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RNA Nucleosides as chiral sensing agents in NMR spectroscopy

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Index

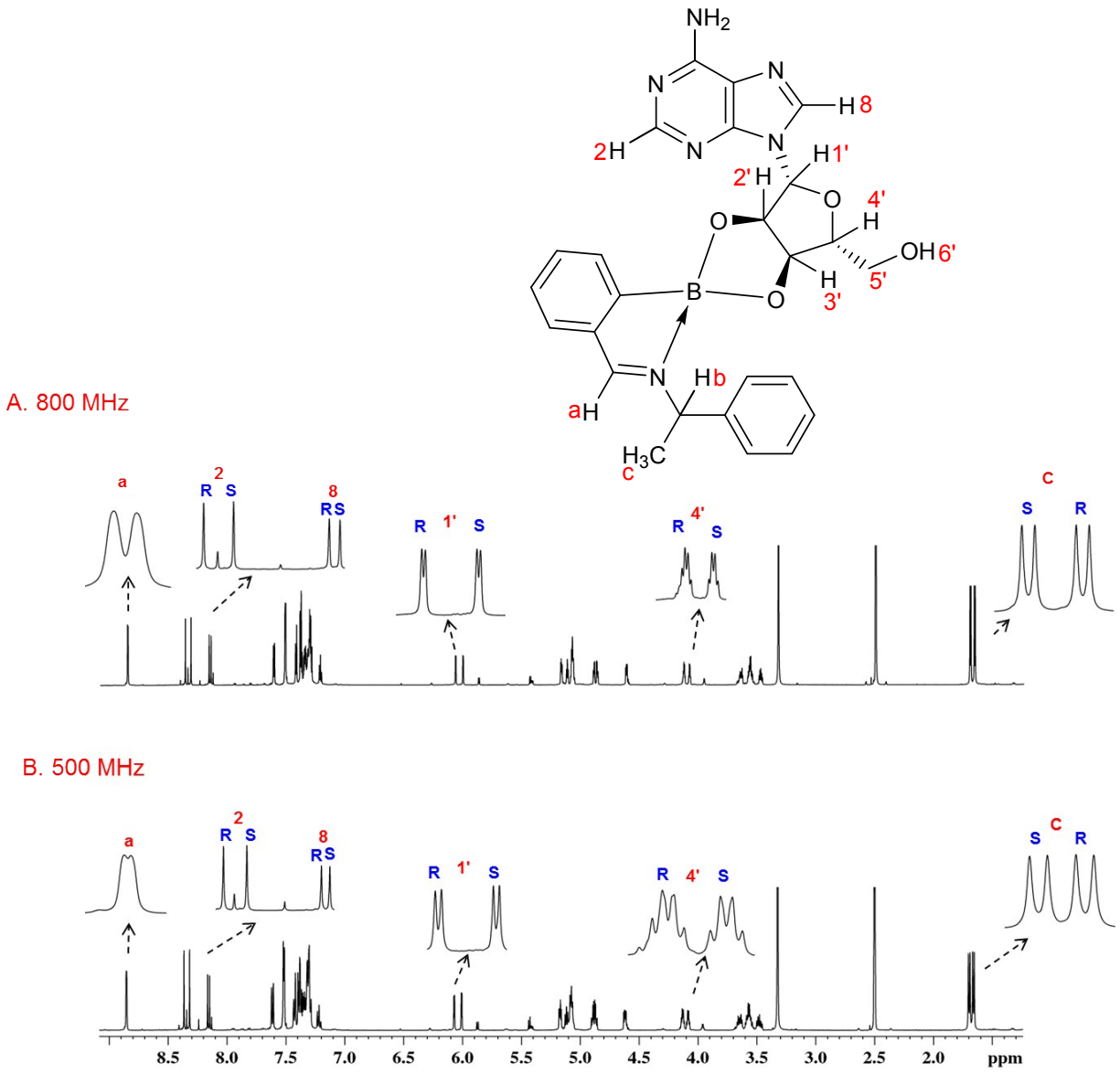


Figure S1. 800 MHz (A) and 500 MHz (B) ^{1}H NMR spectra of diastereomeric complex of adenosine, 2-formylphenylboronic acid and α-methylbenzylamine. Expanded regions in 500 MHz spectrum shows differentiate peaks for diastereomers. Possible measurement of diastereomeric excess.

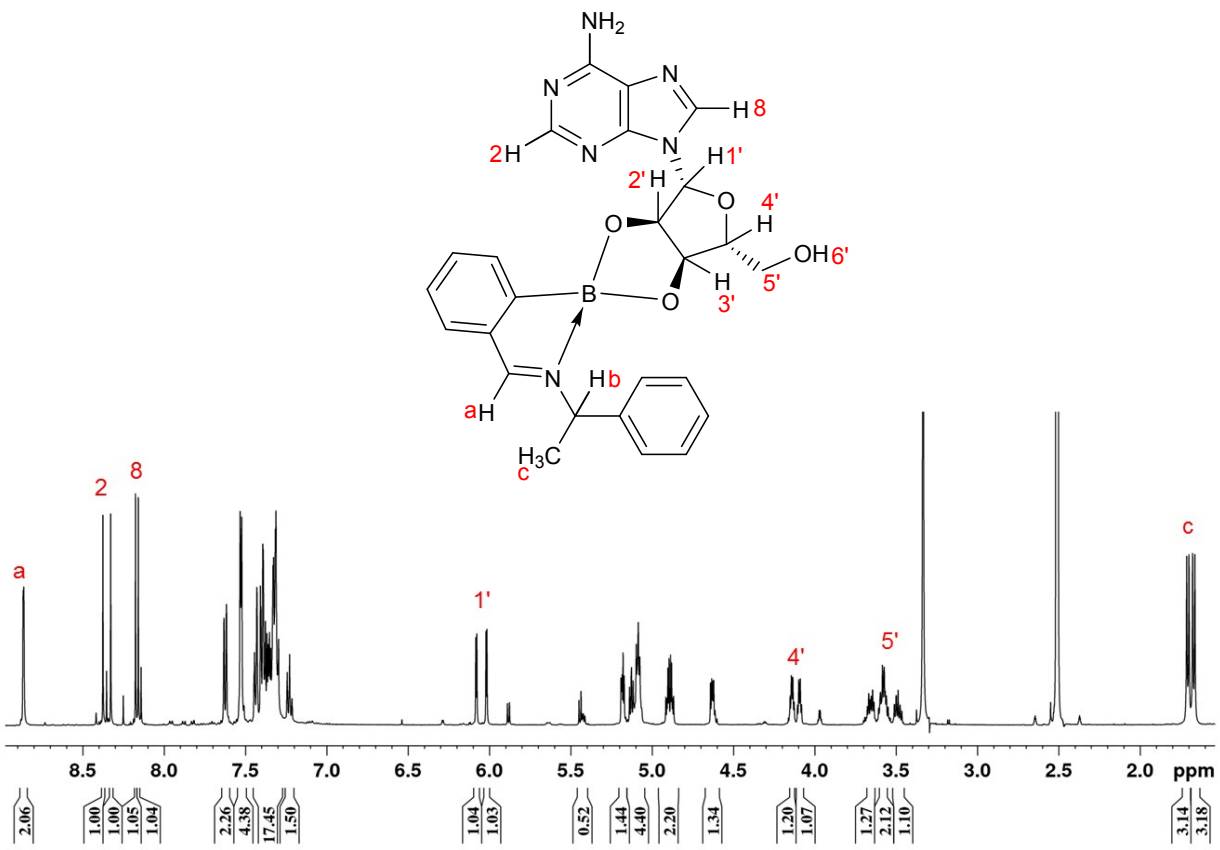


Figure S2. 500 MHz ^{1}H NMR spectrum of adenosine:2-formylphenylboronic acid: α-methylbenzylamine diastreomeric complex with showing peak integration. The peaks shown expected integration within experimental error.

