Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Four- and two-armed hetero porphyrin dimers: their specific recognition and self-sorting behaviours

Masahiro Ueda, Masaki Kimura, Shinobu Miyagawa, Masaya Naito, Hikaru Takaya, and Yuji Tokunaga

Table of contents

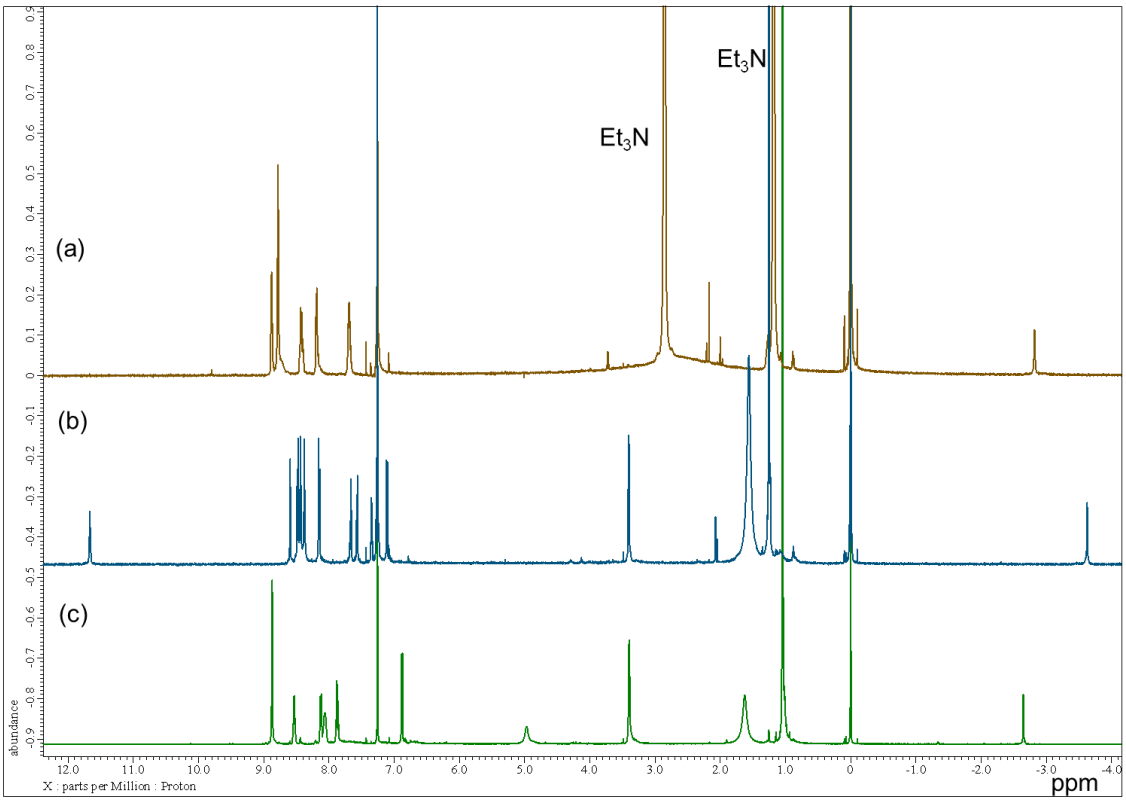


Figure S1. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 25 °C) of (a) the porphyrin derivative **P3** and Et_3N (5.0 eq), (b) an equimolar mixture (0.50 mM) of **P3** and **P4b** (**Cap4**), (c) the porphyrin derivative **P4b**. Fig. 3: Partial spectra of Figure S1.

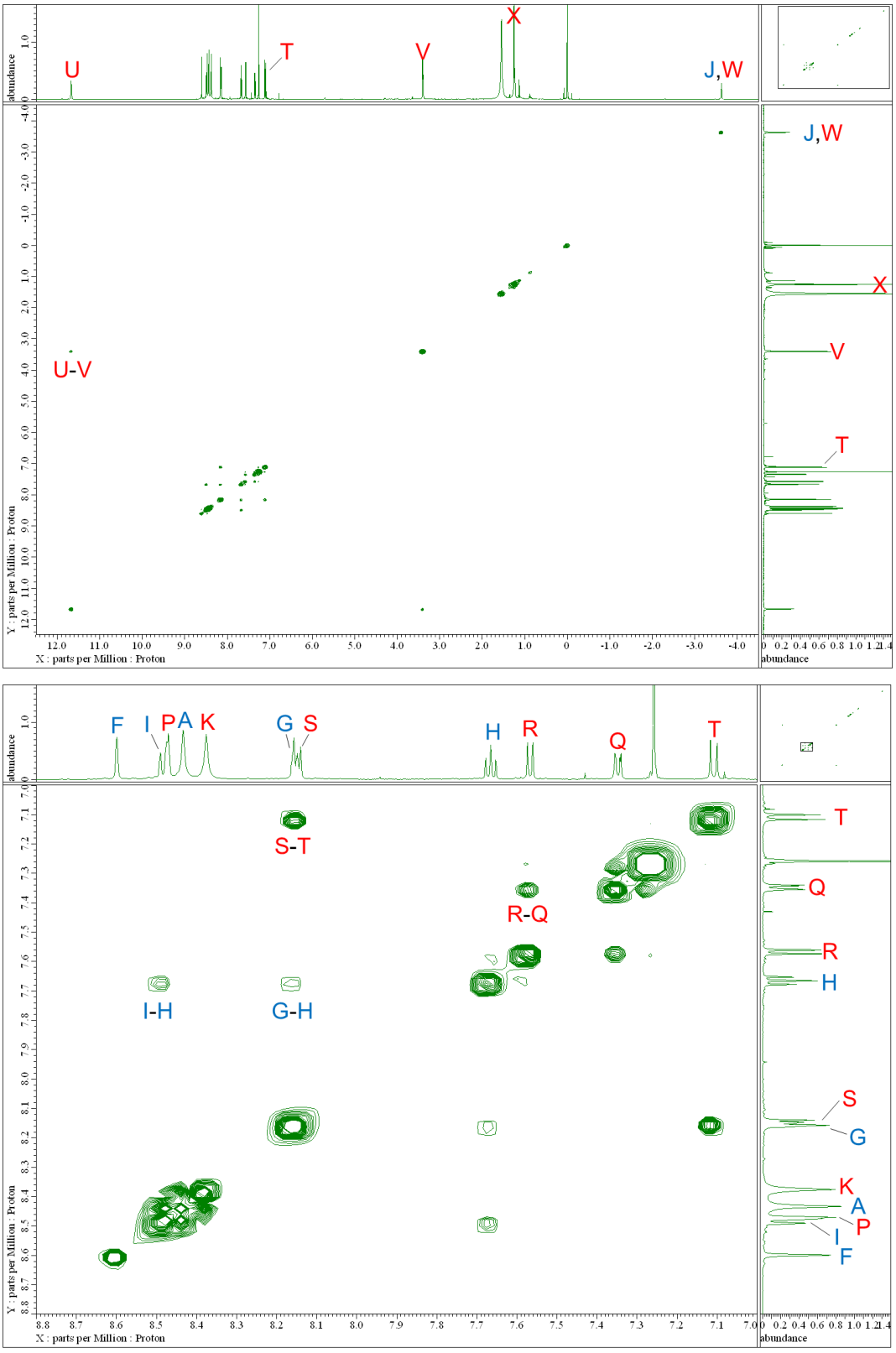


Figure S2. COSY spectrum (600 MHz, $CDCl_3$) of a mixture of **P3** and **P4b** (**Cap4**).

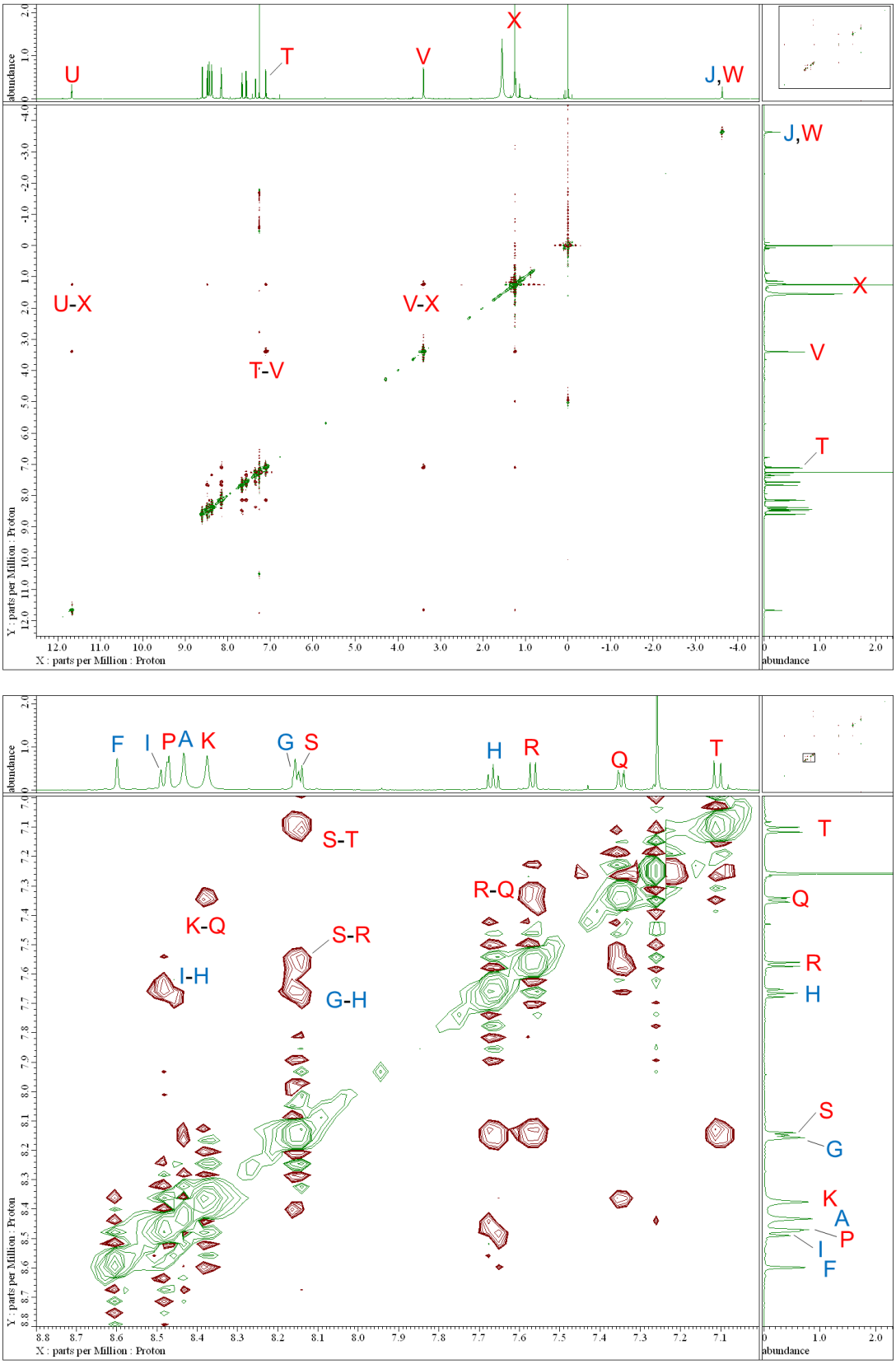


Figure S3. ROESY spectrum (600 MHz, $CDCl_3$) of a mixture of **P3** and **P4b** (**Cap4**).

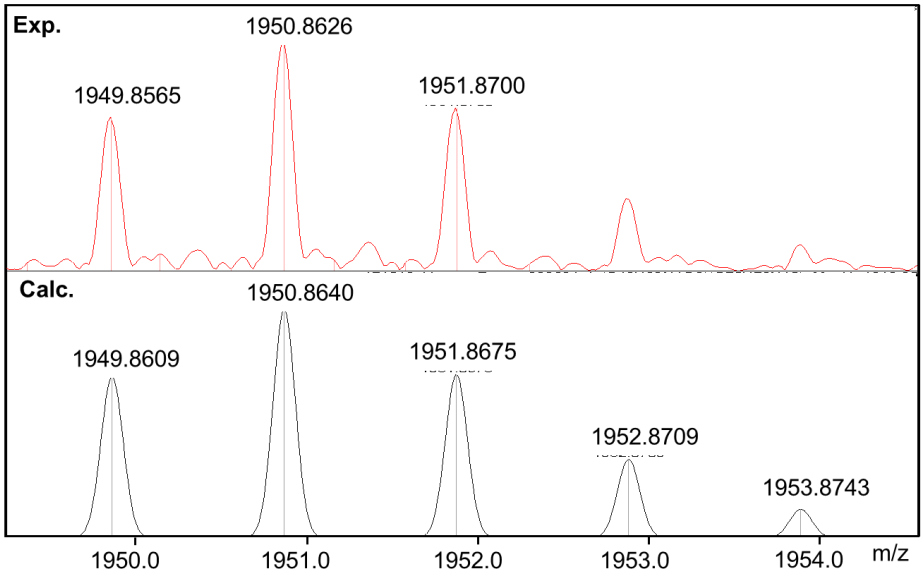


Figure S4. Mass spectrum (ESI) of the four-armed dimer **Cap4**: experimental (top) and calculated (bottom) isotopic patterns.

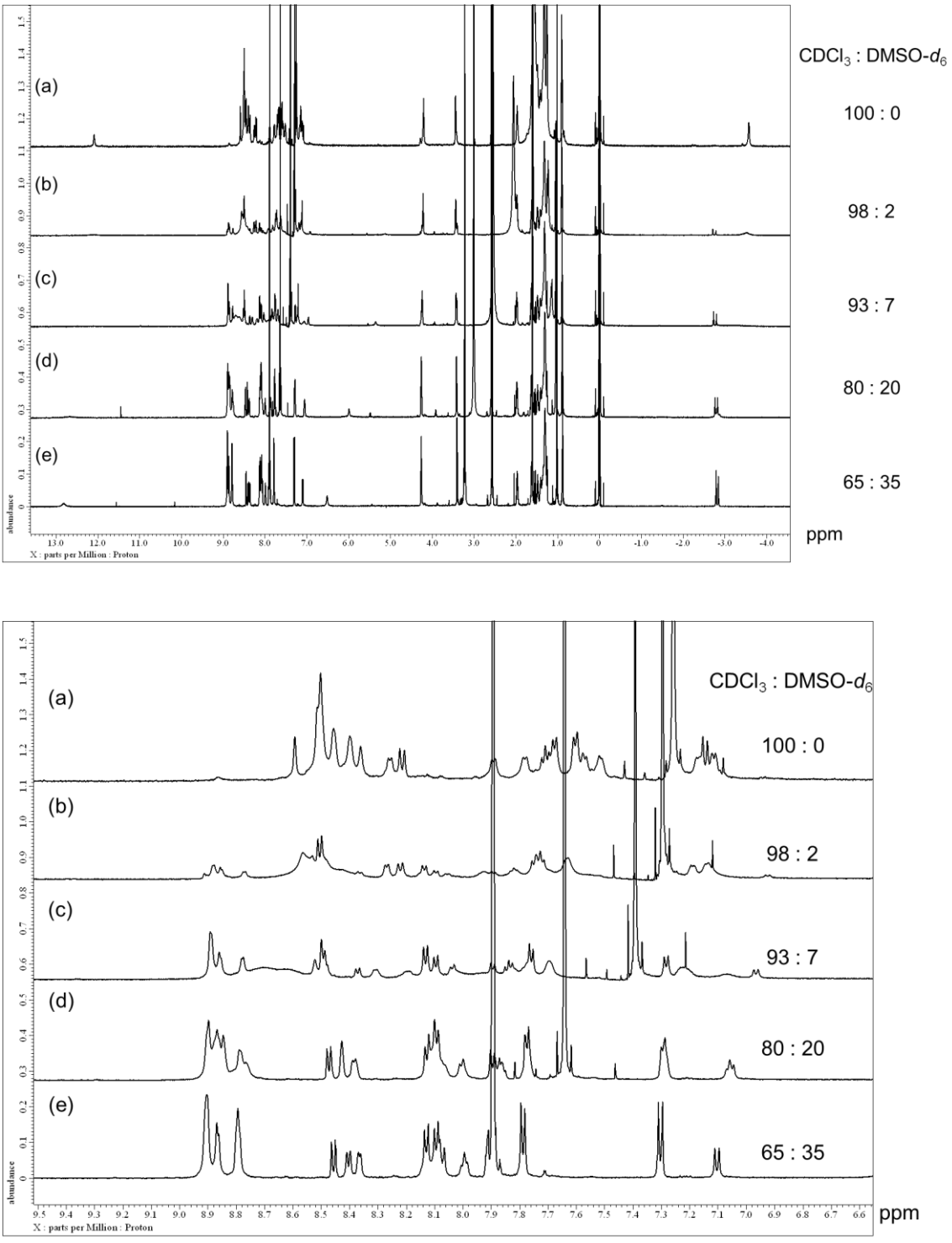


Figure S5. ^{1}H NMR spectra (600 MHz, $CDCl_3$ in the presence of DMSO-d_6, 25 °C) of a 1:1 mixture (0.50 mM) of **P1** and **P2b** (a) in $CDCl_3$, (b) in $CDCl_3$/DMSO-d_6 (98:2), (c) in $CDCl_3$/DMSO-d_6 (93:7), (d) in $CDCl_3$/DMSO-d_6 (80:20), and (e) in $CDCl_3$/DMSO-d_6 (65:35). Fig. 4: Partial spectra of Figure S5.

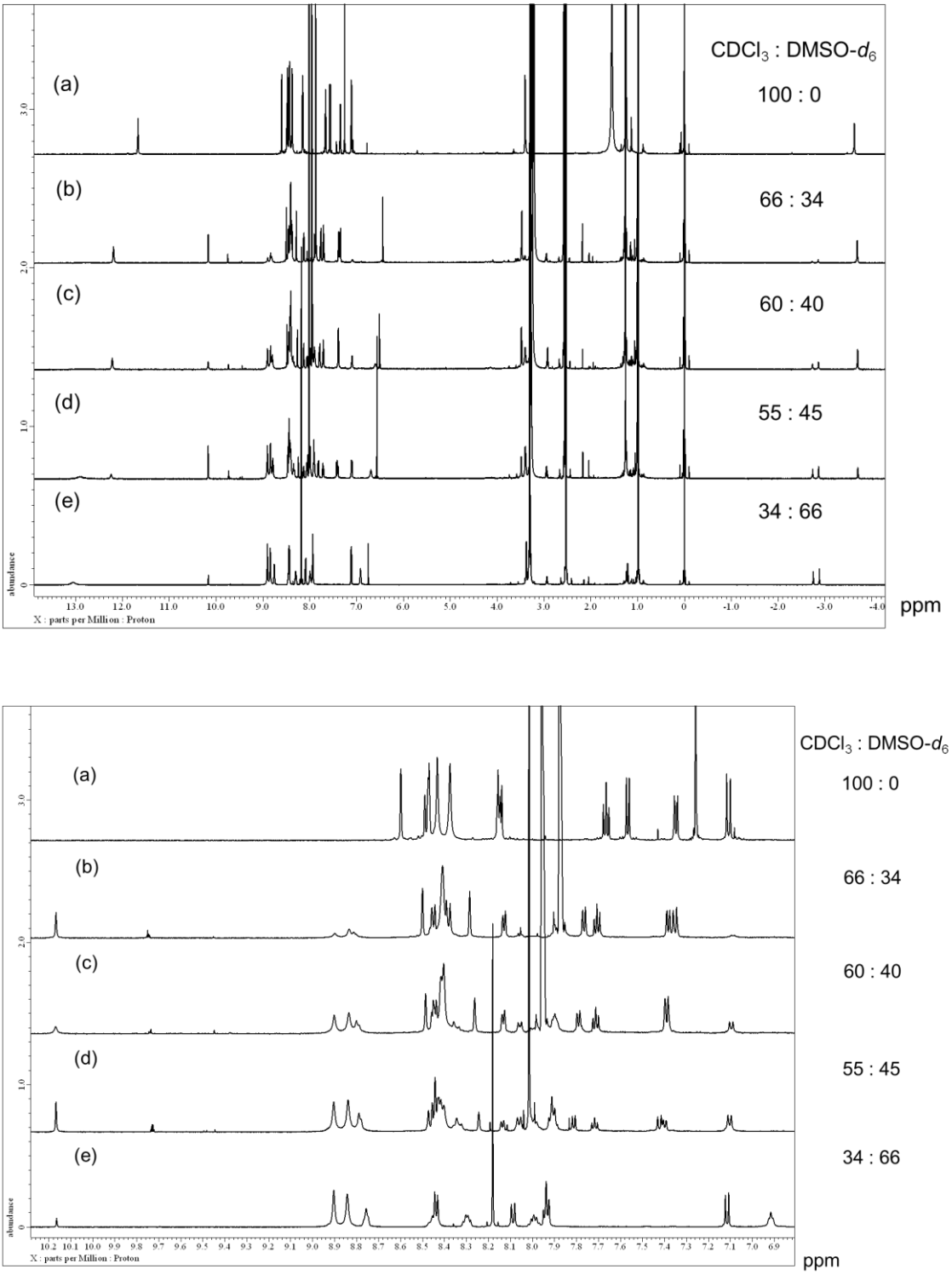


Figure S6. ^{1}H NMR spectra (600 MHz, $CDCl_3$/DMSO-d_6, 25 °C) of a 1:1 mixture (0.50 mM) of **P3** and **P4b** (a) in $CDCl_3$, (b) in $CDCl_3$/DMSO-d_6 (66:34), (c) in $CDCl_3$/DMSO-d_6 (60:40), (d) in $CDCl_3$/DMSO-d_6 (55:45), and (e) in $CDCl_3$/DMSO-d_6 (34:66). Fig. 5: Partial spectra of Figure S6.

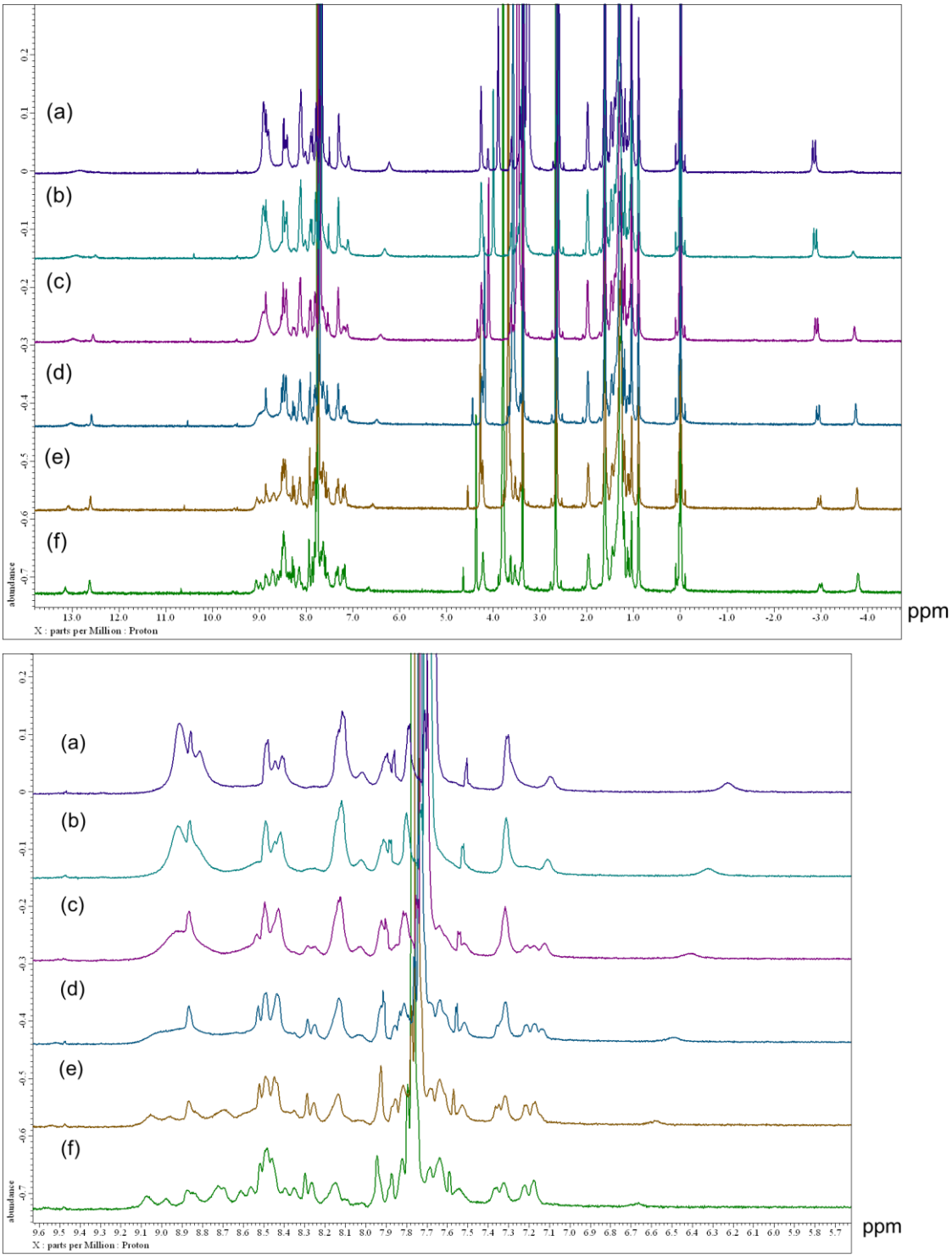


Figure S7. ^{1}H NMR spectra [600 MHz, $CDCl_3$/DMSO-d_6 (80:20), 0.50 mM] of a 1:1 mixture of **P1** and **P2b**. (a) 0 °C; (b) –10 °C, (c) –20 °C, (d) –30 °C, (e) –40 °C and (f) –50 °C. Fig. 6: Partial spectra of Figure S7.

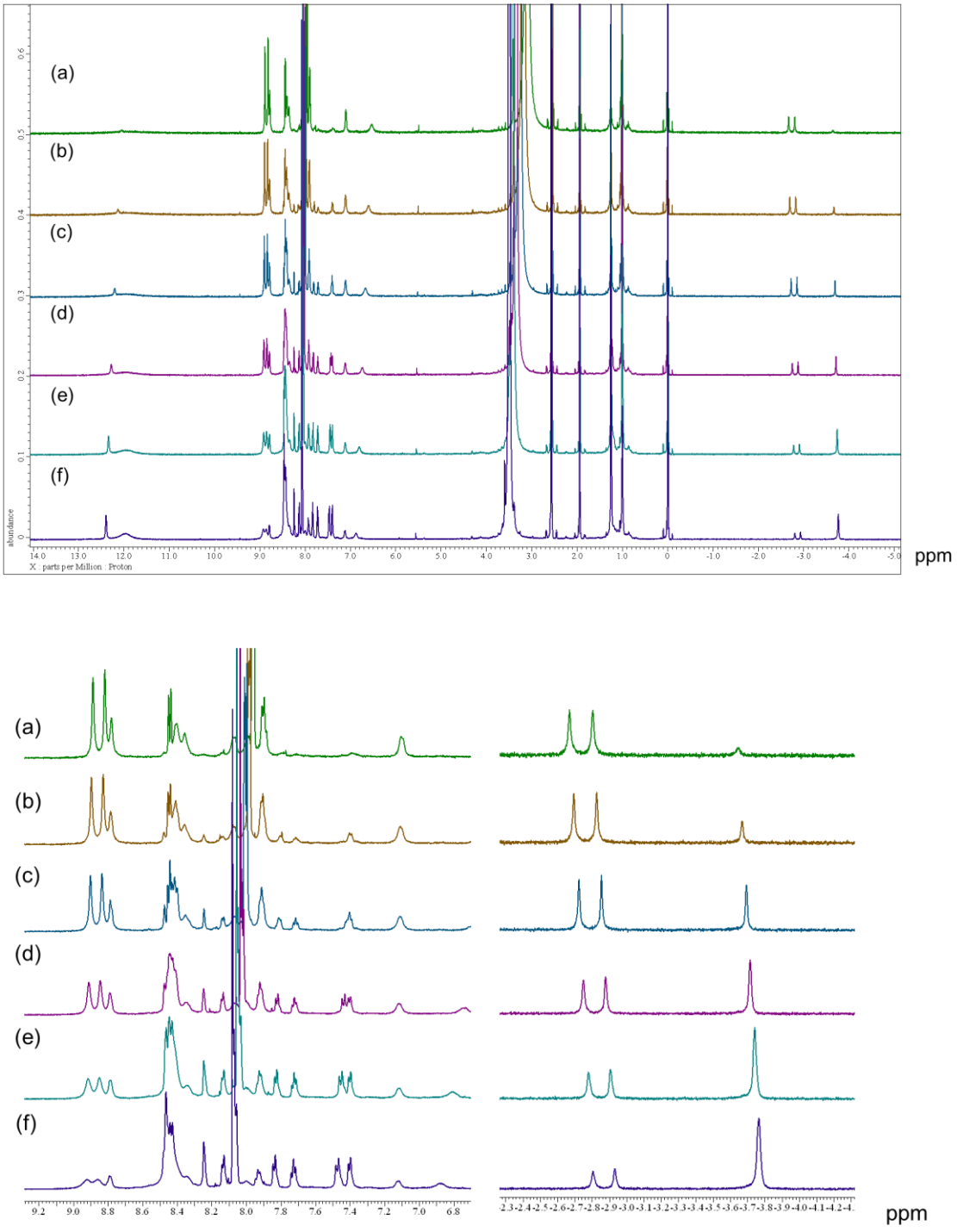


Figure S8. ^{1}H NMR spectra [600 MHz, $CDCl_3$/DMSO-d_6 (55:45), 0.50 mM] of an equimolar mixture of **P3** and **P4b**. (a) 50 °C; (b) 40 °C, (c) 30 °C, (d) 20 °C, (e) 10 °C and (f) 0 °C.

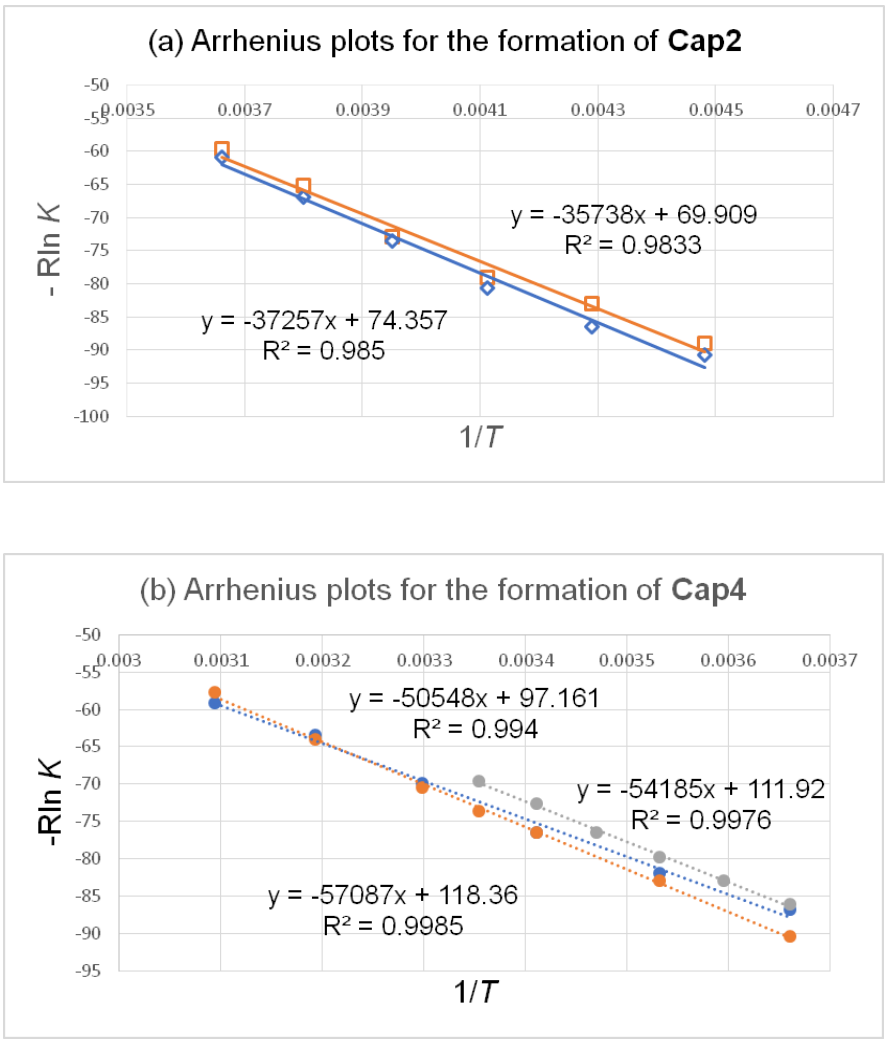
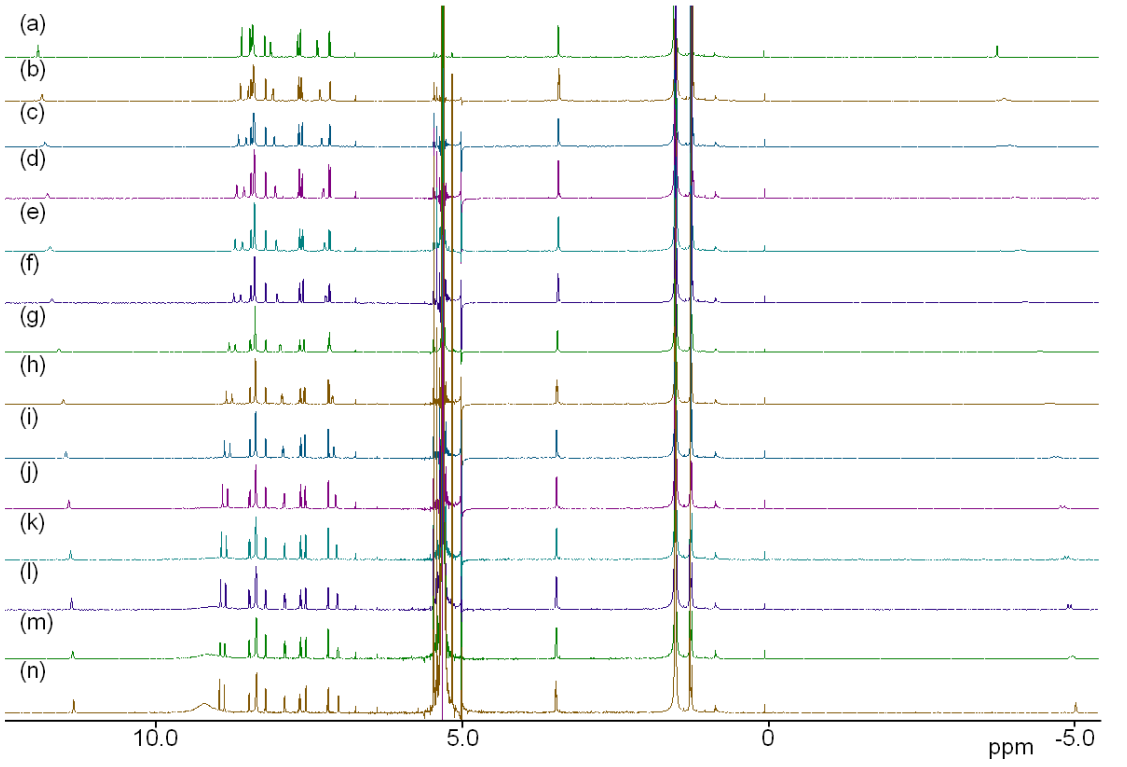
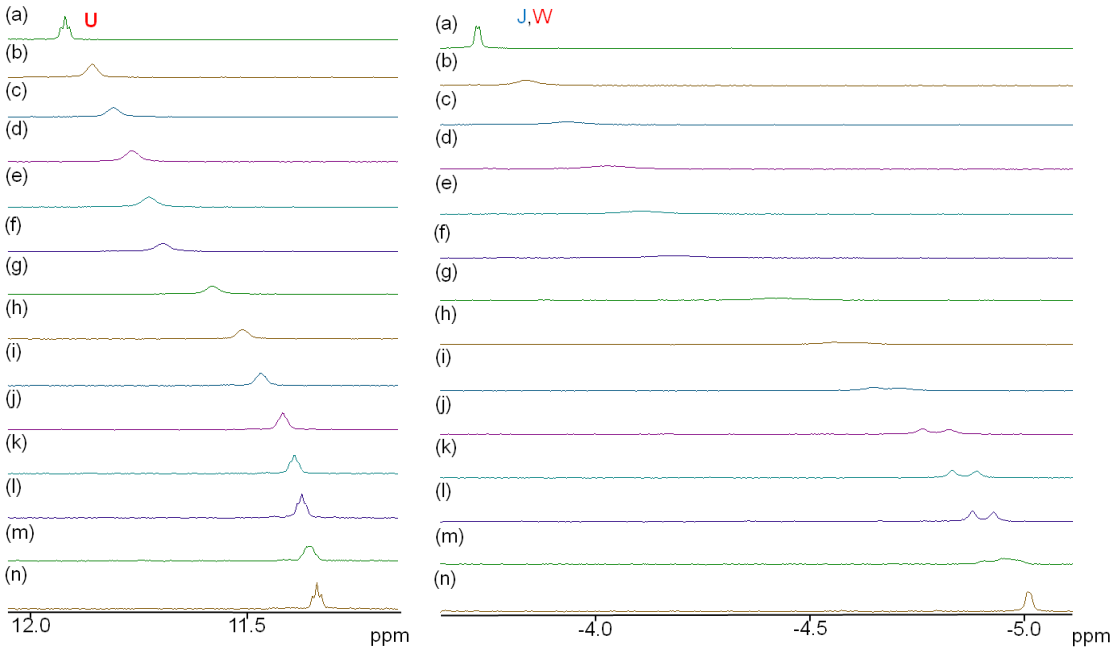


Figure S9. Arrhenius plots for the formation of (a) **Cap2** and (b) **Cap4**.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
10.0
5.0
0
ppm
-5.0


(a)
U
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
12.0
11.5
ppm
(a)
J,W
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
-4.0
-4.5
-5.0
ppm

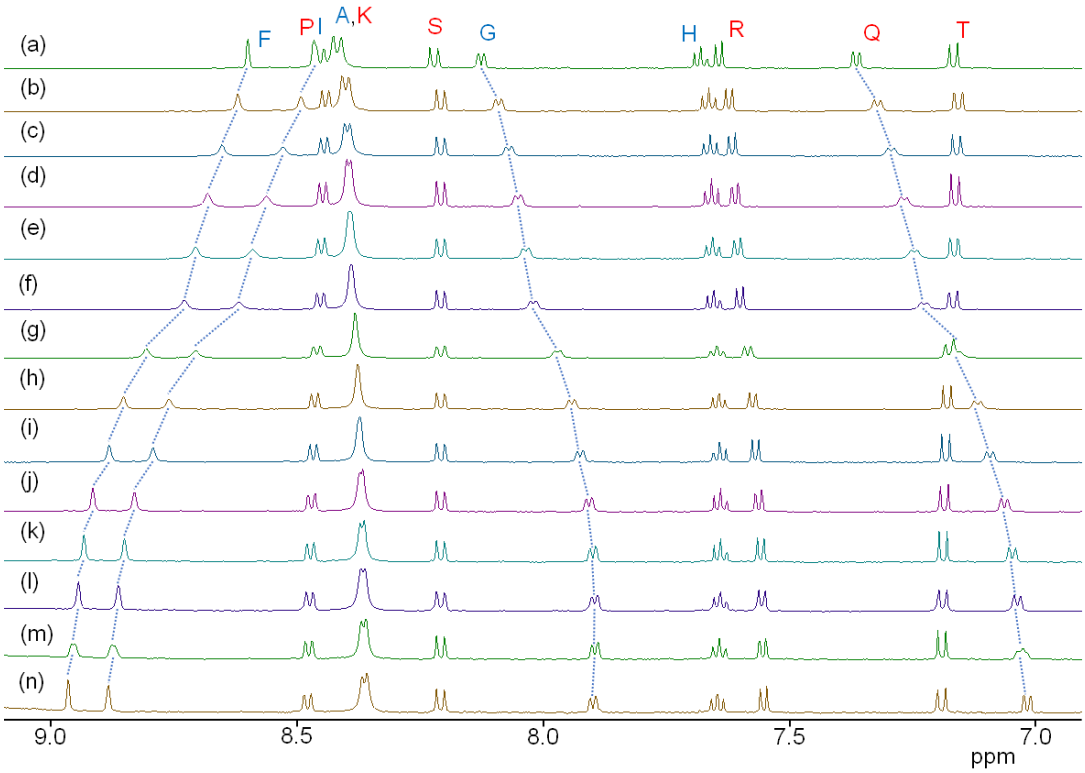


Figure S10a. ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 25 °C) of the dimer **Cap4** (0.50 mM) (a) in the absence of trinitrobenzene **G1** and in the presence of **G1** (b) 0.2 eq, (c) 0.4 eq, (d) 0.6 eq, (e) 0.8 eq, (f) 1.0 eq, (g) 2.0 eq, (h) 3.0 eq, (i) 4.0 eq, (j) 6.0 eq, (k) 8.0 eq, (l) 10 eq, (m) 15 eq, (n) 20 eq.

