

Supporting information for:

Hydrogen-Bonding Complexes of 5-Azauracil and Uracil Derivatives in Organic Medium.

Alba Diez-Martinez, Eun-Kyong Kim and Ramanarayanan Krishnamurthy*

*Department of Chemistry, The Scripps Research Institute,
10550 North Torrey Pines Road,
La Jolla, California 92037, United States

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NMR Spectra of the compounds 1-4 and 10.

6-(((3*R*,4*R*)-3',4'-Bis(*tert*-butyldimethylsilyloxy)pyrrolidine-*N*-yl)methyl)-1,3,5-triazine-2,4-diamine (**1a**)

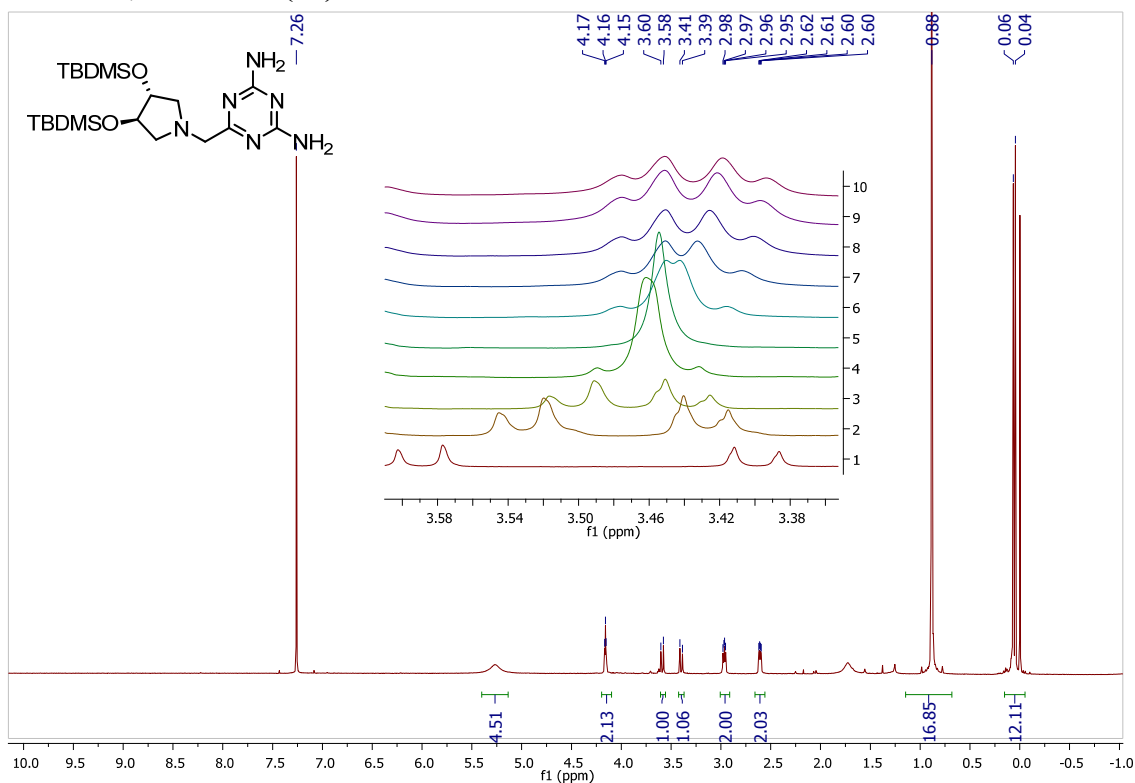


Figure S1: ^1H NMR (600 MHz, CDCl_3) of **1a**. Expansion: influence of the concentration showing the shifting of the diastereomeric protons. $[\mathbf{1a}]_1 = 4.4 \text{ mM}$; $[\mathbf{1a}]_{10} = 120.9 \text{ mM}$.

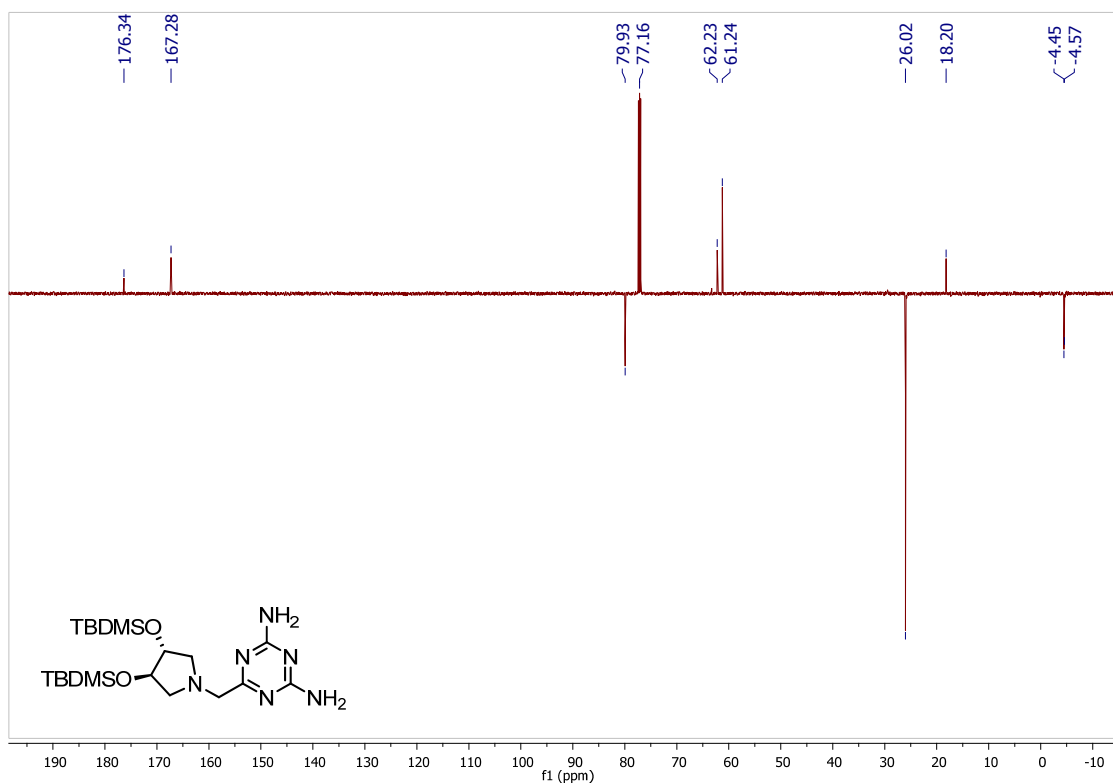


Figure S2: APT NMR (150 MHz, CDCl_3) of **1a**.

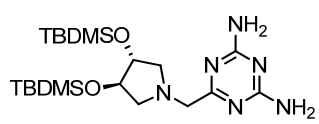


Figure S3: HSQC (^1H - ^{13}C , CDCl_3) of **1a**.

6-(((3*S*,4*S*)-3',4'-Dibenzoyloxypyrrolidine-*N*-yl)methyl)-1,3,5-triazine-2,4-diamine (1b).

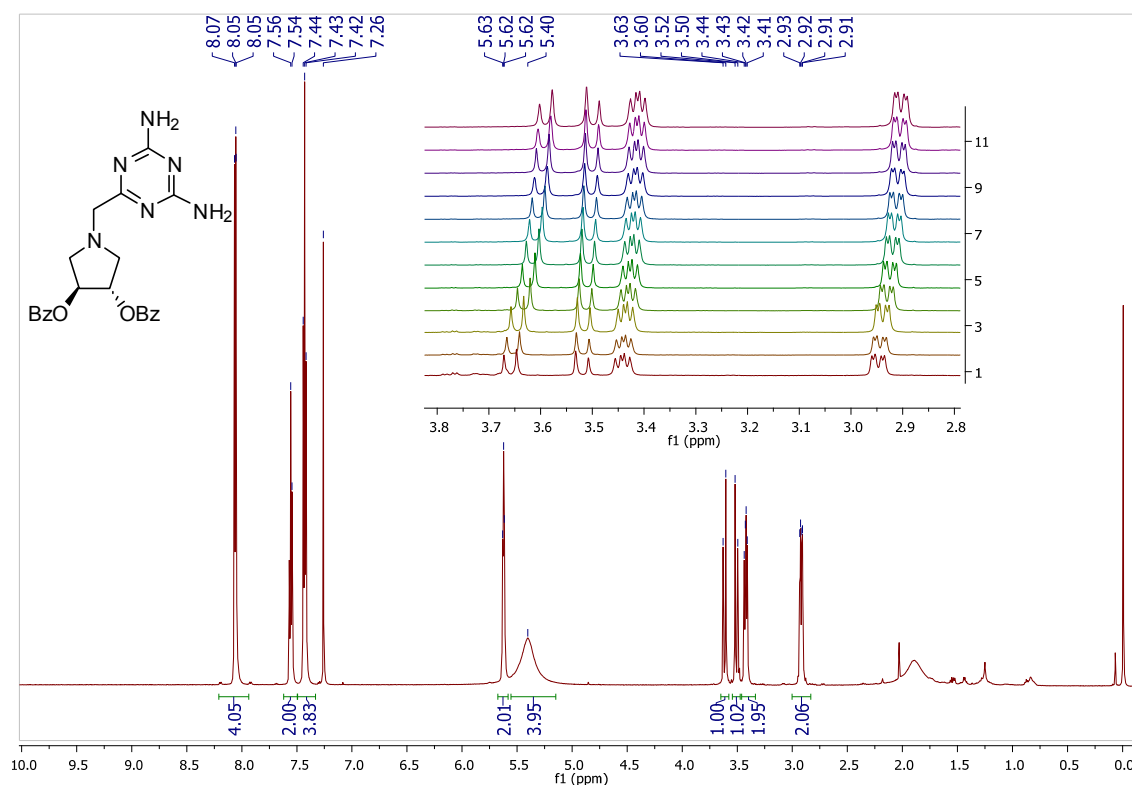


Figure S4: ^1H NMR (600 MHz, CDCl_3) of **1b**. Expansion: influence of the concentration showing the shifting of the diastereomeric protons. $[\mathbf{1b}]_1 = 4.6 \text{ mM}$; $[\mathbf{1b}]_{10} = 60.0 \text{ mM}$.

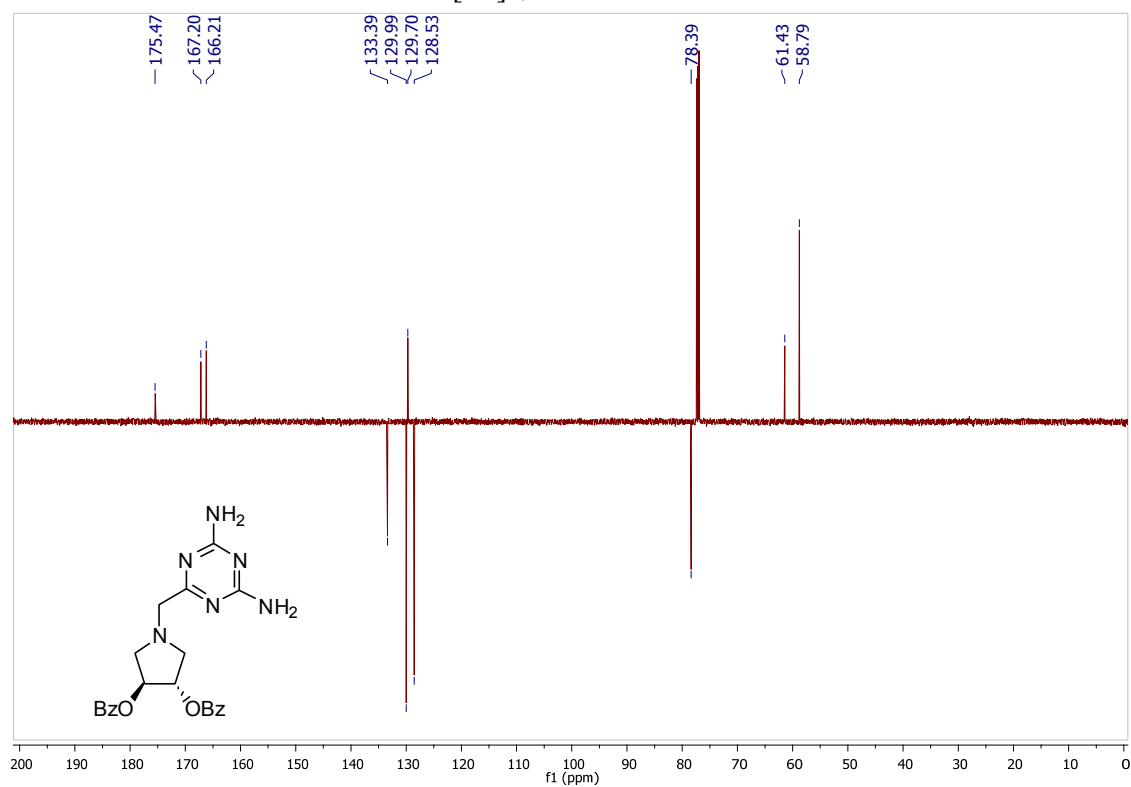


Figure S5: APT NMR (150 MHz, CDCl_3) of **1b**.

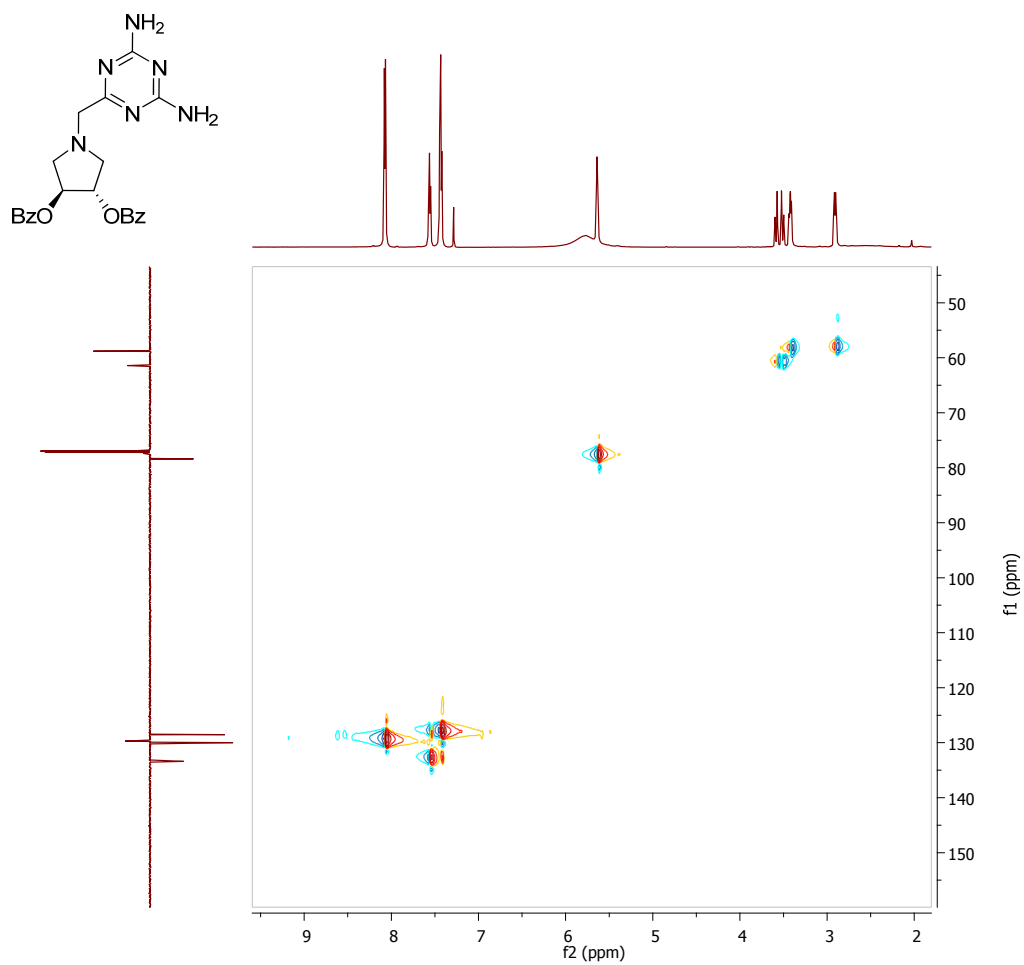


Figure S6: HSQC (^1H - ^{13}C , CDCl_3) of **1b**.

6-(((3*S*,4*S*)-3',4'-Dibenzoyloxy-2'-oxopyrrolidine-*N*-yl)methyl)-1,3,5-triazine-2,4-diamine (**1c**)

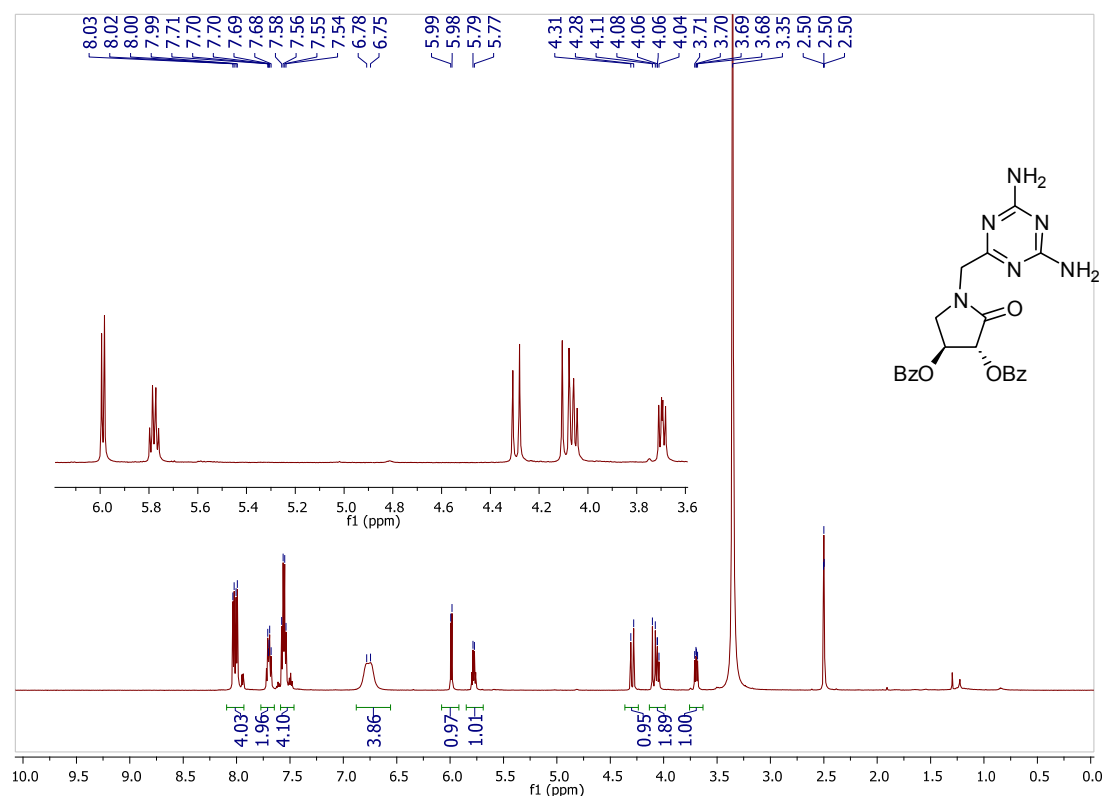


Figure S7: ¹H NMR (600 MHz, DMSO-d₆) of **1c**.

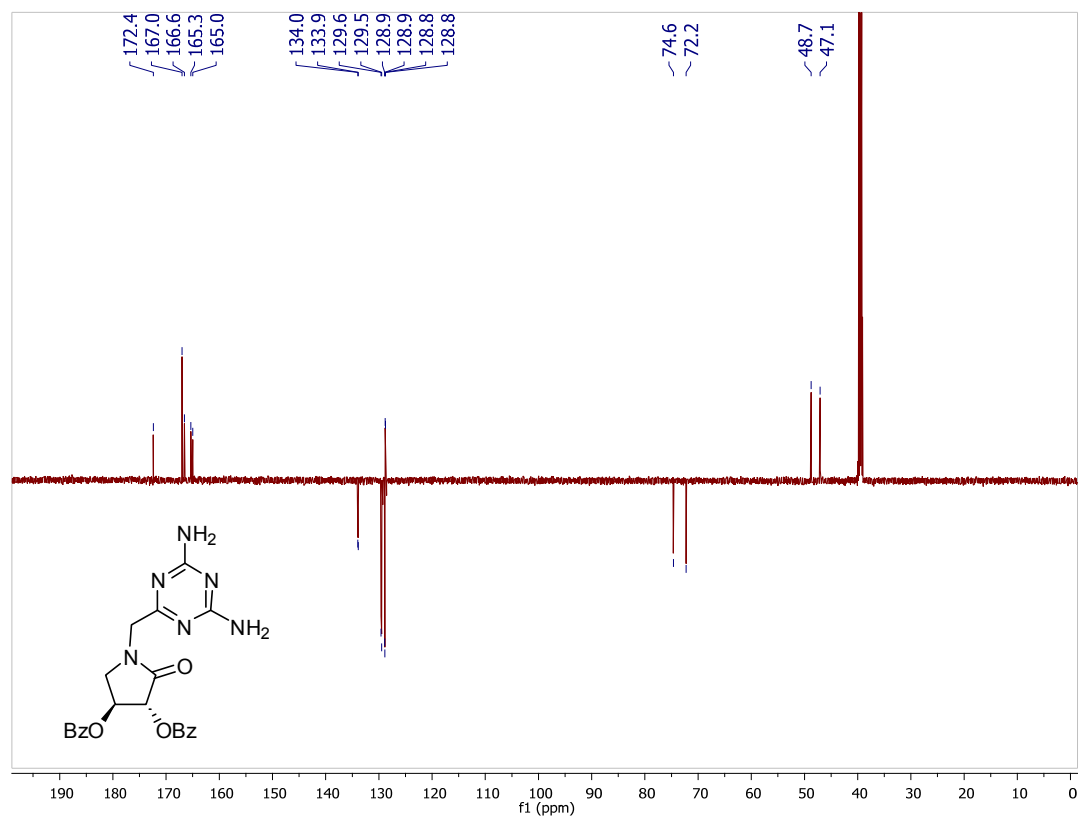


Figure S8: APT NMR (150 MHz, DMSO-d₆) of **1c**.

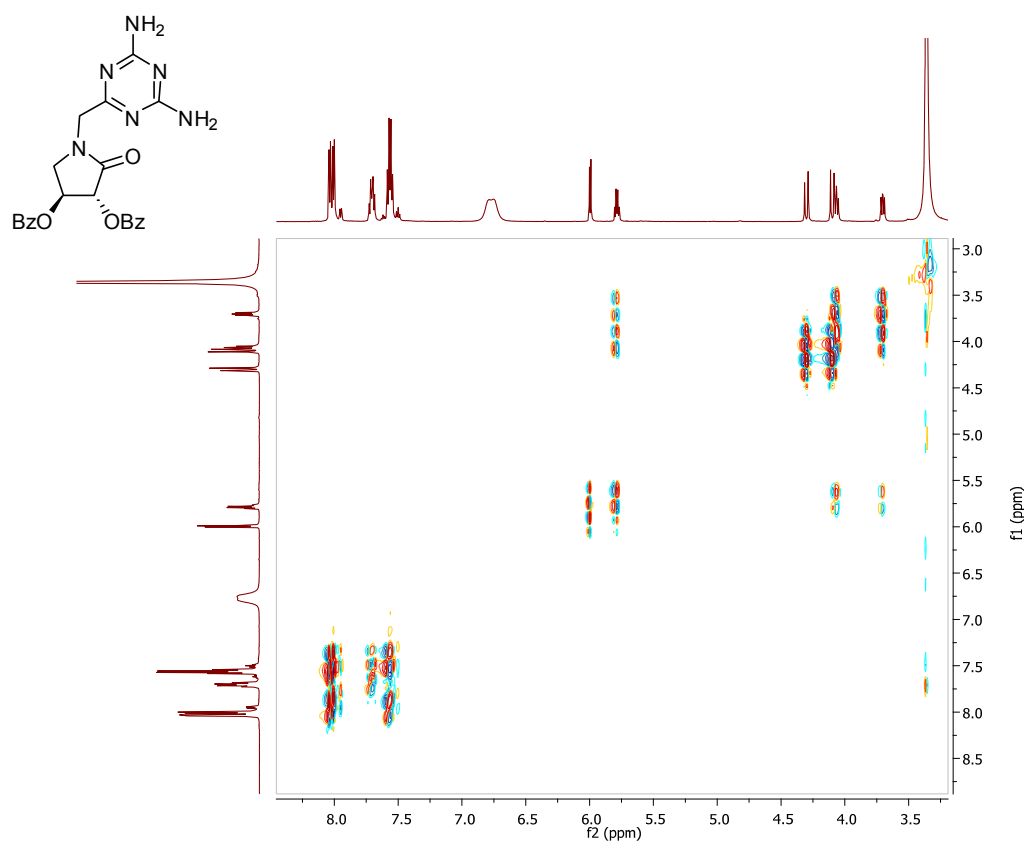


Figure S9: COSY (^1H - ^1H , DMSO- d_6) of **1c**.

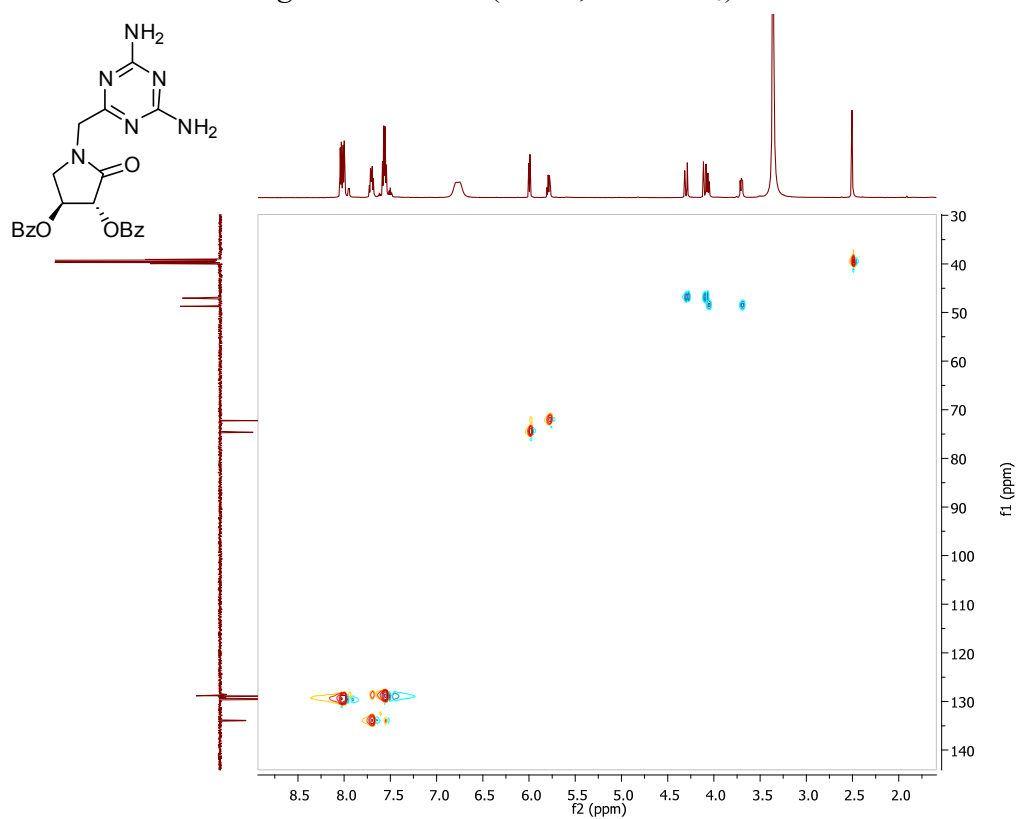


Figure S10: HSQC (^1H - ^{13}C , DMSO- d_6) of **1c**.

Benzyl 2-(*tert*-butoxycarbonylamino)-3-(4,6-diamino-1,3,5-triazin-2-yl)propanoate (1d)

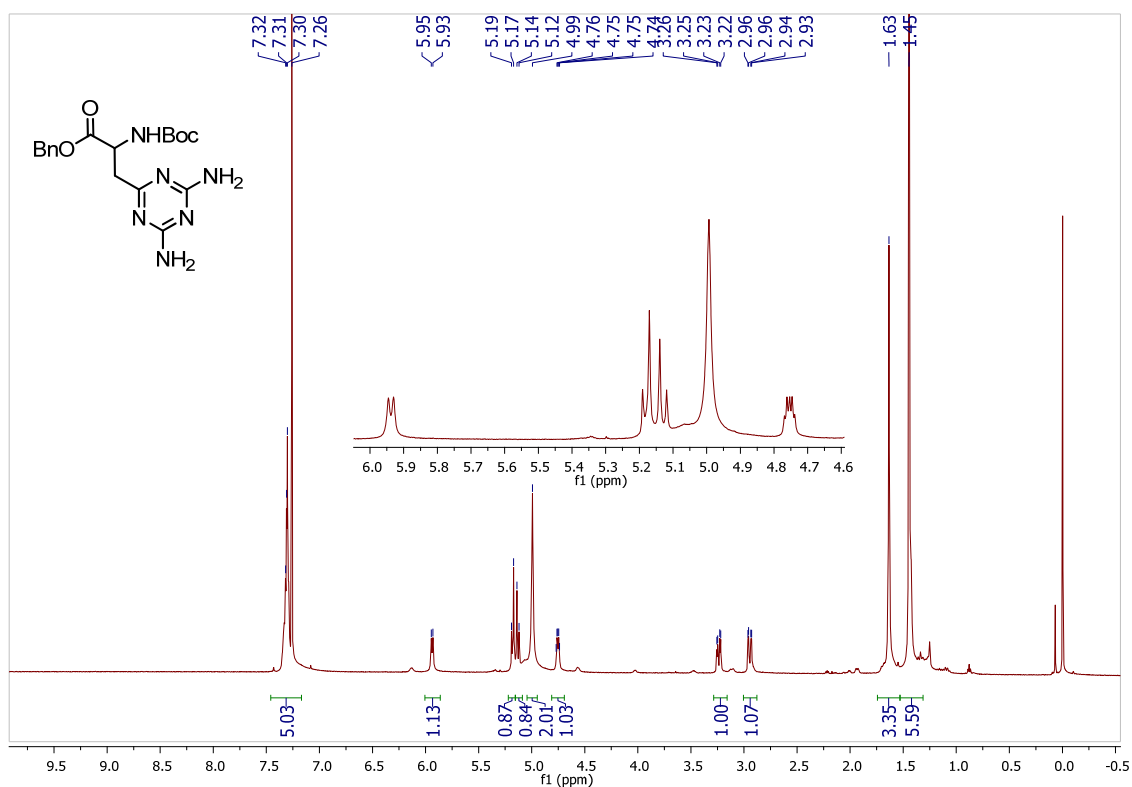


Figure S11: ¹H NMR (600 MHz, CDCl₃) of **1d**.

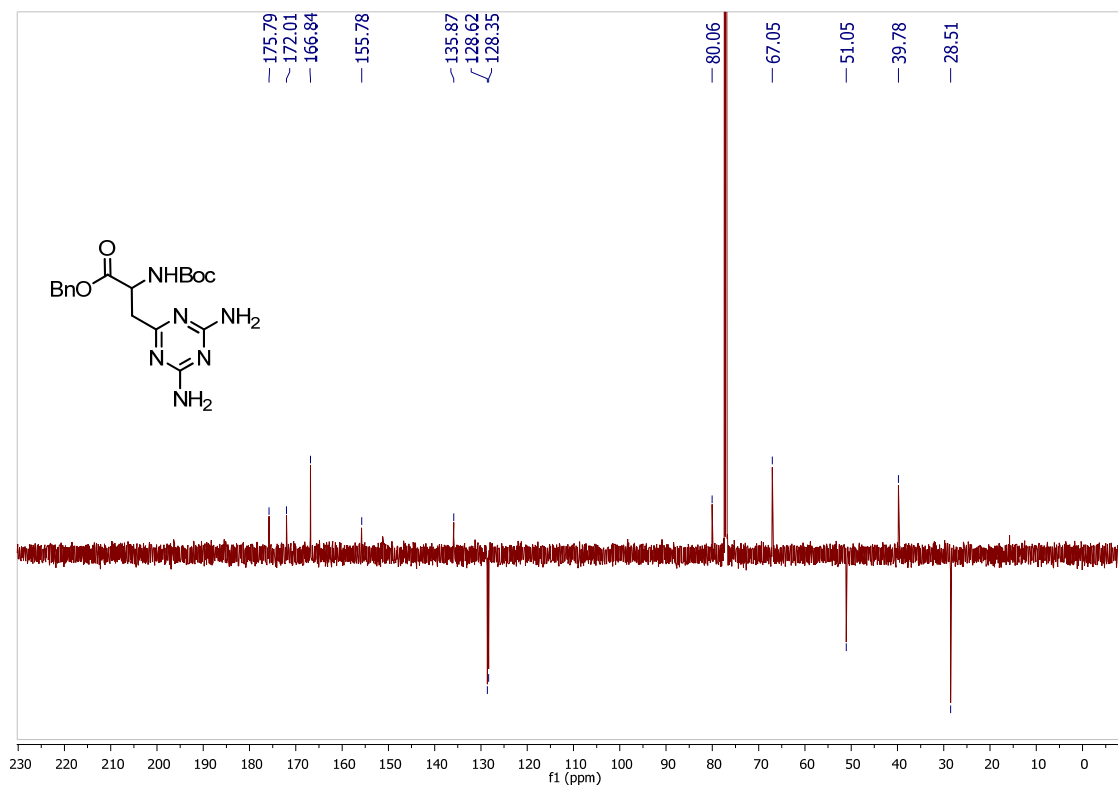


Figure S12: APT NMR (150 MHz, CDCl₃) of **1d**.

Benzyl 2-(*tert*-butoxycarbonyl((4,6-dioxo-1,4,5,6-tetrahydro-1,3,5-triazin-2-yl)methyl)amino)acetate (2)

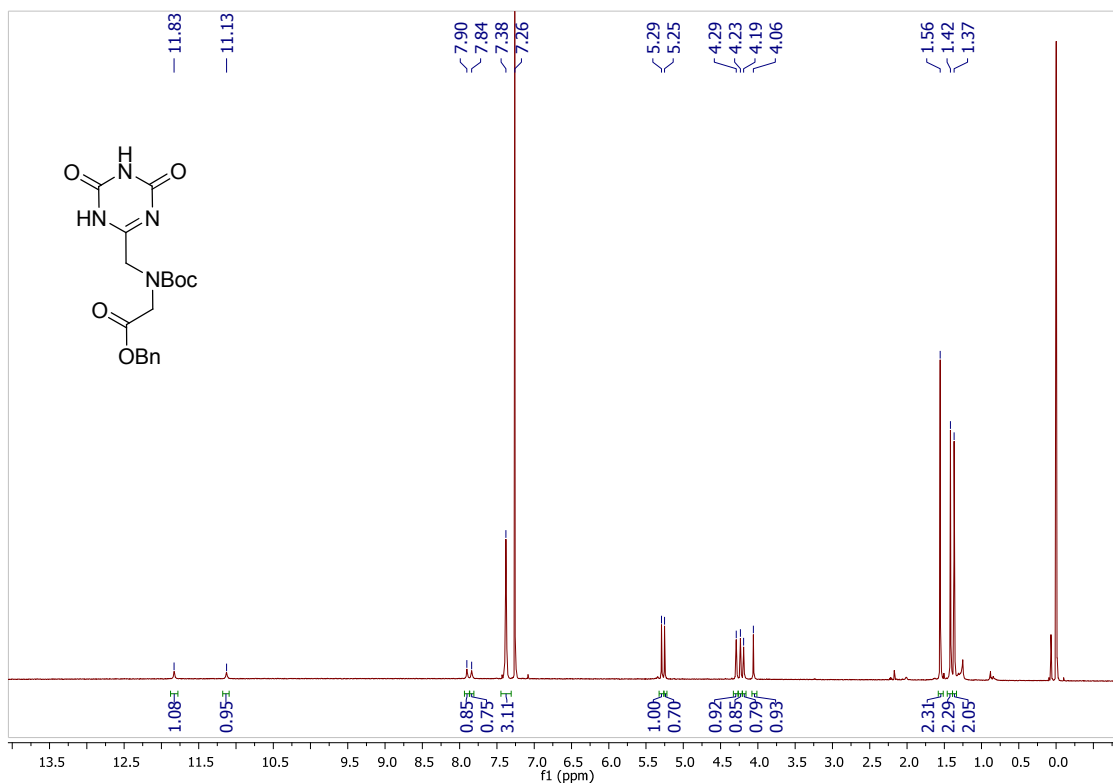


Figure S13: ¹H NMR (600 MHz, CDCl₃) of **2**.

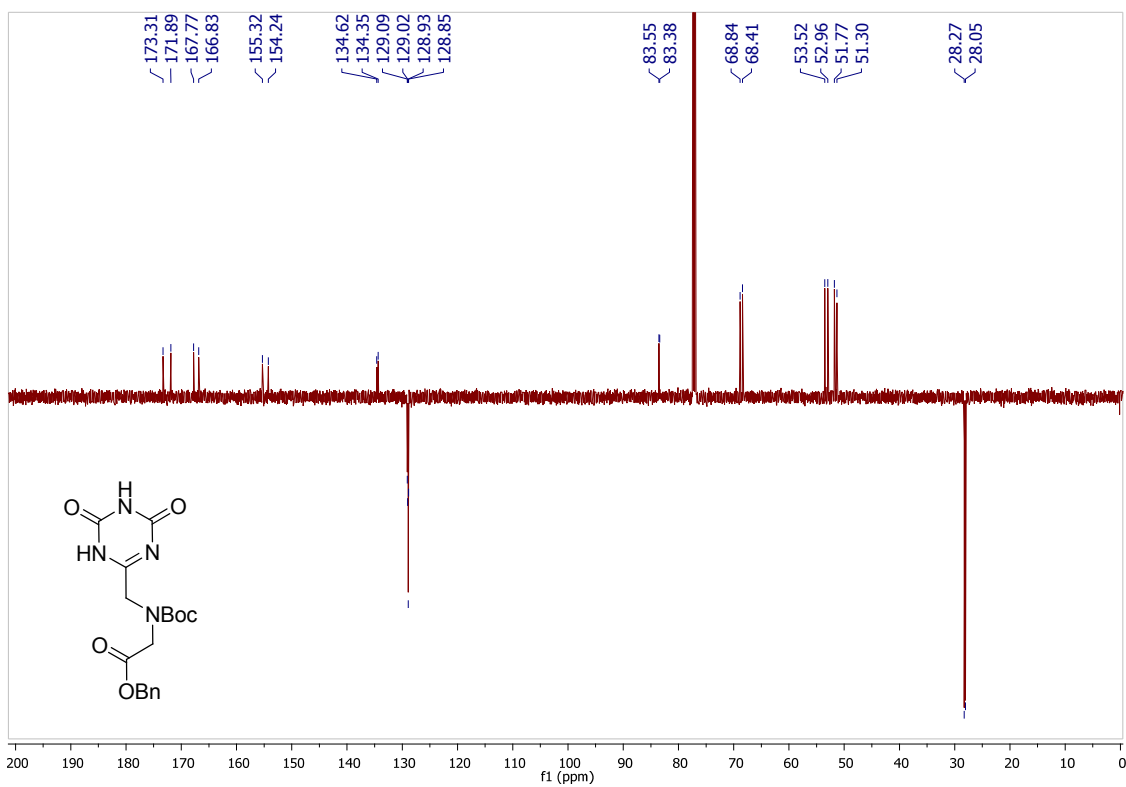


Figure S14: APT NMR (150 MHz, CDCl₃) of **2**.