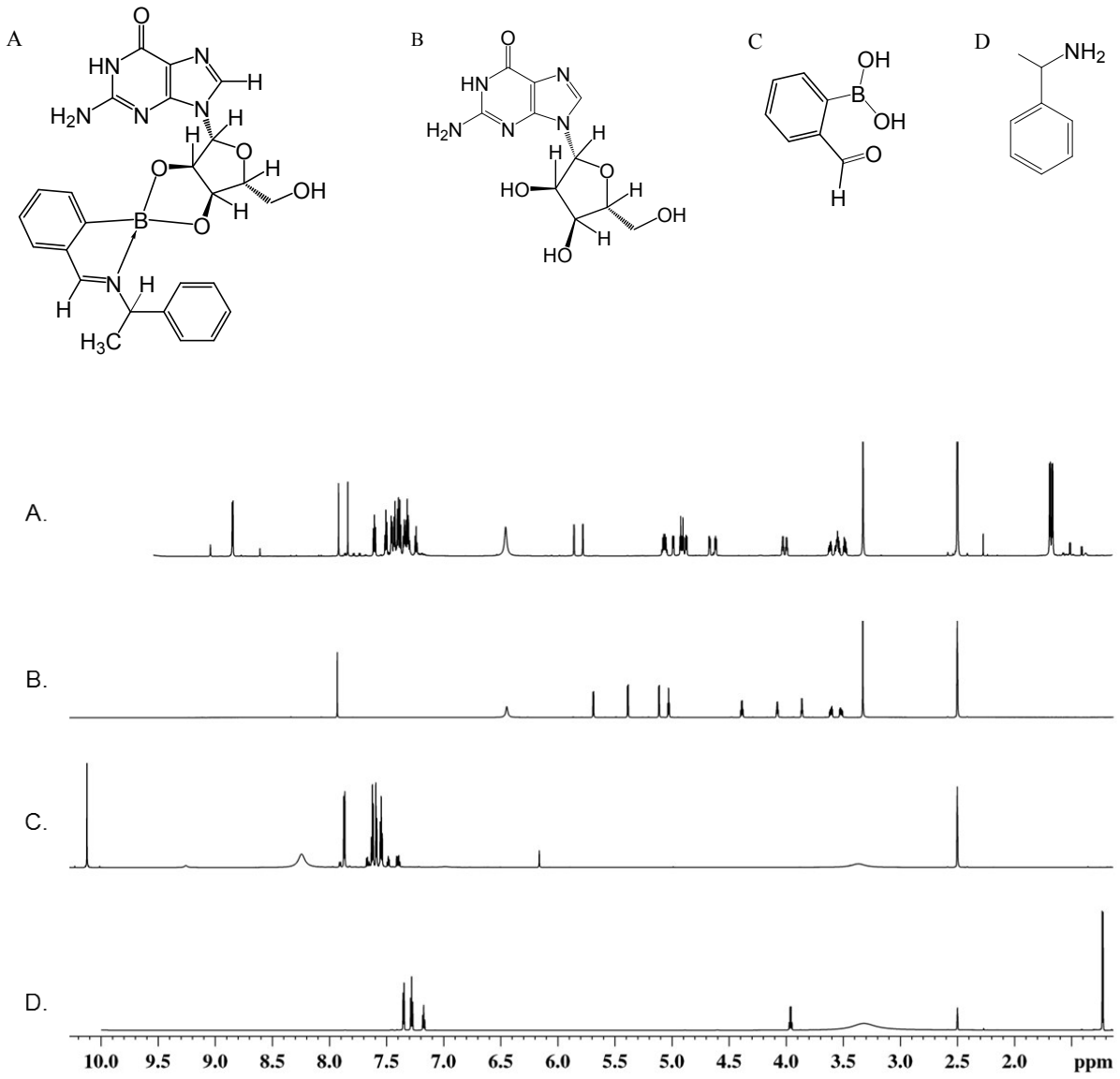


Figure S3. Comparsion of ^{1}H NMR spectra of α-methylbenzylamine (D), 2-formylphenylboronic acid (C), guanosine (B) and guanosine:2-formylphenylboronic acid:4- α-methylbenzylamine diastreomeric complex (A).

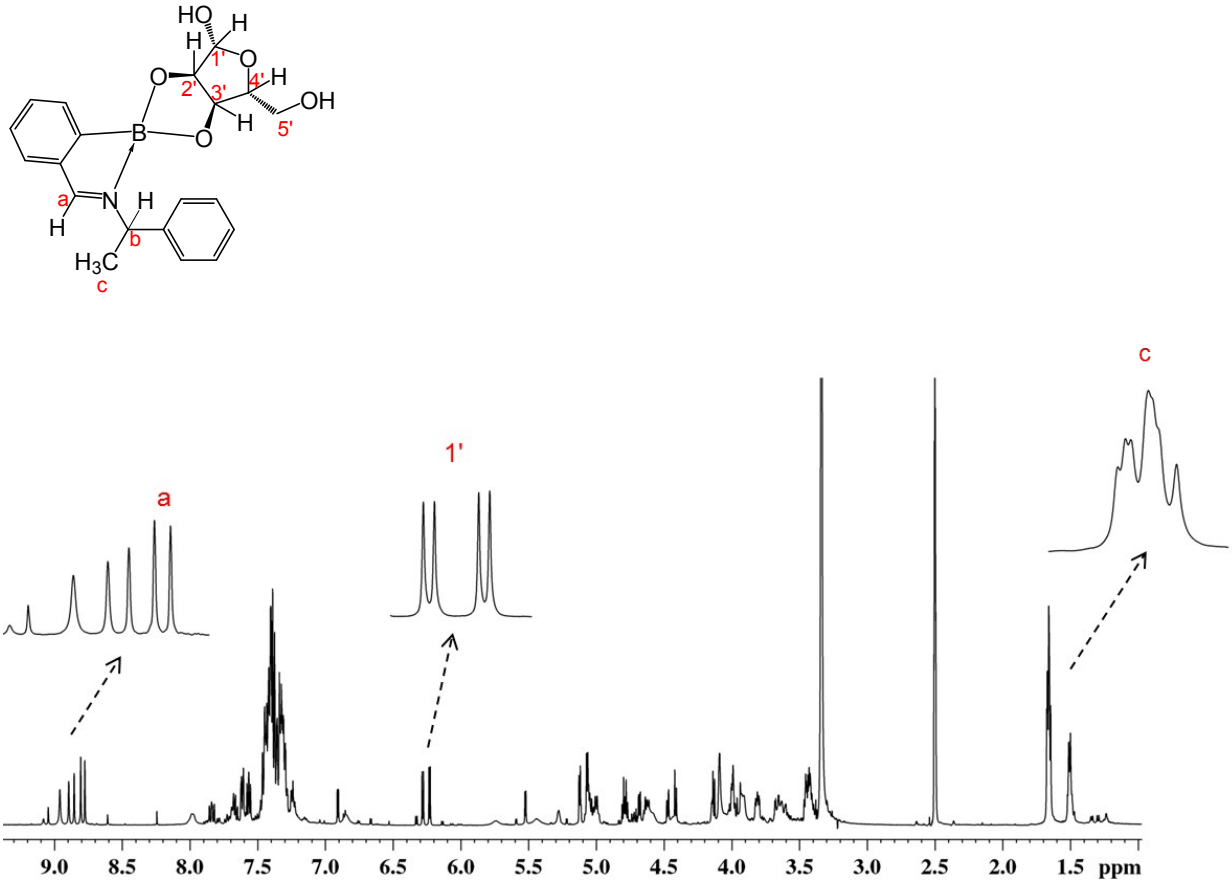


Figure S4. 500 MHz ^{1}H spectra of diastereomeric complexes of ribose, 2-formylphenylboronic acid and α-methylbenzylamine. The spectrum shows enantiomeric differentiation but with many biproduct (impurties peaks) peaks even after heating the reaction mixture for about 30 minutes. This suggests need of nuclear bases to stabilize the complex formatiom.