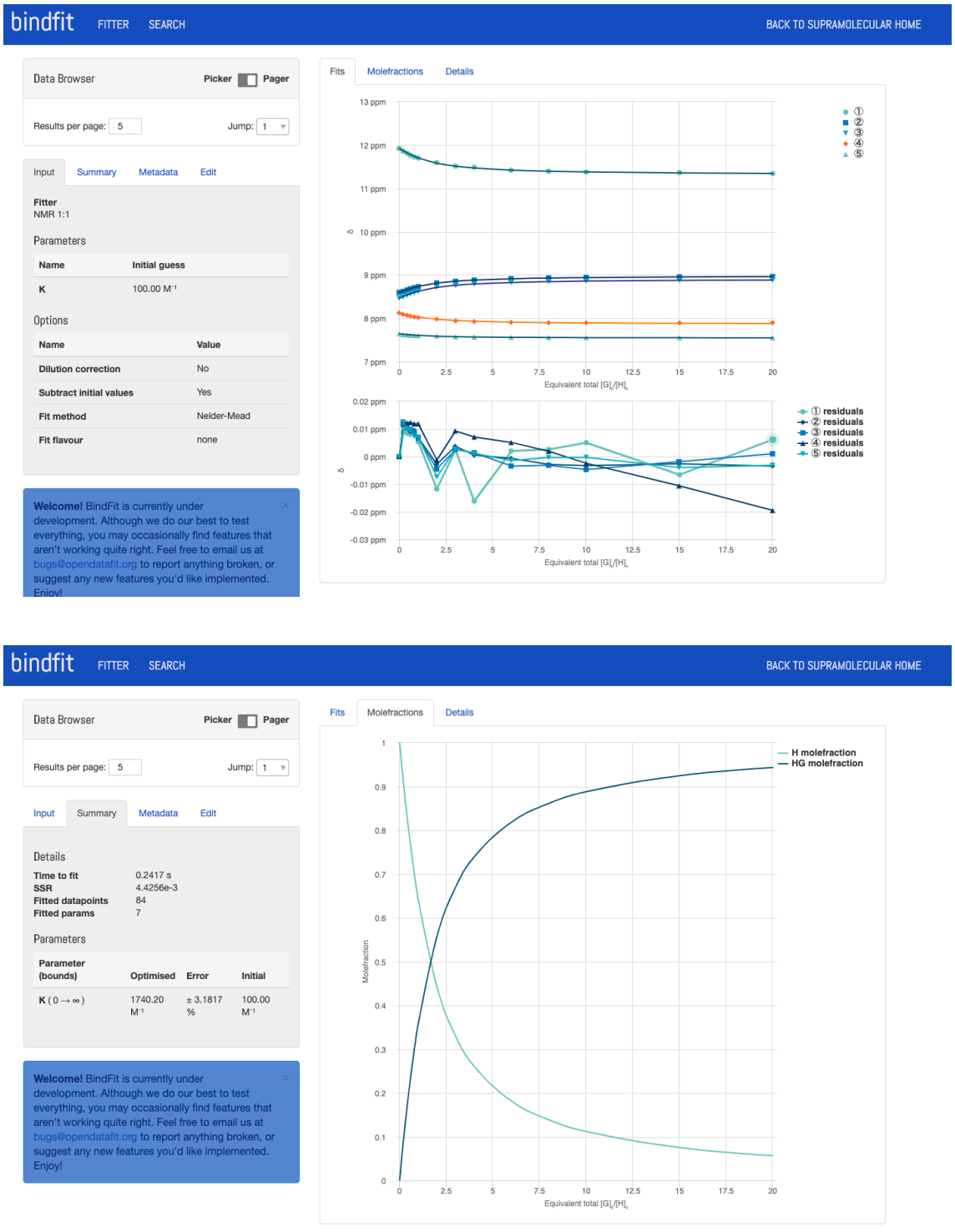


Figure S10b. Simulation of first titrations of **Cap4** and trinitrobenzene **G1** using BindFit.

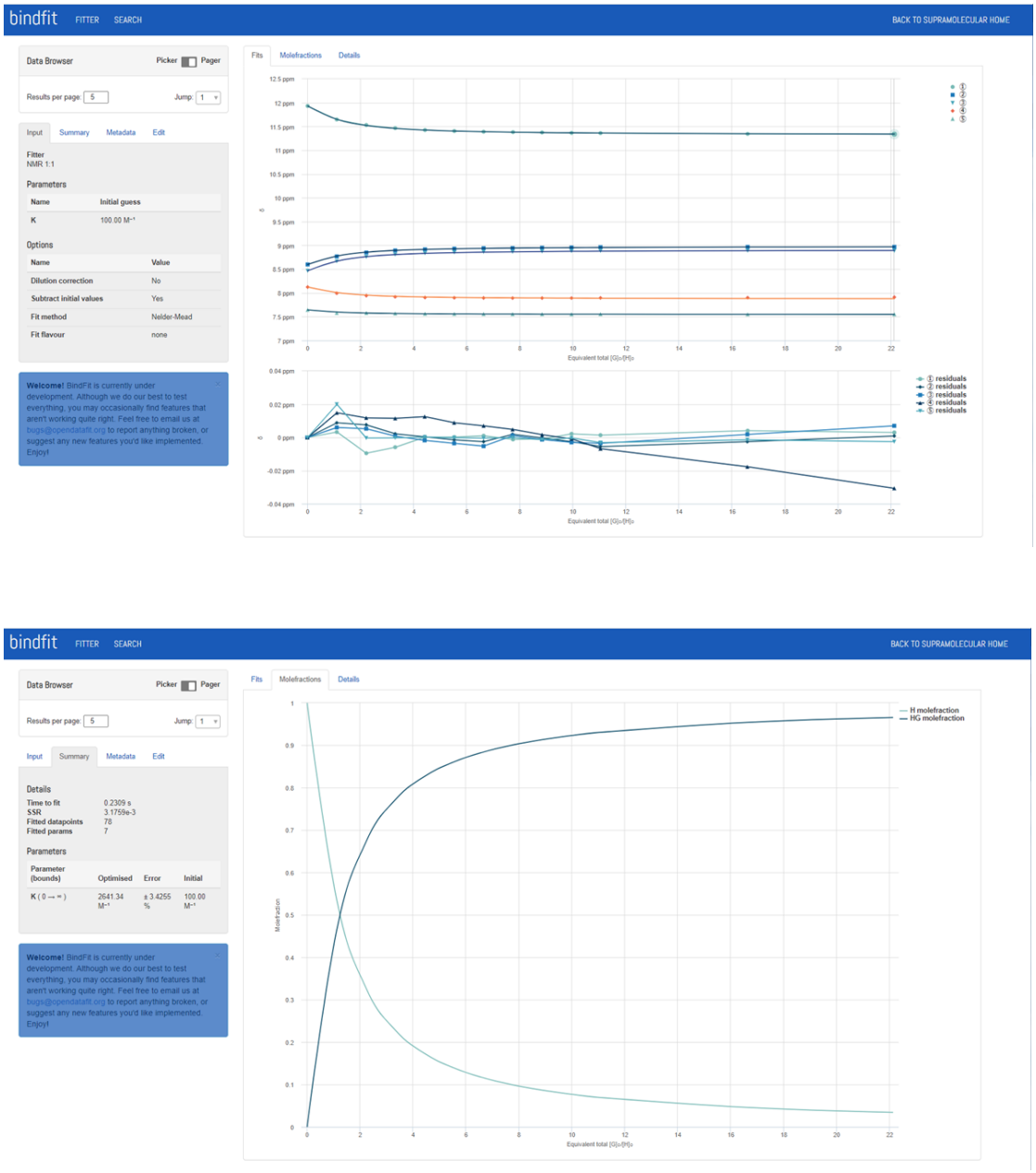


Figure S10c. Simulation of second titrations of **Cap4** and trinitrobenzene **G1** using BindFit.

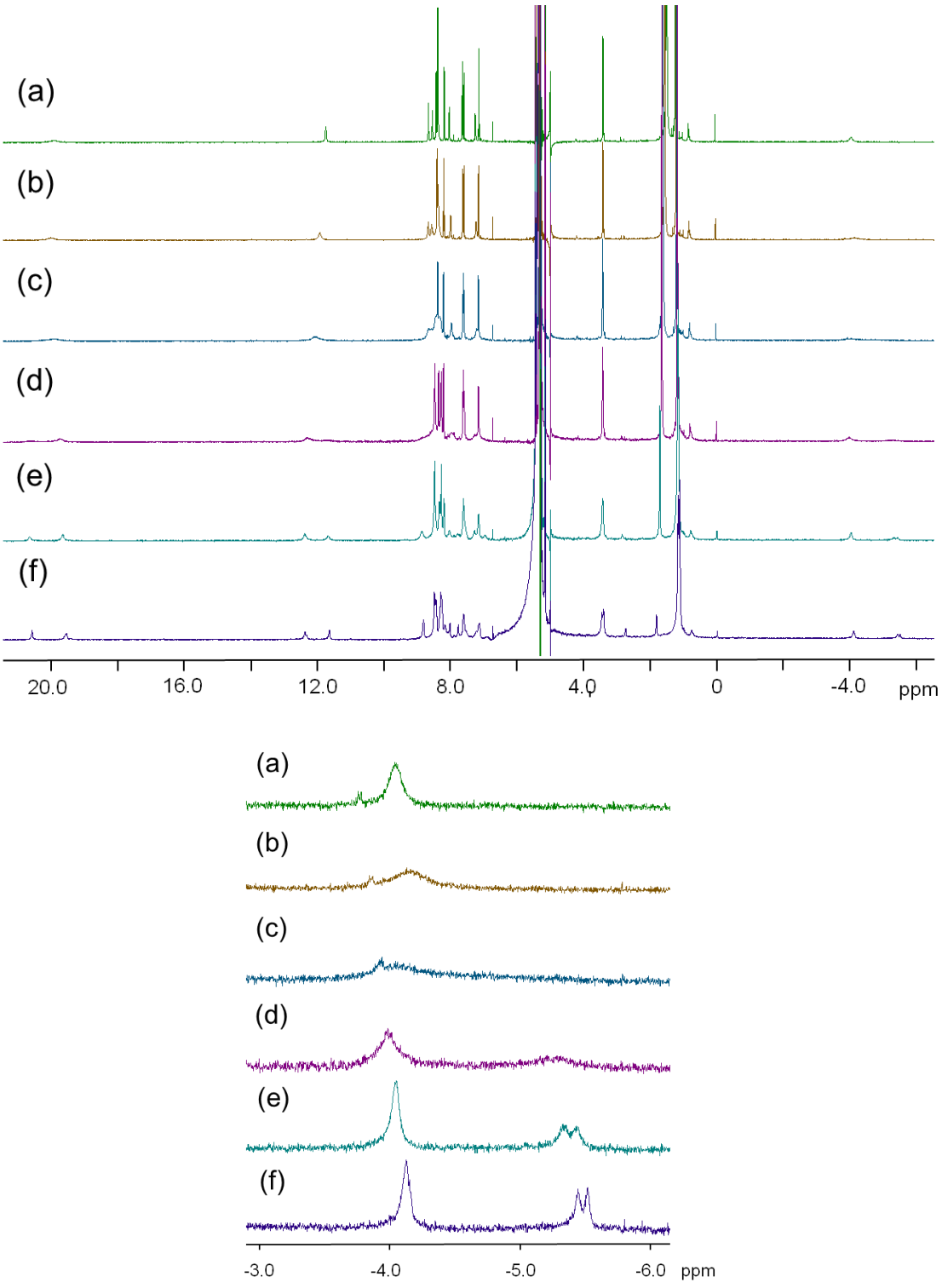
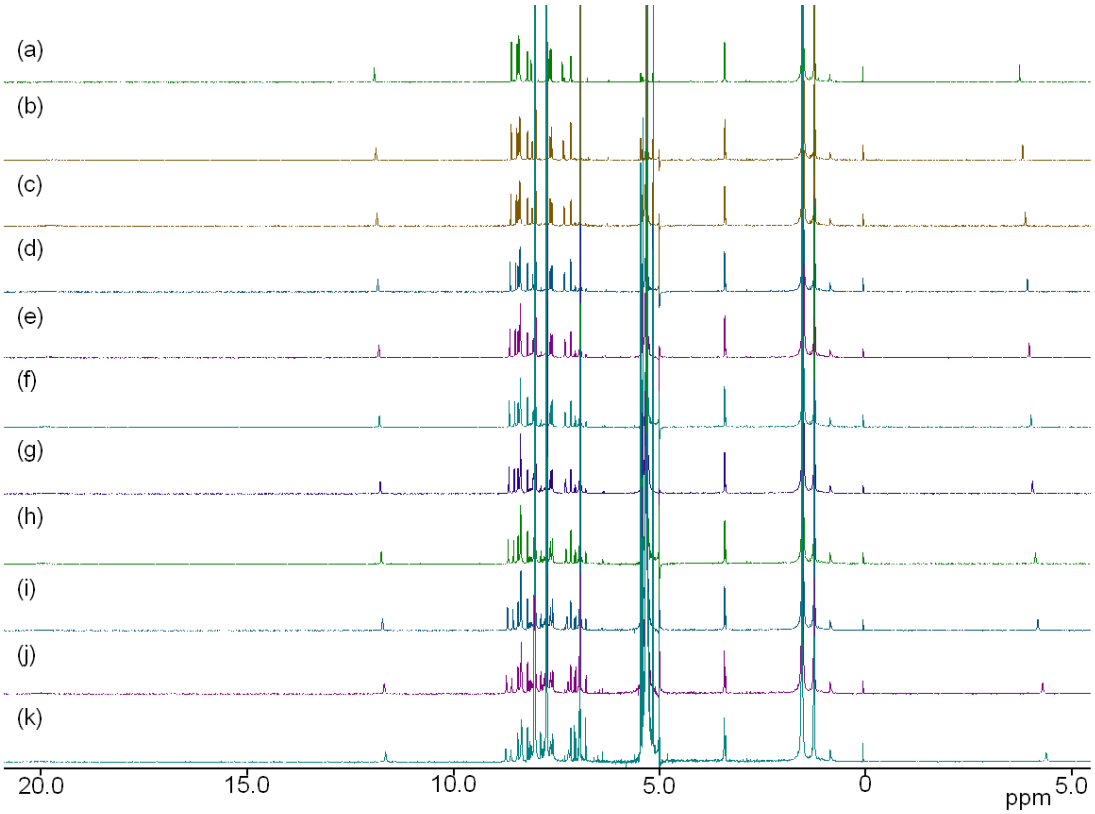
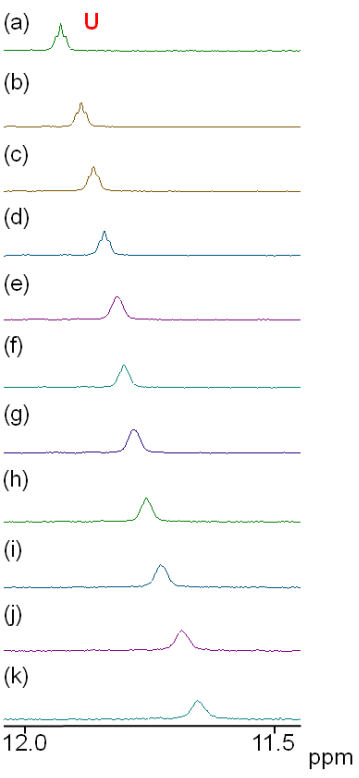
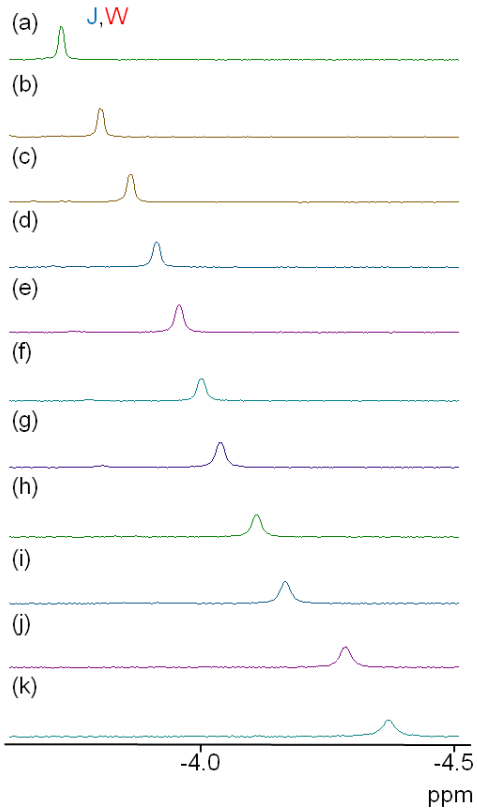


Figure S10d. VT NMR spectra (600 MHz, CD_2Cl_2) of a mixture of the dimer **Cap4** (0.50 mM) and **G1** (0.6 eq) at (a) 25 °C, (b) 0 °C, (c) –20 °C, (d) –40 °C, (e) –60 °C, and (f) –80 °C.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
20.0
15.0
10.0
5.0
0
5.0
ppm


(a)
U
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
12.0
11.5
ppm


(a)
J,W
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
-4.0
-4.5
ppm

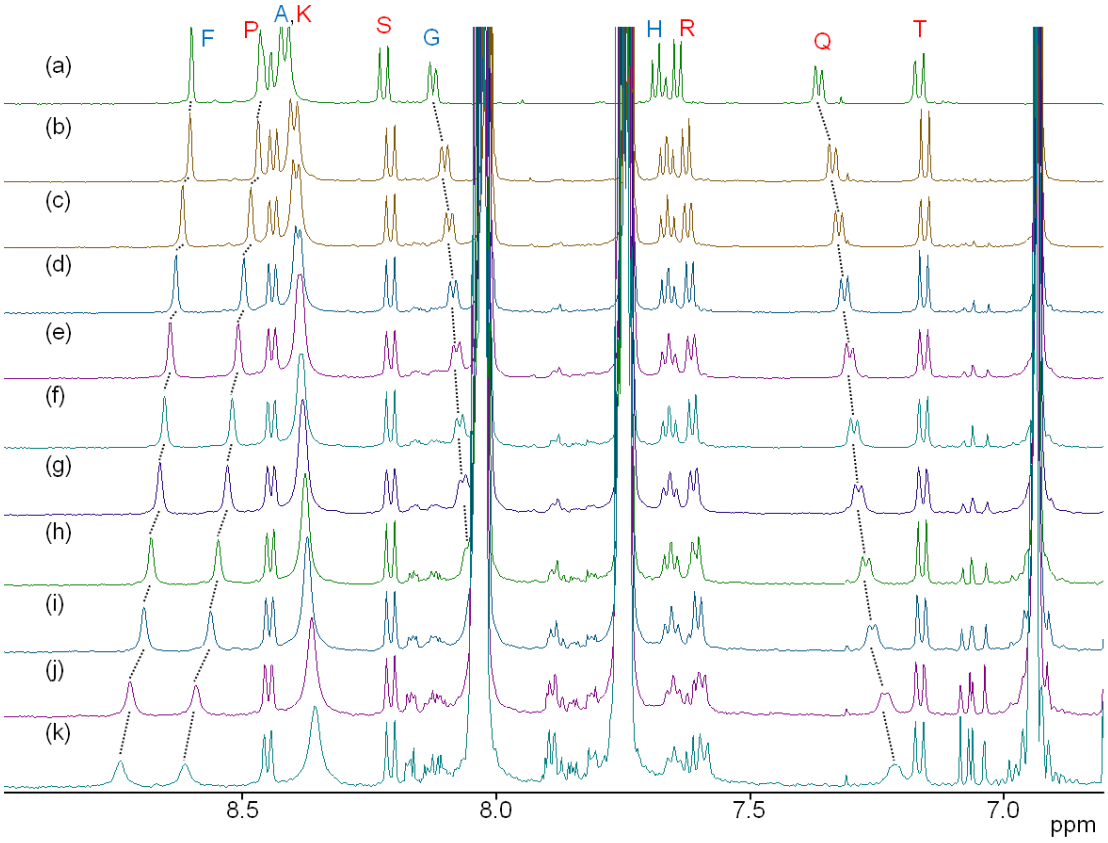


Figure S11a. ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 25 °C) of the dimer **Cap4** (0.50 mM) (a) in the absence of 1,4-naphthoquinone **G2** and in the presence of **G2** (b) 10 eq, (c) 20 eq, (d) 30 eq, (e) 40 eq, (f) 50 eq, (g) 60 eq, (h) 80 eq, (i) 100 eq, (j) 150 eq, (k) 200 eq.

Figure S11b. Simulation of first titrations of **Cap4** and 1,4-naphthoquinone **G2** using BindFit.

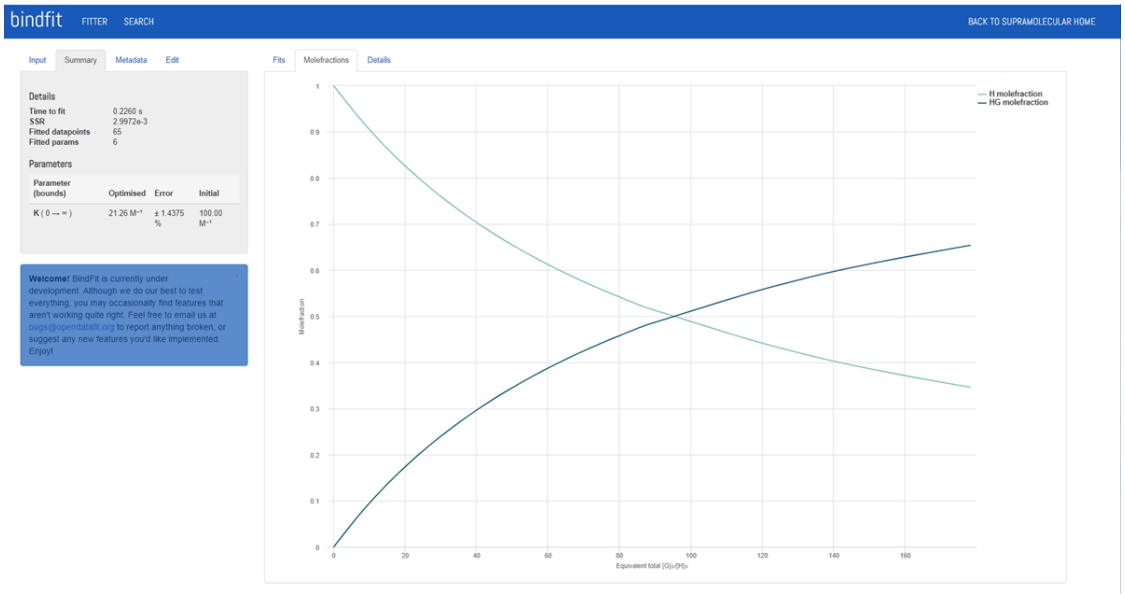
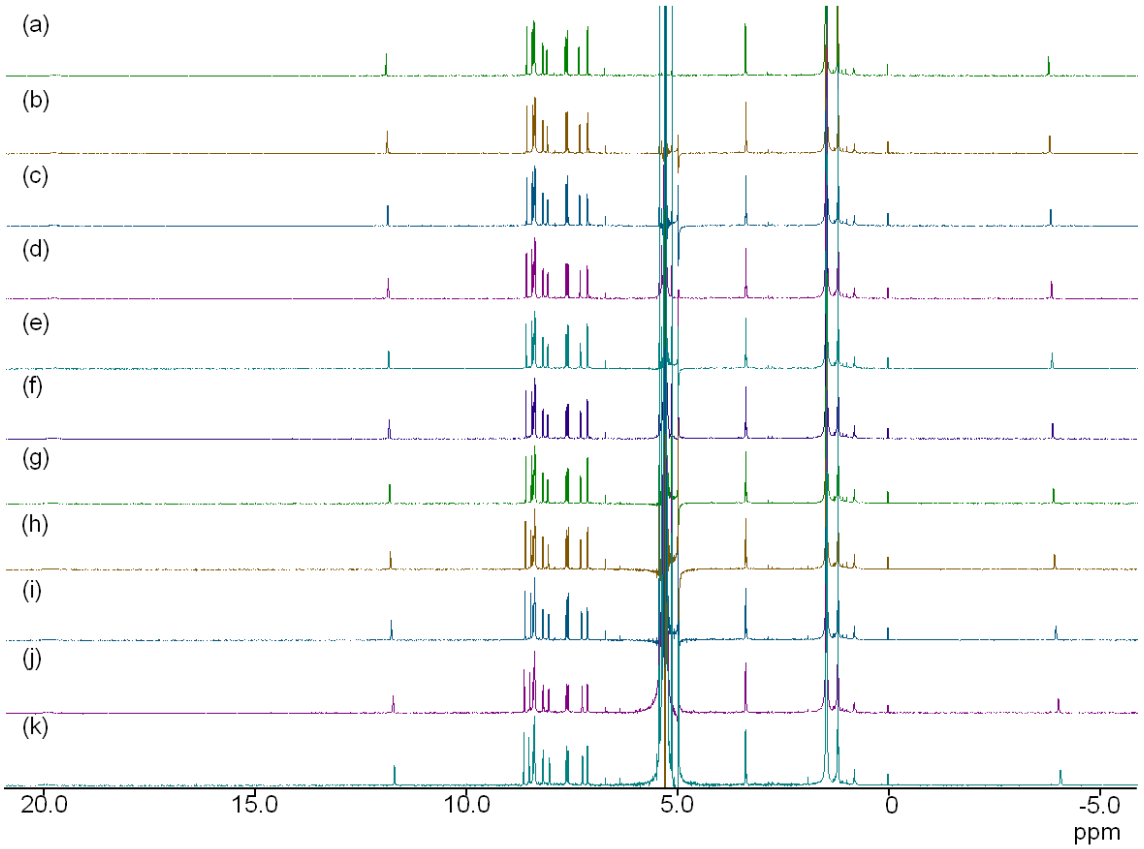
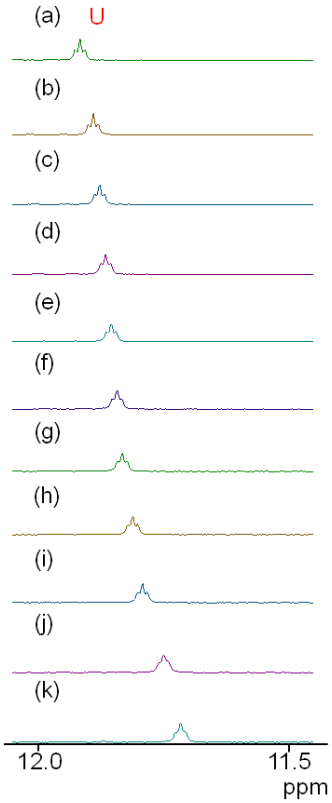
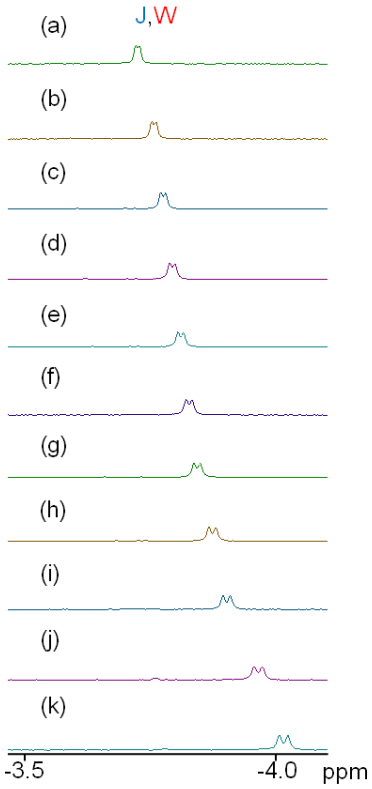


Figure S11c. Simulation of second titrations of **Cap4** and 1,4-naphthoquinone **G2** using BindFit.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
20.0
15.0
10.0
5.0
0
-5.0
ppm


(a) U
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
12.0
11.5
ppm


(a) J,W
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
-3.5
-4.0
ppm

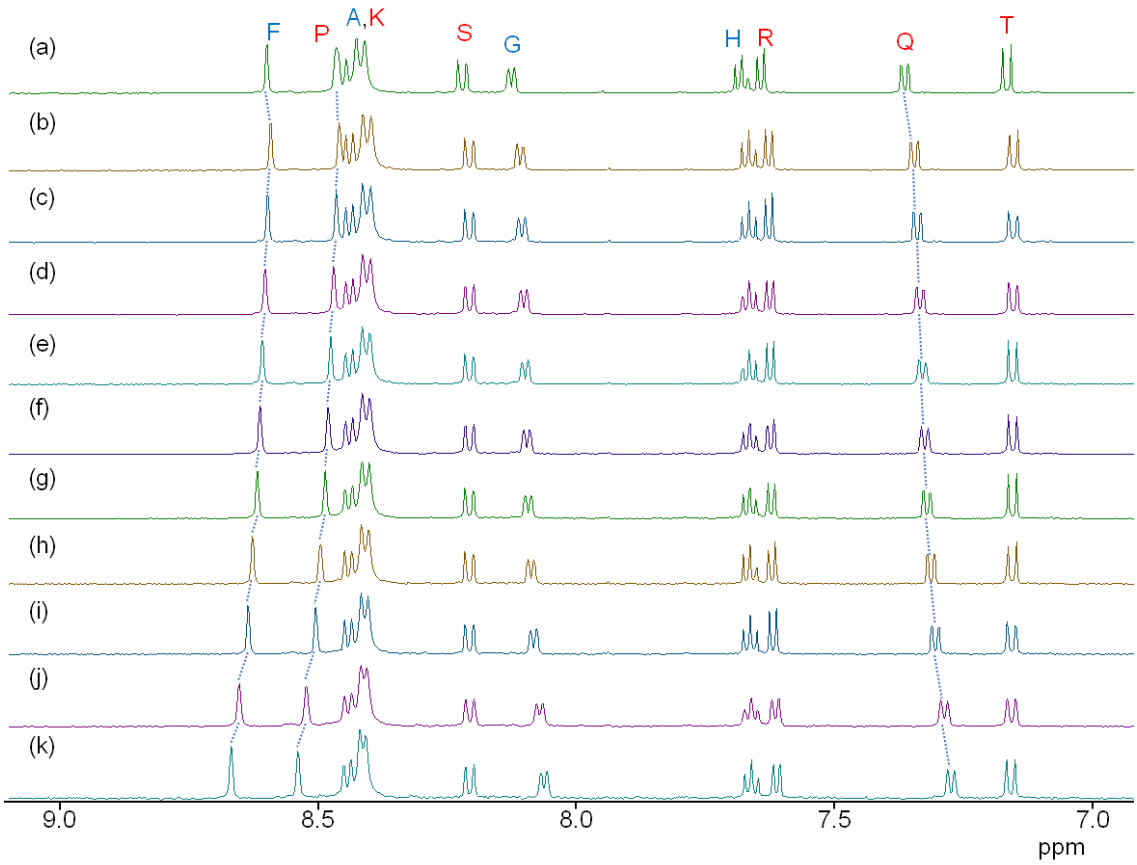
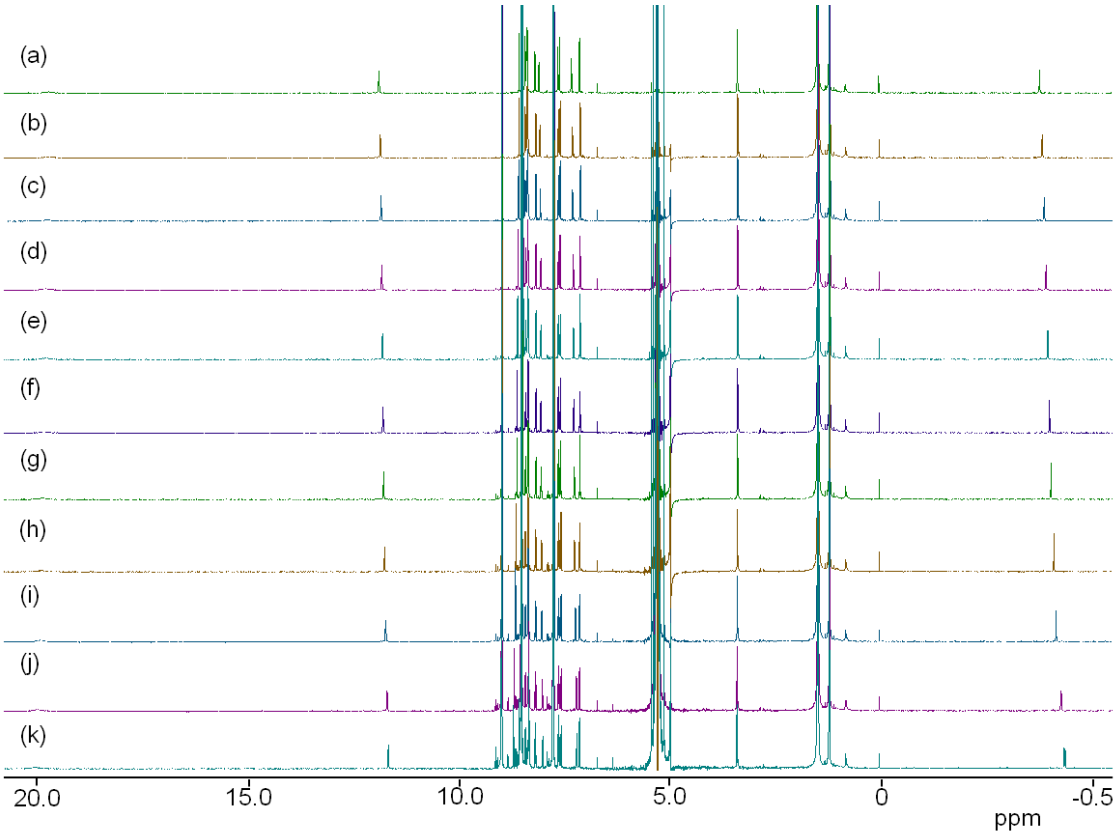
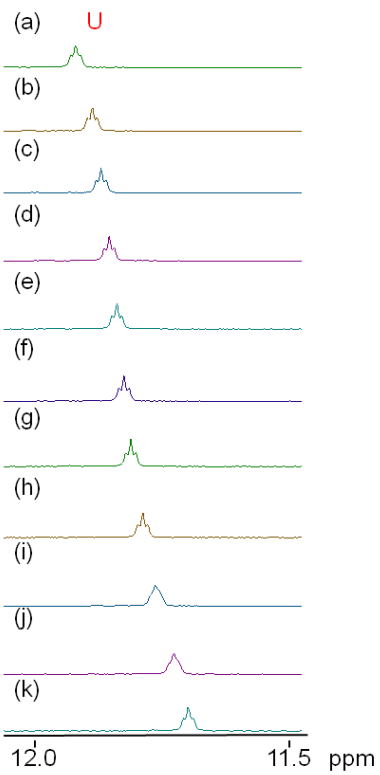


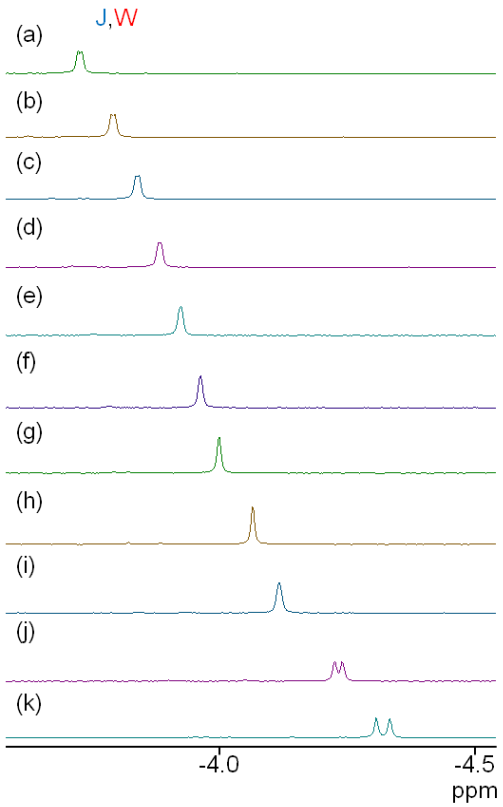
Figure S12a. ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 25 °C) of the dimer **Cap4** (0.50 mM) (a) in the absence of tetrafluoroterephthalonitrile **G3** and in the presence of **G3** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 2.5 eq, (g) 3.0 eq, (h) 4.0 eq, (i) 5.0 eq, (j) 7.5 eq, (k) 10 eq.

Figure S12b. Simulation of first titrations of **Cap4** and tetrafluoroterephthalonitrile **G3** using BindFit.

