Self-Assembly of a Bis-Porphyrinic Supramolecular Rectangle Using Two Orthogonal Binding Strategies

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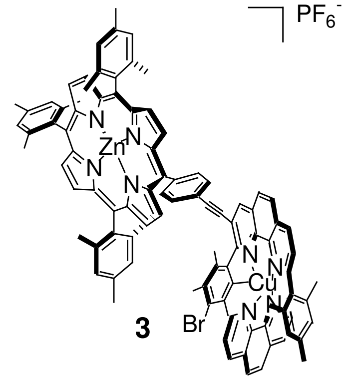
Supporting Information

Synthesis of Cu(I) complexes.



3

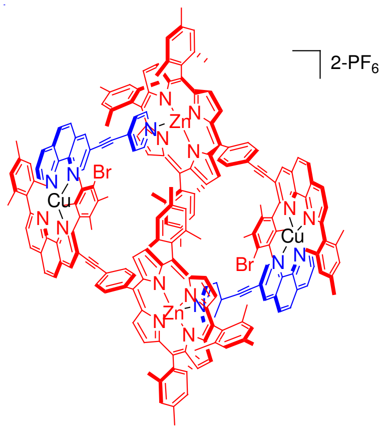
Complex 3: To equimolar amounts of **1** and $[Cu(CH_3CN)_4]PF_6$ in dichloromethane was added one equivalent of anhydrous [1,10]-phenanthroline. The resulting solution showed an instantaneous change in color to deep red. The complex , obtained in quantitative yield, was isolated without any further purification and was found to be **3**.

^{1}H NMR (400 MHz, CD_2Cl_2): δ= 8.95 (s, 1 H, 4-H), 8.72 (d, *J* = 7.8 Hz, 1 H, 7-H), 8.72 (d, *J* = 4.6 Hz, 2 H, pyrrol-H1), 8.68 (d, *J* = 4.8 Hz, 2 H, pyrrol-H3), 8.67 (d, *J* = 4.8 Hz, 2 H, pyrrol-H4), 8.66 (d, *J* = 4.6 Hz, 2 H, pyrrol-H2), 8.52 (dd, ^3J = 4.6 Hz, ^4J = 1.3 Hz, 2 H, 2'-, 9' -H), 8.44 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2 H, 4'-, 7'-H), 8.27 (d, *J* = 9.1 Hz, 1 H, 5-H), 8.24 (d, *J* = 9.1 Hz, 1 H, 6-H), 8.08 (d, *J* = 8.2 Hz, 2 H, Ar-Ha, -Ha'), 7.92 (s, 2 H, 5'-, 6'-H), 7.91 (d, *J* = 7.8 Hz, 1 H, 8-H), 8.27 (dd, ^3J = 8.0 Hz, ^3J = 4.8 Hz, 2 H, 3'-, 8'-H), 7.44 (d, *J* = 8.2 Hz, 2 H, Ar-Hb, -Hb'), 7.26 (s, 6 H, por-mes), 6.02 (s, 2 H, 3'''-, 5'''-H), 2.59 (s, 12H, 7''-, 10''-, 7'''-, 9'''-H), 1.81 (s, 18 H, por-mes-Me), 1.78 (s, 9 H, por-mes-Me), 1.64 (s, 6 H, 8''-, 9''-H), 1.54 (s, 3 H, 8'''-H).

^{13}C NMR (100MHz, CD_2Cl_2): δ= 160.5, 159.0, 149.4, 149.2, 149.2, 148.9, 147.2, 144.4, 143.4, 142.4, 141.8, 139.0, 138.9, 138.5, 137.3, 136.9, 135.9, 134.2, 132.8, 131.8, 131.0, 130.4, 130.1, 129.1, 128.3, 127.8, 127.3, 127.1, 126.6, 126.4, 125.8, 124.2, 122.3, 120.0, 118.1, 117.9, 97.0, 85.3, 21.1, 20.7, 19.6, 19.5 (2), 19.4 (2), 17.7.

ESI-MS *m/z* (%): 1579.6 (100) $[M]^+$.

Elemental analysis calcd(%) for $C_{98}H_{81}BrCuF_6N_8PZn$: C 68.25, H 4.73, N 6.50; found: C 68.77, H 4.68, N 6.56.



6a

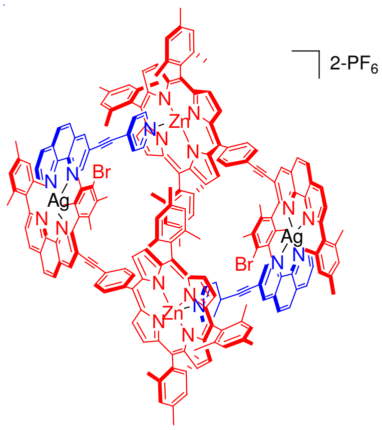
Complex 5a/6a: To equimolar amounts of **1** and $[Cu(CH_3CN)_4]PF_6$ in dichloromethane was added one equivalent of **4**. The resulting solution showed an instantaneous change in color to deep red. The complex was isolated without any further purification and was found to be **5a**, obtained in quantitative yield

^{1}H NMR (400 MHz, CD_2Cl_2): δ= 8.91 (s, 2 H, 4-H), 8.70 (d, J = 8.2 Hz, 2 H, 7-H), 8.68 (d, J = 4.6 Hz, 4 H, pyrrol-H1), 8.65 (d, J = 4.8 Hz, 4 H, pyrrol-H3), 8.62 (s, 8 H, pyrrol-H2, -H4), 8.49 (dd, ^3J = 4.5 Hz, ^4J = 1.2 Hz, 2 H, 9'-H),), 8.42 (dd, ^3J = 8.9 Hz, ^4J = 1.2 Hz, 2 H, 7'-H), 8.28 (br s, 4 H, 5'-, 6'-H), 8.23 (d, J = 9.1 Hz, 2 H, 5-H), 8.22 (d, J = 9.1 Hz, 2 H, 6-H), 8.09 (d, J = 7.9 Hz, 4 H, Ar-Ha, -Ha'), 7.88 (dd, ^3J = 8.7 Hz, ^3J = 4.1 Hz, 2 H, 8'-H), 7.88 (d, ^3J = 4.5 Hz, 2 H, 2'-H), 7.76 (d, ^2J = 8.9 Hz, 2 H, 4'-H), 7.75 (dd, ^3J = 8.1 Hz, ^3J = 4.8 Hz, 2 H, 8'-H), 7.44 (d, J = 7.4 Hz, 4 H, Ar-Hb, -Hb'), 7.26 (s, 12 H, por-mes), 7.07 (br s, 2 H, 3''-H), 6.12 (br s, 2 H, 5''-H), 6.02 (s, 2 H, 3'''-H), 5.87 (s, 2 H, 5'''-H), 2.59 (s, 18 H, por-mes-Me), 1.80 (s, 18 H, por-mes-Me), 1.79 (s, 18 H, por-mes-Me), 1.69 (s, 6 H, 7''-H), 1.68 (s, 6 H, 9''-H), 1.64 (s, 6 H, 7'''-H), 1.56 (s, 6 H, 8''-H), 1.55 (s, 6 H, 10''-H), 1.48 (s, 6 H, 8'''-H), 1.44 (s, 6 H, 9'''-H)

