Supporting Information

Supramolecular Substitution Reactions Between Hydrazide-Based Molecular Duplex Strands: Complexation Induced Non-Symmetry and Dynamic Behavior

Yong Yang, Jun-Feng Xiang, Min Xue, Hai-Yu Hu, and Chuan-Feng Chen*

Beijing National Laboratory for Molecular Sciences, Center for Chemical Biology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail: cchen@iccas.ac.cn

Contents

1. Copies of ^{1}H NMR and ^{13}C NMR spectra for new compounds----------S2
2. Evaluation of supramolecular substitution reaction between **1a-c** and **2a**---------S5
3. Evaluation of supramolecular substitution reaction between **1a-c** and **2b**-------S12
4. Evaluation of supramolecular substitution reaction between **1a-1c** and **2c**------S16

1. Copies of ^{1}H NMR and ^{13}C NMR spectra for new compounds

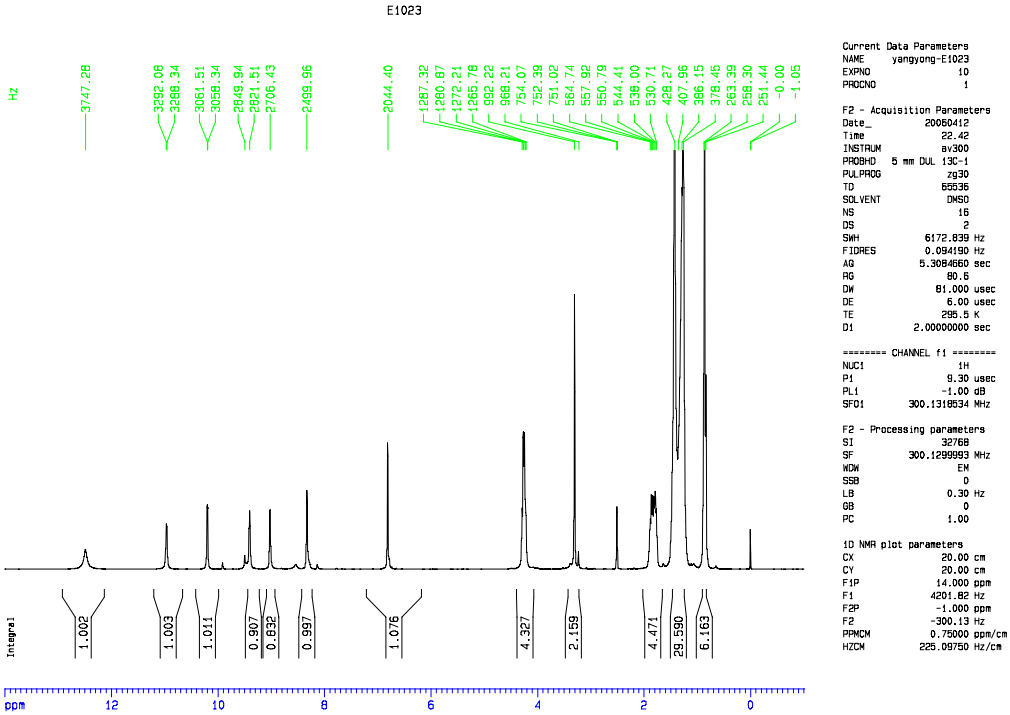


Figure S1. Copy of ^{1}H NMR spectrum for compound **4**.

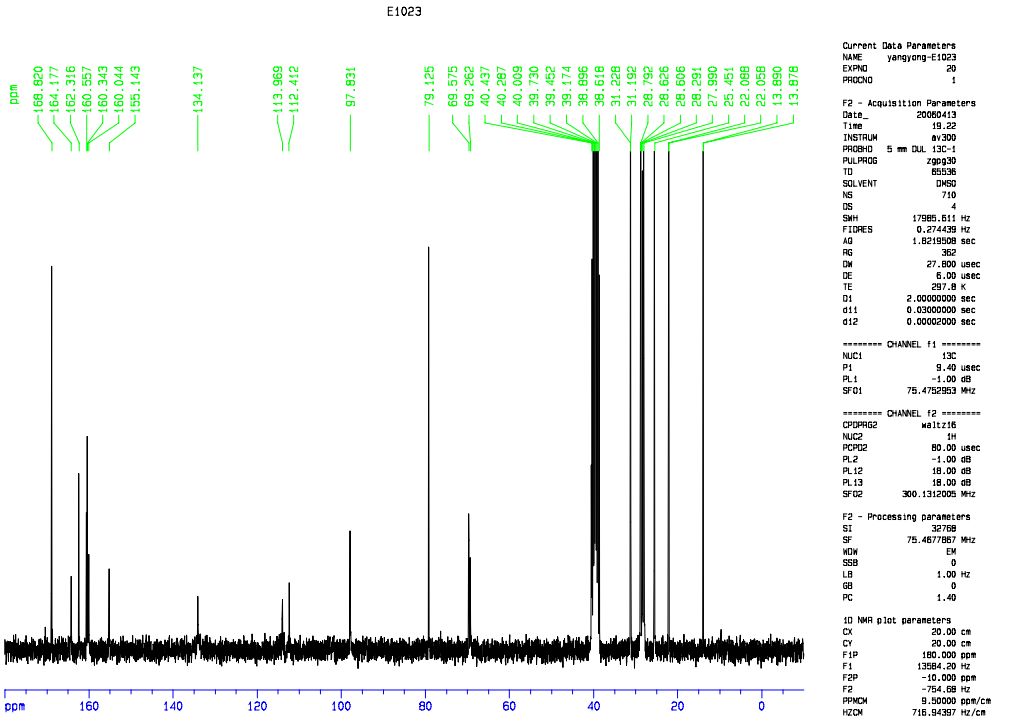


Figure S2. Copy of ^{13}C NMR spectrum for compound **4**.

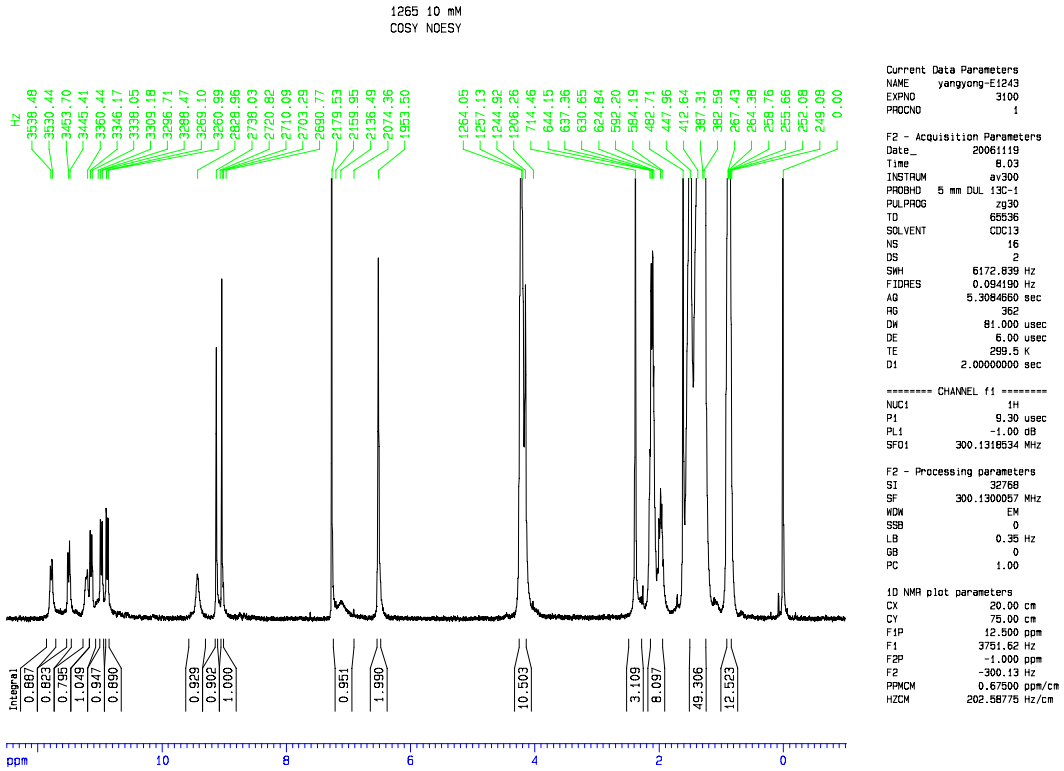


Figure S3. Copy of ^{1}H NMR spectrum for compound **1b**.