Figure S12c. Simulation of second titrations of **Cap4** and tetrafluoroterephthalonitrile **G3** using BindFit.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
20.0
15.0
10.0
5.0
0
-0.5
ppm


(a)
U
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
12.0
11.5
ppm


J,W
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
-4.0
-4.5
ppm

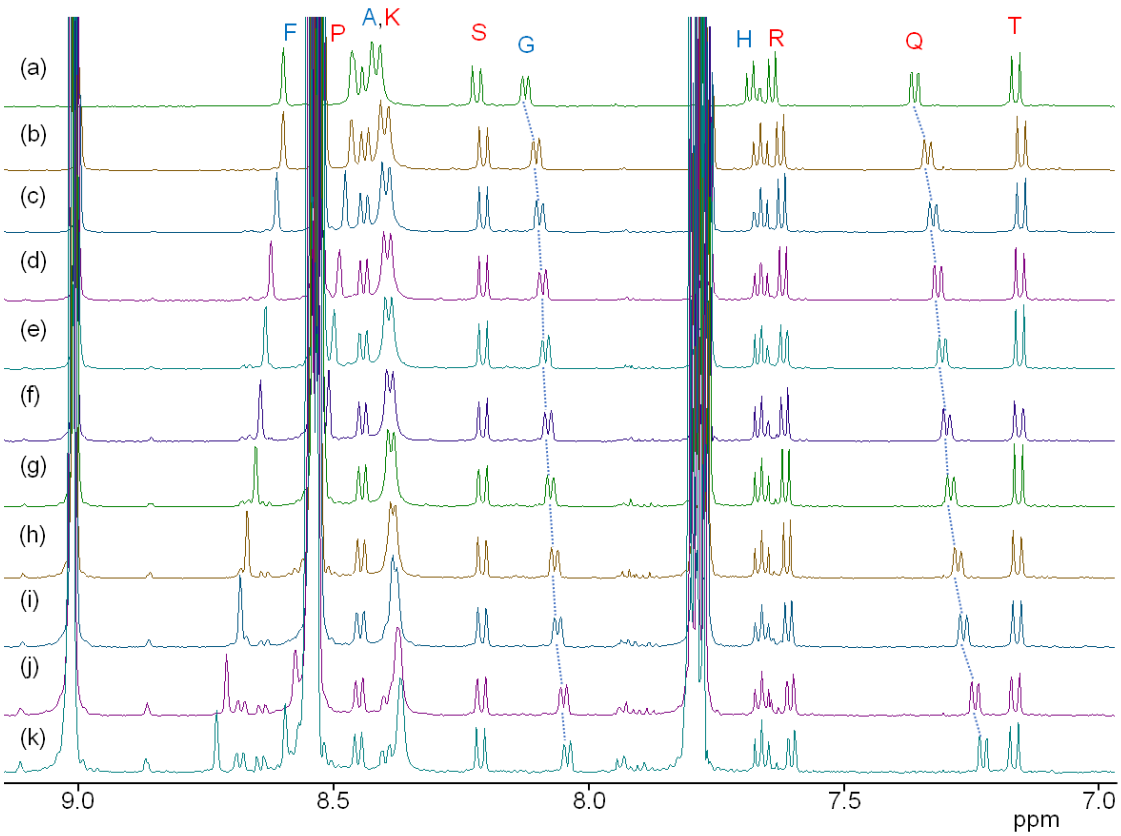


Figure S13a. ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 25 °C) of the dimer **Cap4** (0.50 mM) (a) in the absence of 1,3-dinitrobenzene **G4** and in the presence of **G4** (b) 10 eq, (c) 20 eq, (d) 30 eq, (e) 40 eq, (f) 50 eq, (g) 60 eq, (h) 80 eq, (i) 100 eq, (j) 150 eq, (k) 200 eq.

Figure S13b. Simulation of first titrations of **Cap4** and 1,3-dinitrobenzene **G4** using BindFit.

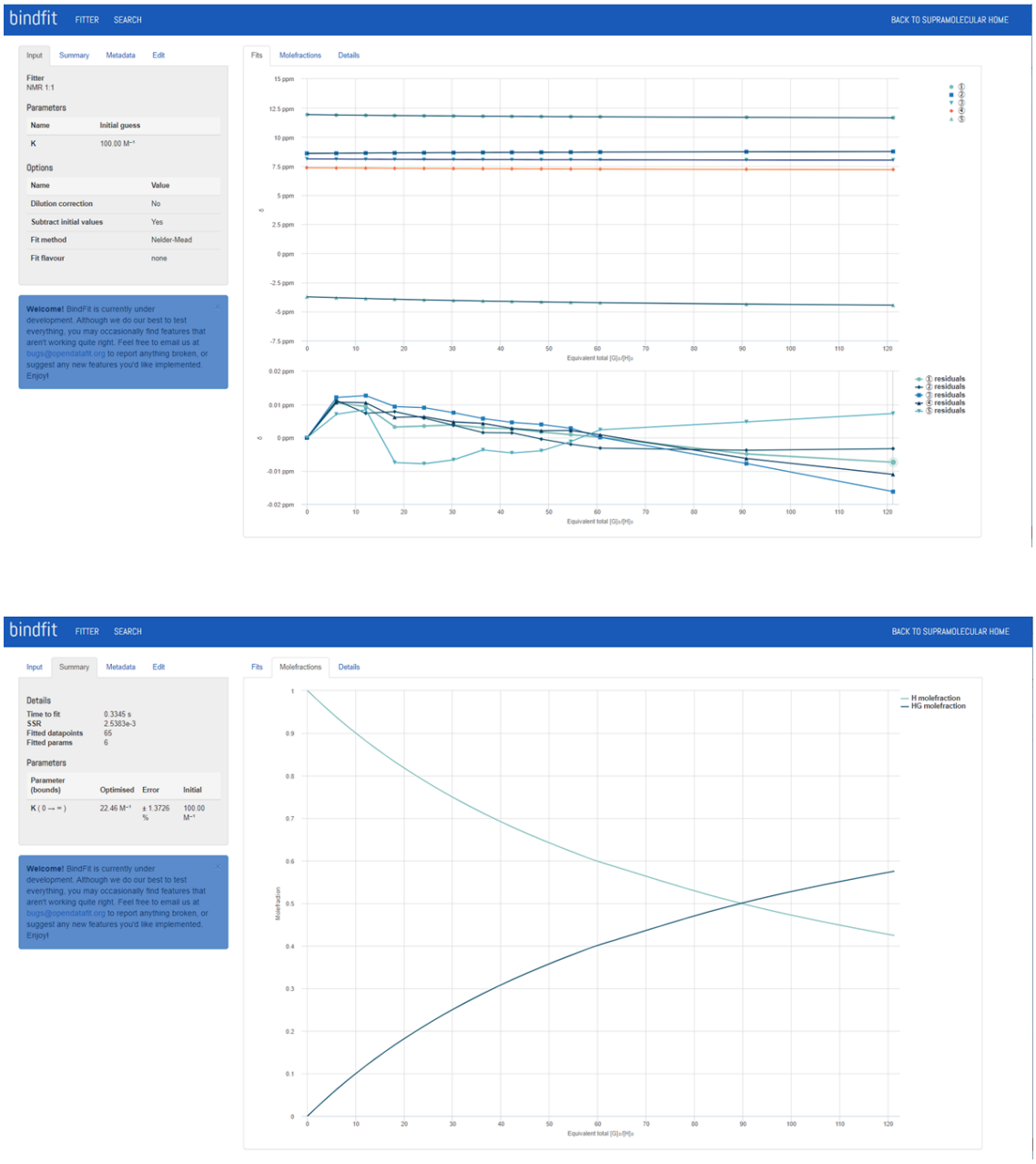
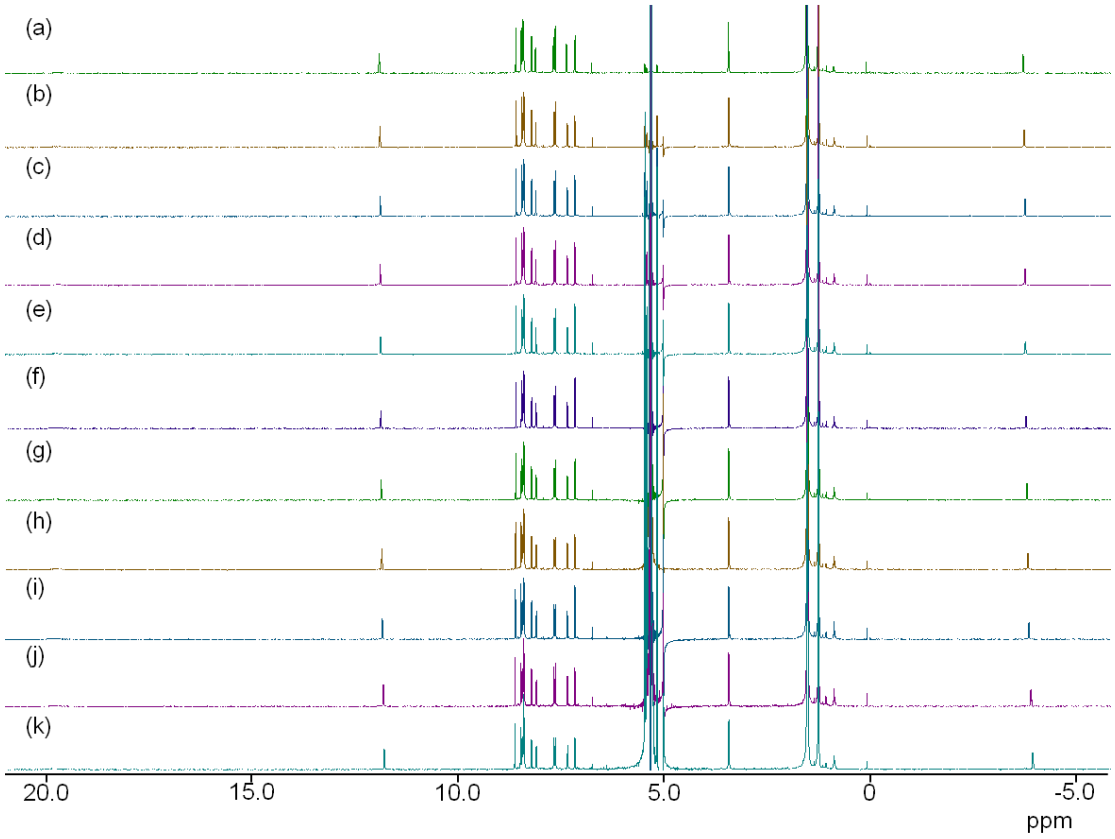
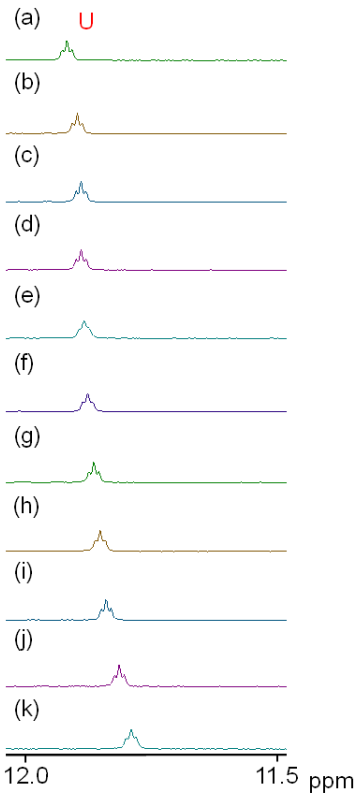
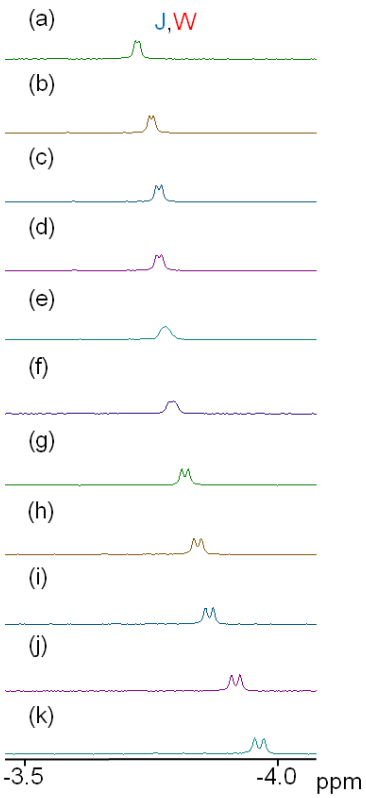


Figure S13c. Simulation of second titrations of **Cap4** and 1,3-dinitrobenzene **G4** using BindFit.


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
20.0
15.0
10.0
5.0
0
-5.0
ppm


(a) U
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
12.0
11.5
ppm


(a) J,W
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
-3.5
-4.0
ppm

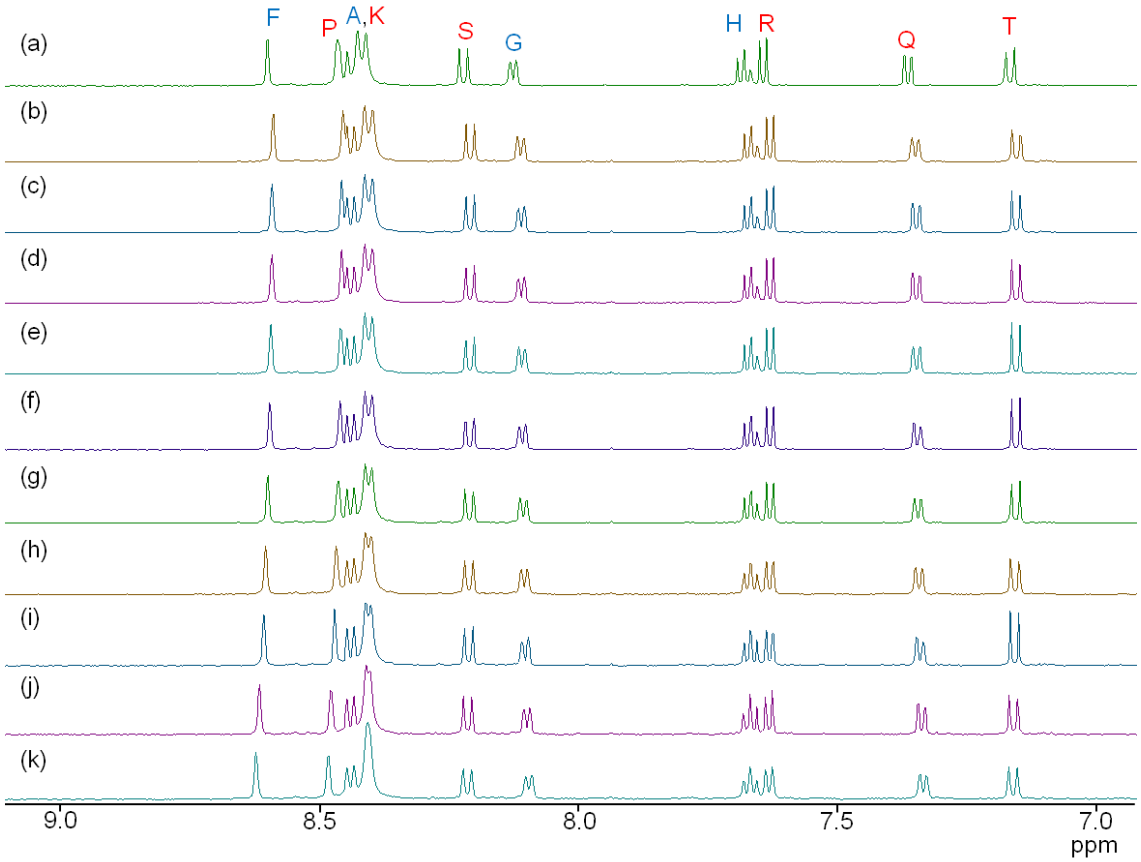


Figure S14a. ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 25 °C) of the dimer **Cap4** (0.50 mM) (a) in the absence of hexafluorobenzene **G5** and in the presence of **G5** (b) 20 eq, (c) 40 eq, (d) 60 eq, (e) 80 eq, (f) 100 eq, (g) 120 eq, (h) 160 eq, (i) 200 eq, (j) 300 eq, (k) 400 eq.

Figure S14b. Simulation of first titrations of **Cap4** and hexafluorobenzene **G5** using BindFit.

Simulation of second titrations of **Cap4** and hexafluorobenzene **G5** using BindFit was performed, however, the values were not obtained.

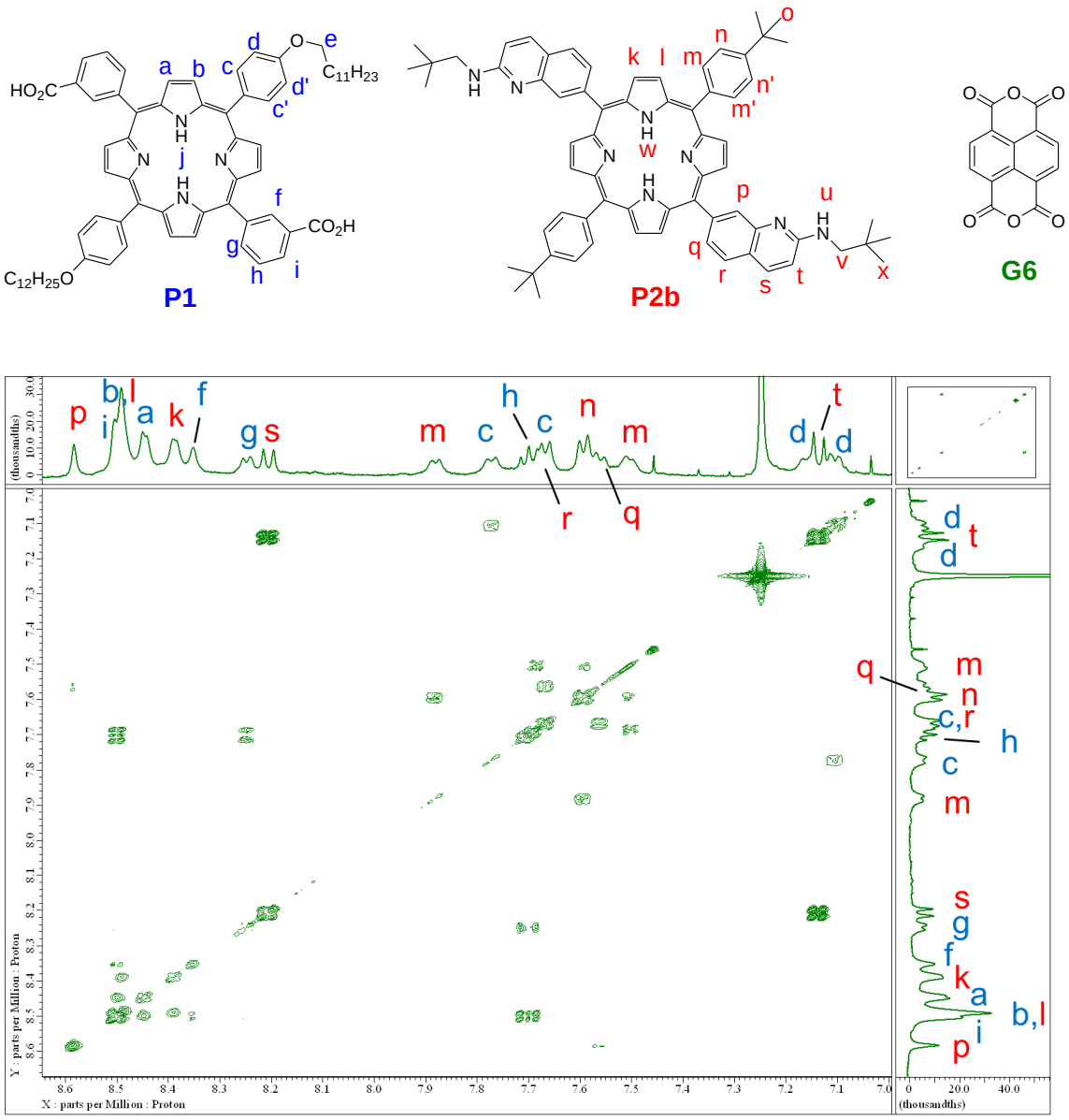


Figure S15. COSY spectrum (600 MHz, $CDCl_3$, 25 °C) of a mixture of **P1** and **P2b** (**Cap2**).

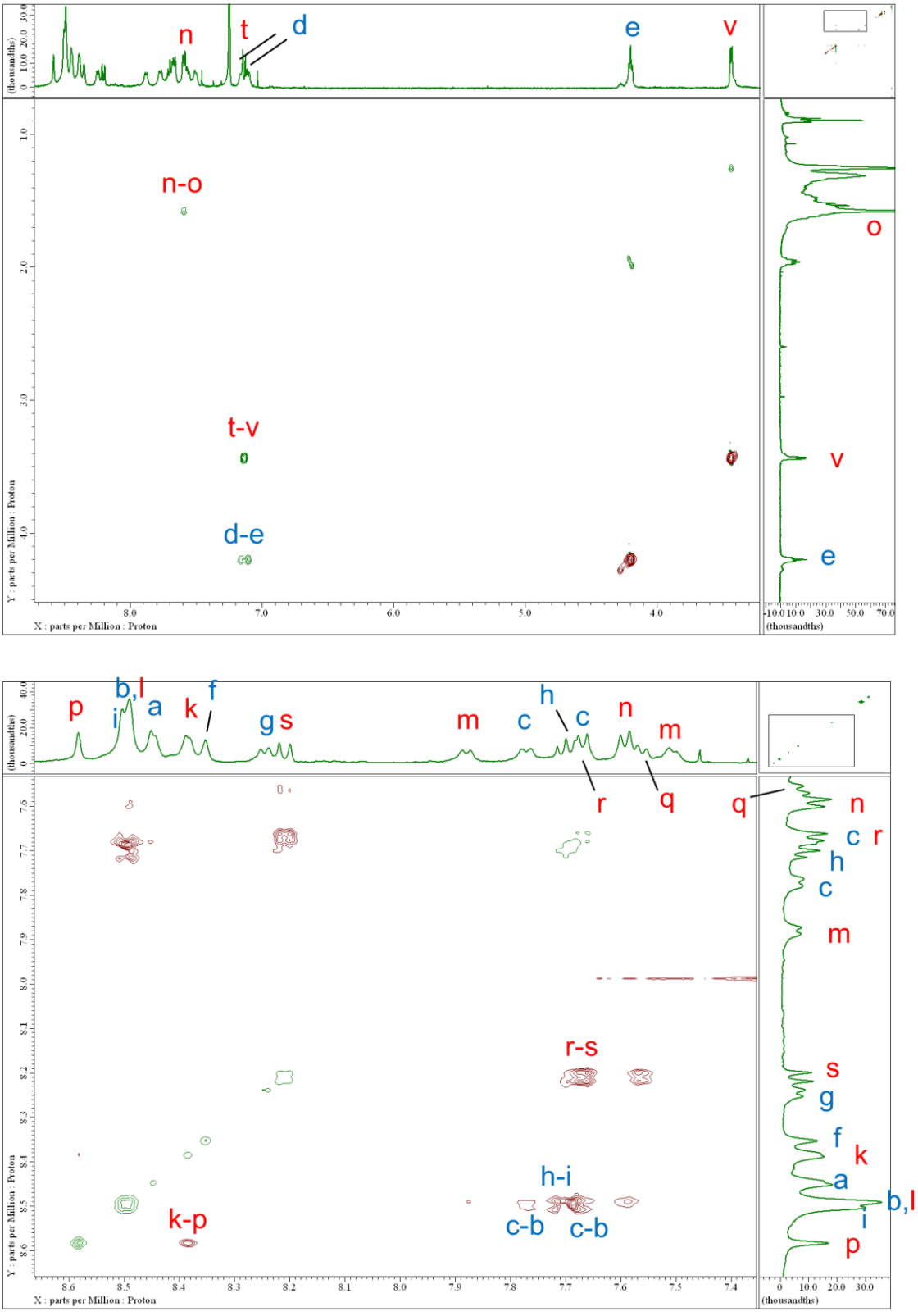
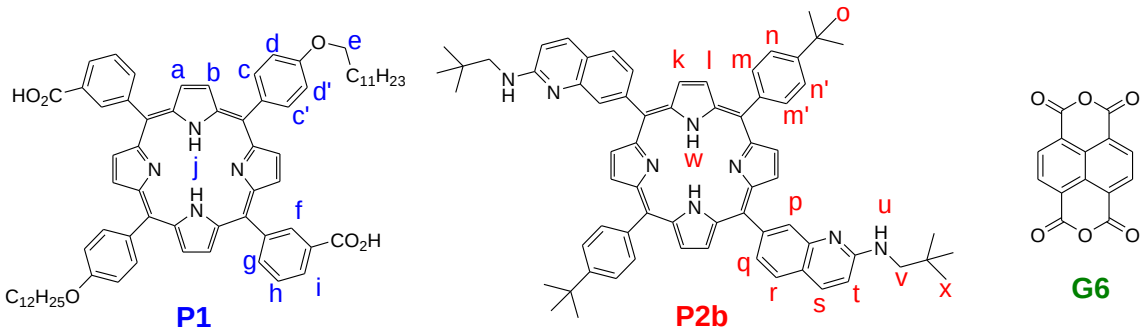
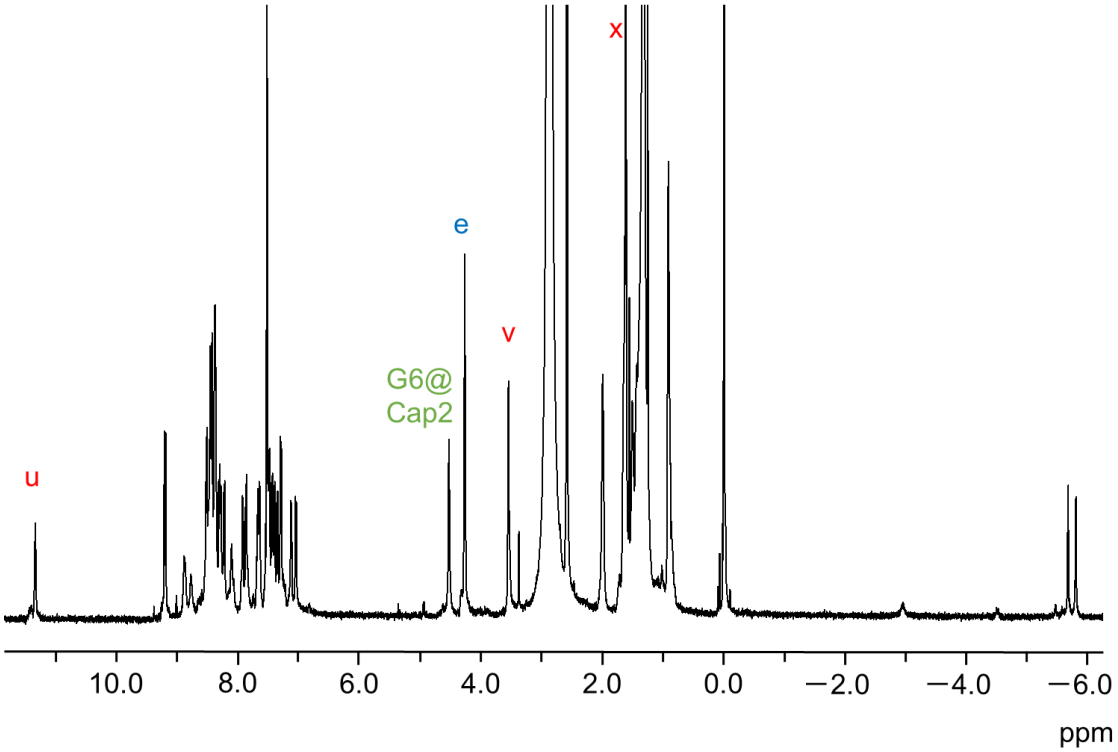


Figure S16. ROESY spectrum (600 MHz, $CDCl_3$, 25 °C) of a mixture of **P1** and **P2b** (**Cap2**).


HO2C
a
b
c
d
O
e
C11H23
d'
c'
N
H
N
j
N
H
f
CO2H
g
h
i
C12H25O
P1
k
l
m
n
o
n'
m'
N
H
N
w
N
H
N
p
u
N
H
q
r
s
t
v
x
P2b
G6


x
e
v
G6@
Cap2
u
10.0
8.0
6.0
4.0
2.0
0.0
−2.0
−4.0
−6.0
ppm

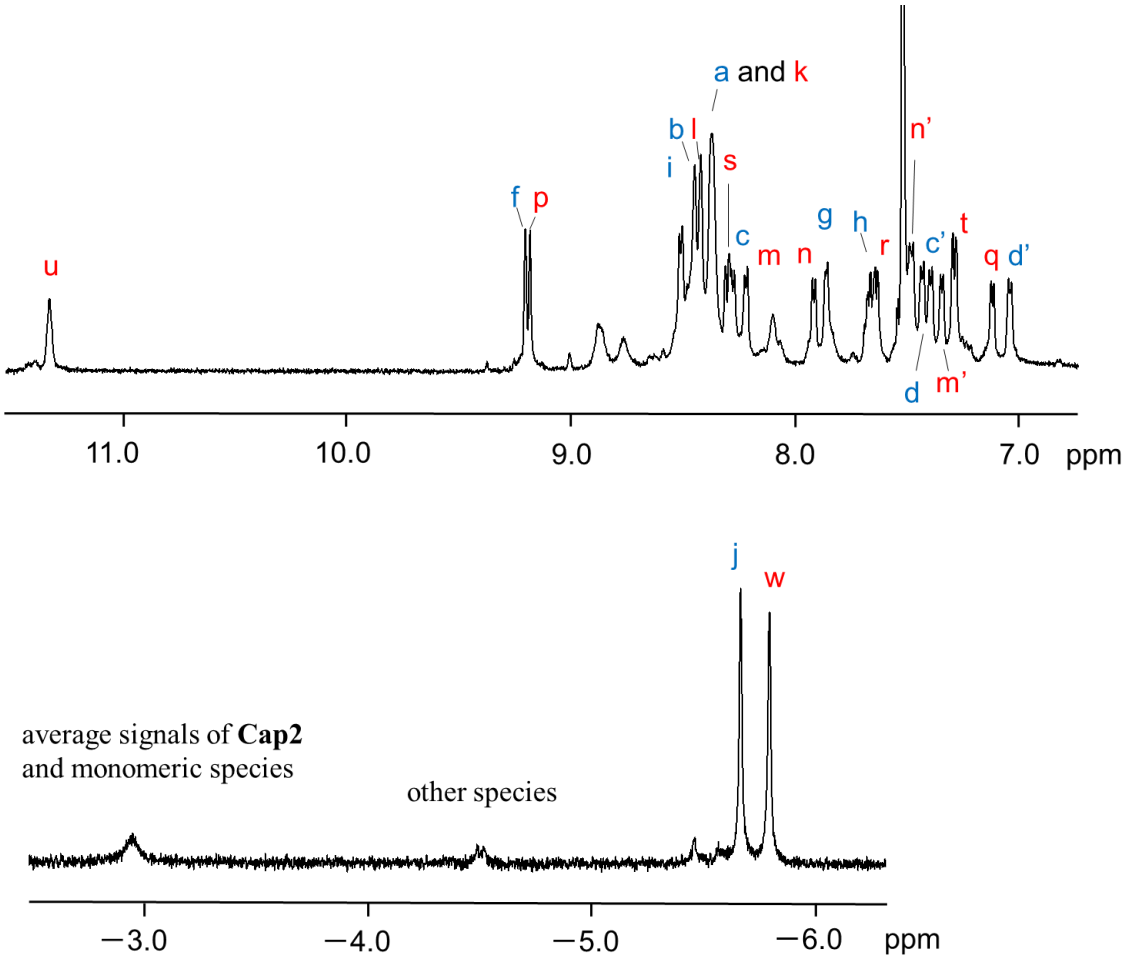
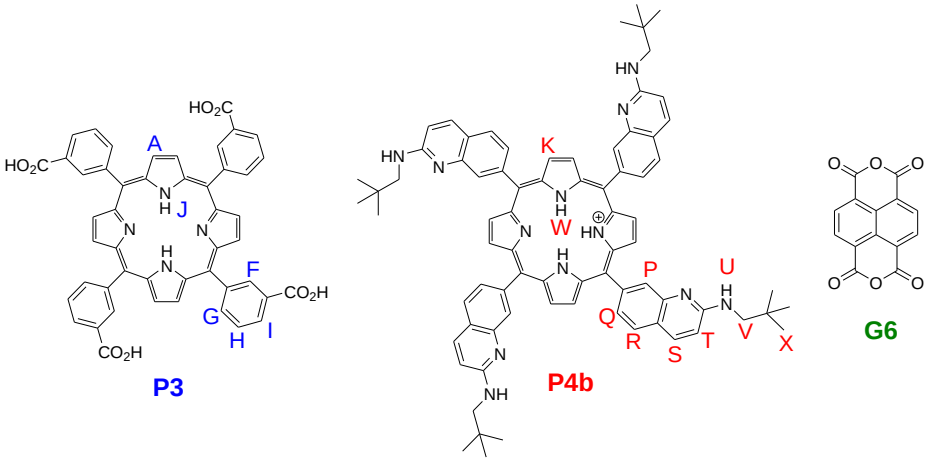
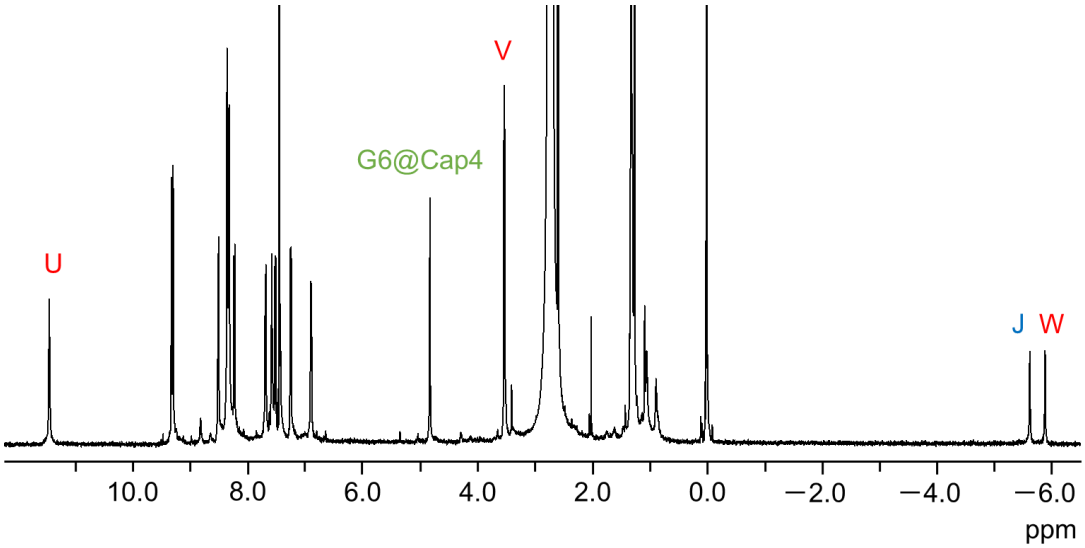
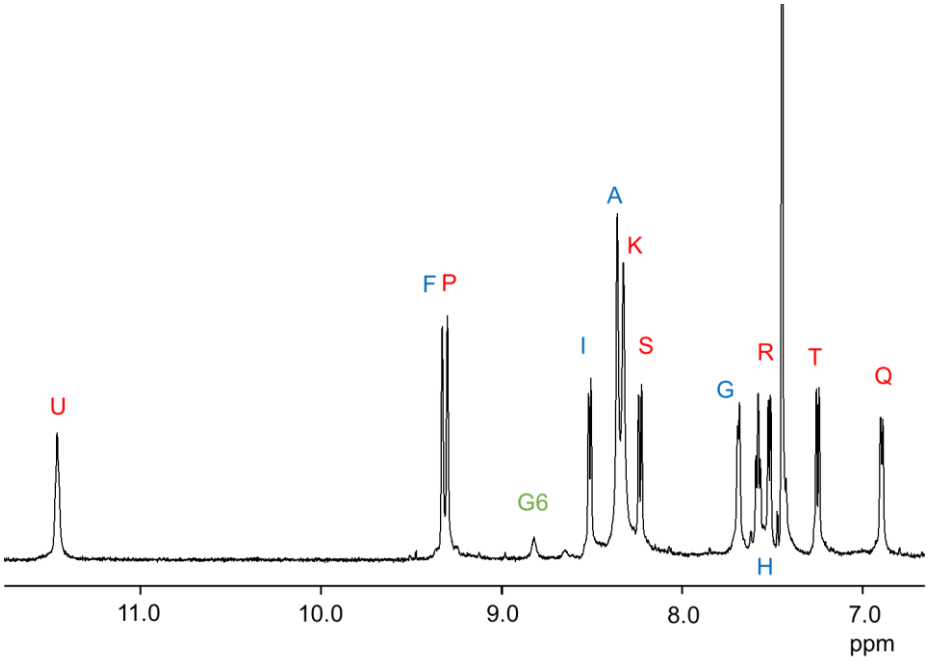


Figure S17. ^{1}H NMR spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (87:13), 25 °C] of the dimer **Cap2** (0.50 mM) in the presence of naphthalenetetracarboxylic dianhydride **G6** (1.5 mM).


HO2C
CO2H
A
J
F
G
H
I
P3
K
W
P
Q
R
S
T
U
V
X
P4b
G6


U
G6@Cap4
V
J W
10.0
8.0
6.0
4.0
2.0
0.0
−2.0
−4.0
−6.0
ppm


U
F P
G6
I
A
K
S
G
H
R
T
Q
11.0
10.0
9.0
8.0
7.0
ppm

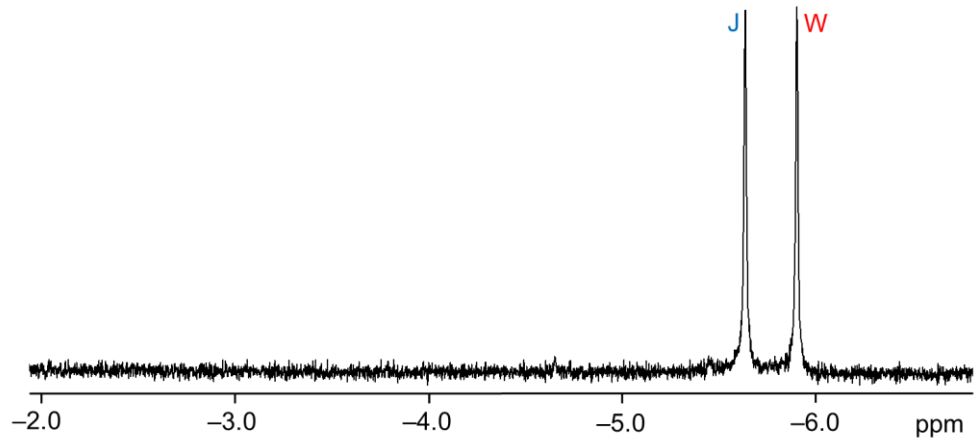


Figure S18a. ^{1}H NMR spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (91:9)] of the dimer **Cap4** (0.50 mM) in the presence of naphthalene tetracarboxylic dianhydride **G6** (1.0 mM).

