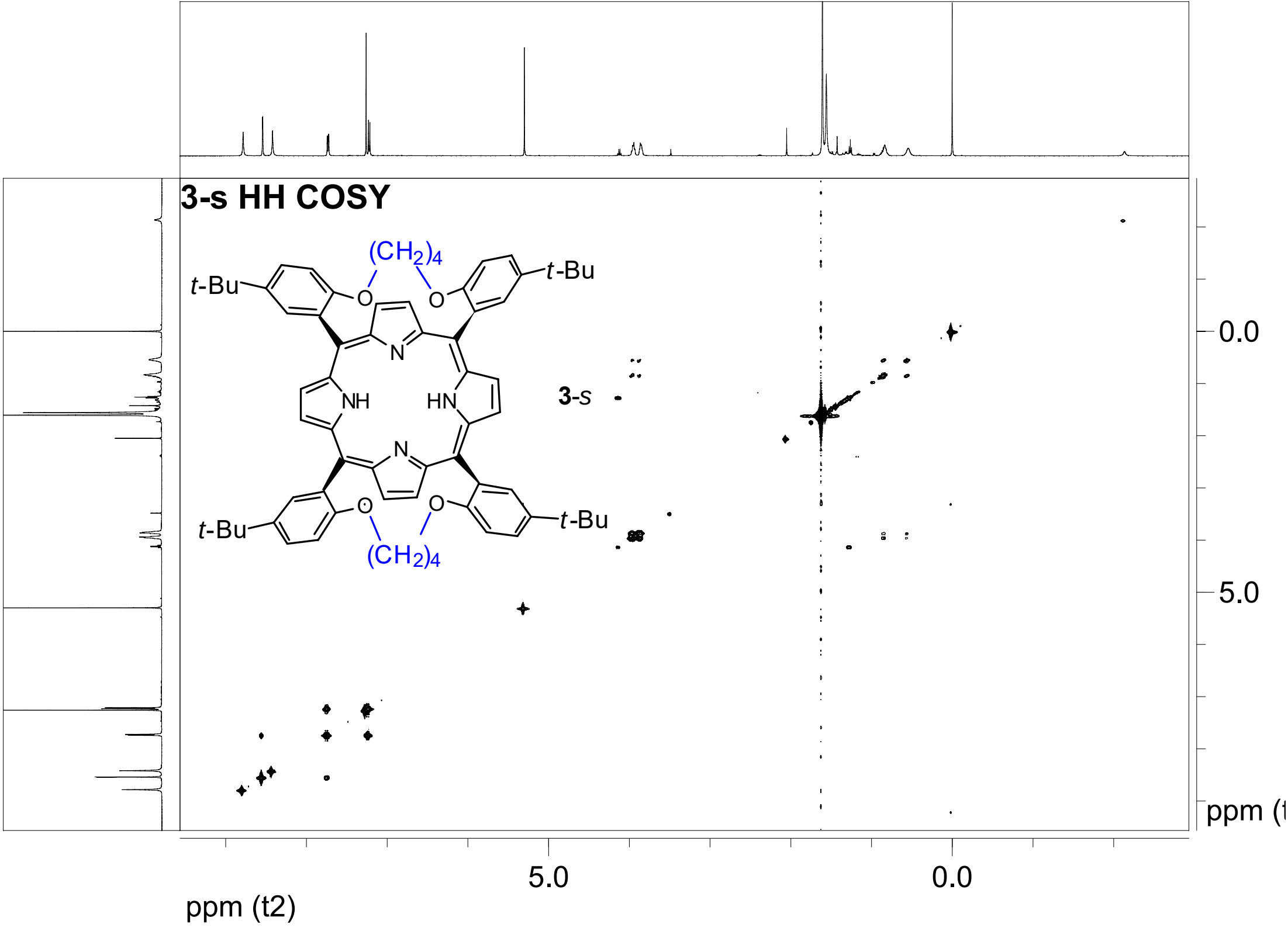

1-s C NMR
157.296
142.532
132.196
130.286
129.198
127.304
126.353
111.915
111.172
65.683
34.514
31.927
(CH2)2
t-Bu
t-Bu
O
O
N
NH
HN
N
O
O
t-Bu
t-Bu
(CH2)2
1-s
150
100
50
0
ppm (t1)

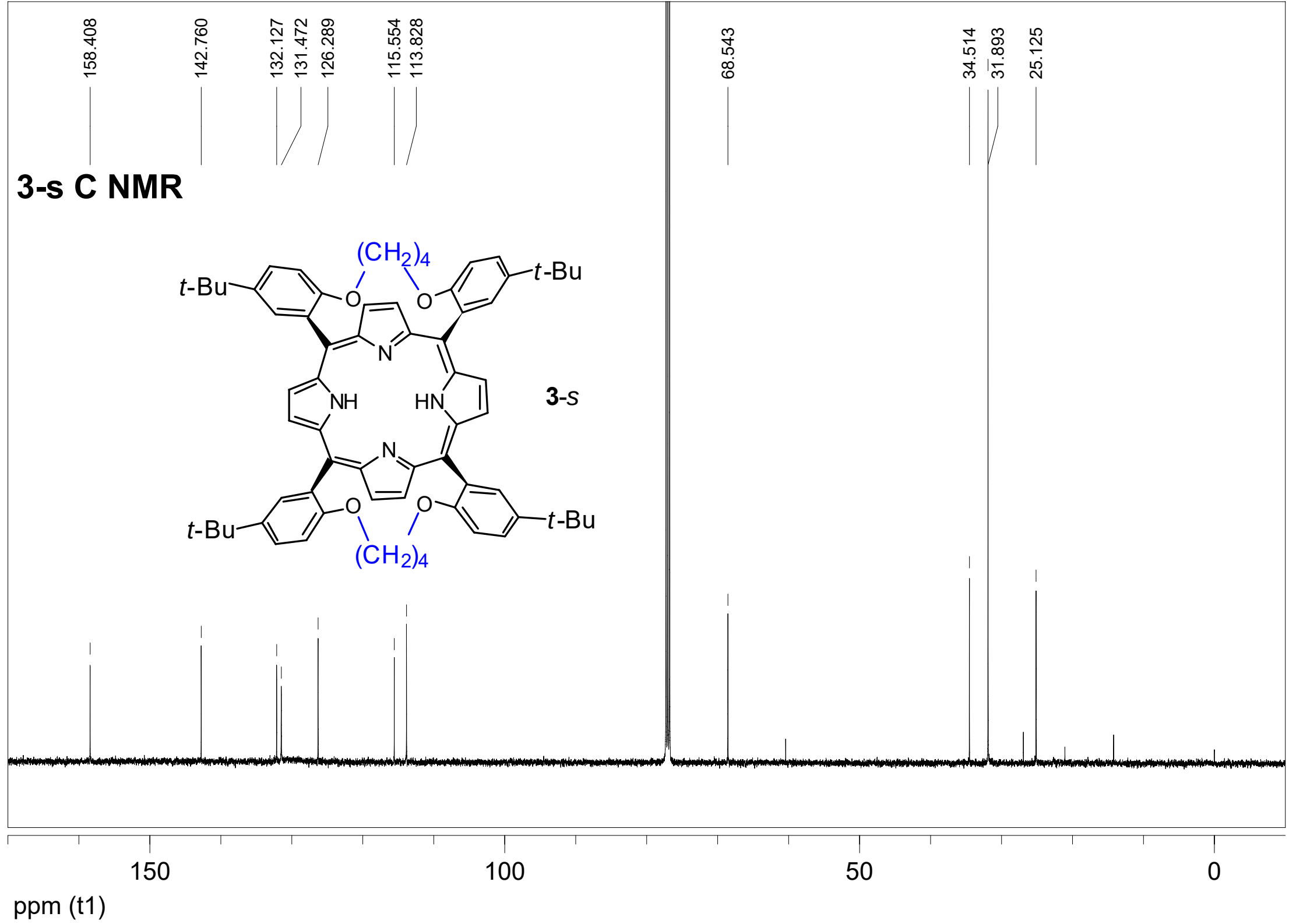

2-s H NMR
8.759
8.754
8.611
8.316
7.706
7.702
7.689
7.685
7.137
7.120
3.703
3.697
3.533
3.529
1.676
1.627
1.620
1.612
1.604
0.643
-1.300
(CH2)3
t-Bu
O
N
NH
HN
2-s
X
3.98
4.00
3.95
4.02
4.02
4.05
3.99
36.16
1.89
1.98
2.00
5.0
0.0
ppm (t1)