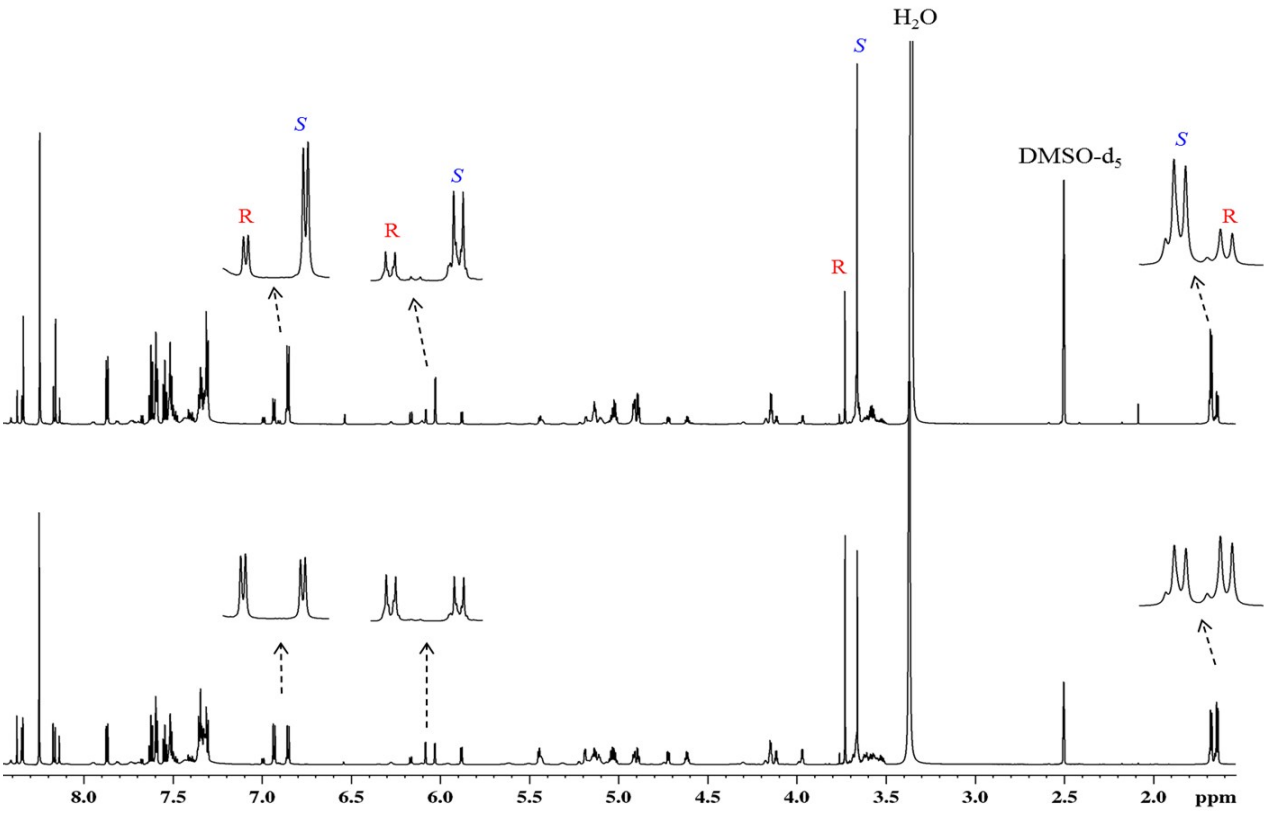


Figure S5. 800 MHz ^{1}H spectra of diastereomeric complexes of adenosine, 2-formylphenylboronic acid and 4-methoxy-α-methylbenzylamine. *R* and *S* amines are in almost equal ratio (bottom spectrum). Excess of *S*- amine (top spectrum). This spiking experiment helped in the assignment of *R*- and *S*-diastreomeric peaks.

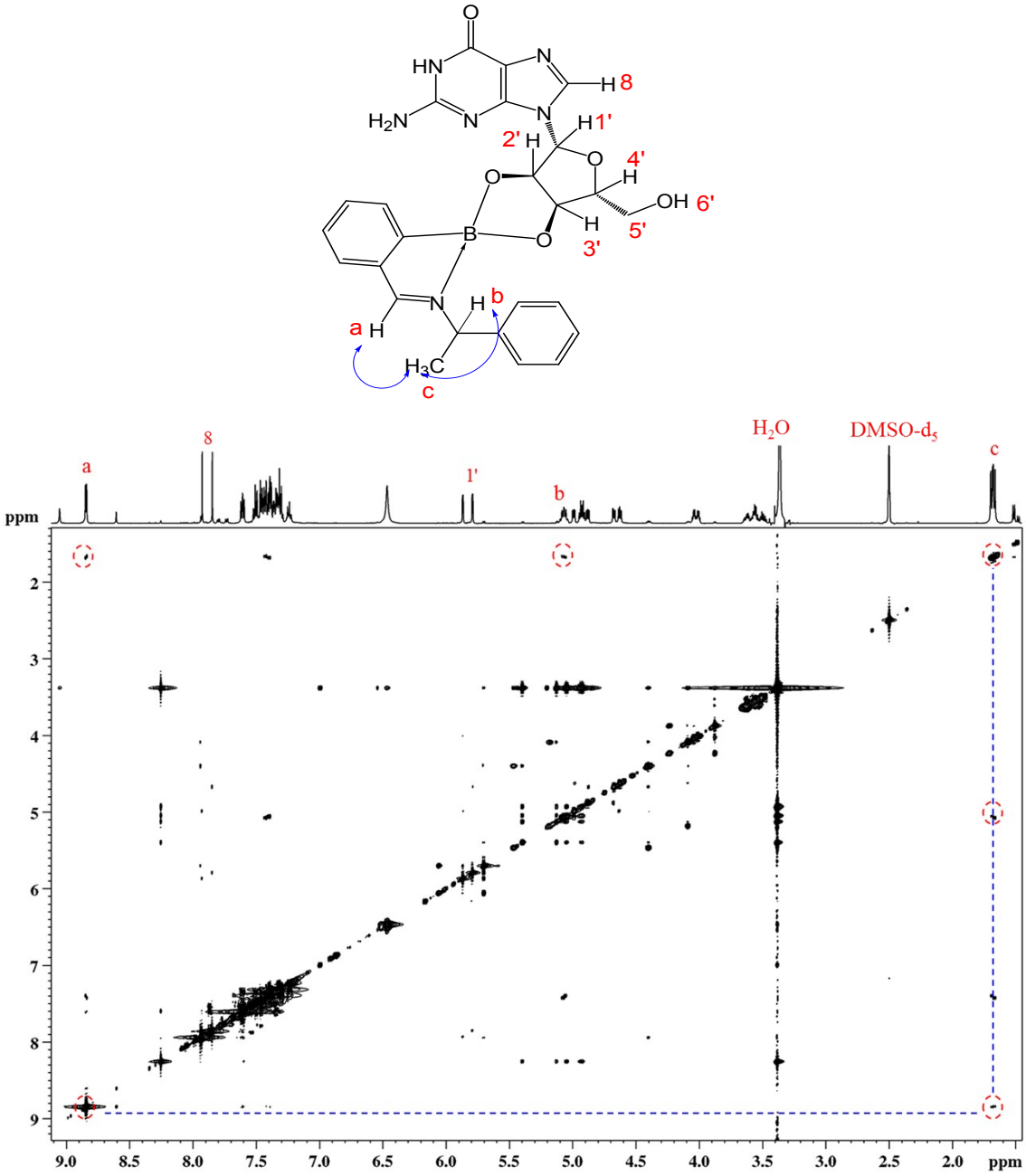


Figure S6. Possible chemical structure and 500 MHz 2D NOESY spectrum of diastereomeric complex formed from guansosine, 2-formylphenylboronic acid and racemic mixture of α-methylbenzylamine. The marked peaks are NOE correlated, suggested the possible structure given above.