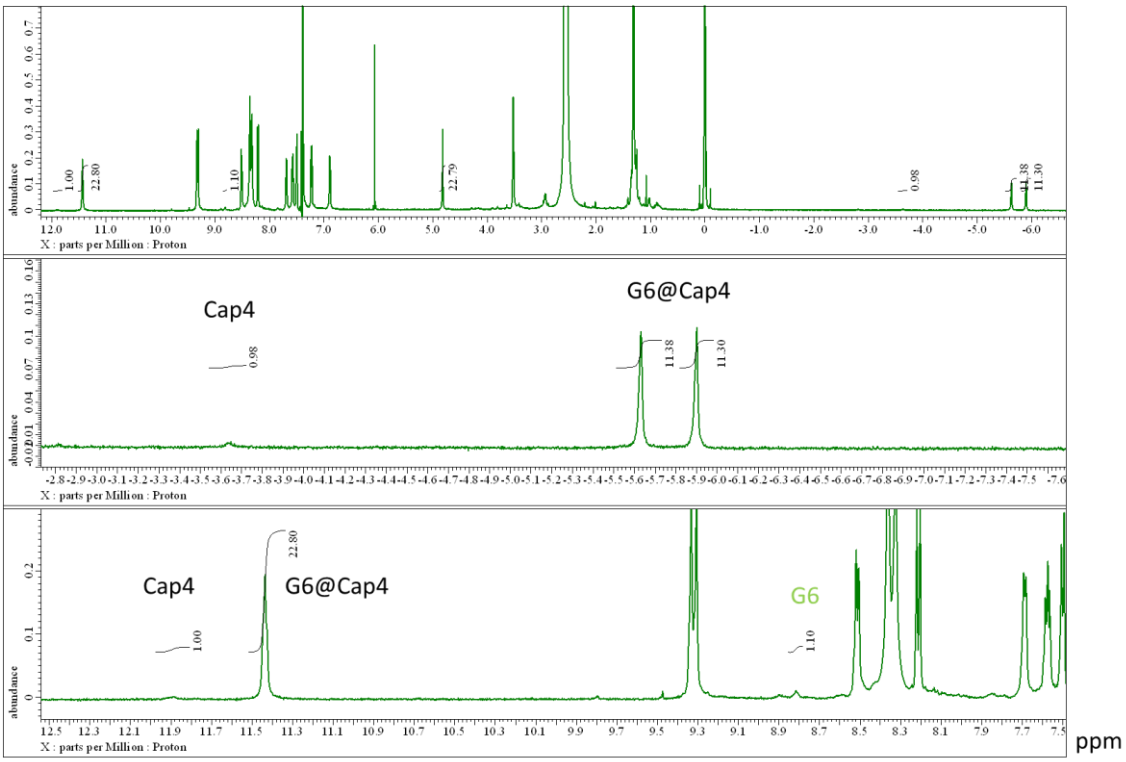
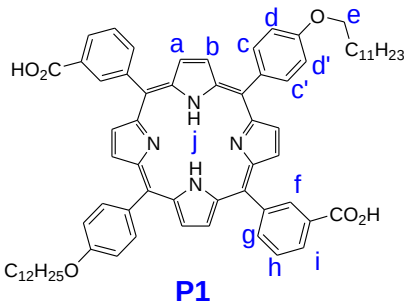
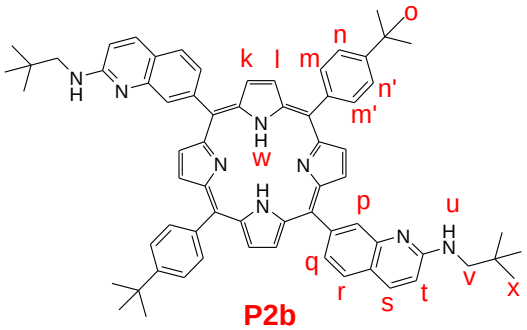


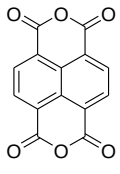
Figure S18b. ^{1}H NMR spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (93:7)] of the dimer **Cap4** (0.50 mM) in the presence of naphthalene tetracarboxylic dianhydride **G6** (0.50 mM).


HO2C
a
b
c
d
O
e
C11H23
d'
c'
N
H
j
N
H
N
f
CO2H
g
h
i
C12H25O

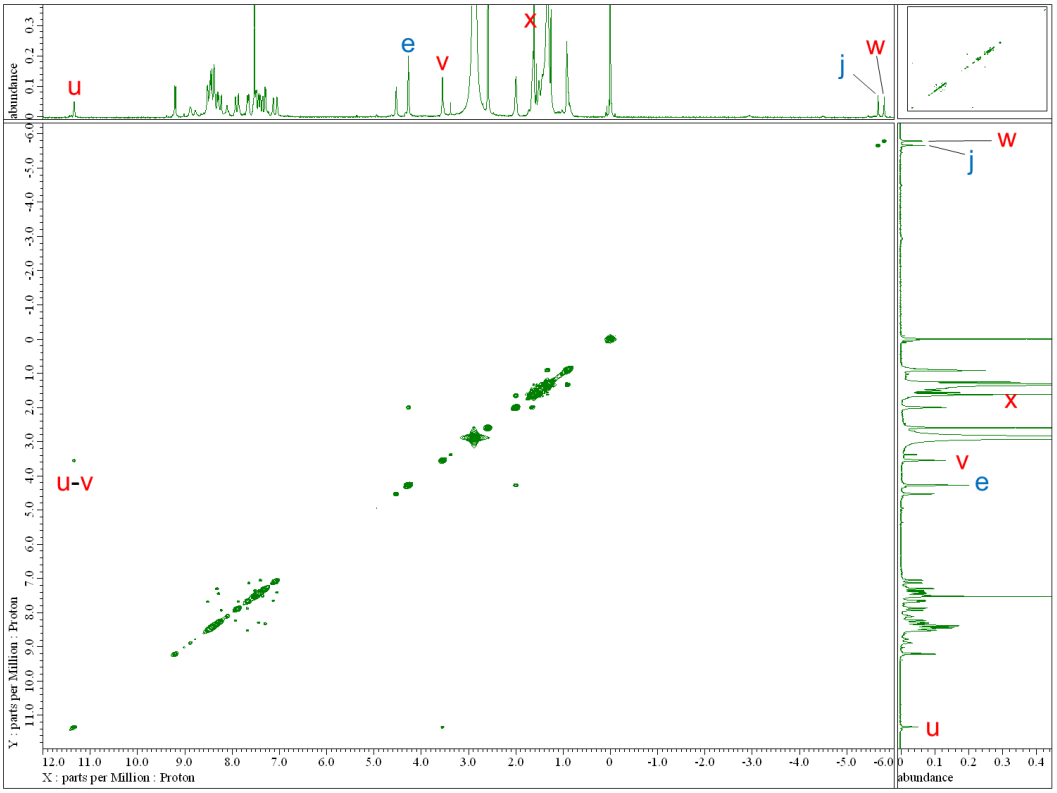
P1


N
H
N
k
l
m
n
o
n'
m'
N
H
w
N
H
N
p
u
N
H
N
q
v
x
r
s
t

P2b


O
O
O
O
O
O

G6


abundance
u
e
v
x
j
w
w
j
x
v
e
u
u-v
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

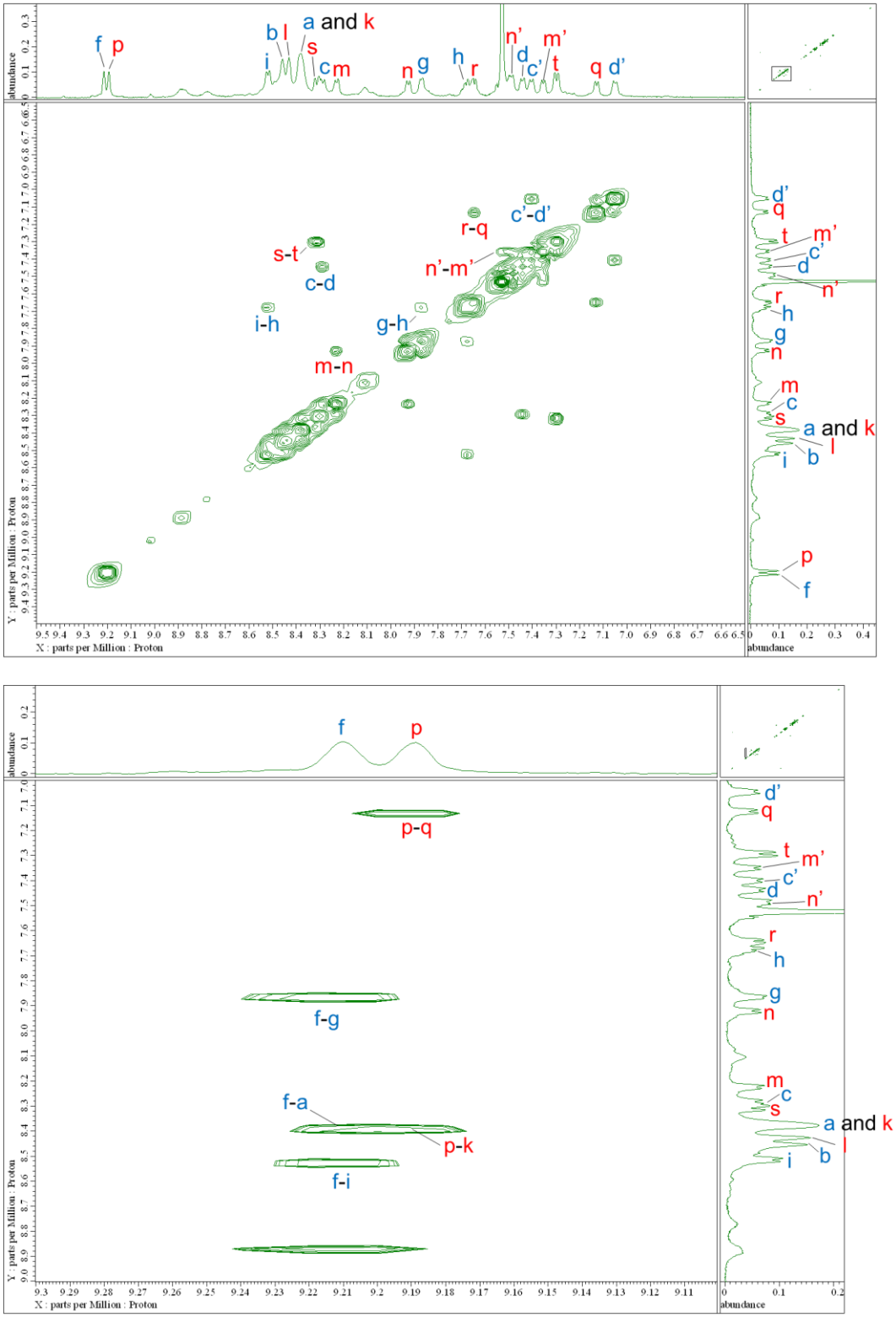


Figure S19. COSY spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (89:11)] of a mixture of **Cap2** (0.50 mM) and naphthalene tetracarboxylic dianhydride **G6** (1.5 mM).

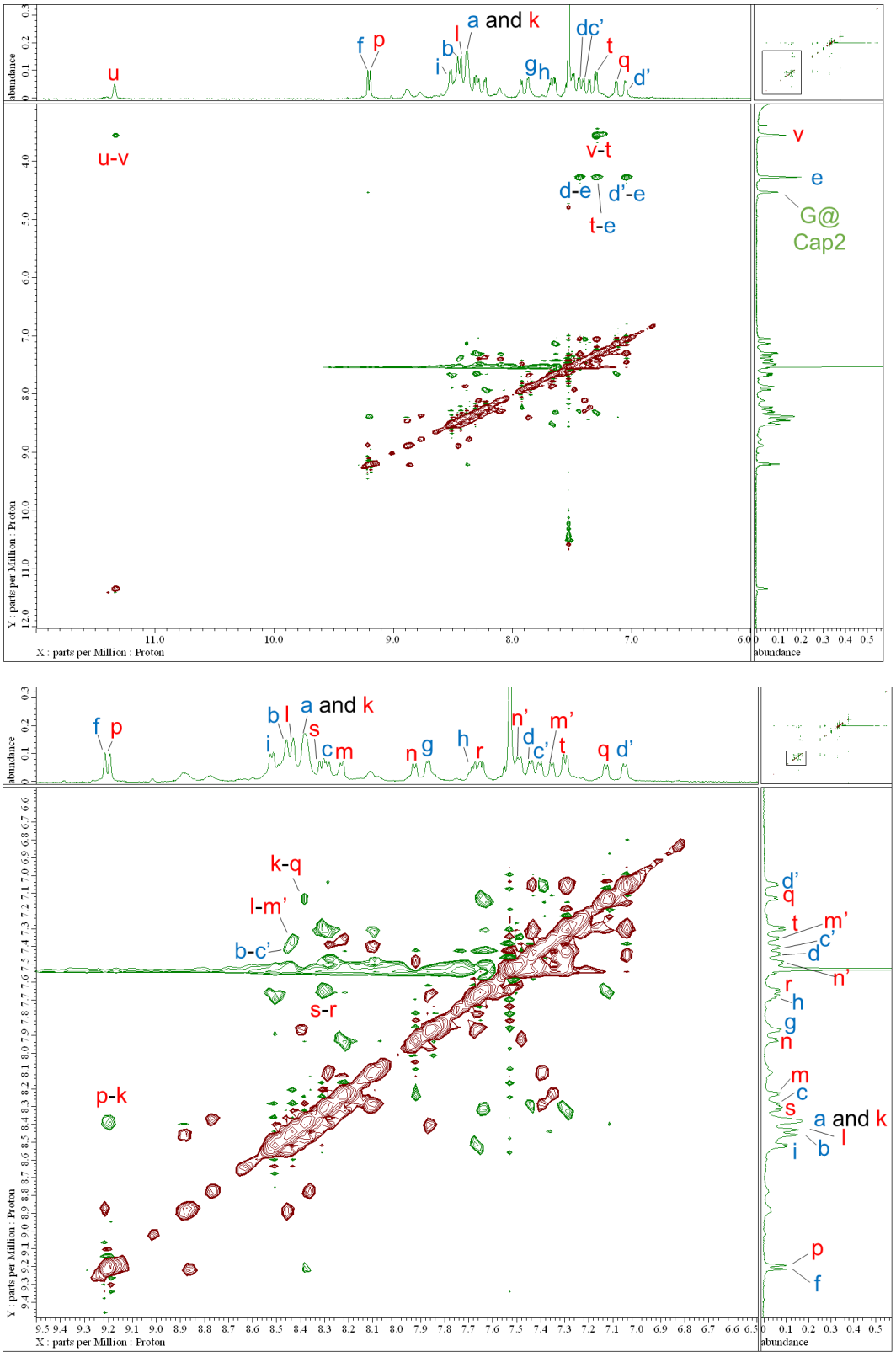
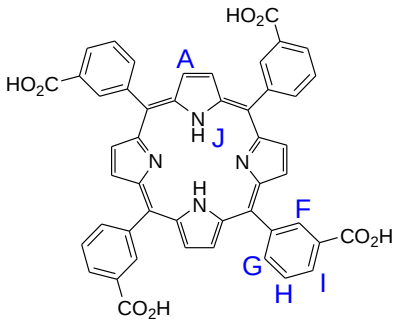
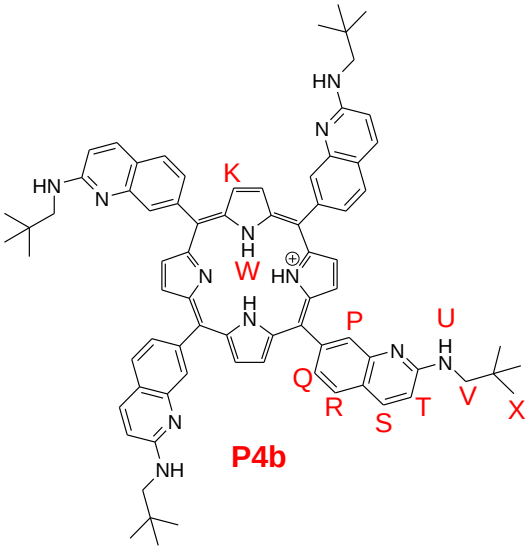


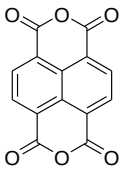
Figure S20. ROESY spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (91:9)] of a mixture of **Cap2** (0.50 mM) and naphthalene tetracarboxylic dianhydride **G6** (1.0 mM).


HO2C
HO2C
CO2H
A
J
F
G
H
I
CO2H

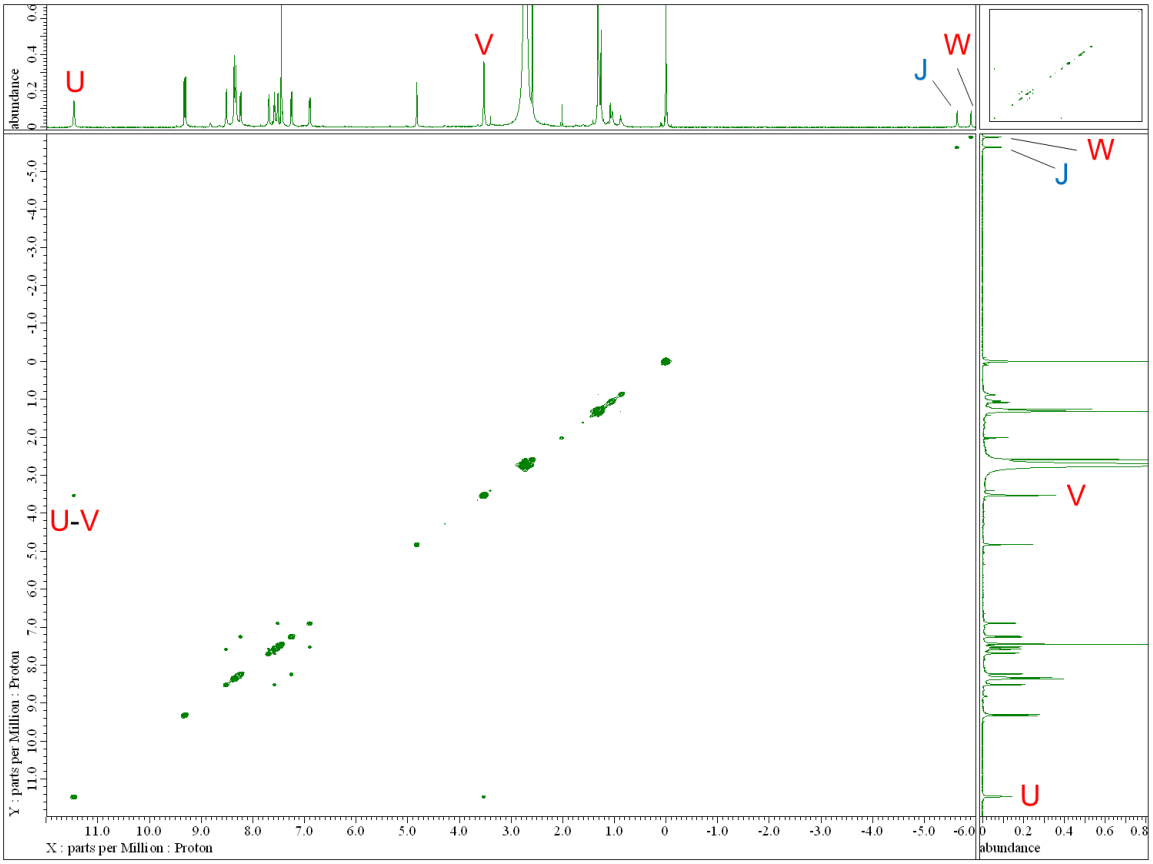
P3


HN
N
HN
N
K
N
H
W
HN
N
H
N
P
U
N
H
N
Q
R
S
T
V
X
N
NH

P4b


O
O
O
O
O
O

G6


abundance
U
V
J
W
U-V
W
J
V
U
Y : parts per Million : Proton
X : parts per Million : Proton
abundance

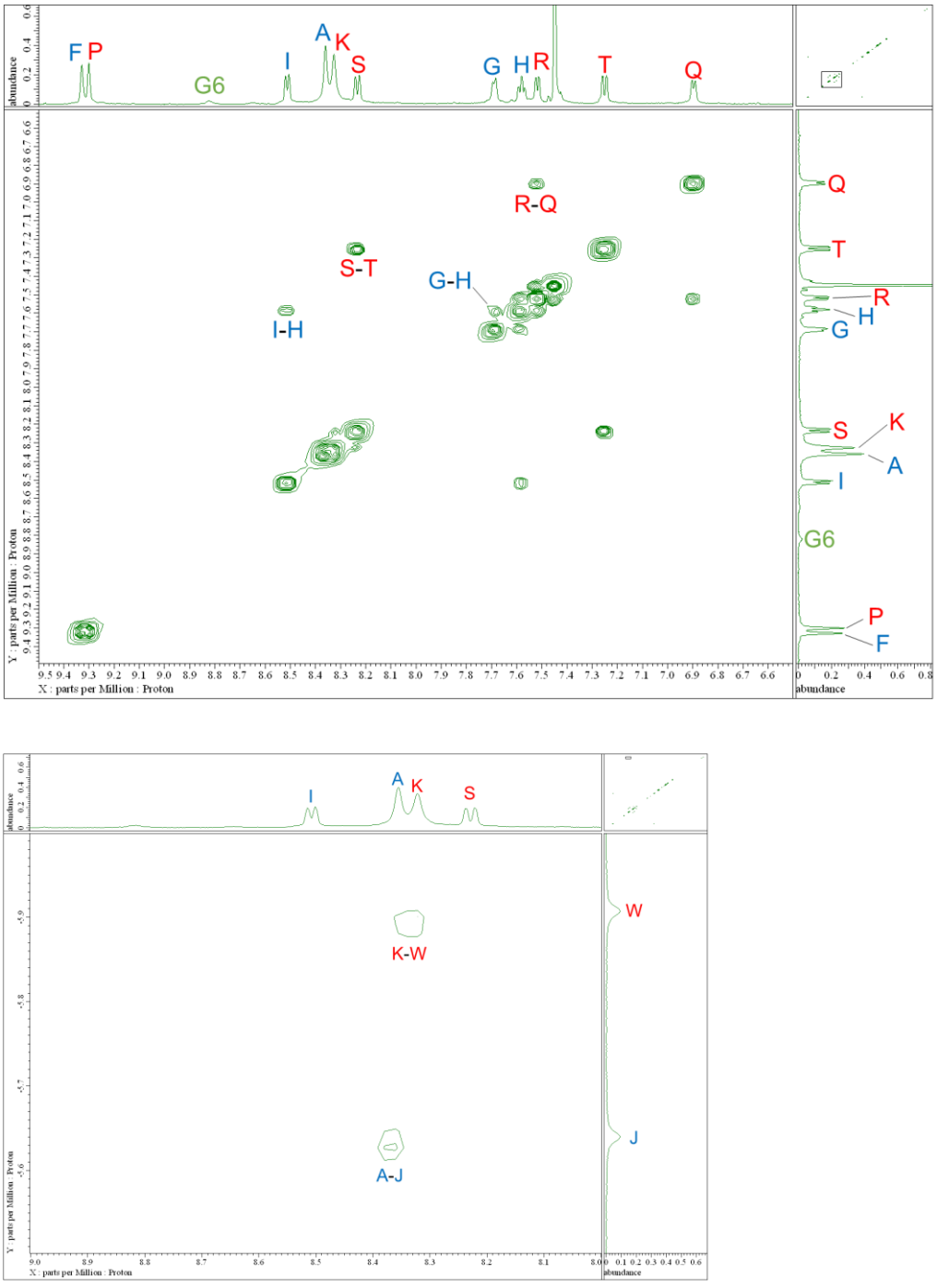
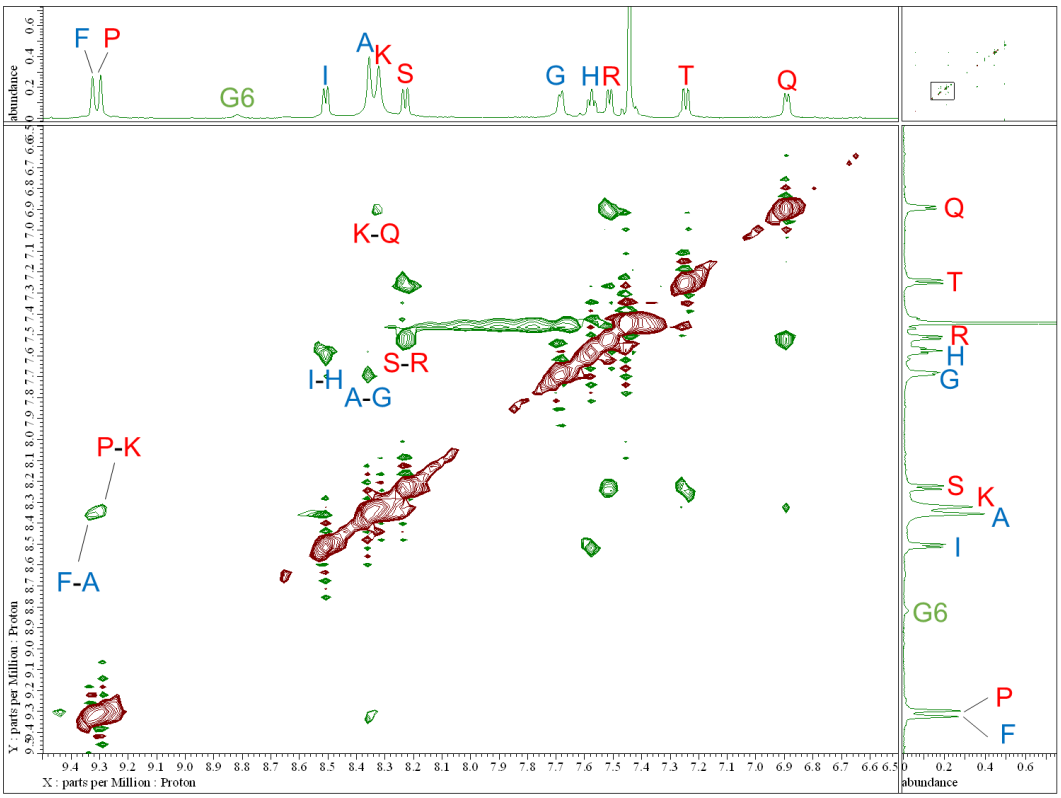
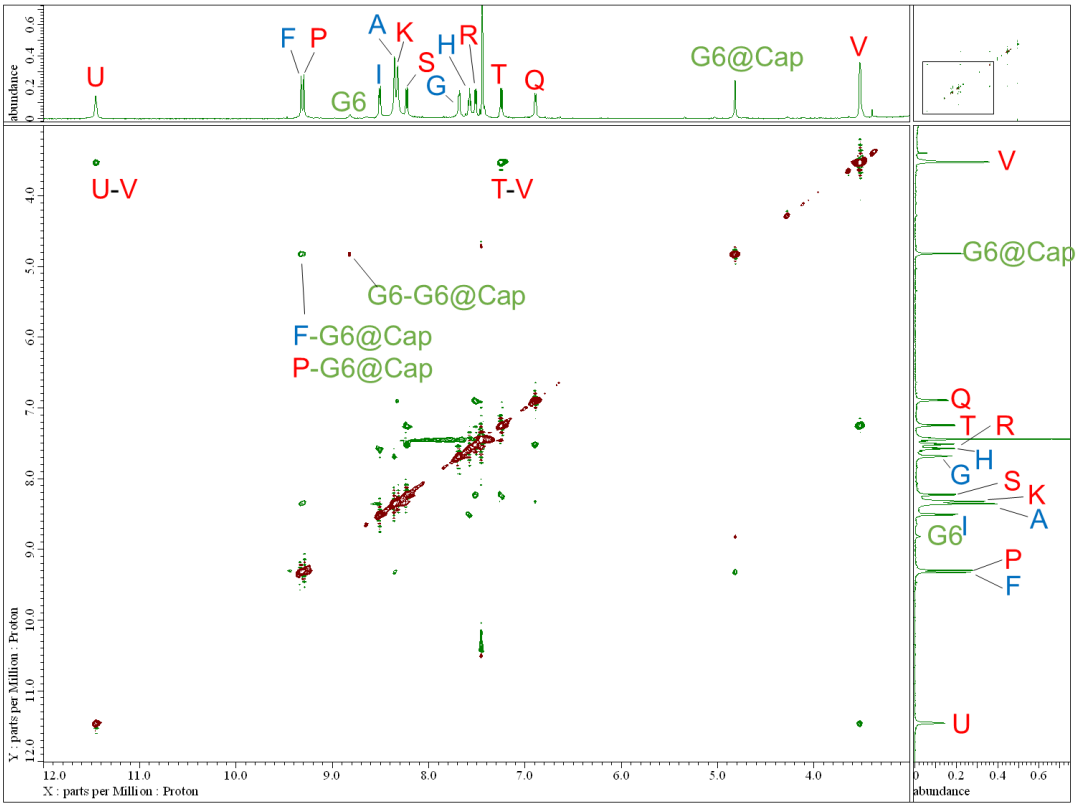


Figure S21. COSY spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (91:9)] of a mixture of **Cap4** (0.50 mM) and naphthalene tetracarboxylic dianhydride **G6** (1.0 mM).


F P
G6
I
A K
S
G HR
T
Q
K-Q
S-R
I-H
A-G
P-K
F-A
Q
T
R
H
G
S K
A
I
G6
P
F
abundance
X : parts per Million : Proton
Y : parts per Million : Proton


U
F P
G6
A K
I
S
G
H
R
T
Q
G6@Cap
V
U-V
T-V
G6-G6@Cap
F-G6@Cap
P-G6@Cap
V
G6@Cap
Q
T
R
H
G
S
K
A
G6
I
P
F
U
abundance
X : parts per Million : Proton
Y : parts per Million : Proton

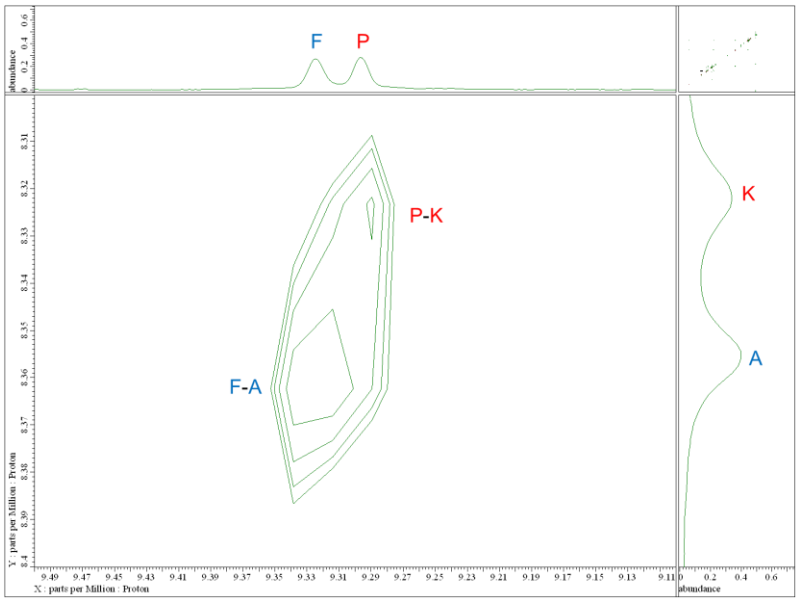


Figure S22. ROESY spectrum [600 MHz, $CDCl_3$/DMSO-d_6 (91:9)] of a mixture of **Cap4** (0.50 mM) and naphthalene tetracarboxylic dianhydride **G6** (1.0 mM).

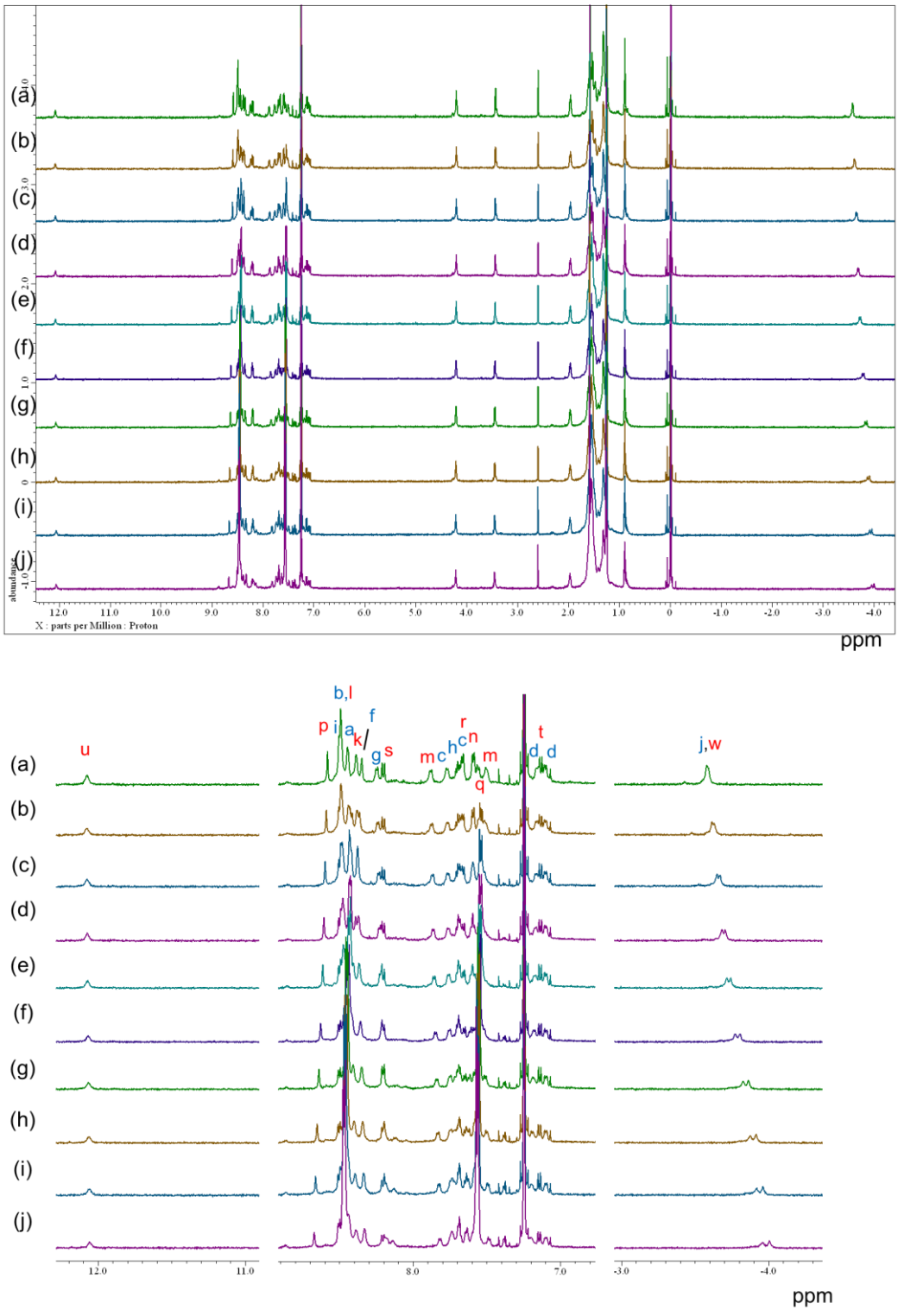


Figure S23a. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 25 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 3.0 eq, (g) 4.0 eq, (h) 5.0 eq, (i) 6.0 eq, (j) 7.0 eq. Fig. 7: Partial spectra of Figure S23a.

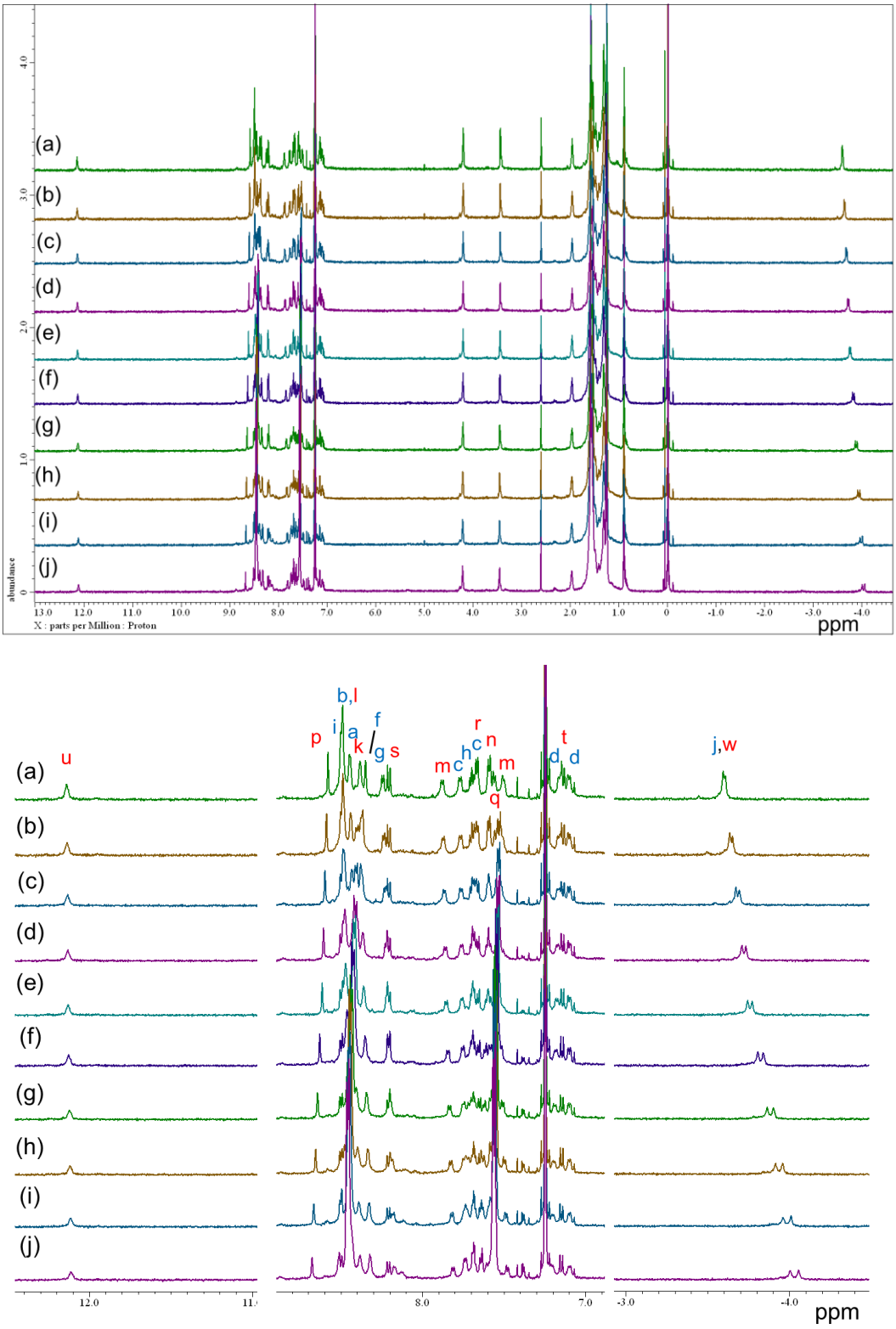


Figure S23b. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 20 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 3.0 eq, (g) 4.0 eq, (h) 5.0 eq, (i) 6.0 eq, (j) 7.0 eq.