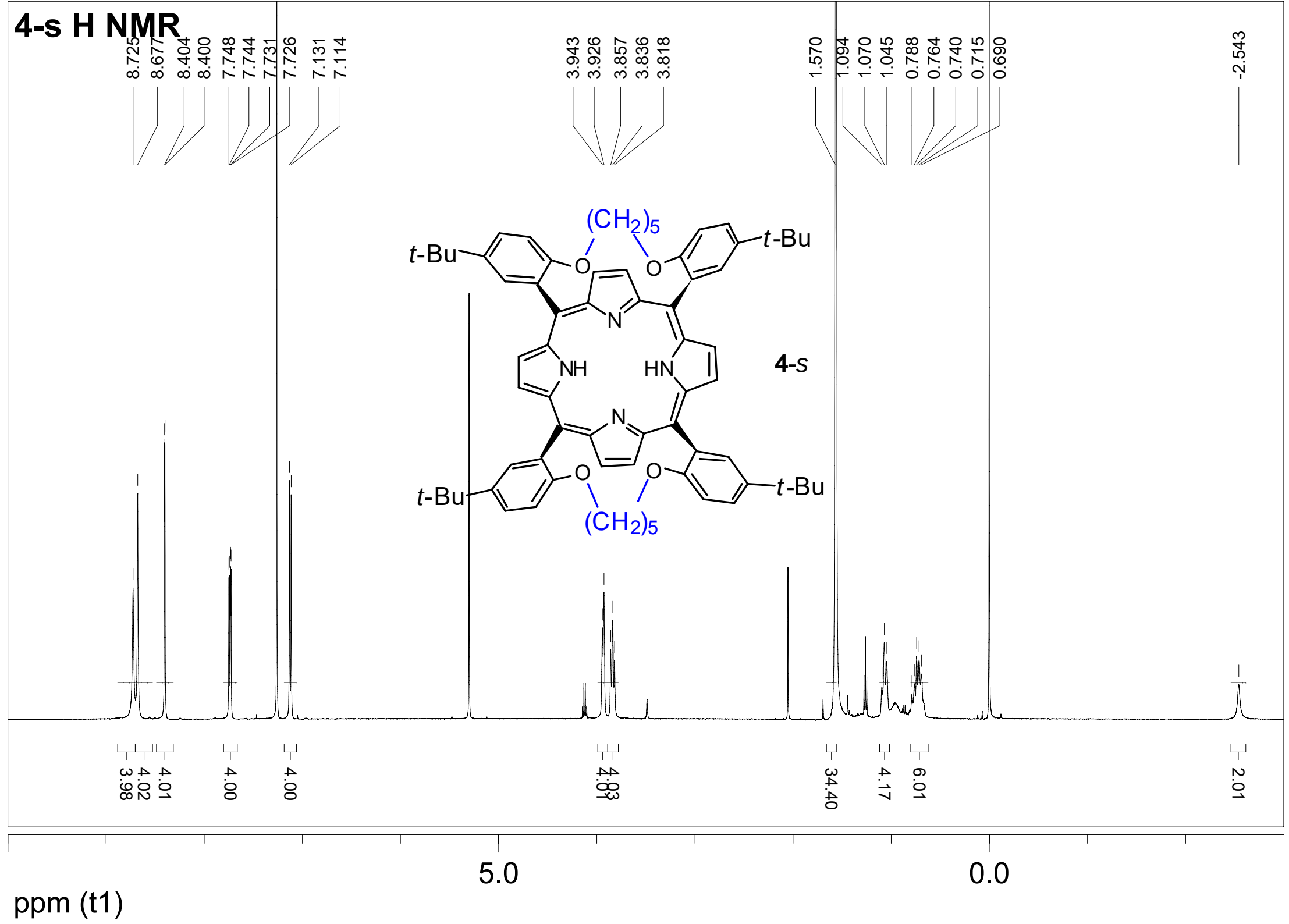

2-s HH COSY
(CH2)3
t-Bu
t-Bu
O
O
N
NH
HN
N
2-s
O
O
t-Bu
t-Bu
(CH2)3
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)

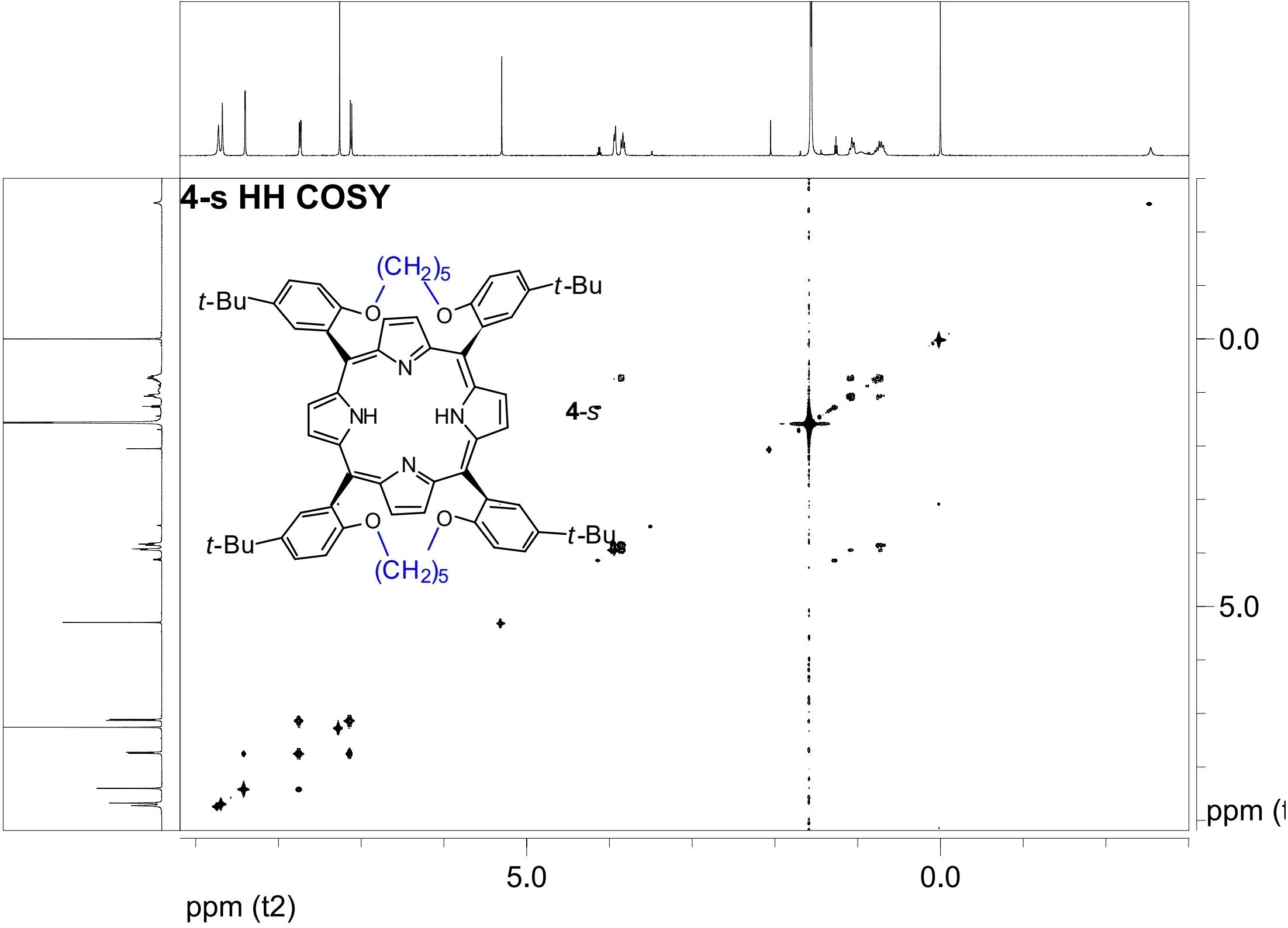

158.165
142.962
131.193
130.713
126.472
114.224
114.046
66.730
34.549
31.935
29.356
2-s C NMR
(CH2)3
t-Bu
t-Bu
O
O
N
NH
HN
N
O
O
t-Bu
t-Bu
(CH2)3
2-s
150
100
50
0
ppm (t1)