6-(((3*R*,4*R*)-3',4'-Bis(*tert*-butyldimethylsilyloxy)pyrrolidine-*N*-yl)methyl)-uracil (3a)

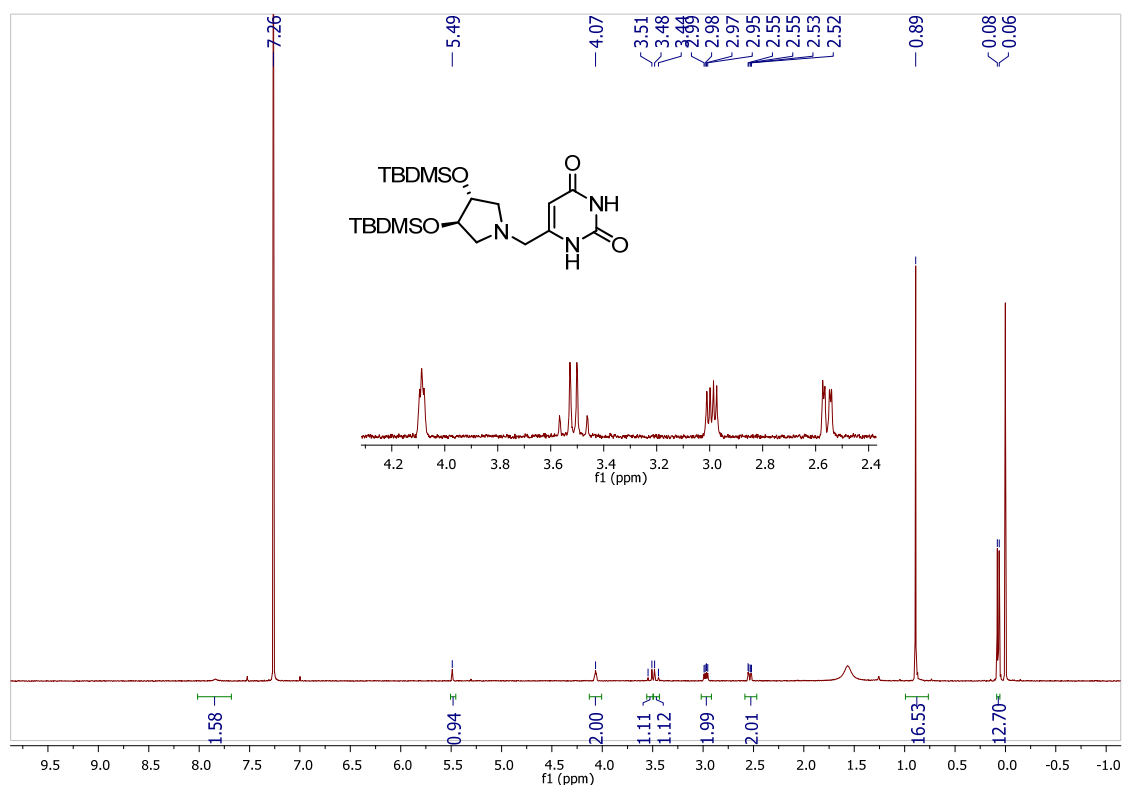


Figure S15: ¹H NMR (600 MHz, CDCl₃) of **3a**.

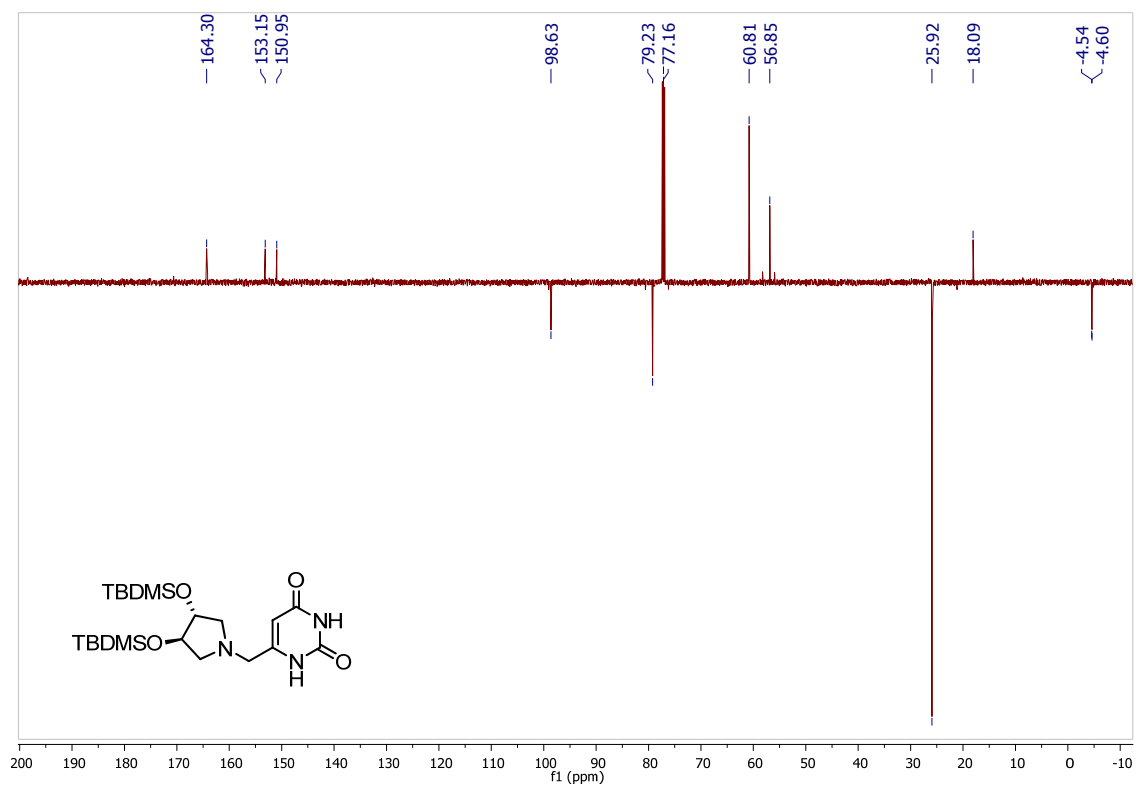


Figure S16: APT NMR (150 MHz, CDCl₃) of **3a**.

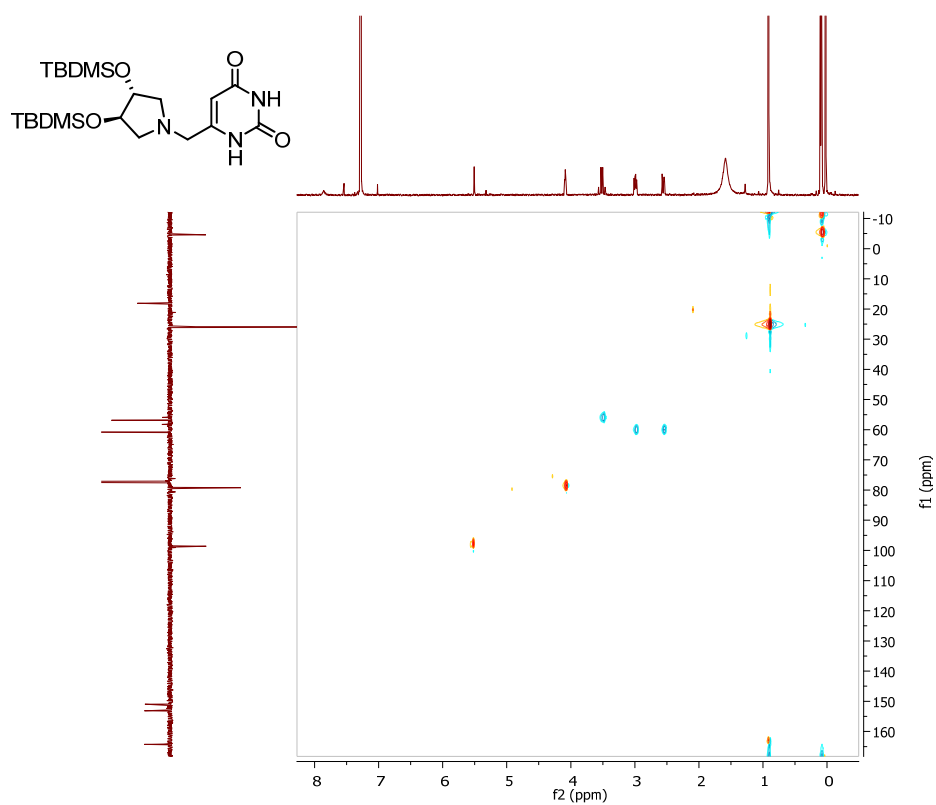


Figure S17: HSQC (^1H - ^{13}C , CDCl_3) of **3a**.

2',3'-*O*-Isopropylidene-5'-*O*-(*tert*-butyldimethylsilyl)-uridine (3b**)**

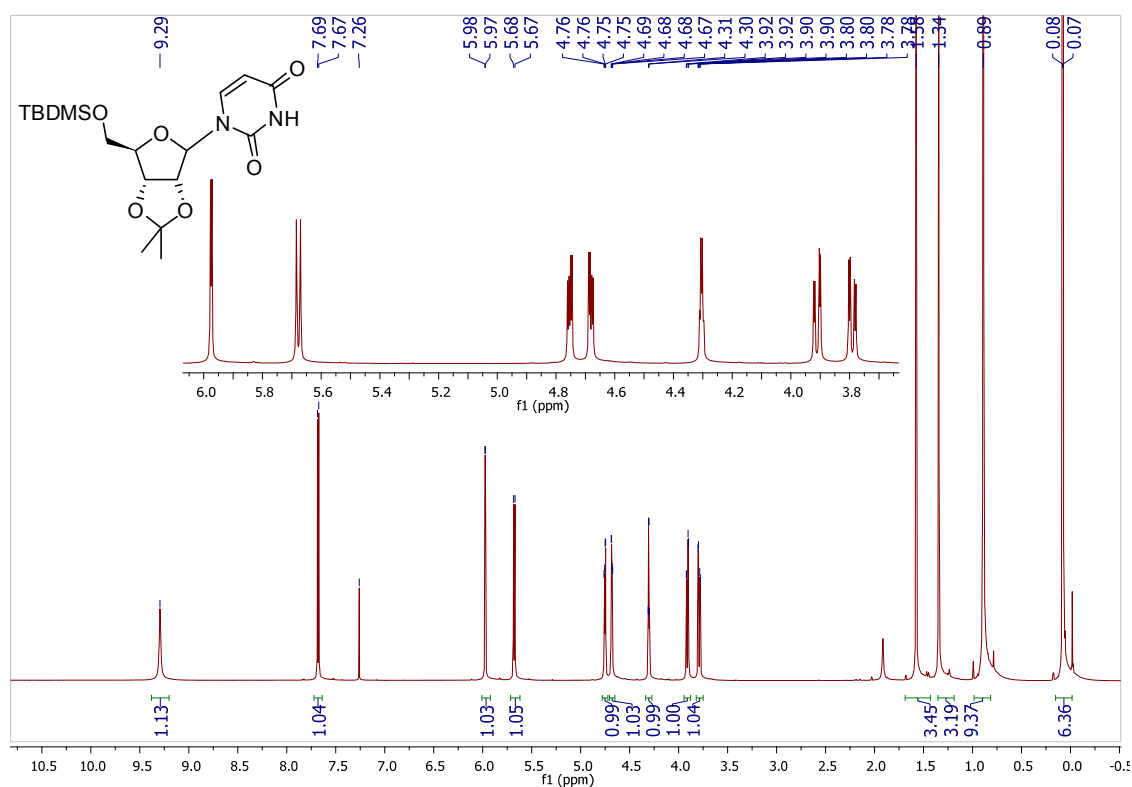


Figure S18: ¹H NMR (600 MHz, CDCl₃) of **3b**.

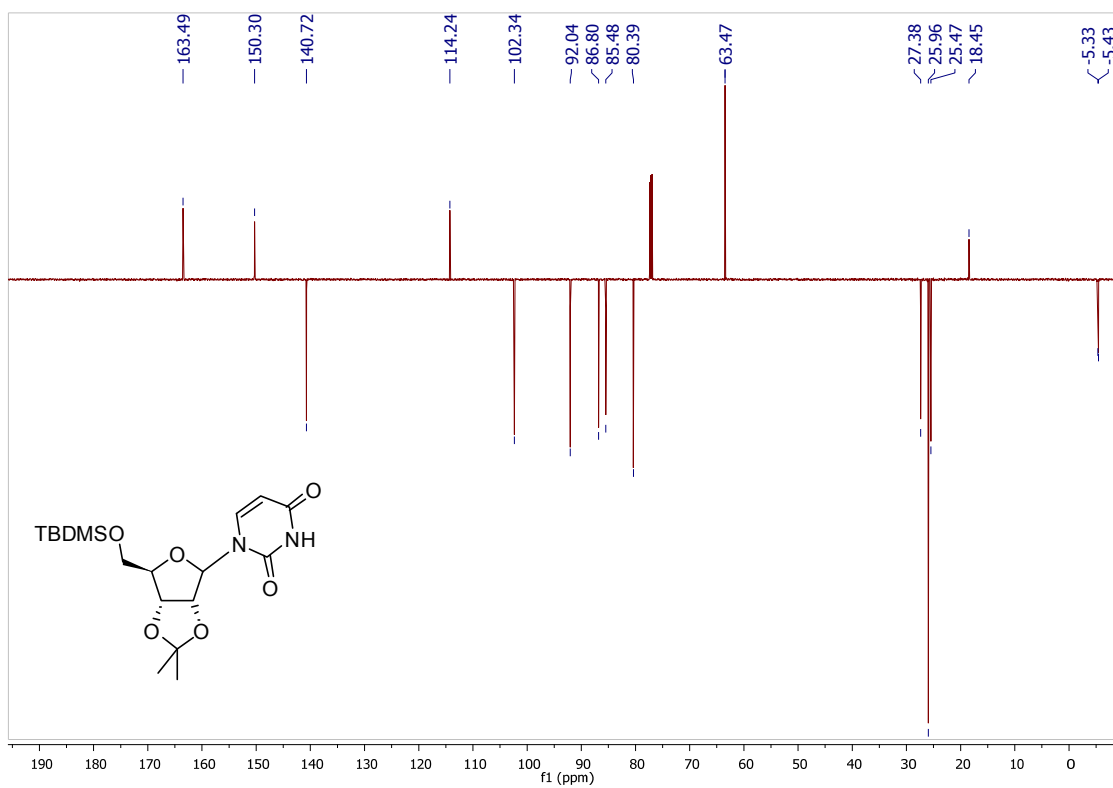


Figure S19: APT NMR (150 MHz, CDCl₃) of **3b**.

2',3'-*O*-Isopropylidene-5'-*O*-(*tert*-butyldimethylsilyl)-orotidine methyl ester (3c**)**

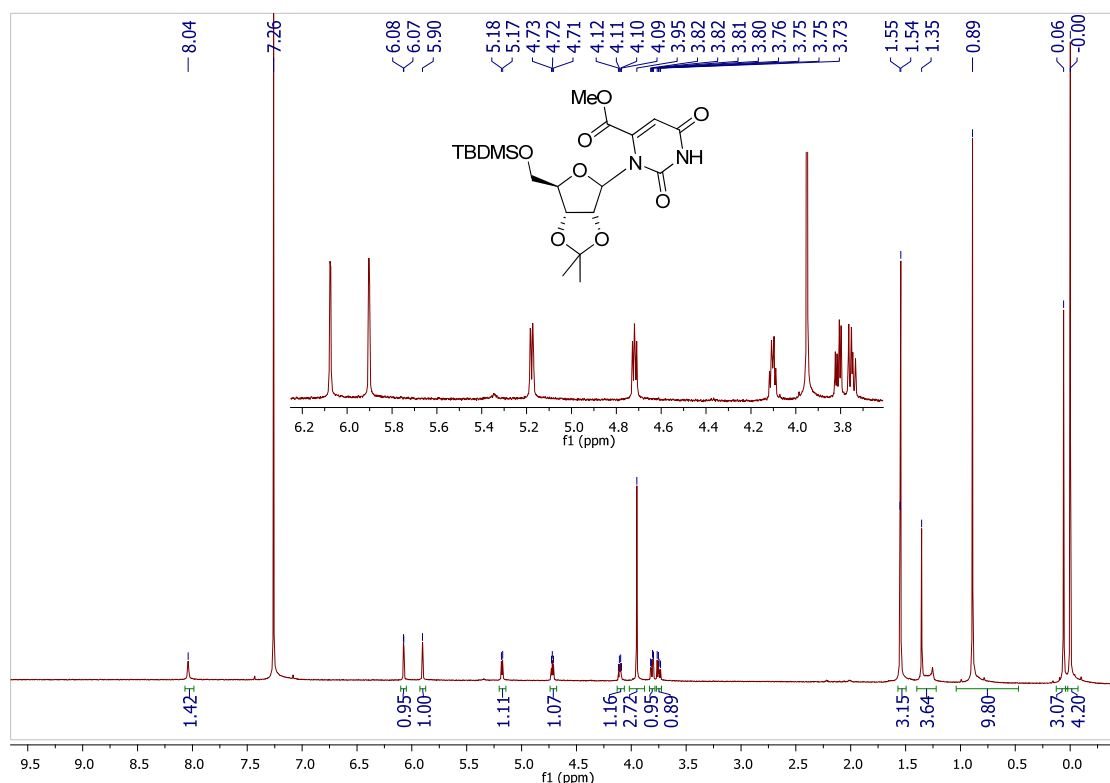


Figure S20: ¹H NMR (600 MHz, CDCl₃) of **3c**.

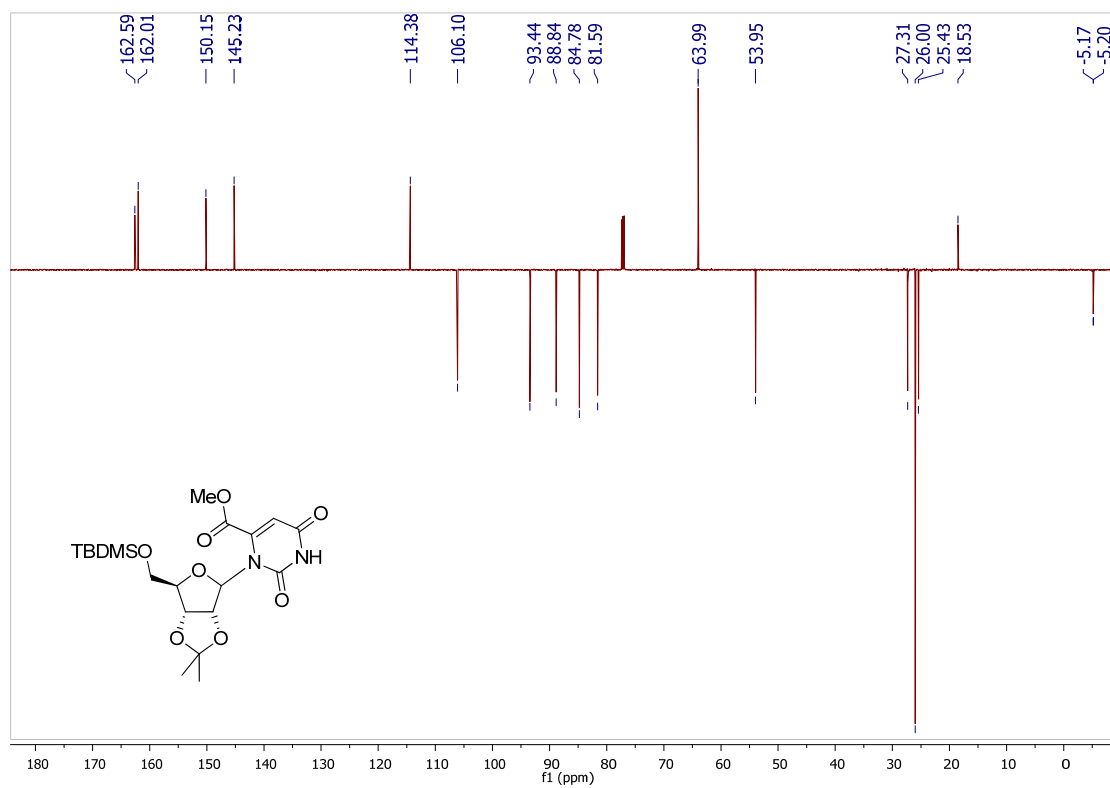


Figure S21: APT NMR (150 MHz, CDCl₃) of **3c**.

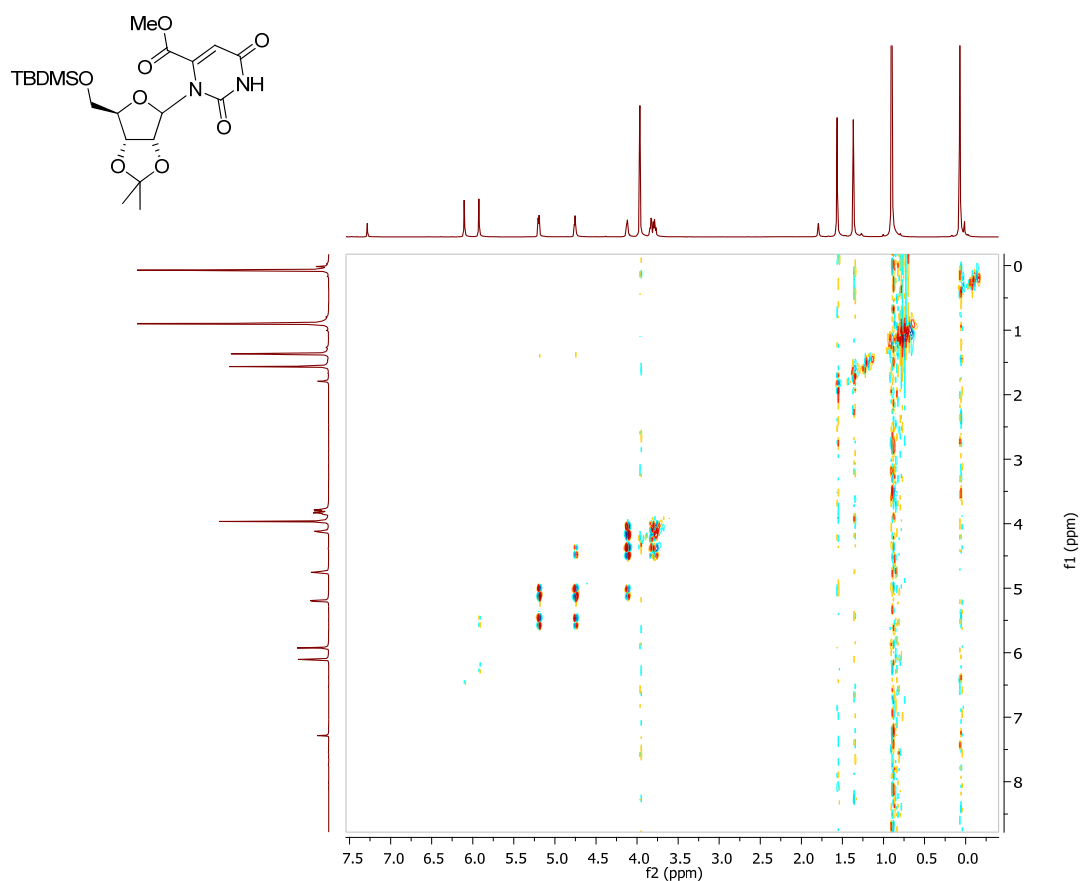


Figure S22: COSY (^1H - ^1H , CDCl_3) of **3c**.

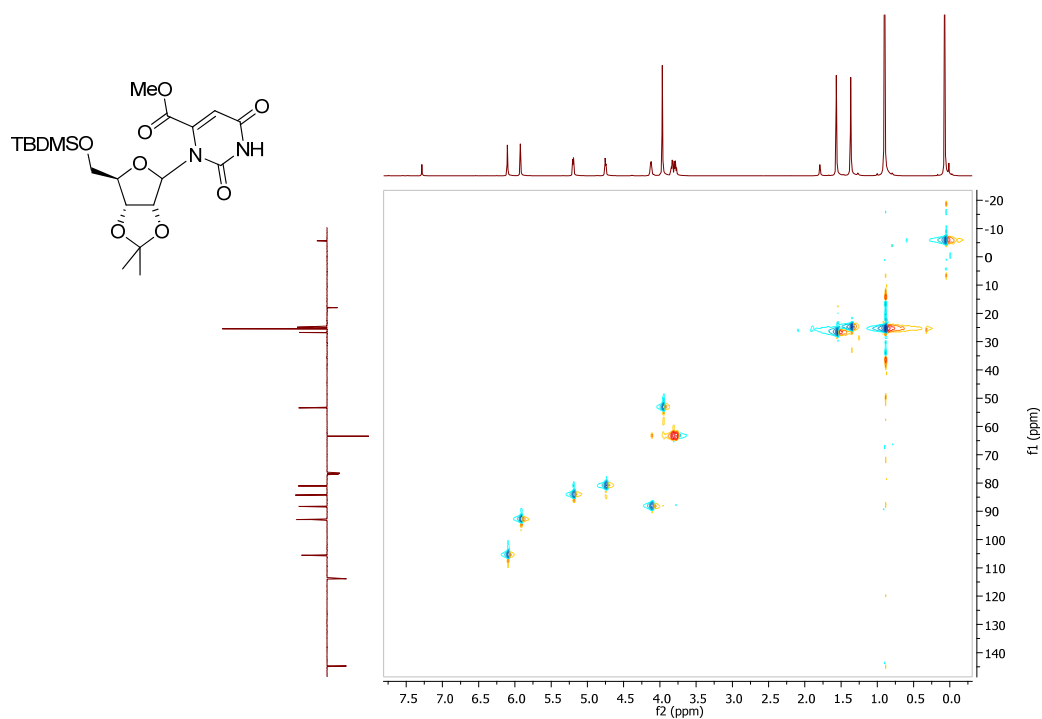


Figure S23: HSQC (^1H - ^{13}C , CDCl_3) of **3c**.

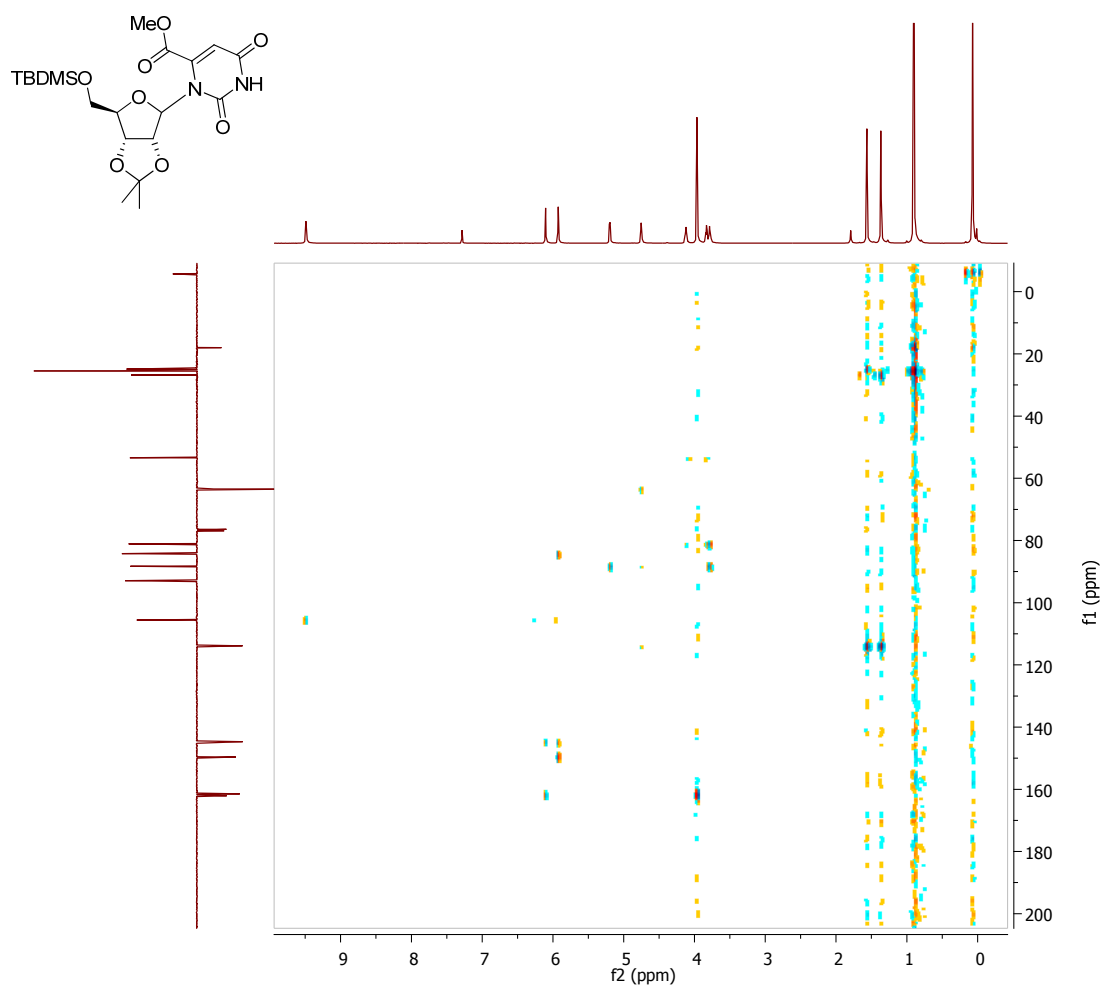


Figure S24: HMBC (^1H - ^{13}C , CDCl_3) of **3c**.

9-(Tetrahydro-2H-pyran-2-yl)-adenine (4a)

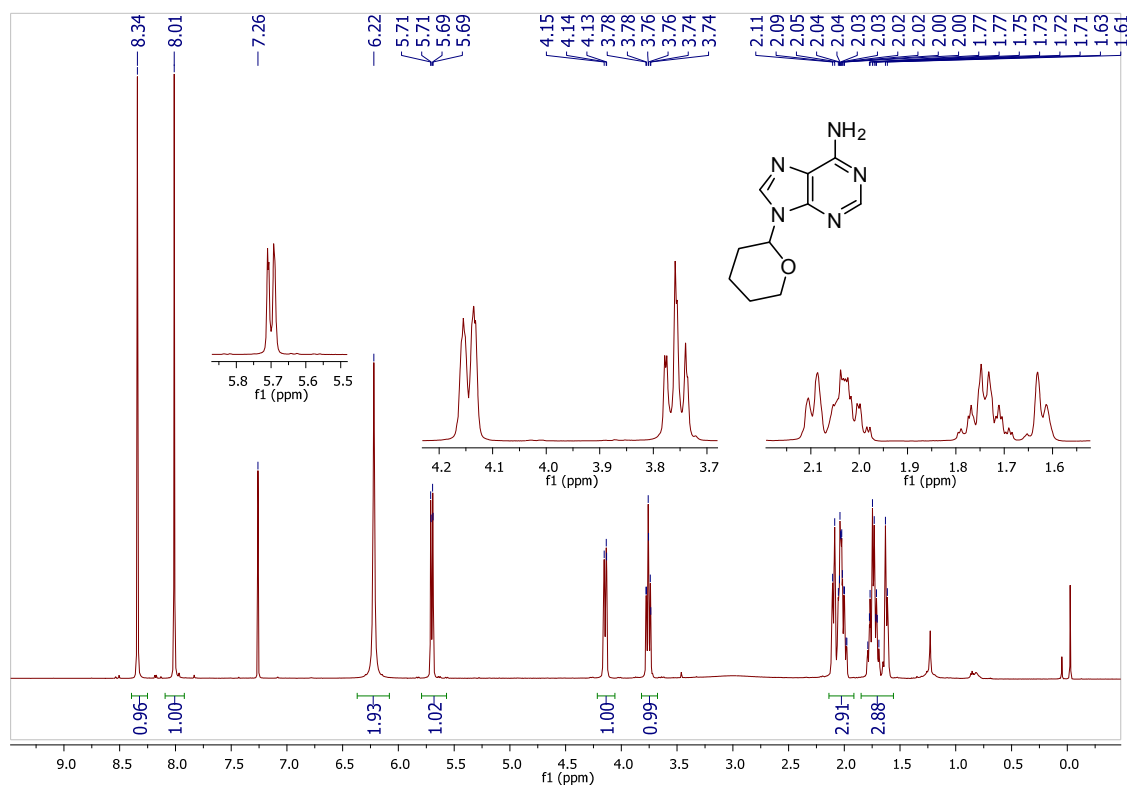


Figure S25: ¹H NMR (600 MHz, CDCl₃) of **4a**.

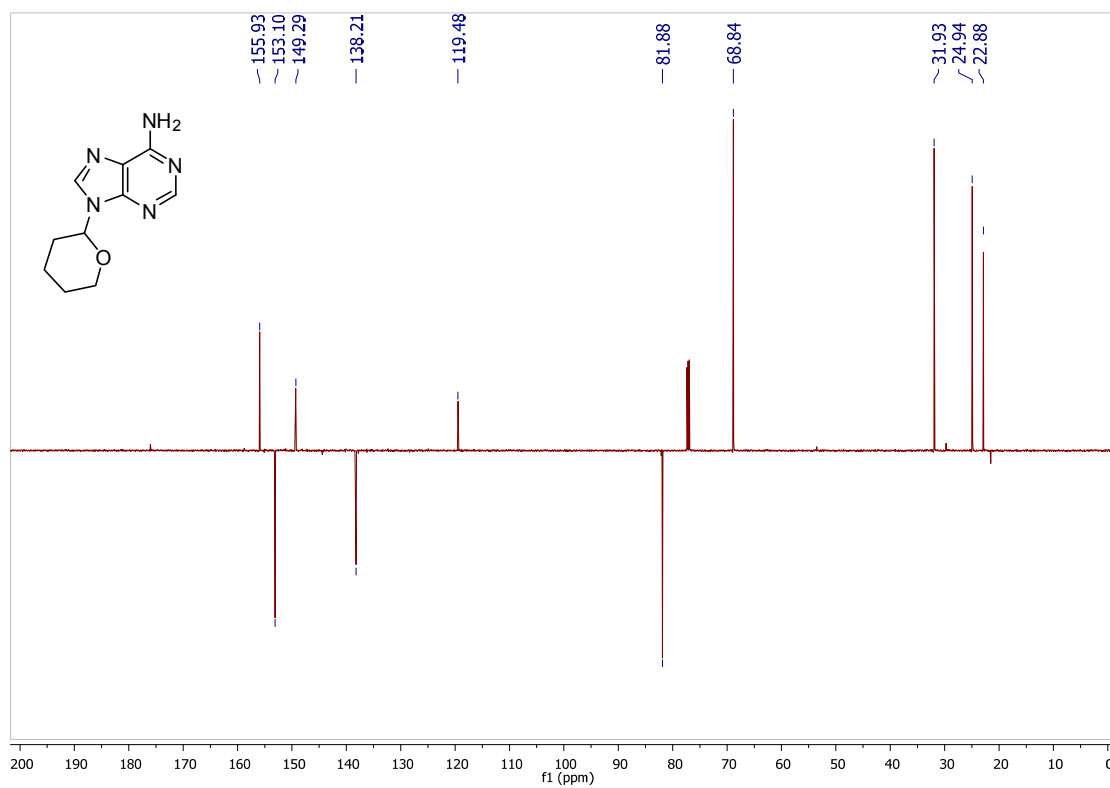


Figure S26: APT NMR (150 MHz, CDCl₃) of **4a**.

3',5'-Di-*O*-(*tert*-butyldimethylsilyl)-8-carboxymethyl-2'-deoxyadenosine (4b)

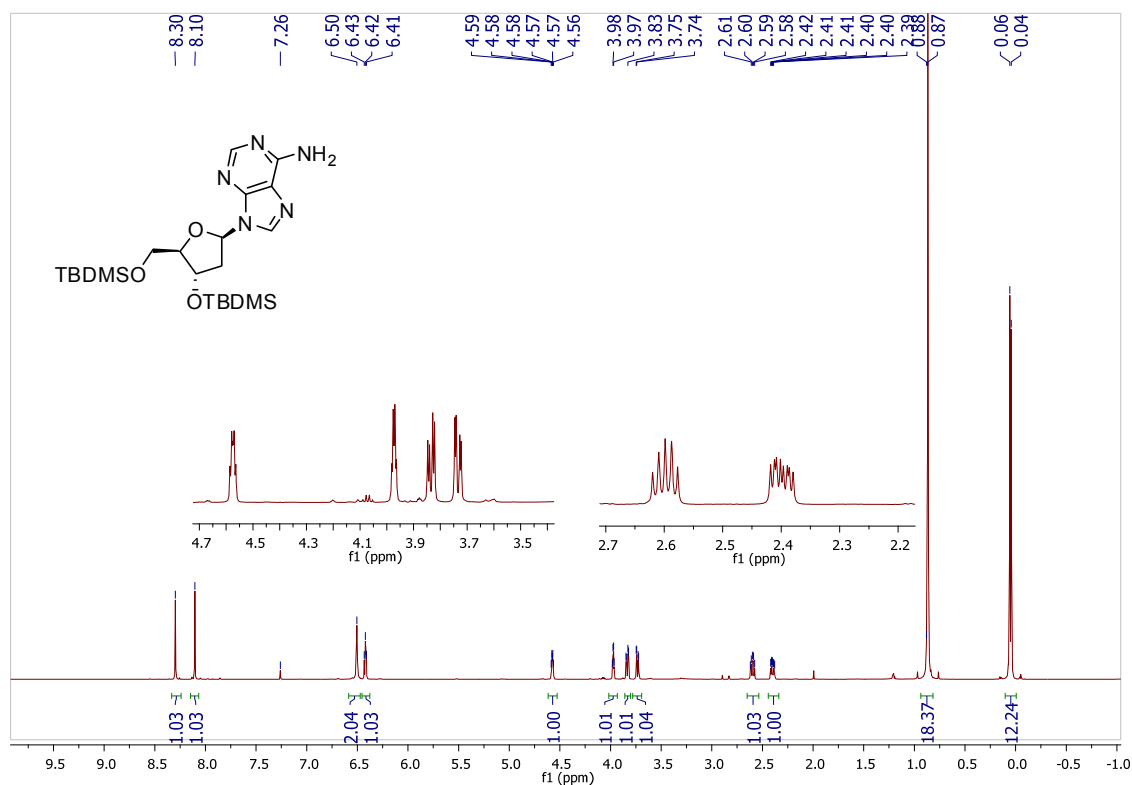


Figure S27: ¹H NMR (600 MHz, CDCl₃) of 4b.