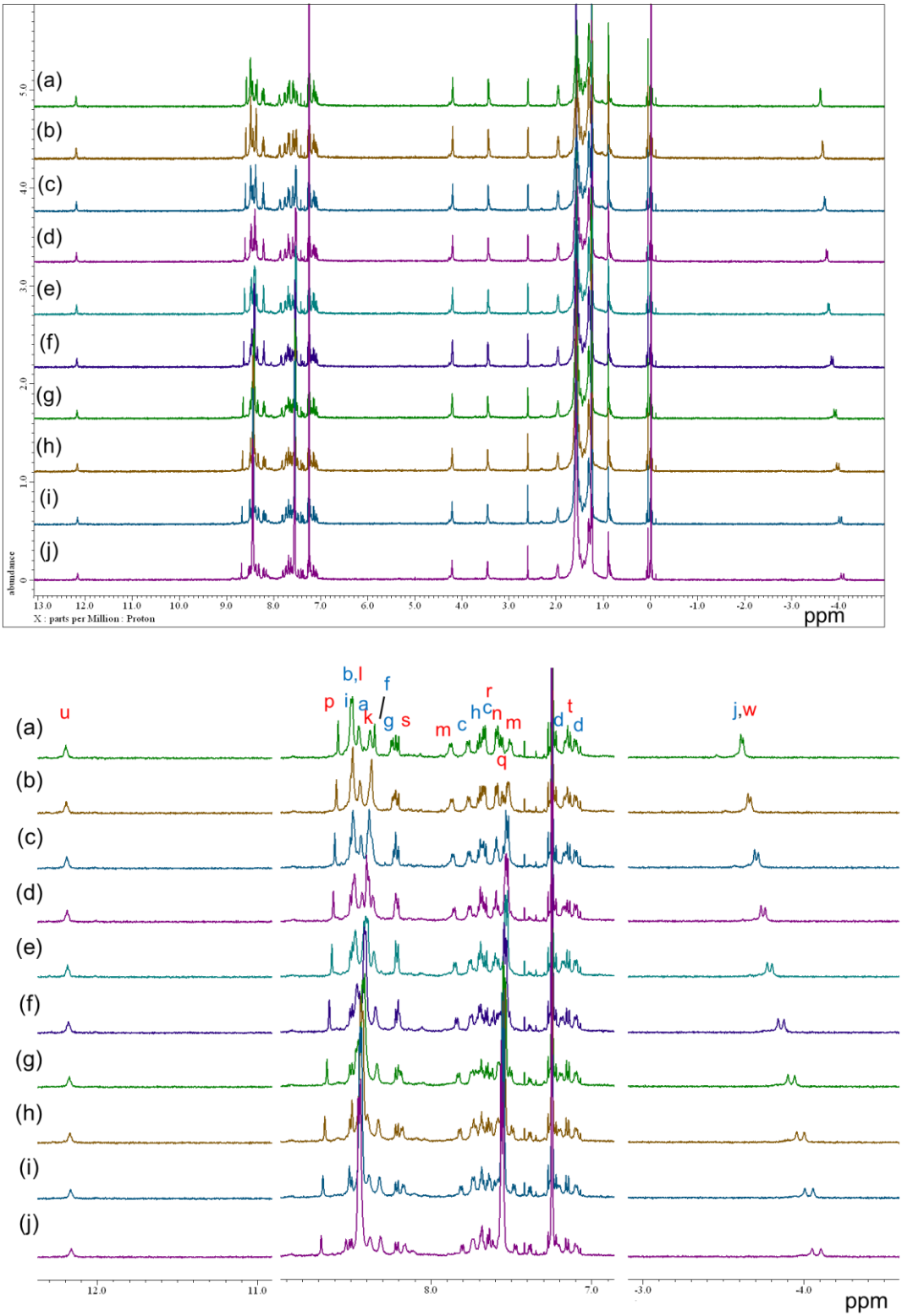


Figure S23c. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 15 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 3.0 eq, (g) 4.0 eq, (h) 5.0 eq, (i) 6.0 eq, (j) 7.0 eq.

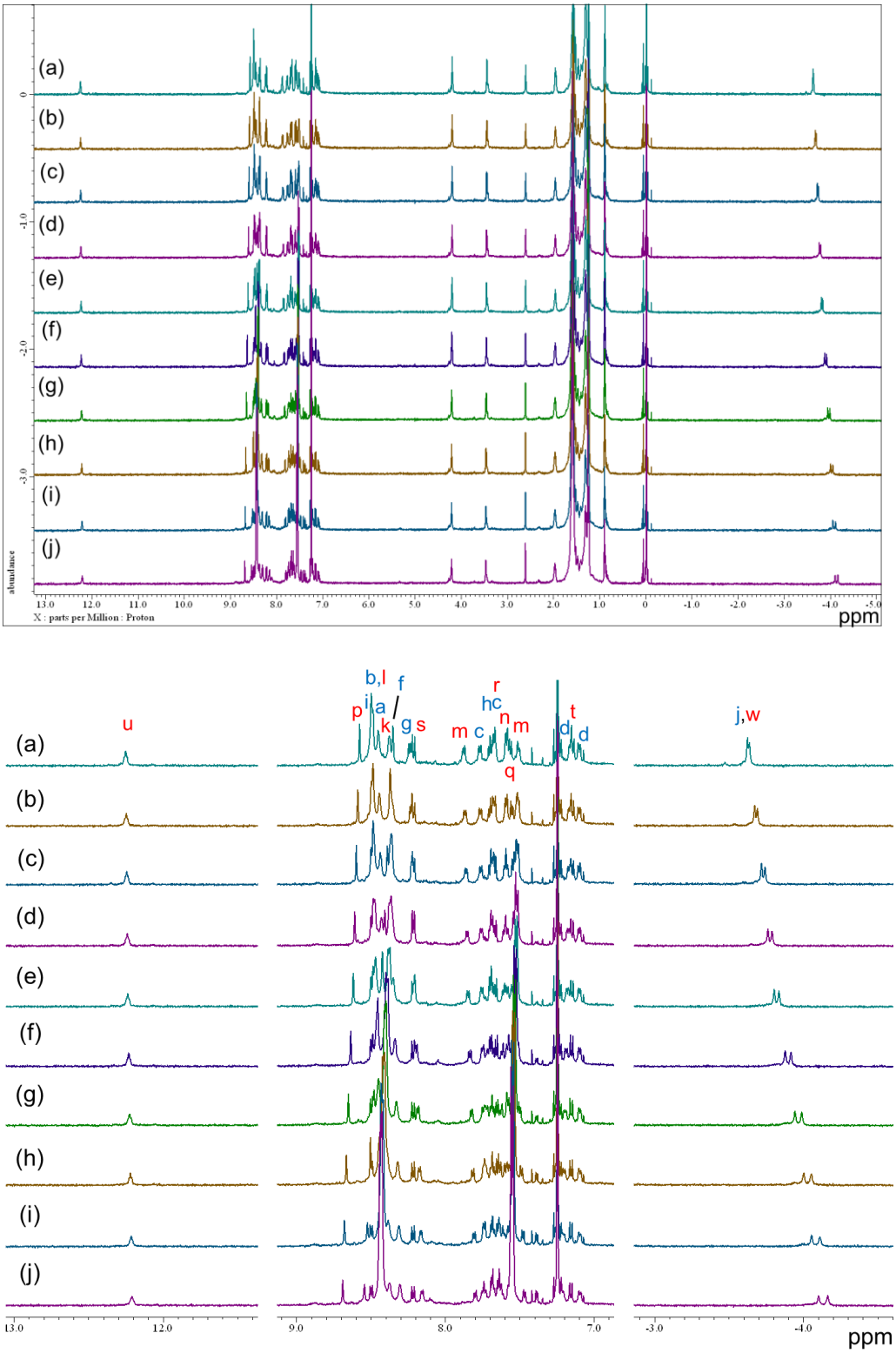


Figure S23d. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 10 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 3.0 eq, (g) 4.0 eq, (h) 5.0 eq, (i) 6.0 eq, (j) 7.0 eq.

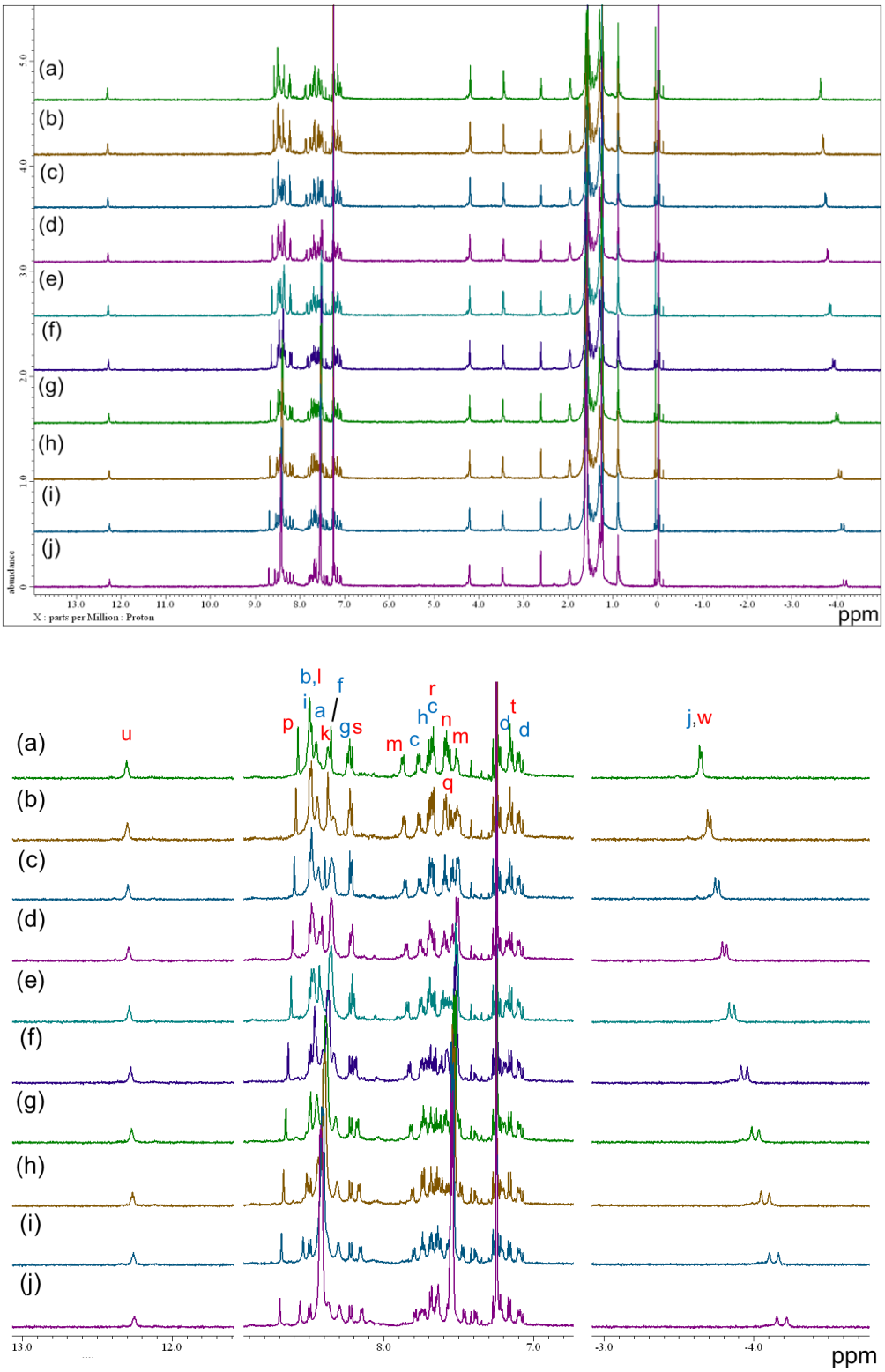


Figure S23e. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 5 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 3.0 eq, (g) 4.0 eq, (h) 5.0 eq, (i) 6.0 eq, (j) 7.0 eq.

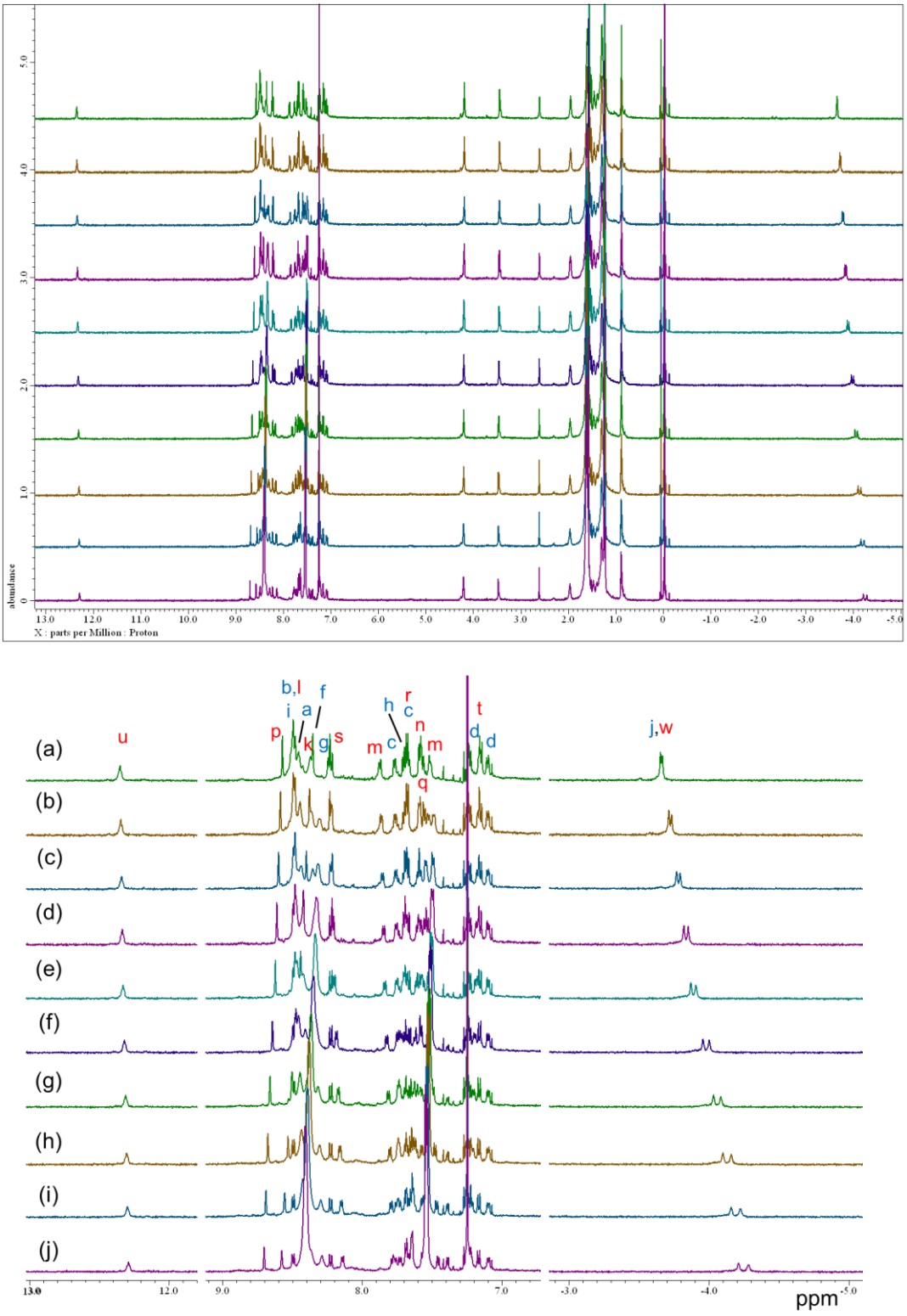
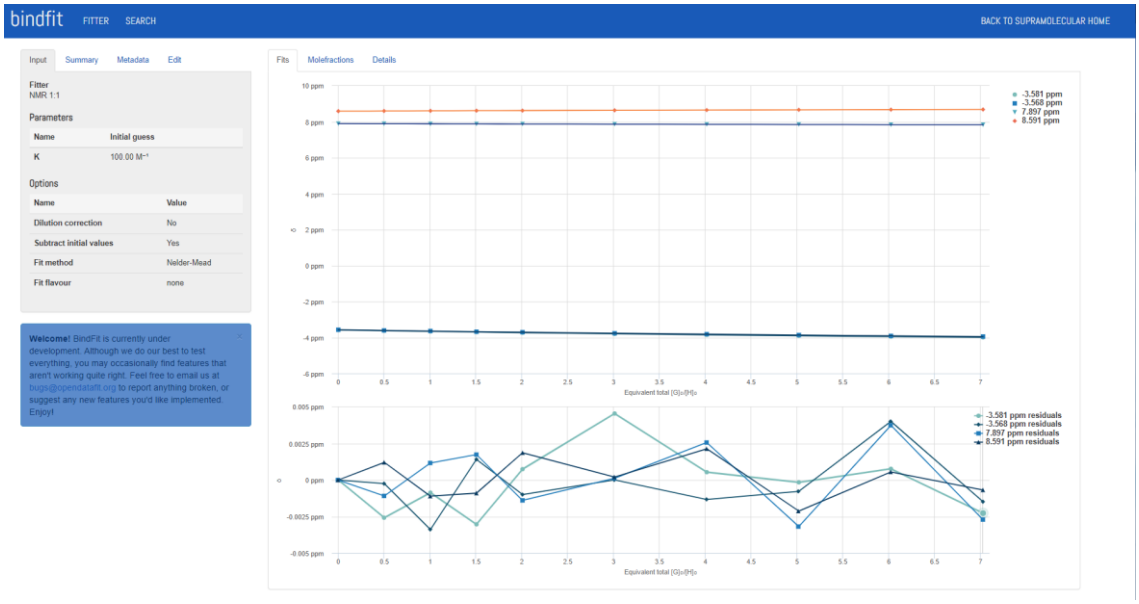
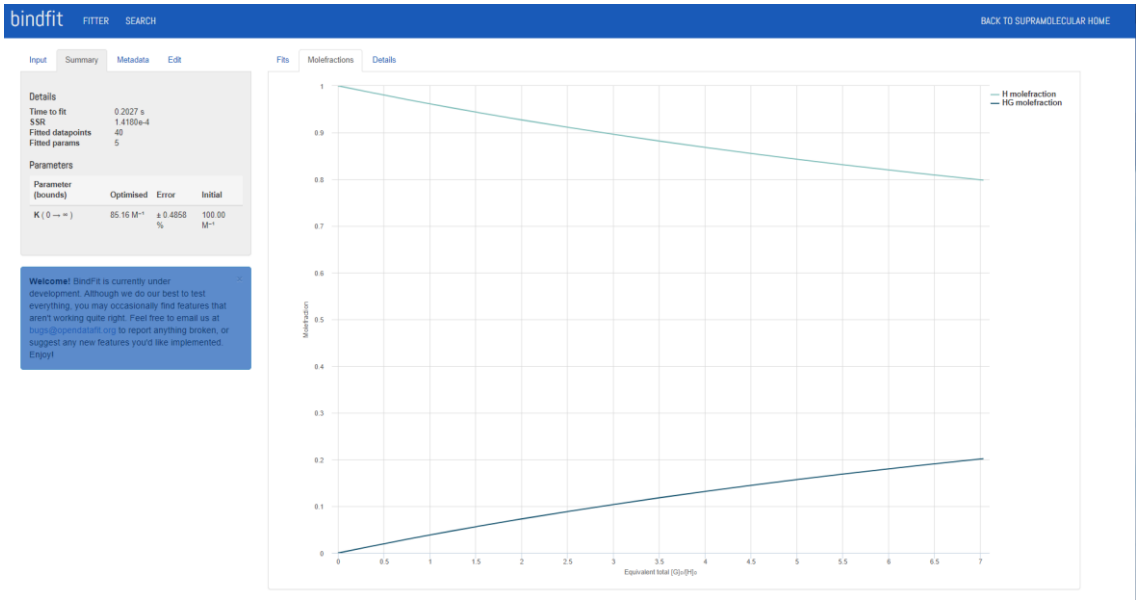


Figure S23f. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 0 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 1.5 eq, (e) 2.0 eq, (f) 3.0 eq, (g) 4.0 eq, (h) 5.0 eq, (i) 6.0 eq, (j) 7.0 eq.


bindfit
FITTER
SEARCH
BACK TO SUPRAMOLECULAR HOME
Input
Summary
Metadata
Edit
Fitter
NMR 1:1
Parameters
Name
Initial guess
K
100.00 M⁻¹
Options
Name
Value
Dilution correction
No
Subtract initial values
Yes
Fit method
Nelder-Mead
Fit flavour
none
Welcome! BindFit is currently under development. Although we do our best to test everything, you may occasionally find features that aren't working quite right. Feel free to email us at bugs@opendatafit.org to report anything broken, or suggest any new features you'd like implemented. Enjoy!
Fits
Molefractions
Details
-3.581 ppm
-3.568 ppm
7.897 ppm
8.591 ppm
Equivalent total [G]ₜ/[H]₀
-3.581 ppm residuals
-3.568 ppm residuals
7.897 ppm residuals
8.591 ppm residuals


bindfit
FITTER
SEARCH
BACK TO SUPRAMOLECULAR HOME
Input
Summary
Metadata
Edit
Details
Time to fit 0.2027 s
SSR 1.4180e-4
Fitted datapoints 40
Fitted params 5
Parameters
Parameter (bounds)
Optimised
Error
Initial
K (0 → ∞)
85.16 M⁻¹
± 0.4858 %
100.00 M⁻¹
Welcome! BindFit is currently under development. Although we do our best to test everything, you may occasionally find features that aren't working quite right. Feel free to email us at bugs@opendatafit.org to report anything broken, or suggest any new features you'd like implemented. Enjoy!
Fits
Molefractions
Details
H molefraction
HG molefraction
MoleFraction
Equivalent total [G]ₜ/[H]₀

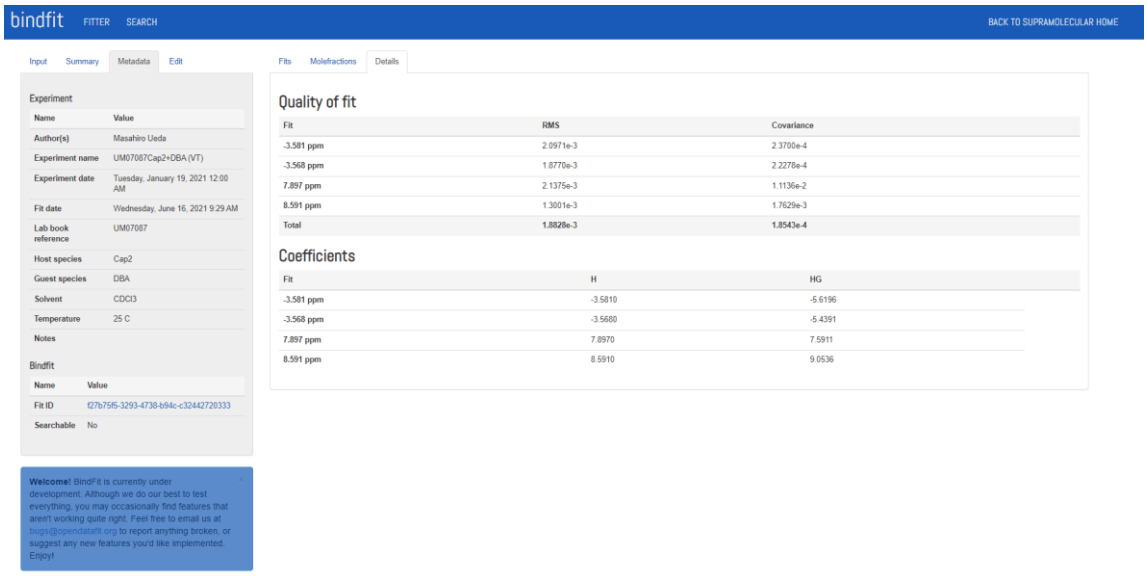
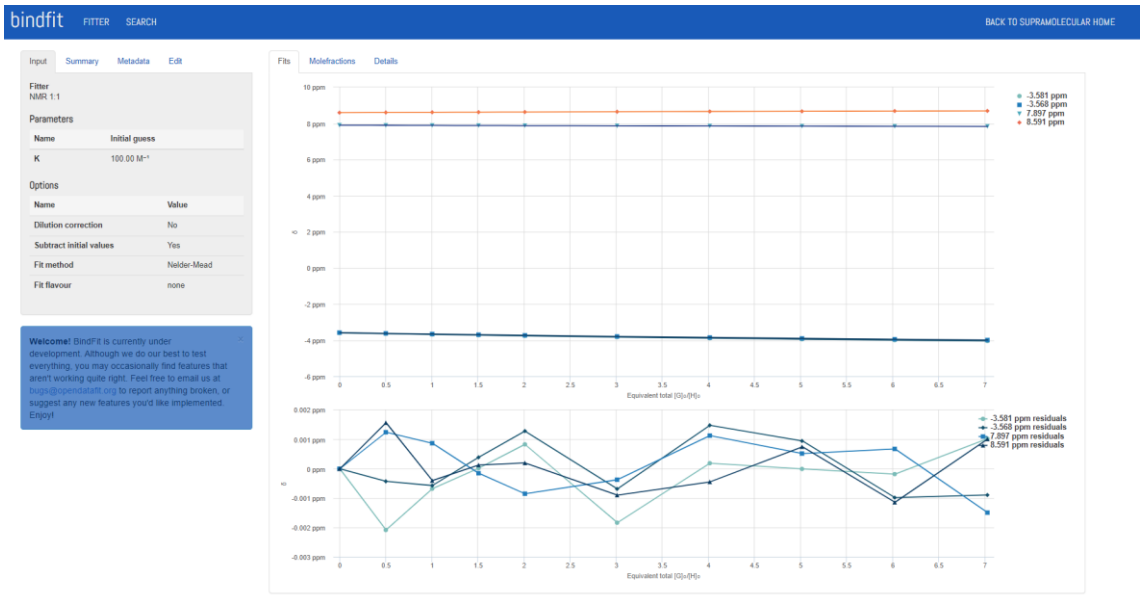


Figure S24a. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 25 °C.



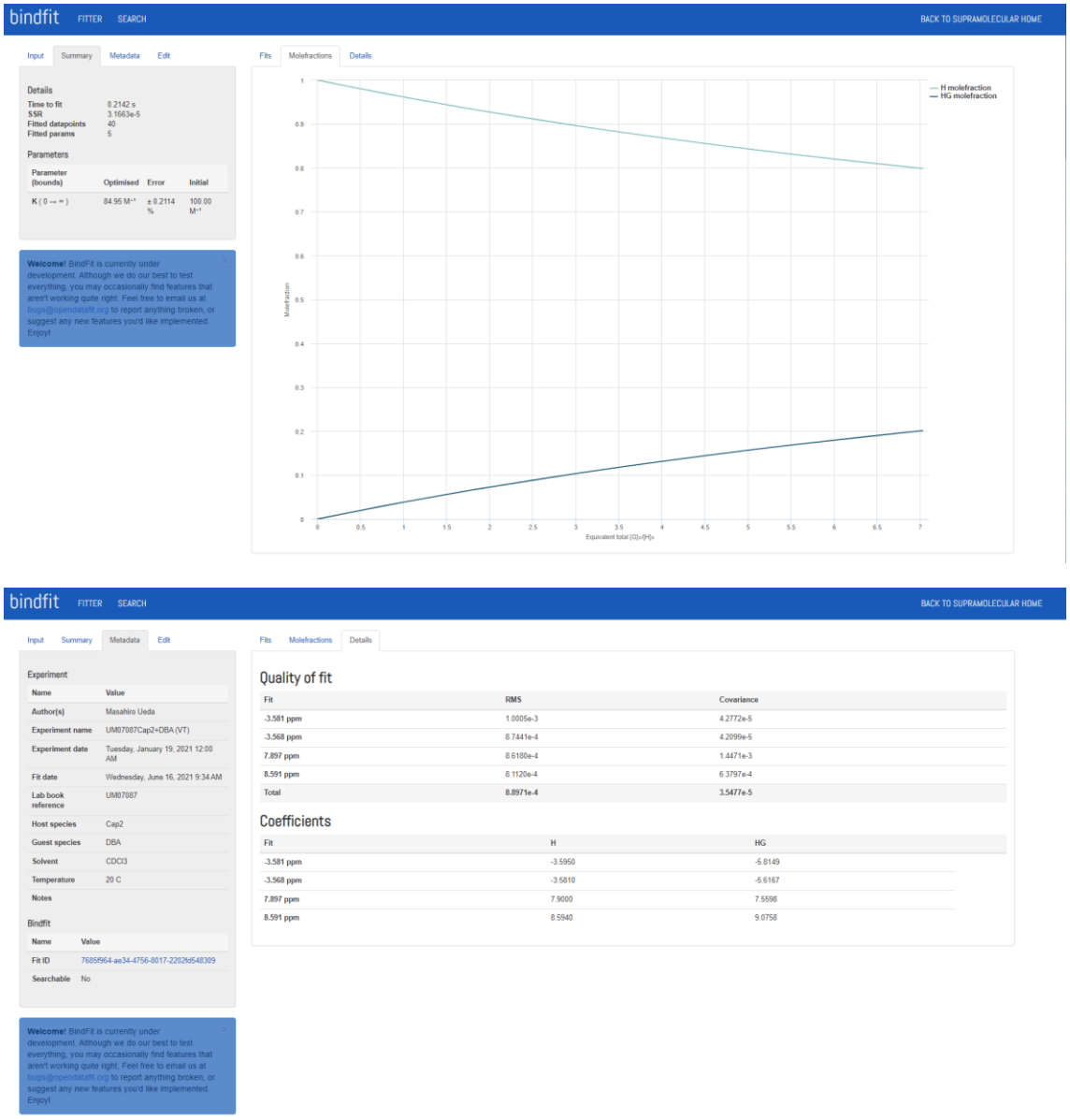
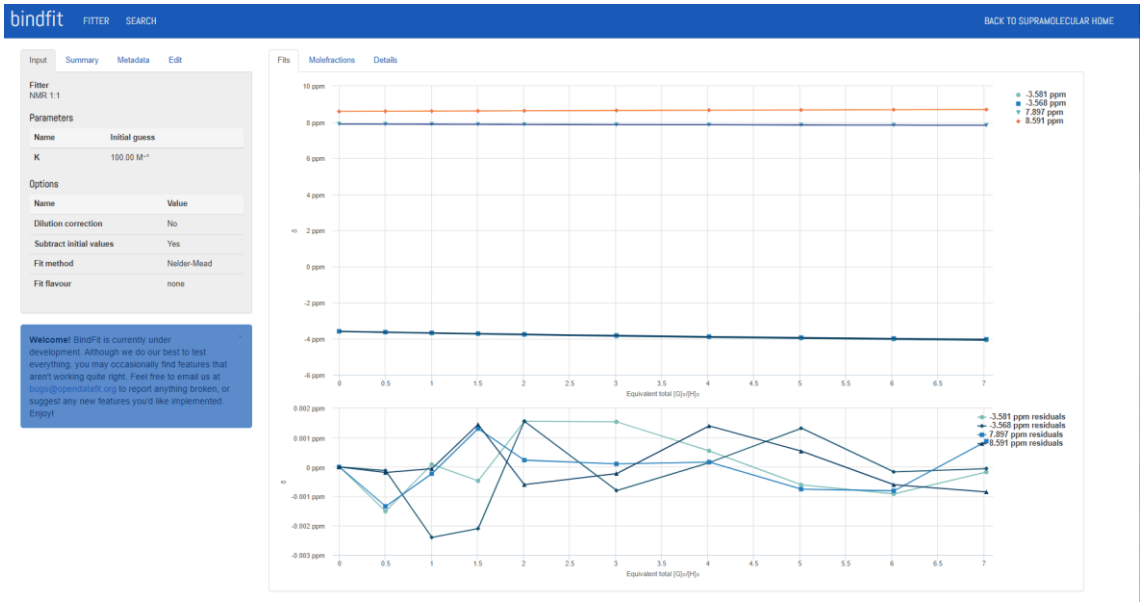
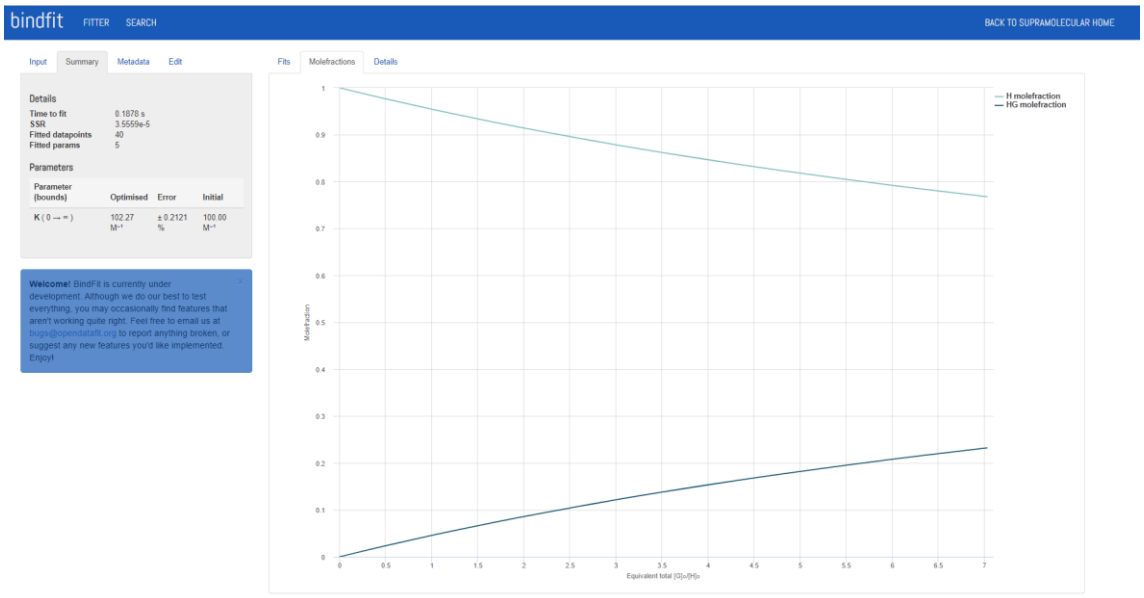


Figure S24b. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 20 ℃.


bindfit
FITTER
SEARCH
BACK TO SUPRAMOLECULAR HOME
Input
Summary
Metadata
Edit
Fitter
NMR 1:1
Parameters
Name
Initial guess
K
100.00 M⁻¹
Options
Name
Value
Dilution correction
No
Subtract initial values
Yes
Fit method
Nelder-Mead
Fit flavour
none
Welcome! BindFit is currently under development. Although we do our best to test everything, you may occasionally find features that aren't working quite right. Feel free to email us at bugs@opendatafit.org to report anything broken, or suggest any new features you'd like implemented. Enjoy!
Fits
Molefractions
Details
-3.581 ppm
-3.568 ppm
7.897 ppm
8.591 ppm
Equivalent total [G]₀/[H]₀
-3.581 ppm residuals
-3.568 ppm residuals
7.897 ppm residuals
8.591 ppm residuals


bindfit
FITTER
SEARCH
BACK TO SUPRAMOLECULAR HOME
Input
Summary
Metadata
Edit
Details
Time to fit
0.1878 s
SSR
3.5559e-5
Fitted datapoints
40
Fitted params
5
Parameters
Parameter (bounds)
Optimised
Error
Initial
K (0 → ∞)
102.27 M⁻¹
± 0.2121 %
100.00 M⁻¹
Welcome! BindFit is currently under development. Although we do our best to test everything, you may occasionally find features that aren't working quite right. Feel free to email us at bugs@opendatafit.org to report anything broken, or suggest any new features you'd like implemented. Enjoy!
Fits
Molefractions
Details
H molefraction
HG molefraction
MoleFraction
Equivalent total [G]₀/[H]₀

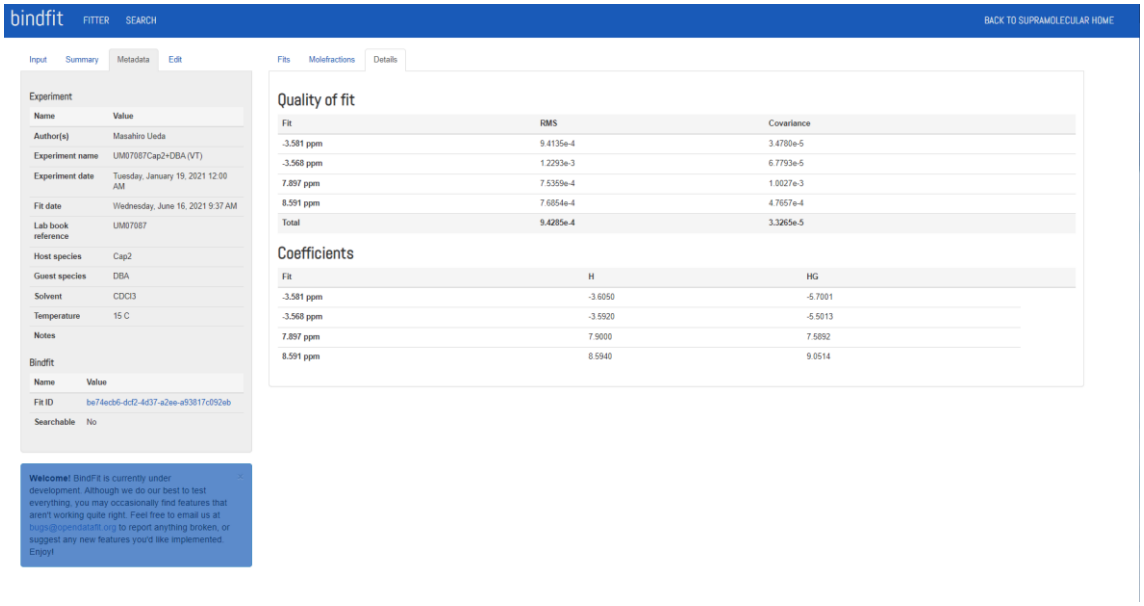


Figure S24c. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 15 °C.