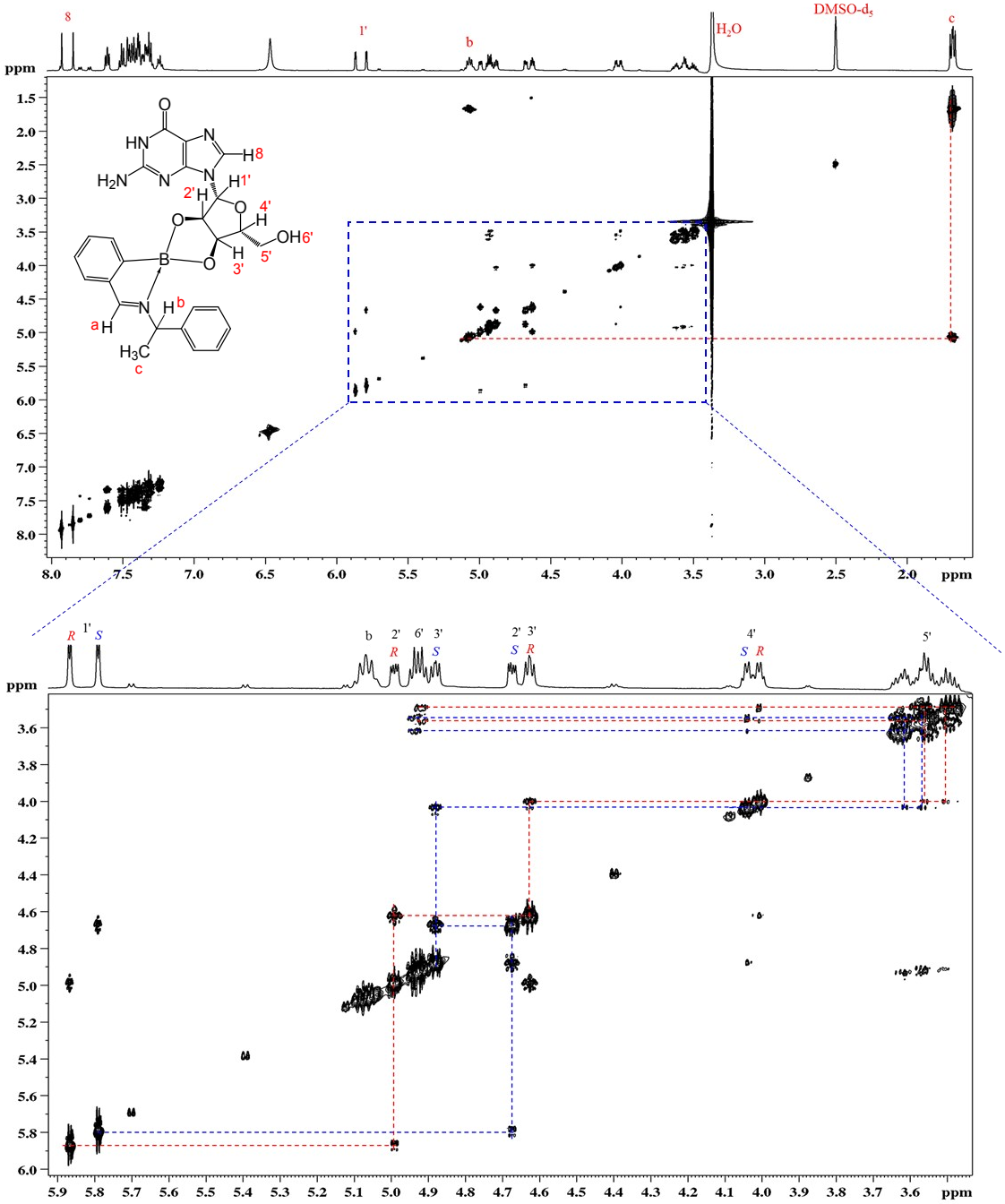


Figure S7. 500 MHz 2D COSY spectrum of diastereomeric complex formed from guansosine, 2-formylphenylboronic acid and the racemic mixture of α-methylbenzylamine. Blue lines and red lines shows correlation of *S* and *R* diastereomeric peaks respectively (as assigned above).

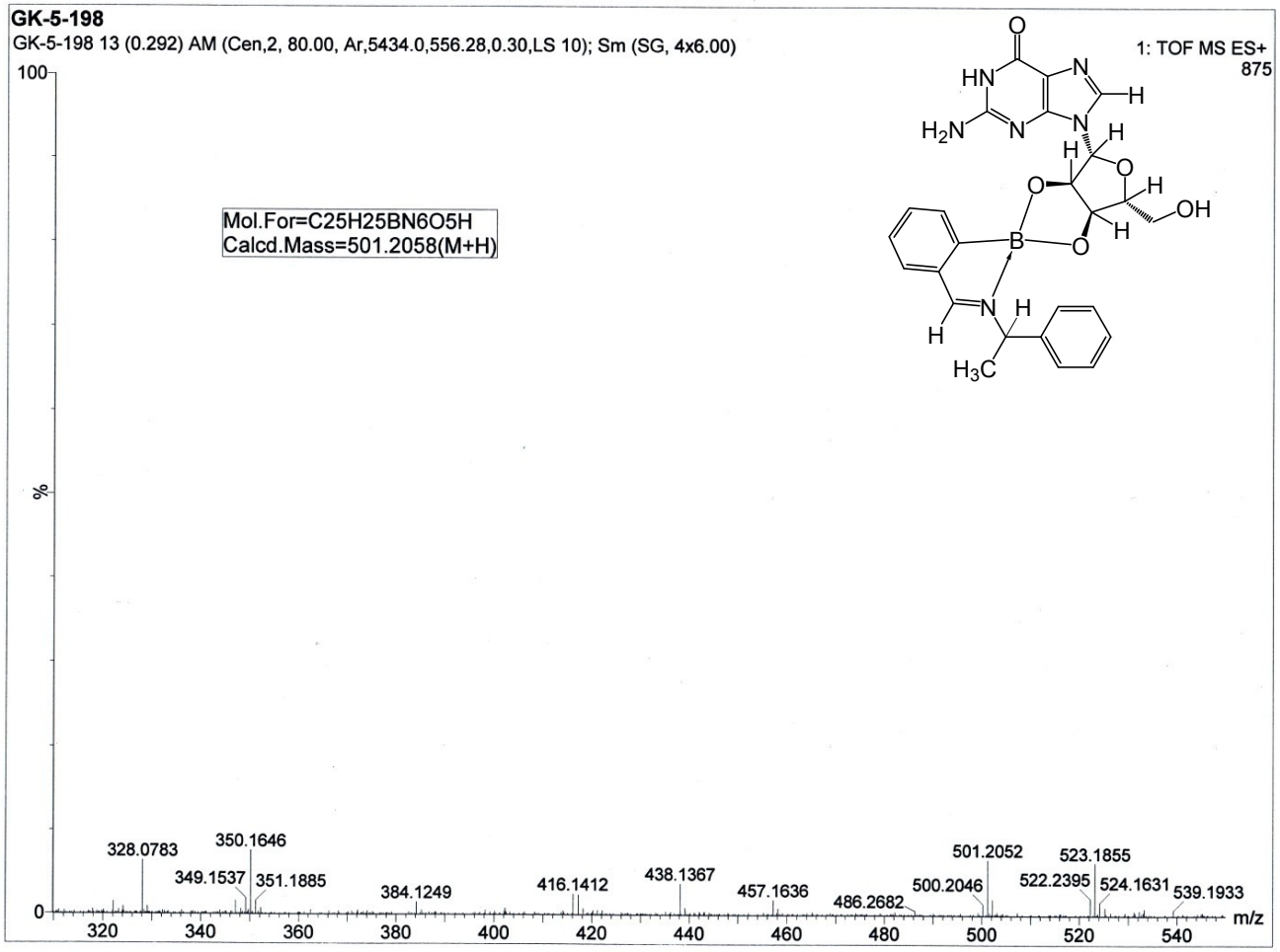

GK-5-198
GK-5-198 13 (0.292) AM (Cen,2, 80.00, Ar,5434.0,556.28,0.30,LS 10); Sm (SG, 4x6.00)
1: TOF MS ES+
875
100
%
0
Mol.For=C25H25BN6O5H
Calcd.Mass=501.2058(M+H)
328.0783
350.1646
349.1537
351.1885
384.1249
416.1412
438.1367
457.1636
486.2682
500.2046
501.2052
522.2395
523.1855
524.1631
539.1933
320
340
360
380
400
420
440
460
480
500
520
540
m/z

Figure S8. HR-MS spectrum showing the M+H (mass= 501.2052) and M+Na (mass = 523.1855) mass peaks. M is mass of guanosine:2-formylphenylboronic acid:α-methylbenzylamine diastreomeric complex

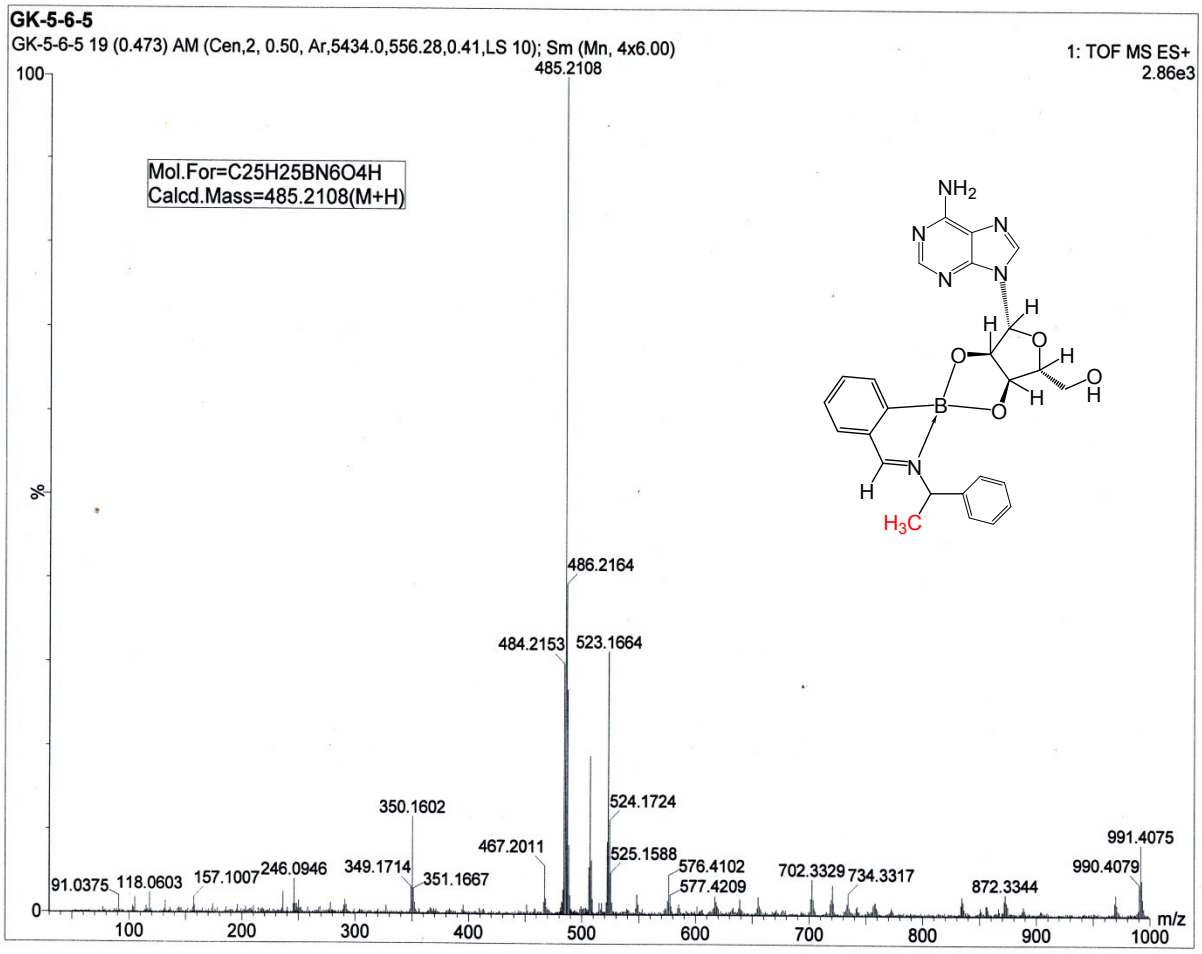


Figure S9: HR-MS spectrum of adenosine:2-formylphenylboronic acid:α-methylbenzylamine diastreomeric complex