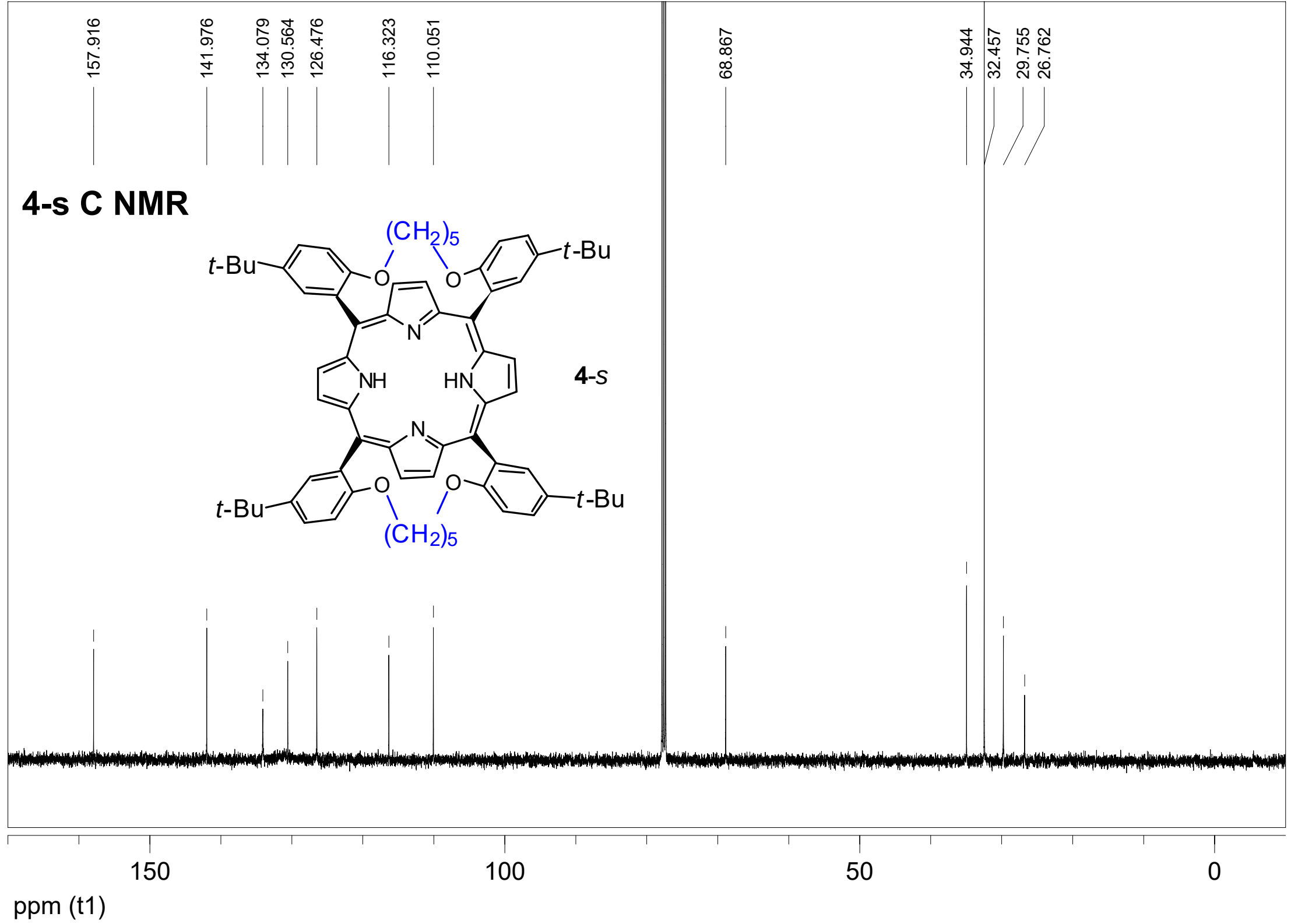

3-s H NMR
8.784
8.544
8.539
8.419
7.743
7.738
7.726
7.721
7.231
7.214
3.958
3.955
3.942
3.863
3.854
3.846
1.608
0.835
0.546
-2.135
(CH2)4
t-Bu
t-Bu
O
O
N
NH
HN
N
3-s
t-Bu
t-Bu
O
O
(CH2)4
4.01
3.80
3.90
4.04
4.05
4.33
4.62
35.55
5.23
4.22
2.02
5.0
0.0
ppm (t1)

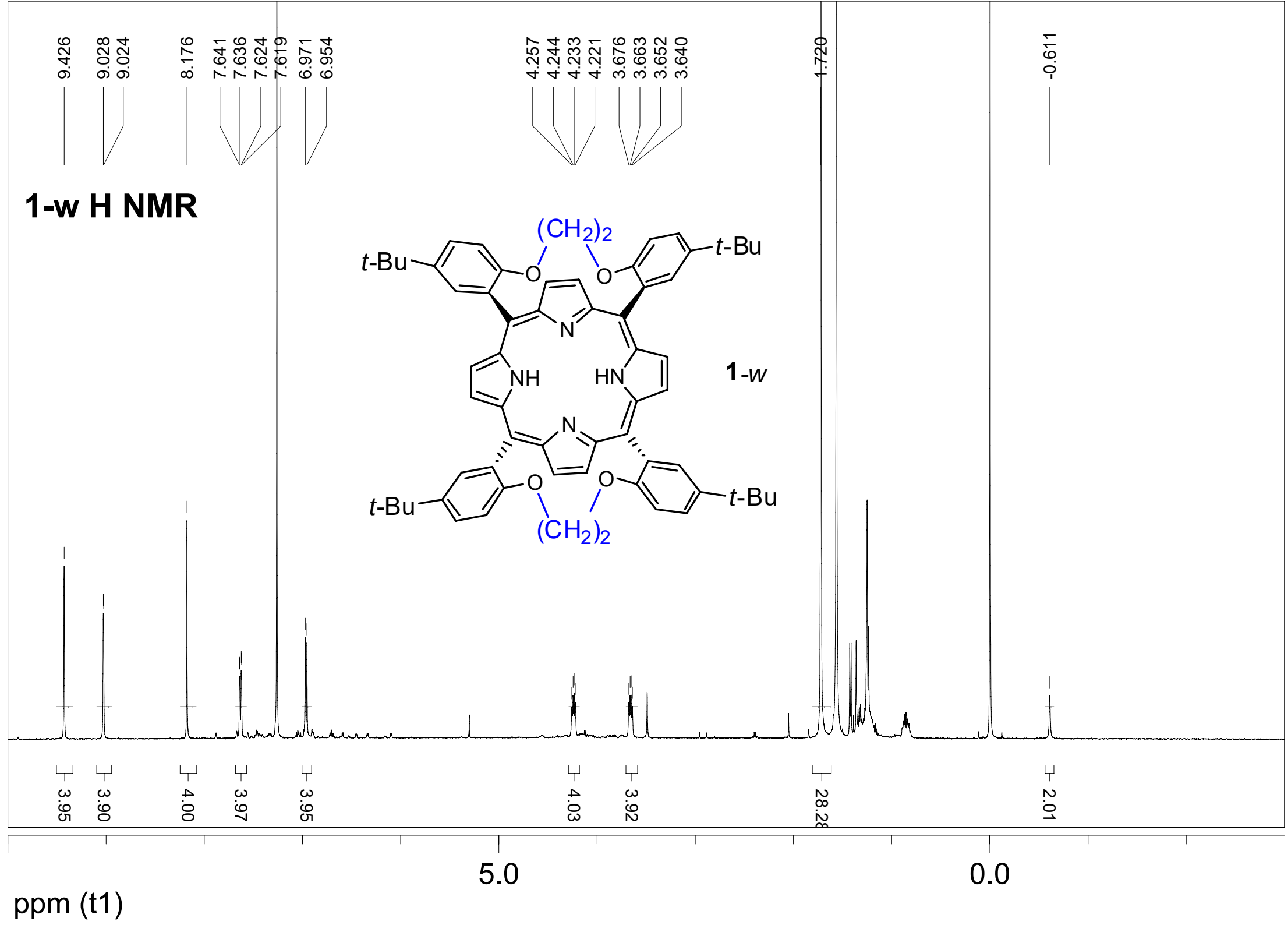

3-s HH COSY
(CH2)4
t-Bu
t-Bu
O
O
N
NH
HN
N
3-s
t-Bu
t-Bu
O
O
(CH2)4
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)