^{13}C NMR (100MHz, CD_2Cl_2): δ= 161.4, 159.9, 150.4, 150.2, 150.1, 149.8, 149.4, 148.6, 145.5, 144.3, 142.8, 142.7, 142.2, 140.0, 139.9, 139.8, 139.6, 139.5, 139.4, 139.1, 138.4, 138.1, 137.9, 137.8, 137.1, 135.2, 135.1, 134.0, 133.6, 132.9, 132.6, 131.9, 131.5, 131.3, 130.9, 130.0, 129.7, 129.2, 128.7, 128.4, 128.3 (2), 128.1, 127.7, 127.5, 127.3, 126.9, 126.8, 125.6, 125.2, 123.3, 120.9, 120.1, 119.0, 118.7, 98.1, 91.6, 89.7, 86.1, 22.1(2), 21.7, 20.6, 20.4, 20.3, 18.8, 18.6.

ESI-MS *m/z* (%): 1680 (100) $[M]^+$,

Elemental analysis calcd(%) for $C_{105}H_{84}BrCuF_6N_9PZn*CH_3CN$: C 68.85, H 4.70, N 7.50; found C 68.54, H 4.64, N 7.61;



6b

Complex 5b/6b: To equimolar amounts of **1** and $AgPF_6$ in dichloromethane-acetonitrile (10:1) was added one equivalent of **4**. The resulting solution showed an instantaneous darkening in color. The solvents were then removed and the solid was redissolved in dichloromethane. The complex was isolated without any further purification and was found to be **5b**, obtained in quantitative yield

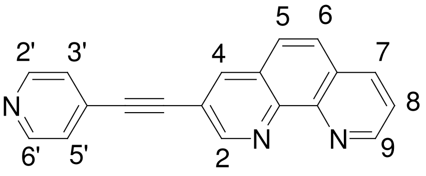
^{1}H NMR (400 MHz, CD_2Cl_2): δ= 8.86 (s, 2 H, 4-H), 8.72-8.60 (m, 18 H, Pyrrol H, 7-H), 8.44 (br s, 4 H, 7', 4'-H),), 8.31 (s, 2 H, 2'-H), 8.25 (s, 2 H, 9'-H), 8.20 (d, J = 9.1 Hz, 2 H, 5-H), 8.18 (d, J = 9.1 Hz, 2 H, 6-H), 8.09 (d, J = 7.9 Hz, 4 H, Ar-Ha, -Ha'), 7.90(br s, 4 H, 5'-, 6'-H), 7.79 (d, ^3J = 4.5 Hz, 4 H, 8', 8-H), 7.37 (d, J = 7.4 Hz, 4 H, Ar-Hb, -Hb'), 7.23 (s, 12 H, por-mes), 7.02 (br s, 4 H, 3''-H), 6.19 (s, 6 H, 3'''-H), 5.87 (s, 6 H, 5''', 5''-H), H), 2.53 (s, 18 H, por-mes-Me), 2.00 (s, 6 H, 7''-H), 1.92 (s, 6 H, 9''-H), 1.86 (s, 6 H, 7'''-H), 1.78 (s, 36 H, por-mes-Me), , 1.66 (s, 6 H, 8''-H), 1.56 (s, 6 H, 10''-H), 1.32 (s, 6 H, 8'''-H), 1.23 (s, 6 H, 9'''-H)

^{13}C NMR (100MHz, CD_2Cl_2): δ= 162.7, 161.6, 151.4, 150.9, 150.4, 150.3, 150.2, 149.9, 149.9, 147.0, 146.9, 146.8, 146.8, 145.9, 145.5, 142.9, 142.1, 141.5, 141.3, 140.8, 140.7, 140.4, 140.1, 139.9, 139.6, 139.0, 138.9, 138.7, 137.9, 135.6, 135.3, 131.9, 131.6, 131.5, 131.4, 131.0, 130.5, 130.2, 130.0, 129.6, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.5, 127.0, 126.7, 125.2, 120.9, 119.0, 118.7, 117.3, 98.2, 98.1, 91.7, 90.0, 86.4, 22.1, 21.7, 20.8, 20.7, 20.6, 20.4, 19.1, 18.8.

ESI-MS *m/z* (%): 1724 (100) $[M]^+$.

Elemental analysis calcd(%) for $C_{105}H_{84}AgBrF_6N_9PZn{\ast}CH_3CN{\ast}0.5CH_2Cl_2$: C 66.09, H 4.54, N 7.17, found : C 66.04, H, 4.51, N 7.36