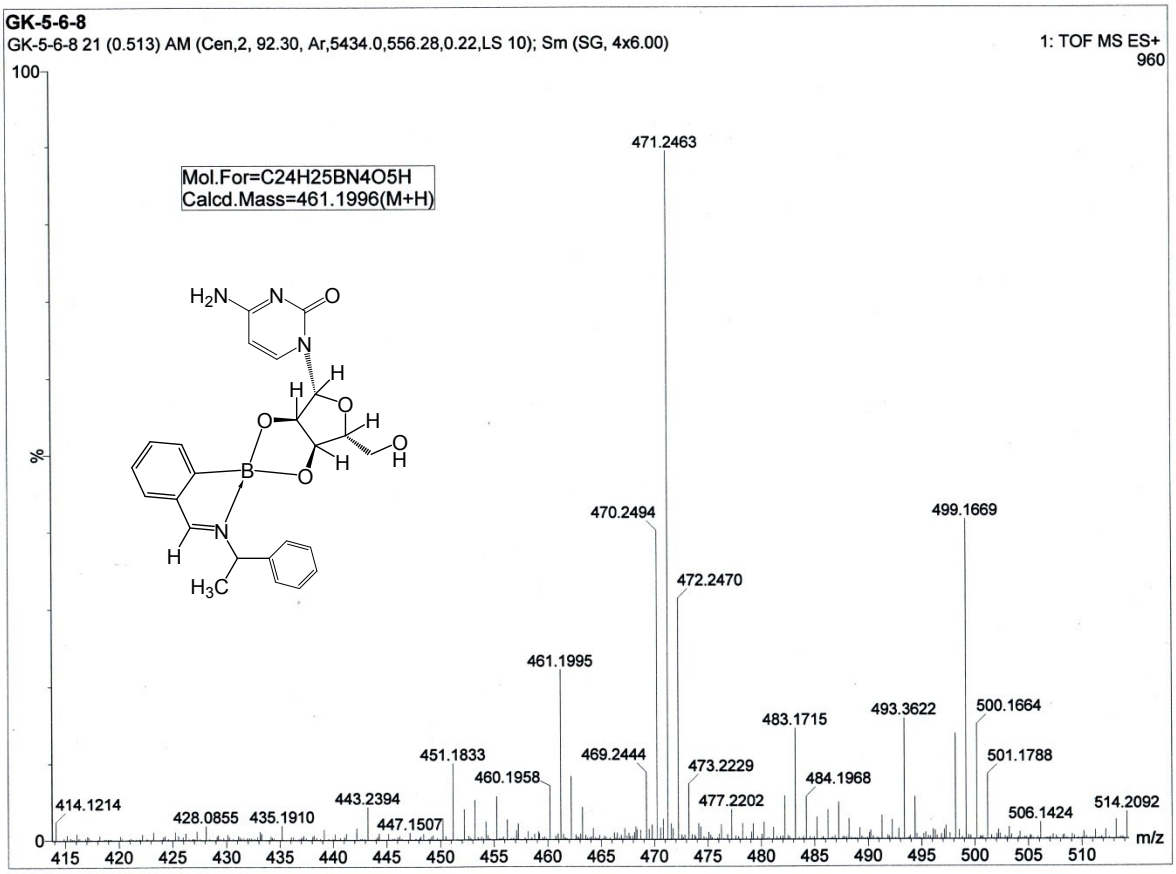


Figure S10: HR-MS spectrum of cytidine:2-formylphenylboronic acid:α-methylbenzylamine diastreomeric complex

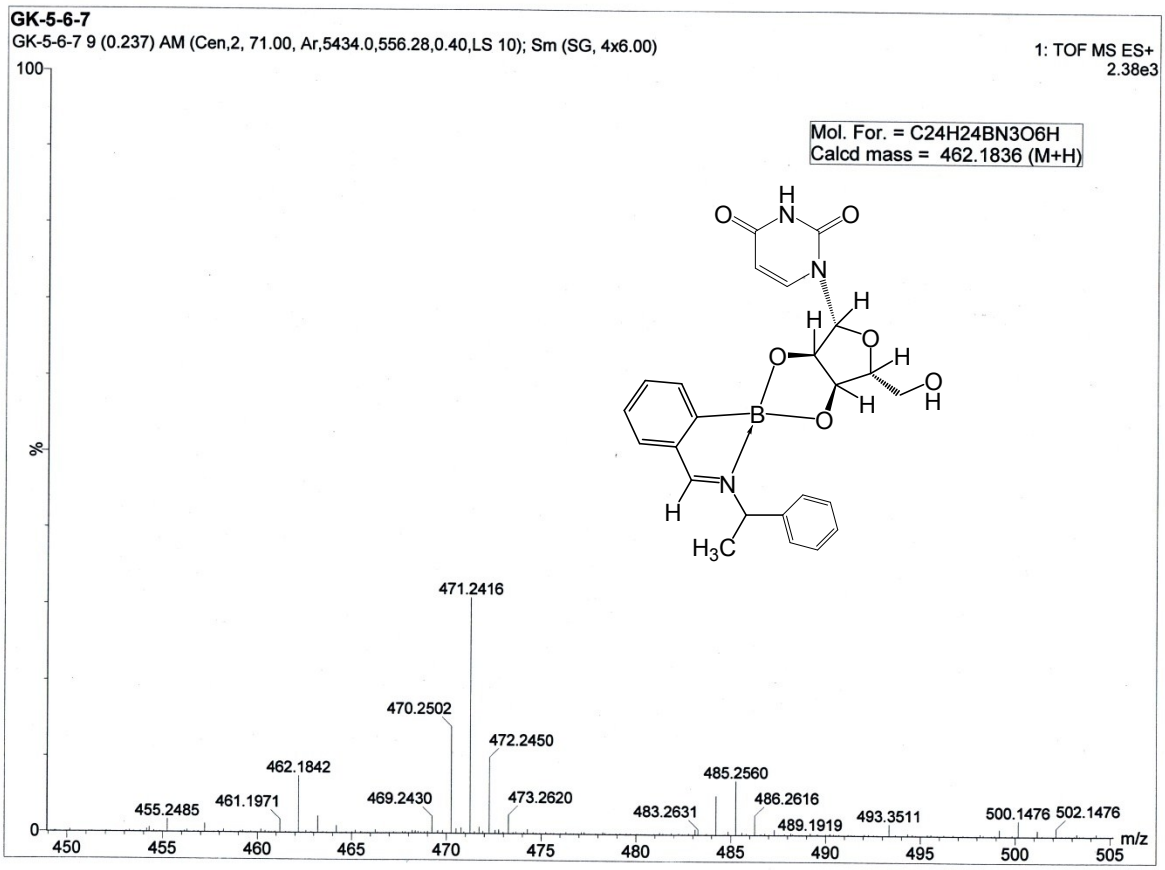


Figure S11: HR-MS spectrum of uridine:2-formylphenylboronic acid: α-methylbenzylamine diastreomeric complex