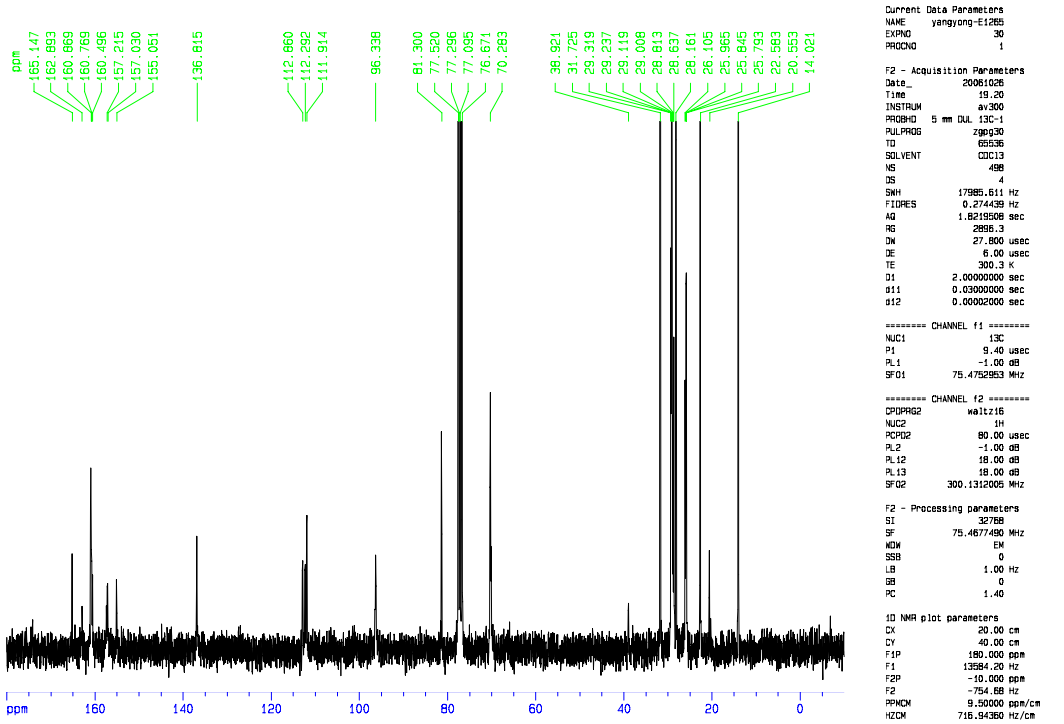


Figure S4. Copy of ^{13}C NMR spectrum for compound **1b**.

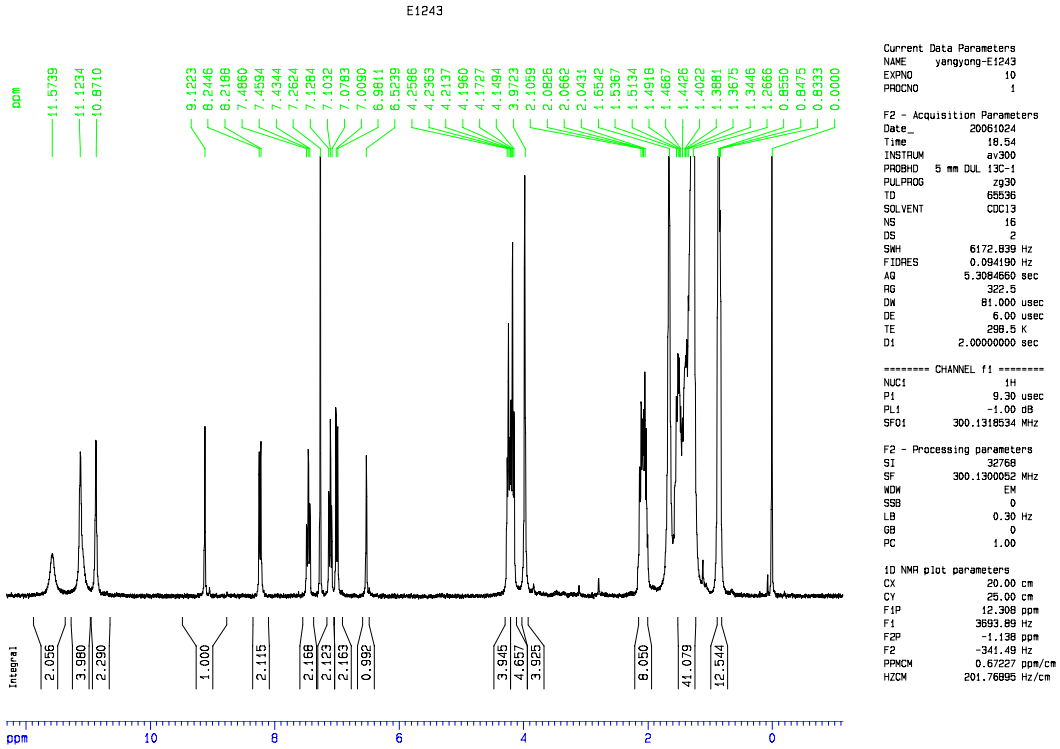


Figure S5. Copy of ^{1}H NMR spectrum for compound **2a**.