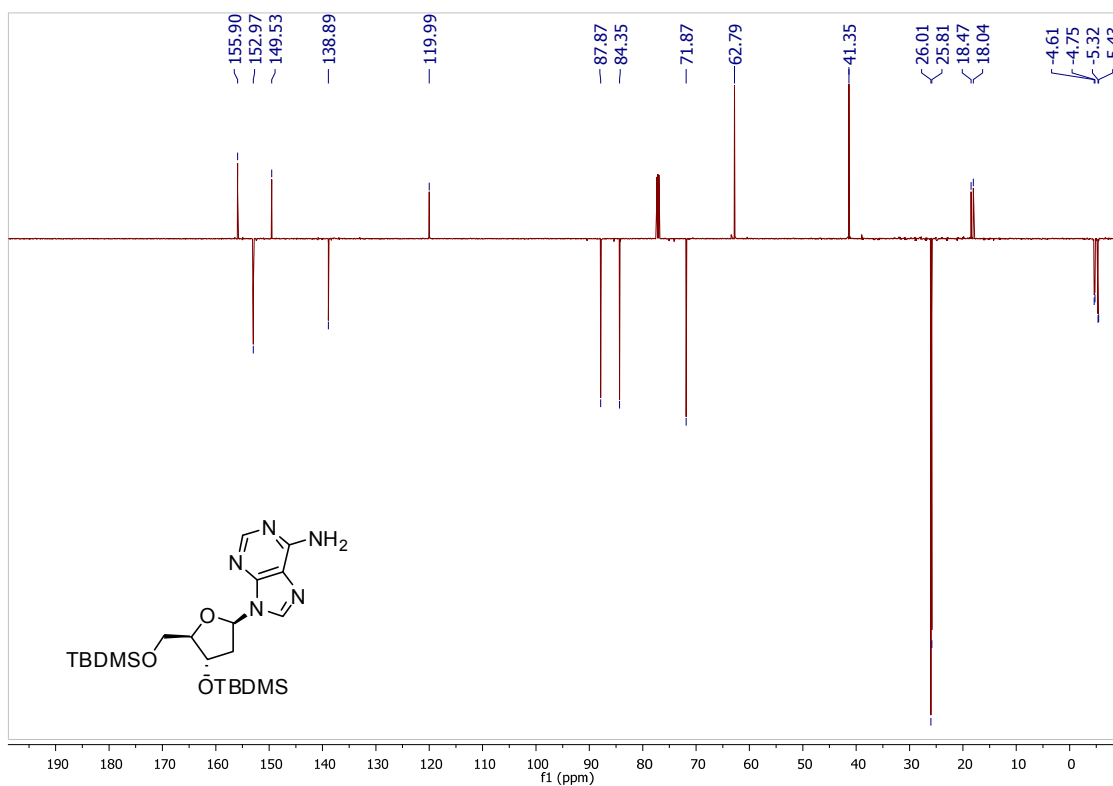


Figure S28: APT NMR (150 MHz, CDCl₃) of 4a.

5'-O-(*Tert*-butyldimethylsilyl)-8-carboxymethyl-2'-deoxyadenosine (4c)

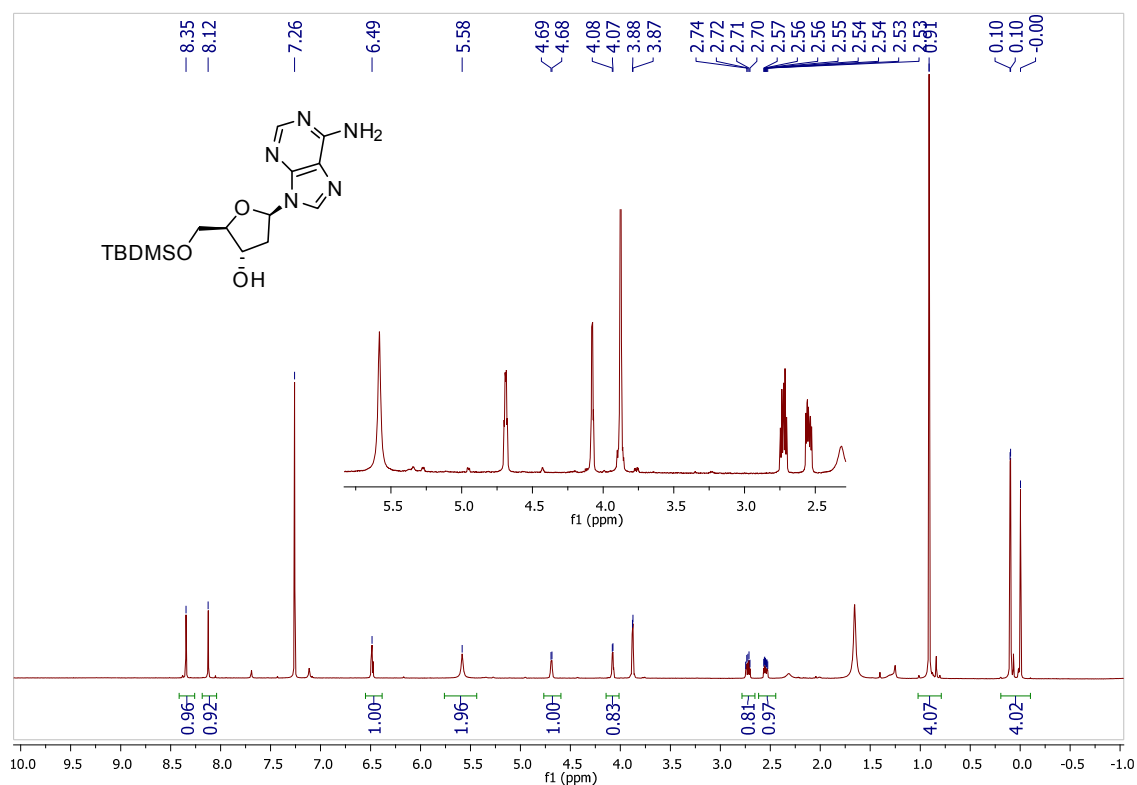


Figure S29: ¹H NMR (600 MHz, CDCl₃) of **4c**.

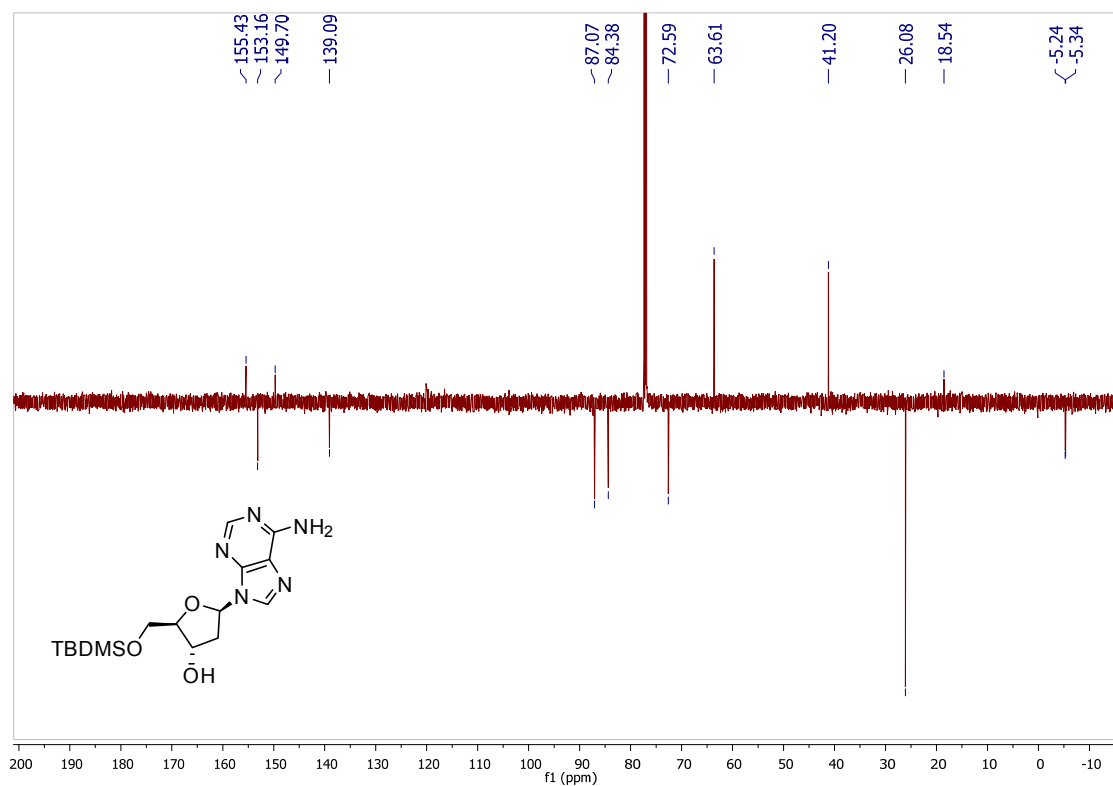


Figure S30: APT NMR (150 MHz, CDCl₃) of **4c**.

***N*⁶-Benzoyl 2',3'-*O*-isopropylidene-5'-*O*-(*tert*-butyldimethylsilyl)-adenosine (4d)**

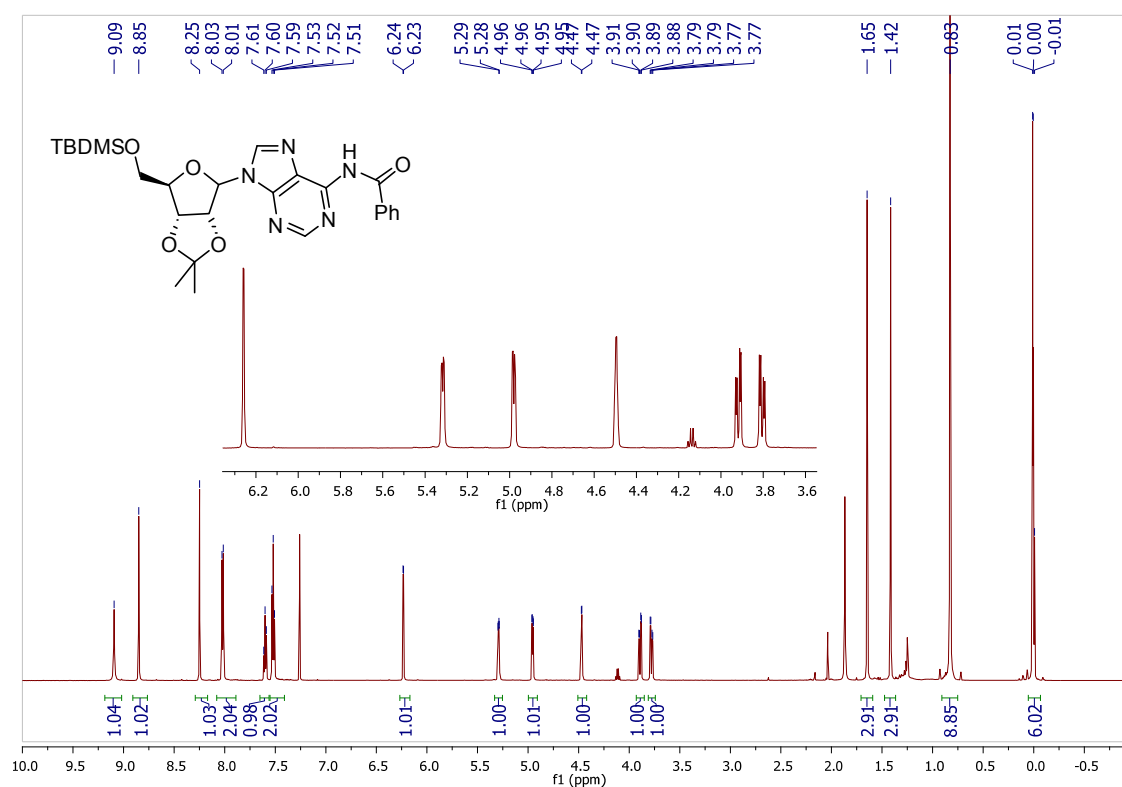


Figure S31: ¹H NMR (600 MHz, CDCl₃) of 4d.

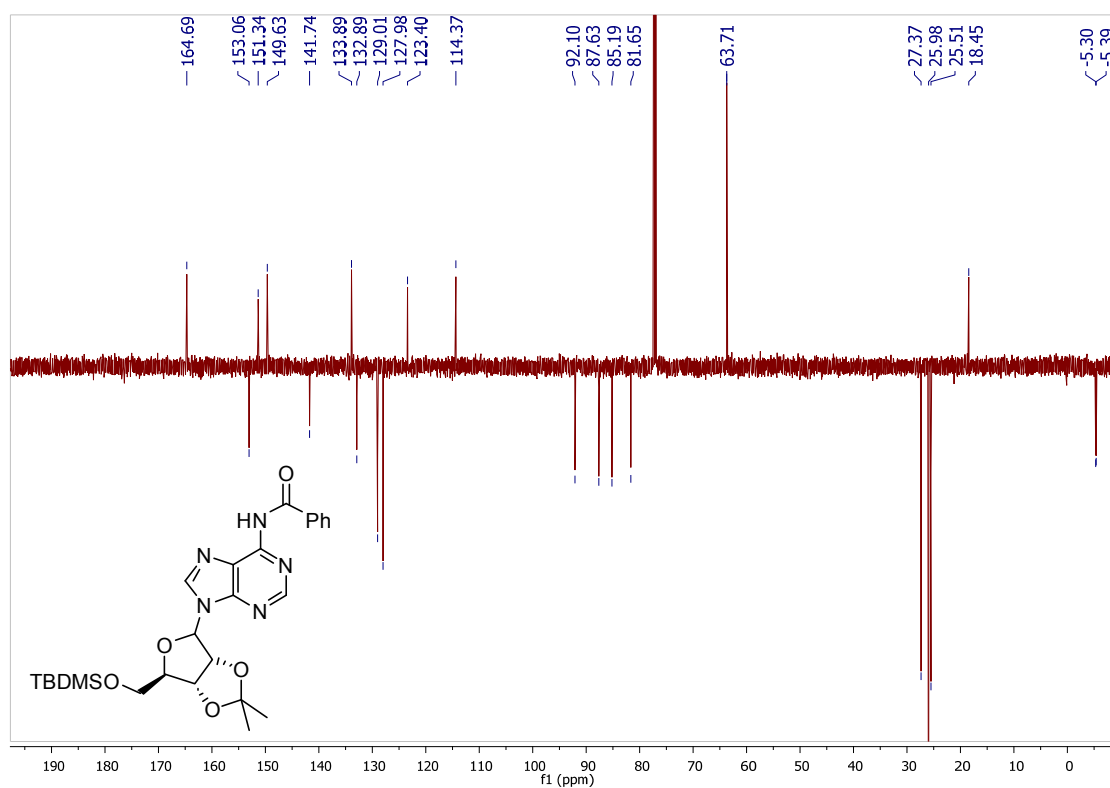


Figure S32: APT NMR (150 MHz, CDCl₃) of 4d.

2',3'-*O*-Isopropylidene-5'-*O*-(*tert*-butyldimethylsilyl)-adenosine (4e)

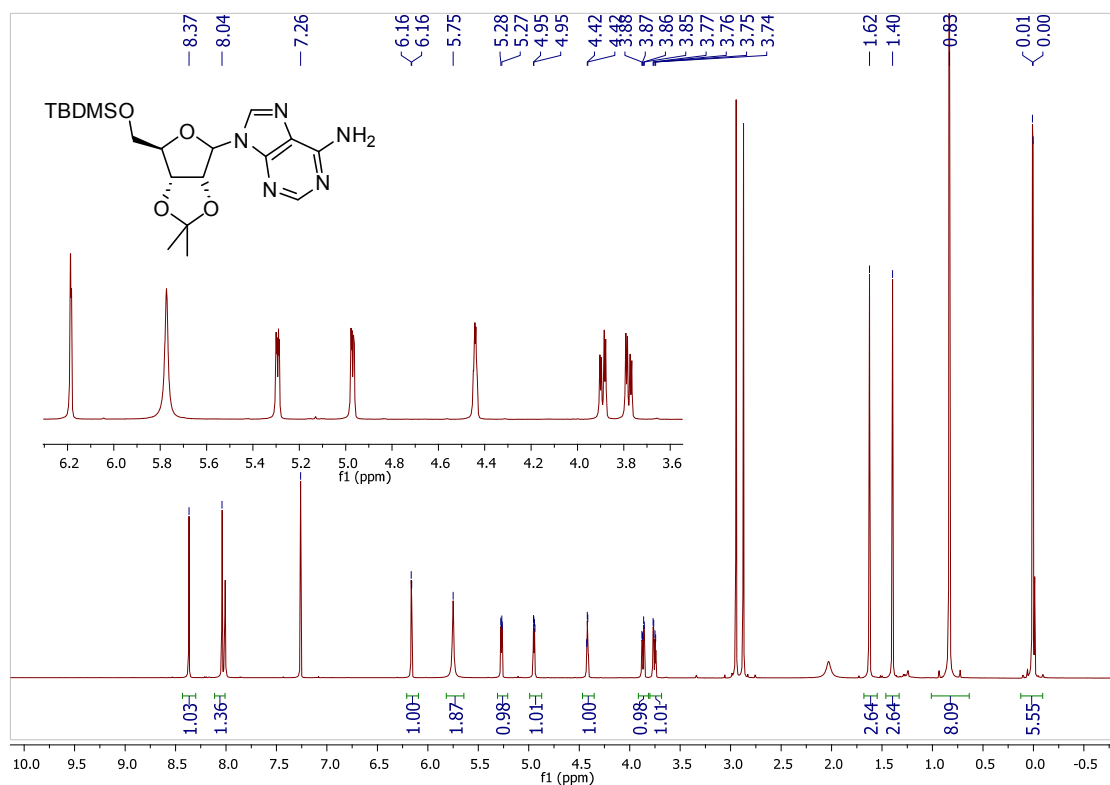


Figure S33: ¹H NMR (600 MHz, CDCl₃) of 4e.

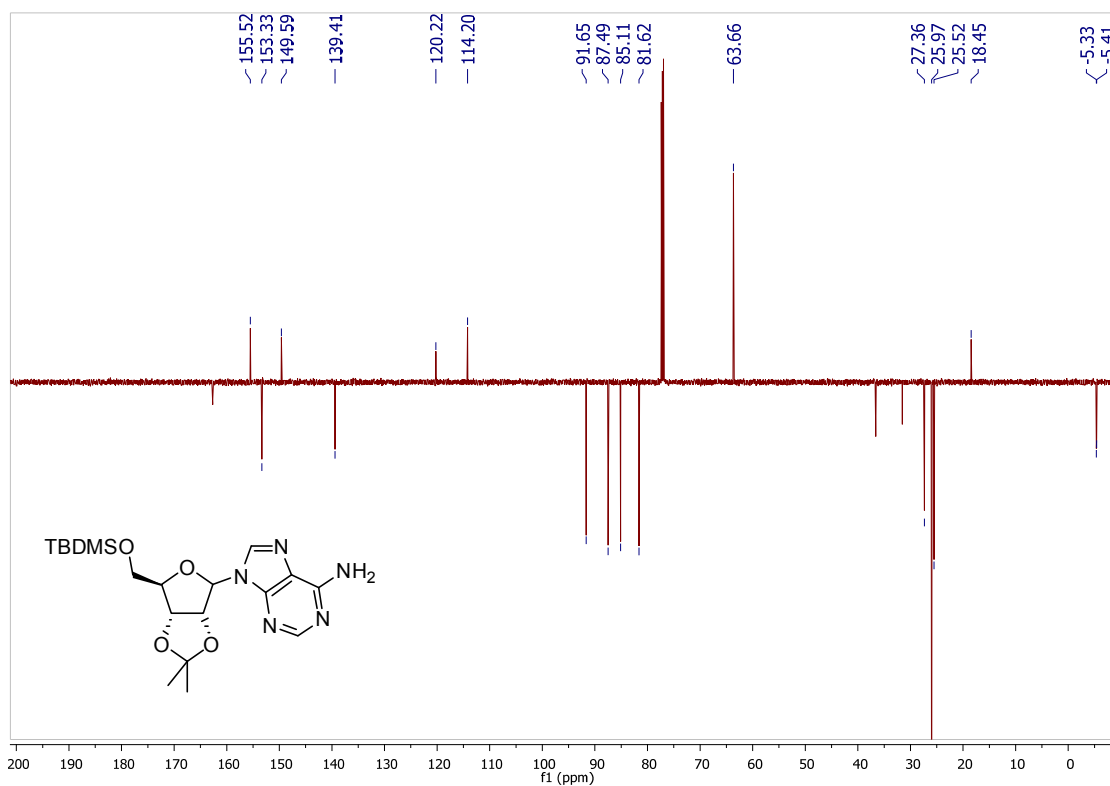


Figure S34: APT NMR (150 MHz, CDCl₃) of 4e.

***N*⁶-Benzoyl 2',3'-*O*-isopropylidene-5'-*O*-(*tert*-butyldimethylsilyl)-8-carboxymethyl-adenosine (**10**)**

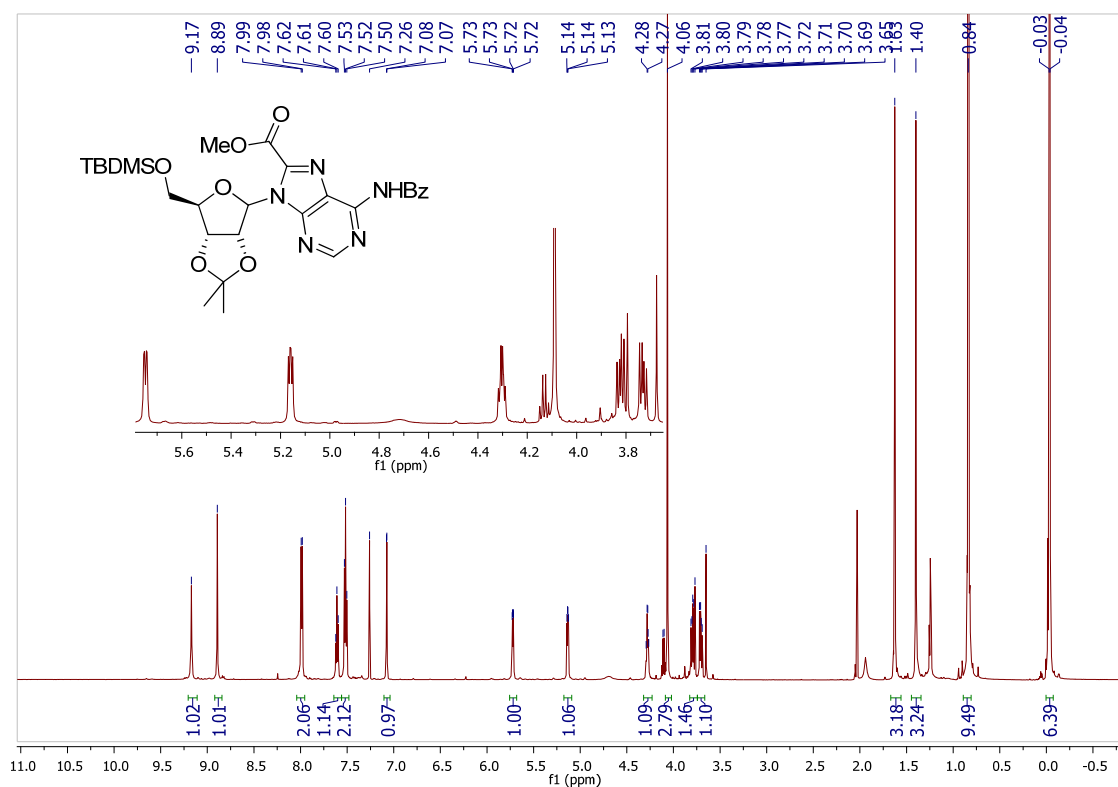


Figure S35: ¹H NMR (600 MHz, CDCl₃) of **10**.

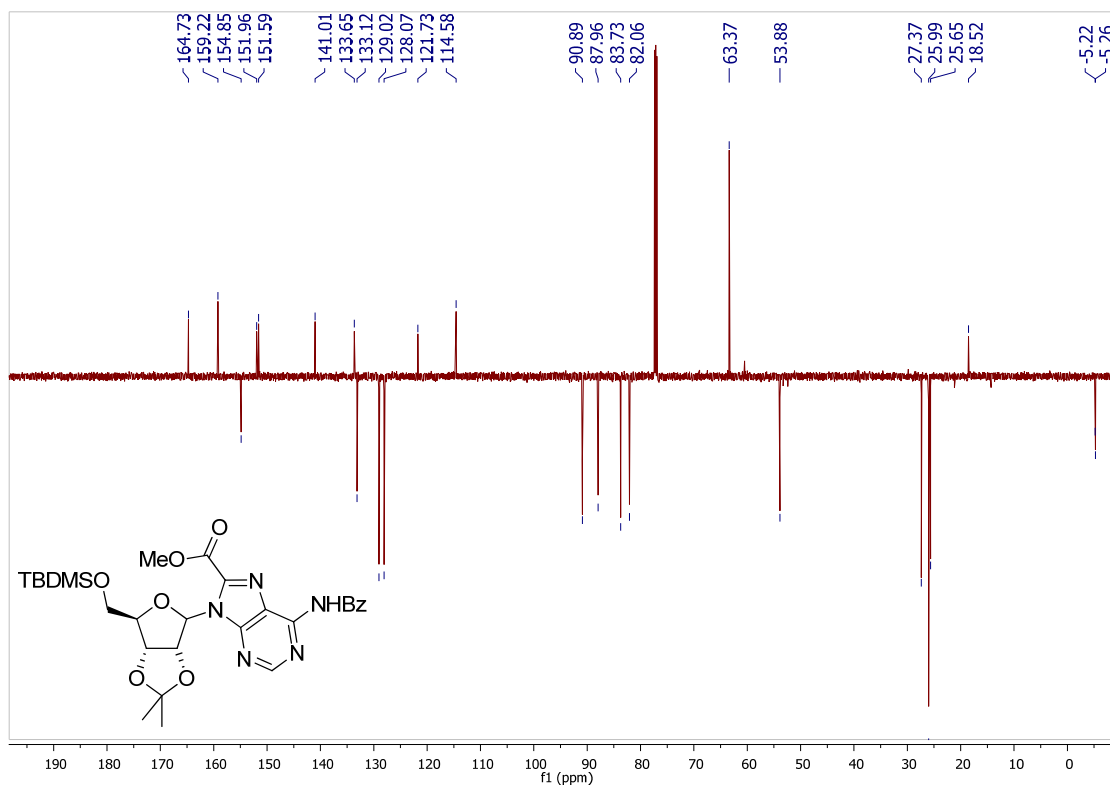
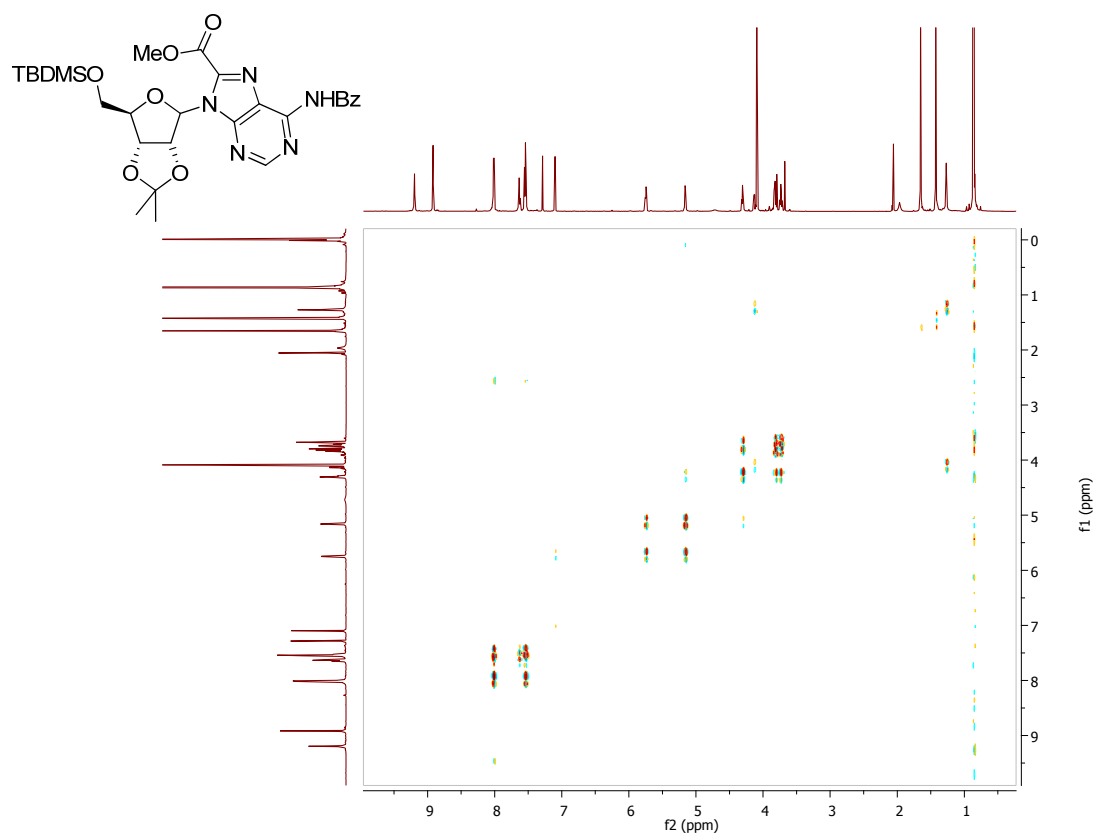
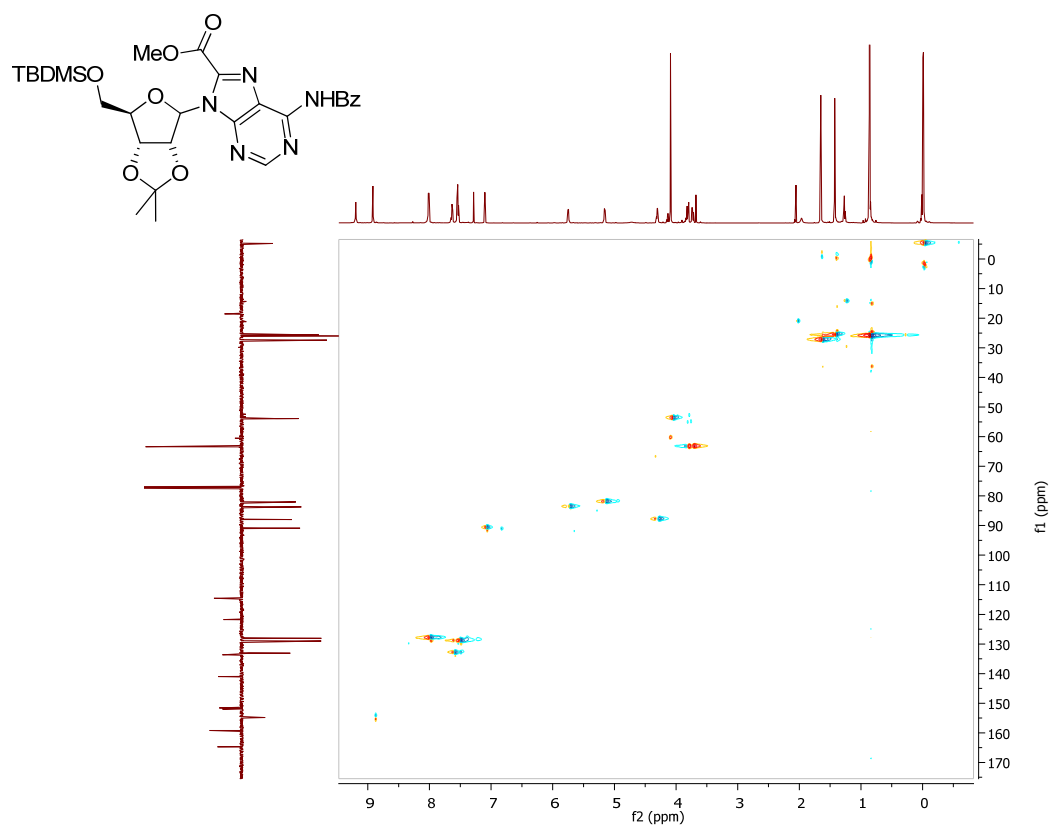


Figure S36: APT NMR (150 MHz, CDCl₃) of **10**.



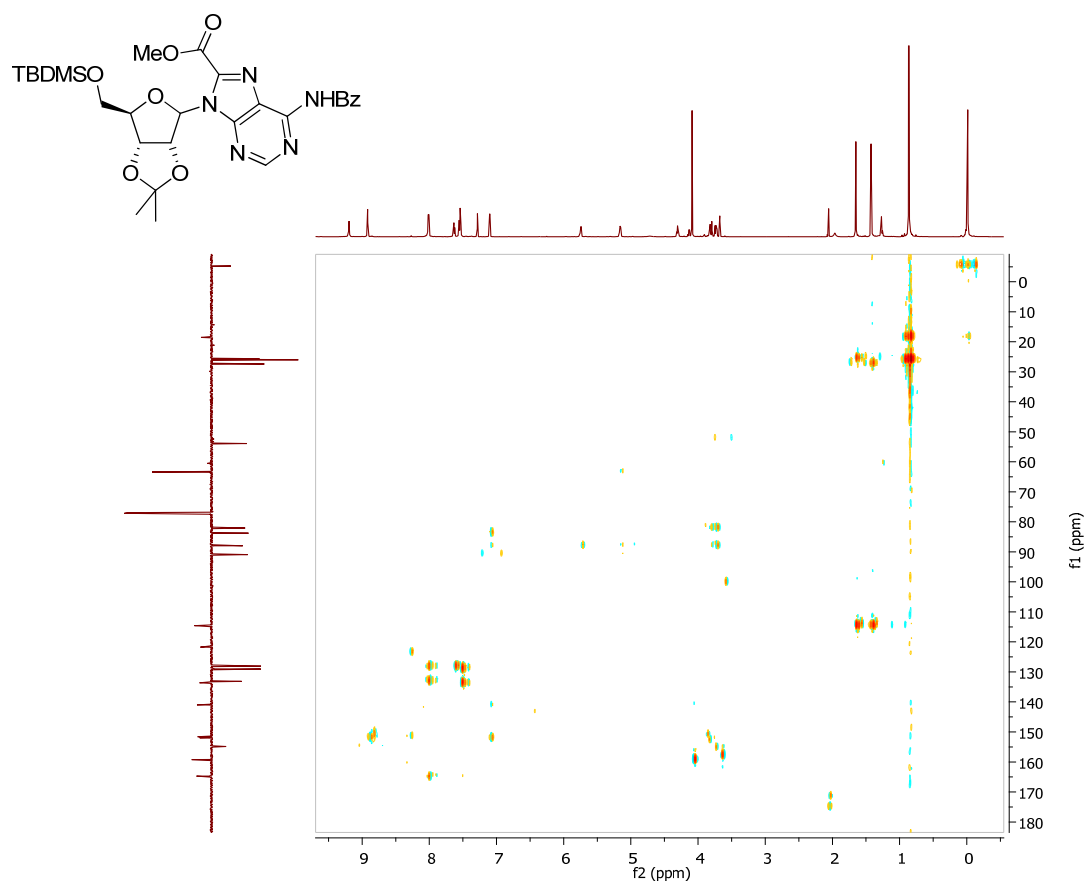


Figure S39: HMBC (^1H - ^{13}C , CDCl_3) of **10**.

2',3'-*O*-Isopropylidene-5'-*O*-(*tert*-butyldimethylsilyl)-8-carboxymethyl-adenine (4f)

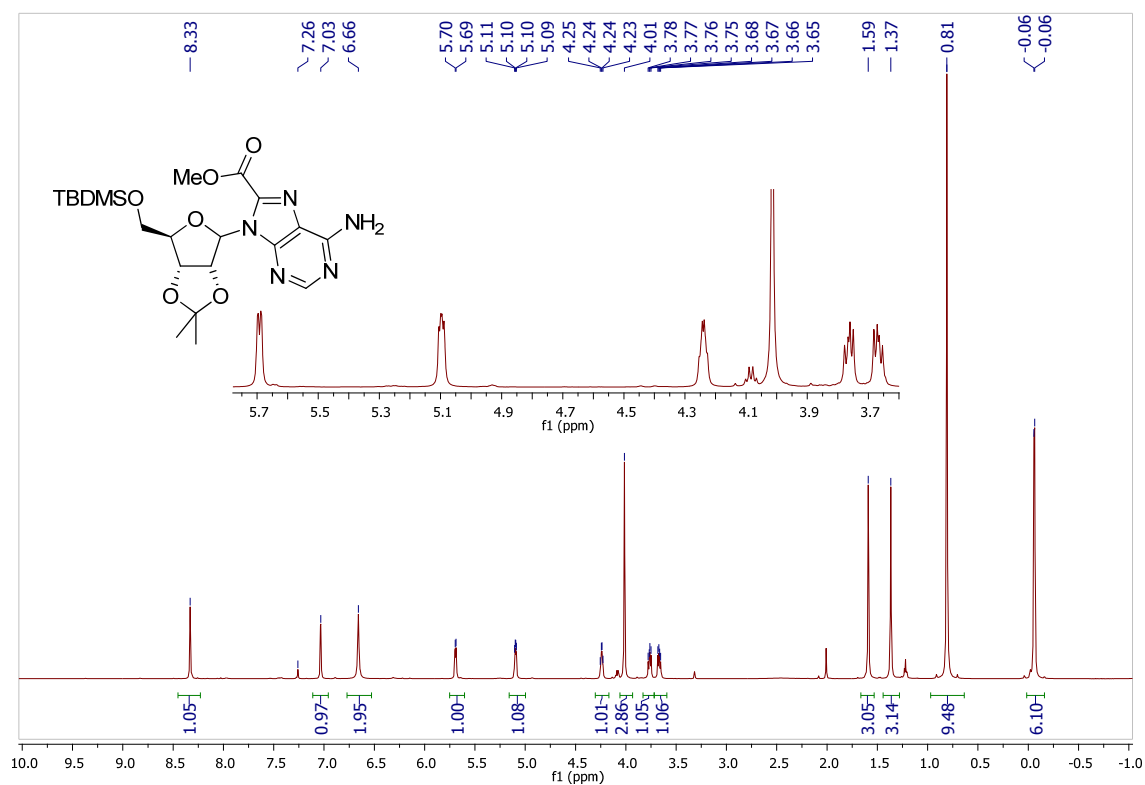


Figure S40: ¹H NMR (600 MHz, CDCl₃) of **4f**.