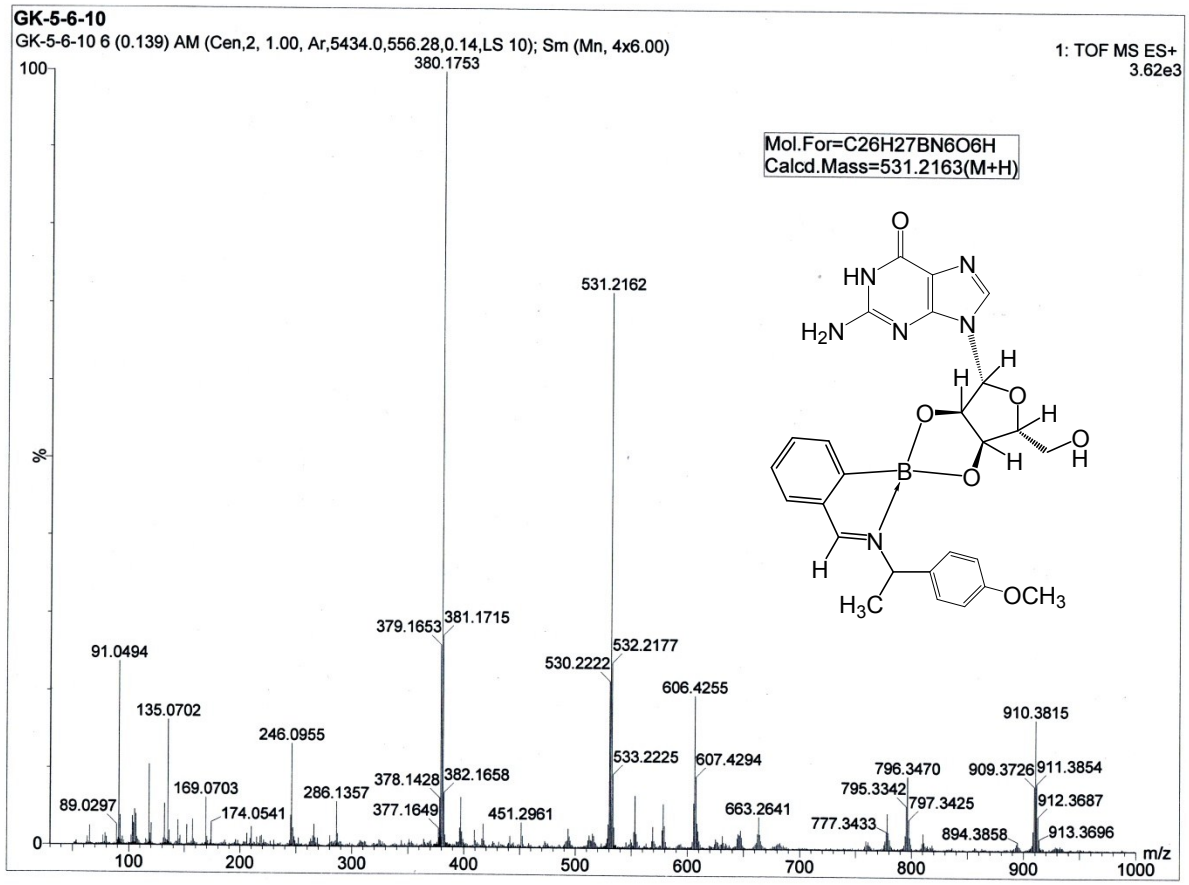


Figure S12: HR-MS spectrum of guanosine:2-formylphenylboronic acid: 4-methoxy-α-methylbenzylamine diastreomeric complex

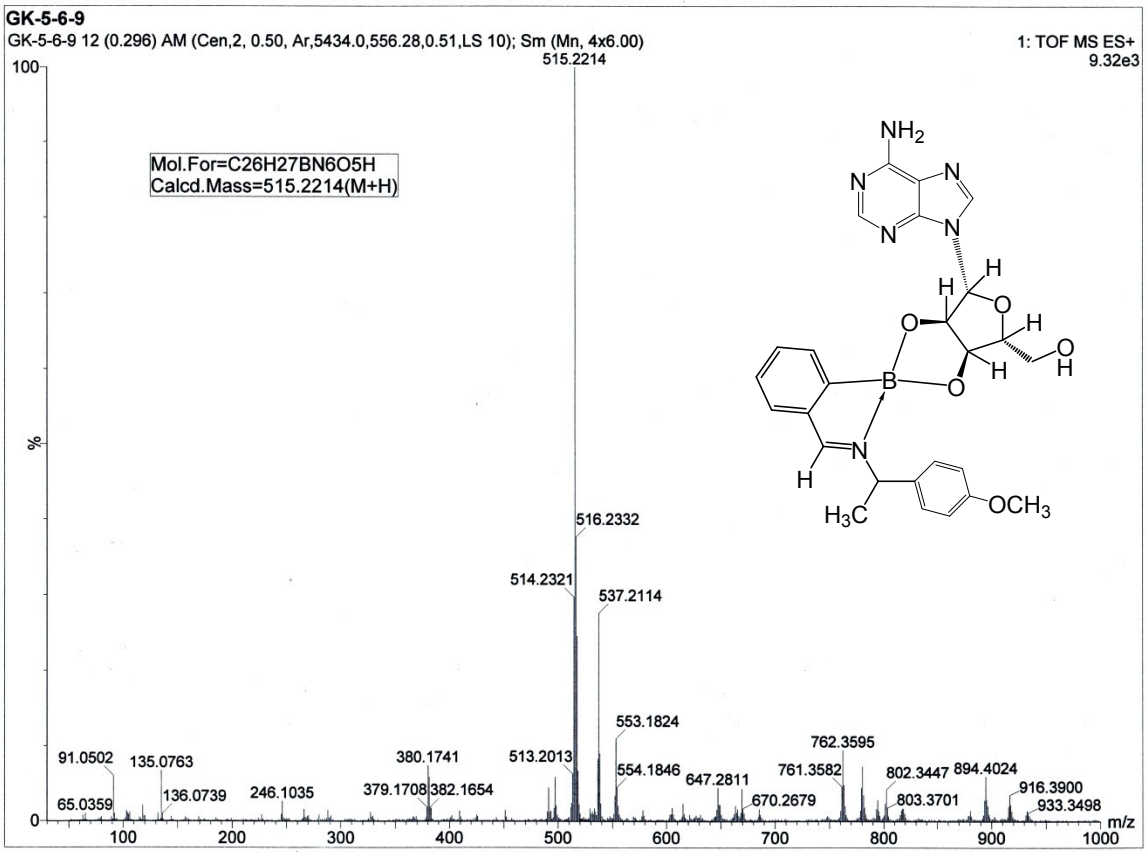


Figure S13: HR-MS spectrum of adenosine:2-formylphenylboronic acid: 4-methoxy-α-methylbenzylamine diastreomeric complex

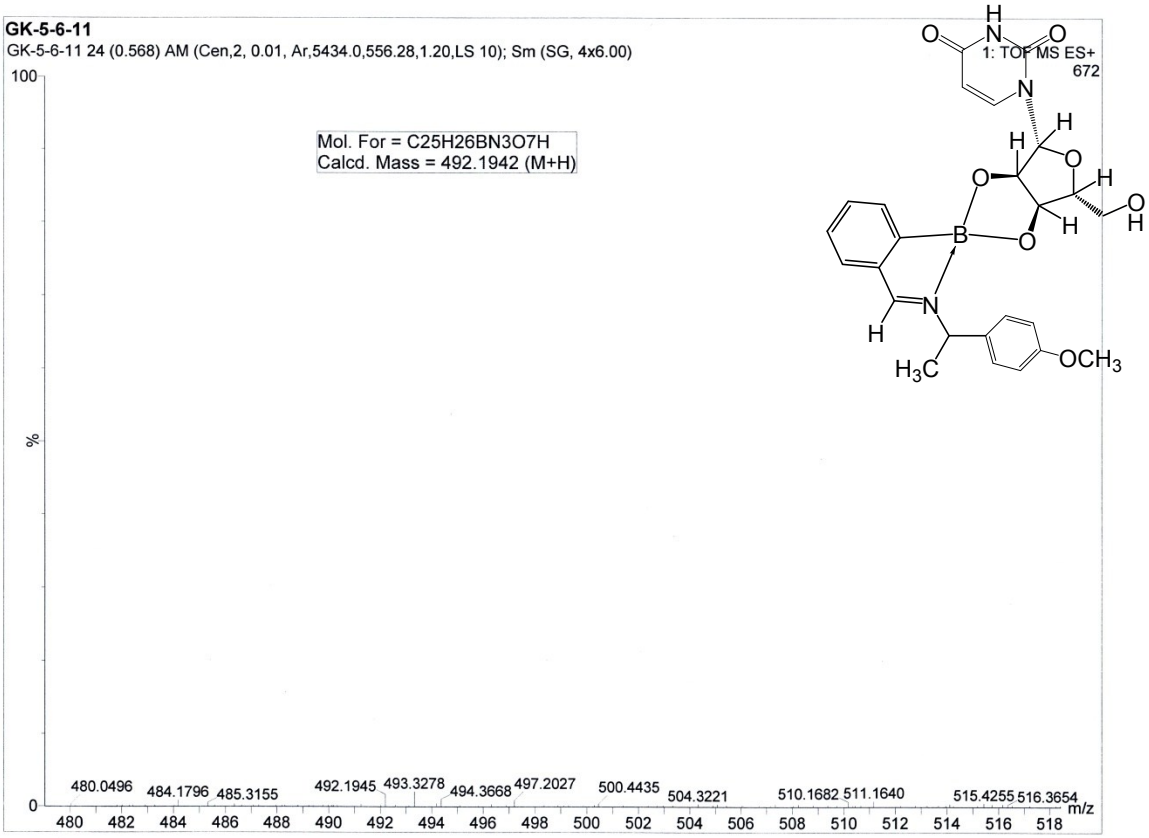


Figure S14: HR-MS spectrum of uridine:2-formylphenylboronic acid: 4-methoxy-α-methylbenzylamine diastreomeric complex