3-Pyridin-4-ylethynyl-[1,10]phenanthroline



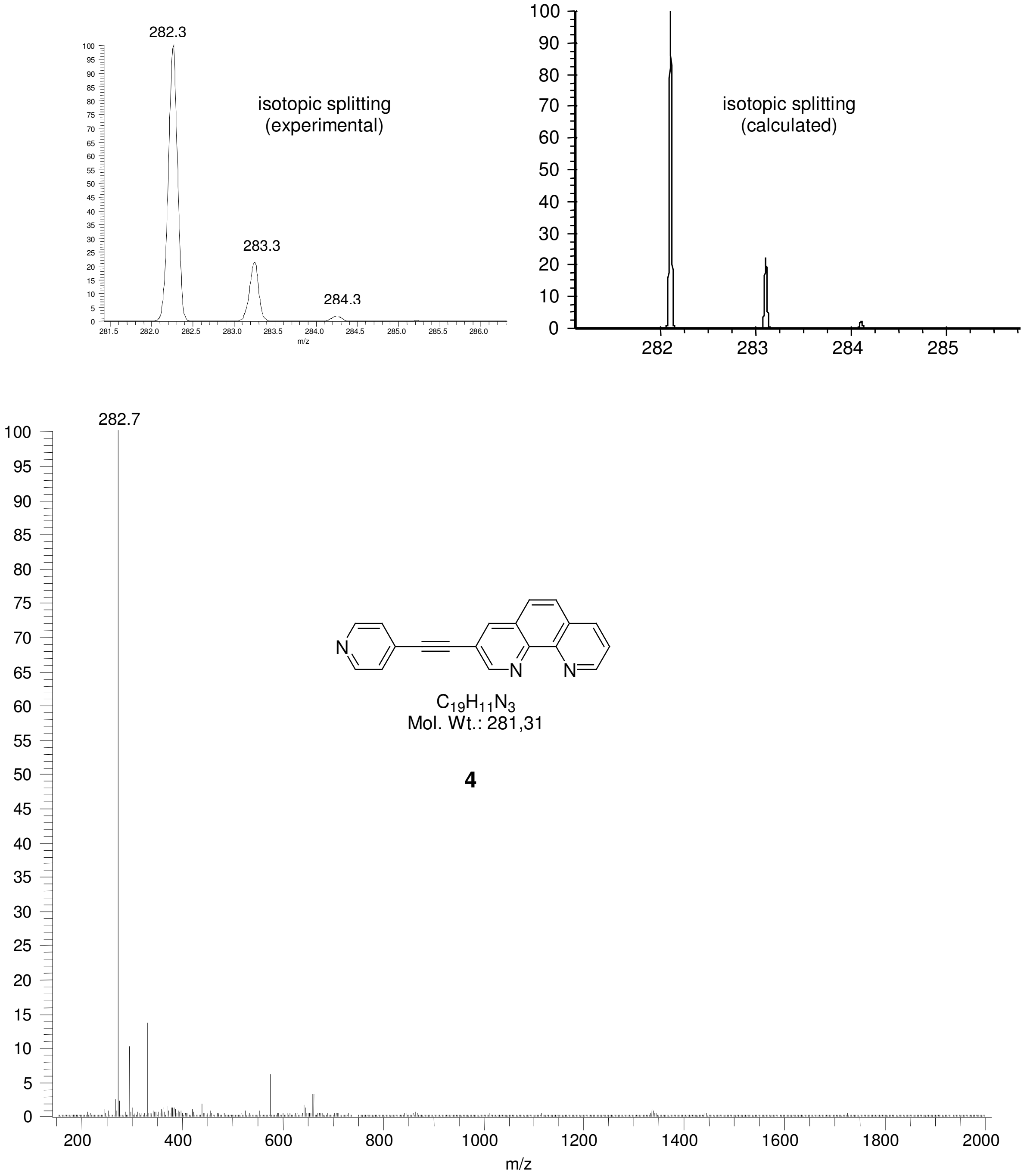
4

^{1}H NMR (400 MHz, CD_2Cl_2): 9.25 (s, 1 H, 2-H), 9.15 (s, 1 H, 9-H), 8.64 (dd, ^3J=4.5 Hz, ^4J= 1.5 Hz, 2 H, 2', 6'-H), 8.45 (s, 1 H, 4-H), 8.29 (d, J=8.0 Hz, 1 H, 7-H), 7.88 (d, J=8.6 Hz, 1 H, 5-H), 7.82 (d, J=8.6 Hz, 1 H, 6-H), 7.67 (br. s, 1 H, 8-H), 7.48 (dd, ^3J=4.5 Hz, ^4J= 1.5 Hz, 2 H, 3', 5'-H).

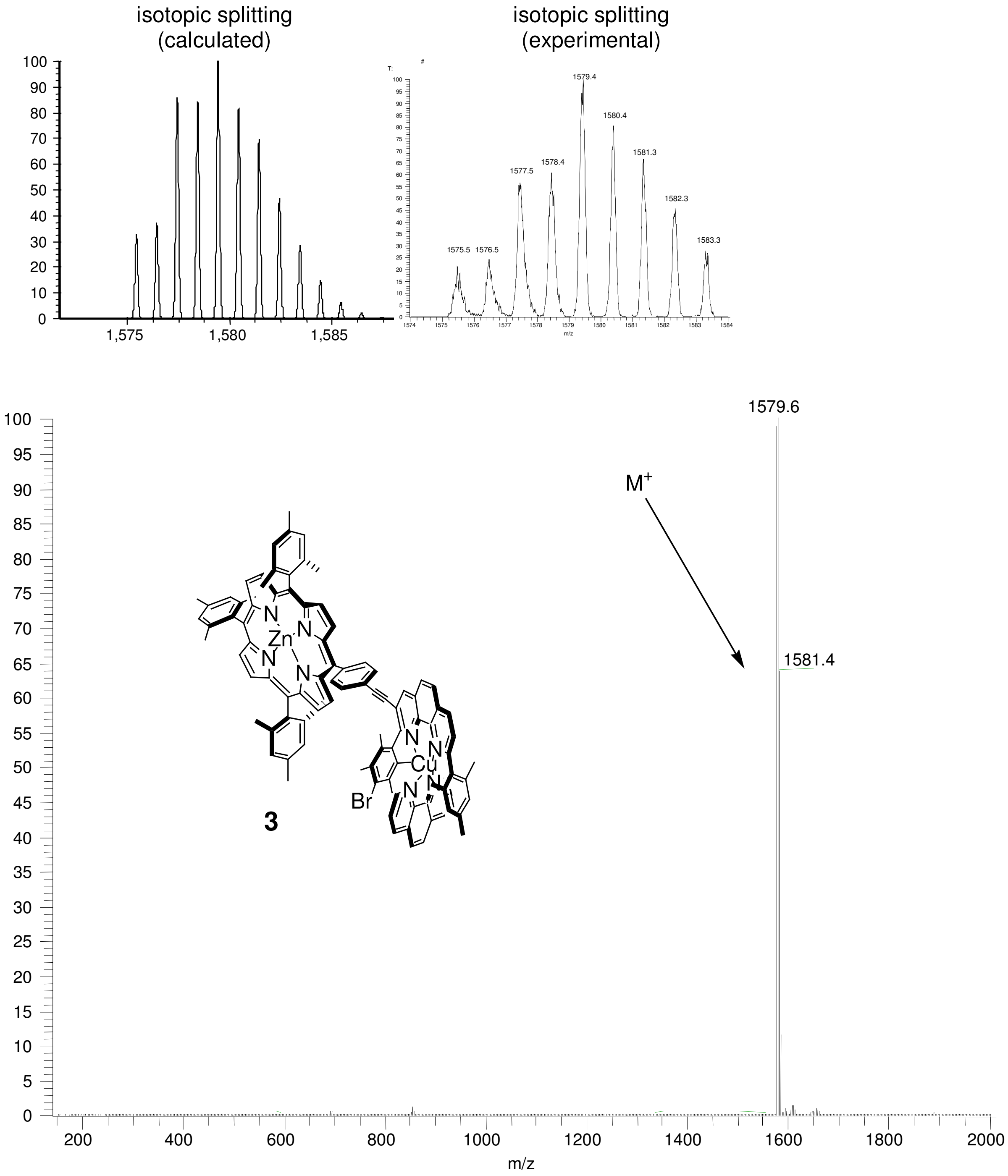
^{13}C NMR (100MHz, CD_2Cl_2): δ=152.2, 150.9, 150.4, 146.3, 145.8, 139.1, 136.4, 130.9, 129.7, 128.1, 126.4, 125.9, 123.9, 118.7, 110.1, 91.0, 90.9.