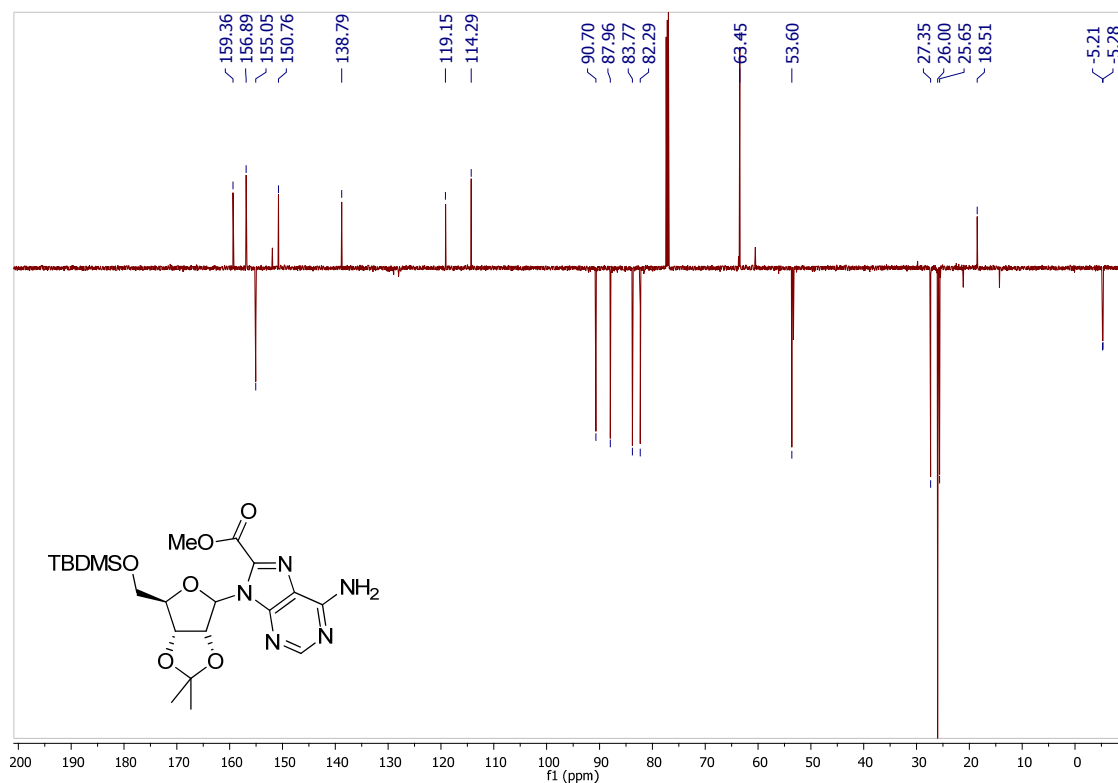


Figure S41: APT NMR (150 MHz, CDCl₃) of **4f**.

Self-association experiments

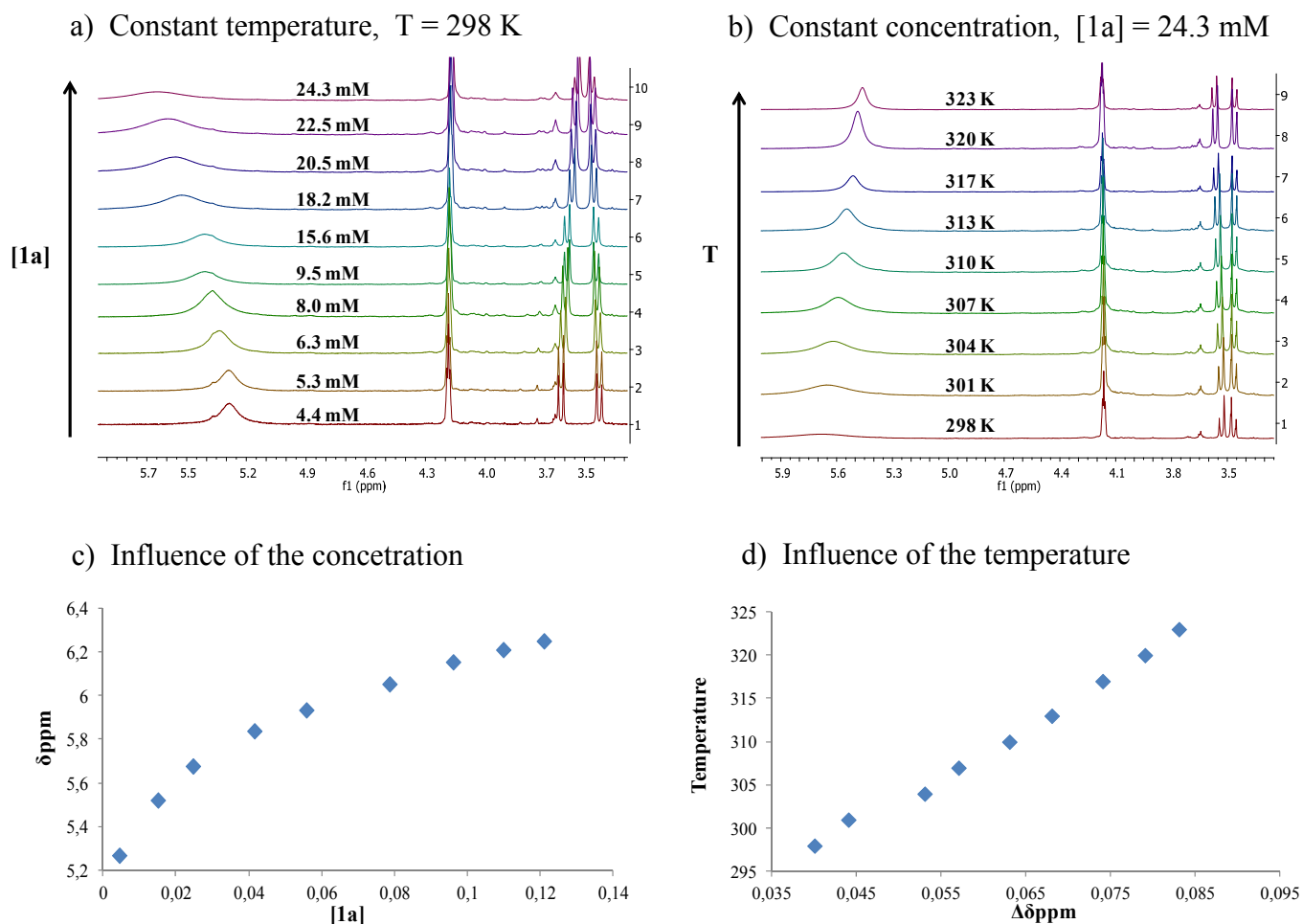
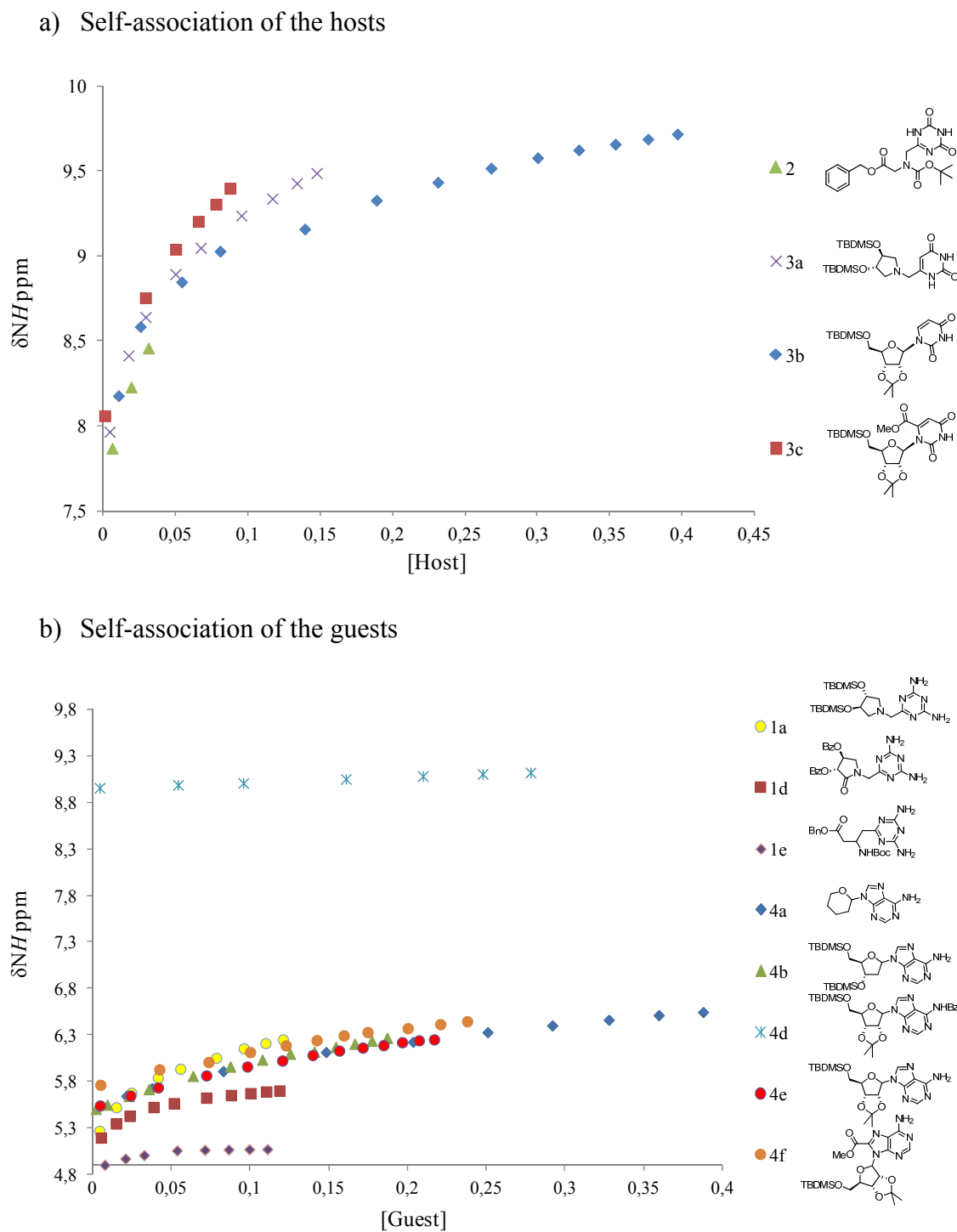


Figure S42. Self-association study of **1a** varying concentration and temperature conditions. a) ^1H NMR (600 MHz, CDCl_3) of **1a** at different concentration showing the shift of the exocyclic methylene diastereomeric CH_2 and exchangeable NH protons. b) ^1H NMR (600 MHz, CDCl_3) of **1a** at different temperatures showing the shifting of the diastereomeric and exchangeable protons. c) Graphic representation of the influence of the concentration by $[1a]$ vs δ ppm. d) Graphic representation of the influence of the temperature by the $\Delta\delta$ ppm vs T for **1a**.



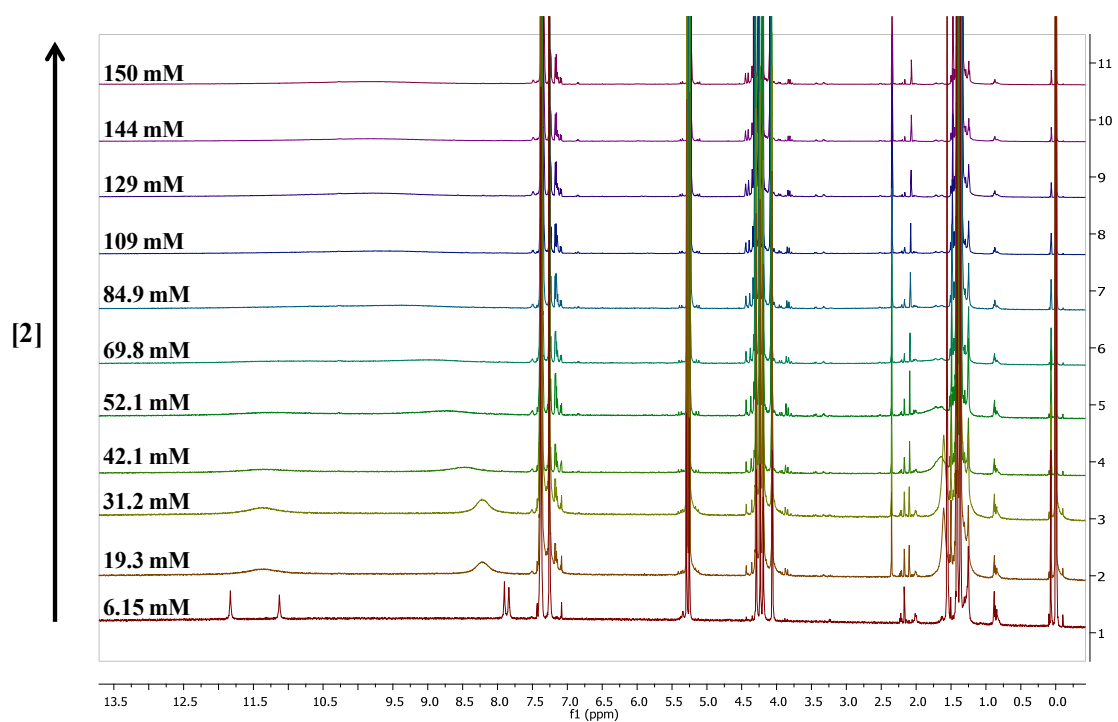


Figure S44. Self-association ^1H NMR (298K, CDCl_3) study of **2**. The exchangeable protons of the dioxotriazine (5-azauracil) vanished while the concentration is increasing.

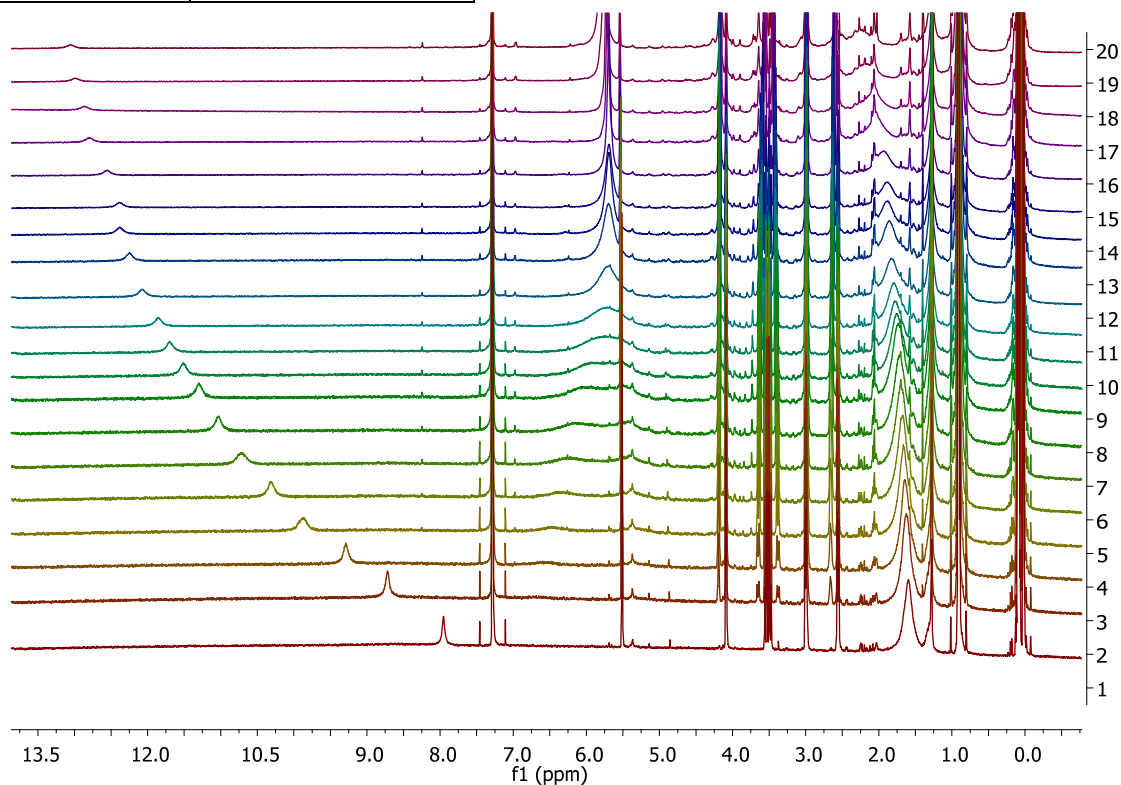
Titration experiments

Titration 1

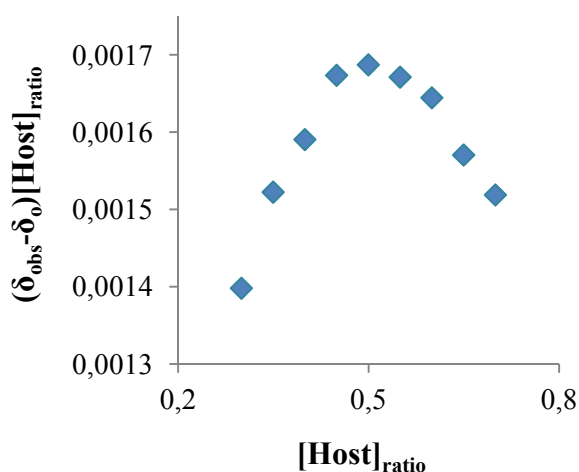
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	2.194 mM
Guest: 1a	21.989 mM

K_a binding constant	error
317 M^{-1}	$\pm 7 \text{ M}^{-1}$



b) Job's Plot



c) Binding curve fitting

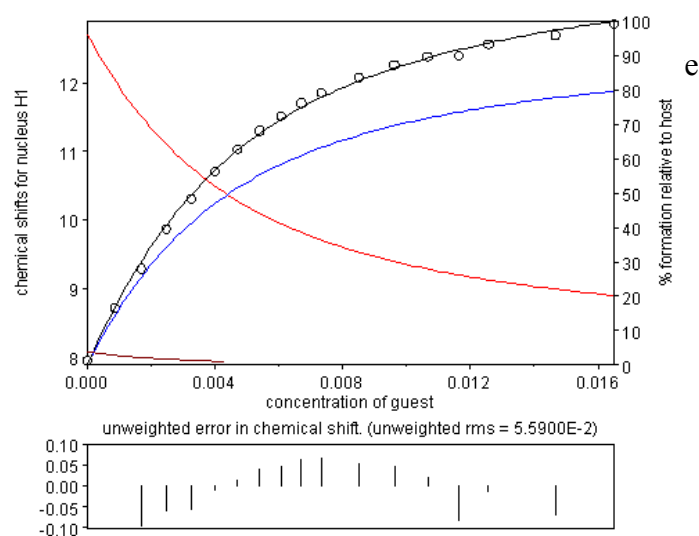


Figure S45. Titration 1. a) Representative ^1H NMR titration of **3a** with **1a** spectra, **1a** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**:**1a**. c) Representative fit curve from the Titration 1.

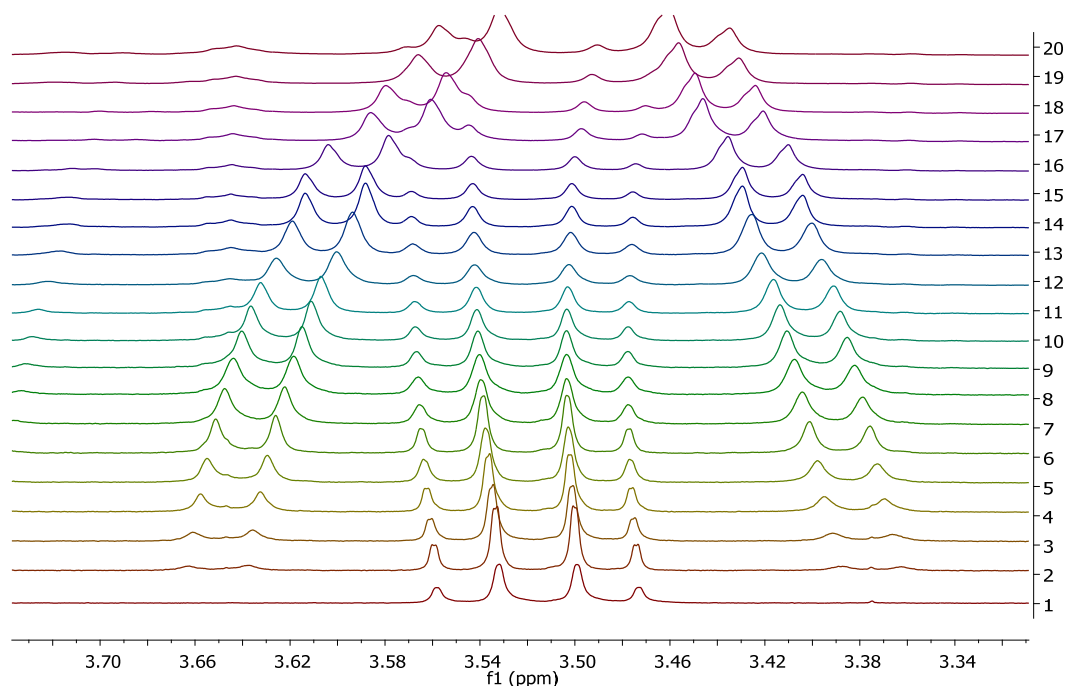


Figure S46. a) Expansion of the ^1H NMR of the figure S41 a) (Titration 1) showing the shift of the exocyclic diastereotopic CH_2 protons of **3a** and **1a**.

Titration 1-reverse

	Final concentration
Host: 1a	2.42 mM
Guest: 3a	23.04 mM

K_a binding constant	error
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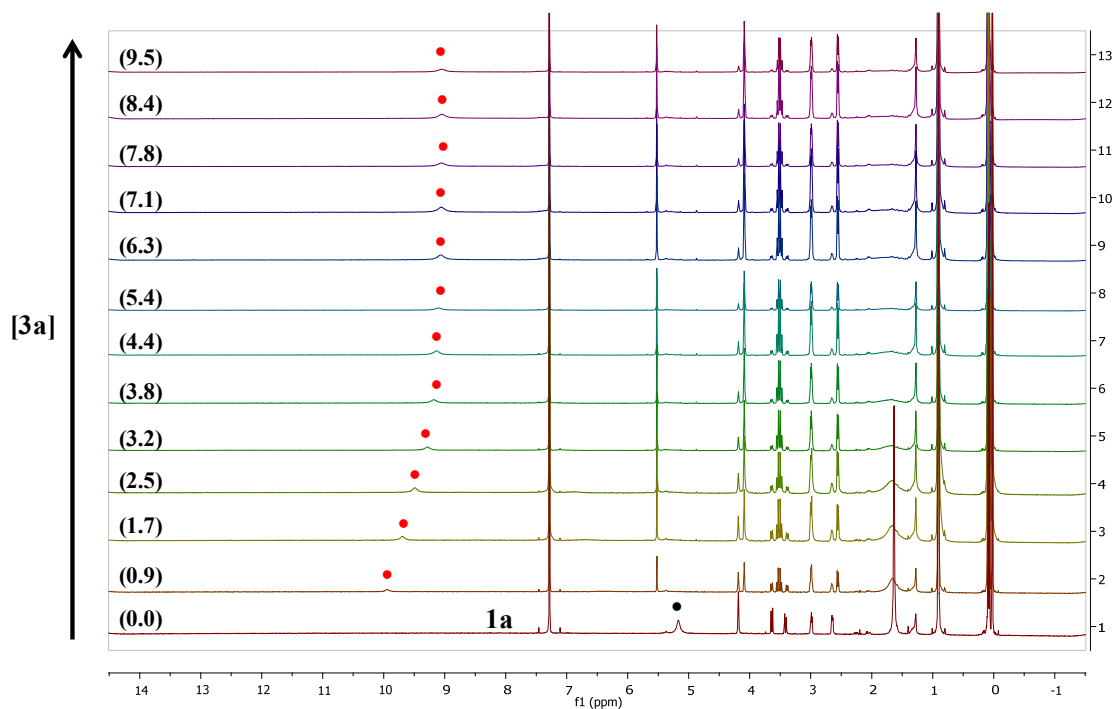


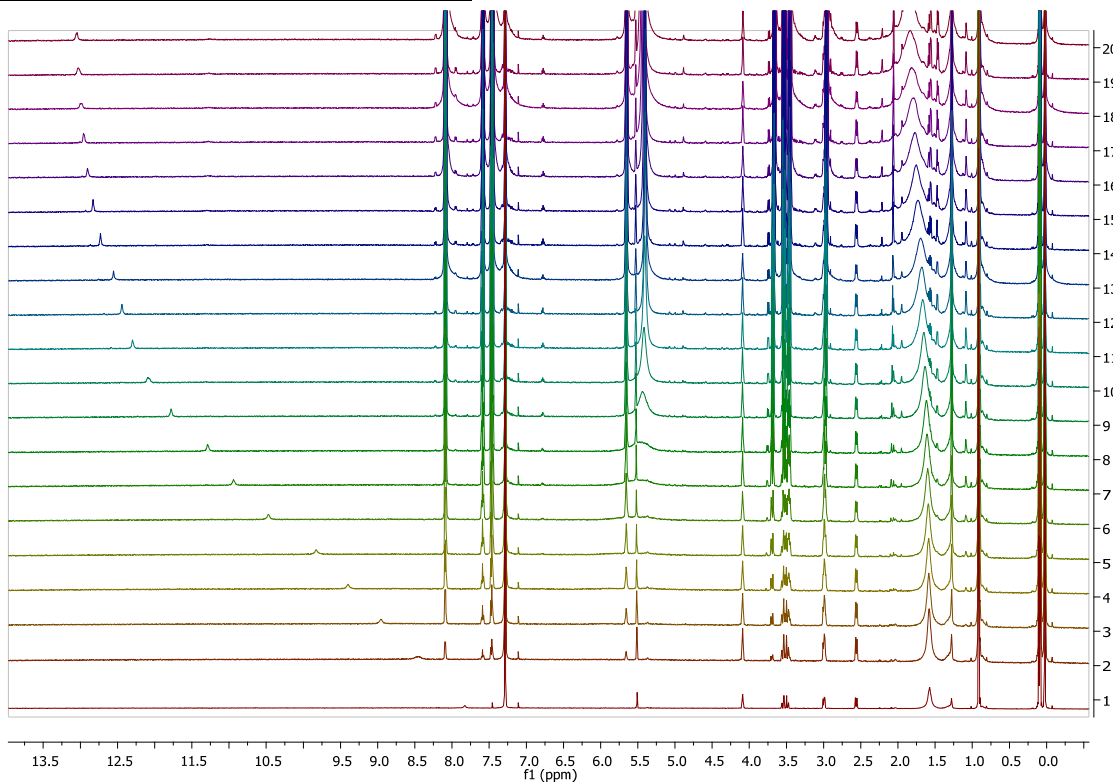
Figure S47: ^1H NMR (600 MHz, CDCl_3) Titration experiment of **1a** (host) with **3a** (guest). In black: exchangeable proton of the **1a** vanished after the addition of **3a**. In red: exchangeable proton of **3a**. In parenthesis: number of eq. of **3a**.

Titration 2

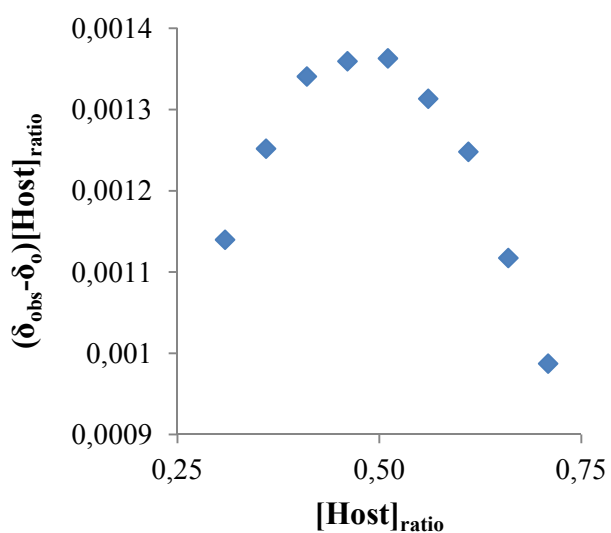
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	2.194 mM
Guest: 1b	23.018 mM

K_a binding constant	error
550 M^{-1}	± 2



b) Job's Plot



c) Binding curve fitting

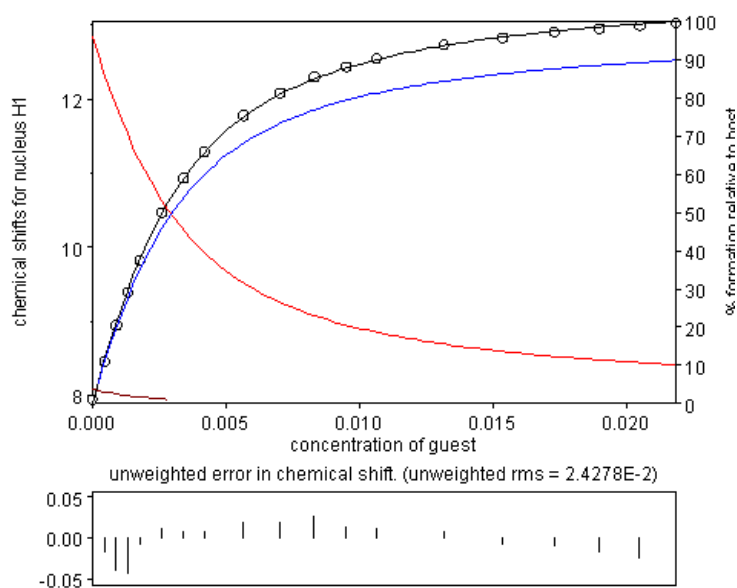


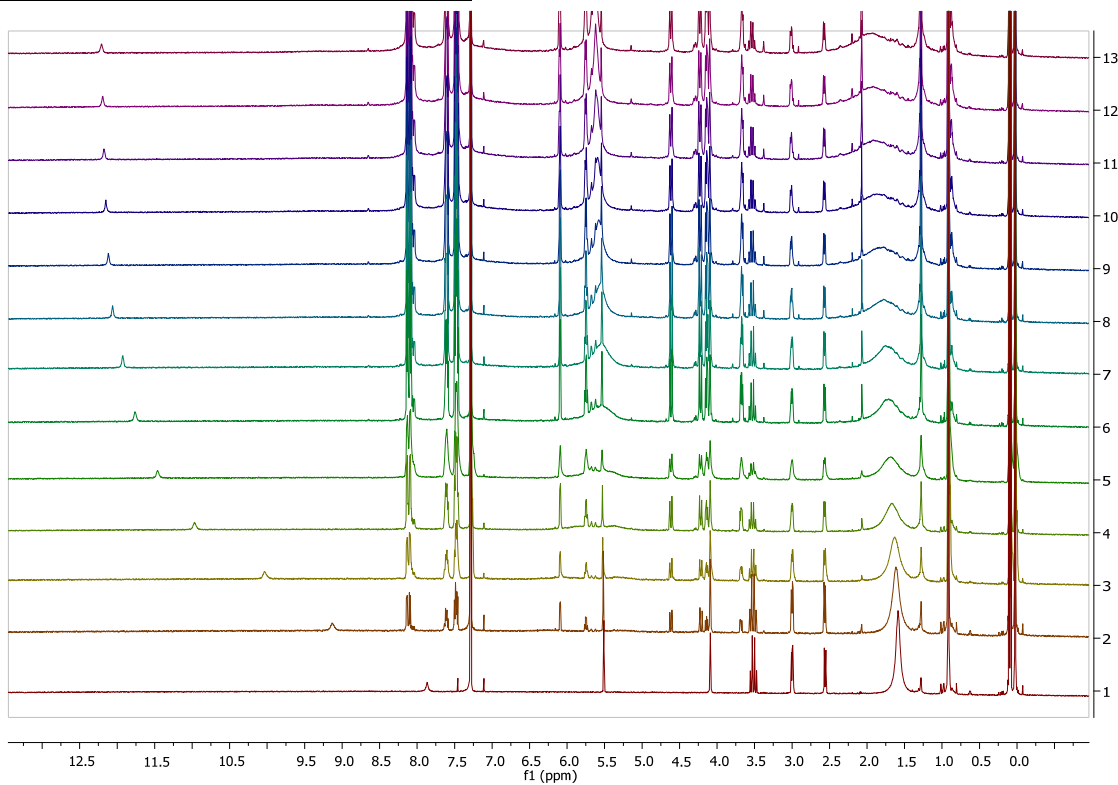
Figure S48. Titration 2. a) Representative ^1H NMR titration of **3a** with **1b** spectra, **1b** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**1b**. c) Representative fit curve from the Titration 2.

Titration 3

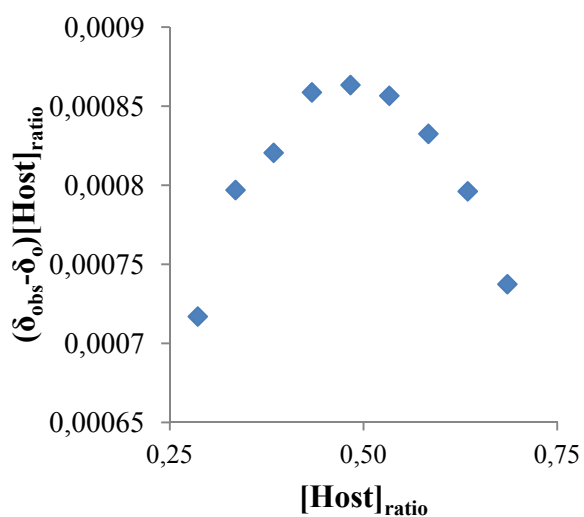
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	2.194 mM
Guest: 1c	21.989 mM

K_a binding constant	error
496 M^{-1}	± 6



b) Job's Plot



c) Binding curve fitting

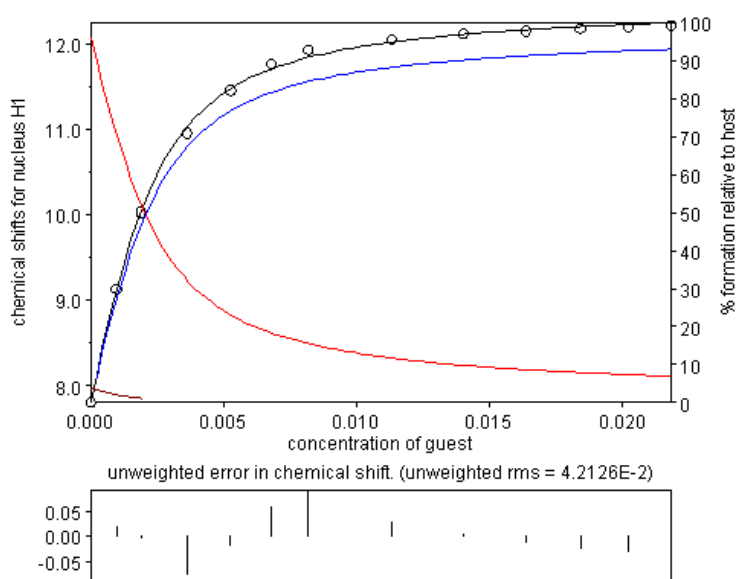


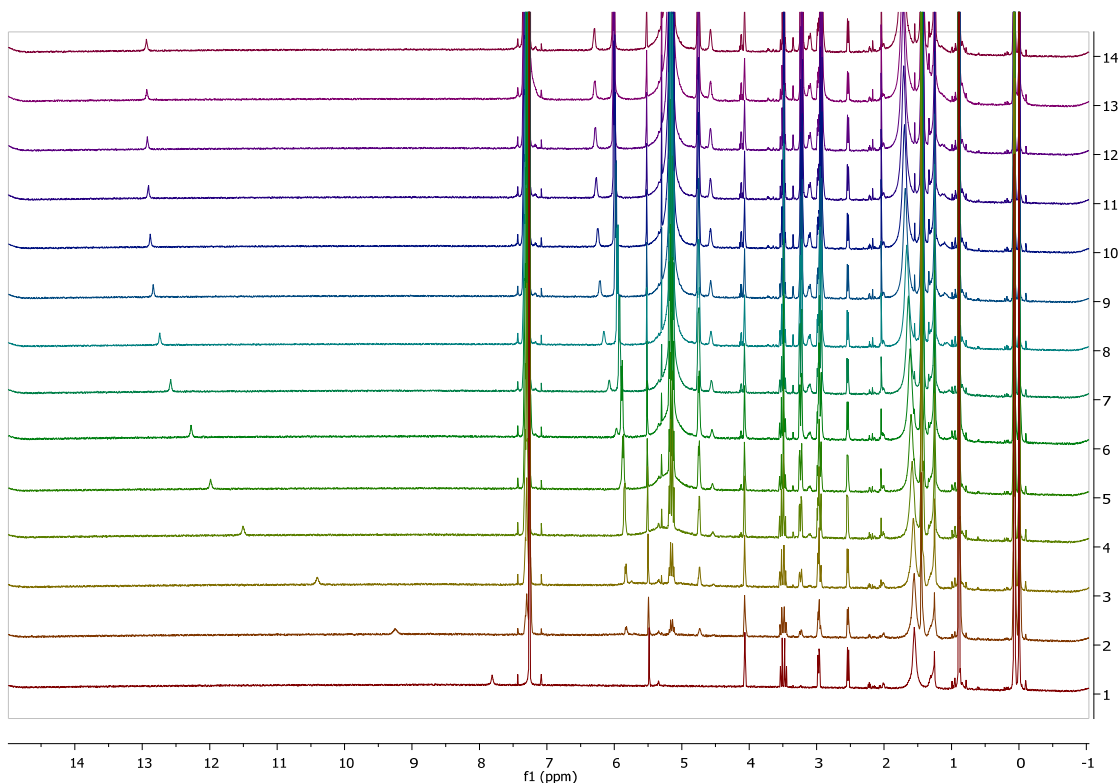
Figure S49. Titration 3. a) Representative ^1H NMR titration of **3a** with **1c** spectra, **1c** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a-1c**. c) Representative fit curve from the Titration 3.