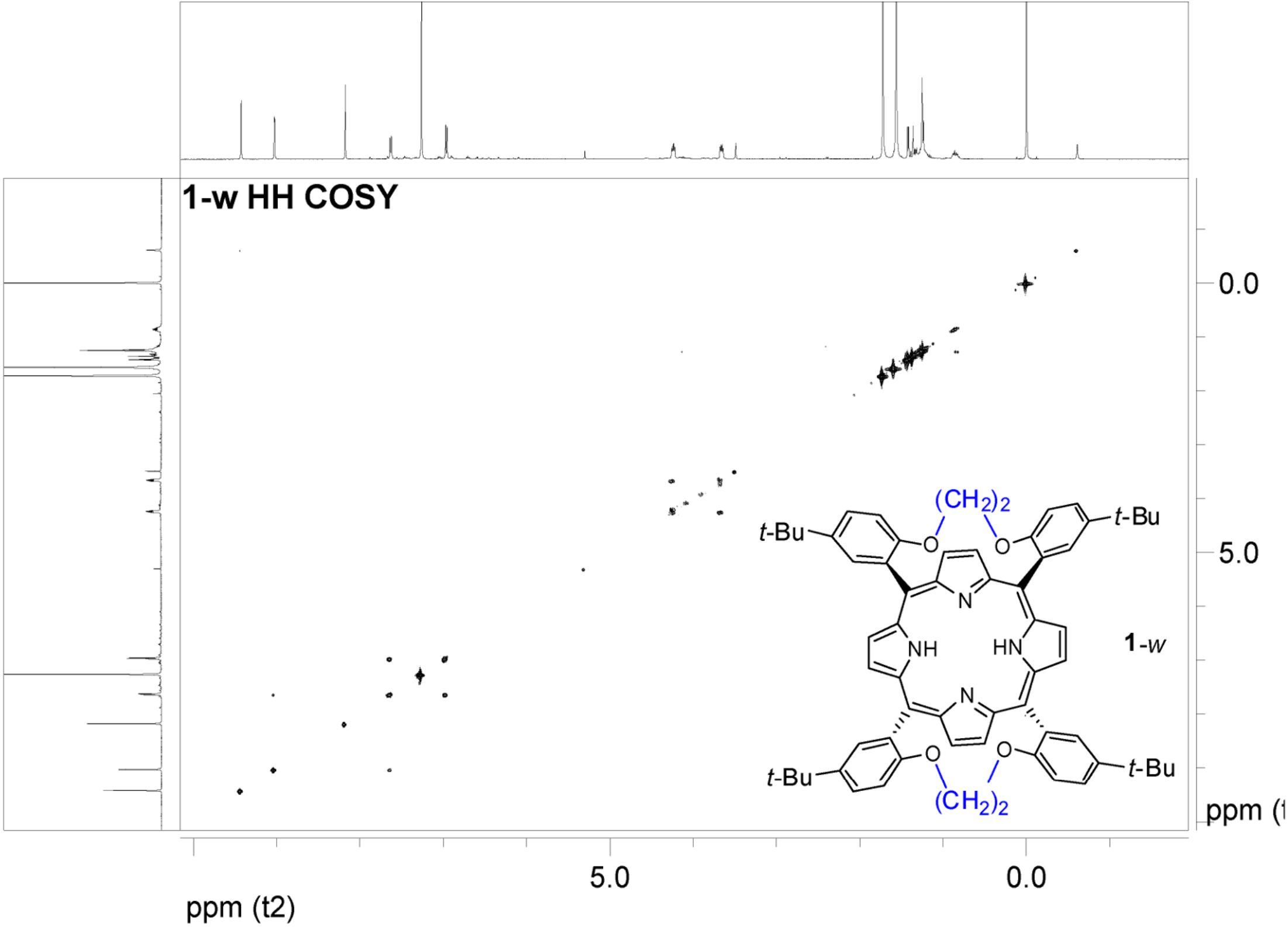

158.408
142.760
132.127
131.472
126.289
115.554
113.828
68.543
34.514
31.893
25.125
3-s C NMR
(CH2)4
t-Bu
t-Bu
O
O
N
NH
HN
N
3-s
O
O
t-Bu
t-Bu
(CH2)4
150
100
50
0
ppm (t1)

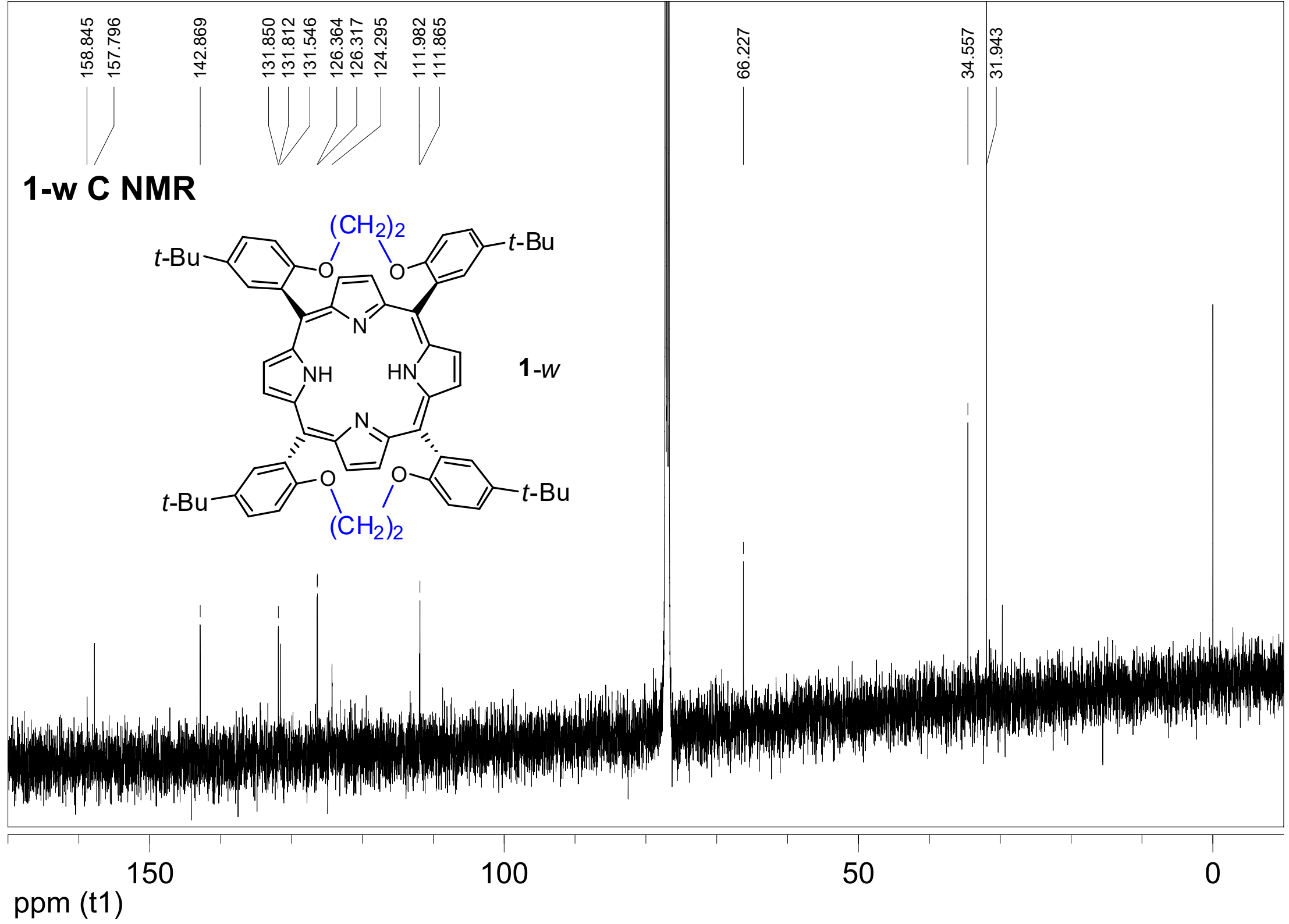

4-s H NMR
8.725
8.677
8.404
8.400
7.748
7.744
7.731
7.726
7.131
7.114
3.943
3.926
3.857
3.836
3.818
1.570
1.094
1.070
1.045
0.788
0.764
0.740
0.715
0.690
-2.543
(CH2)5
t-Bu
t-Bu
O
O
N
NH
HN
N
4-s
t-Bu
t-Bu
O
O
(CH2)5
3.98
4.02
4.01
4.00
4.00
4.01
4.03
34.40
4.17
6.01
2.01
5.0
0.0
ppm (t1)