ESI-MS *m/z* (%): 282.7 (100) $[M+H]^+$

ESI-MS



ESI-MS of **4.**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1,580
1,585
isotopic splitting
(experimental)
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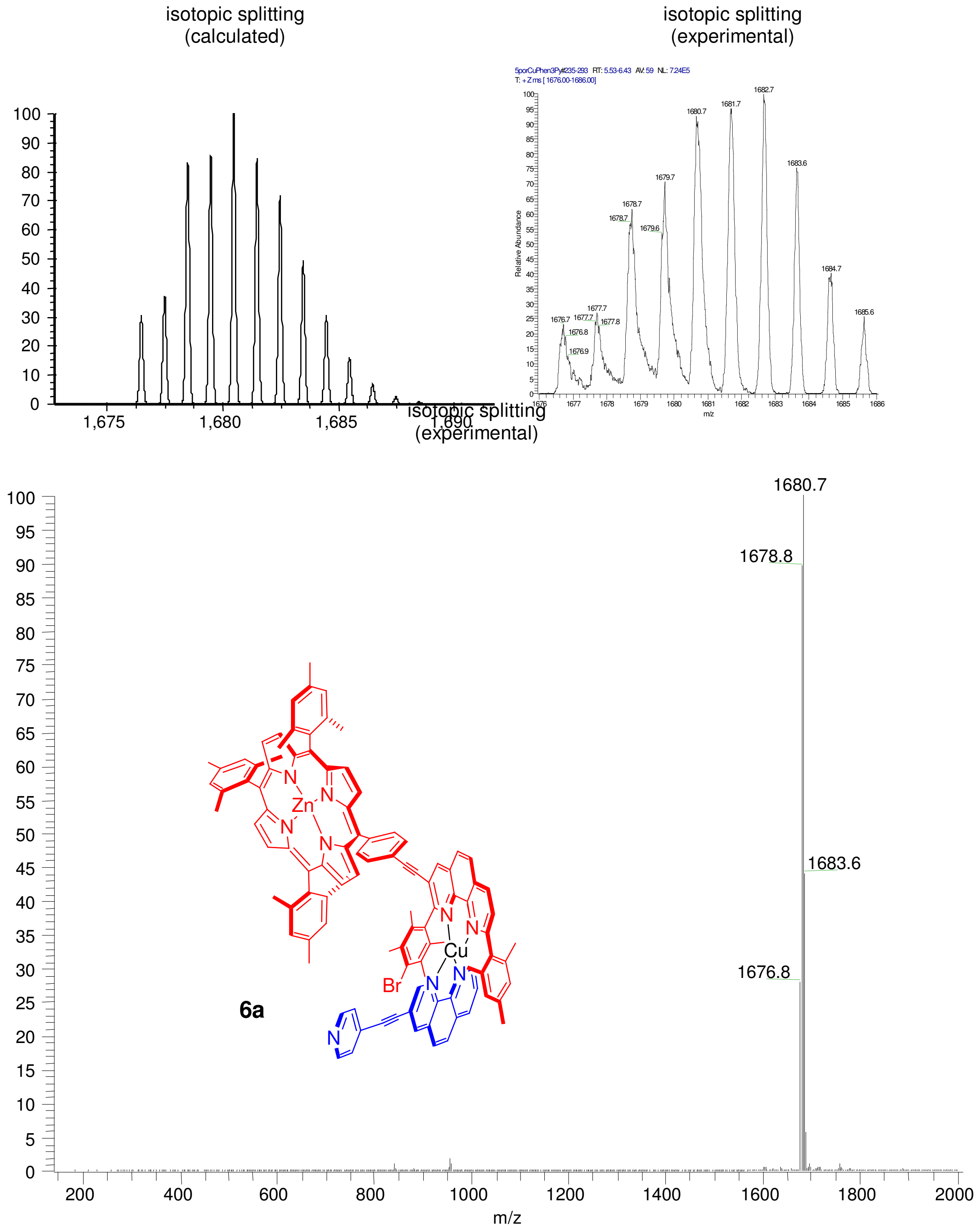
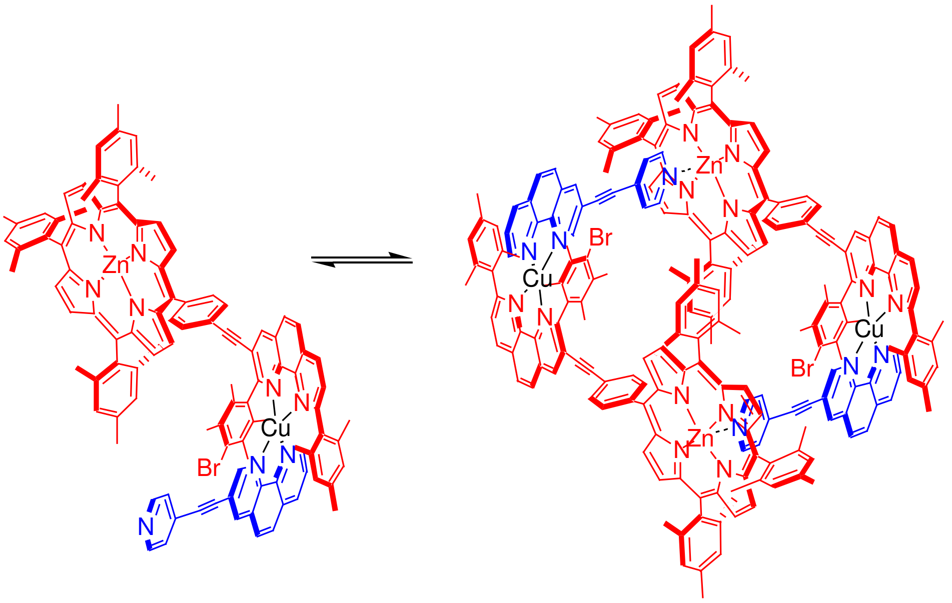
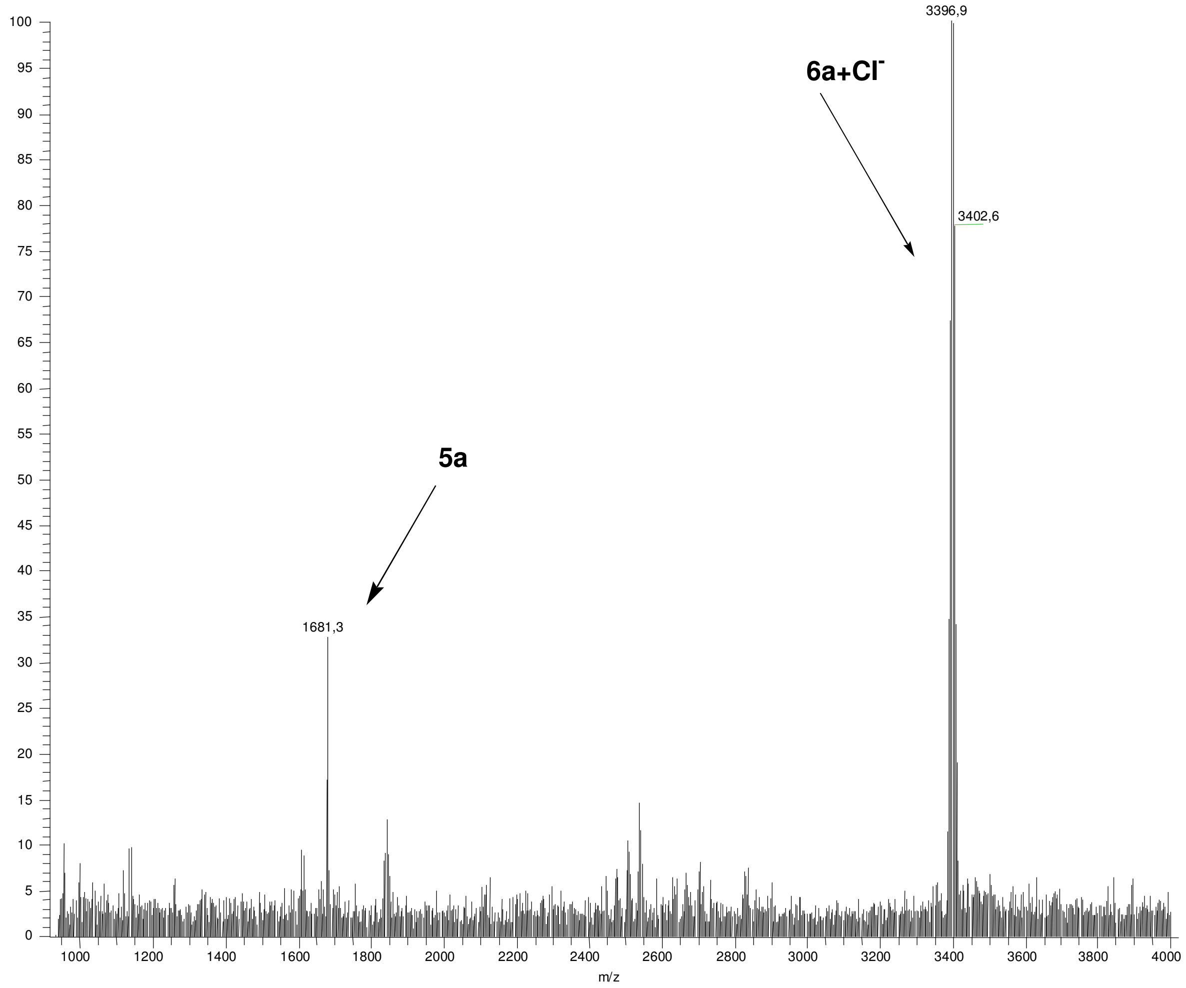
1576.5
1577.5
1578.4
1579.4
1580.4
1581.3
1582.3
1583.3
m/z
1579.6
1581.4
M+
Zn
Cu
N
Br
3
m/z