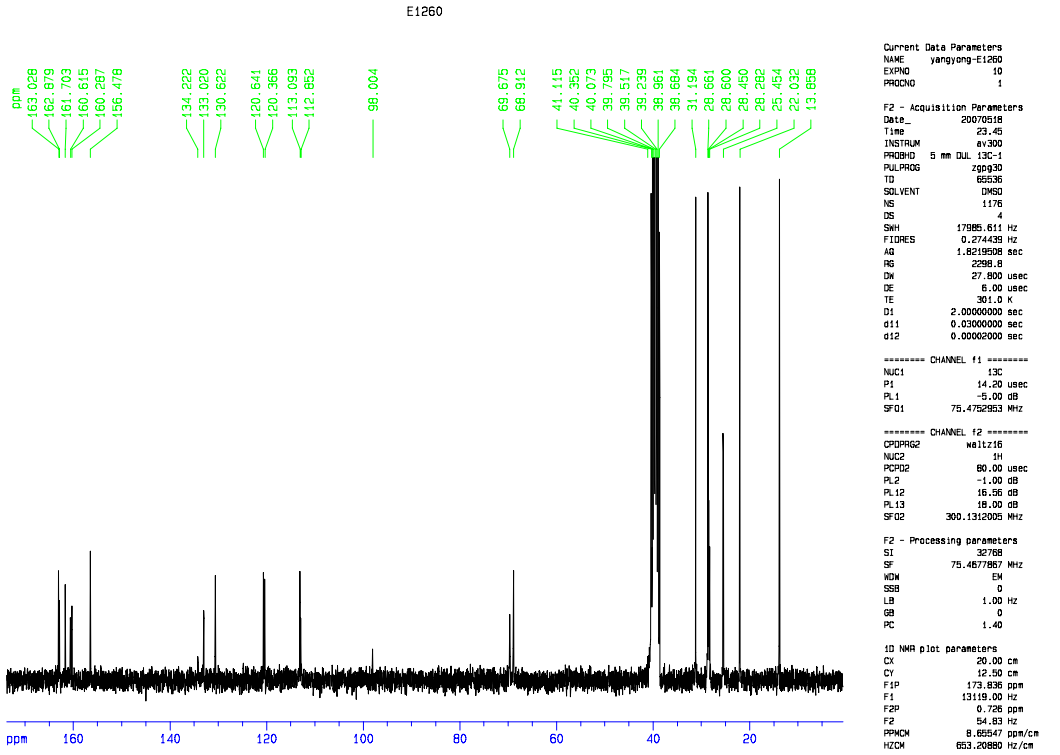
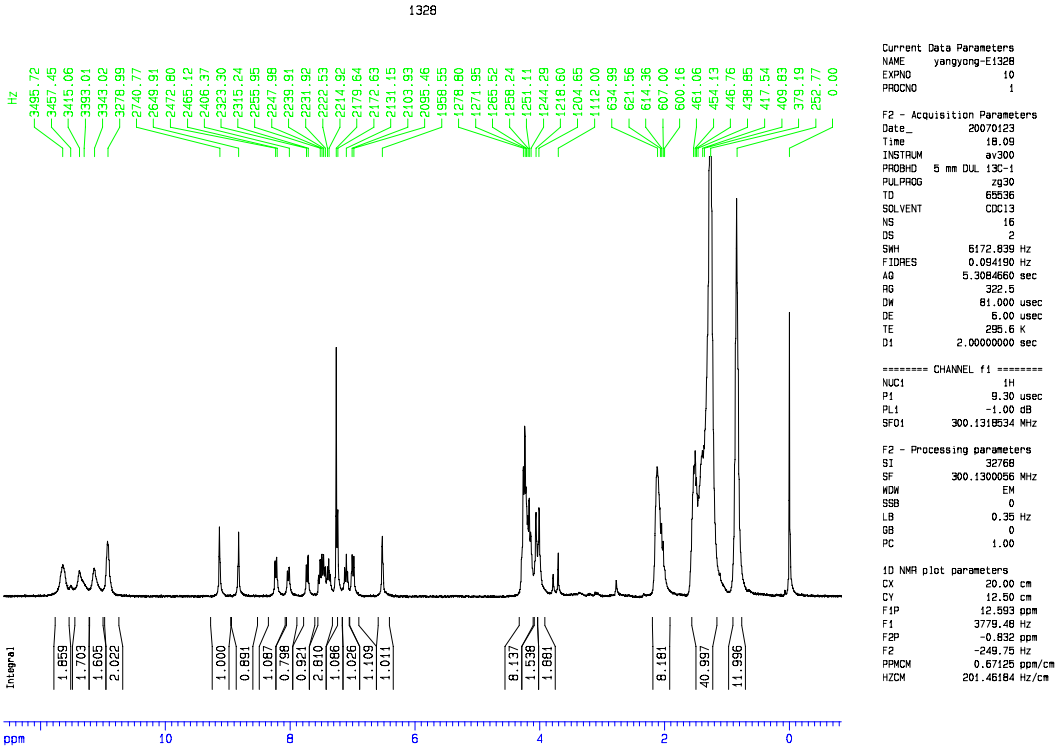
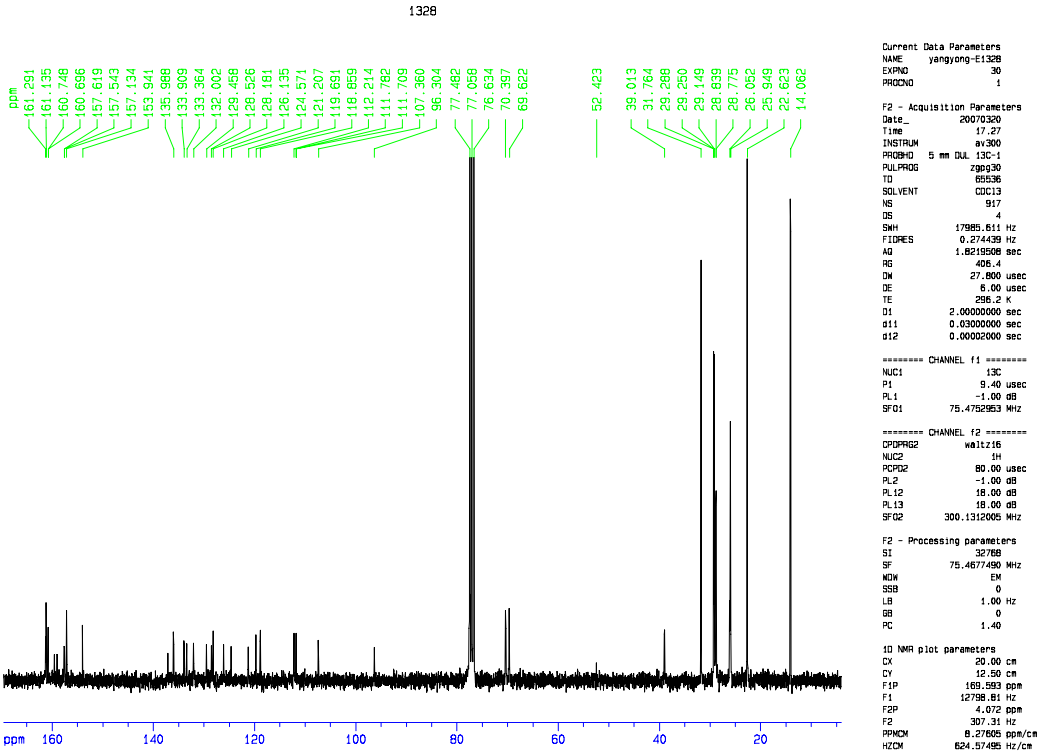


Figure S6. Copy of ^{13}C NMR spectrum for compound **2a**.




```
Current Data Parameters
NAME      yangyong-E1328
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070123
Time               18.09
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ            5.3084660 sec
RG                 322.5
DW                81.000 usec
DE                  6.00 usec
TE                 295.6 K
D1           2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.30 usec
PL1                -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300056 MHz
WDW                   EM
SSB                    0
LB                  0.35 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P               12.593 ppm
F1                3779.48 Hz
F2P                -0.832 ppm
F2                -249.75 Hz
PPMCM             0.67125 ppm/cm
HZCM            201.46184 Hz/cm
```

Figure S7. Copy of ^{1}H NMR spectrum for compound **2b**.




```
Current Data Parameters
NAME      yangyong-E1328
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070320
Time               17.27
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   917
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ            1.8219508 sec
RG                 406.4
DW                27.800 usec
DE                  6.00 usec
TE                 296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PL1                -1.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               18.00 dB
PL13               18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P               169.593 ppm
F1               12798.81 Hz
F2P                 4.072 ppm
F2                307.31 Hz
PPMCM             8.27605 ppm/cm
HZCM            624.57495 Hz/cm
```

Figure S8. Copy of ^{13}C NMR spectrum for compound **2b**.