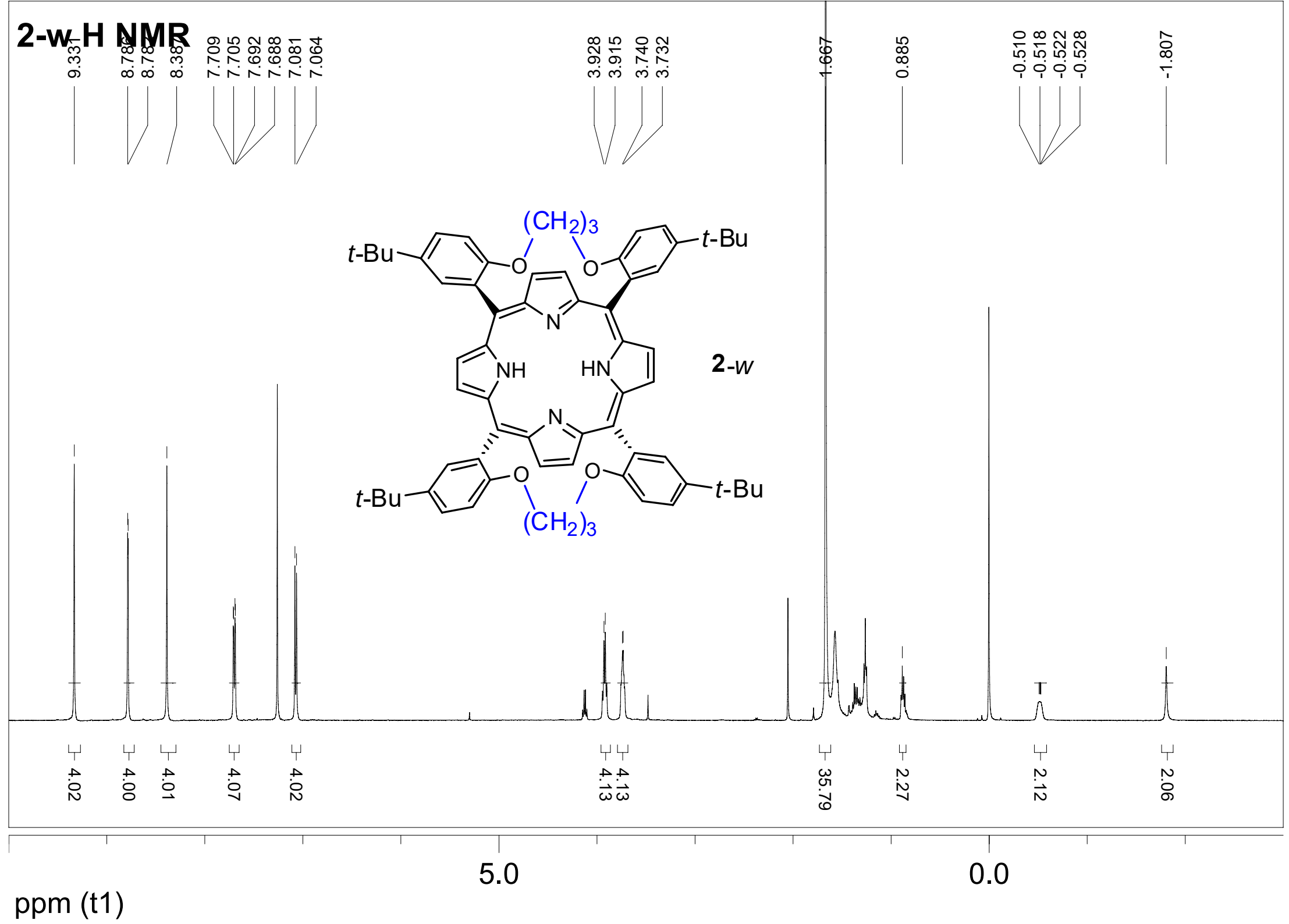

4-s HH COSY
(CH2)5
t-Bu
t-Bu
O
O
N
NH
HN
N
4-s
O
O
t-Bu
t-Bu
(CH2)5
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)

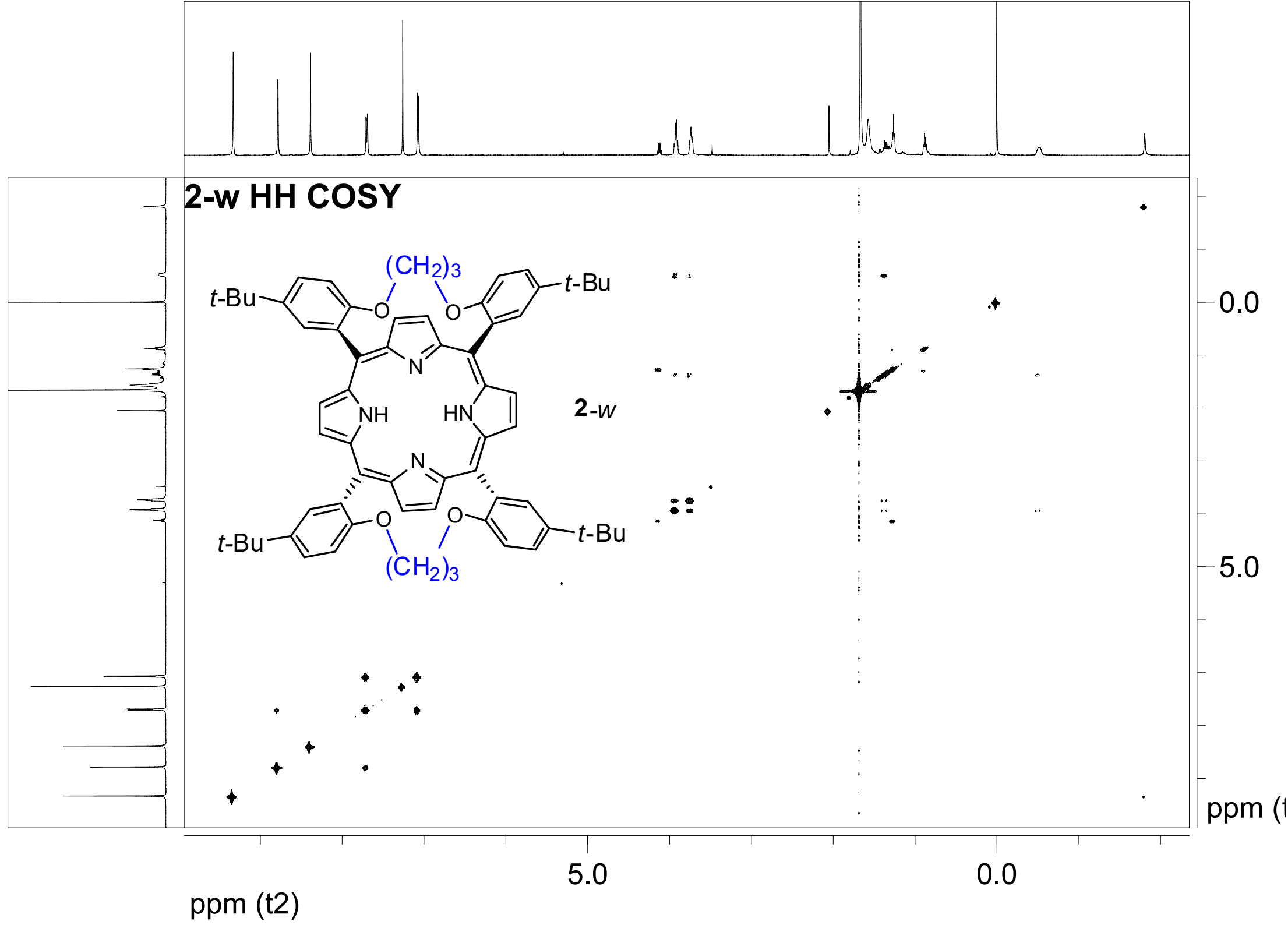

157.916
141.976
134.079
130.564
126.476
116.323
110.051
68.867
34.944
32.457
29.755
26.762
4-s C NMR
(CH2)5
t-Bu
t-Bu
O
O
N
NH
HN
N
4-s
O
O
t-Bu
t-Bu
(CH2)5
150
100
50
0
ppm (t1)