ESI-MS of **3.**

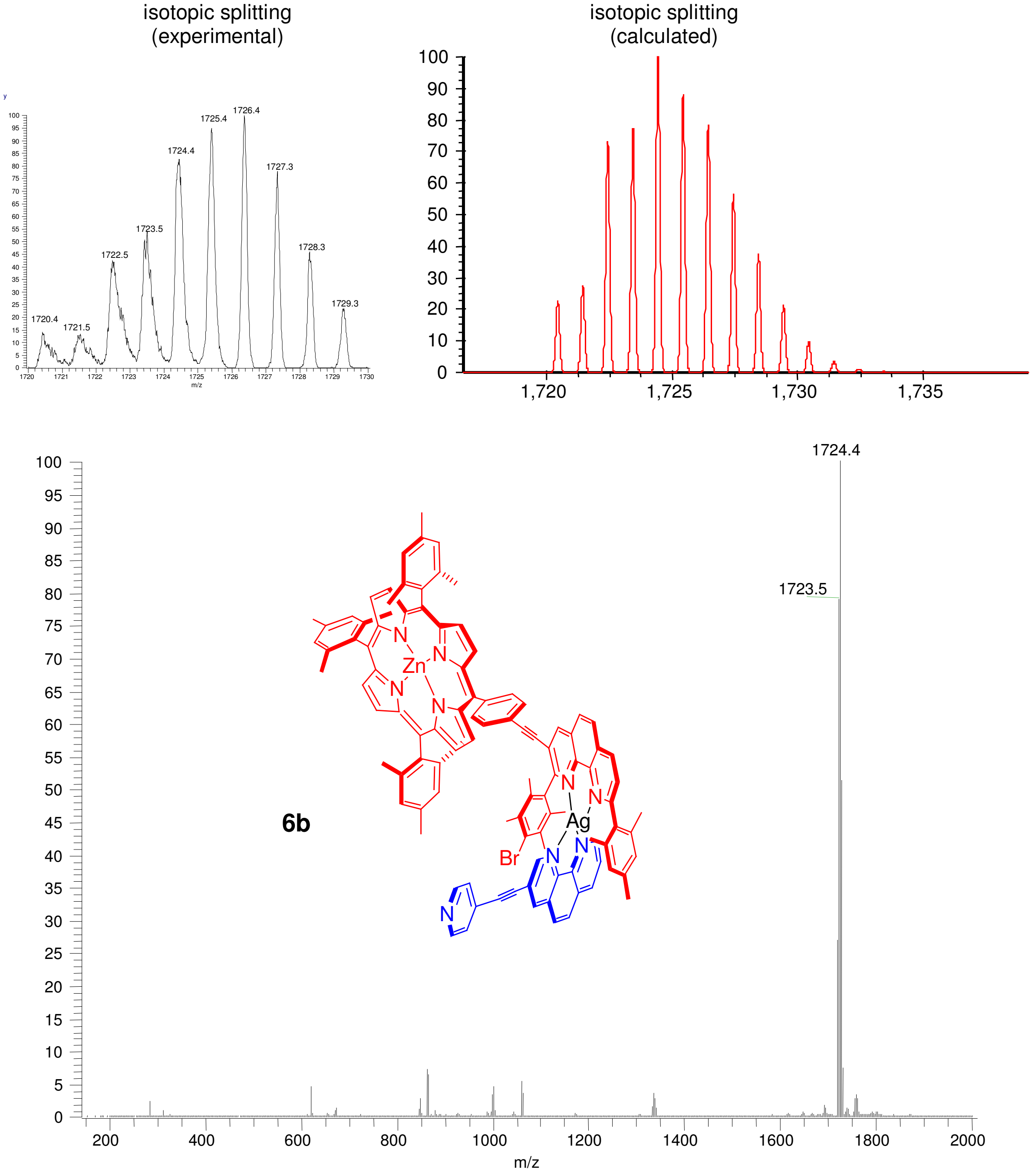

isotopic splitting
(calculated)
0
10
20
30
40
50
60
70
80
90
100
1,675
1,680
1,685
1,690
isotopic splitting
(experimental)
5porCuPhen3Py#235-293 RT: 5.53-6.43 AV: 59 NL: 7.24E5
T: + Z ms [1676.00-1686.00]
Relative Abundance
m/z
1676.7
1676.8
1676.9
1677.7
1677.7
1677.8
1678.7
1678.7
1679.6
1679.7
1680.7
1681.7
1682.7
1683.6
1684.7
1685.6
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
isotopic splitting
(experimental)
1680.7
1678.8
1683.6
1676.8
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
200
400
600
800
1000
1200
1400
1600
1800
2000
m/z
N
Zn
N
N
N
N
N
Cu
N
N
Br
N
6a