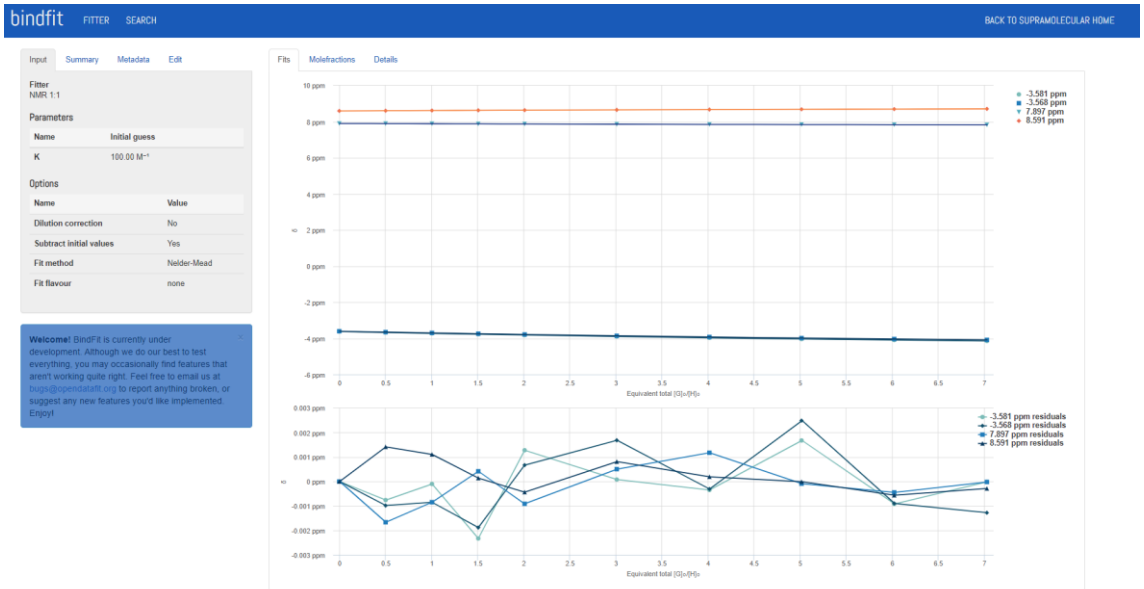
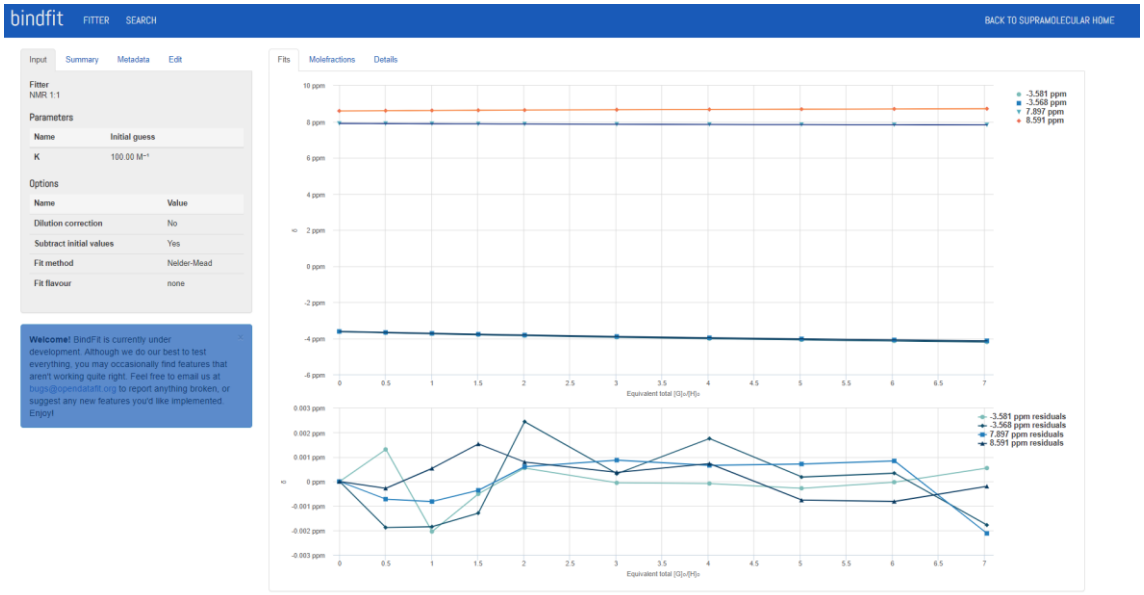
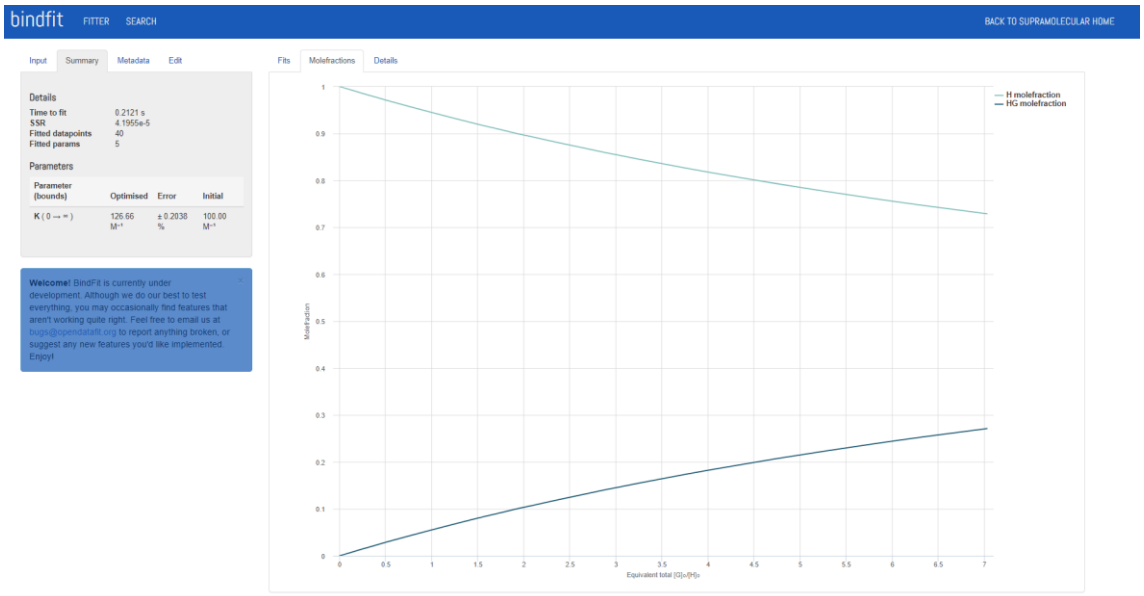


Figure S24d. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 10 °C.


bindfit
FITTER
SEARCH
BACK TO SUPRAMOLECULAR HOME
Input
Summary
Metadata
Edit
Fitter
NMR 1:1
Parameters
Name
Initial guess
K
100.00 M⁻¹
Options
Name
Value
Dilution correction
No
Subtract initial values
Yes
Fit method
Nelder-Mead
Fit flavour
none
Welcome! BindFit is currently under development. Although we do our best to test everything, you may occasionally find features that aren't working quite right. Feel free to email us at bugs@opendatafit.org to report anything broken, or suggest any new features you'd like implemented. Enjoy!
Fits
Molefractions
Details
-3.581 ppm
-3.568 ppm
7.897 ppm
8.591 ppm
δ
Equivalent total [G]ₒ/[H]ₒ
-3.581 ppm residuals
-3.568 ppm residuals
7.897 ppm residuals
8.591 ppm residuals


bindfit
FITTER
SEARCH
BACK TO SUPRAMOLECULAR HOME
Input
Summary
Metadata
Edit
Details
Time to fit 0.2121 s
SSR 4.1955e-5
Fitted datapoints 40
Fitted params 5
Parameters
Parameter (bounds)
Optimised
Error
Initial
K (0 → ∞)
126.66 M⁻¹
± 0.2038 %
100.00 M⁻¹
Welcome! BindFit is currently under development. Although we do our best to test everything, you may occasionally find features that aren't working quite right. Feel free to email us at bugs@opendatafit.org to report anything broken, or suggest any new features you'd like implemented. Enjoy!
Fits
Molefractions
Details
H molefraction
HG molefraction
MoleFraction
Equivalent total [G]ₒ/[H]ₒ

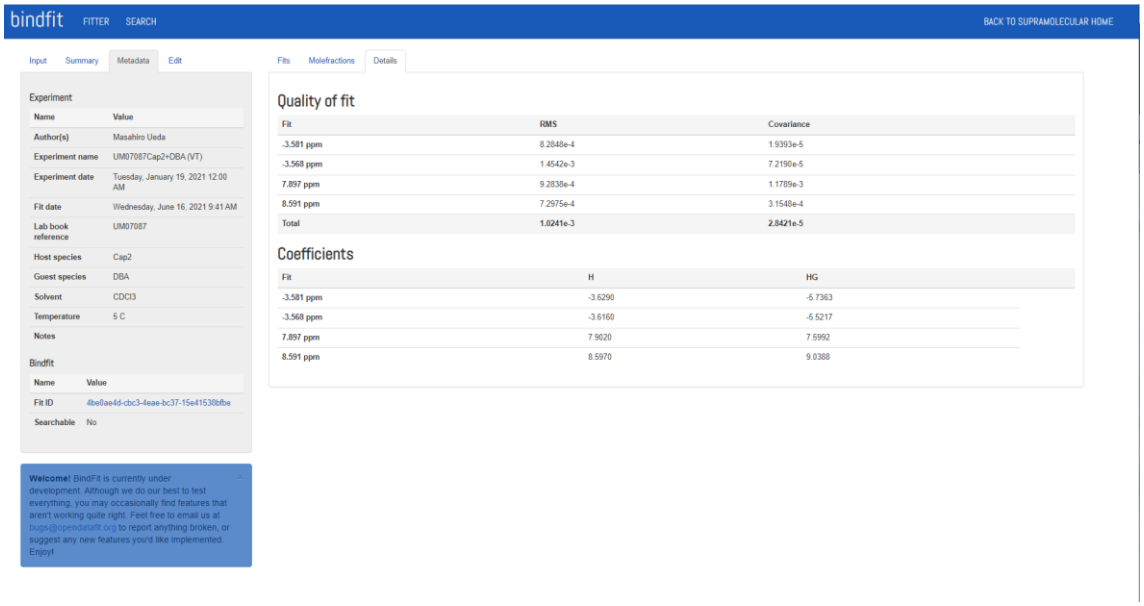
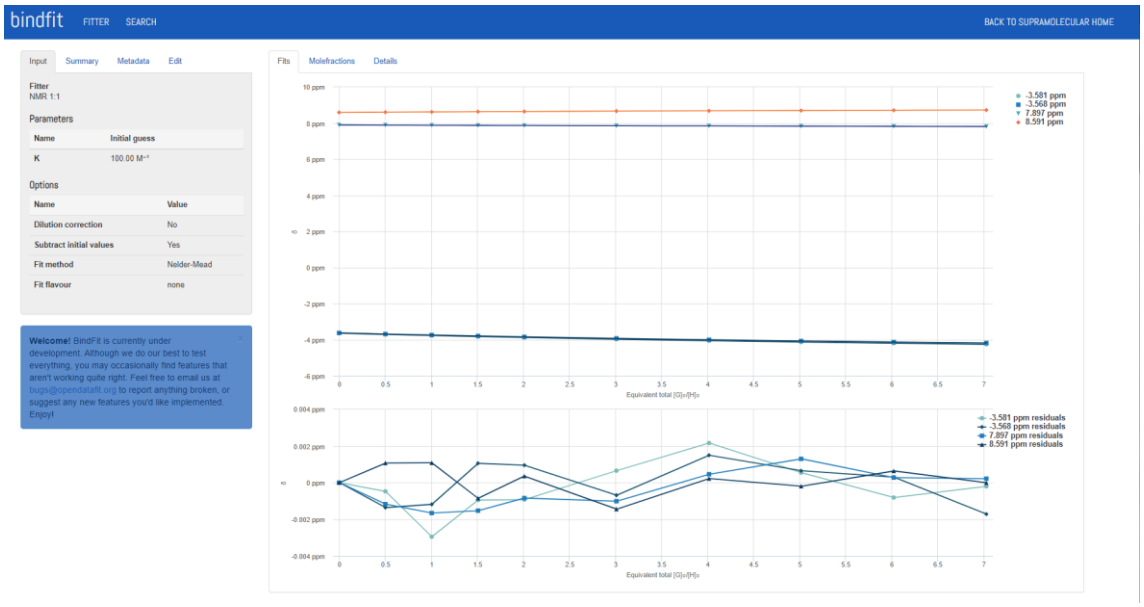
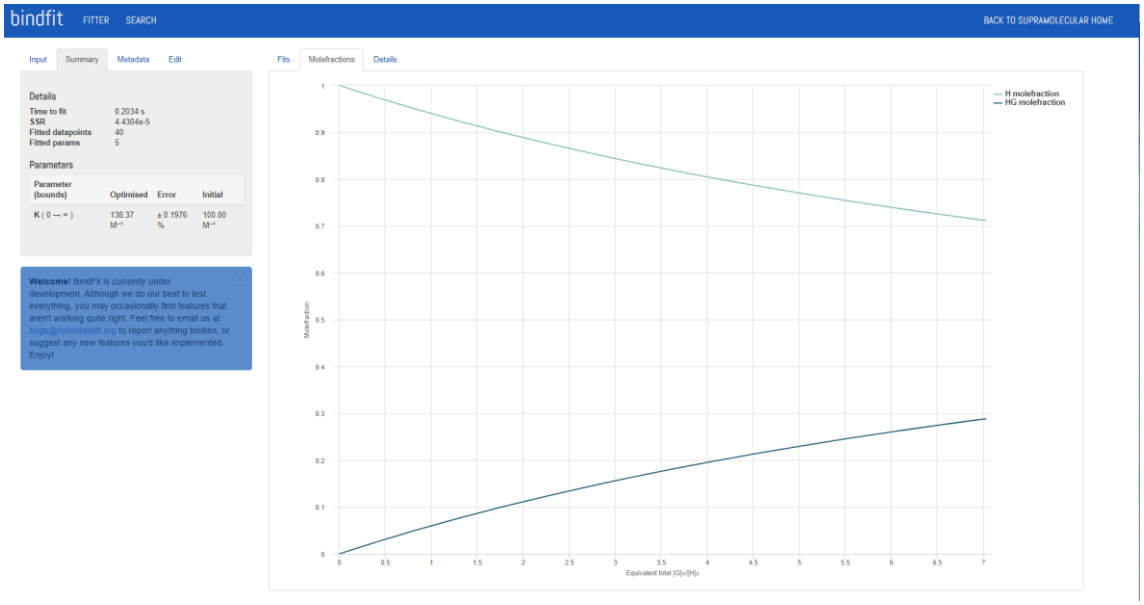


Figure S24e. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 5 °C.





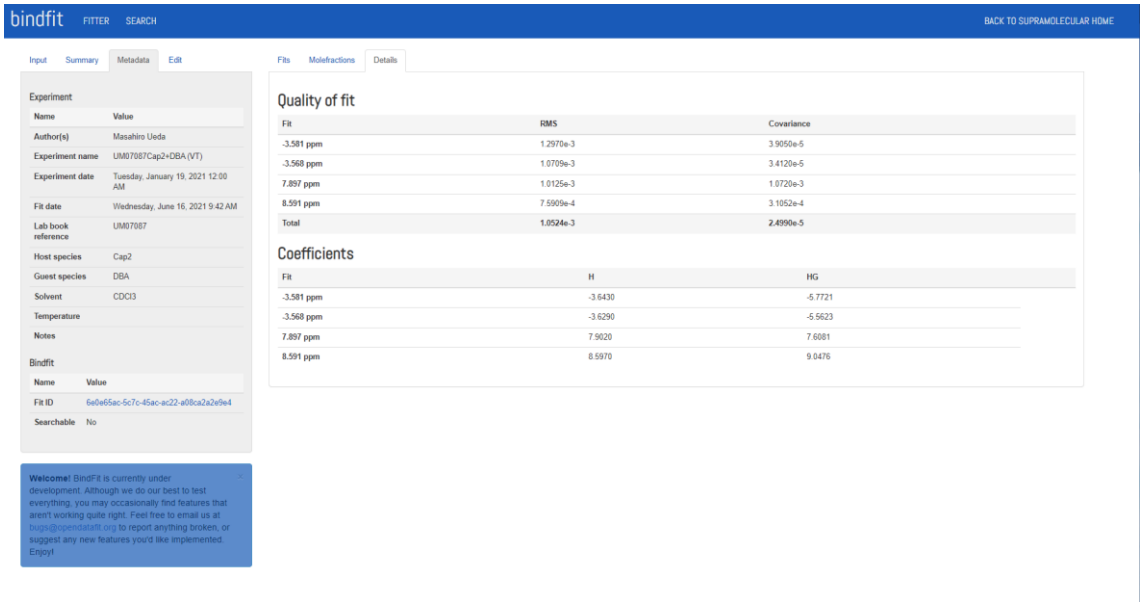


Figure S24f. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 0 °C.

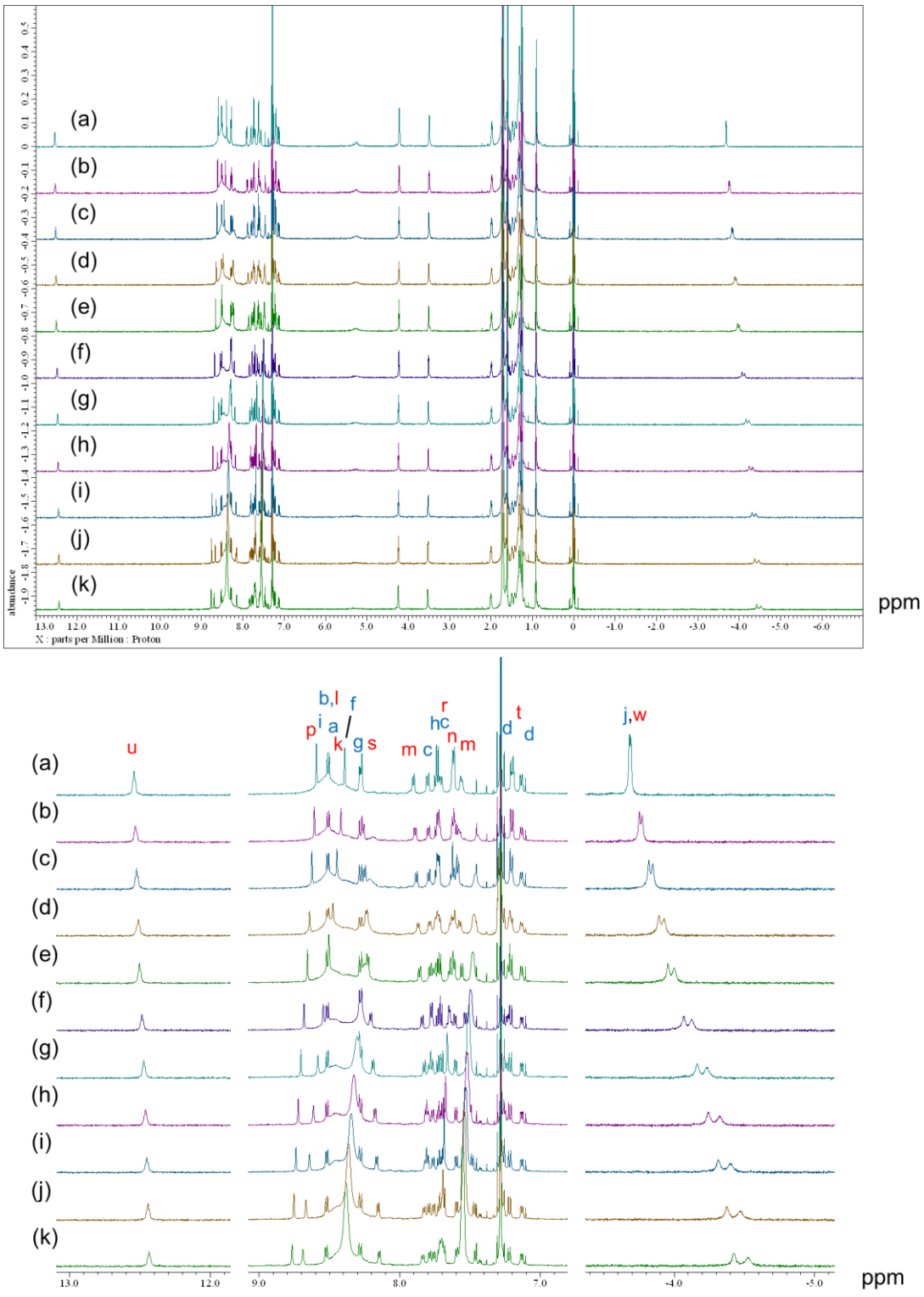


Figure S25a. ^{1}H NMR spectra (600 MHz, $CDCl_3$, −20 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

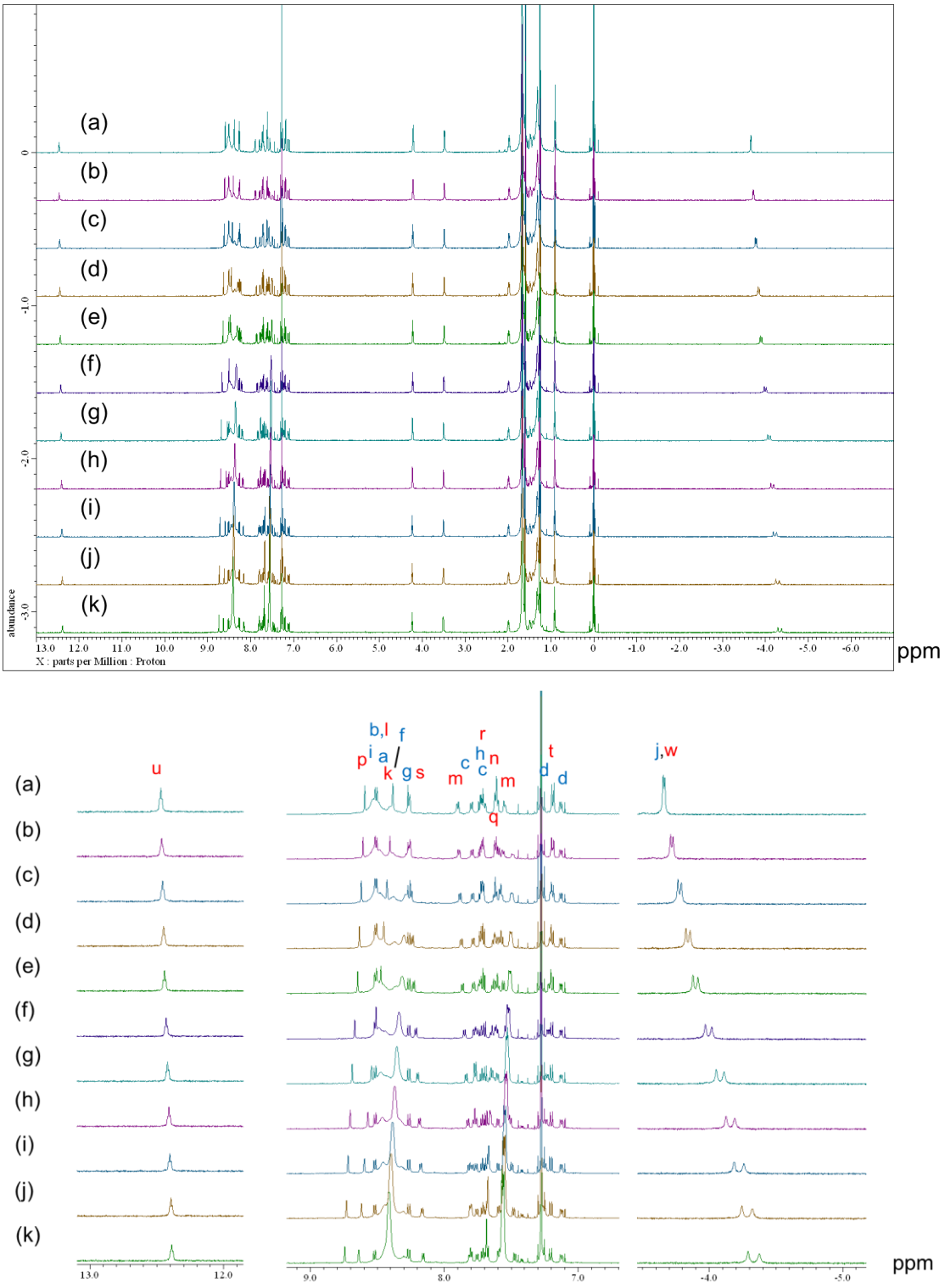


Figure S25b. ^{1}H NMR spectra (600 MHz, $CDCl_3$, −10 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

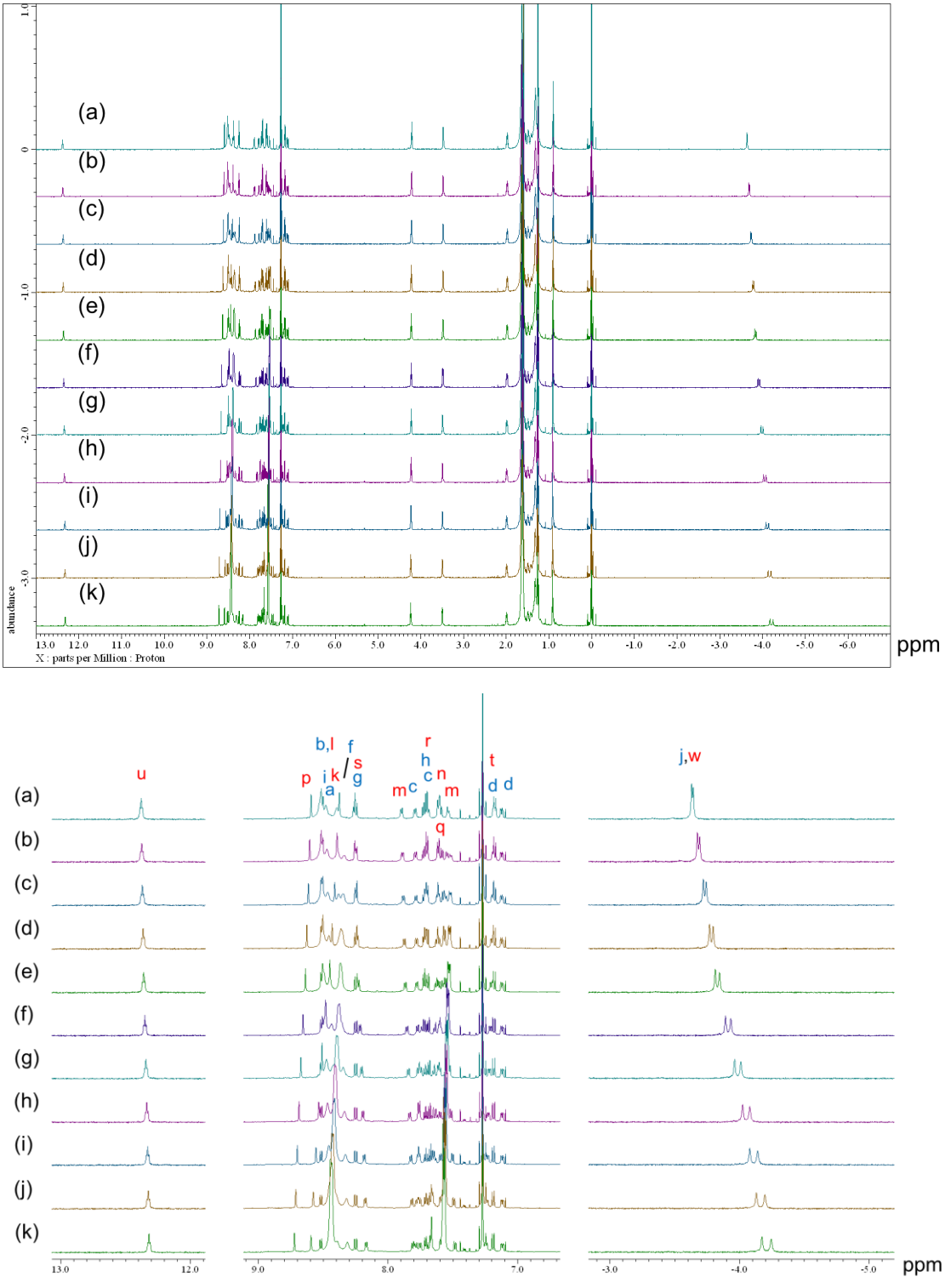


Figure S25c. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 0 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

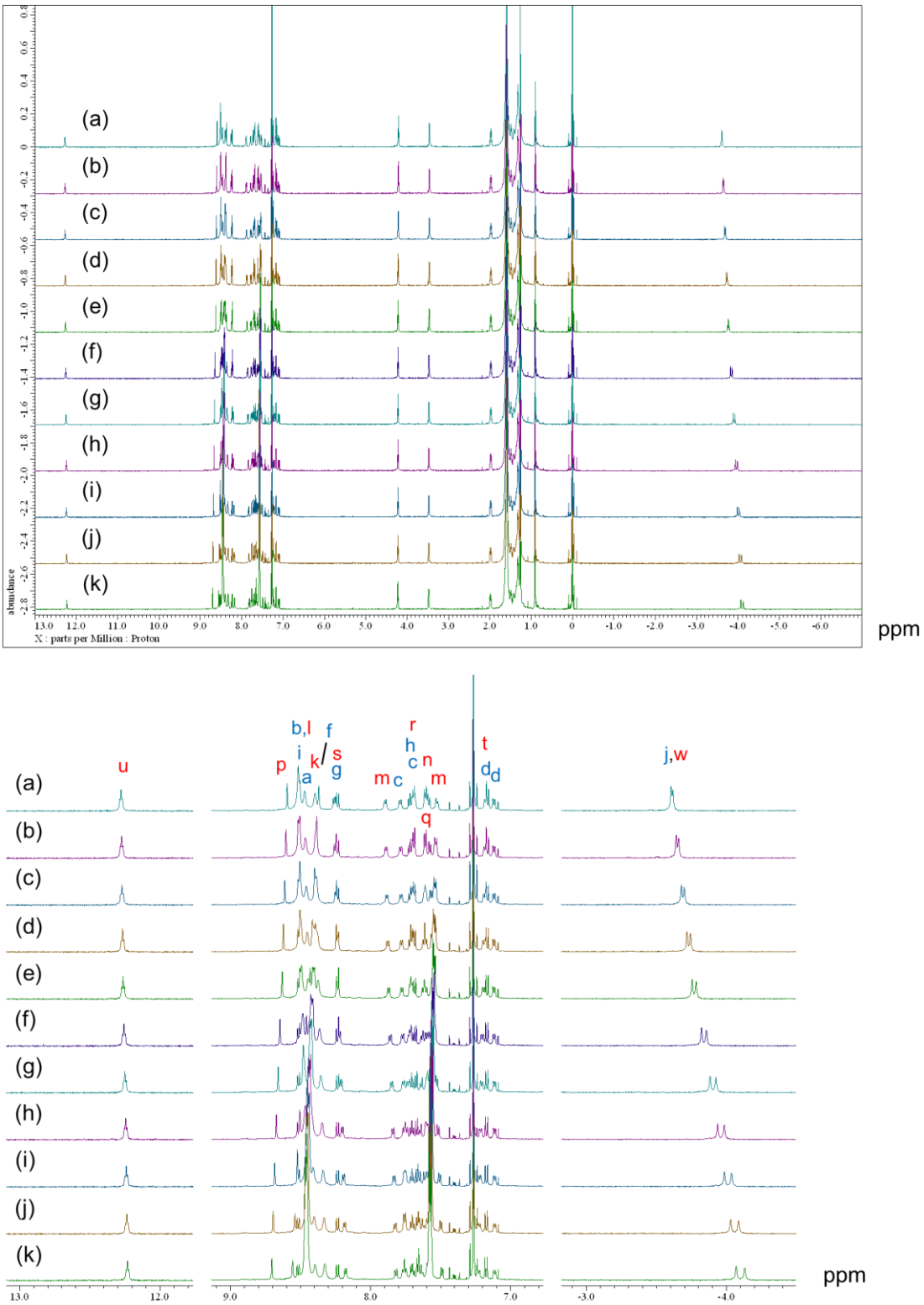


Figure S25d. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 10 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

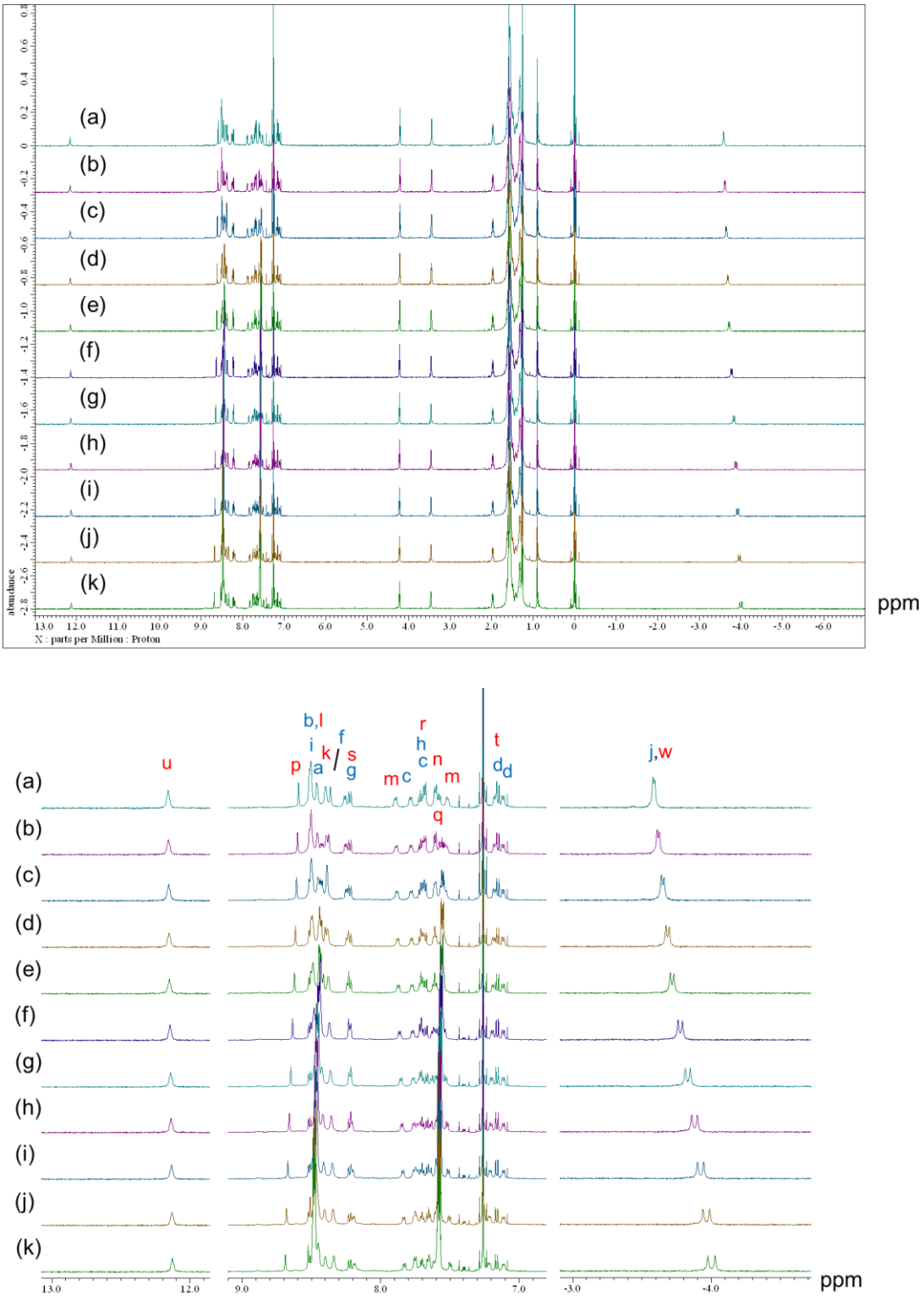


Figure S25e. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 20 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

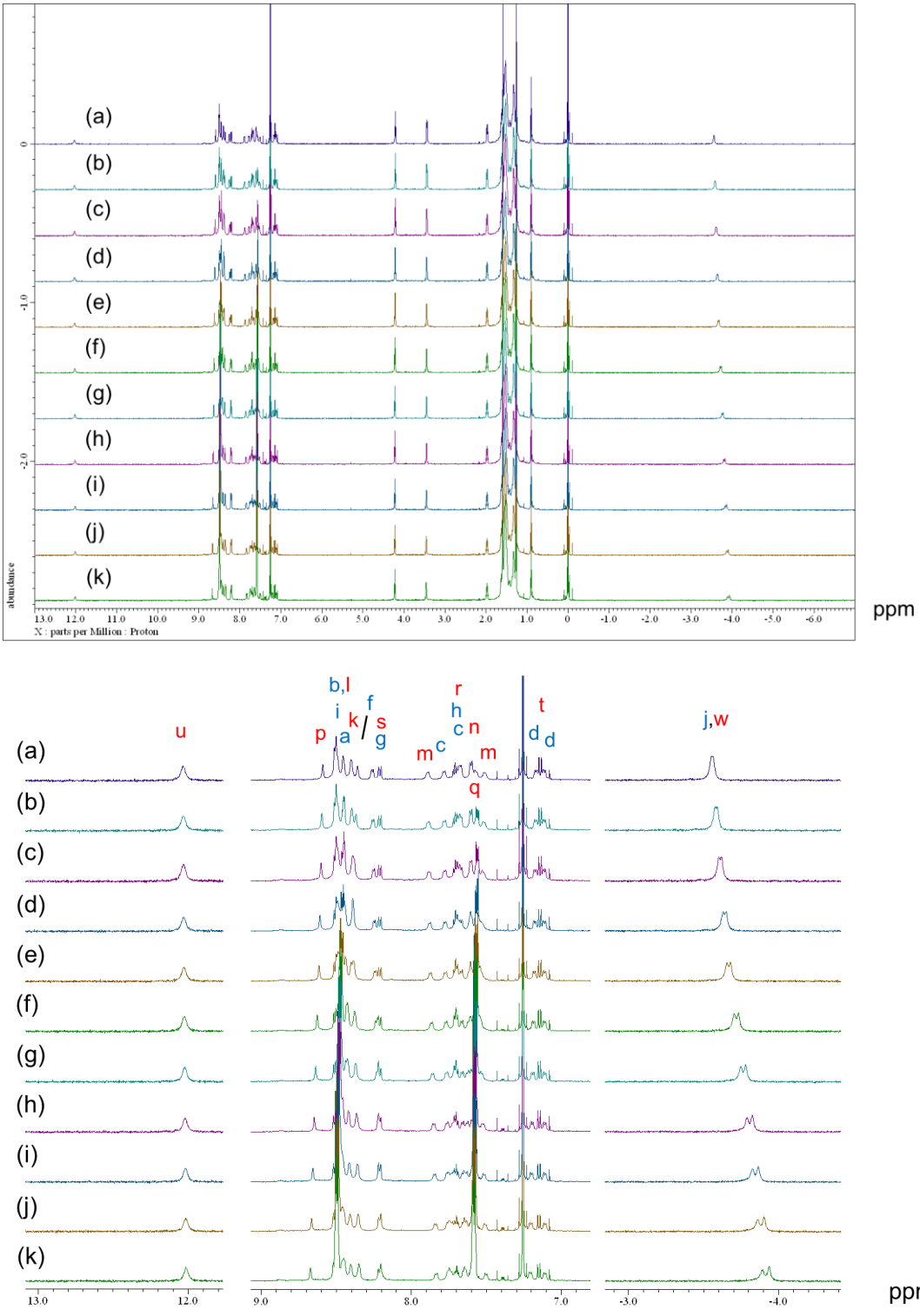


Figure S25f. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 30 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