2. Evaluation of supramolecular substitution reaction between 1a, 1b, 1c and 2a.

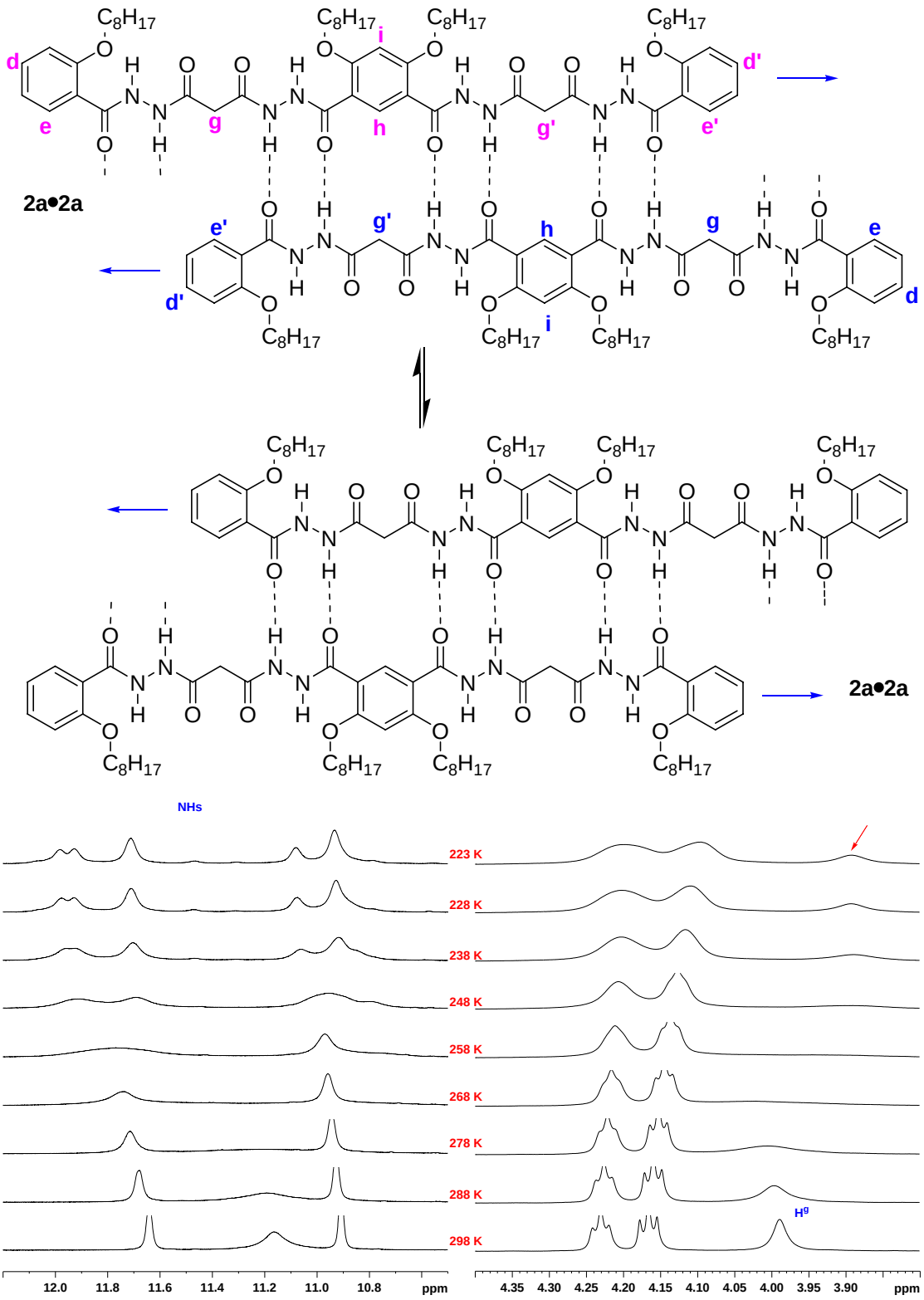


Figure S9. Stacked partial ^{1}H NMR spectra of **2a** at different temperatures, 600 MHz, 10 mM in $CDCl_3$. With lowering of temperature, partial signals for NHs shifted

upfield; signals for g zone splitted into two peaks: one shifted downfield and one shifted upfield.

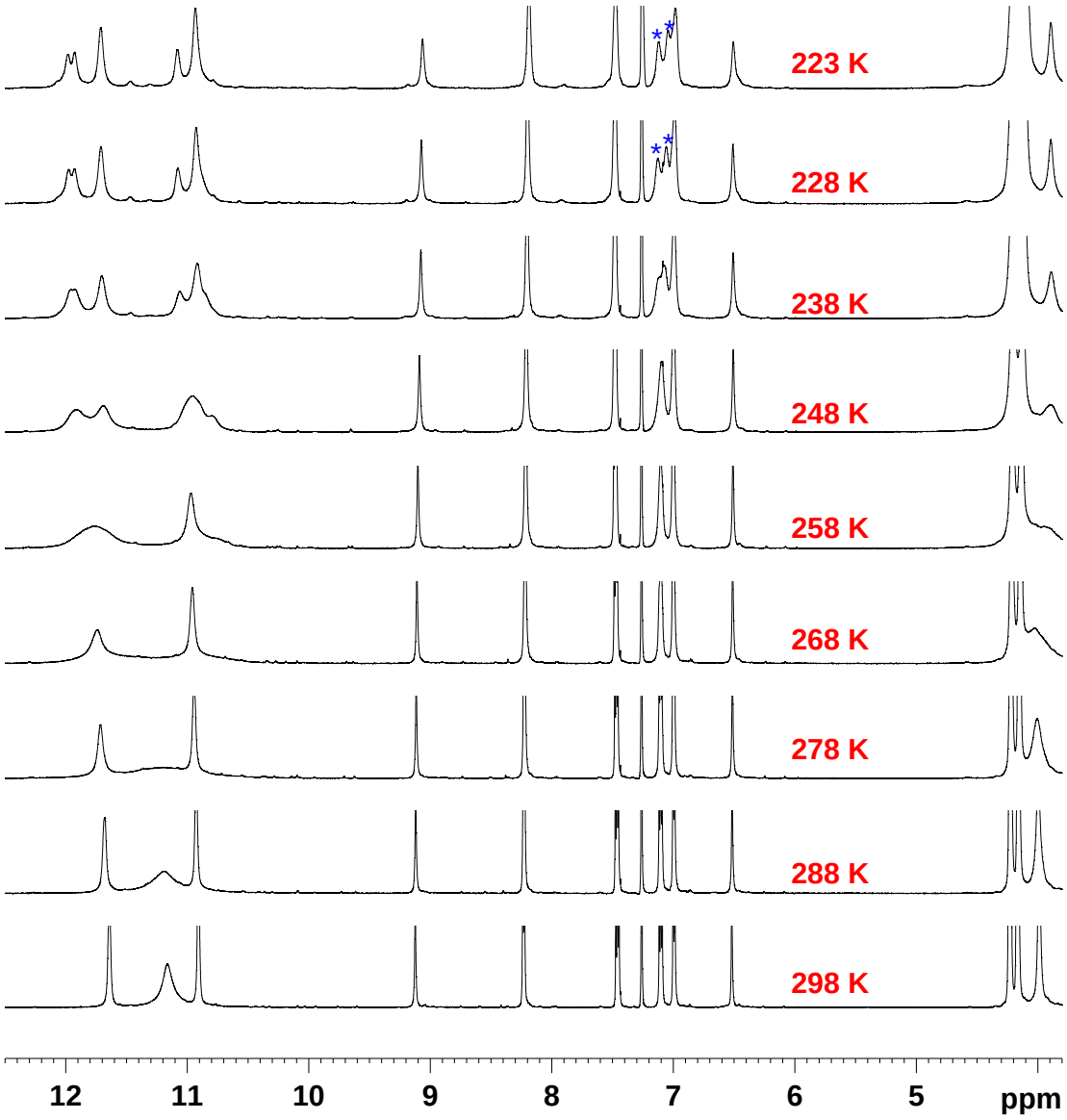


Figure S10. Stacked partial ^{1}H NMR spectra of **2a** at different temperatures, 600 MHz, 10 mM in $CDCl_3$. With splitting of signals for H^{d} ($H^{d'}$) highlighted.