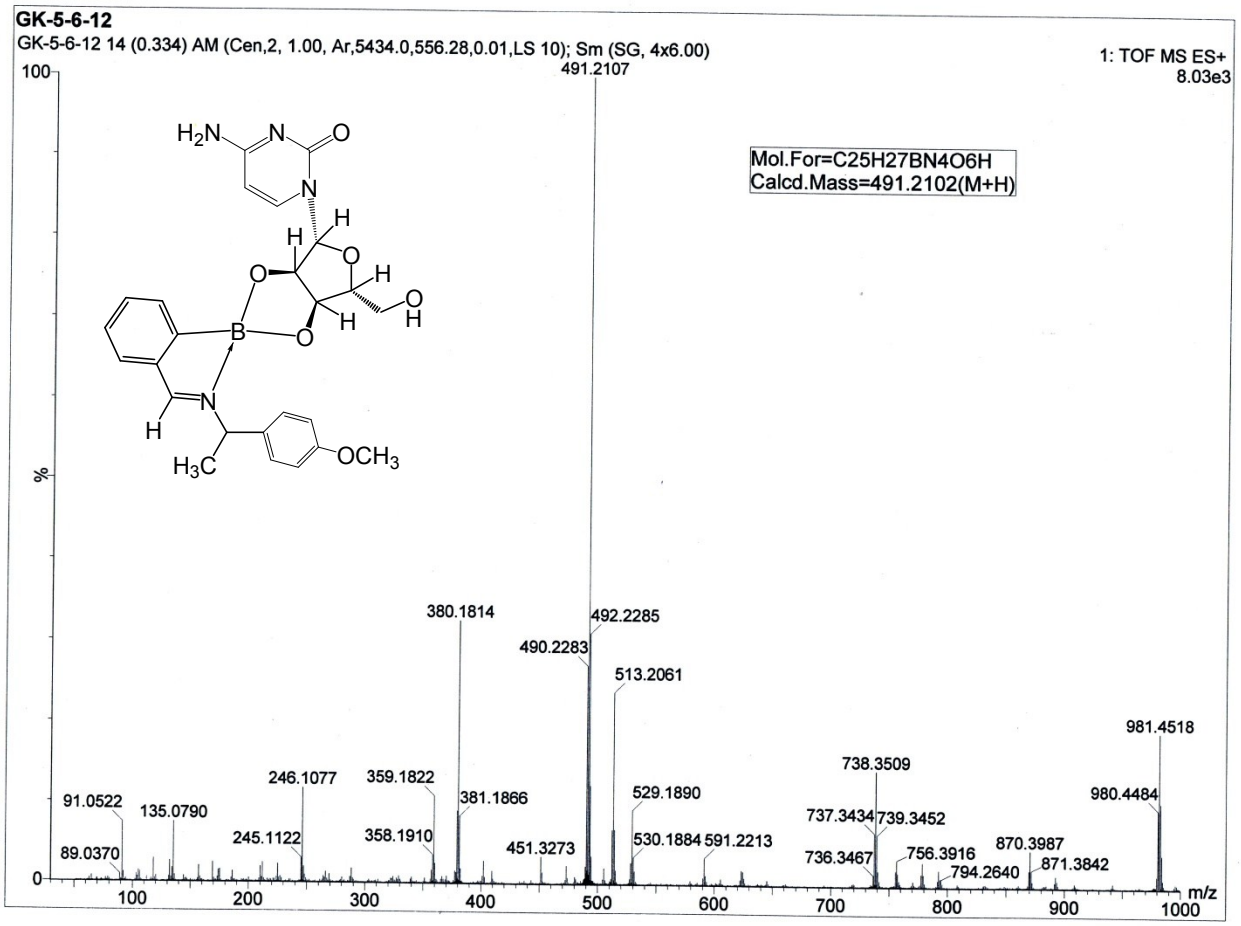


Figure S15: HR-MS spectrum of cytidine:2-formylphenylboronic acid: 4-methoxy-α-methylbenzylamine diastreomeric complex

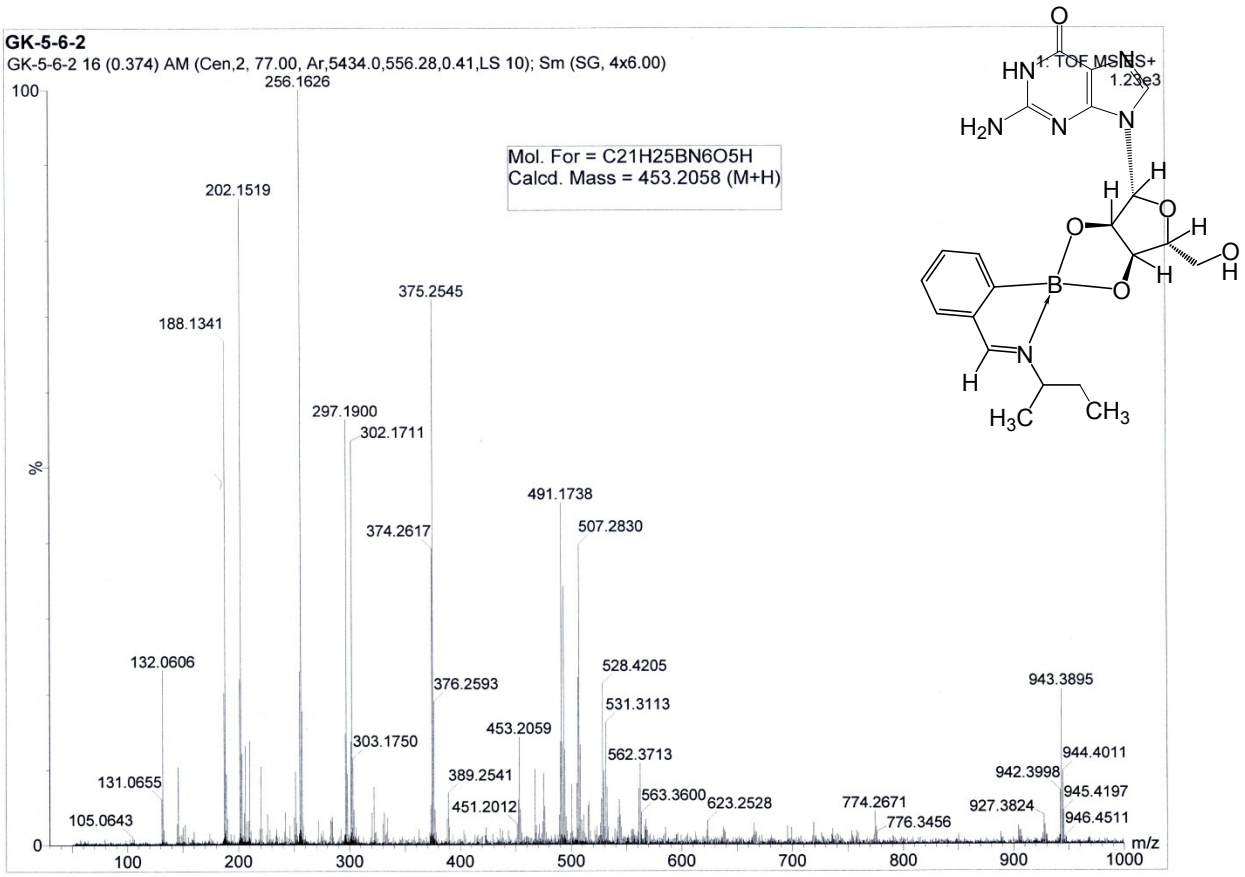


Figure S16: HR-MS spectrum of guanosine:2-formylphenylboronic acid: sec-butylamine diastreomeric complex