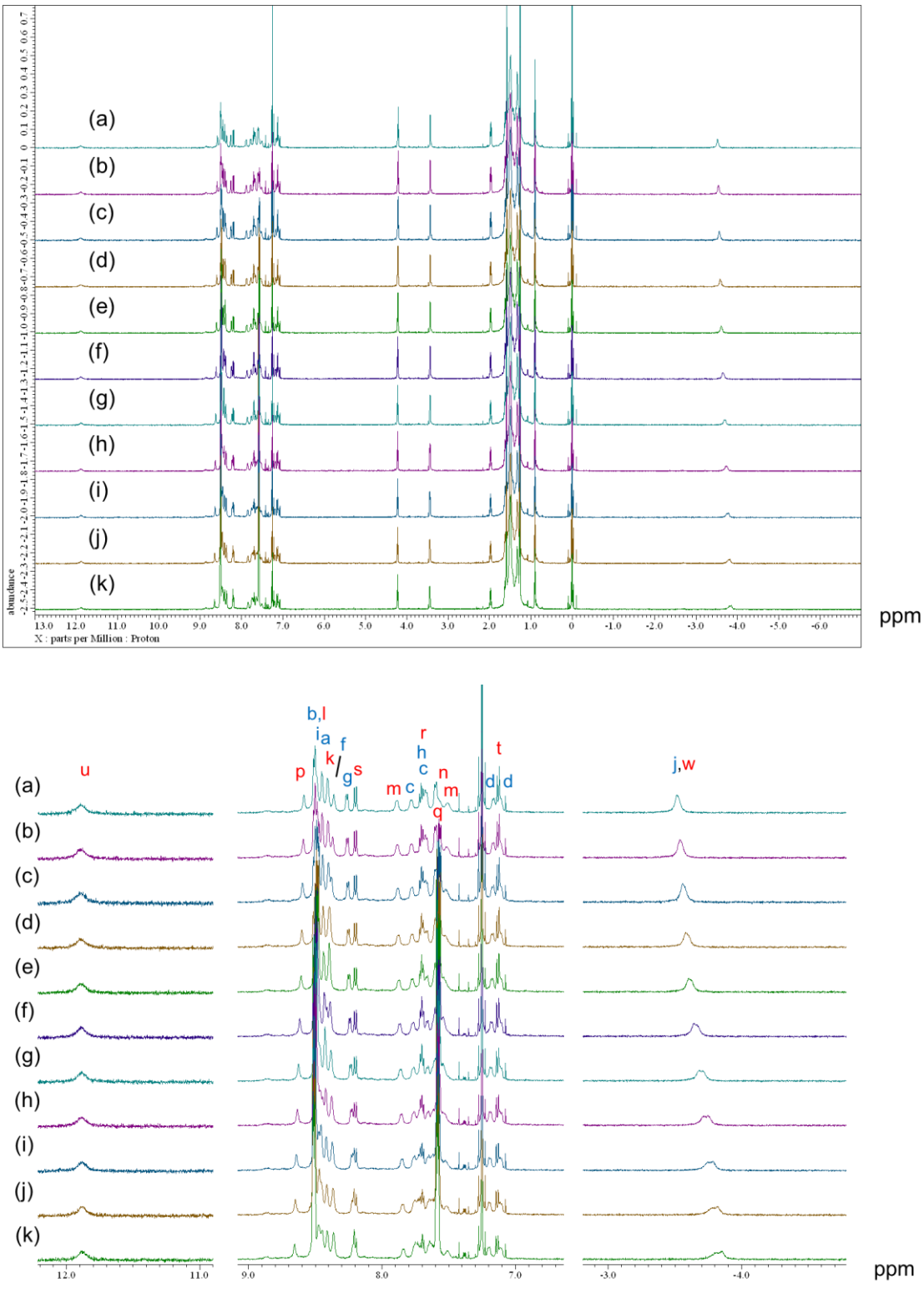


Figure S25g. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 40 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

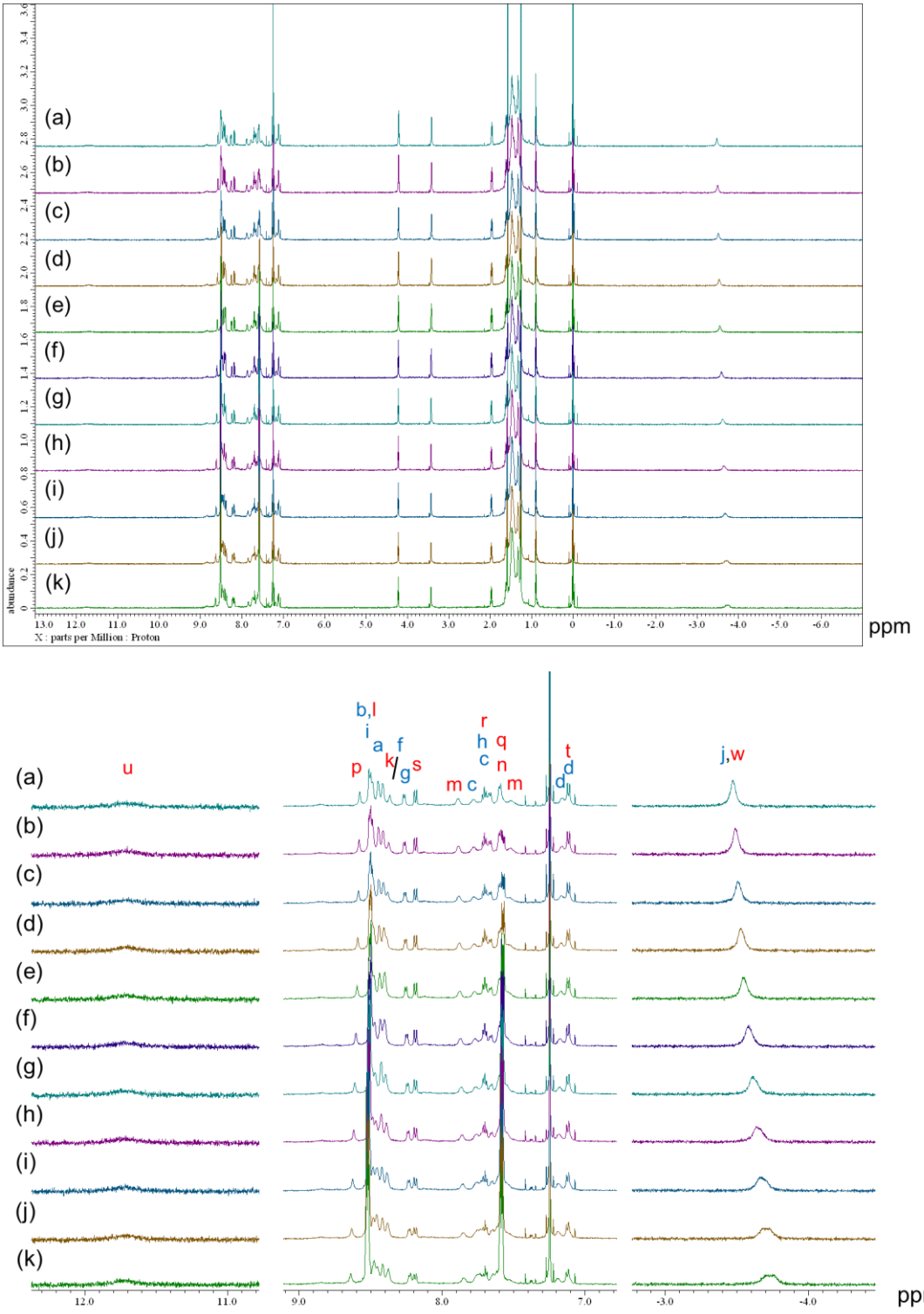


Figure S25h. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 50 °C) of **Cap2** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.40 eq, (c) 0.80 eq, (d) 1.2 eq, (e) 1.6 eq, (f) 2.5 eq, (g) 3.3 eq, (h) 4.2 eq, (i) 5.1 eq, (j) 6.0 eq, (k) 6.9 eq.

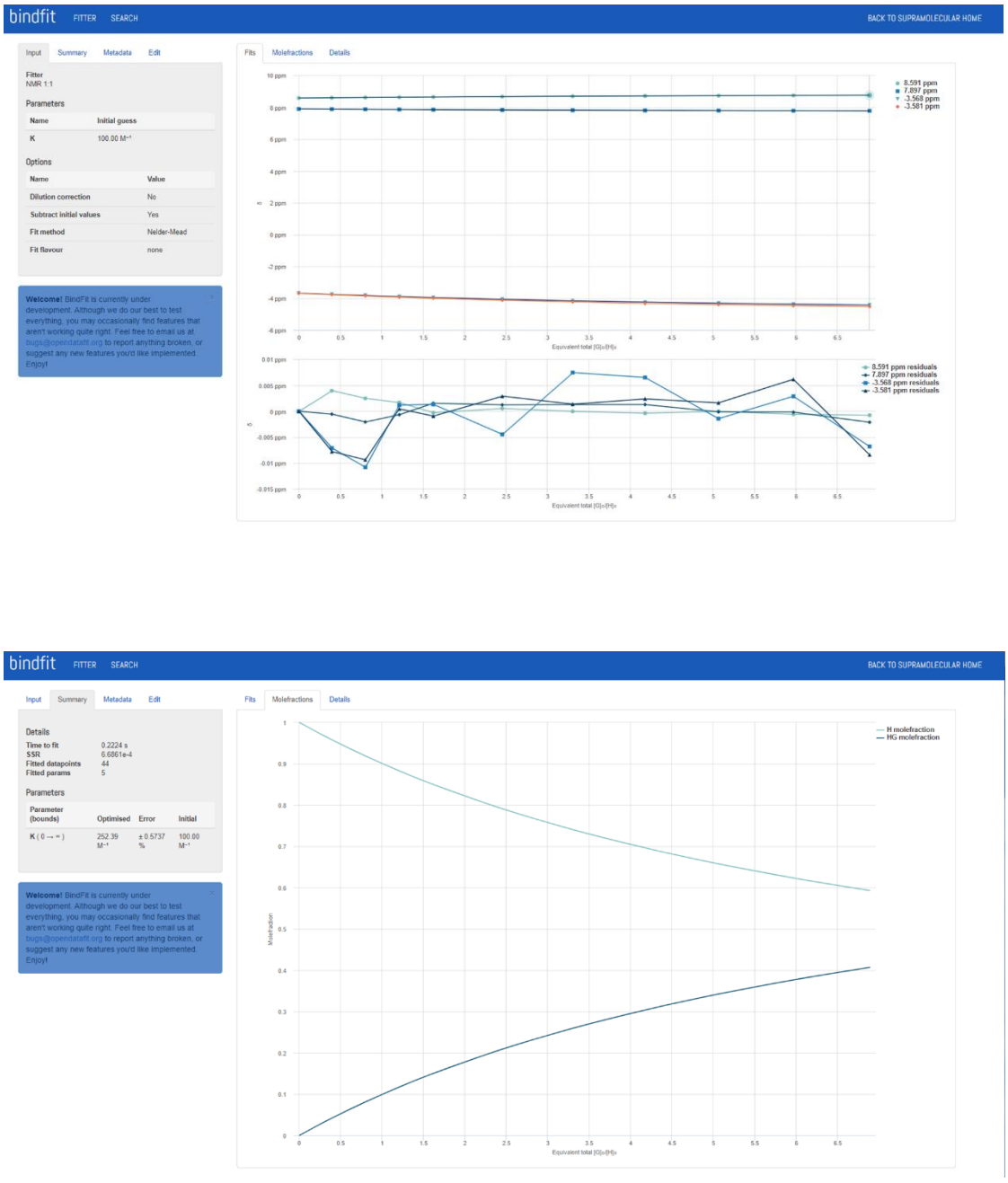


Figure S26a. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at −20 °C.

Figure S26b. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at −10 °C.

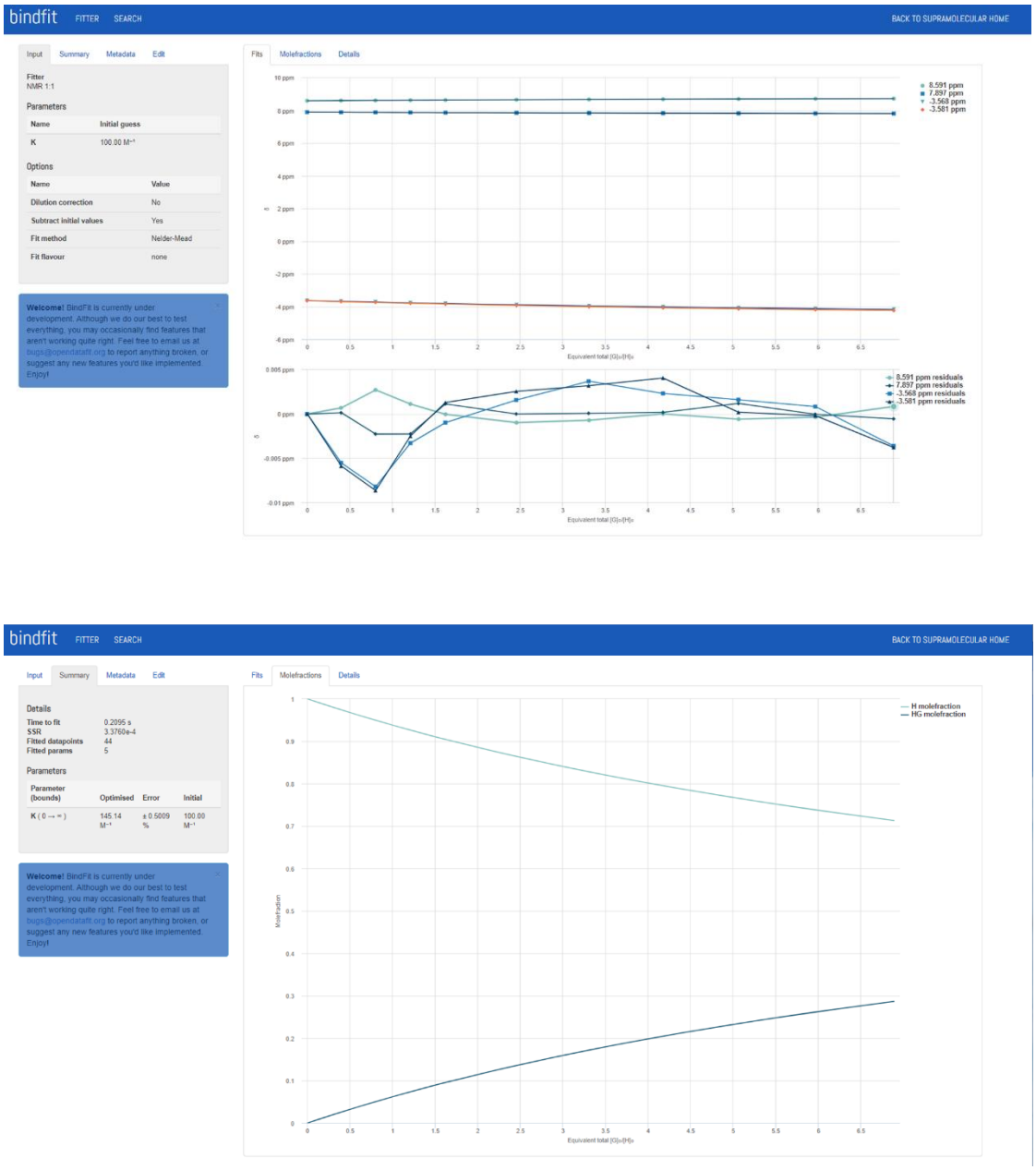


Figure S26c. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 0 °C.

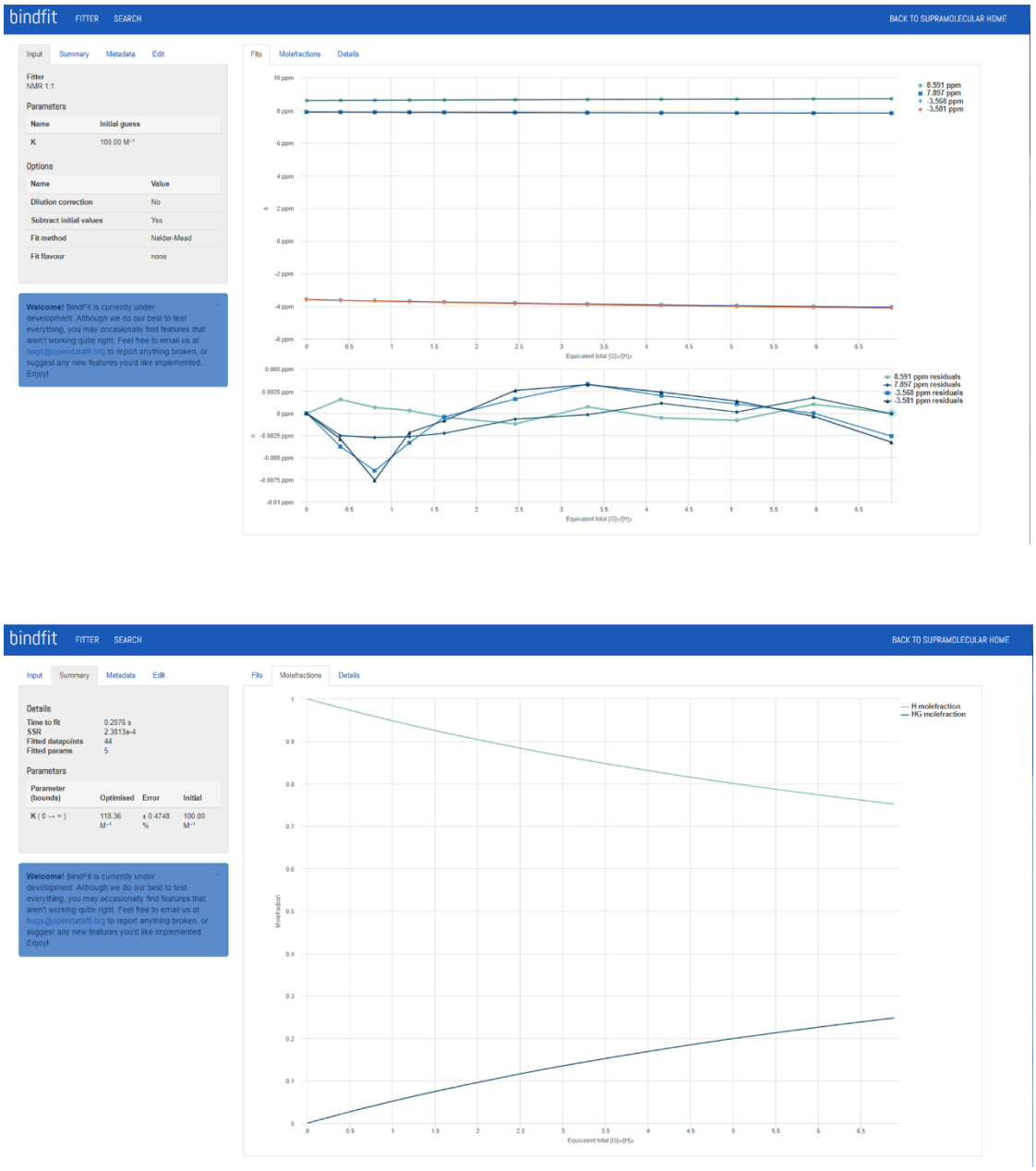


Figure S26d. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 10 °C.

Figure S26e. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 20 °C.

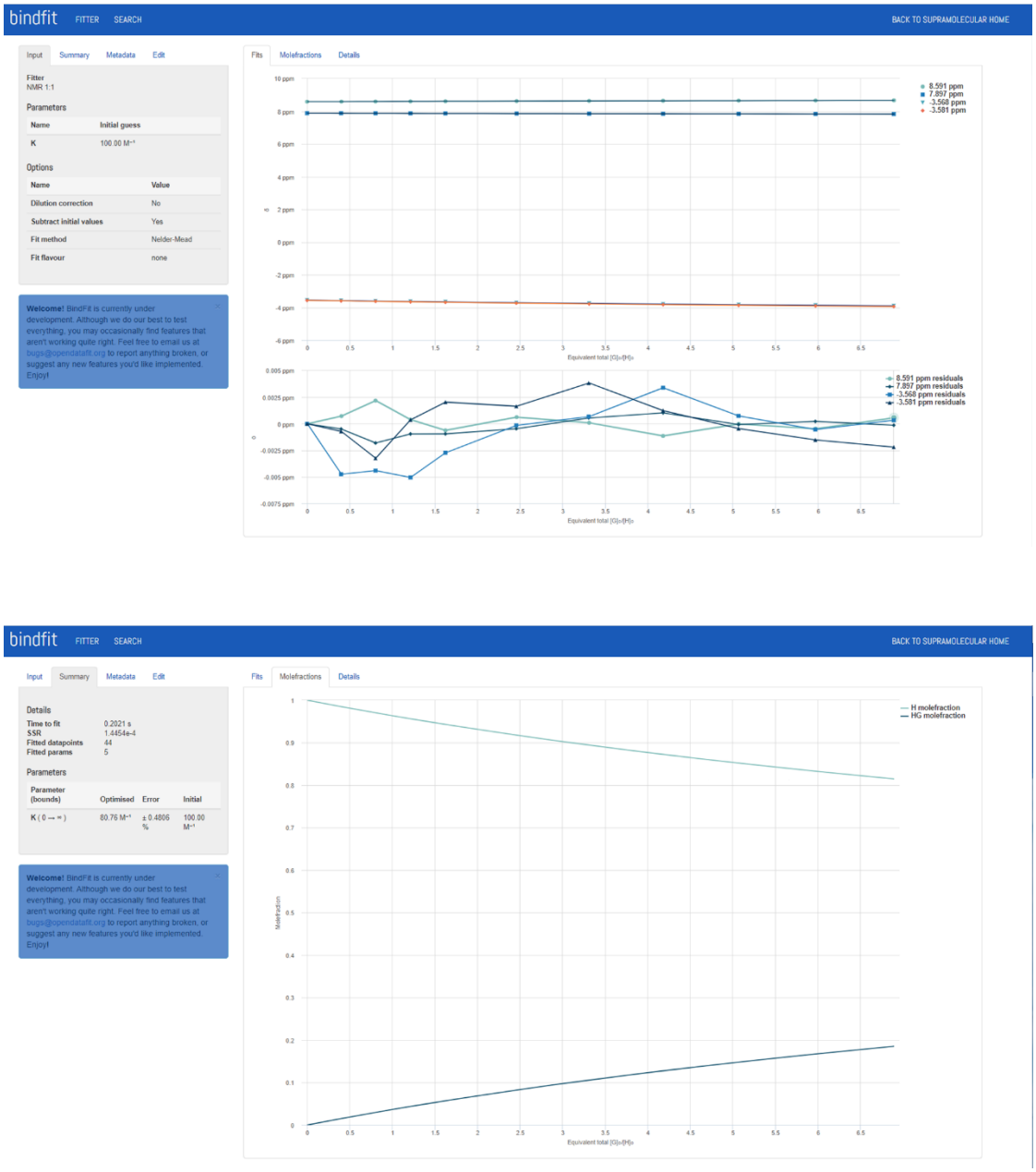


Figure S26f. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 30 °C.

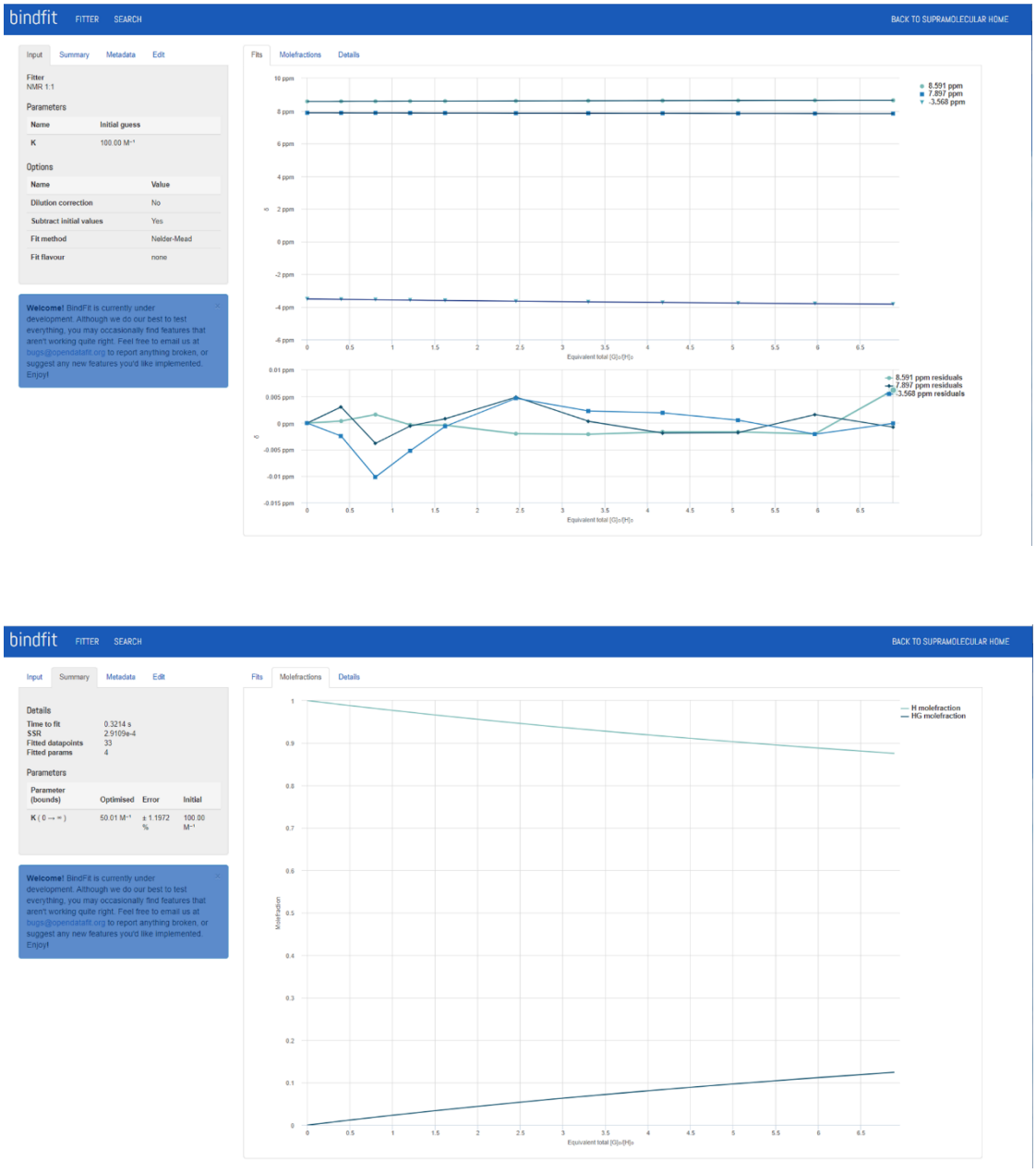


Figure S26g. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 40 °C.

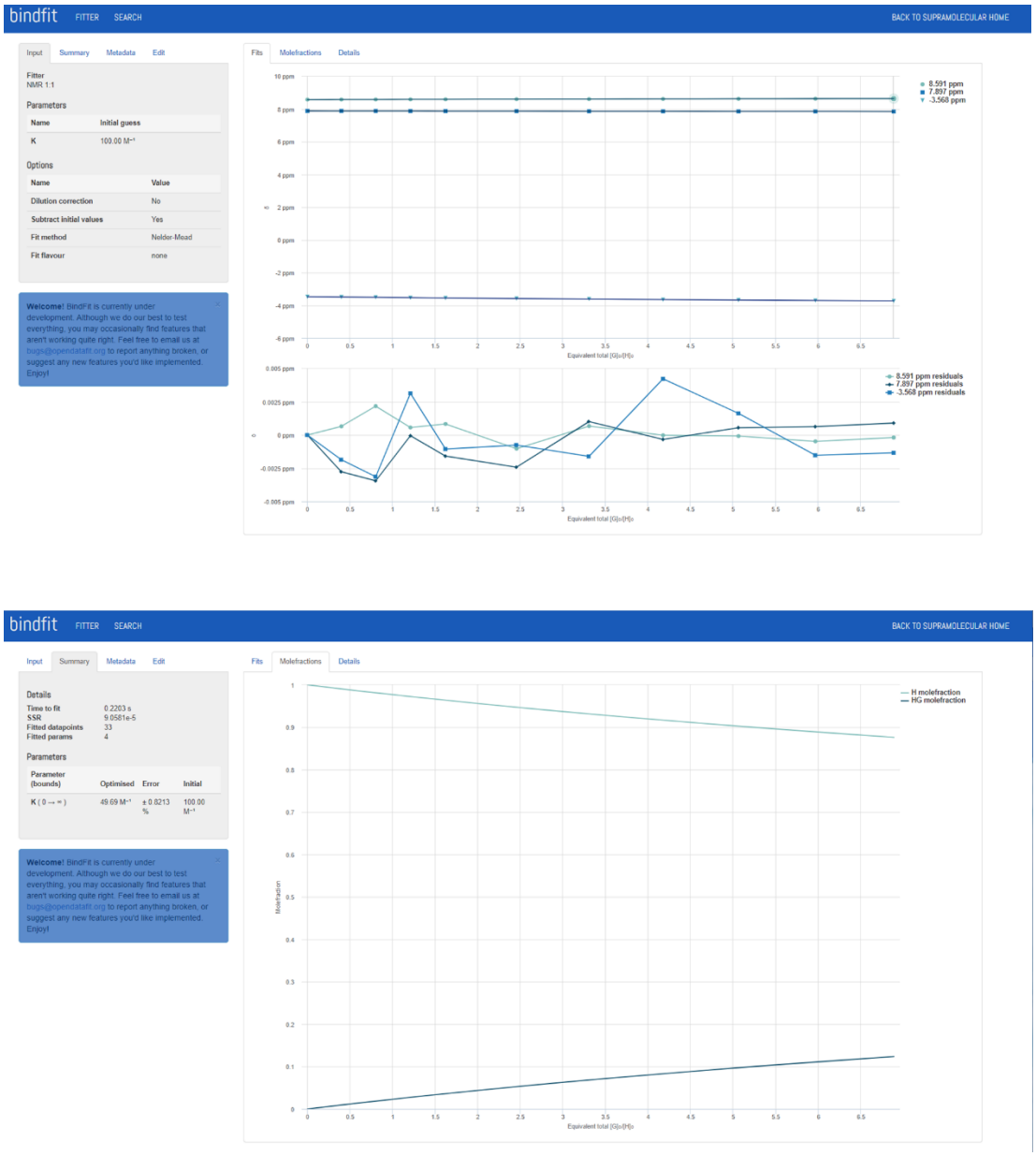


Figure S26h. Determination of the association constants *K*a of the dimer **Cap2** with the guest **G7** at 50 °C.

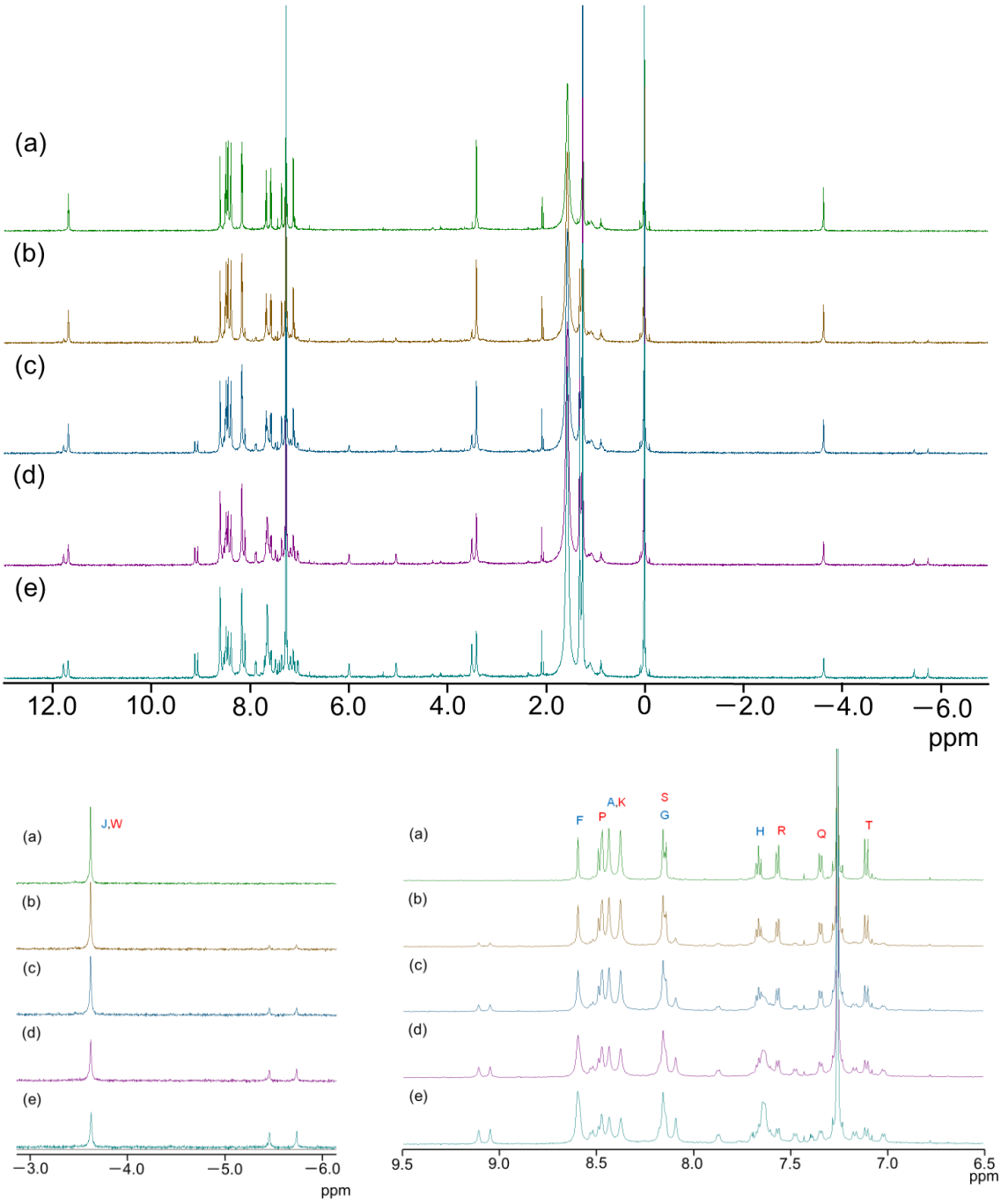


Figure S27a. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 25 °C) of the dimer **Cap4** (0.50 mM) (a) in the absence of 9,10-dibromoanthracene **G7** and in the presence of **G7** (b) 0.50 eq, (c) 1.0 eq, (d) 2.0 eq, (e) 3.0 eq. Fig. 8: Partial spectra of Figure S27a.

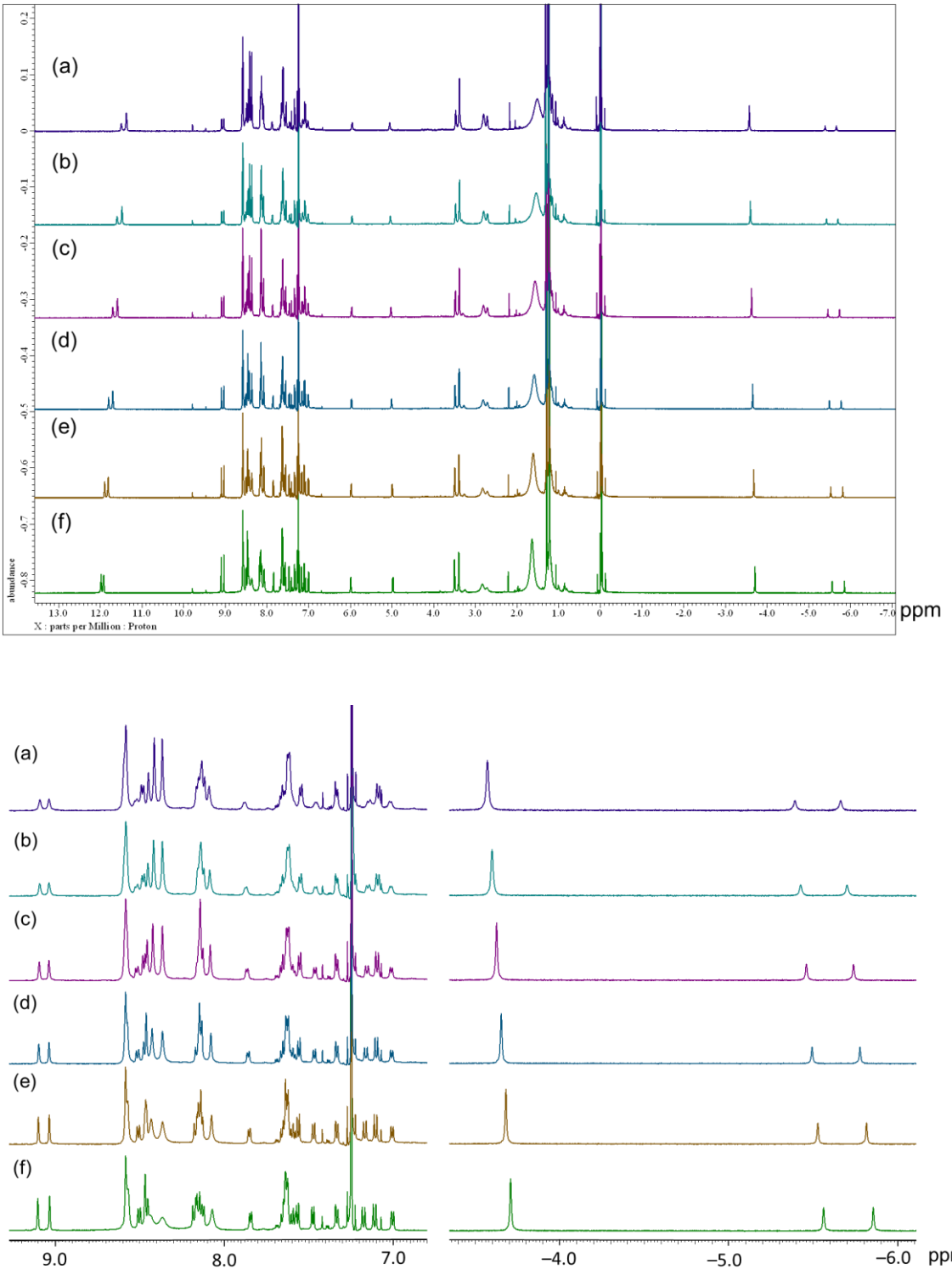


Figure S27b. ^{1}H NMR spectra (600 MHz, $CDCl_3$) of a mixture **Cap4** (0.50 mM) and 9,10-dibromoanthracene **G7** (1.0 mM) at (a) 50 ℃, (b) 40 ℃, (c) 30 ℃, (d) 20 ℃, (e) 10 ℃, and (f) 0 ℃.