ESI-MS of **6a**





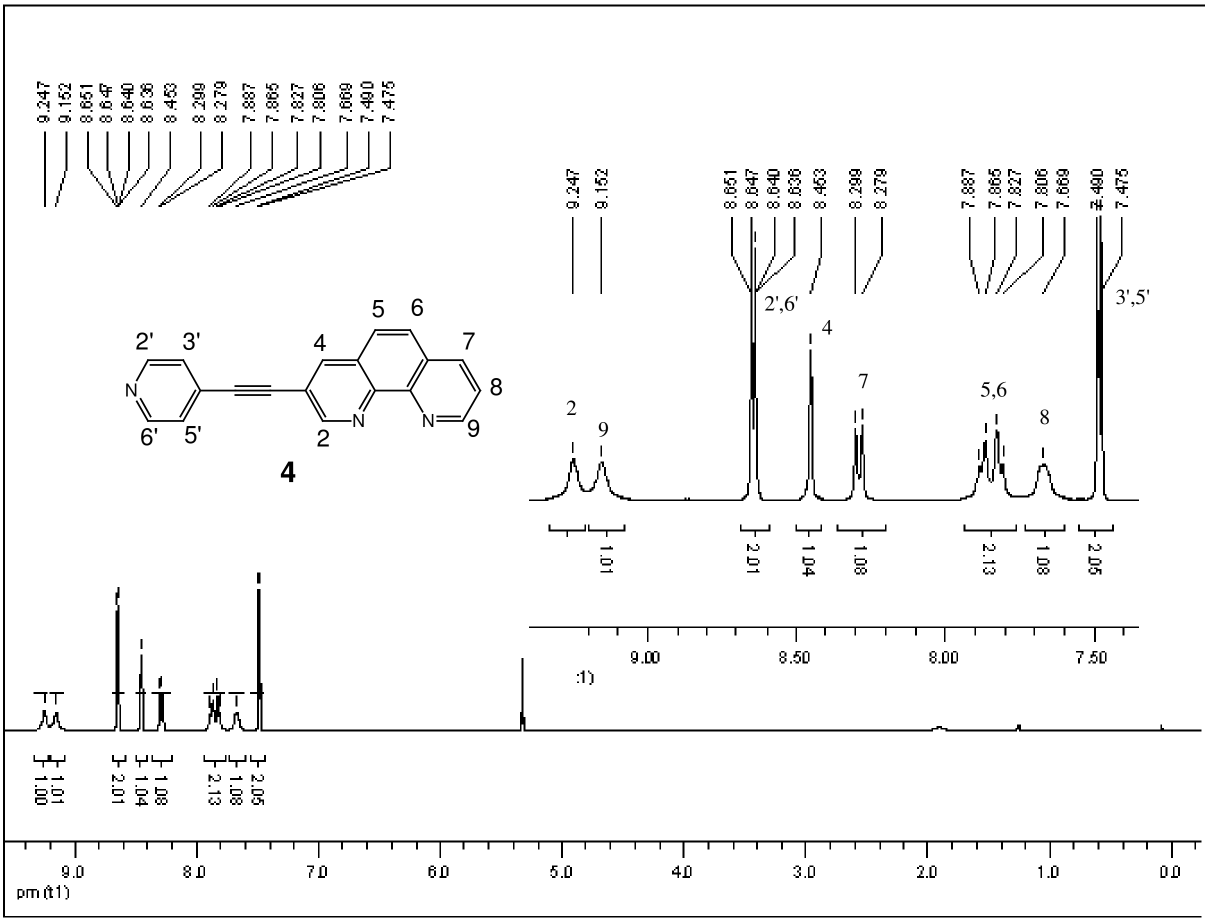
ESI-MS of **6a** and **5a** in equilibrium.



isotopic splitting (experimental)
isotopic splitting (calculated)
1720.4
1721.5
1722.5
1723.5
1724.4
1725.4
1726.4
1727.3
1728.3
1729.3
m/z
1,720
1,725
1,730
1,735
1724.4
1723.5
6b
Zn
Ag
Br
N
200
400
600
800
1000
1200
1400
1600
1800
2000
m/z