Titration 4

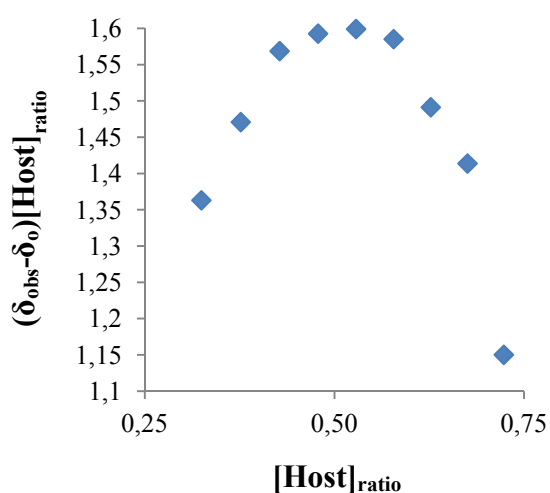
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	1.54 mM
Guest: 1d	31.86 mM

K_a binding constant	error
521 M^{-1}	± 10



b) Job's Plot



c) Binding curve fitting

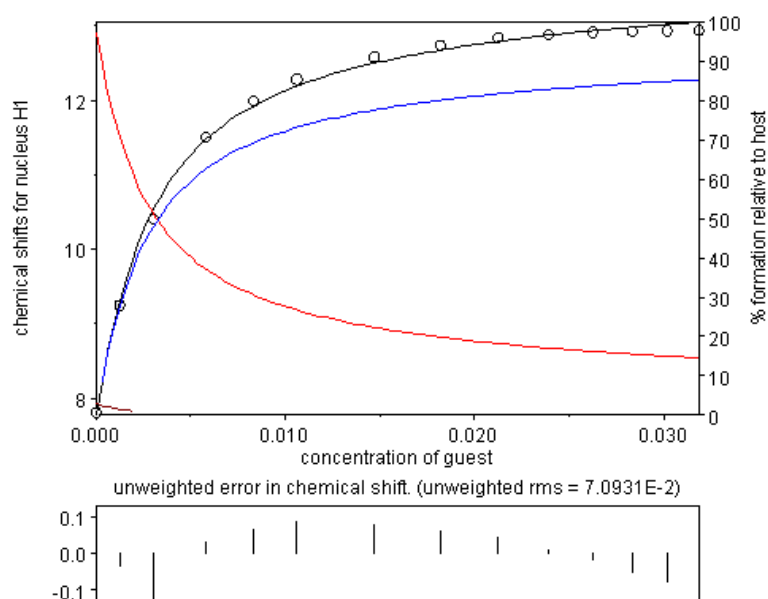


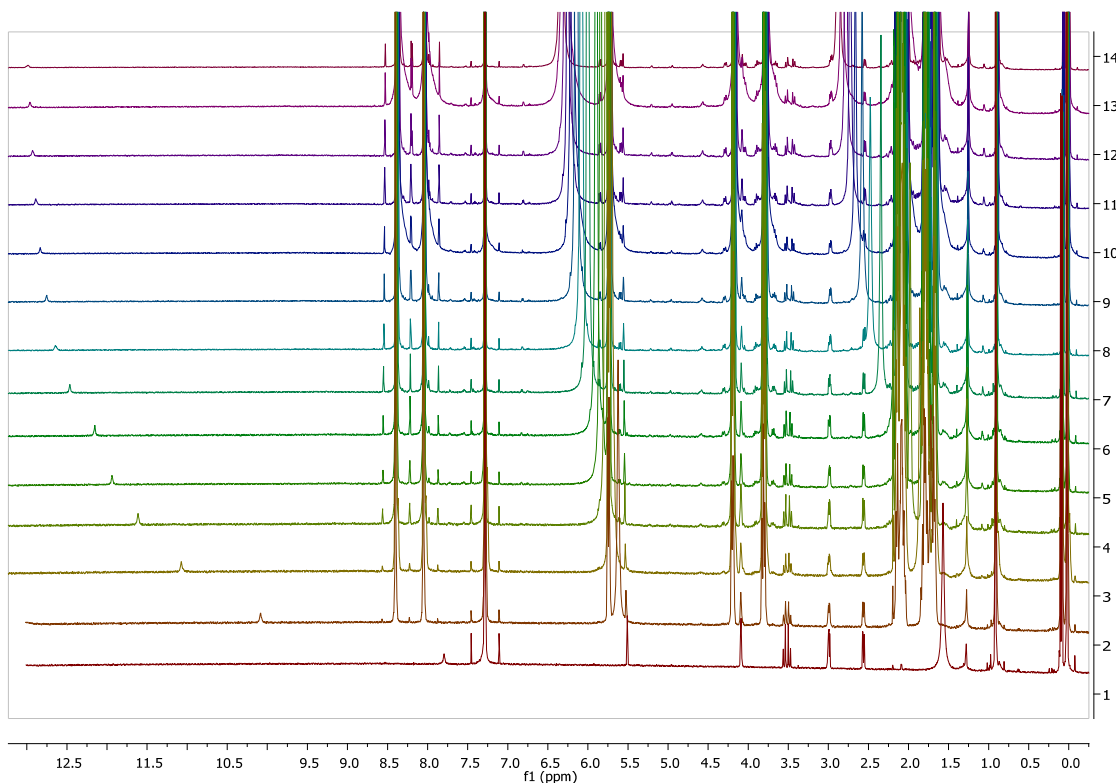
Figure S50. Titration 4. a) Representative ^1H NMR titration of **3a** with **1d** spectra, **1d** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**:**1d**. c) Representative fit curve from the Titration 4.

Titration 5

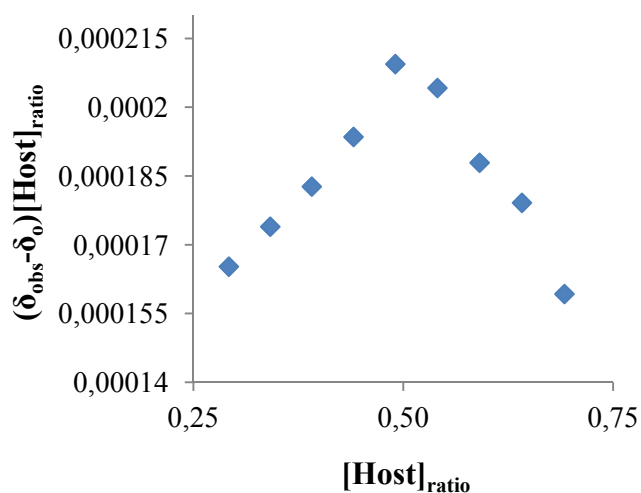
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	1.097 mM
Guest: 4a	125.43 mM

K_a binding constant	error
83 M^{-1}	± 2



b) Job's Plot



c) Binding curve fitting

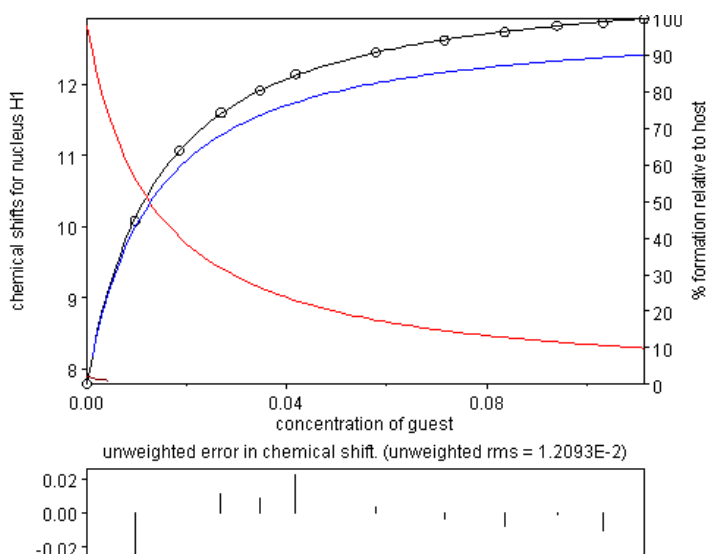


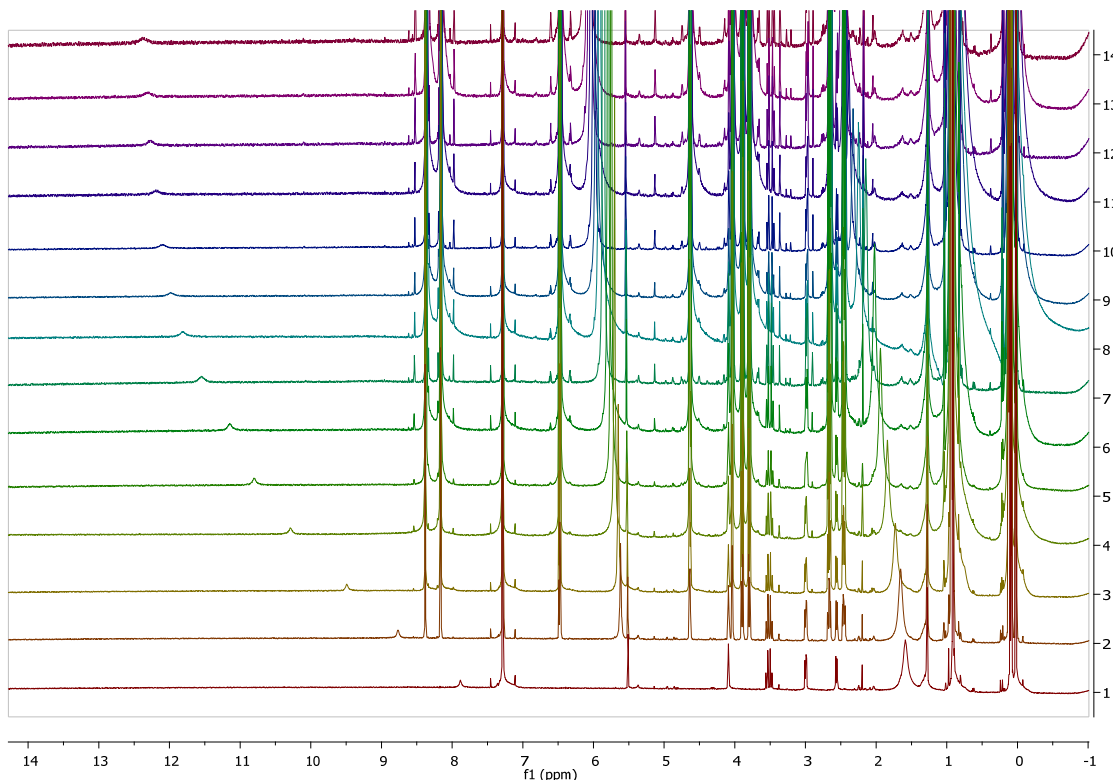
Figure S51. Titration 5. a) Representative ^1H NMR titration of **3a** with **4a** spectra, **4a** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**4a**. c) Representative fit curve from the Titration 5.

Titration 6

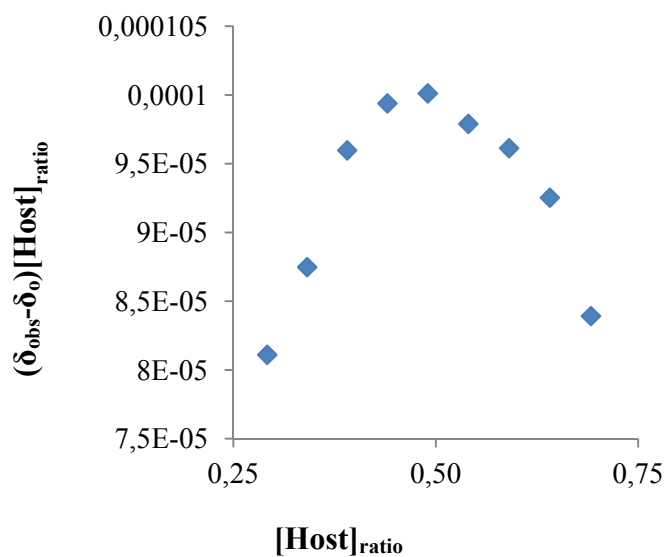
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	1.97 mM
Guest: 4b	120.26 mM

K_a binding constant	error
38 M^{-1}	± 1



b) Job's Plot



c) Binding curve fitting

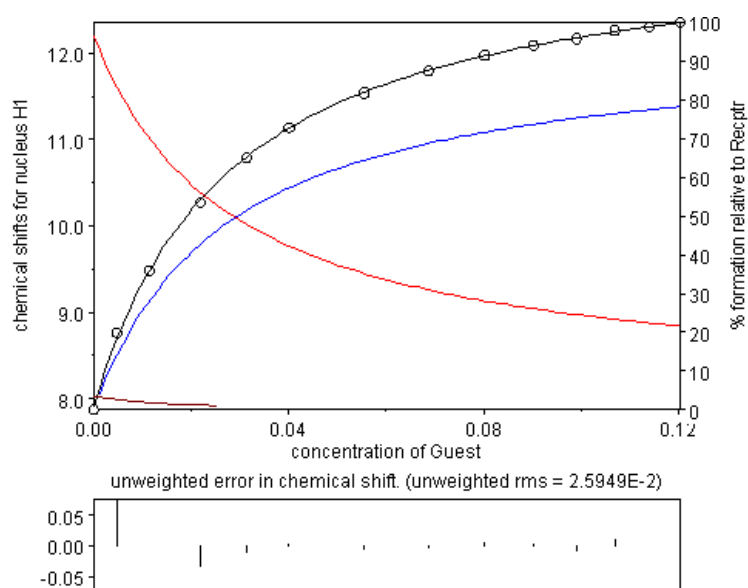


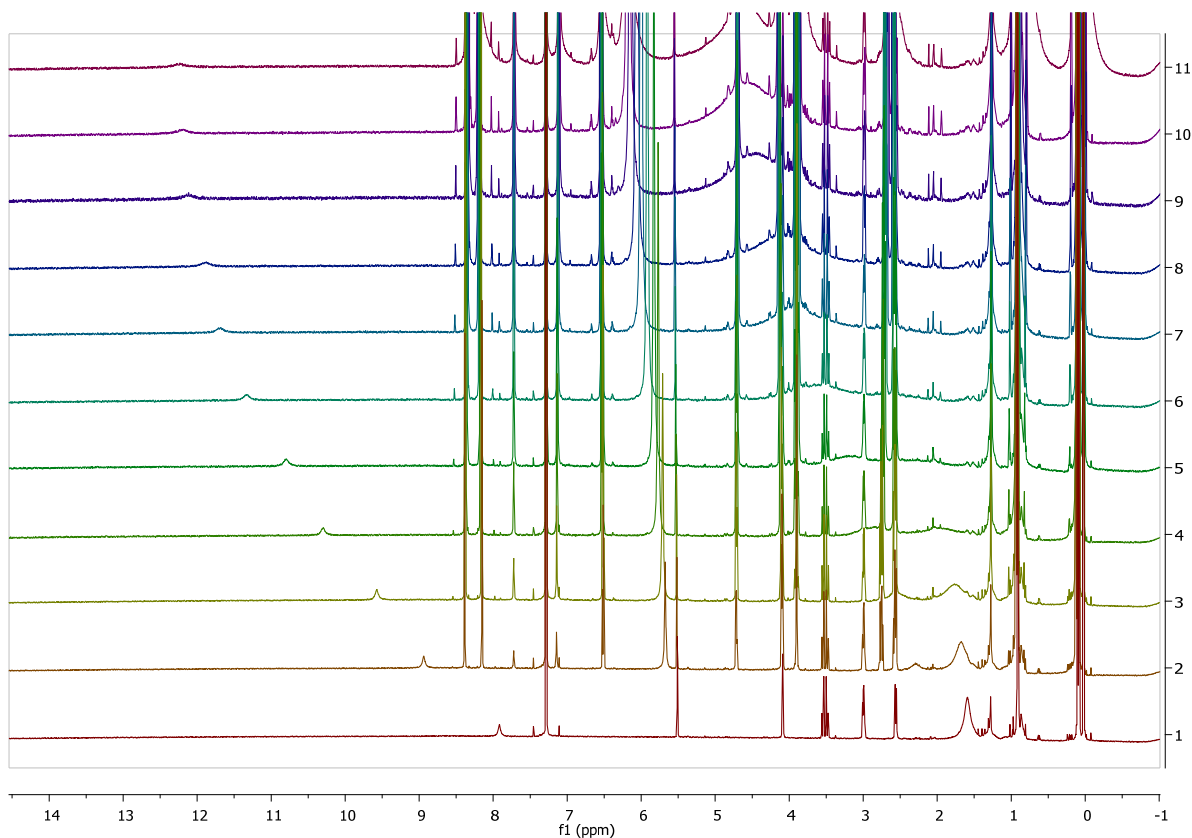
Figure S52. Titration 6. a) Representative ^1H NMR titration of **3a** with **4b** spectra, **4b** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**4b**. c) Representative fit curve from the Titration 6.

Titration 7

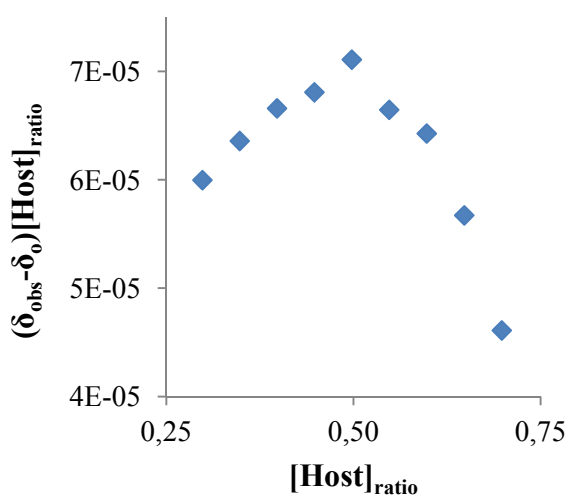
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	2.194 mM
Guest: 4c	112.7 mM

K_a binding constant	error
33 M^{-1}	± 1



b) Job's Plot



c) Binding curve

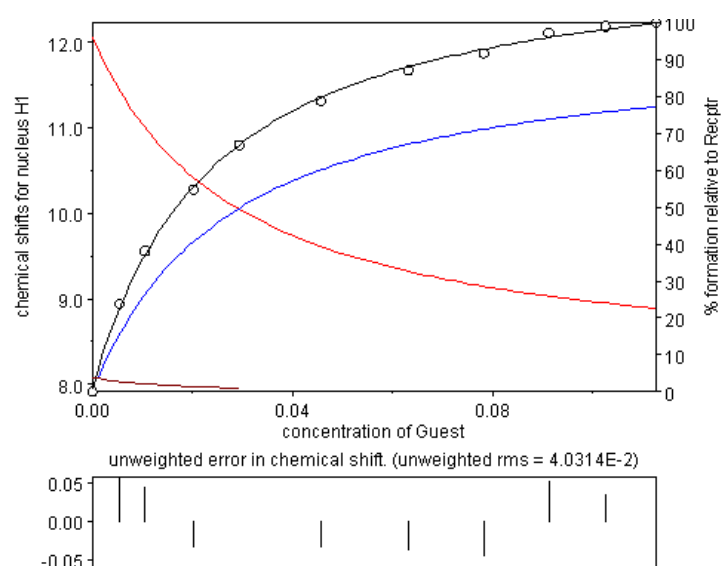


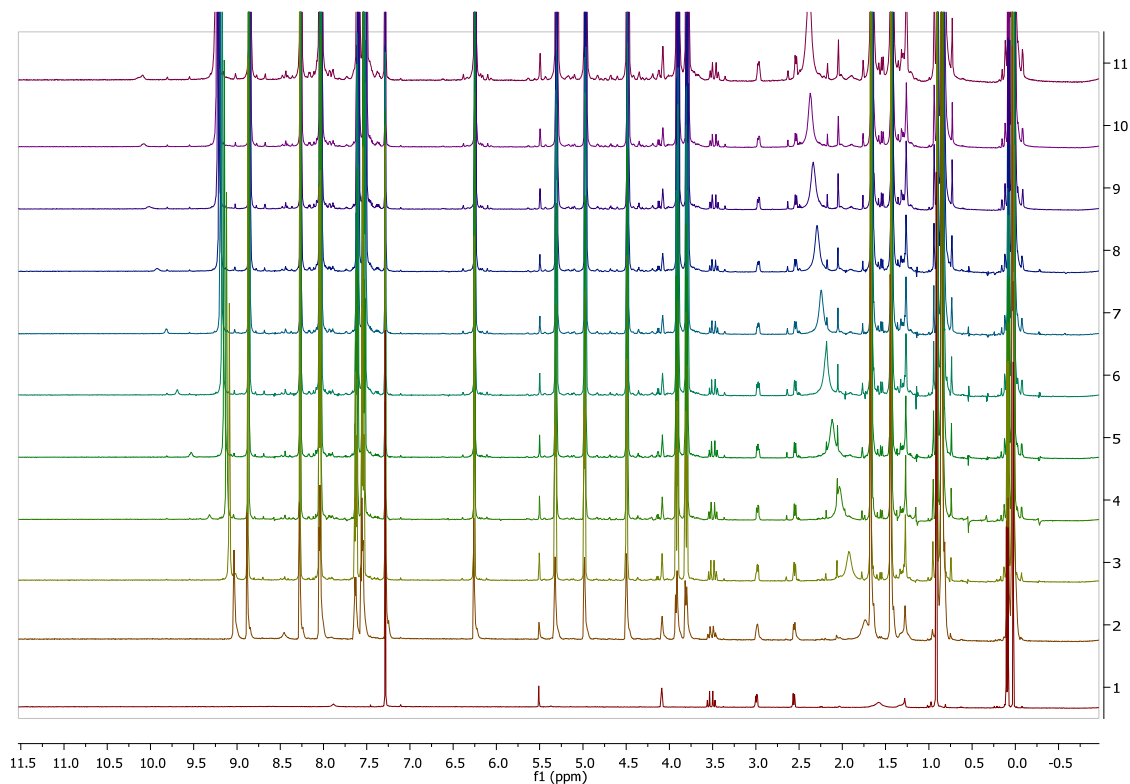
Figure S53. Titration 7. a) Representative ^1H NMR titration of **3a** with **4c** spectra, **4c** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**4c**. c) Representative fit curve from the Titration 7.

Titration 8

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	2.41mM
Guest: 4d	123.65 mM

K_a binding constant	error
10 M^{-1}	± 4



b) Job's Plot

^1H NMR Job's method of continuous variation of **3a**·**4d** did not show significant shift of the exchangeable protons.

c) Binding curve

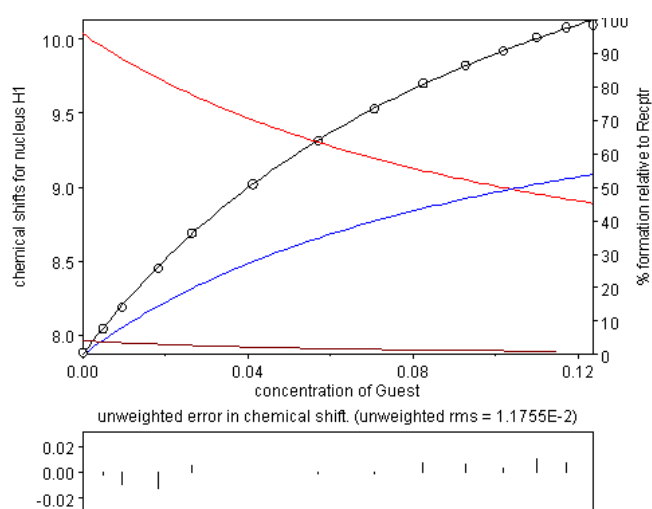


Figure S54. Titration 8. a) Representative ^1H NMR titration of **3a** with **4d** spectra, **4d** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**4d**. c) Representative fit curve from the Titration 8.

Titration 9

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	1.097 mM
Guest: 4e	60.029 mM

K_a binding constant	error
38 M^{-1}	± 2

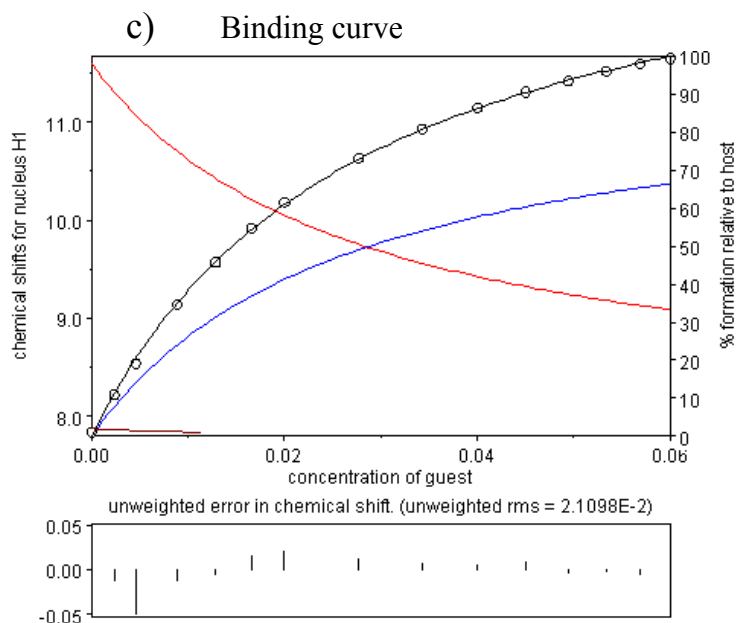
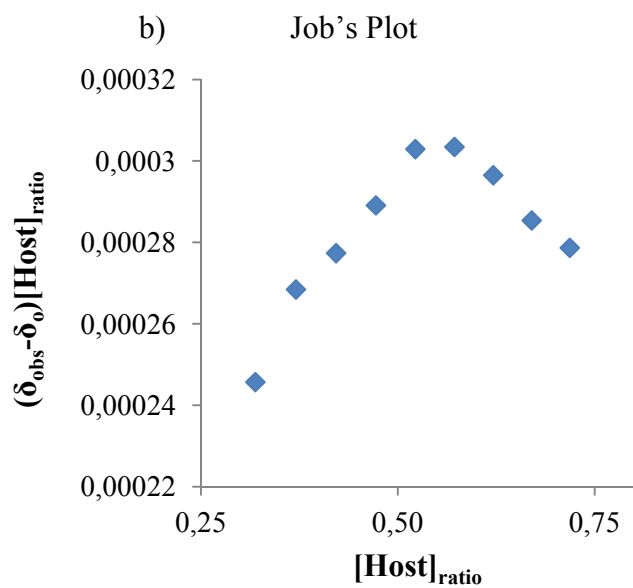
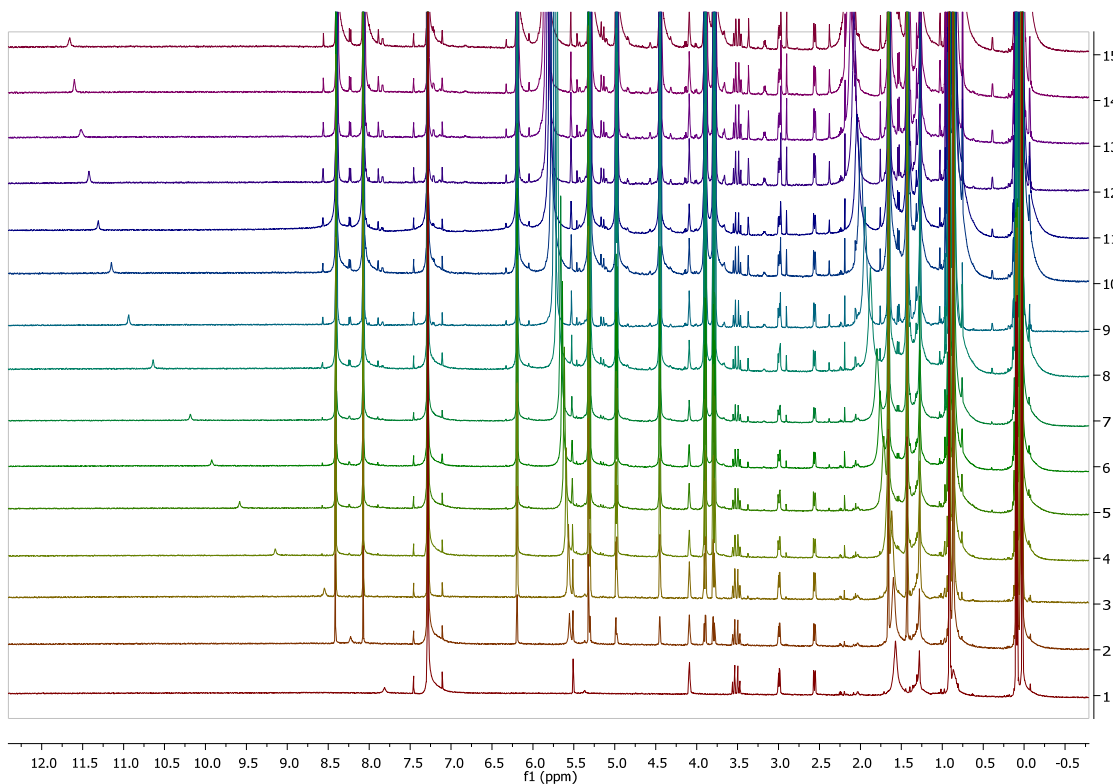


Figure S55. Titration 9. a) Representative ^1H NMR titration of **3a** with **4e** spectra, **4e** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**4e**. c) Representative fit curve from the Titration 9.

Titration 10

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3a	1.09 mM
Guest: 4f	52.5 mM

K_a binding constant	error
26 M^{-1}	± 1

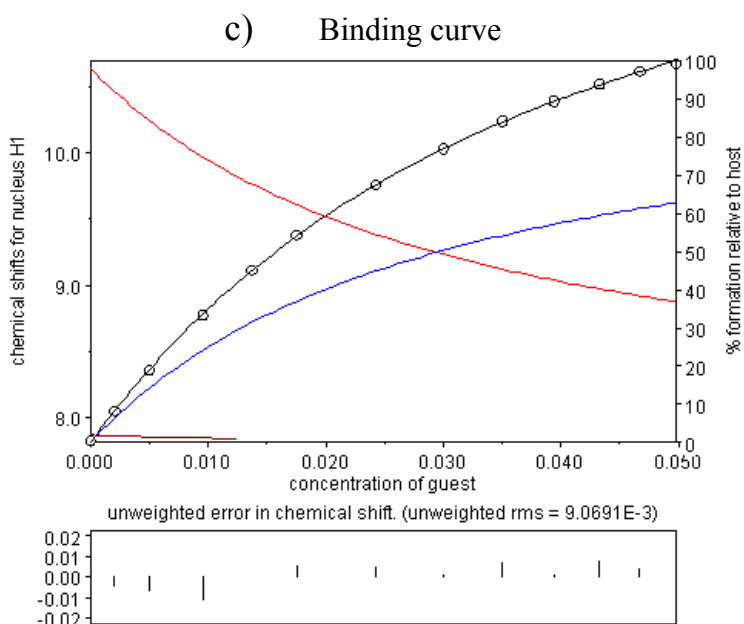
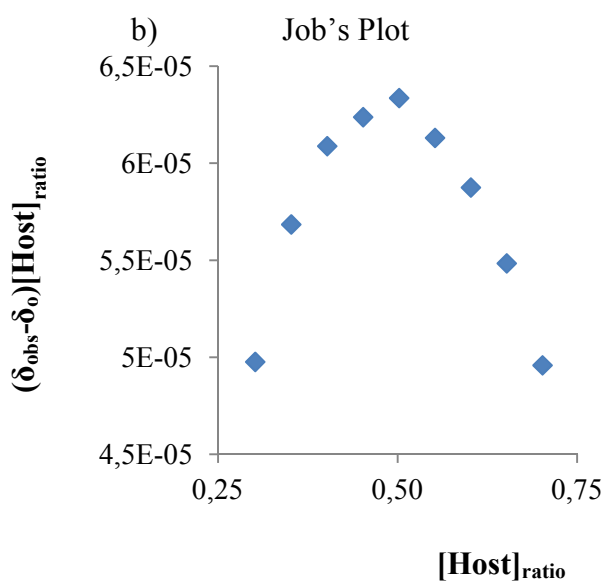
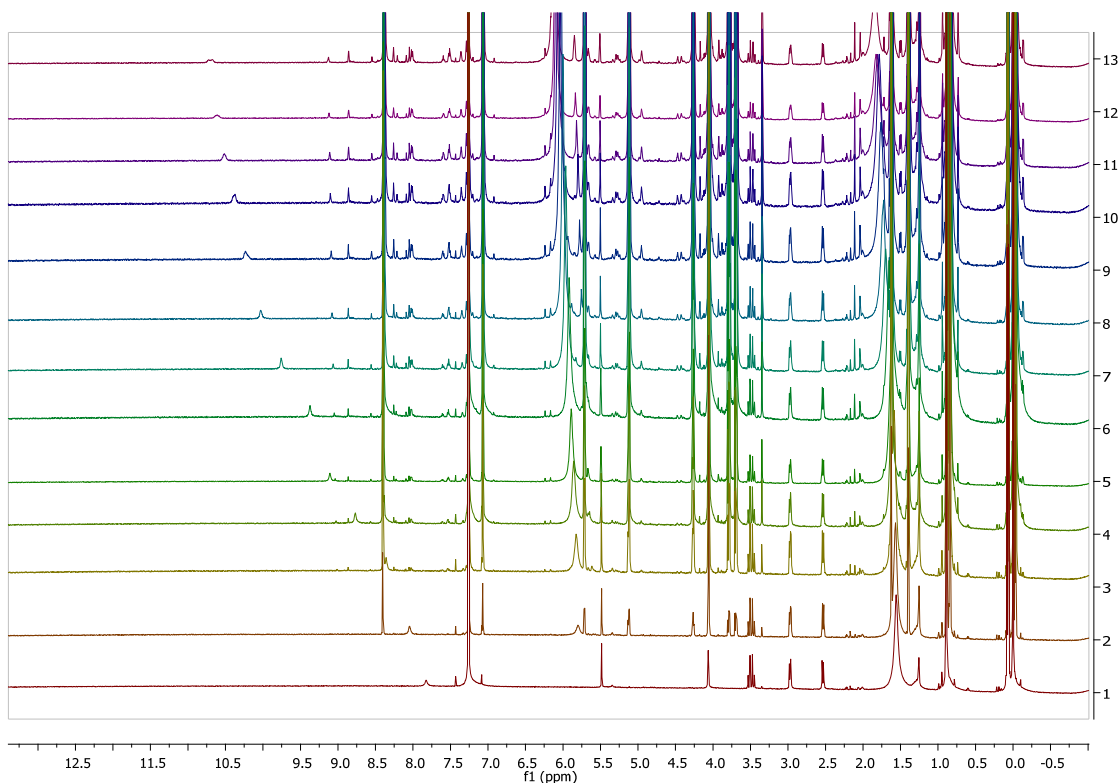


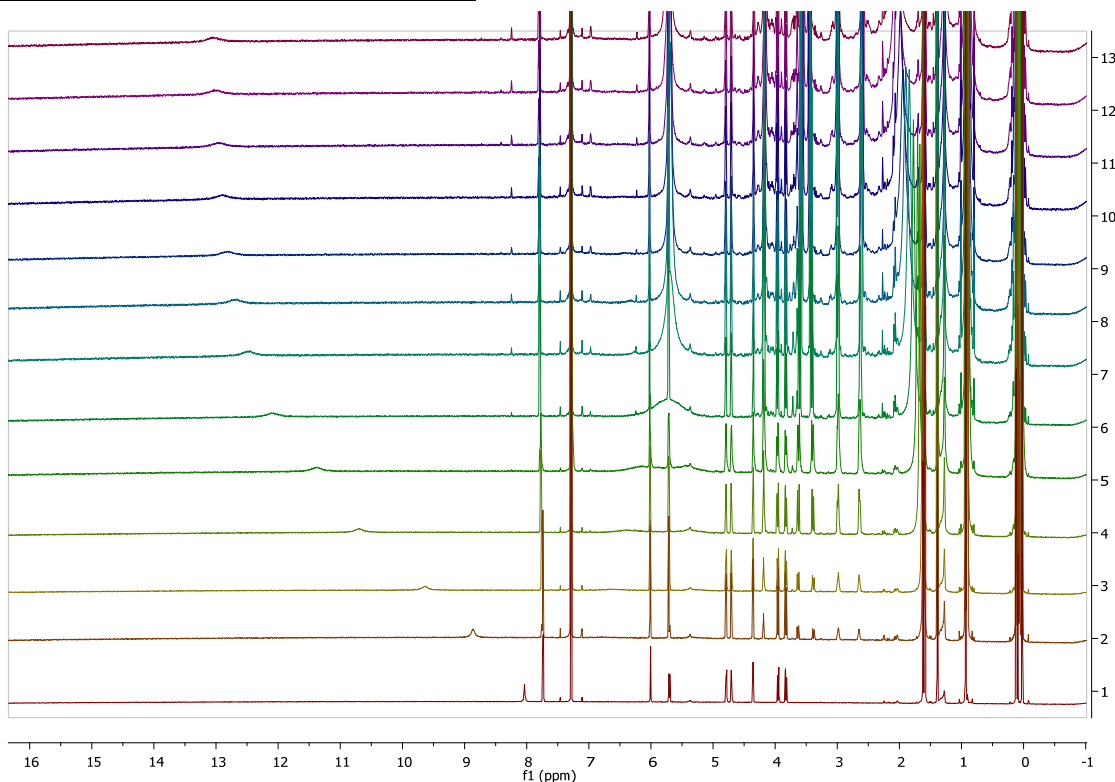
Figure S56. Titration 10. a) Representative ^1H NMR titration of **3a** with **4f** spectra, **4f** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3a**·**4f**. c) Representative fit curve from the Titration 10.