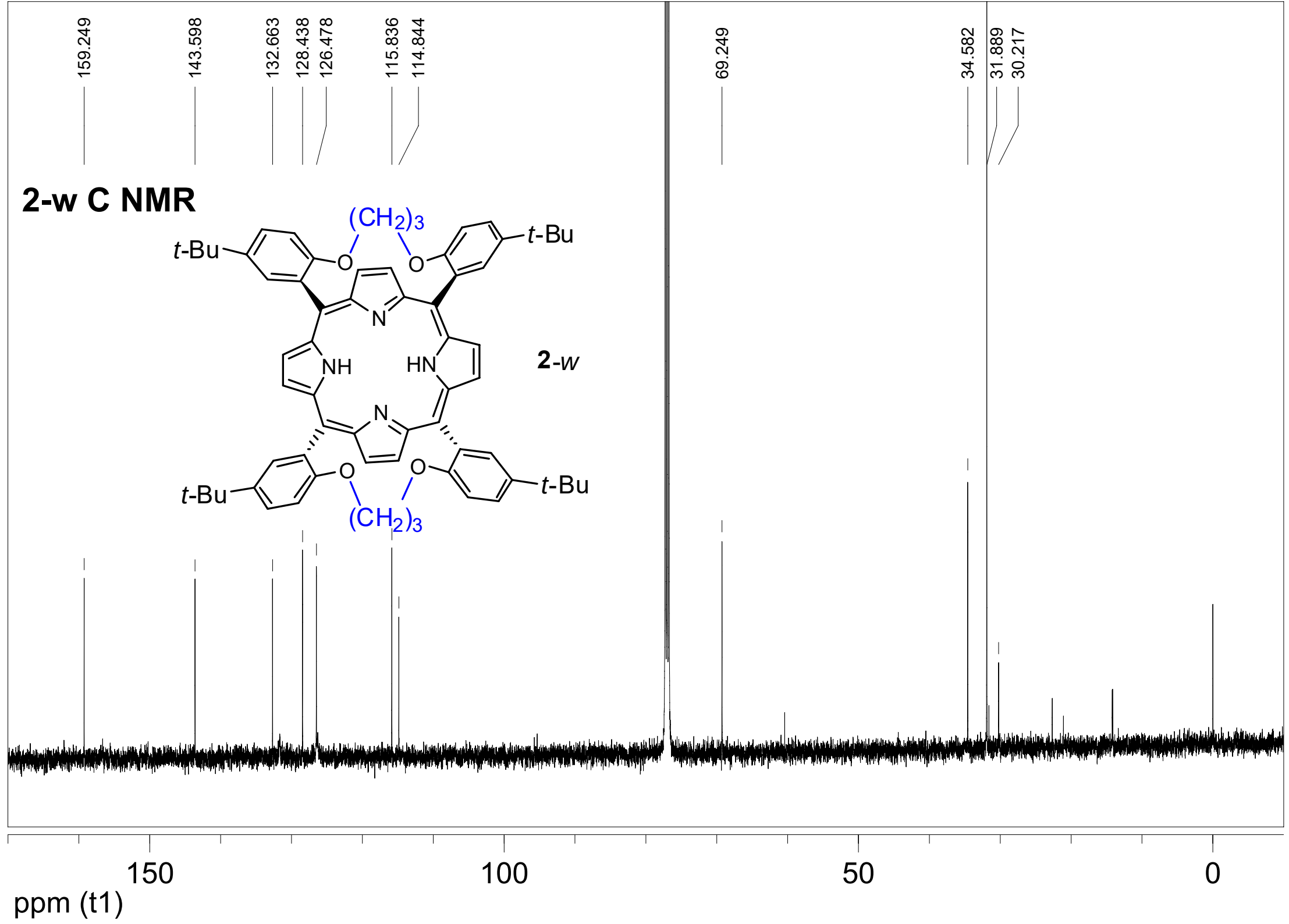

9.426
9.028
9.024
8.176
7.641
7.636
7.624
7.619
6.971
6.954
4.257
4.244
4.233
4.221
3.676
3.663
3.652
3.640
1.720
-0.611
1-w H NMR
(CH2)2
t-Bu
t-Bu
O
O
N
NH
HN
N
1-w
t-Bu
t-Bu
O
O
(CH2)2
3.95
3.90
4.00
3.97
3.95
4.03
3.92
28.28
2.01
5.0
0.0
ppm (t1)

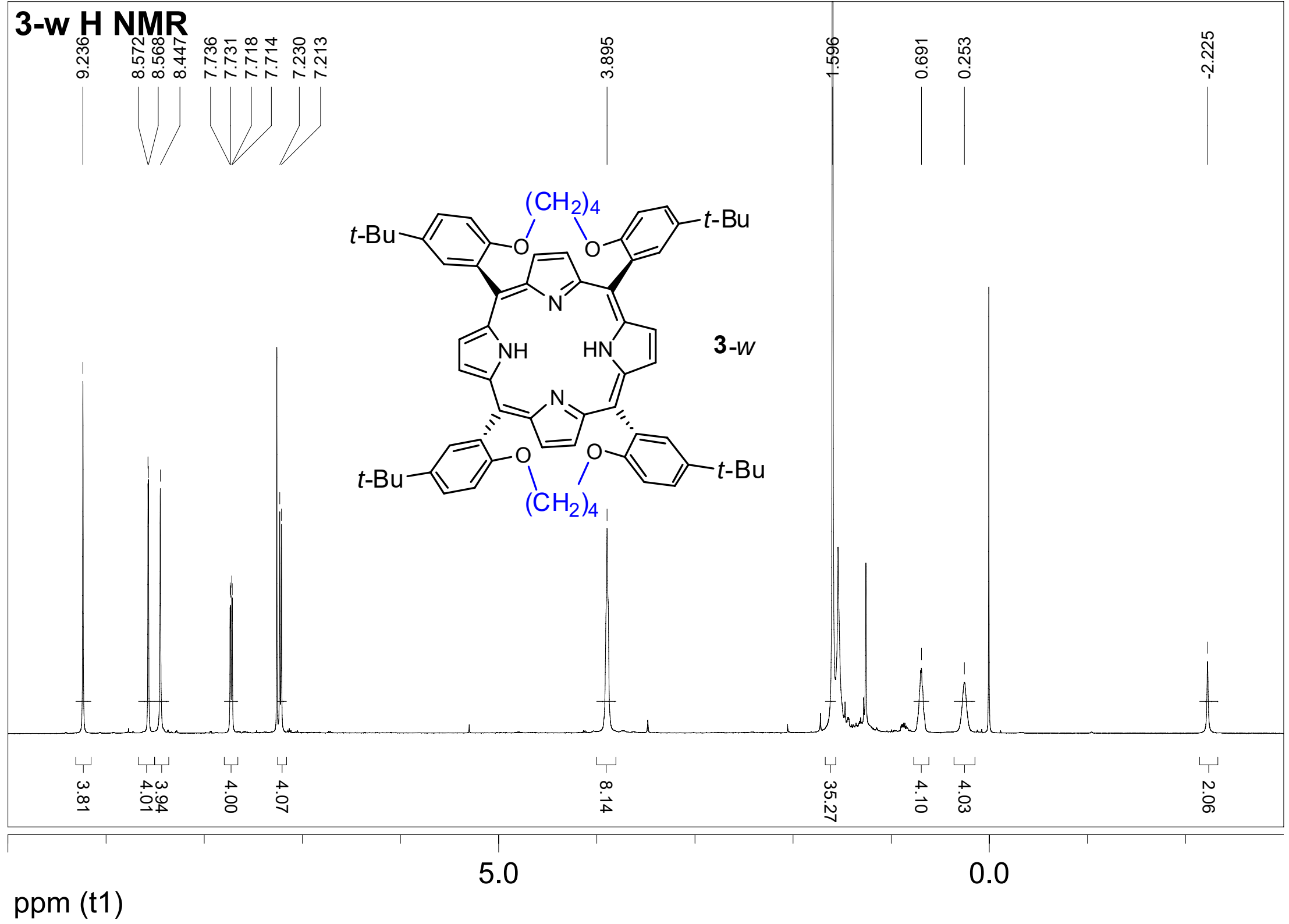

1-w HH COSY
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)
(CH2)2
t-Bu
t-Bu
O
O
N
NH
HN
N
1-w
t-Bu
t-Bu
O
O
(CH2)2