ESI-MS of **6b**

NMR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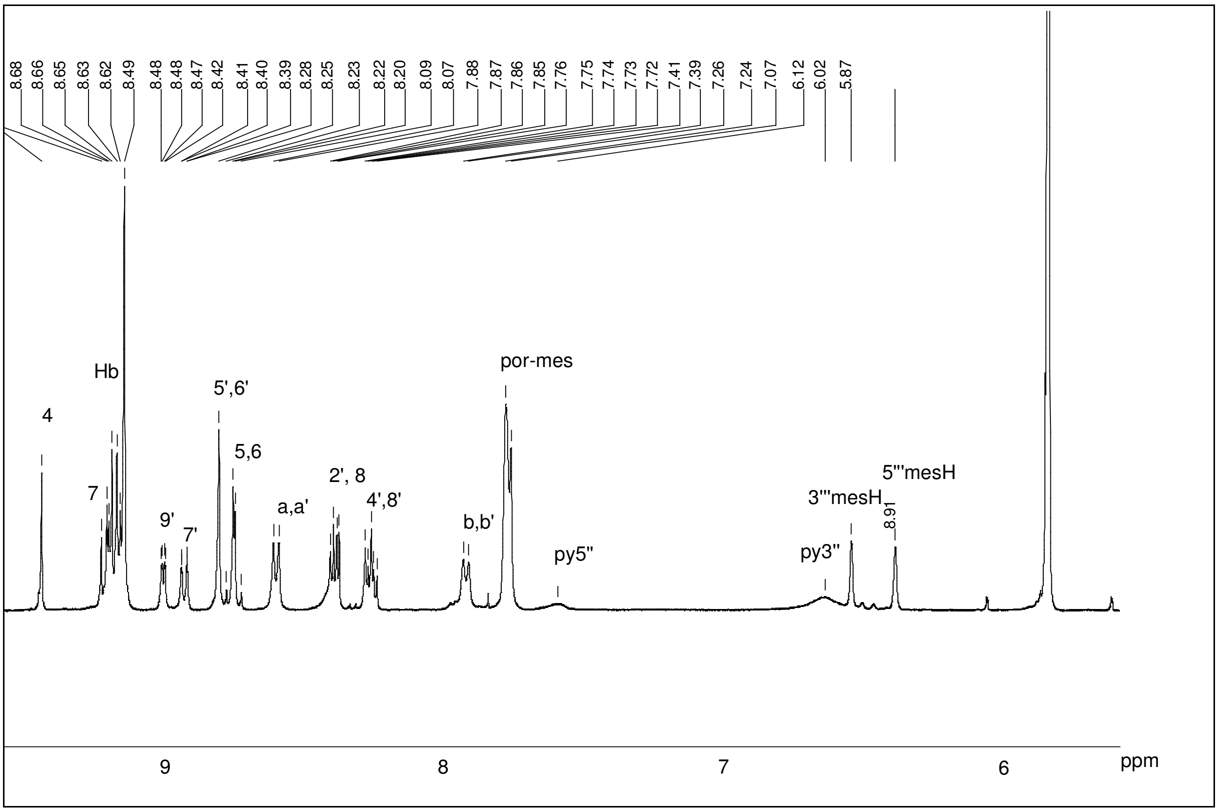
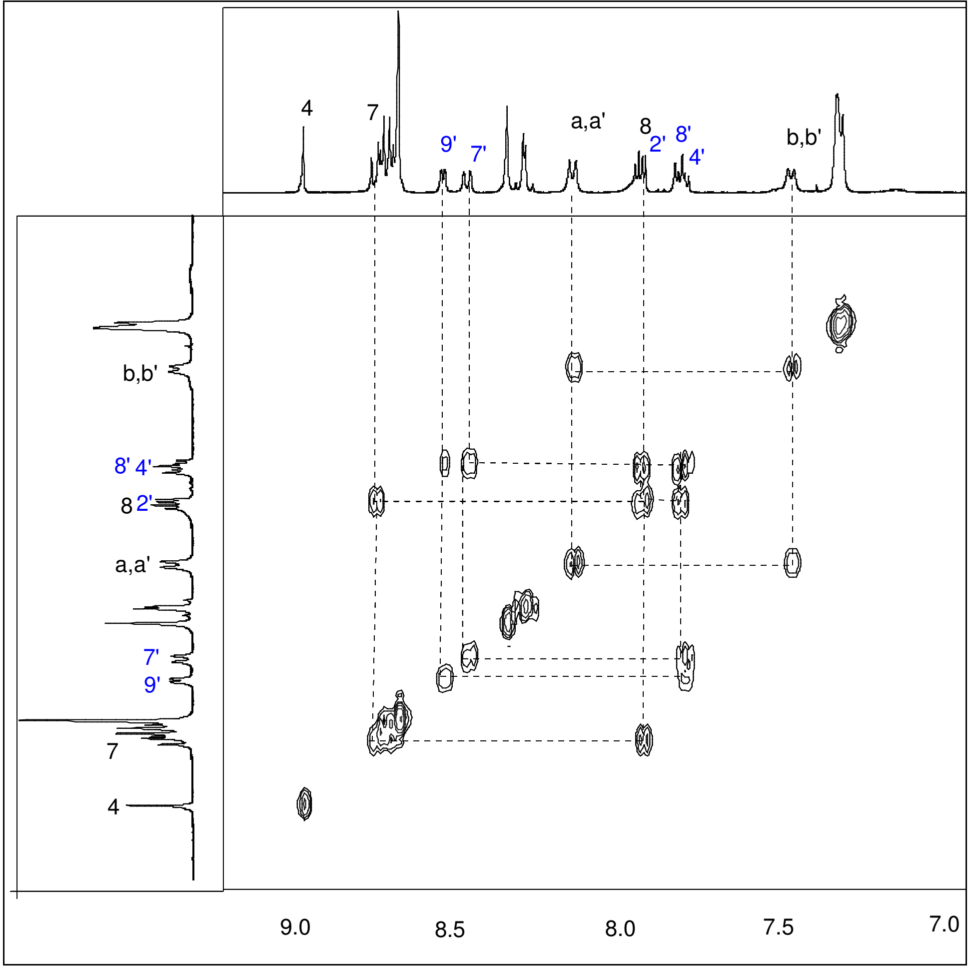
9.152
8.651
8.647
8.640
8.636
8.463
8.299
8.279
7.887
7.865
7.827
7.806
7.669
7.490
7.475
2',6'
4
7
5,6
8
3',5'
2
9
2.01
1.04
1.08
2.13
1.08
2.05
1.00
1.01
9.00
8.50
8.00
7.50
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
pm (t1)
2'
3'
N
6'
5'
4
5
6
7
8
2
N
N
9
4

NMR of **4**

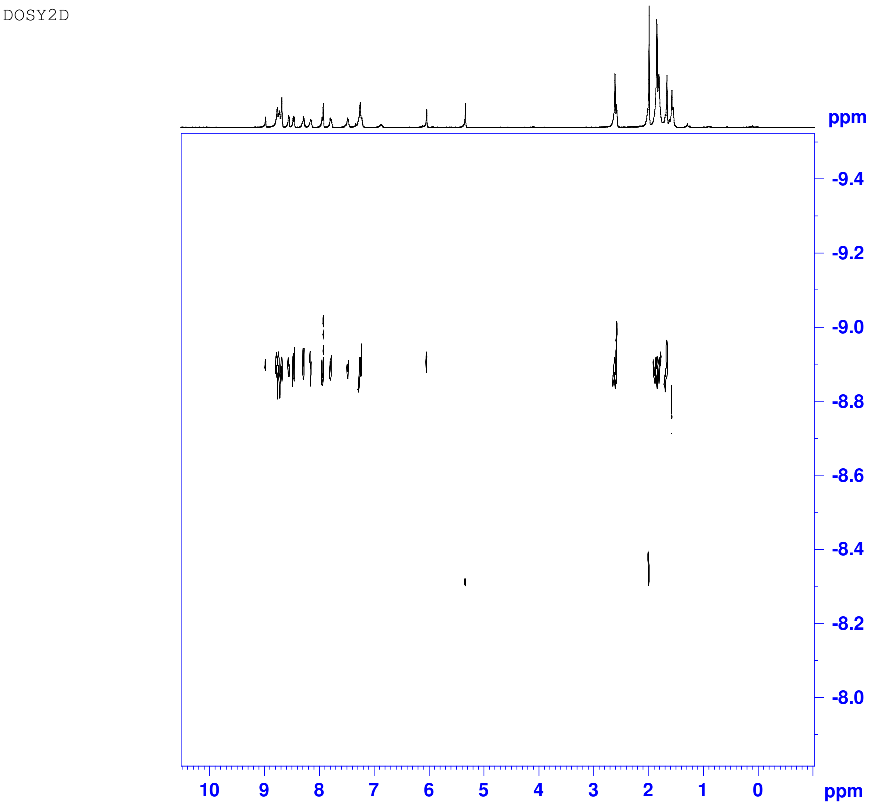


Aromatic region of **6a**



COSY of **6a**

DOSY NMR



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PROCNO                   1

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SOLVENT              CDCl3
NS                       8
DS                       4
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FIDRES            0.537281 Hz
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RG                   3.175
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DE                    6.50 usec
TE                   298.0 K
D1              2.00000000 sec
D16             0.00020000 sec
D20             0.05000000 sec
D21             0.00500000 sec
DELTA1          0.04467700 sec
DELTA2          0.00244600 sec
MCREST          0.00000000 sec
MCWRK           2.00000000 sec