Titration 11

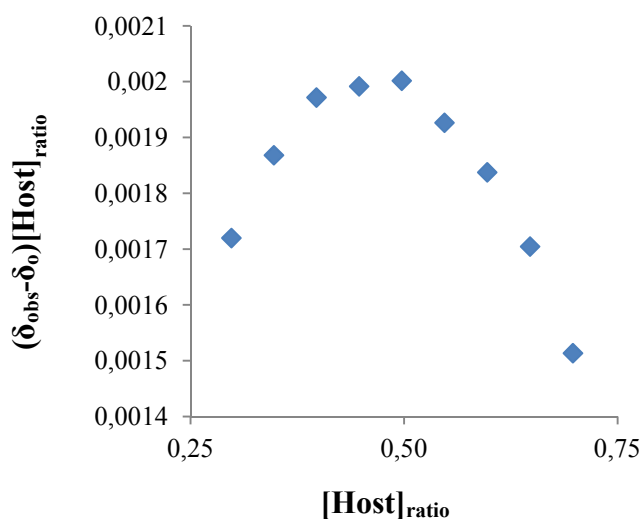
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3b	2.509 mM
Guest: 1a	26.65 mM

K_a binding constant	error
350 M^{-1}	± 4



b) Job's Plot



c) Binding curve

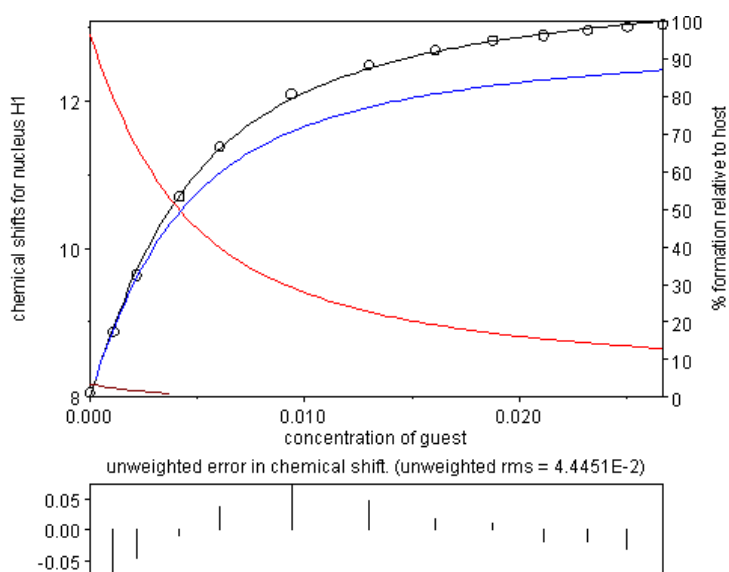


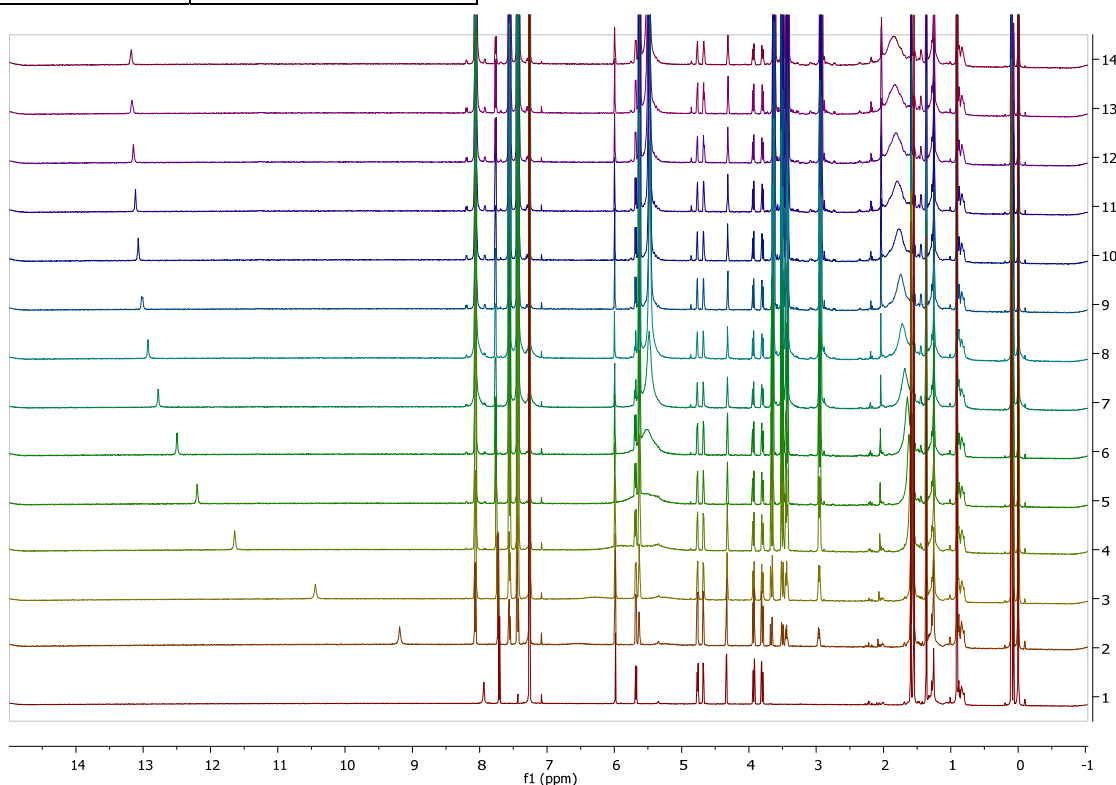
Figure S57. Titration 11. a) Representative ^1H NMR titration of **3b** with **1a** spectra, **1a** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**·**1a**. c) Representative fit curve from the Titration 11.

Titration 12

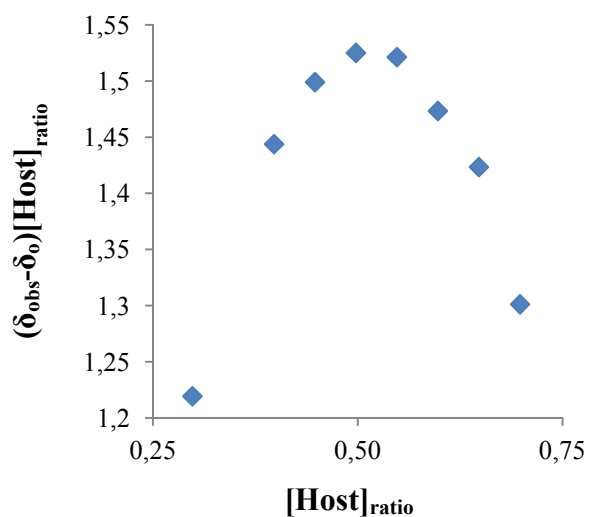
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3b	2.76 mM
Guest: 1b	33.66 mM

K_a binding constant	error
467 M^{-1}	± 1



b) Job's Plot



c) Binding curve

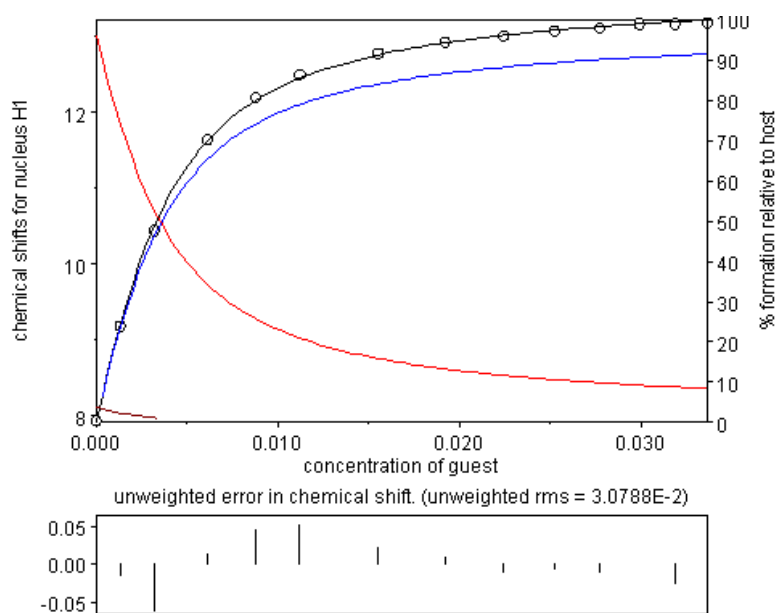


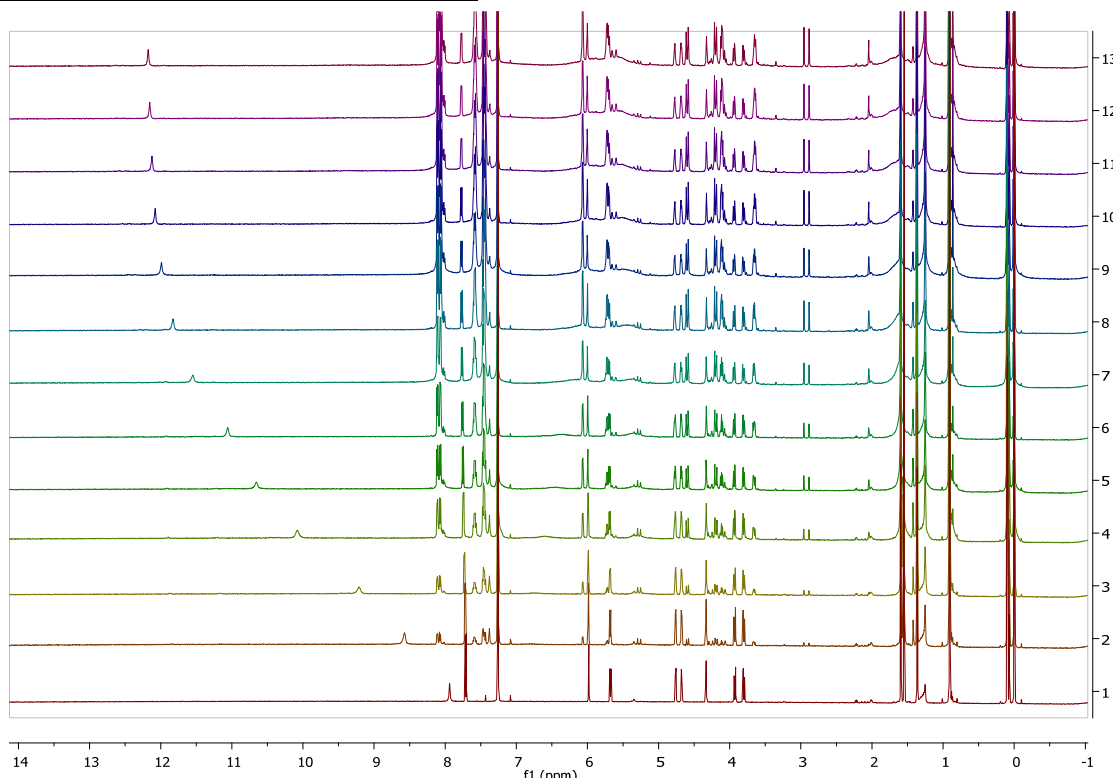
Figure S58. Titration 12. a) Representative ^1H NMR titration of **3b** with **1b** spectra, **1b** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**·**1b**. c) Representative fit curve from the Titration 12.

Titration 13

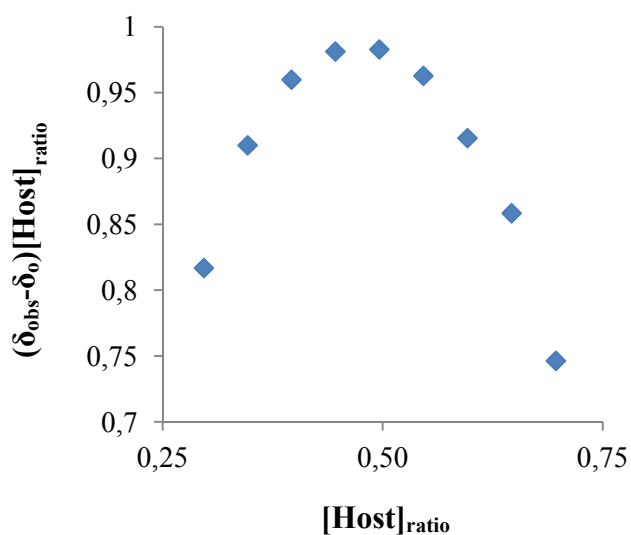
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3b	3.01 mM
Guest: 1c	23.24 mM

K_a binding constant	error
230 M^{-1}	± 11



b) Job's Plot



c) Binding curve

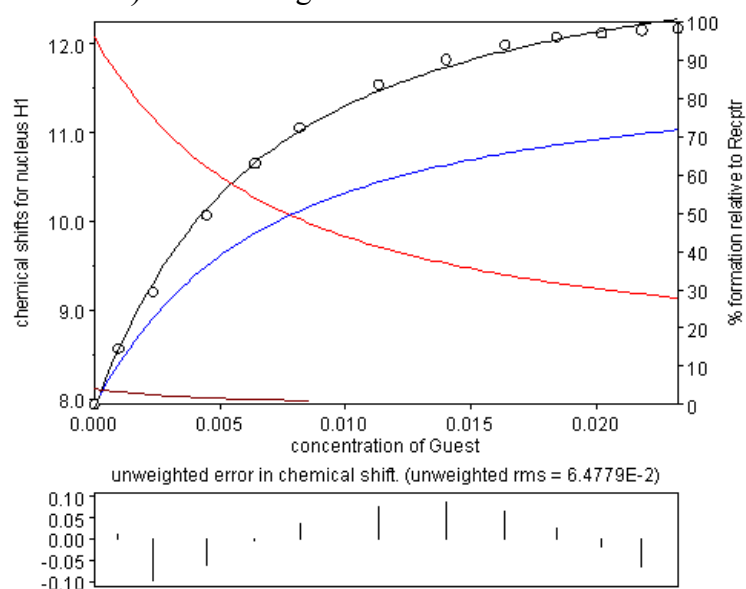


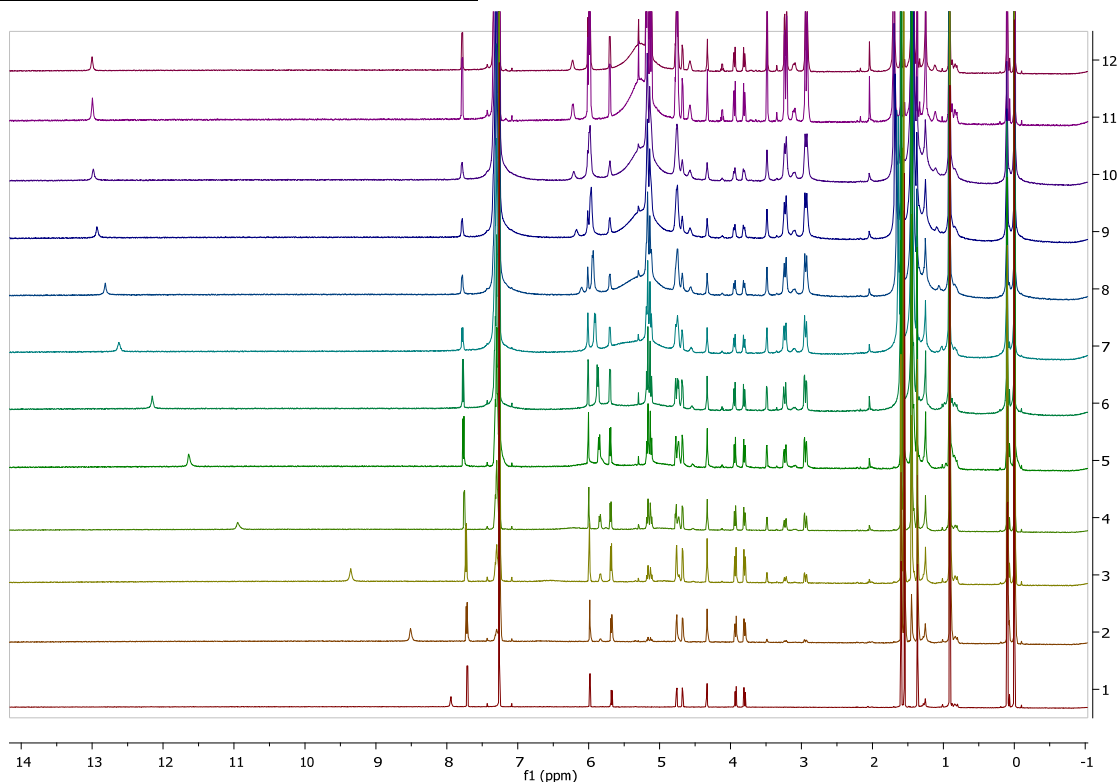
Figure S59. Titration 13. a) Representative ^1H NMR titration of **3b** with **1c** spectra, **1c** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**·**1c**. c) Representative fit curve from the Titration 13.

Titration 14

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3b	2.76 mM
Guest: 1d	30.04 mM

K_a binding constant	error
336 M^{-1}	± 24



b) Job's Plot

c) Binding curve

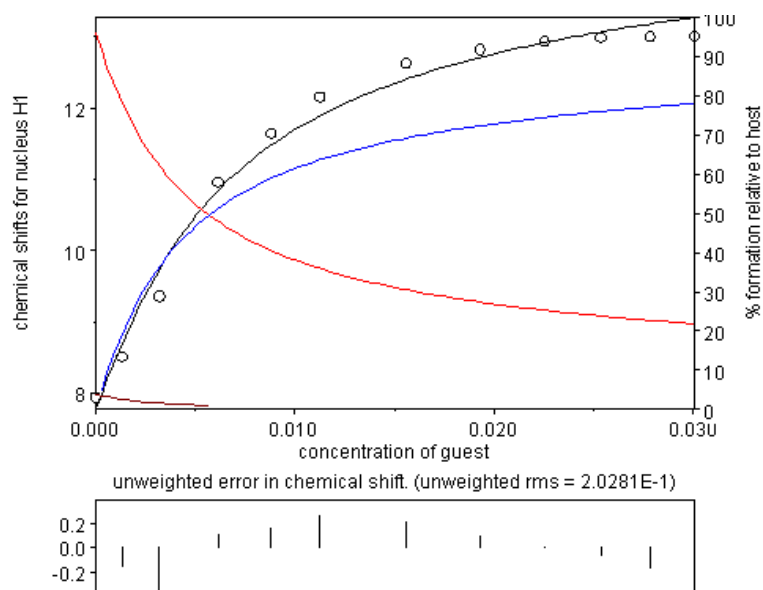
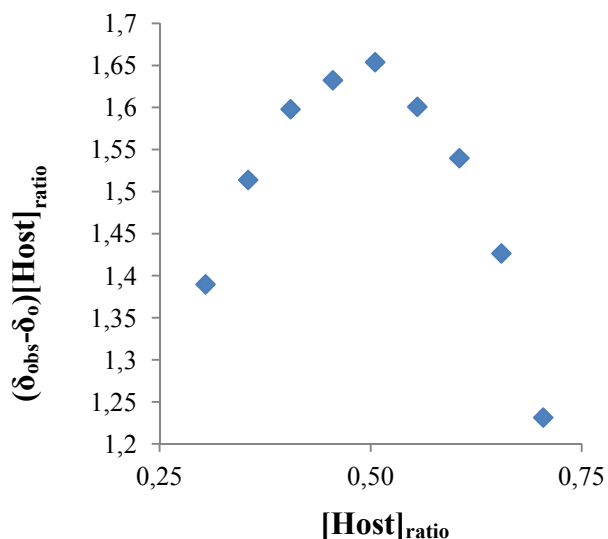


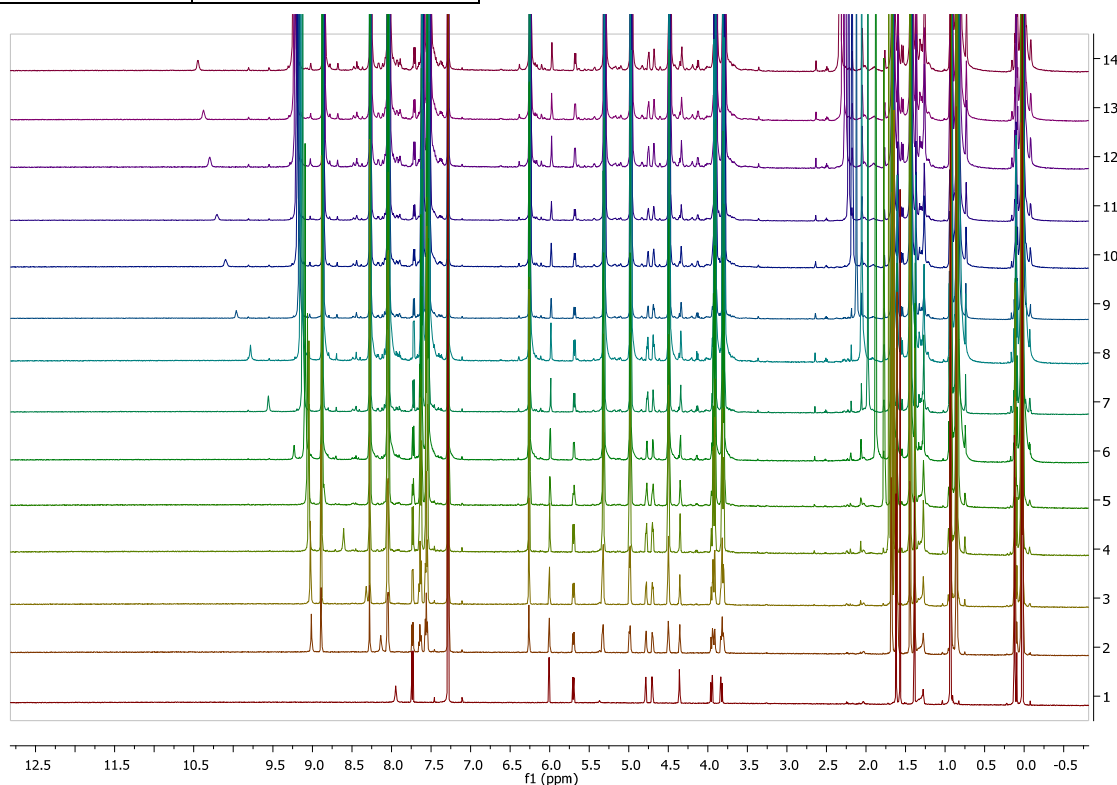
Figure S60. Titration 14. a) Representative ^1H NMR titration of **3b** with **1d** spectra, **1d** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**·**1d**. c) Representative fit curve from the Titration 14.

Titration 15

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3b	2.509 mM
Guest: 4d	111.48 mM

K_a binding constant	error
6 M^{-1}	± 2



b) Job's Plot

^1H NMR Job's method of continuous variation of **3b**·**4d** did not show significant shift of the exchangeable protons.

c) Binding curve

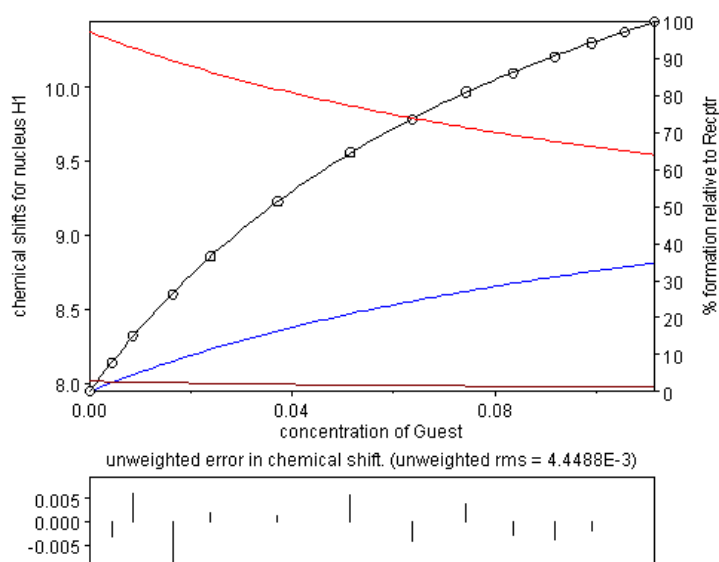
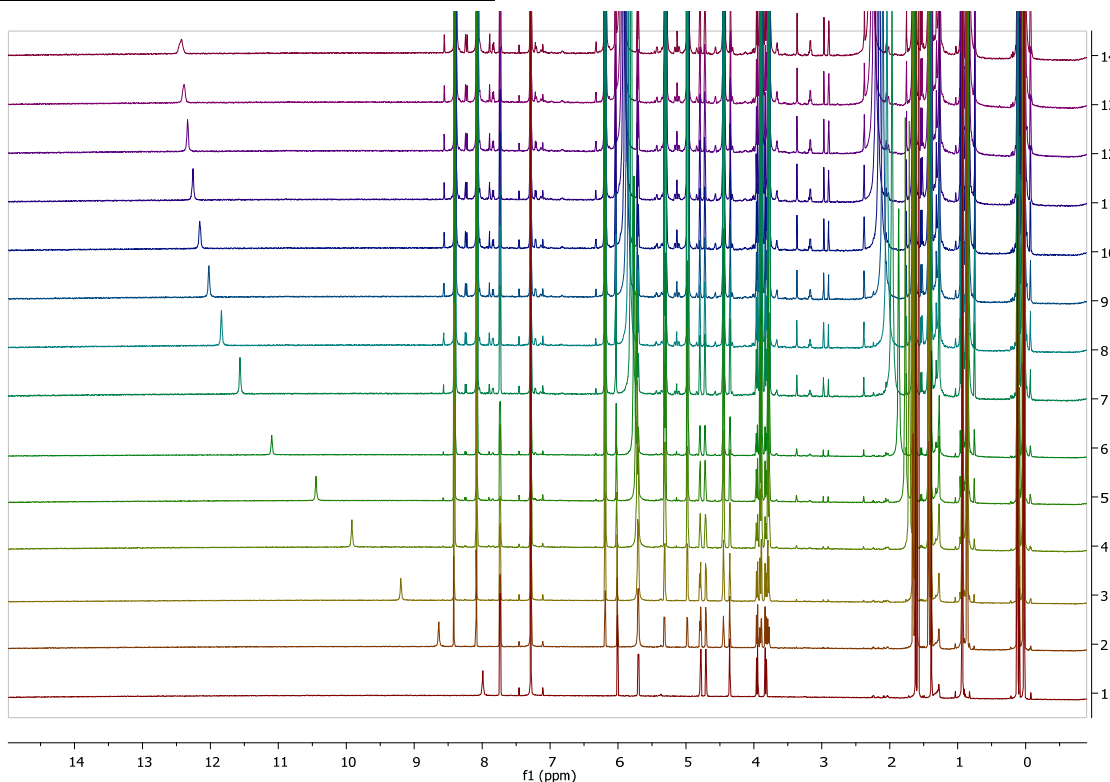


Figure S61. Titration 15. a) Representative ^1H NMR titration of **3b** with **4d** spectra, **4d** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**·**4d**. c) Representative fit curve from the Titration 15.

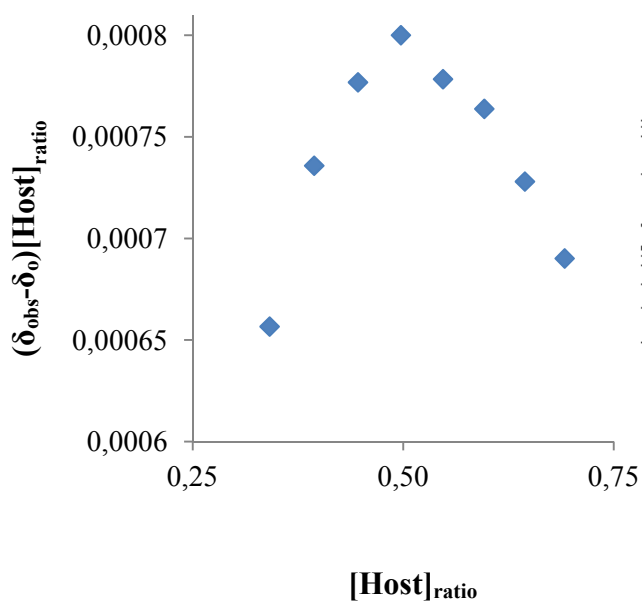
Titration 16

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration	K_a binding constant	error
Host: 3b	3.513 mM	59 M^{-1}	± 2
Guest: 4e	71.163 mM		



b) Job's Plot



c) Binding curve

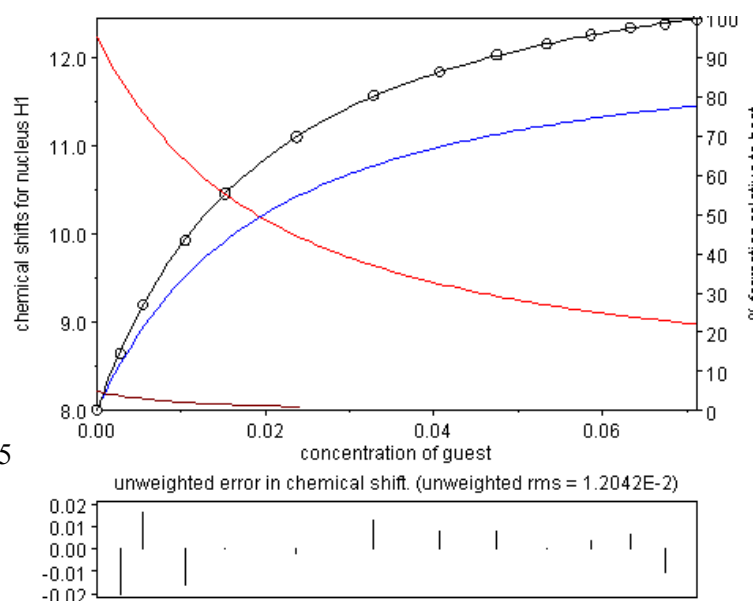
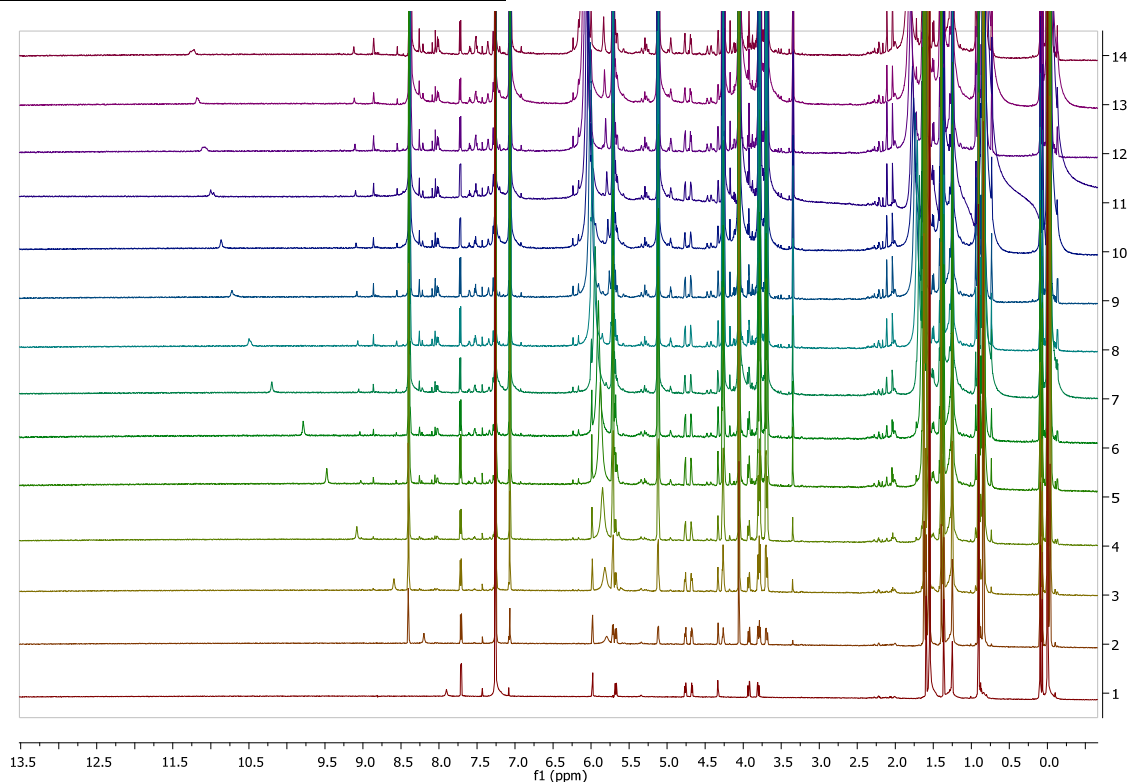


Figure S62. Titration 16. a) Representative ^1H NMR titration of **3b** with **4e** spectra, **4e** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**•**4e**. c) Representative fit curve from the Titration 16.

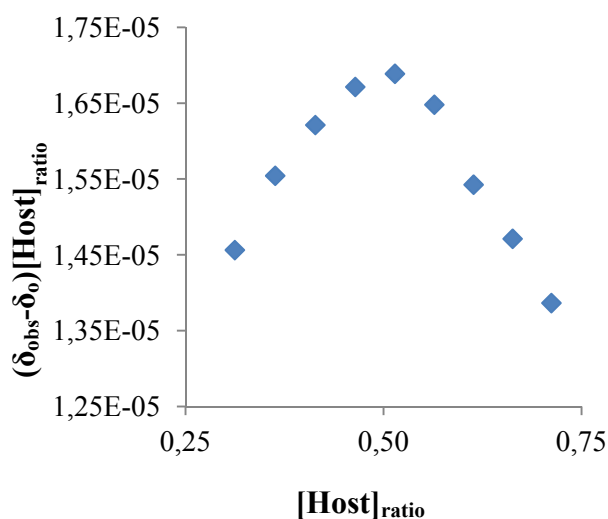
Titration 17

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration	K_a binding constant	error
Host: 3b	1.25 mM	45 M^{-1}	± 2
Guest: 4f	50.25 mM		



b) Job's Plot



c) Binding curve

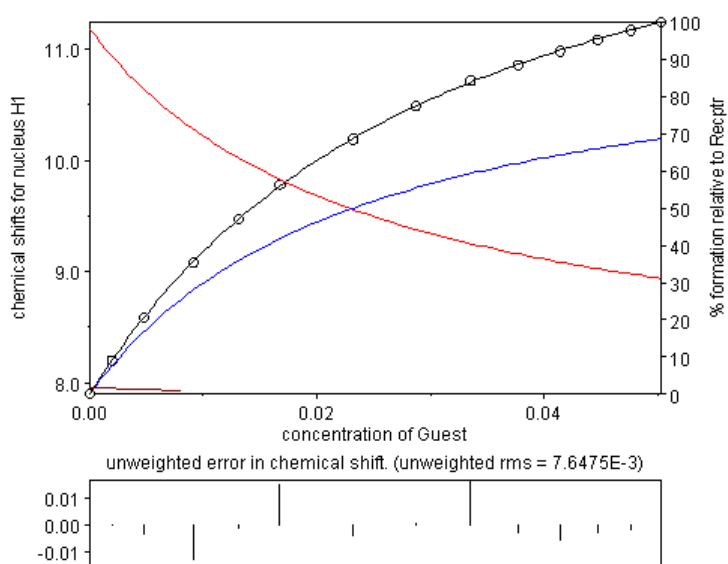


Figure S63. Titration 17. a) Representative ^1H NMR titration of **3b** with **4f** spectra, **4f** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3b**·**4f**. c) Representative fit curve from the Titration 17.

Titration 18

¹H NMR (600MHz, CDCl₃)

	Final concentration
Host: 3c	2.43 mM
Guest: 1a	--- mM

<i>K</i> _a binding constant	error
---	---

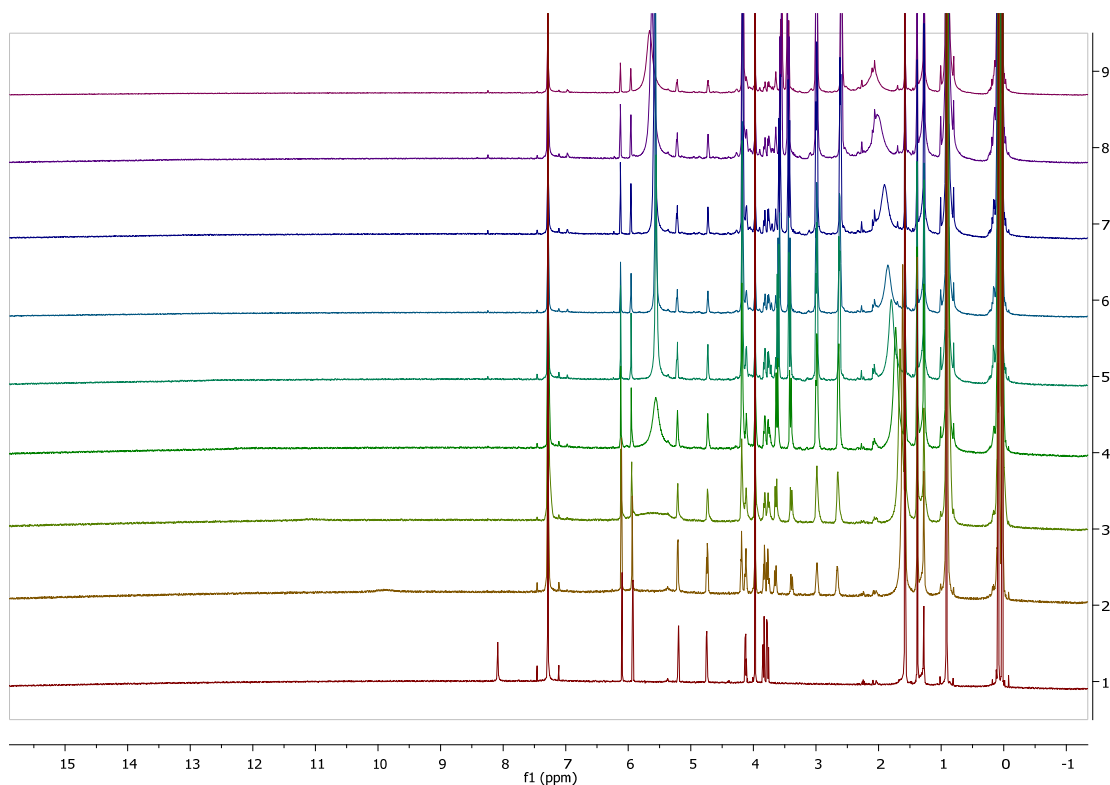


Figure S64. Titration 18. Representative ¹H NMR titration of **3c** with **1a** spectra, **1a** concentration increasing bottom to top in CDCl₃. Saturation was not achieved. Exchangeable NH proton of **3c** disappeared during the titration with **1a**.