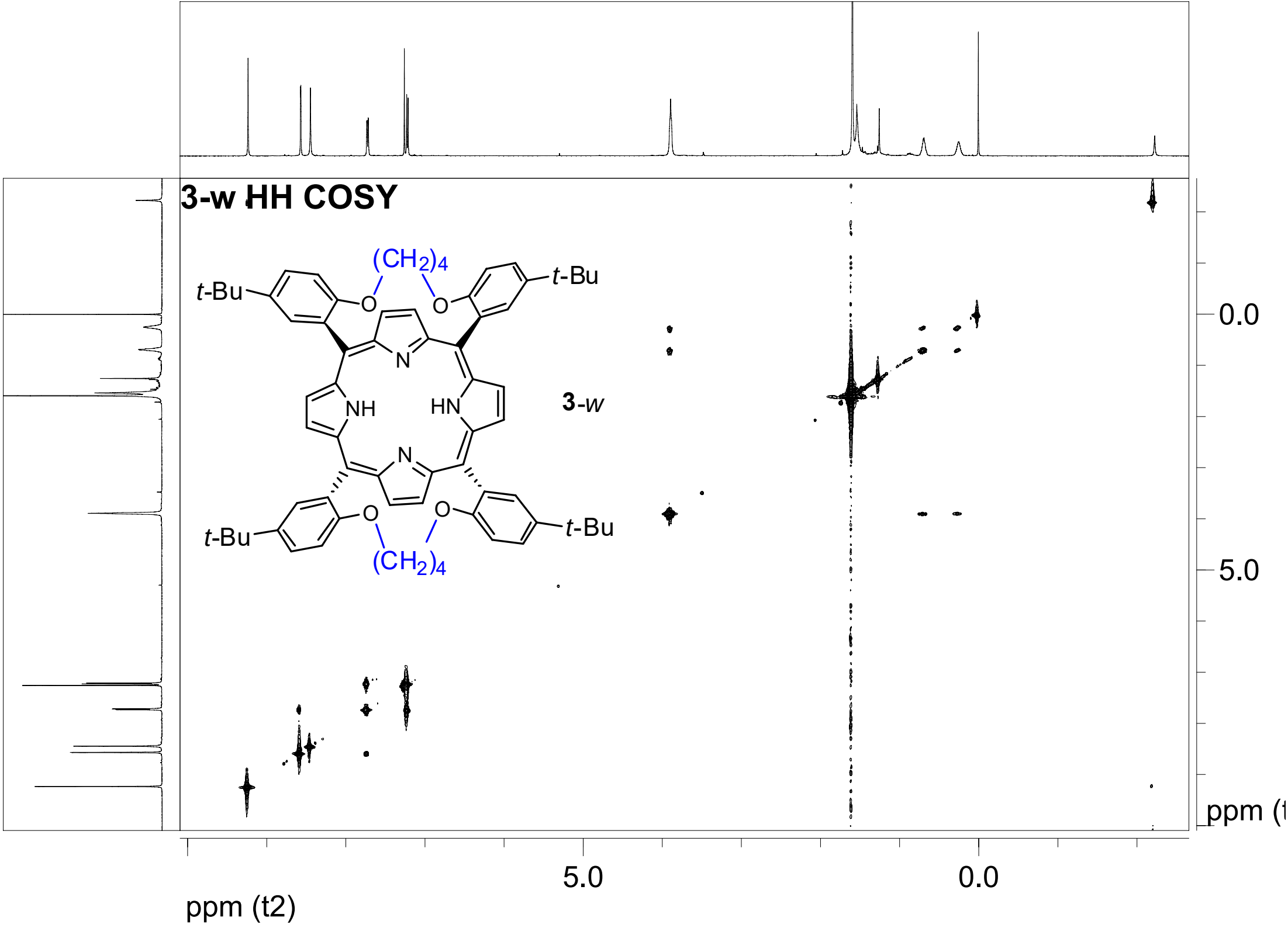

158.845
157.796
142.869
131.850
131.812
131.546
126.364
126.317
124.295
111.982
111.865
66.227
34.557
31.943
1-w C NMR
(CH2)2
t-Bu
t-Bu
O
O
N
NH
HN
N
1-w
t-Bu
t-Bu
O
O
(CH2)2
150
100
50
0
ppm (t1)

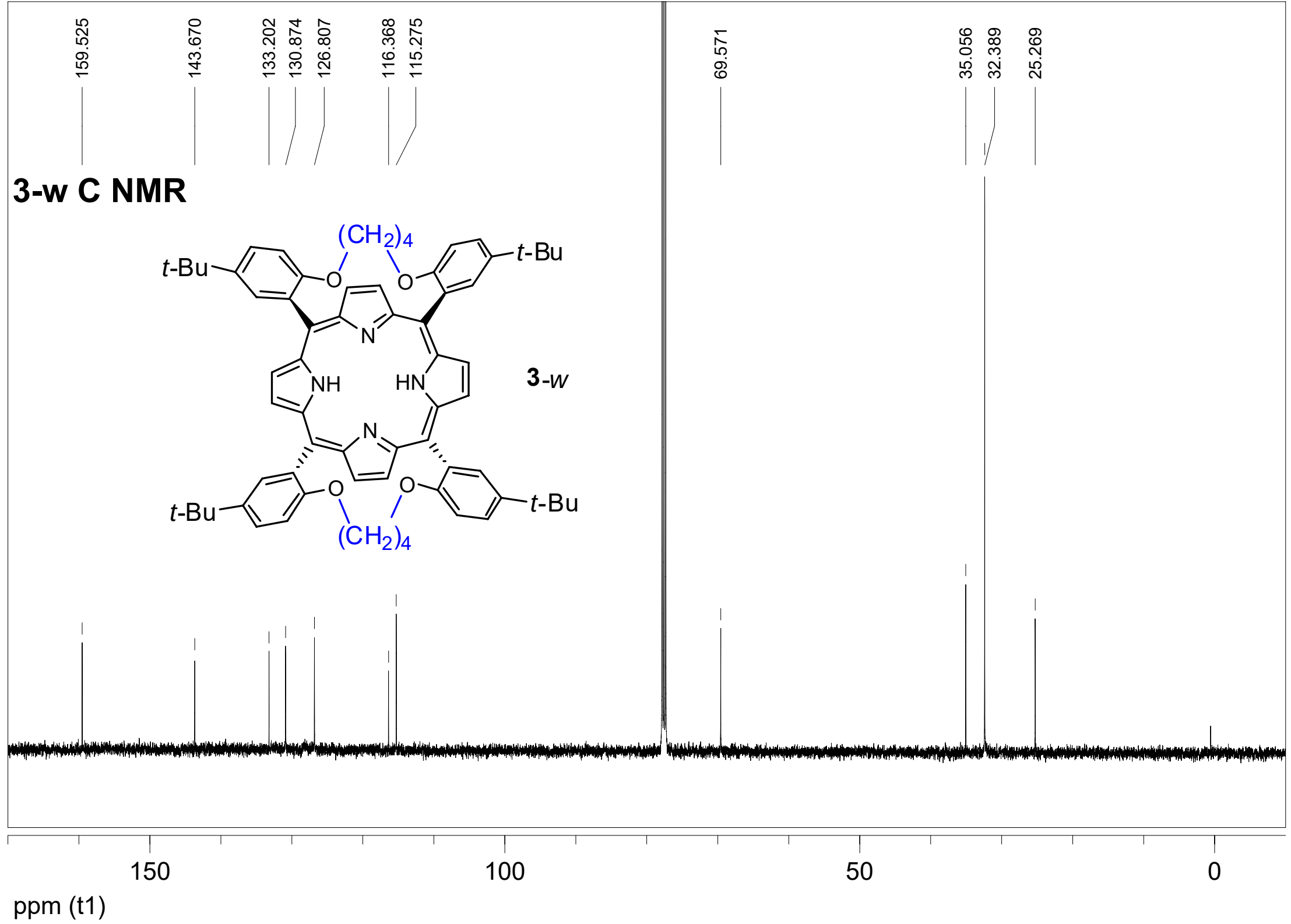

2-w H NMR
9.331
8.787
8.787
8.387
7.709
7.705
7.692
7.688
7.081
7.064
3.928
3.915
3.740
3.732
1.667
0.885
-0.510
-0.518
-0.522
-0.528
-1.807
(CH2)3
t-Bu
t-Bu
O
O
N
NH
HN
N
2-w
t-Bu
t-Bu
O
O
(CH2)3
4.02
4.00
4.01
4.07
4.02
4.13
4.13
35.79
2.27
2.12
2.06
5.0
0.0
ppm (t1)


2-w HH COSY
(CH2)3
t-Bu
t-Bu
O
O
N
NH
HN
N
O
O
t-Bu
t-Bu
(CH2)3
2-w
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)

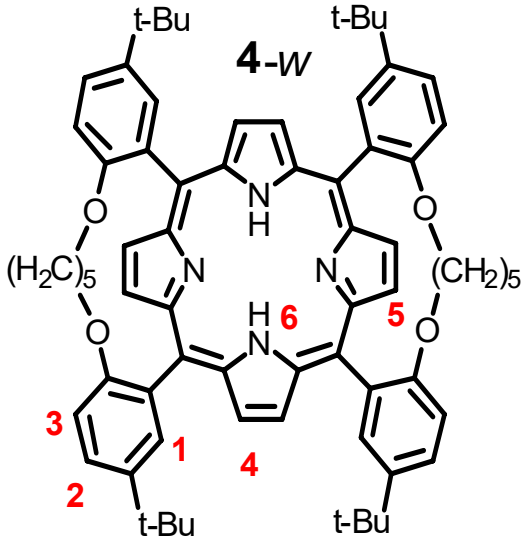

159.249
143.598
132.663
128.438
126.478
115.836
114.844
69.249
34.582
31.889
30.217
2-w C NMR
(CH2)3
t-Bu
t-Bu
O
O
N
NH
HN
N
2-w
O
O
t-Bu
t-Bu
(CH2)3
150
100
50
0
ppm (t1)


3-w H NMR
9.236
8.572
8.568
8.447
7.736
7.731
7.718
7.714
7.230
7.213
3.895
1.596
0.691
0.253
-2.225
(CH2)4
t-Bu
t-Bu
O
O
N
NH
HN
N
3-w
O
O
t-Bu
t-Bu
(CH2)4
3.81
4.01
3.94
4.00
4.07
8.14
35.27
4.10
4.03
2.06
5.0
0.0
ppm (t1)