======== CHANNEL f1 ========
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P1                    5.75 usec
p2                   11.50 usec
PL1                   0.00 dB
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====== GRADIENT CHANNEL =====
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GPNAM7            sine.100
GPNAM8            sine.100
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GPX7                  0.00 %
GPX8                  0.00 %
GPY6                  0.00 %
GPY7                  0.00 %
GPY8                  0.00 %
GPZ6                100.00 %
GPZ7                -17.13 %
GPZ8                -13.17 %
P19                2350.00 usec
P30                1175.00 usec

F1 - Acquisition parameters
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TD                     128
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FIDRES            7.812500 Hz
SW                   2.499 ppm
FnMODE                  QF

F2 - Processing parameters
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WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
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MC2                     QF
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WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
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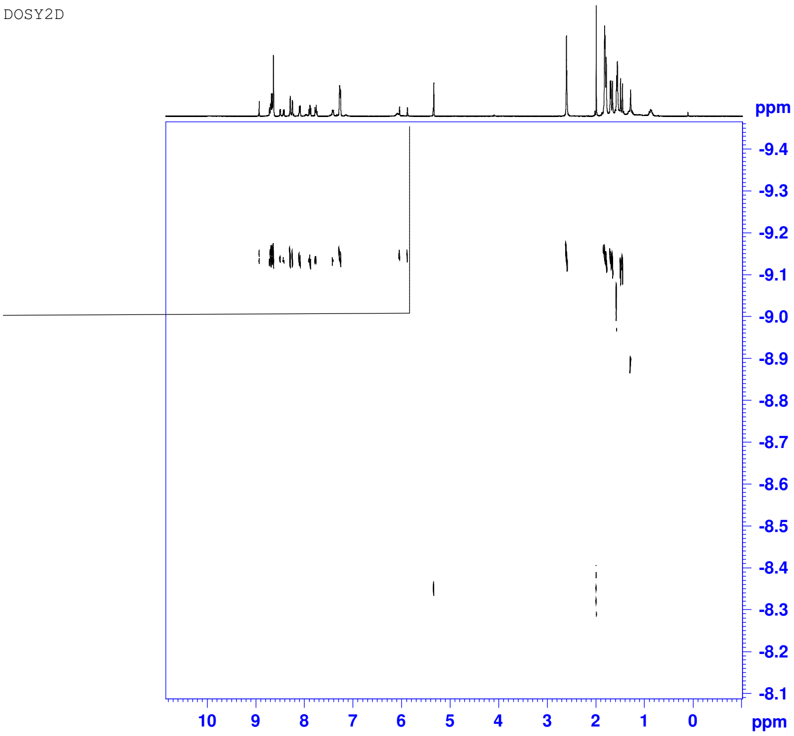
DOSY plot of **3**



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PROCNO                   1

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NS                      16
DS                       4
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FIDRES            0.537281 Hz
AQ               0.9306612 sec
RG                   3.175
DW                  56.800 usec
DE                    6.50 usec
TE                   298.0 K
D1              2.00000000 sec
D16             0.00020000 sec
D20             0.05000000 sec
D21             0.00500000 sec
DELTA1          0.04397700 sec
DELTA2          0.00209600 sec
MCREST          0.00000000 sec
MCWRK           2.00000000 sec

======== CHANNEL f1 ========
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PL1                   0.00 dB
SFO1           400.1340013 MHz

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GPNAM8            sine.100
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GPX7                  0.00 %
GPX8                  0.00 %
GPY6                  0.00 %
GPY7                  0.00 %
GPY8                  0.00 %
GPZ6                100.00 %
GPZ7                -17.13 %
GPZ8                -13.17 %
P19                2700.00 usec
P30                1350.00 usec

F1 - Acquisition parameters
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TD                     128
SFO1               400.134 MHz
FIDRES            7.812500 Hz
SW                   2.499 ppm
FnMODE                  QF

F2 - Processing parameters
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SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
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GB                       0
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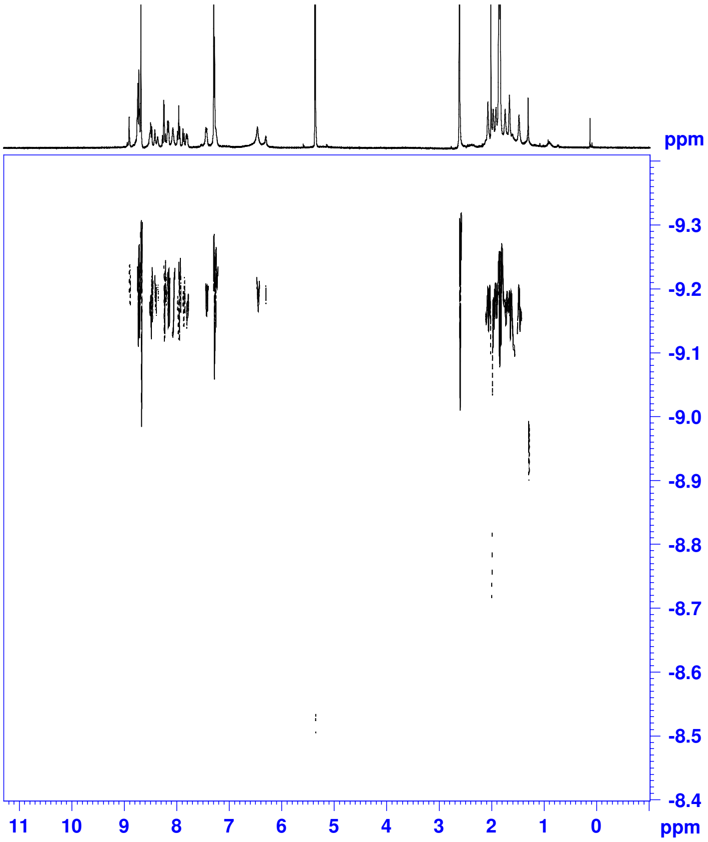
DOSY plot of **6a**

DOSY2D



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PROCNO                 1

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D16           0.00020000 sec
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MCWRK         2.00000000 sec

======== CHANNEL f1 ========
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p2                 18.70 usec
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GPNAM7          sine.100
GPNAM8          sine.100
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GPX7                0.00 %
GPX8                0.00 %
GPY6                0.00 %
GPY7                0.00 %
GPY8                0.00 %
GPZ6              100.00 %
GPZ7              -17.13 %
GPZ8              -13.17 %
P19              2800.00 usec
P30              1400.00 usec

F1 - Acquisition parameters
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FIDRES          2.500000 Hz
SW                 2.499 ppm
FnMODE                QF

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WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00

F1 - Processing parameters
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MC2                   QF
SF           400.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
```

DOSY plot of **6b**