Titration 19

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3c	2.43 mM
Guest: 1b	27.11 mM

K_a binding constant	error
480 M^{-1}	± 3

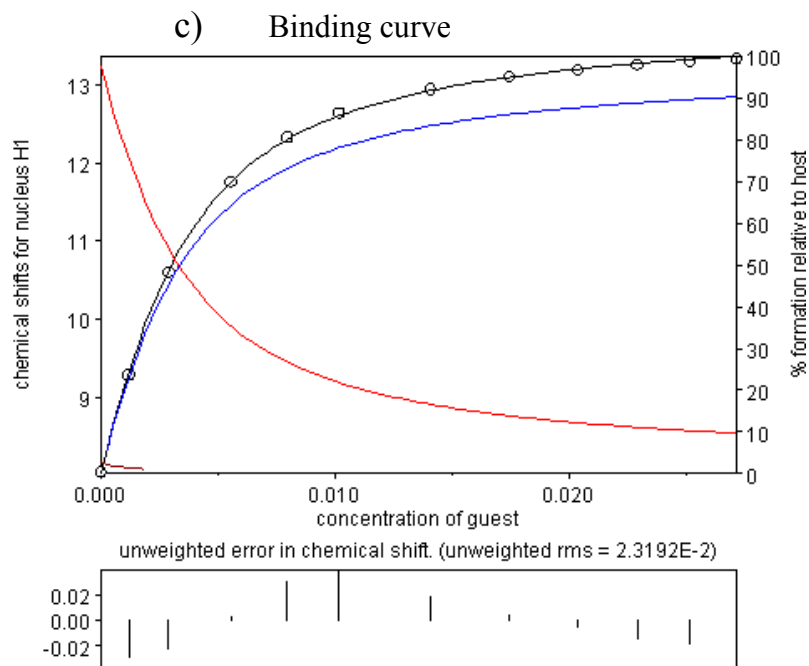
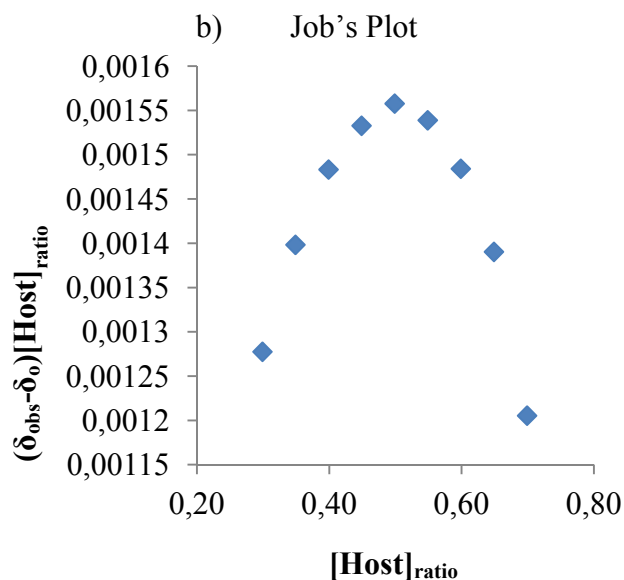
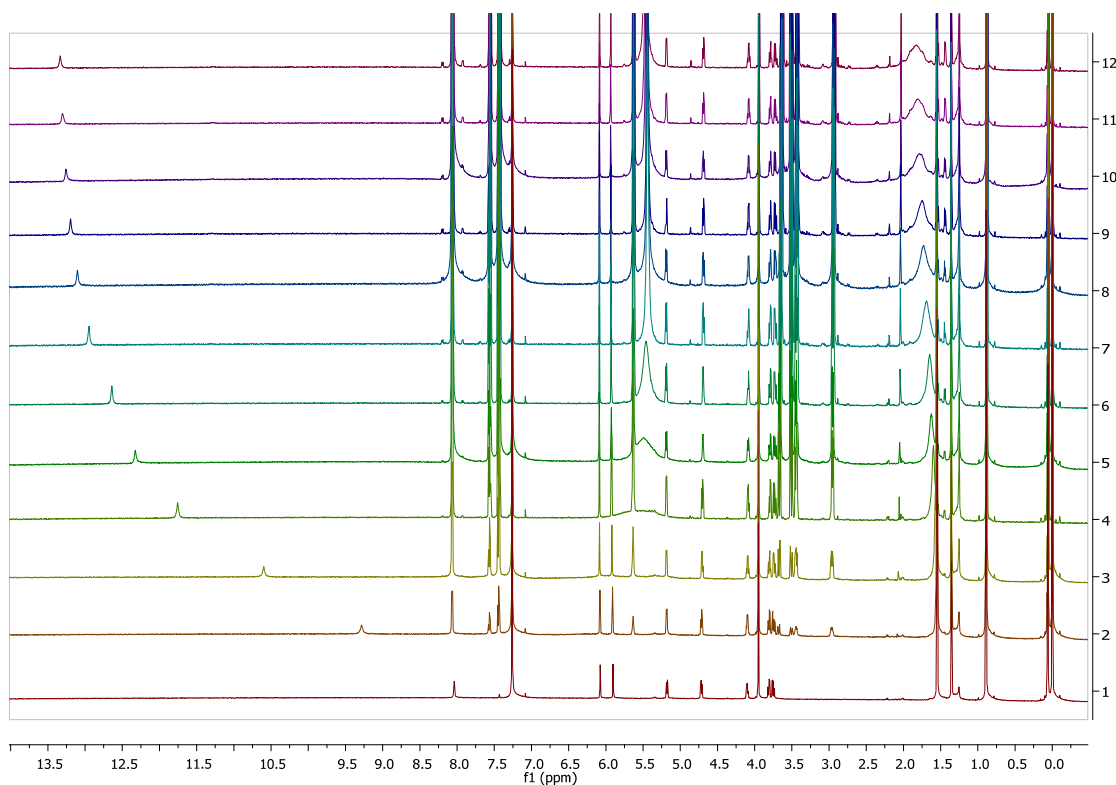


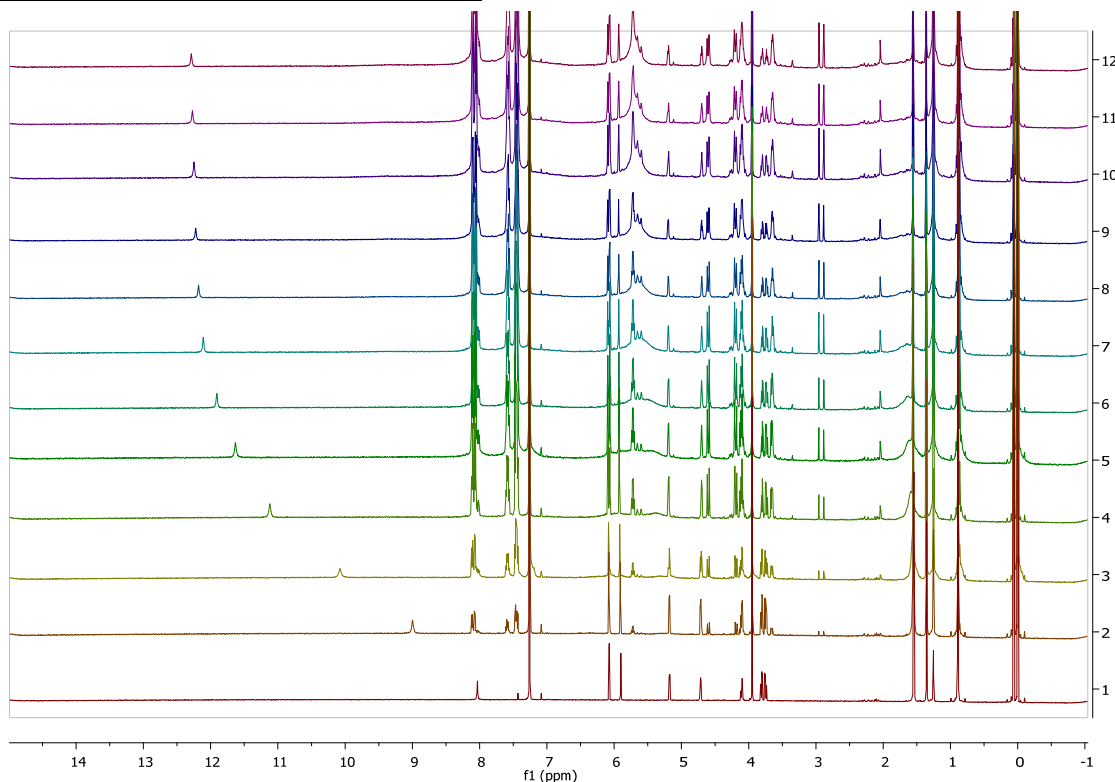
Figure S65. Titration 19. a) Representative ^1H NMR titration of **3c** with **1b** spectra, **1b** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3c**: **1b**. c) Representative fit curve from the Titration 19.

Titration 20

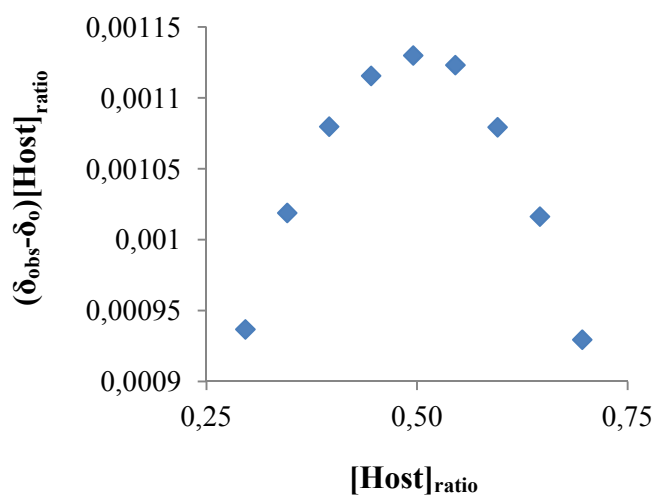
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3c	2.19 mM
Guest: 1c	25.99 mM

K_a binding constant	error
633 M^{-1}	± 12



b) Job's Plot



c) Binding curve

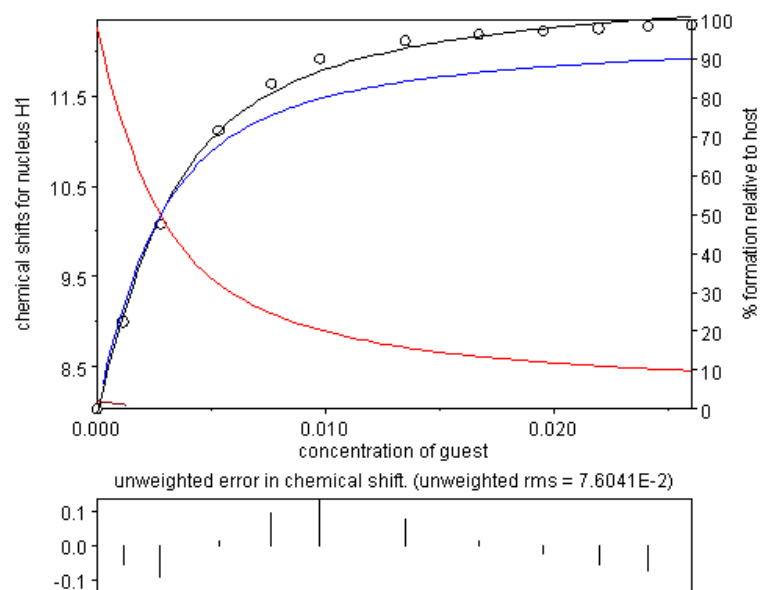


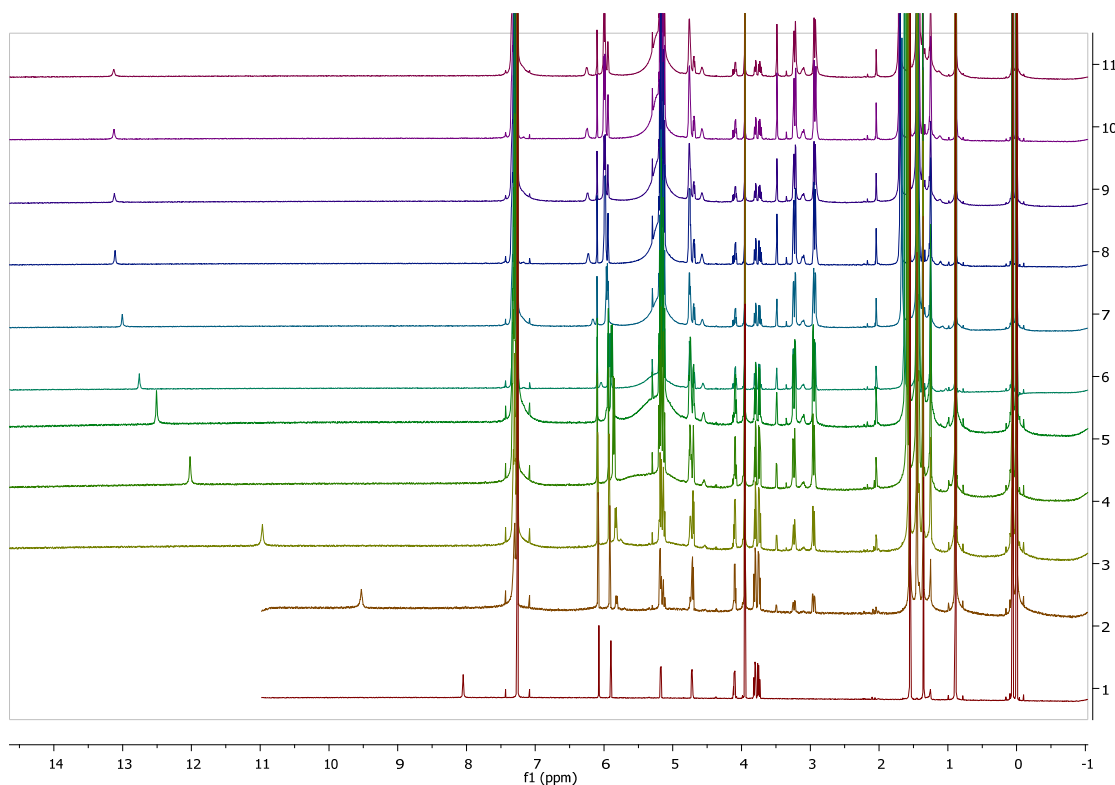
Figure S66. Titration 20. a) Representative ^1H NMR titration of **3c** with **1c** spectra, **1c** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3c**: **1c**. c) Representative fit curve from the Titration 20.

Titration 21

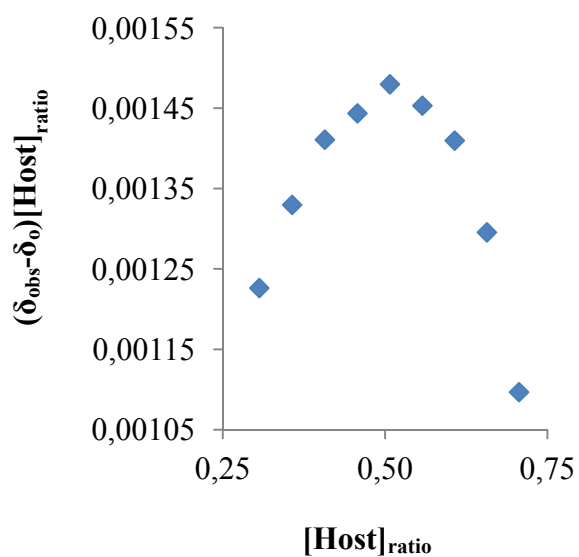
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3c	3.13 mM
Guest: 1d	30.89 mM

K_a binding constant	error
754 M^{-1}	± 11



b) Job's Plot



c) Binding curve

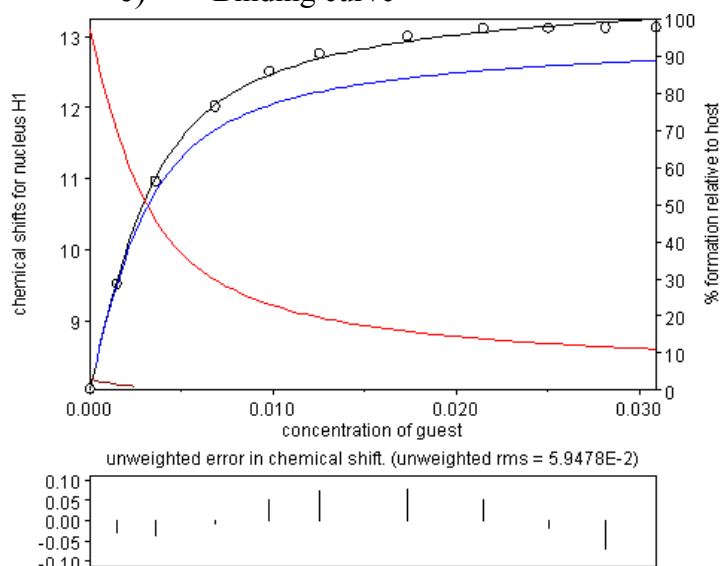


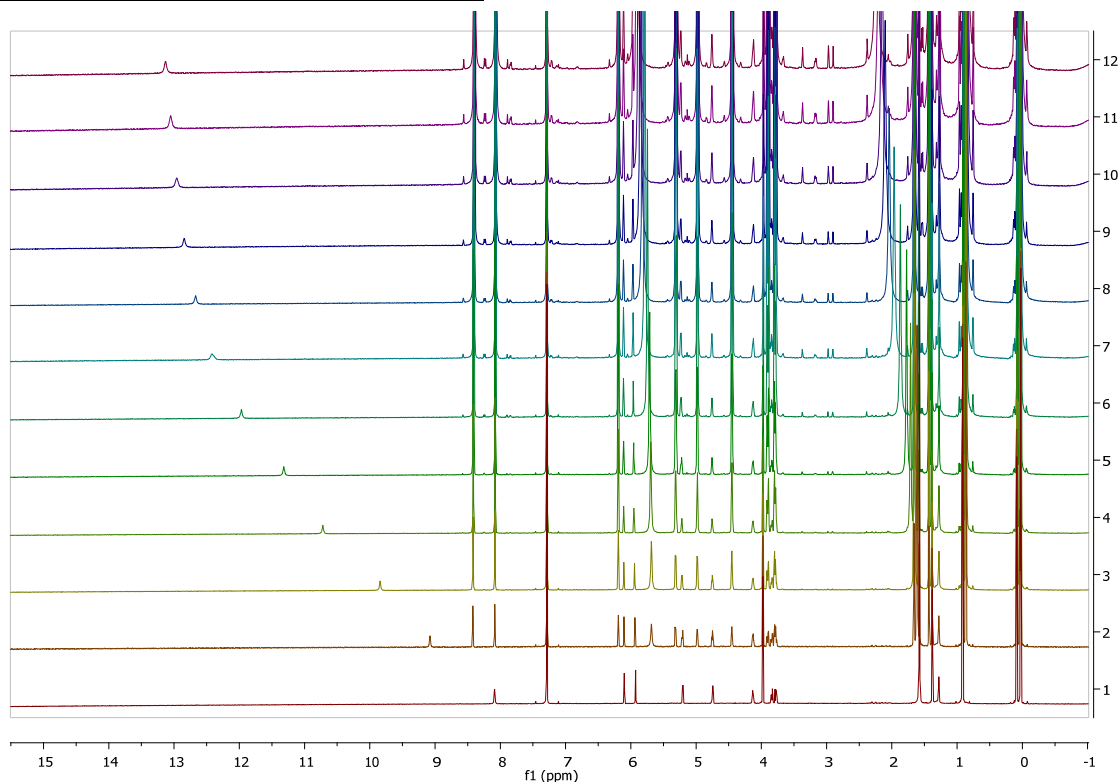
Figure S67. Titration 21. a) Representative ^1H NMR titration of **3c** with **1d** spectra, **1d** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3c**·**1d**. c) Representative fit curve from the Titration 21.

Titration 22

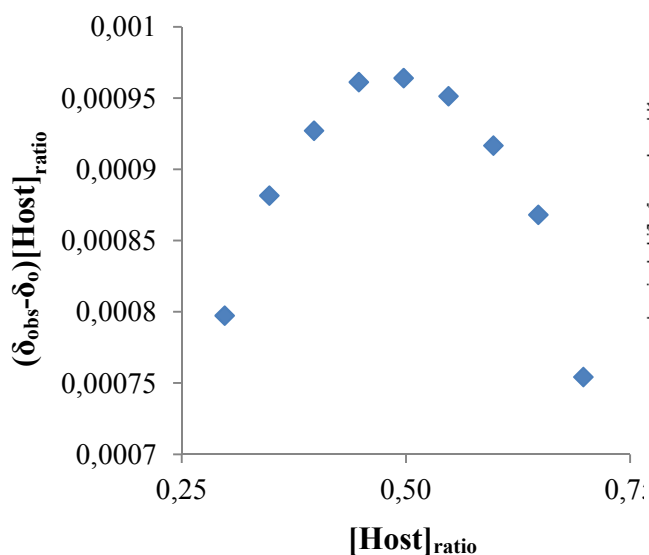
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3c	2.19 mM
Guest: 4e	59.04 mM

K_a binding constant	error
87 M^{-1}	± 2



b) Job's Plot



c) Binding curve

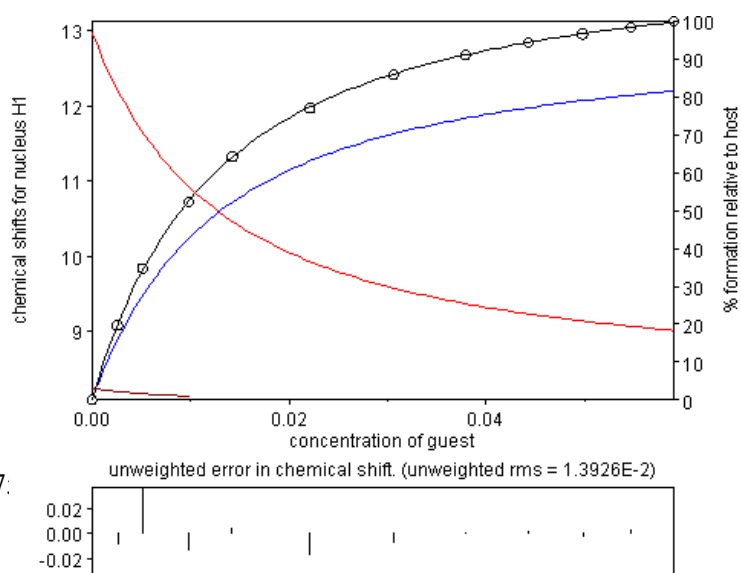


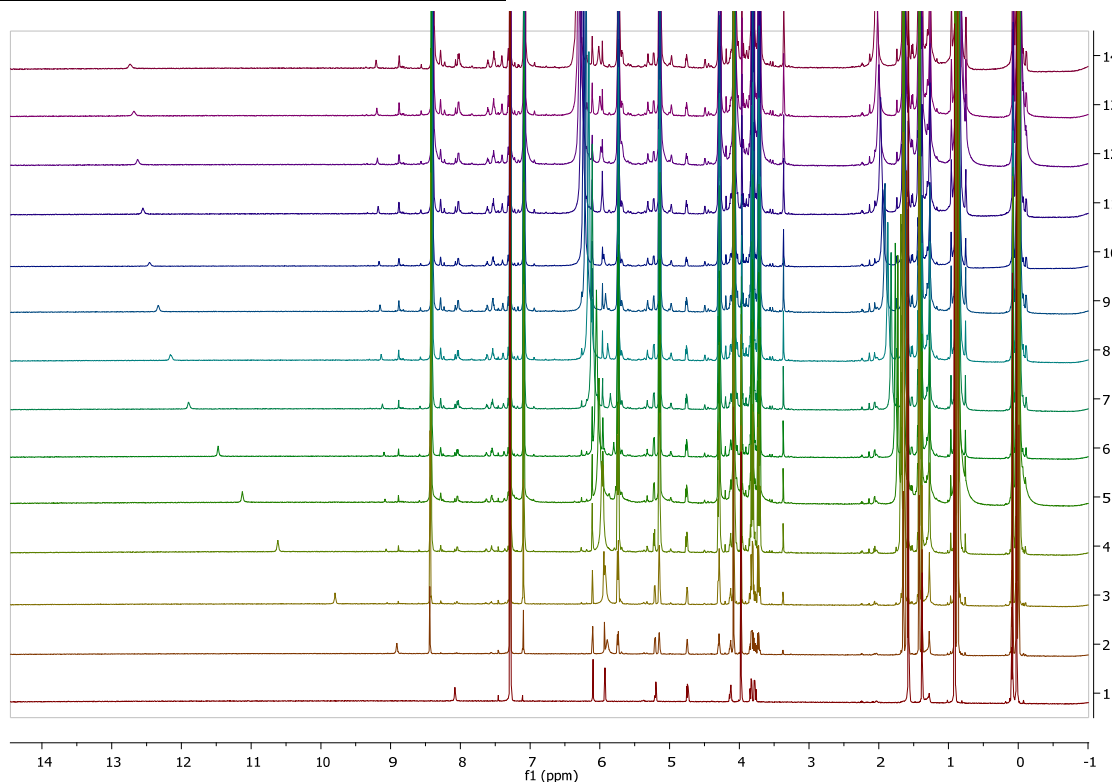
Figure S68. Titration 22. a) Representative ^1H NMR titration of **3c** with **4e** spectra, **4e** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3c**·**4e**. c) Representative fit curve from the Titration 22.

Titration 23

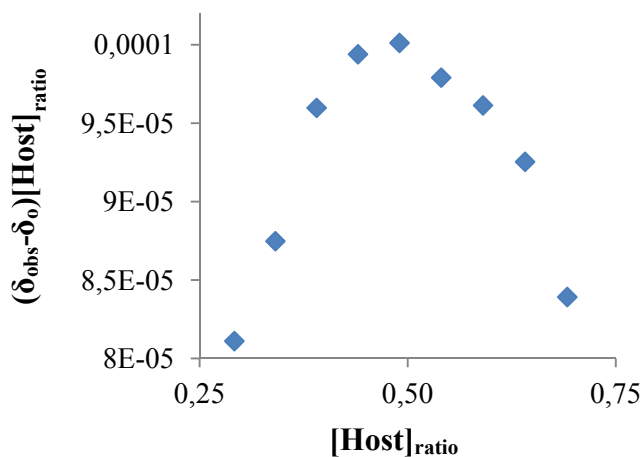
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 3c	2.19 mM
Guest: 4f	99.46 mM

K_a binding constant	error
47 M^{-1}	± 1



b) Job's Plot



c) Binding curve

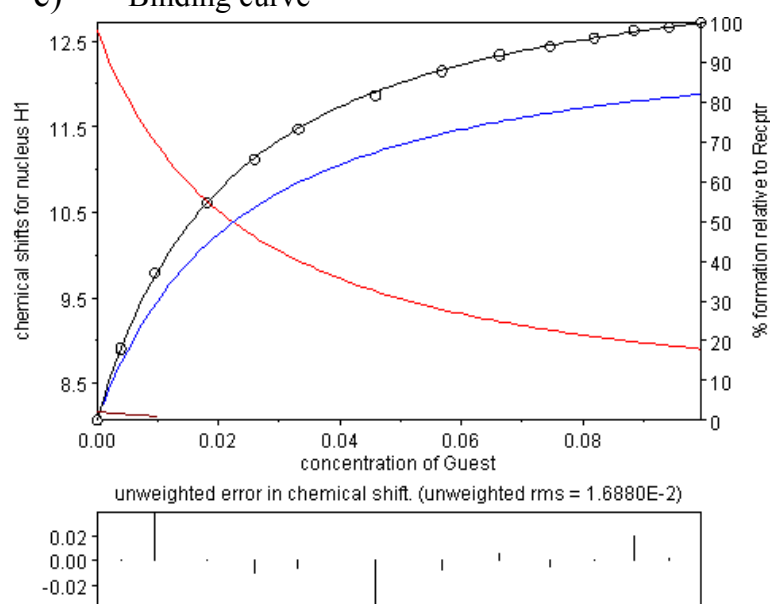


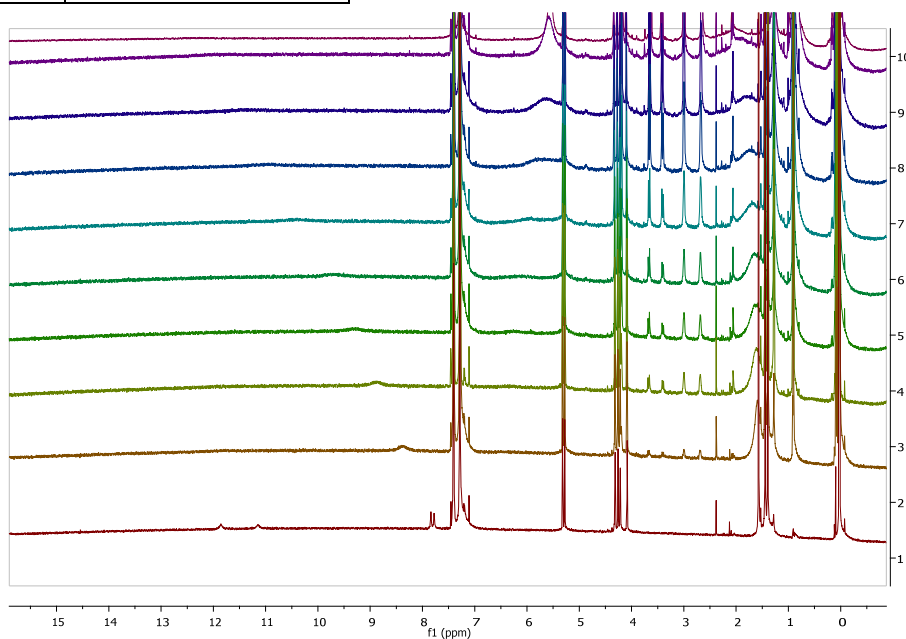
Figure S69. Titration 23. a) Representative ^1H NMR titration of **3c** with **4f** spectra, **4f** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **3c**: **4f**. c) Representative fit curve from the Titration 23.

Titration 24

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 2	1.79 mM
Guest: 1a	20.82 mM

K_a binding constant	error
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b) ^1H NMR Comparison (600MHz, CDCl_3) at 298K (bottom) and 276K (top)

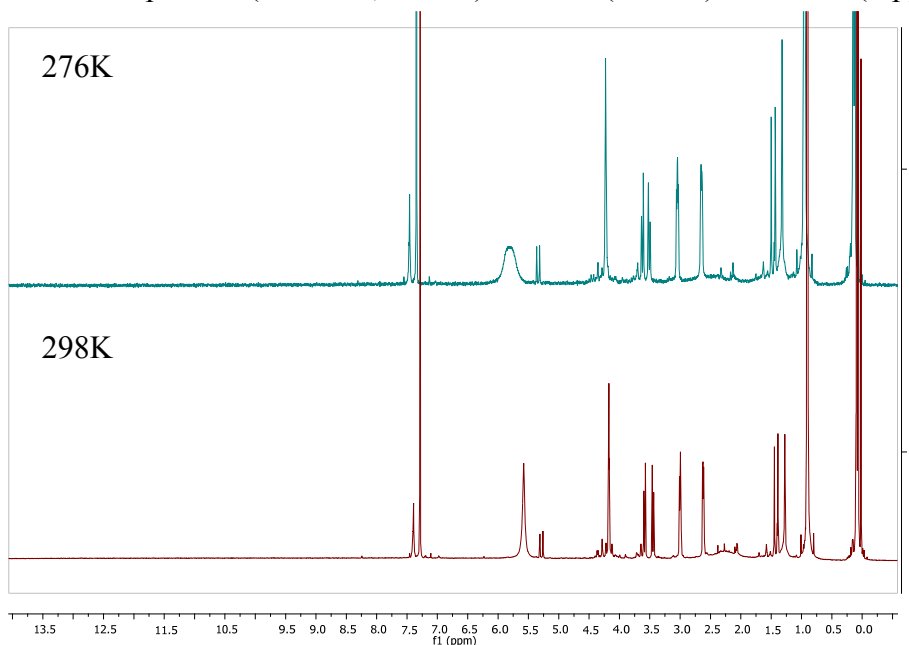


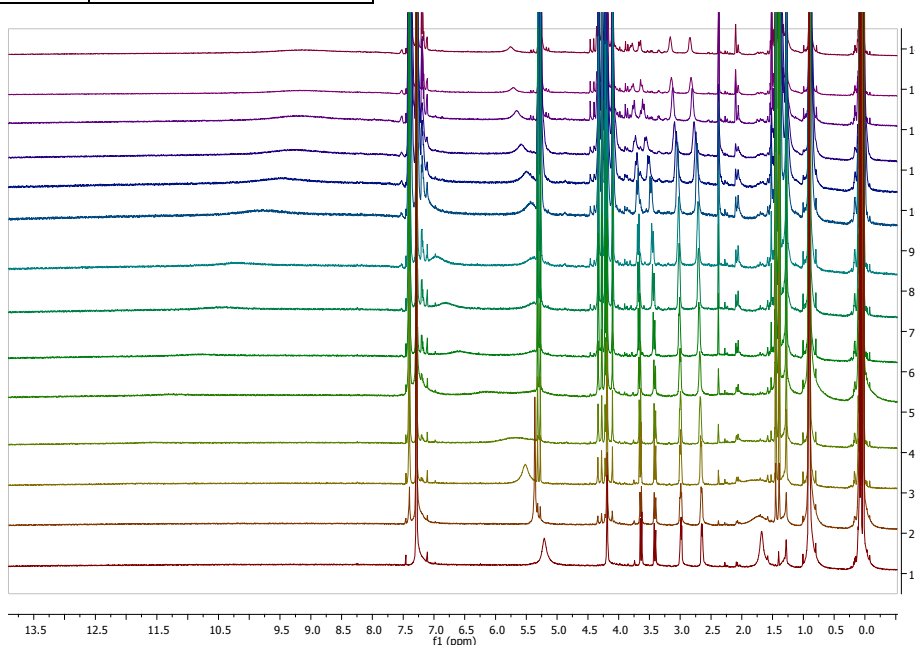
Figure S70. Titration 24. a) Representative ^1H NMR titration of **2** with **1a** spectra, **1a** concentration increasing bottom to top in CDCl_3 . Saturation was not achieved. Exchangeable NH proton of **2** disappeared during the titration with **1a**. b) ^1H NMR comparison at different temperatures of the mixture **1a:2** (11.31 eq. of **1a**). Exchangeable NH protons of **2** disappeared.

Titration 24-reverse

a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 1a	1.10 mM
Guest: 2	28.82 mM

K_a binding constant	error
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b) ^1H NMR Comparison (600MHz, CDCl_3) at 298K (bottom) and 276K (top)

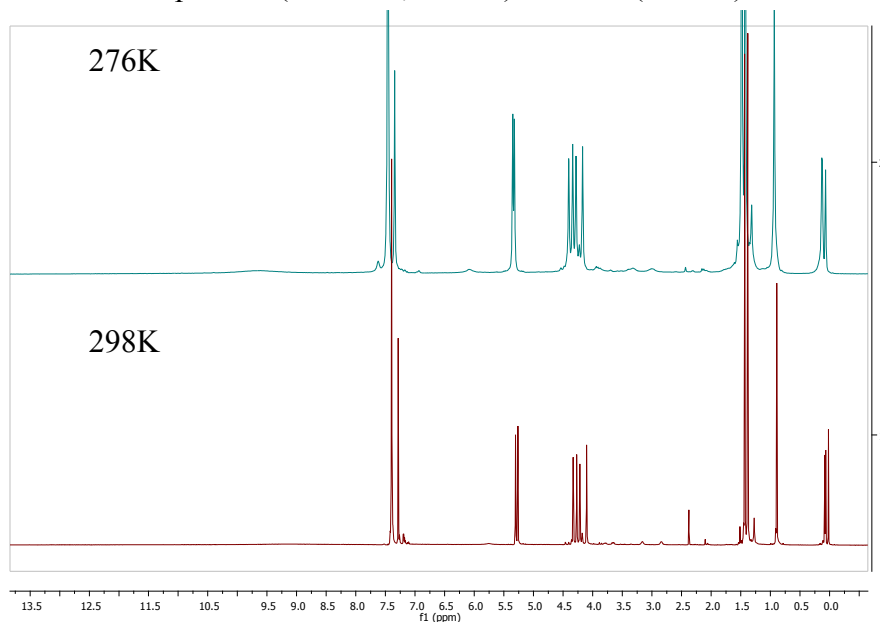


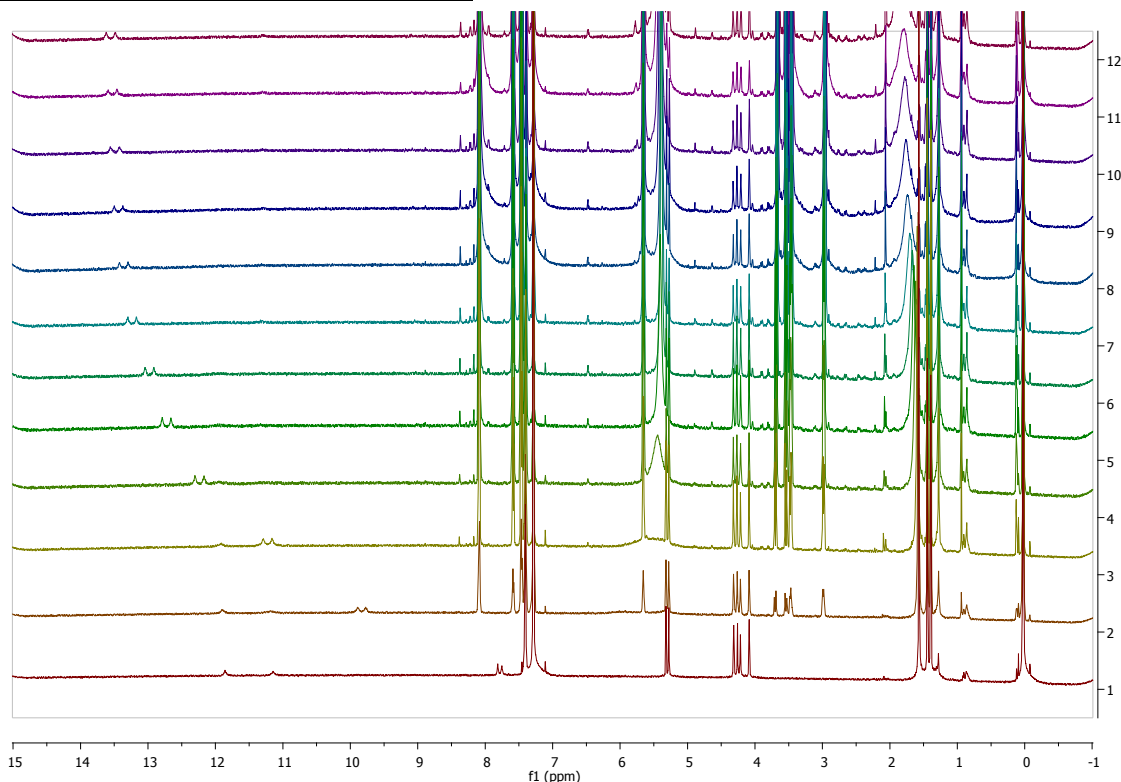
Figure S71. Titration 24-reverse. a) Representative ^1H NMR titration of **1a** with **2** spectra, **2** concentration increasing bottom to top in CDCl_3 . Saturation could not be achieved. Exchangeable NH_2 protons of **1a** disappeared during the titration with **2**. b) ^1H NMR comparison at different temperatures of the mixture **2:1a** (26.21 eq. of **2**). Exchangeable NH_2 protons of **1a** disappeared.