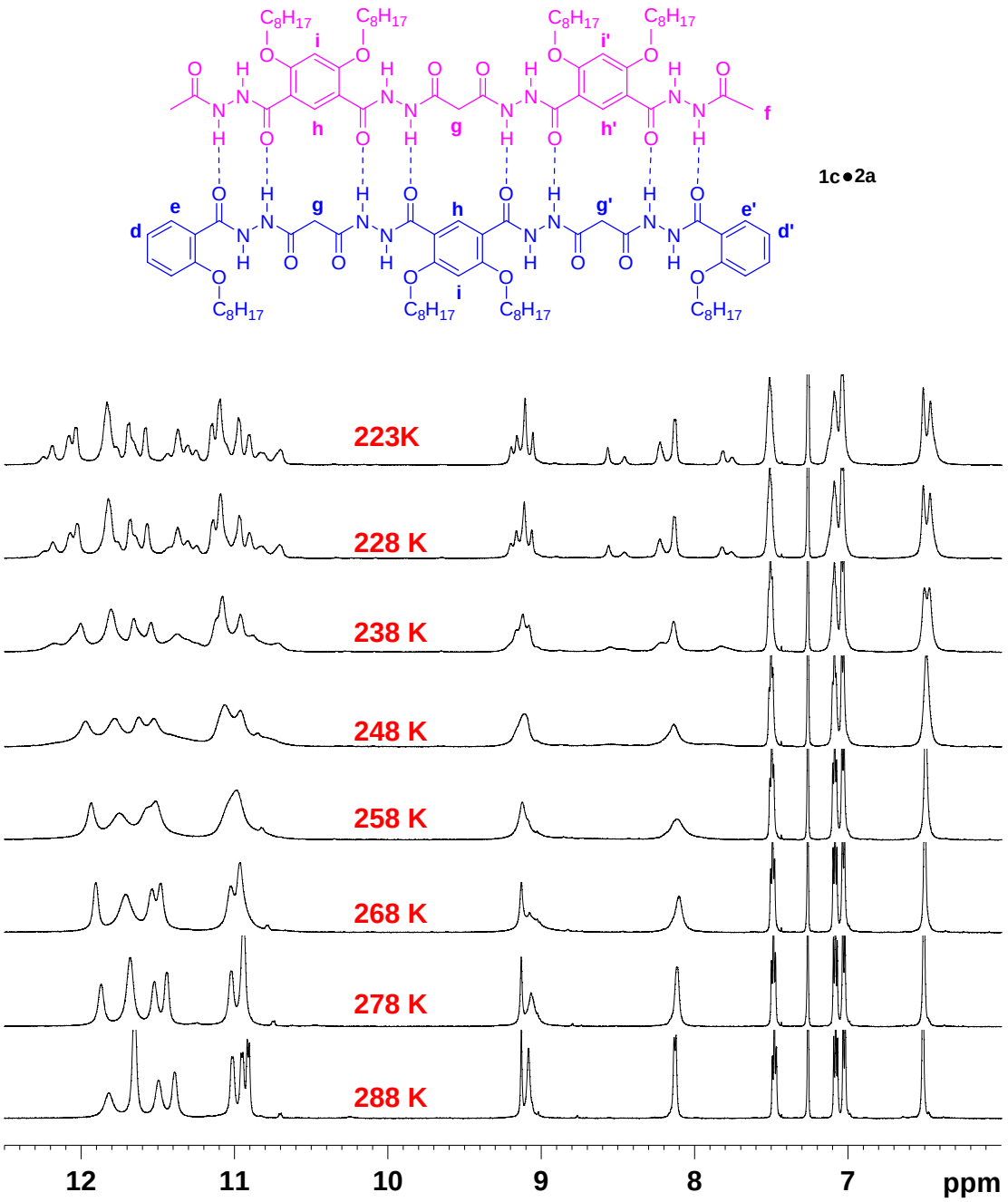


Figure S11. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1c** and **2a** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$.

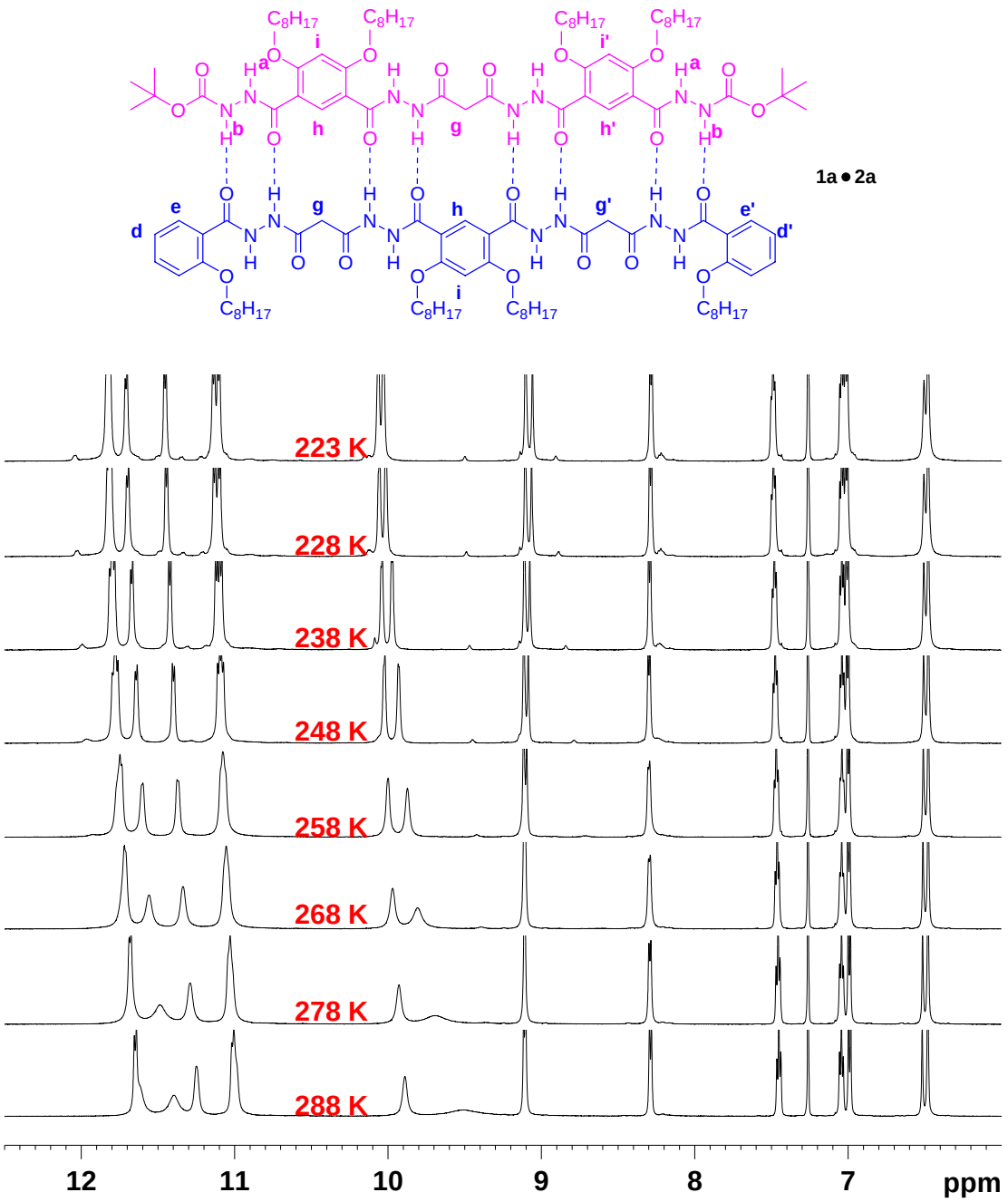


Figure S12. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1a** and **2a** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$.

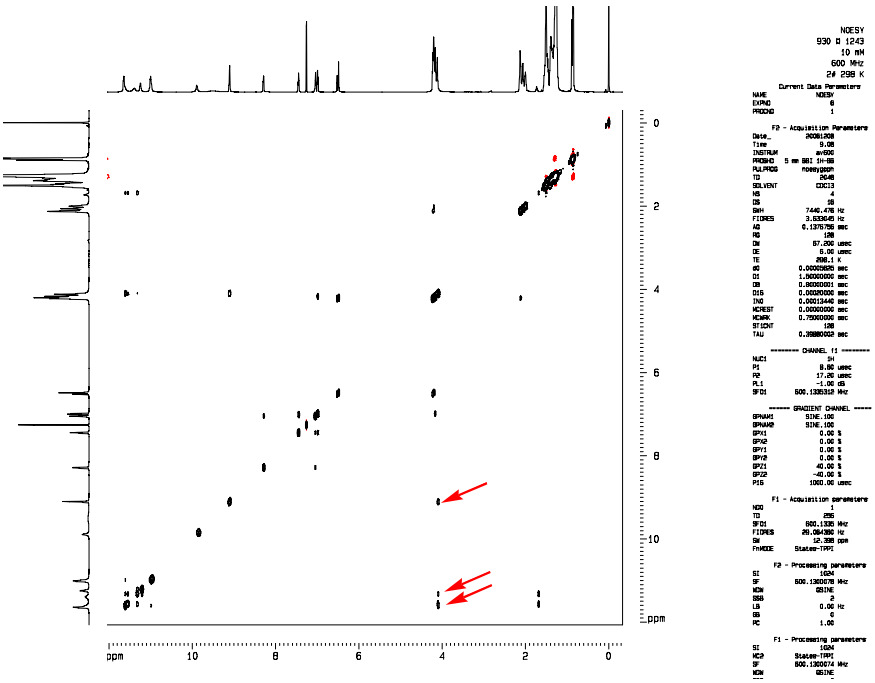


Figure S13. NOESY spectrum of 1:1 mixed **1a** and **2a** at 298 K, 600 MHz, each 10 mM in $CDCl_3$, with contacts between *g* zone and *h* zone, among NHs highlighted.