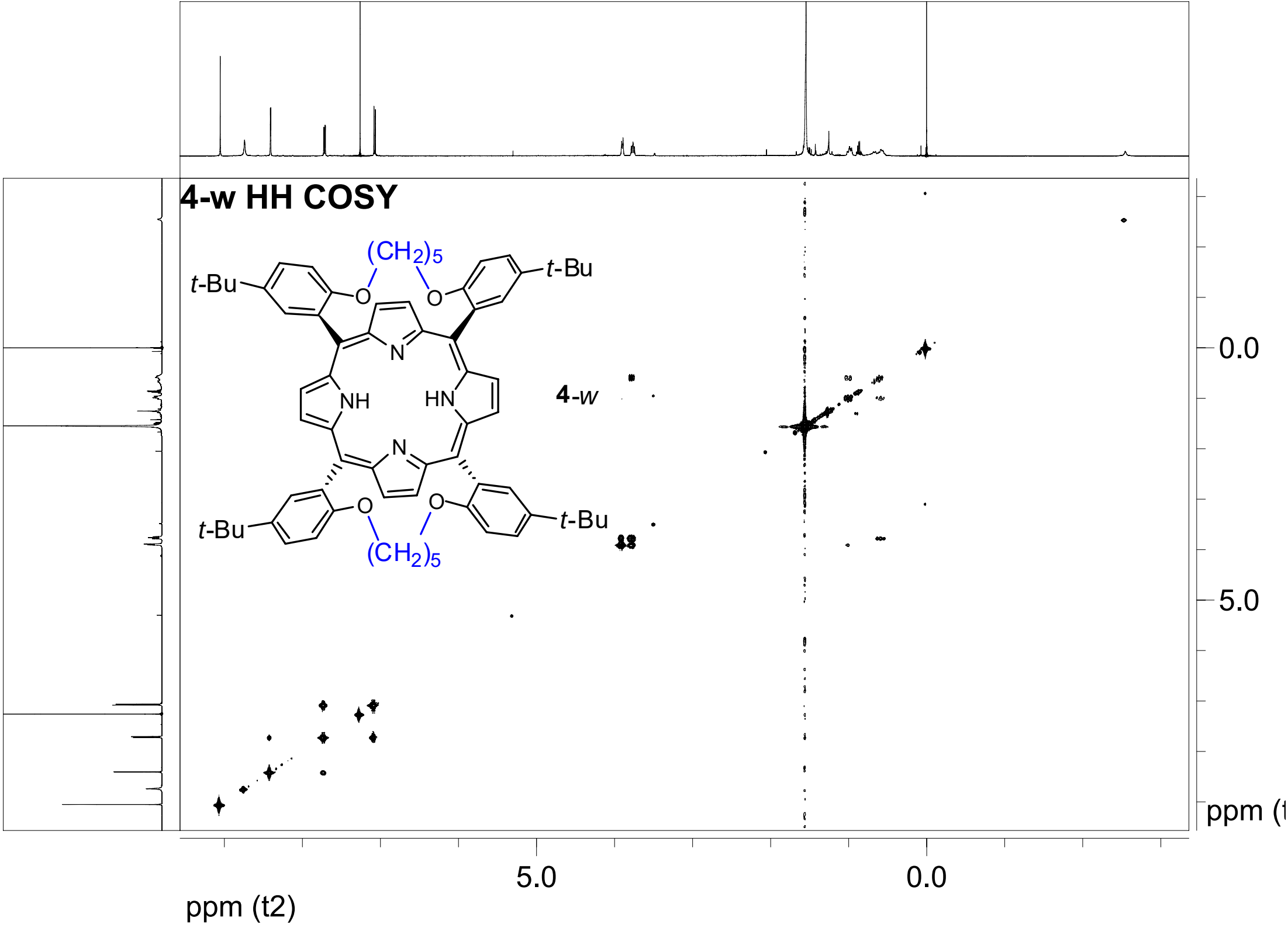

3-w HH COSY
(CH2)4
t-Bu
t-Bu
O
O
N
NH
HN
N
3-w
t-Bu
t-Bu
O
O
(CH2)4
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)

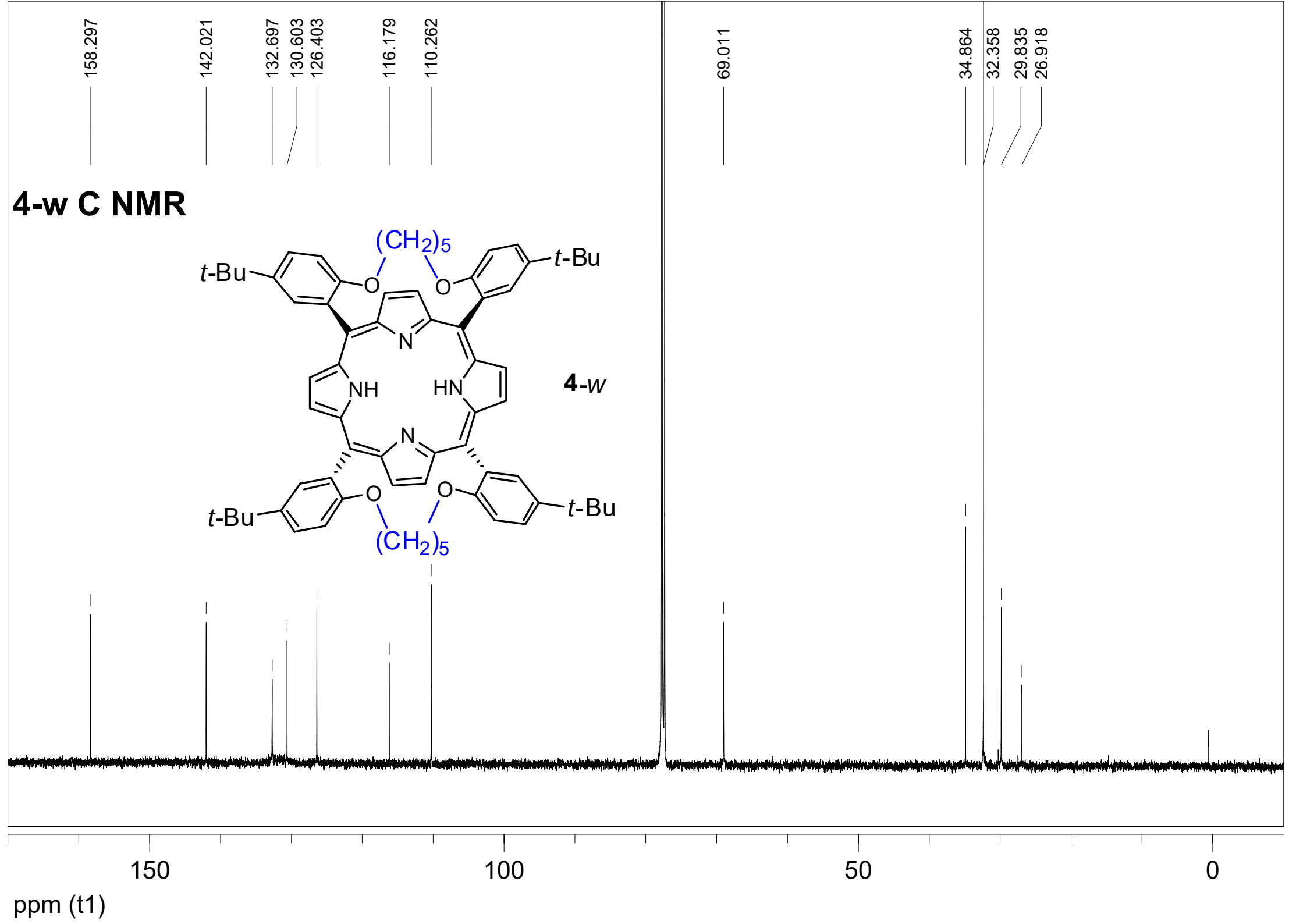

159.525
143.670
133.202
130.874
126.807
116.368
115.275
69.571
35.056
32.389
25.269
3-w C NMR
(CH2)4
t-Bu
t-Bu
O
O
N
NH
HN
N
3-w
O
O
t-Bu
t-Bu
(CH2)4
150
100
50
0
ppm (t1)

4-w H NMR


t-Bu
t-Bu
4-w
O
(H2C)5
O
N
H
N
N
H
O
(CH2)5
O
6
5
3
1
4
2
t-Bu
t-Bu

9.052
8.740
8.410
8.405
7.727
7.722
7.709
7.704
7.082
7.065
3.891
3.763
1.546
0.989
0.682
0.679
0.655
0.586
0.584
-2.549
4
1
2
3
5
6
3.77
3.80
3.88
3.99
4.00
4.04
4.04
35.48
4.05
2.26
2.00
5.0
0.0
ppm (t1)


4-w HH COSY
(CH2)5
t-Bu
t-Bu
O
O
N
NH
HN
N
4-w
O
O
t-Bu
t-Bu
(CH2)5
0.0
5.0
ppm (t
5.0
0.0
ppm (t2)


158.297
142.021
132.697
130.603
126.403
116.179
110.262
69.011
34.864
32.358
29.835
26.918
4-w C NMR
(CH2)5
t-Bu
t-Bu
O
O
N
NH
HN
N
4-w
O
O
t-Bu
t-Bu
(CH2)5
150
100
50
0
ppm (t1)