Titration 25

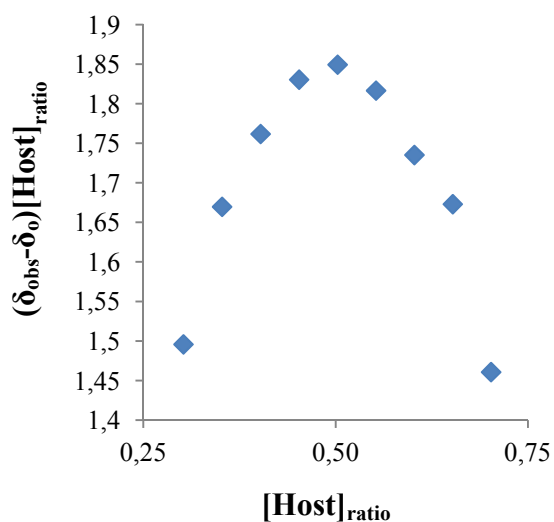
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 2	1.79 mM
Guest: 1b	25.8 mM

K_a binding constant	error
711 M^{-1}	± 3



b) Job's Plot



c) Binding curve

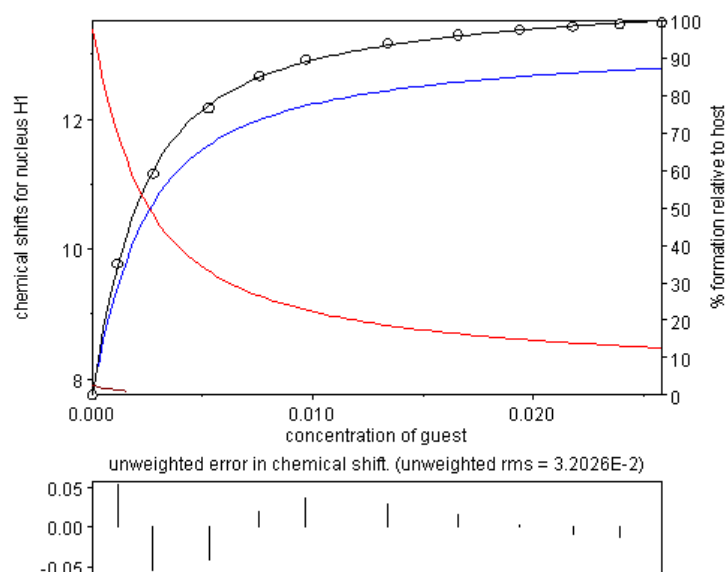


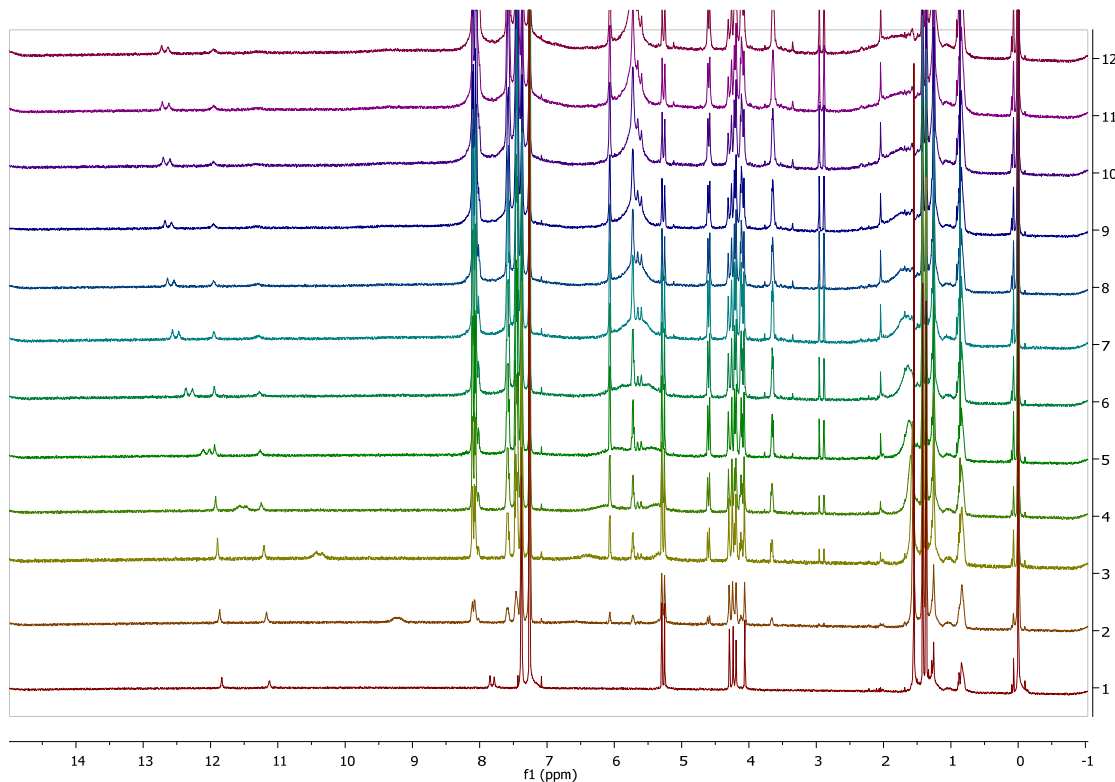
Figure S72. Titration 25. a) Representative ^1H NMR titration of **2** with **1b** spectra, **1b** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **2**:**1b**. c) Representative fit curve from the Titration 25.

Titration 26

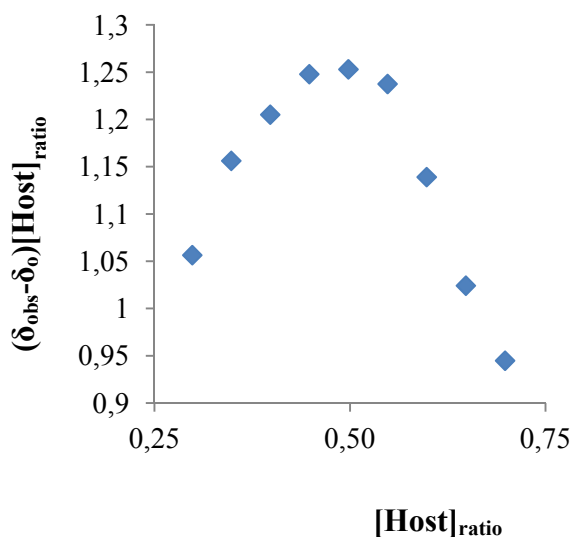
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 2	2.82 mM
Guest: 1c	36.67 mM

K_a binding constant	error
484 M^{-1}	± 10



b) Job's Plot



c) Binding curve

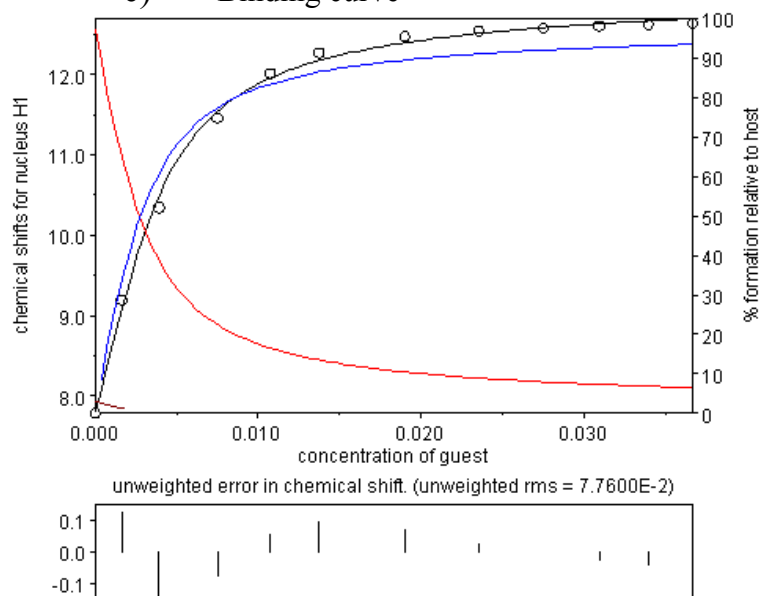


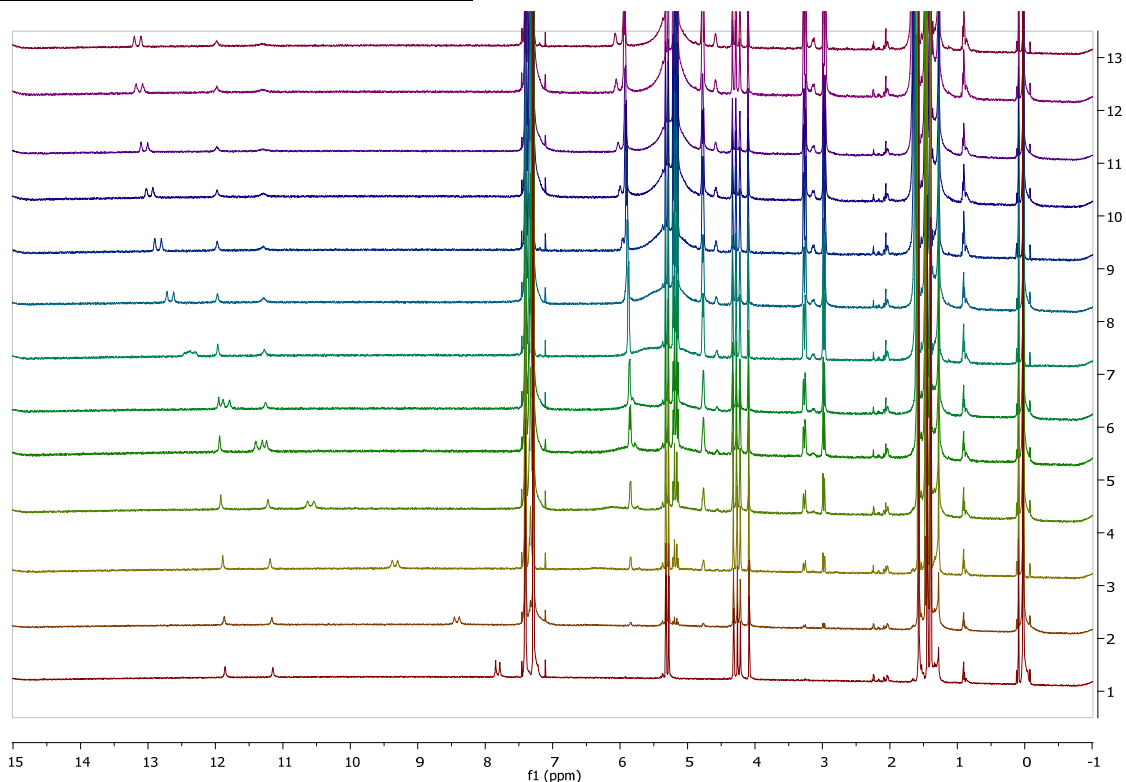
Figure S73. Titration 26. a) Representative ^1H NMR titration of **2** with **1c** spectra, **1c** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **2**·**1c**. c) Representative fit curve from the Titration 26.

Titration 27

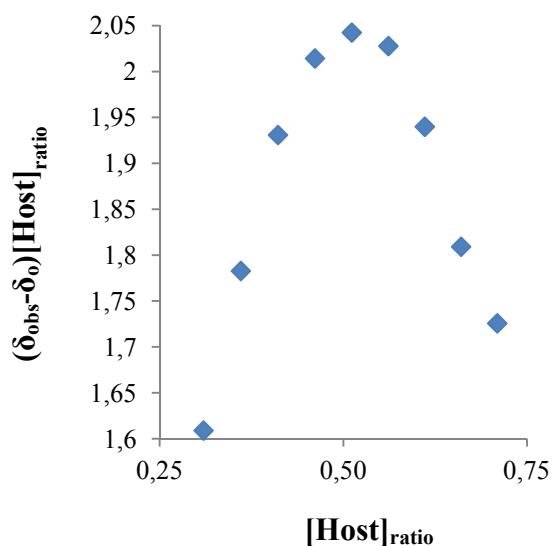
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 2	1.29 mM
Guest: 1d	25.6 mM

K_a binding constant	error
320 M^{-1}	± 24



b) Job's Plot



c) Binding curve

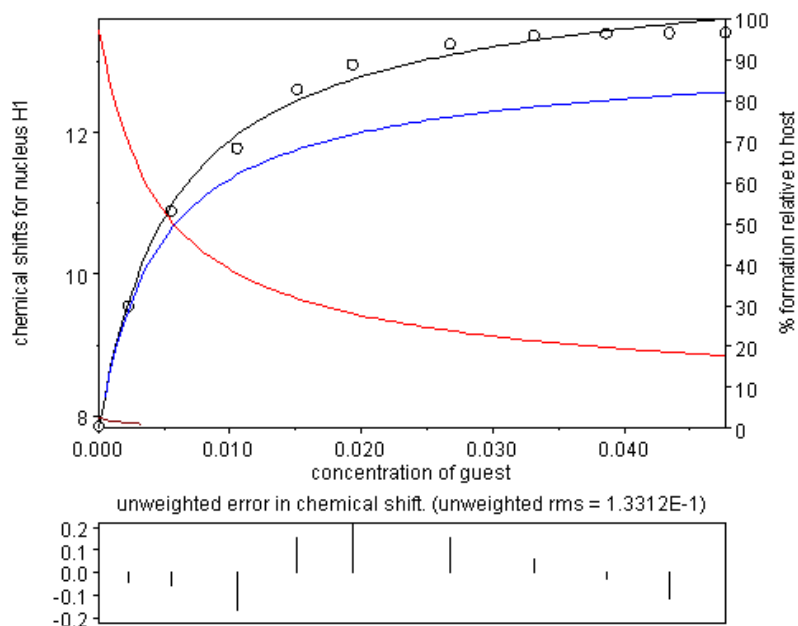


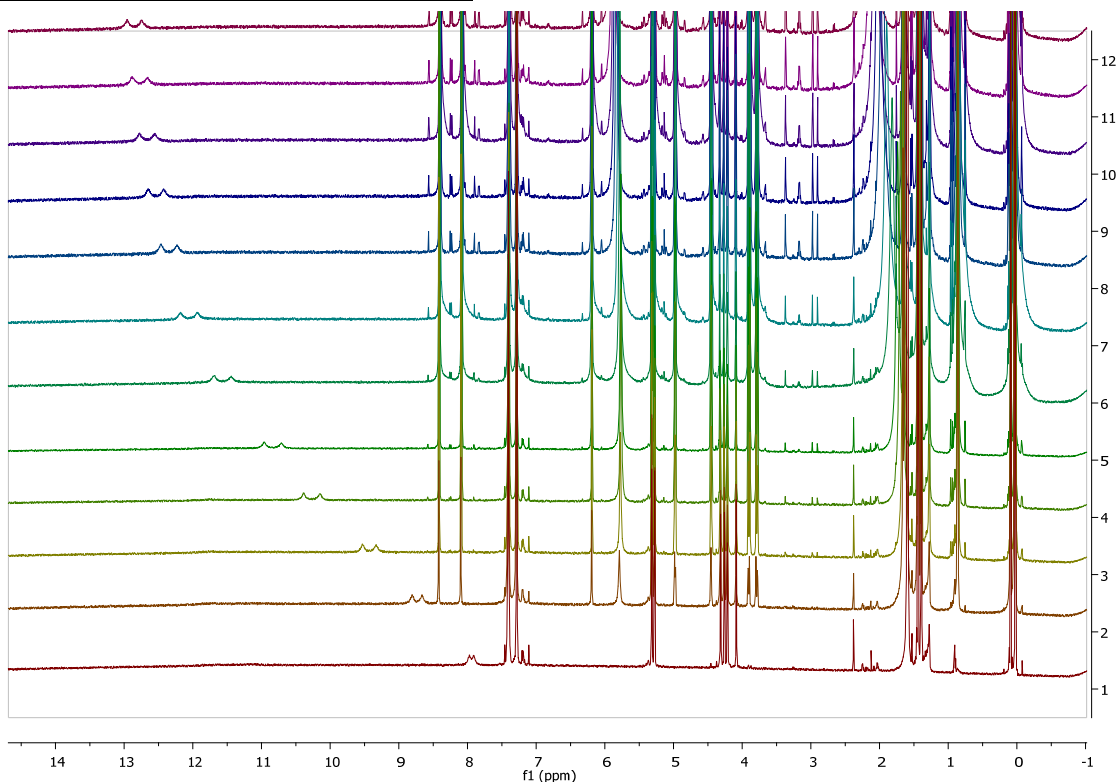
Figure S74. Titration 27. a) Representative ^1H NMR titration of **2** with **1d** spectra, **1d** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **2**:**1d**. c) Representative fit curve from the Titration 27.

Titration 28

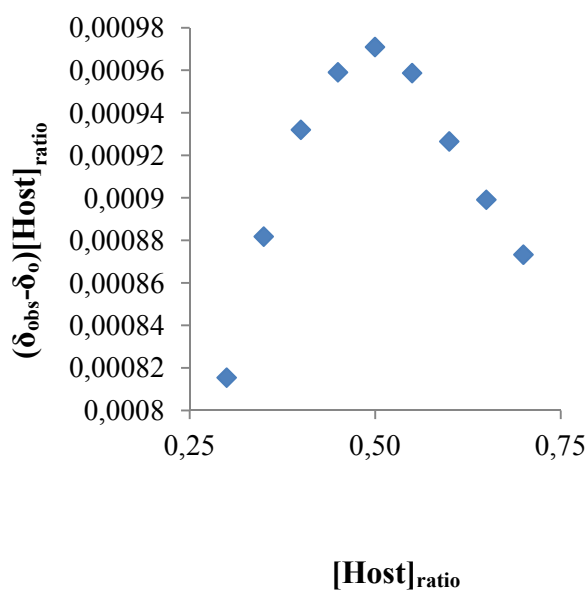
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 2	2.56 mM
Guest: 4e	47.65 mM

K_a binding constant	error
89 M^{-1}	± 2



b) Job's Plot



c) Binding curve

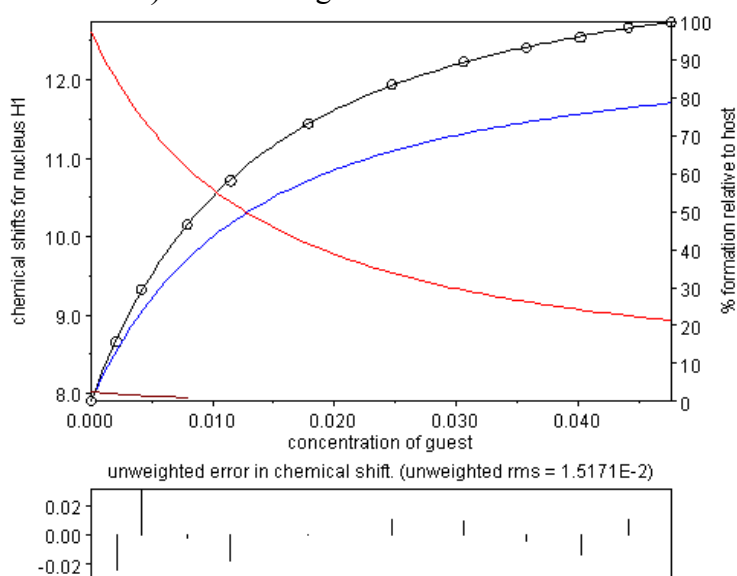


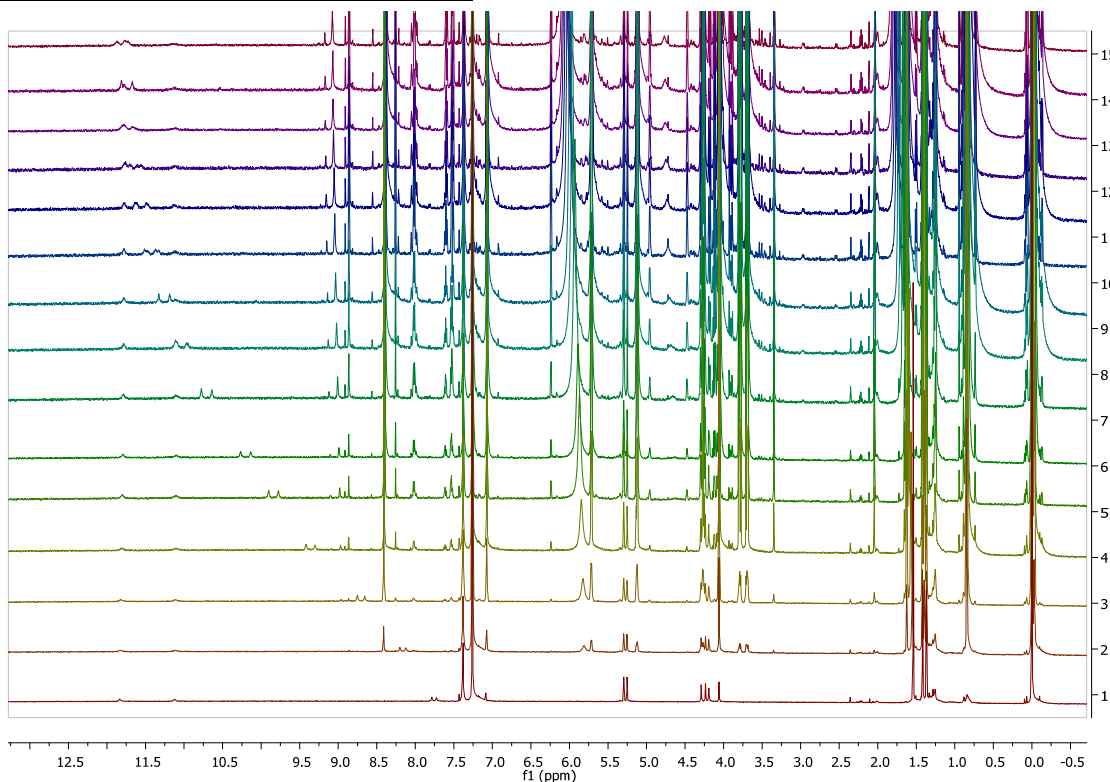
Figure S75. Titration 28. a) Representative ^1H NMR titration of **2** with **4e** spectra, **4e** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **2**·**4e**. c) Representative fit curve from the Titration 28.

Titration 29

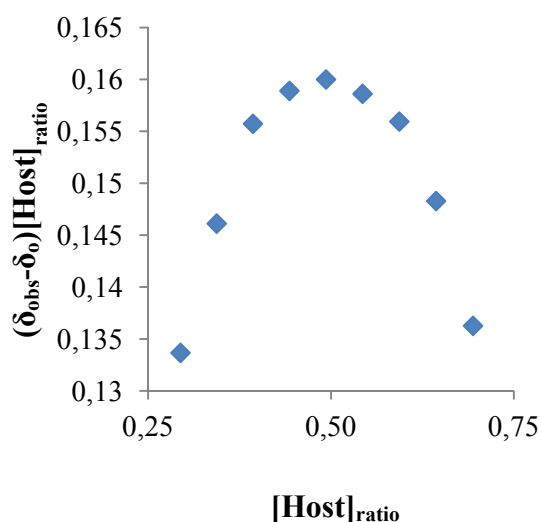
a) ^1H NMR (600MHz, CDCl_3)

	Final concentration
Host: 2	2.82 mM
Guest: 4f	36.67 mM

K_a binding constant	error
39 M^{-1}	± 1



b) Job's Plot



c) Binding curve

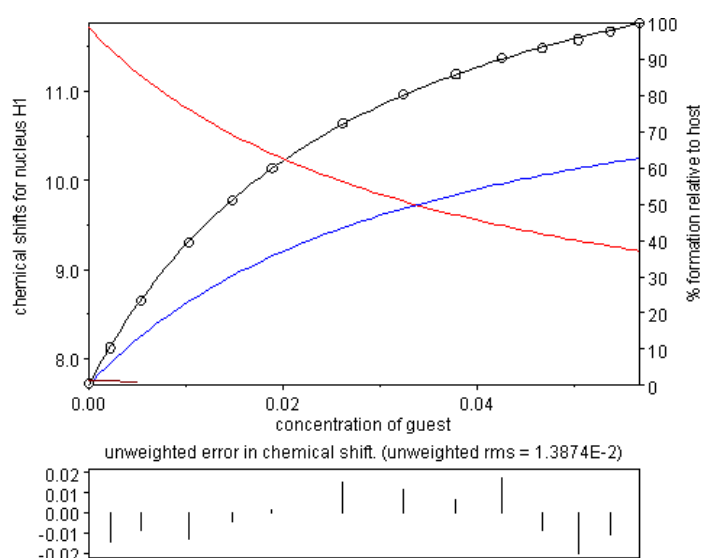


Figure S76. Titration 29. a) Representative ^1H NMR titration of **2** with **4f** spectra, **4f** concentration increasing bottom to top in CDCl_3 . b) ^1H NMR Job's method of continuous variation of **2**·**4f**. c) Representative fit curve from the Titration 29.

TRIAZINES vs ADENINES

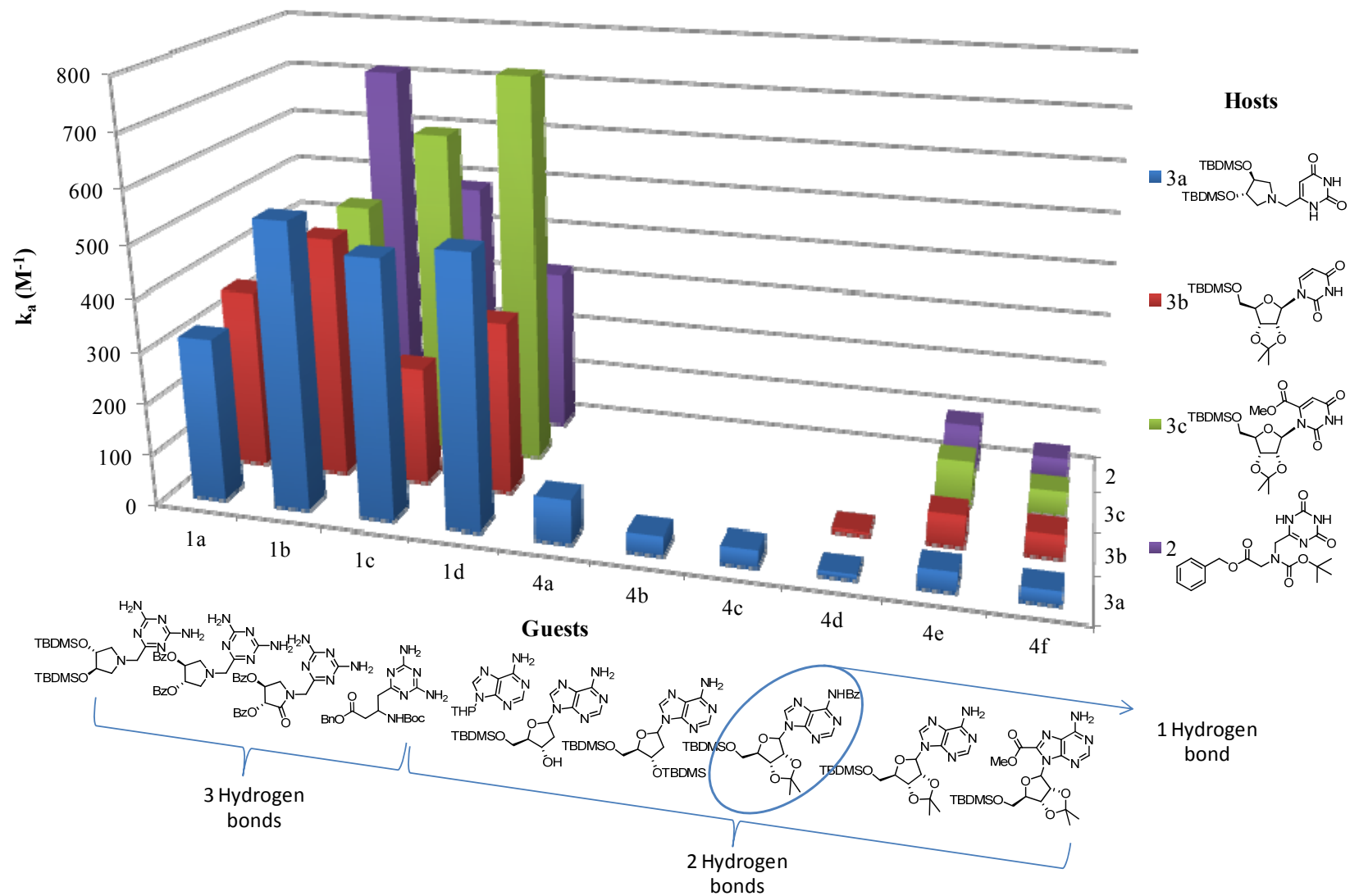


Figure S77. Summary of binding isothermal cross association constant values for the complexation of uracil and 5-azauracil with adenine and 2,4-diaminotriazine derivatives.

Table S1. Free Energy associated to the complexation with triazines.

nH = number of hydrogens bonding (nH = 3).
 $\Delta G = -RT \ln K$; $R = 1,9872041 \times 10^{-3} \text{ Kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $T = 298 \text{ K}$.
 K_a = value obtained for the corresponding titration experiment.

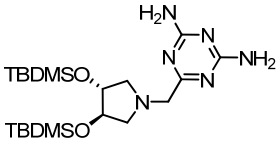
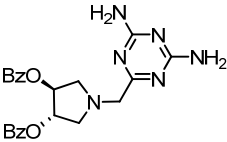
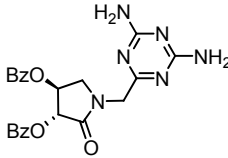
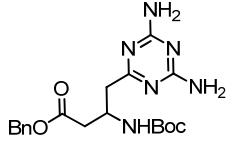
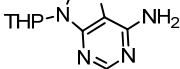
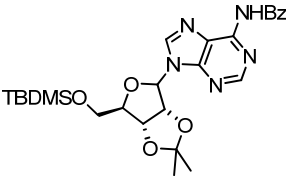
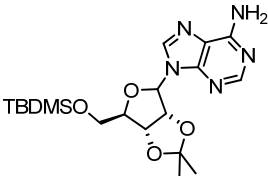
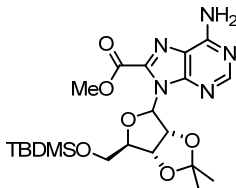
												
	1a			1b			1c			1d		
	K_a	ΔG	$\Delta G/nH$	K_a	ΔG	$\Delta G/nH$	K_a	ΔG	$\Delta G/nH$	K_a	ΔG	$\Delta G/nH$
3a	317	-3,41	-1,14	550	-3,74	-1,25	496	-3,68	-1,23	521	-3,70	-1,24
3b	350	-3,47	-1,16	467	-3,64	-1,21	230	-3,22	-1,07	336	-3,44	-1,15
3c				480	-3,66	-1,22	633	-3,82	-1,27	754	-3,92	-1,31
2				711	-3,89	-1,29	484	-3,66	-1,22	320	-3,42	-1,14

Table S2. Free Energy associated to the complexation with adenines.

nH = number of hydrogens bonding (nH = 2).
 $\Delta G = -RT \ln K$; $R = 1,9872041 \times 10^{-3} \text{ Kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $T = 298 \text{ K}$.
 K_a = value obtained for the corresponding titration experiment.

													
	4a			4d				4e			4f		
	K_a	ΔG	$\Delta G/nH$	K_a	ΔG	$\Delta G/nH$	$\Delta G/nH^*$	K_a	ΔG	$\Delta G/nH$	K_a	ΔG	$\Delta G/nH$
3a	83	-2,61	-1,31	10	-1,36	-0,68	-1,36	38	-2,15	-1,08	26	-1,93	-0,96
3b				6	-1,06	-0,53	-1,06	59	-2,41	-1,21	45	-2,25	-1,12
3c								87	-2,64	-1,32	47	-2,28	-1,14
2								88	-2,66	-1,33	39	-2,17	-1,08

* nH involved in the complexation with compound 4d is just one (nH=1).

Table S3. Crystal data and structure refinement for **3a**.

Empirical formula	C ₂₁ H ₄₁ N ₃ O ₄ Si ₂	
Formula weight	455.75	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 6.7380(3) Å	α = 90°.
	b = 10.5506(4) Å	β = 99.501(2)°.
	c = 19.1623(8) Å	γ = 90°.
Volume	1343.56(10) Å ³	
Z	2	
Density (calculated)	1.127 Mg/m ³	
Absorption coefficient	0.160 mm ⁻¹	
F(000)	496	
Crystal size	0.270 x 0.200 x 0.080 mm ³	
Theta range for data collection	2.155 to 26.412°.	
Index ranges	-8 ≤ h ≤ 8, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23	
Reflections collected	20474	
Independent reflections	5519 [R(int) = 0.0363]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Multi-scan	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5519 / 1 / 281	
Goodness-of-fit on F ²	1.009	
Final R indices [I > 2σ(I)]	R1 = 0.0359, wR2 = 0.0990	
R indices (all data)	R1 = 0.0395, wR2 = 0.1013	
Absolute structure parameter	0.04(3) [stereochem. confirmed]	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.546 and -0.398 e.Å ⁻³	

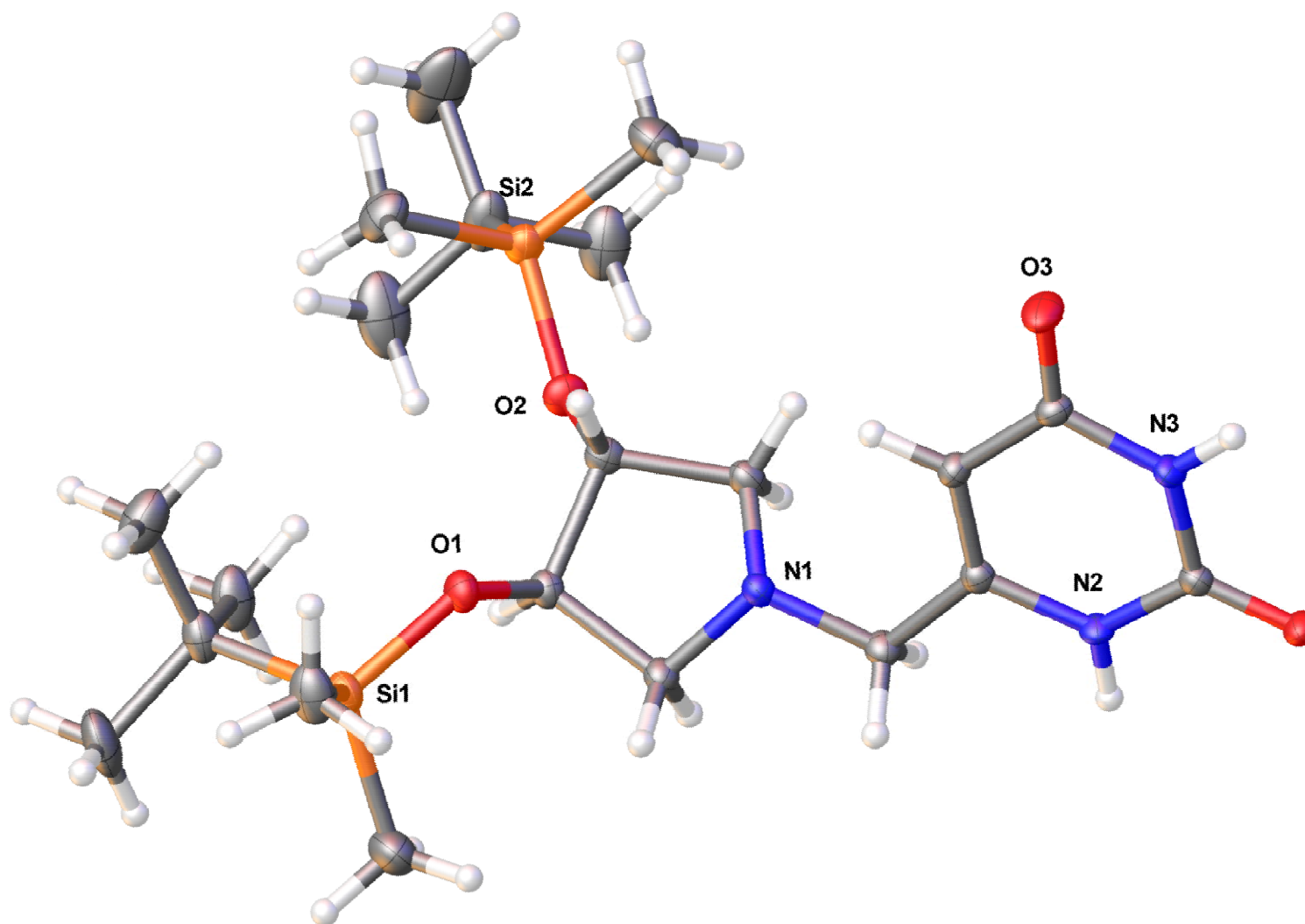


Figure S78. X-ray structure of the compound **3a** with 50% ellipsoid probability. CCDC-1056406 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data%5Frequest/cif