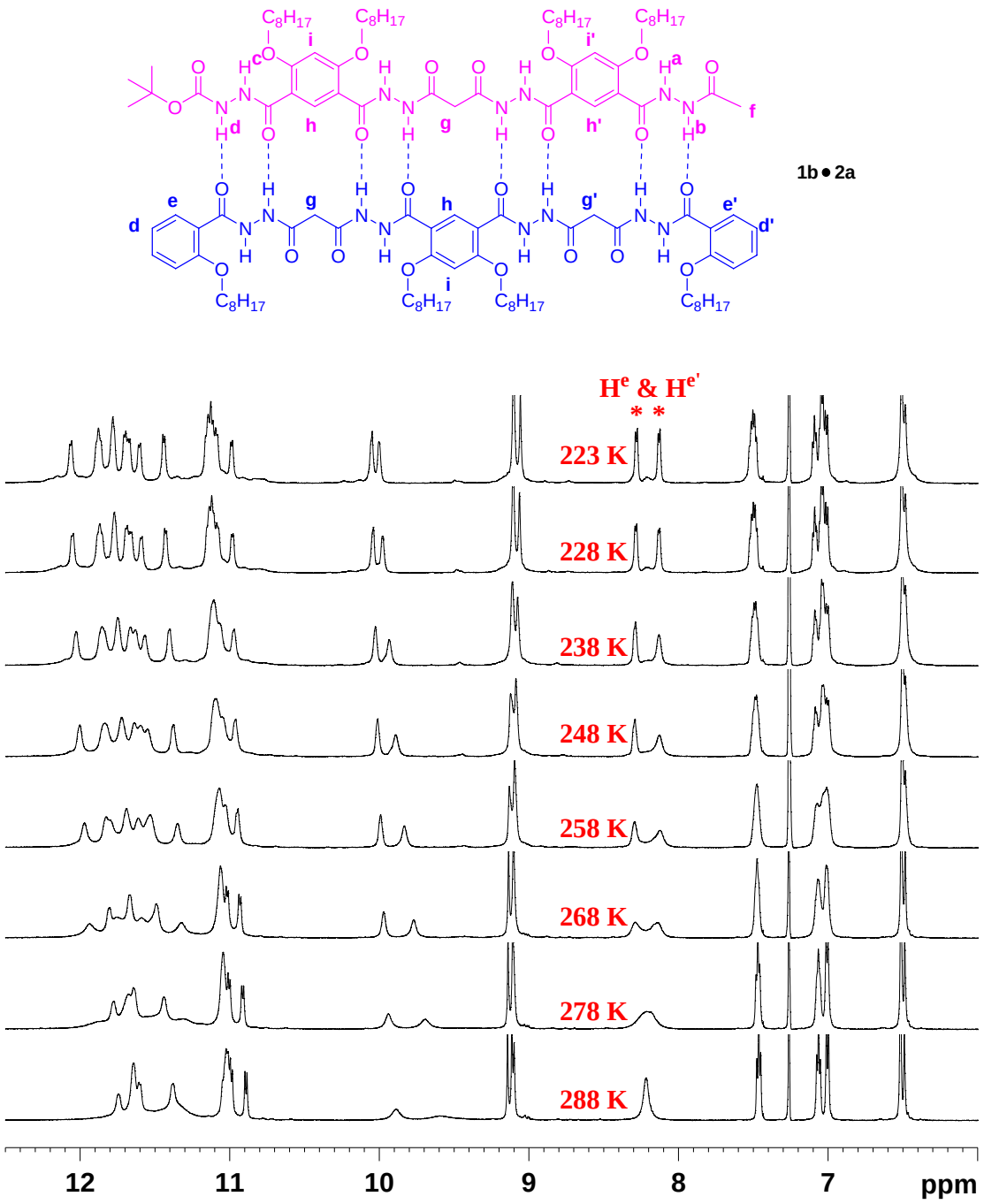


Figure S14. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1b** and **2a** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$, with splitting of signals for **2a**-H^{e} ($H^{e'}$) highlighted.

3. Evaluation of supramolecular substitution reaction between 1a, 1b, 1c and 2b.

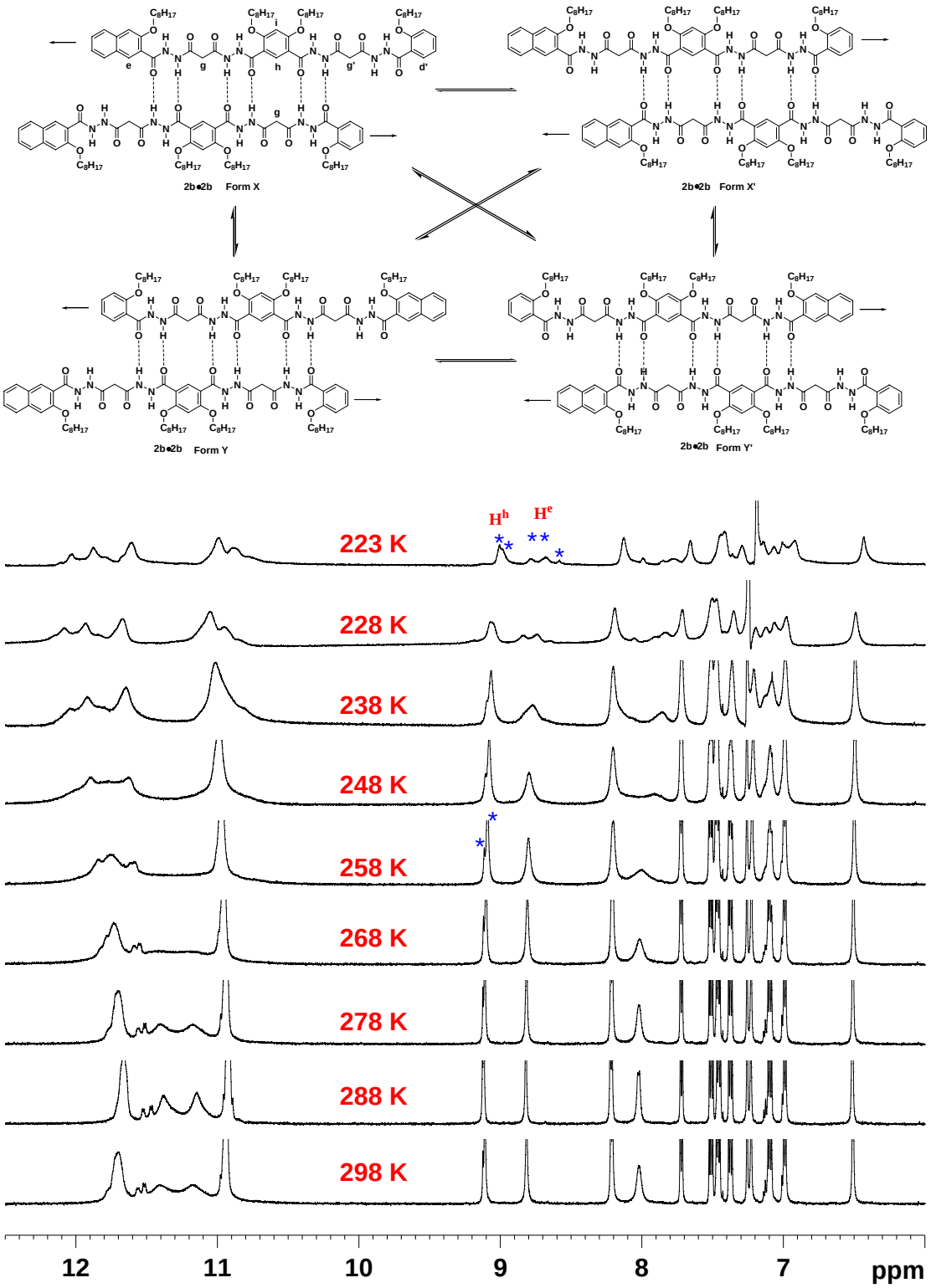


Figure S15. Stacked partial ^{1}H NMR spectra of **2b** at different temperatures, 600 MHz, 10 mM in $CDCl_3$, with splitting of signals for H^e and H^h highlighted.