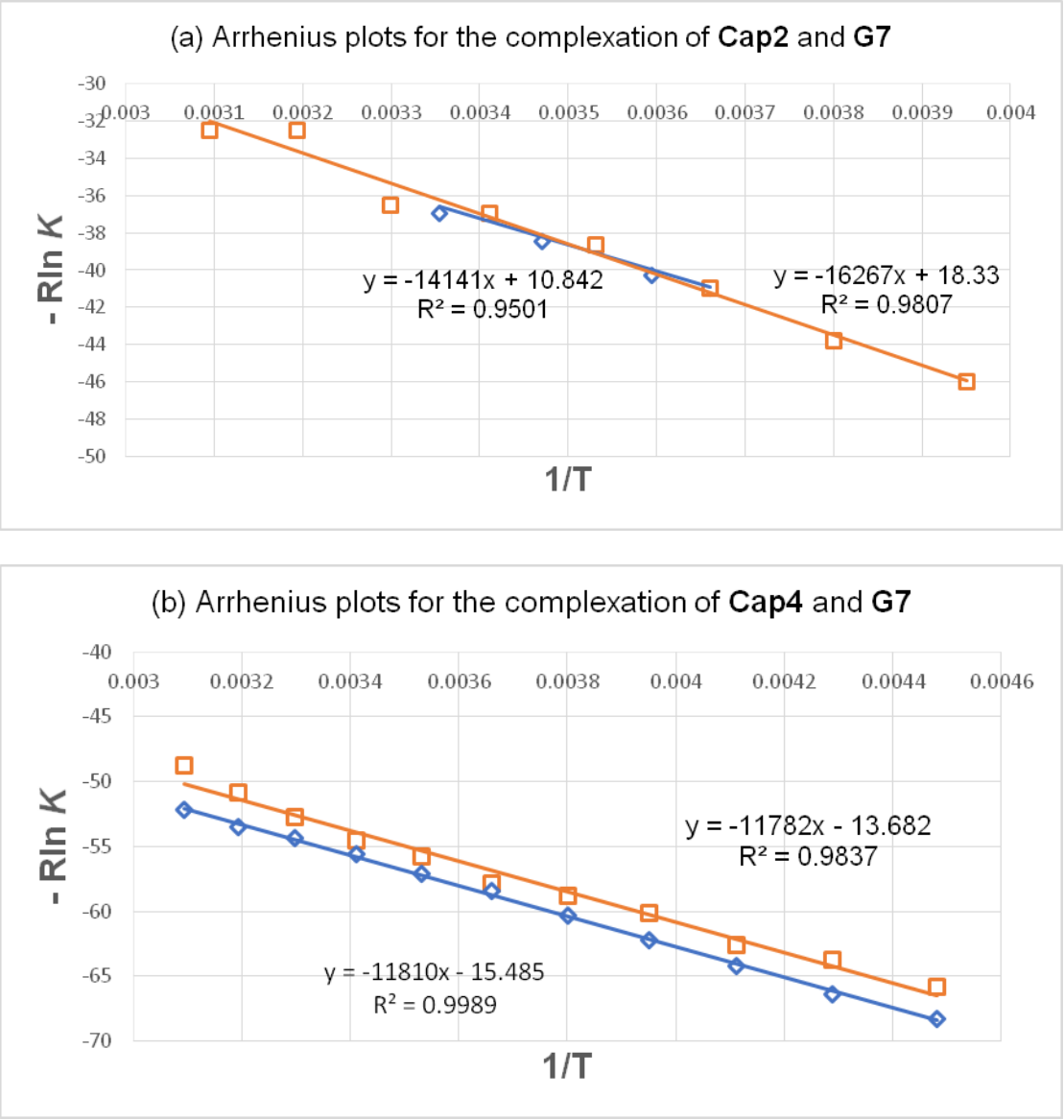


Figure S28. Arrhenius plots for the complexation of the dimers **Cap2** and **Cap4** with 9,10-dibromoanthracene **G7**.

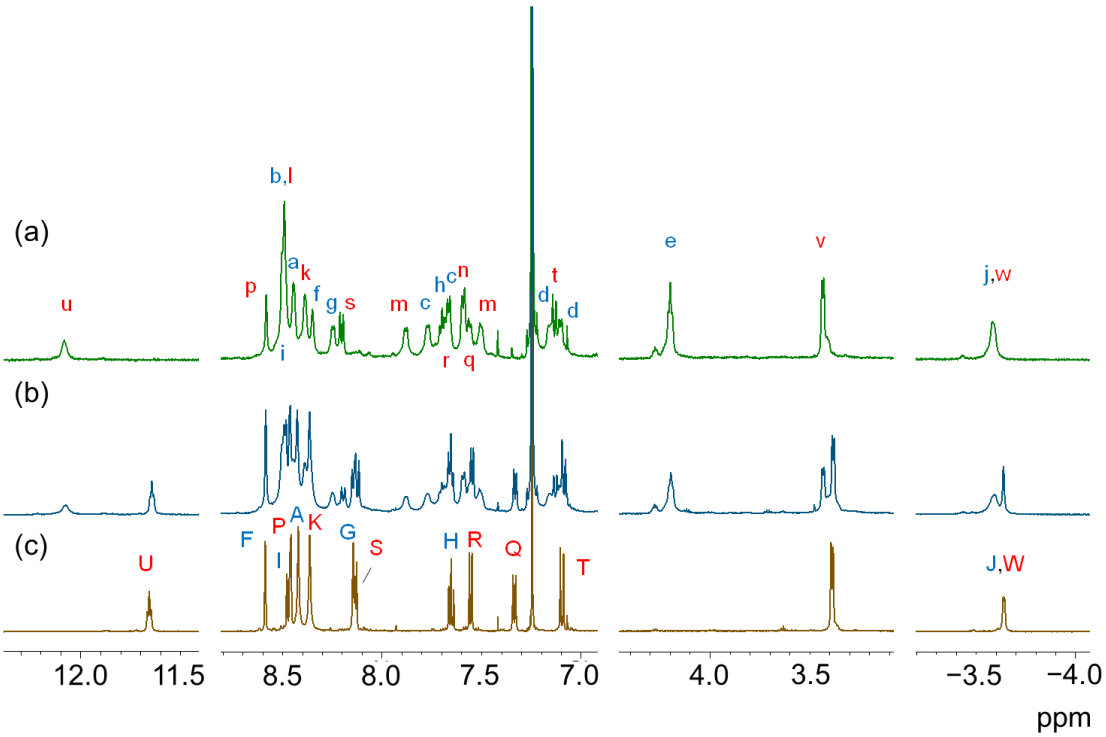


Figure S29. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 25 °C) of equimolar mixtures of porphyrin derivatives (0.50 mM). (a) **P1** and **P2b** (**Cap2**), (b) **P1**, **P2b**, **P3**, and **P4b**, (c) **P3** and **P4b** (**Cap4**). Fig. 9: Partial spectra of Figure S29.

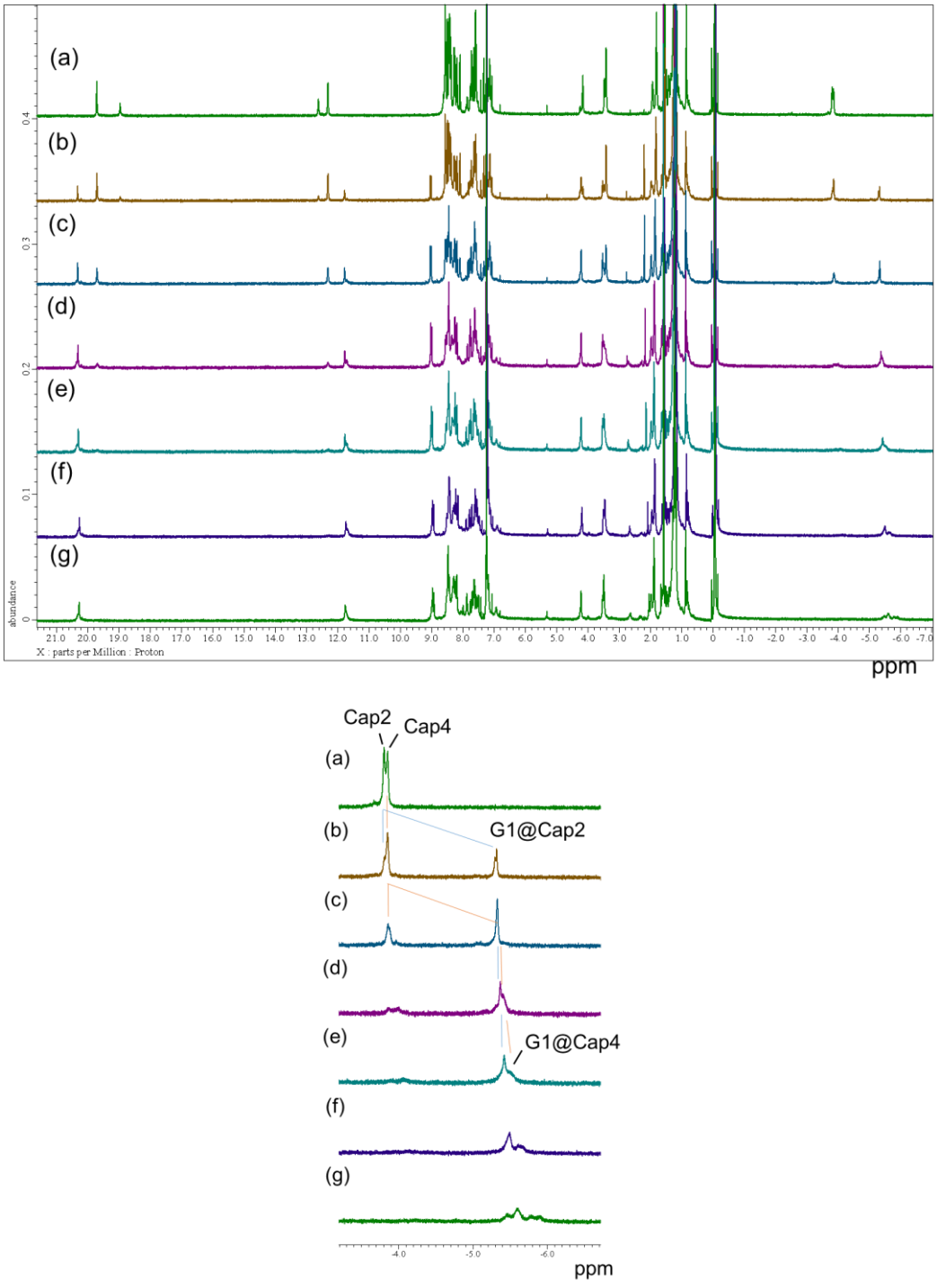


Figure S30a. ^{1}H NMR (600 MHz, $CDCl_3$, –50 °C) spectra of mixtures of **Cap2** (0.5 mM), **Cap4** (0.5 mM), and **G1** (0–2.0 mM). (a) **Cap2** and **Cap4**, (b) **Cap2**, **Cap4**, and **G1** (0.25 mM), (c) **Cap2**, **Cap4**, and **G1** (0.50 mM), (d) **Cap2**, **Cap4**, and **G1** (0.75 mM), (e) **Cap2**, **Cap4**, and **G1** (1.0 mM), (f) **Cap2**, **Cap4**, and **G1** (1.25 mM), (g) **Cap2**, **Cap4**, and **G1** (2.0 mM). Fig. 10: Partial spectra of Figure S30a.

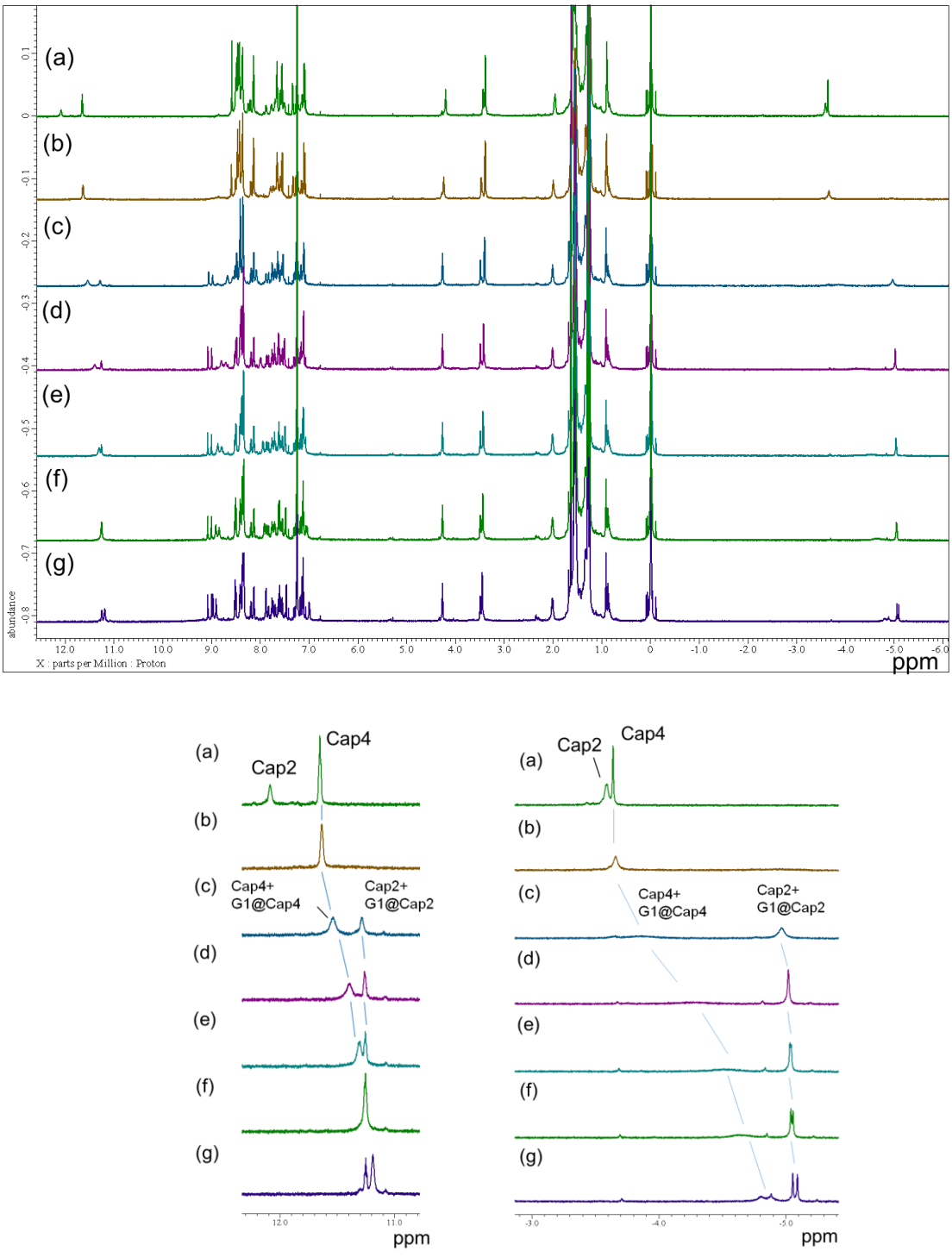


Figure S30b. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) spectra of mixtures of **Cap2** (0.5 mM), **Cap4** (0.5 mM), and **G1** (0–2.0 mM). (a) **Cap2** and **Cap4**, (b) **Cap2**, **Cap4**, and **G1** (0.25 mM), (c) **Cap2**, **Cap4**, and **G1** (0.50 mM), (d) **Cap2**, **Cap4**, and **G1** (0.75 mM), (e) **Cap2**, **Cap4**, and **G1** (1.0 mM), (f) **Cap2**, **Cap4**, and **G1** (1.25 mM), (g) **Cap2**, **Cap4**, and **G1** (2.0 mM).

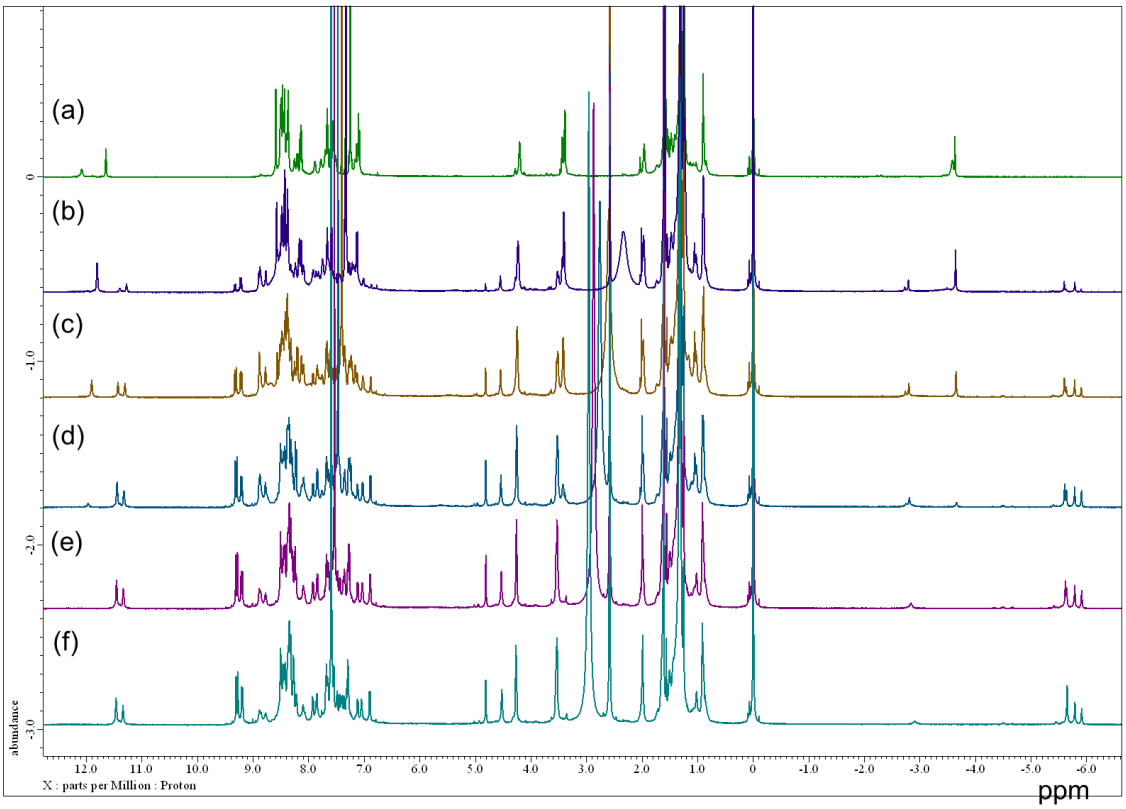
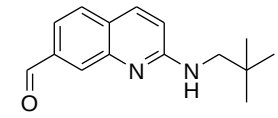


Figure S31. ^{1}H NMR spectra (600 MHz, 25 °C) of mixtures of **Cap2** (0.50 mM) and **Cap4** (0.50 mM), and **G6** (0–1.25 mM). (a) **Cap2** and **Cap4** in $CDCl_3$, (b) **Cap2**, **Cap4**, and **G6** (0.25 mM) in $CDCl_3$/DMSO-d_6 (96:4), (c) **Cap2**, **Cap4**, and **G6** (0.50 mM) in $CDCl_3$/DMSO-d_6 (92:8), (d), **Cap2**, **Cap4**, and **G6** (0.75 mM) in $CDCl_3$/DMSO-d_6 (89:11), (e) **Cap2**, **Cap4**, and **G6** (1.00 mM) in $CDCl_3$/DMSO-d_6 (86:14), (f) **Cap2**, **Cap4**, and **G6** (1.25 mM) in $CDCl_3$/DMSO-d_6 (83:17). Fig. 11: Partial spectra of Figure S31.



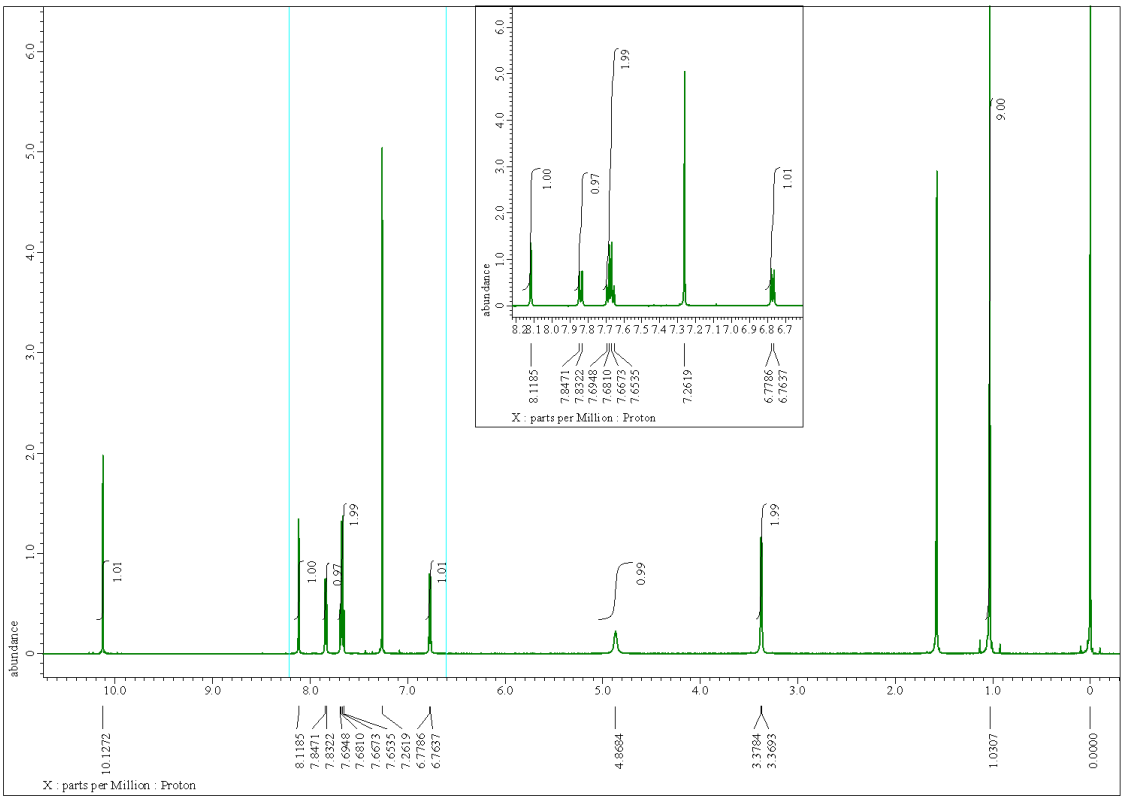


Figure S32a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound **2**.

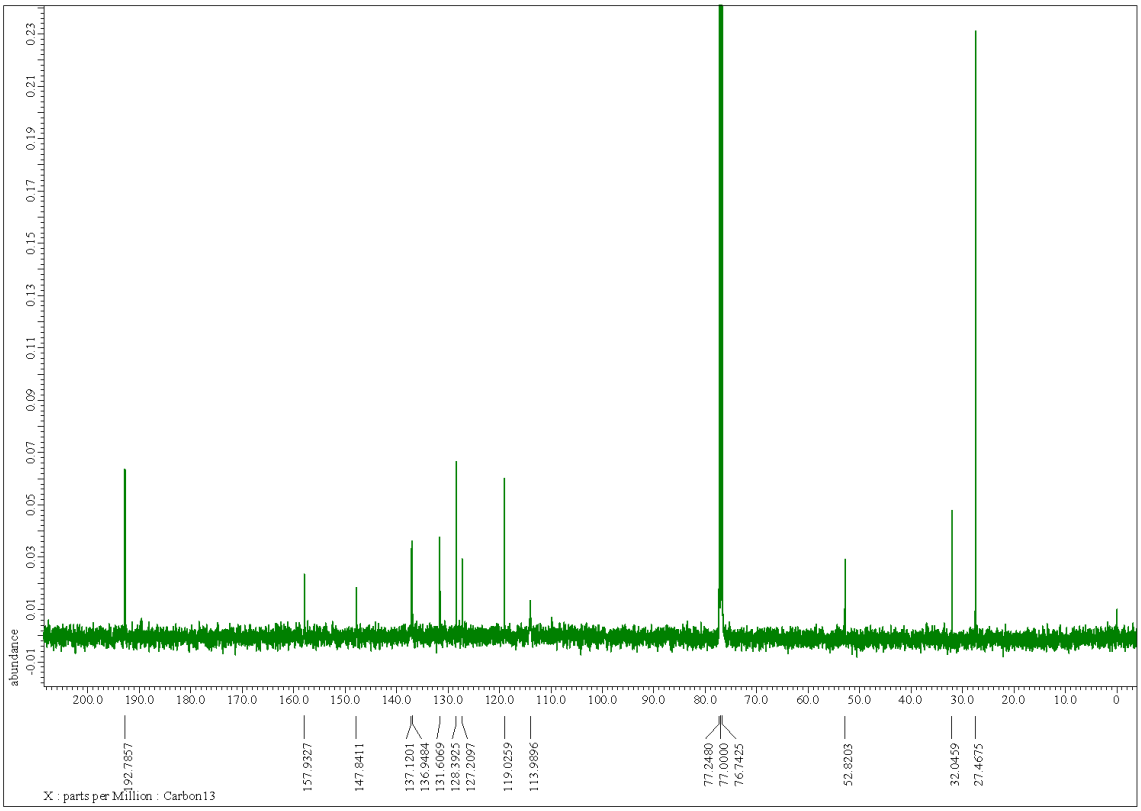


Figure S32b. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **2**.

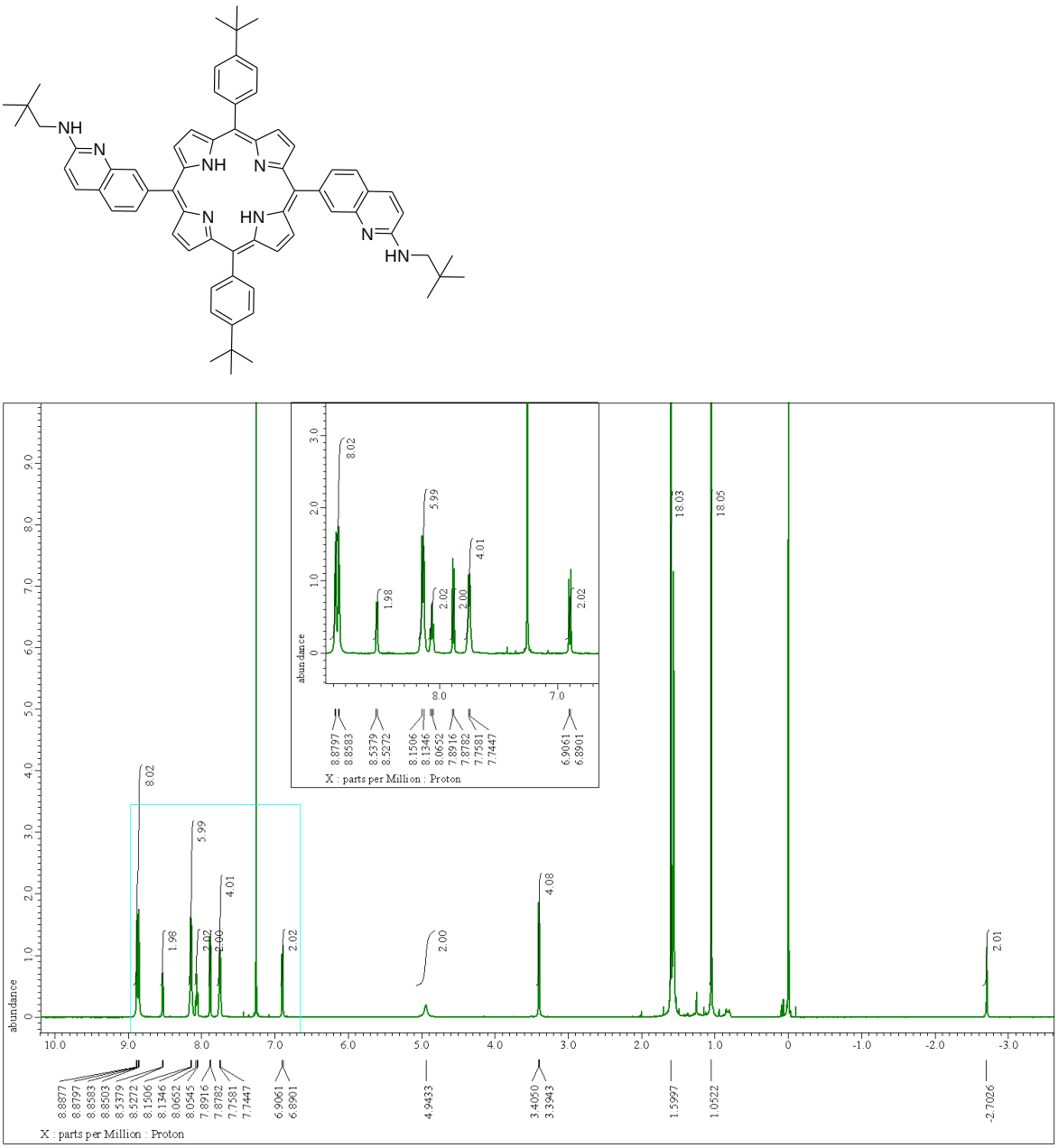


Figure S33a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the porphyrin derivative **P2b**.

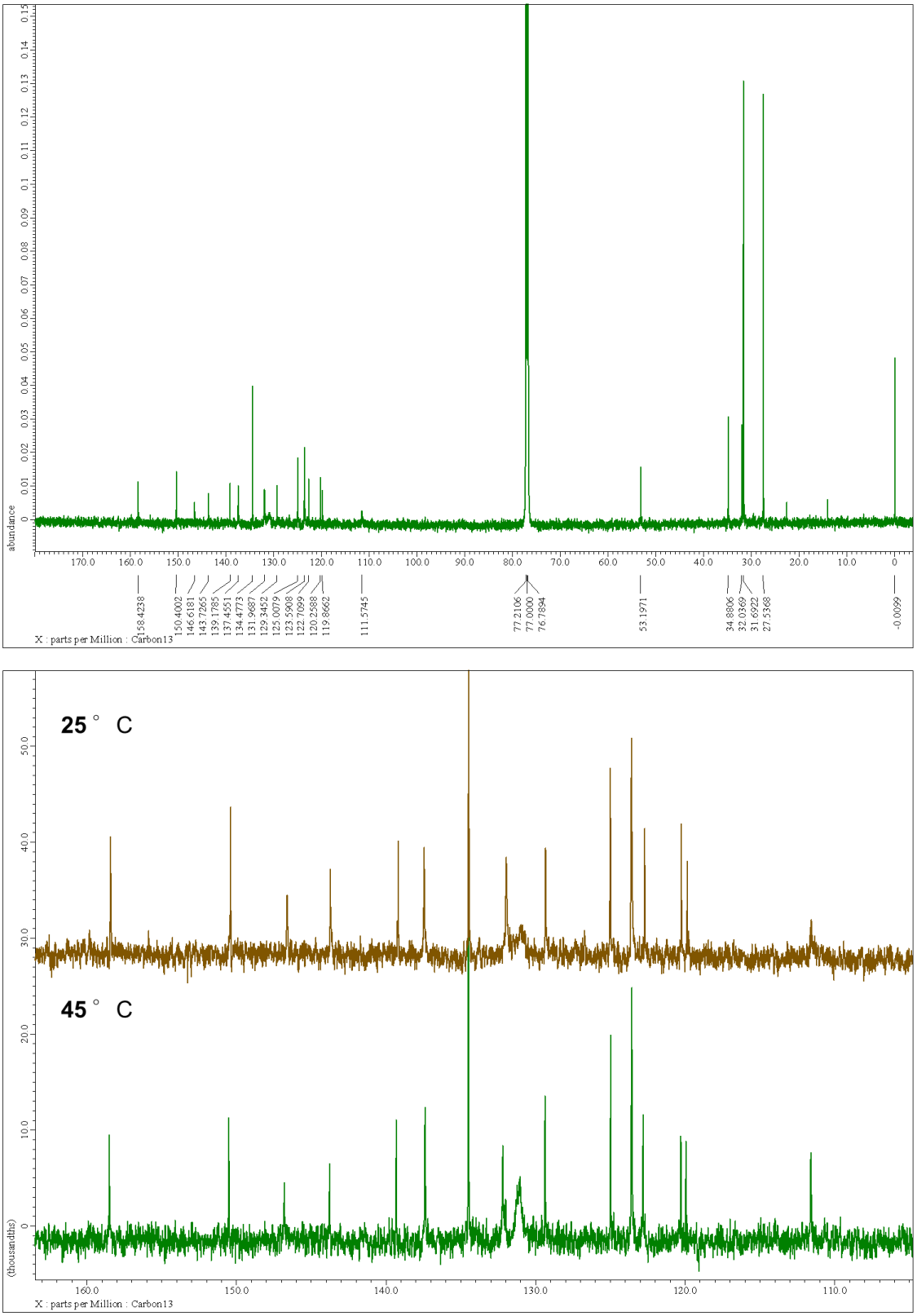


Figure S33b. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of the porphyrin derivative **P2b**.

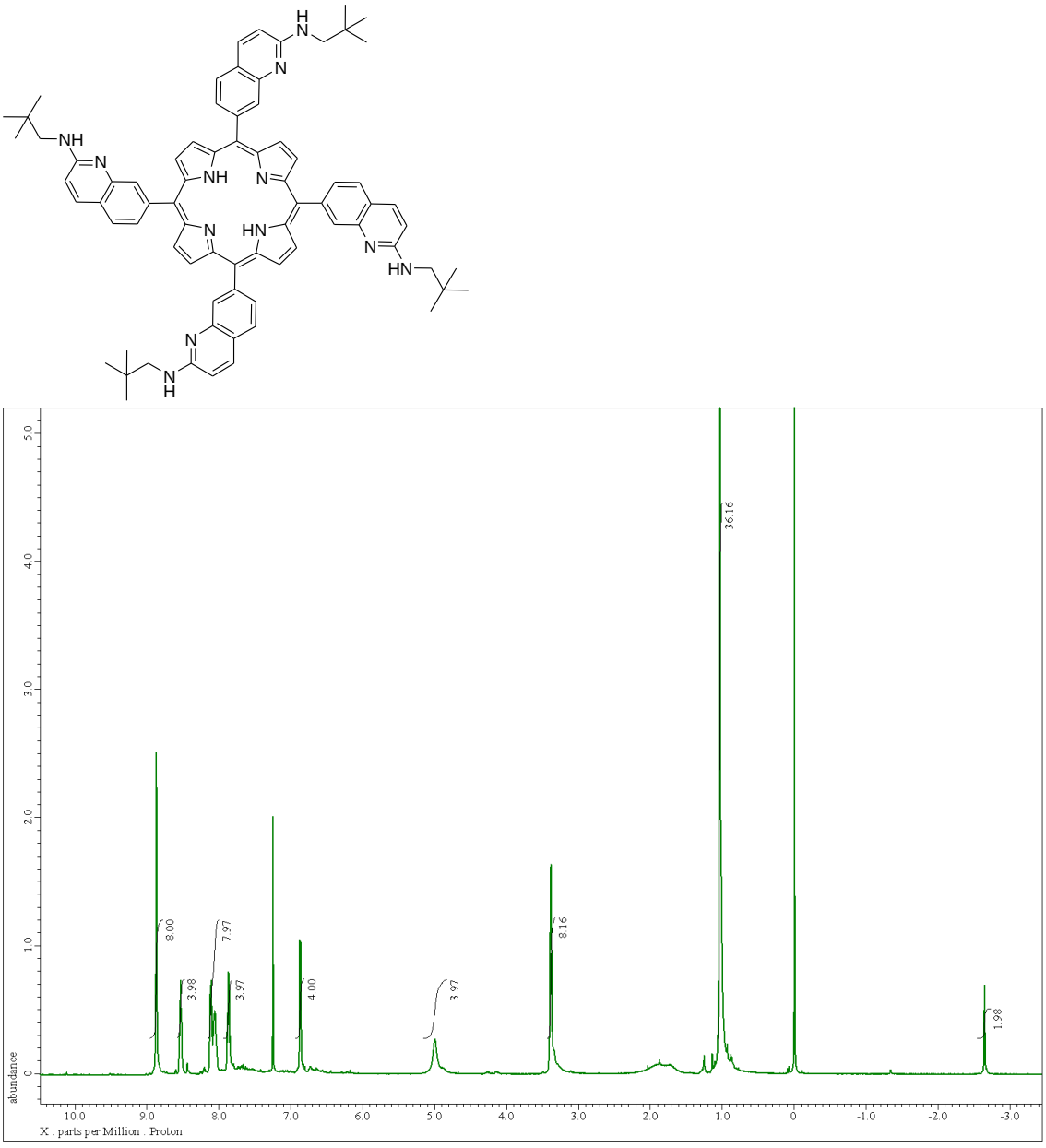


Figure S34a. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the porphyrin derivative **P4b**.

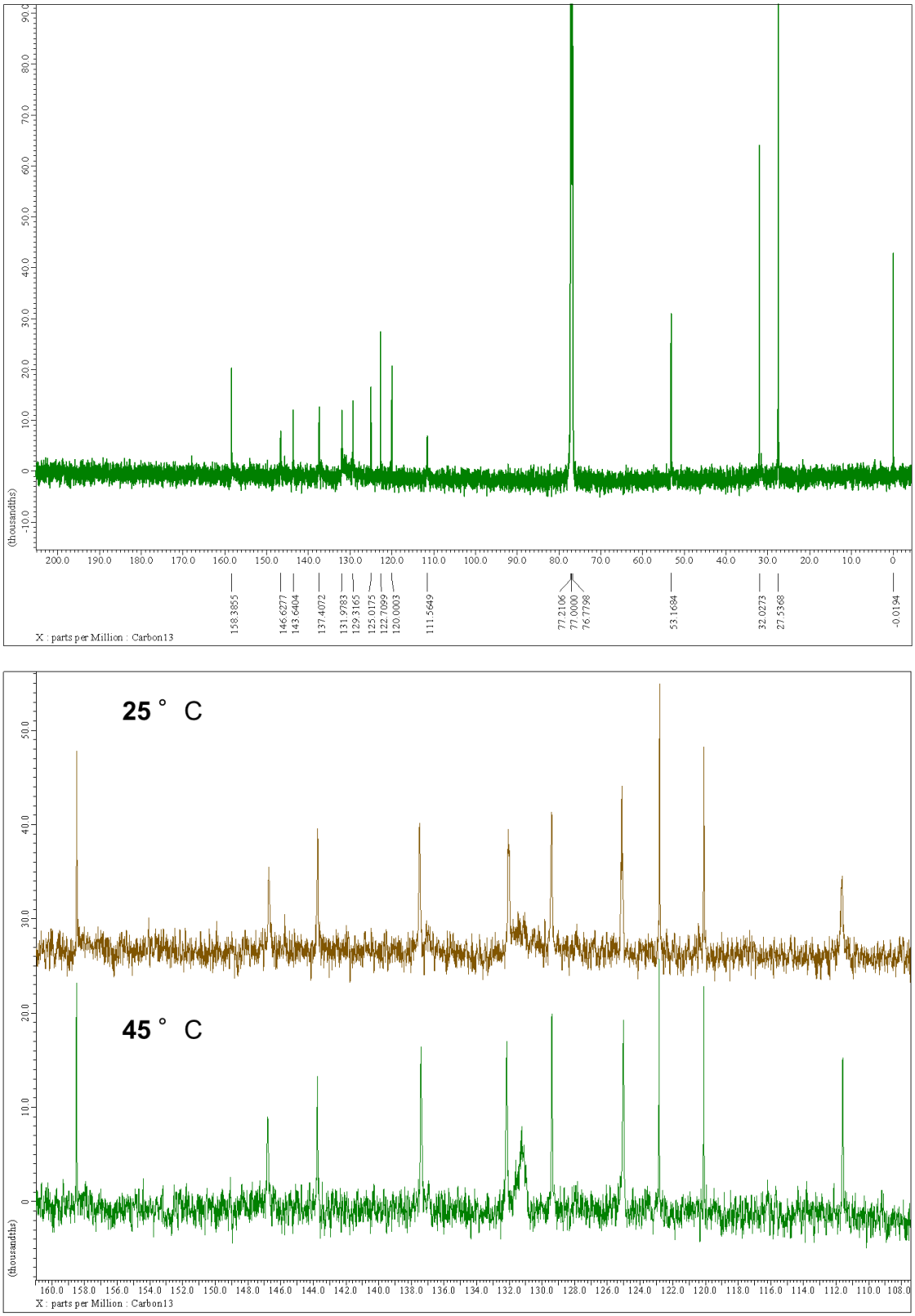


Figure S34b. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of the porphyrin derivative **P4b**.