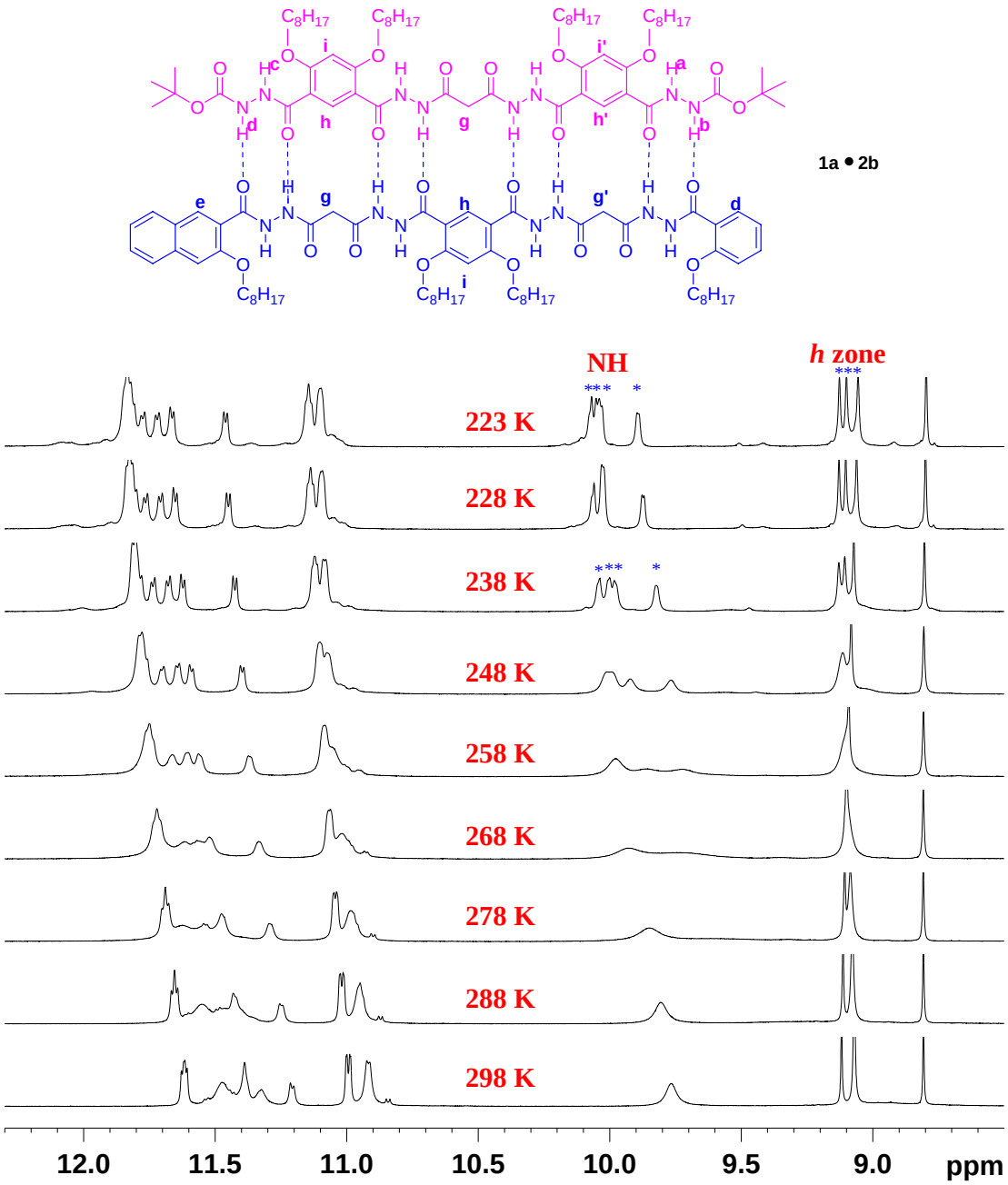


Figure S16. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1a** and **2b** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$, with splitting of signals for NH and *h* zone highlighted.

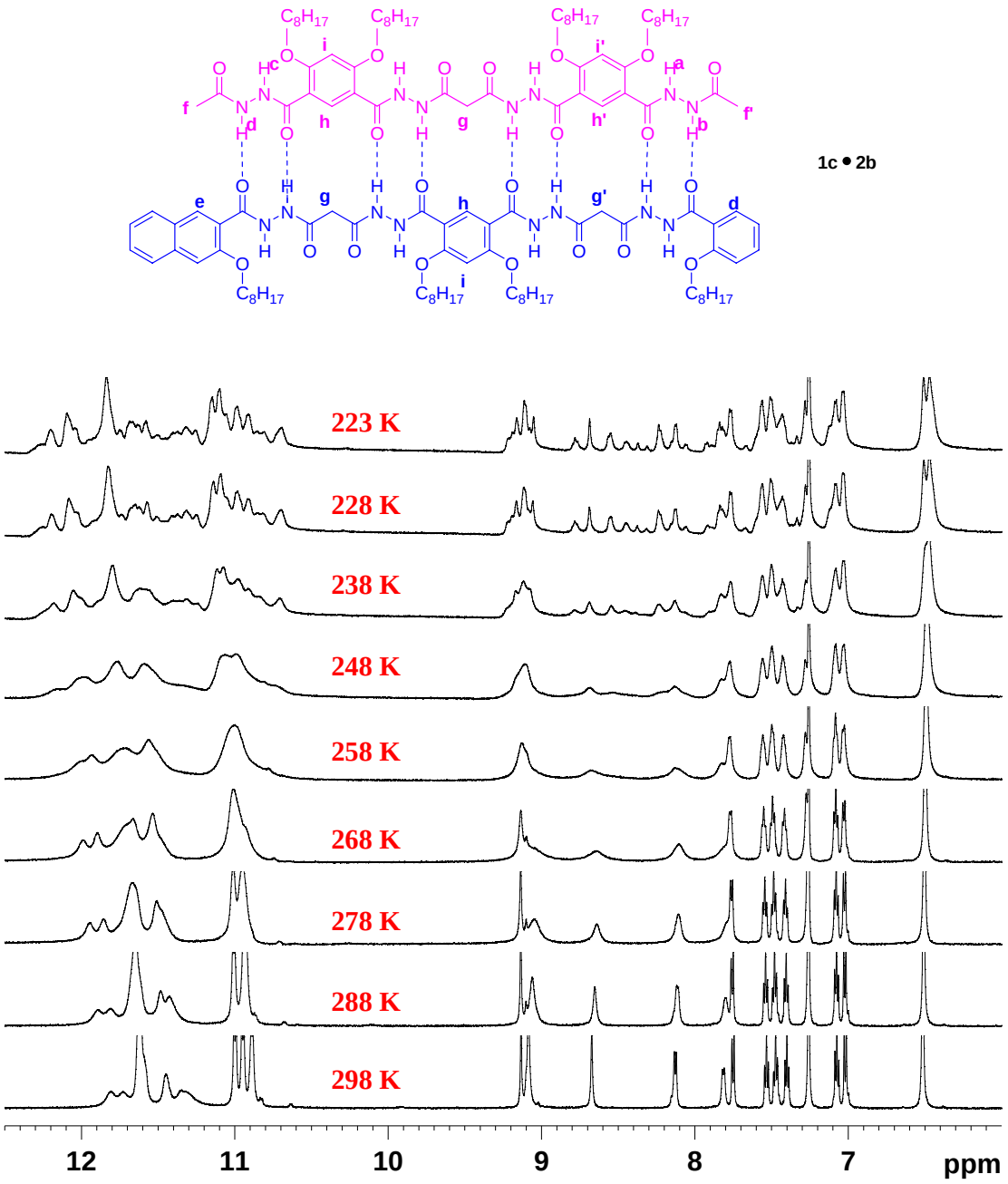


Figure S17. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1c** and **2b** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$.

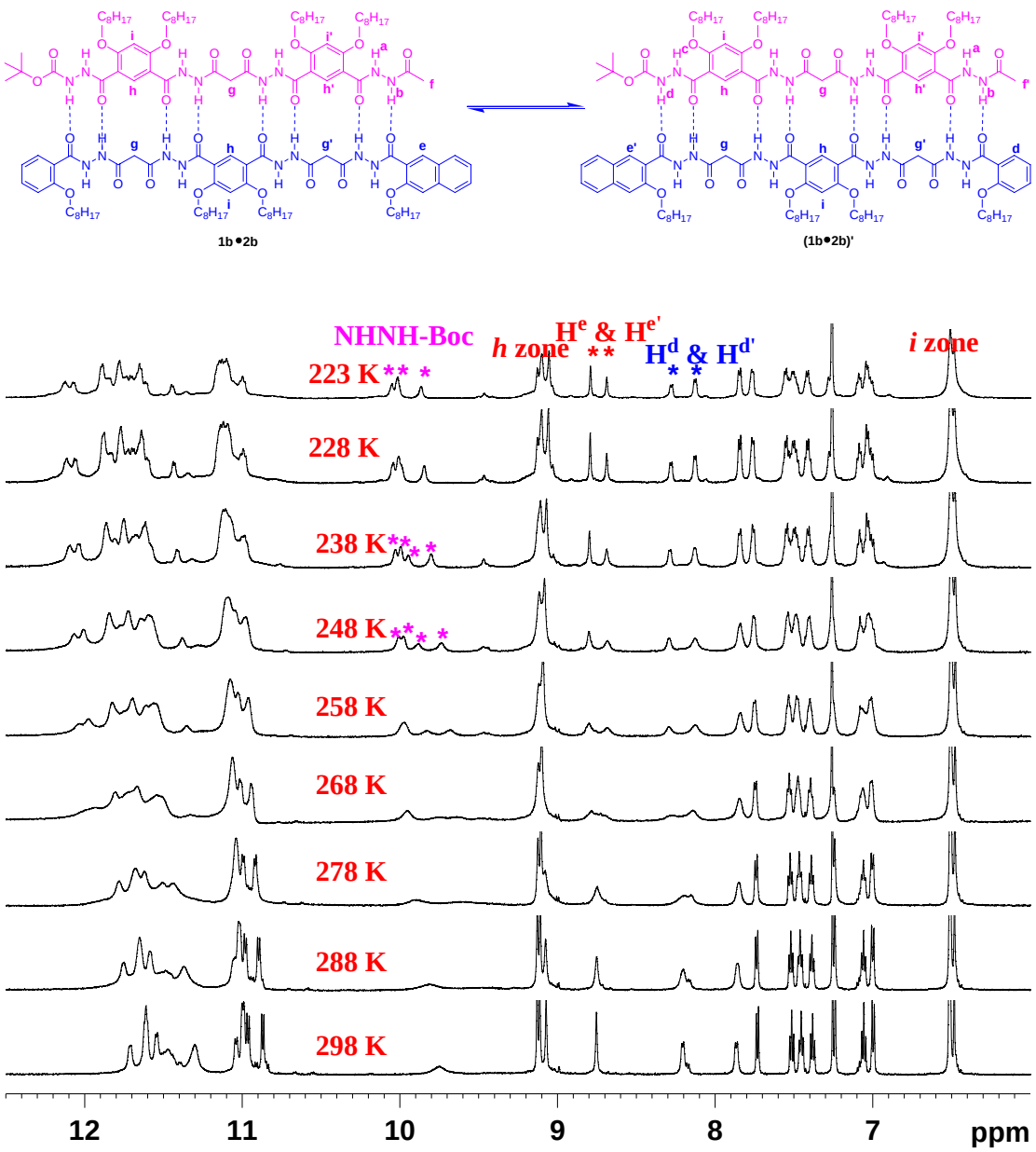


Figure S18. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1b** and **2b** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$, with splitting of signals for NHNH-Boc, **2b**-H^{d}($H^{d'}$), **2b**-H^{e}($H^{e'}$) highlighted.

4. Evaluation of supramolecular substitution reaction between 1a, 1b, 1c and 2c.

Figure S19. Digital photograph of gel formed from **2c** (left, ca. 0.8% (*w*/*w*). and **1b**&**2c** (right) in $CDCl_3$ (each 10 mM).

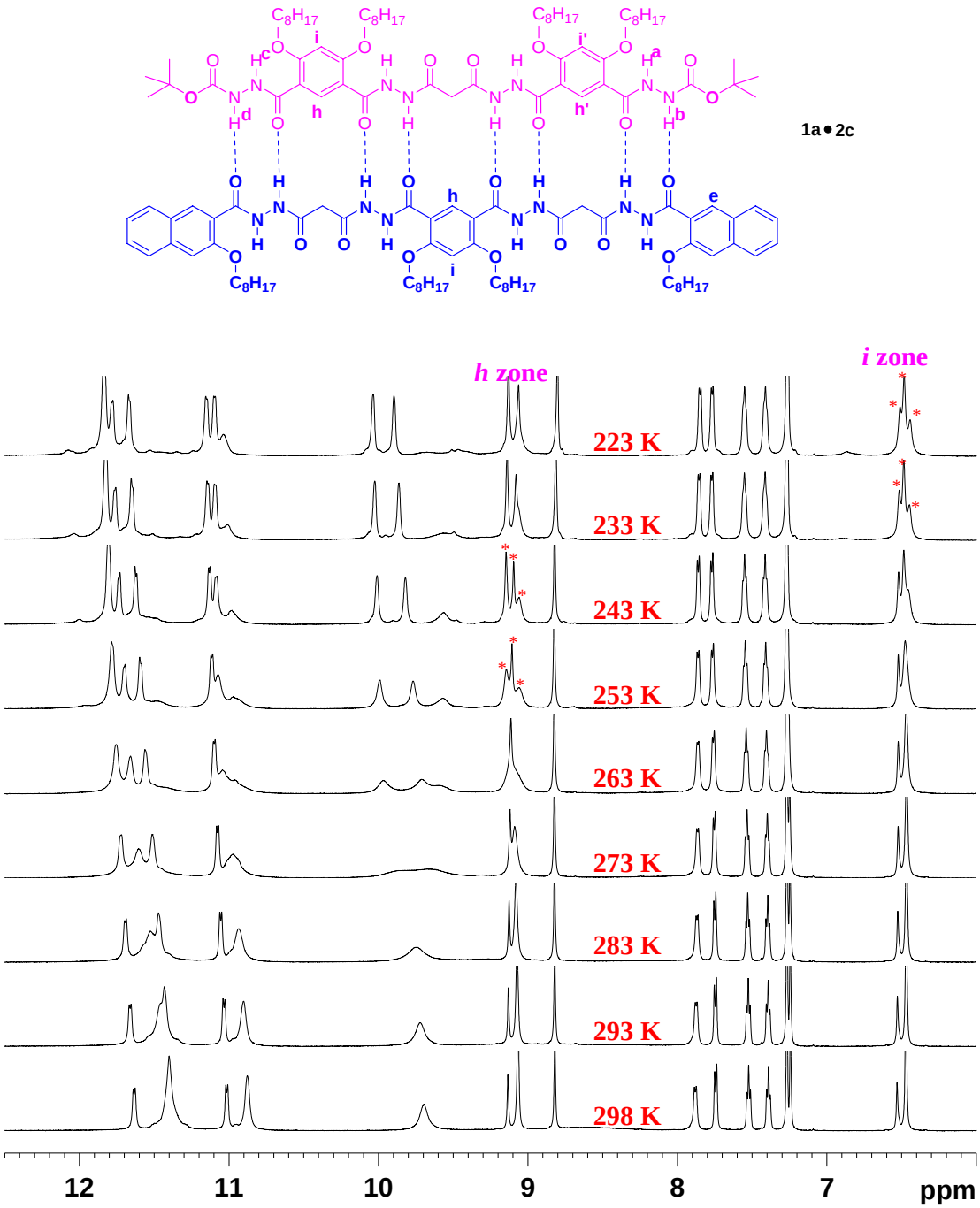


Figure S20. Stacked partial ^{1}H NMR spectra of 1:1 mixed **1a** and **2c** at different temperatures, 600 MHz, each 10 mM in $CDCl_3$, with splitting of signals for *h* zone and *i* zone highlighted.