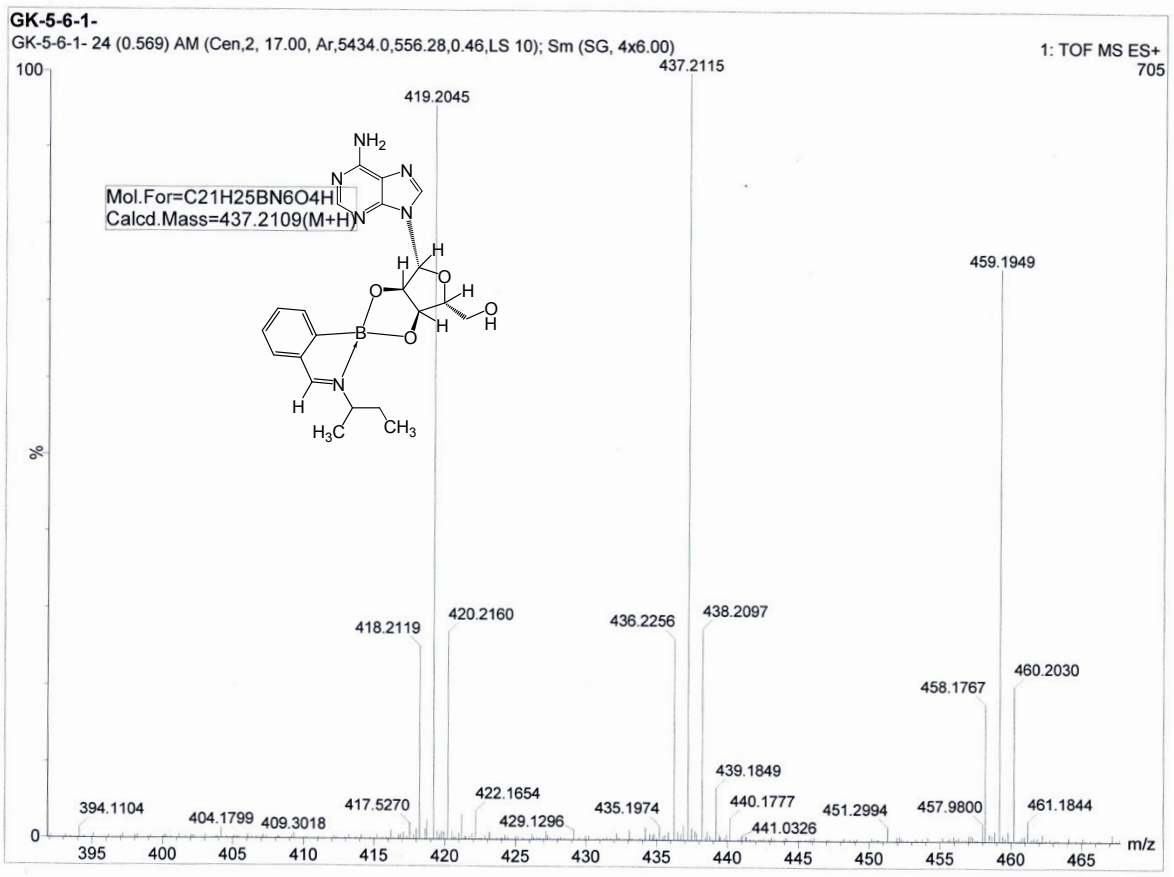


Figure S17: HR-MS spectrum of adenosine:2-formylphenylboronic acid: sec-butylamine diastreomeric complex

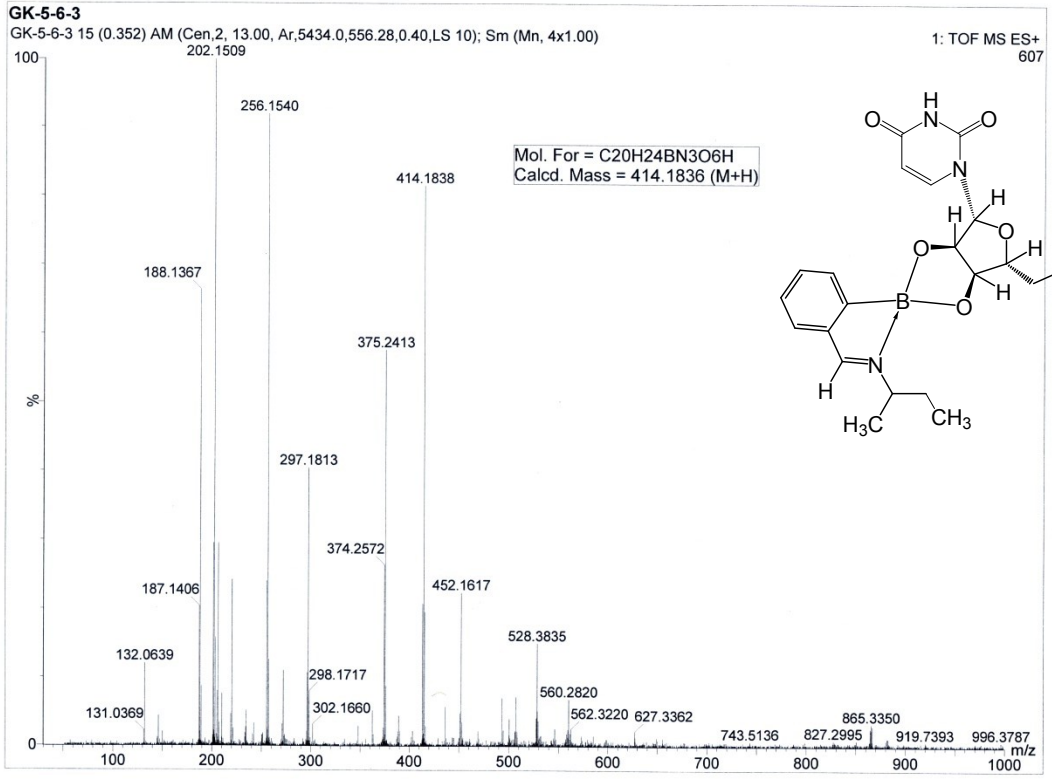


Figure S18: HR-MS spectrum of uridine:2-formylphenylboronic acid: sec-butylamine diastreomeric complex

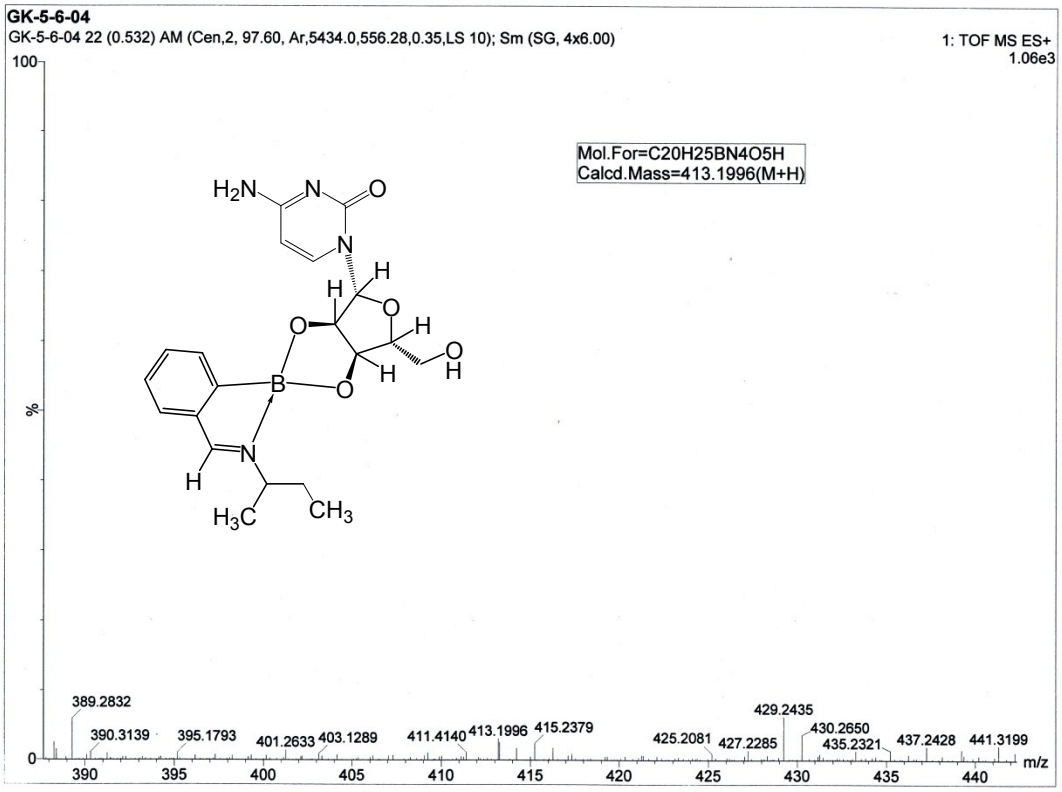


Figure S19: HR-MS spectrum of cytidine:2-formylphenylboronic acid: sec-butylamine diastreomeric complex

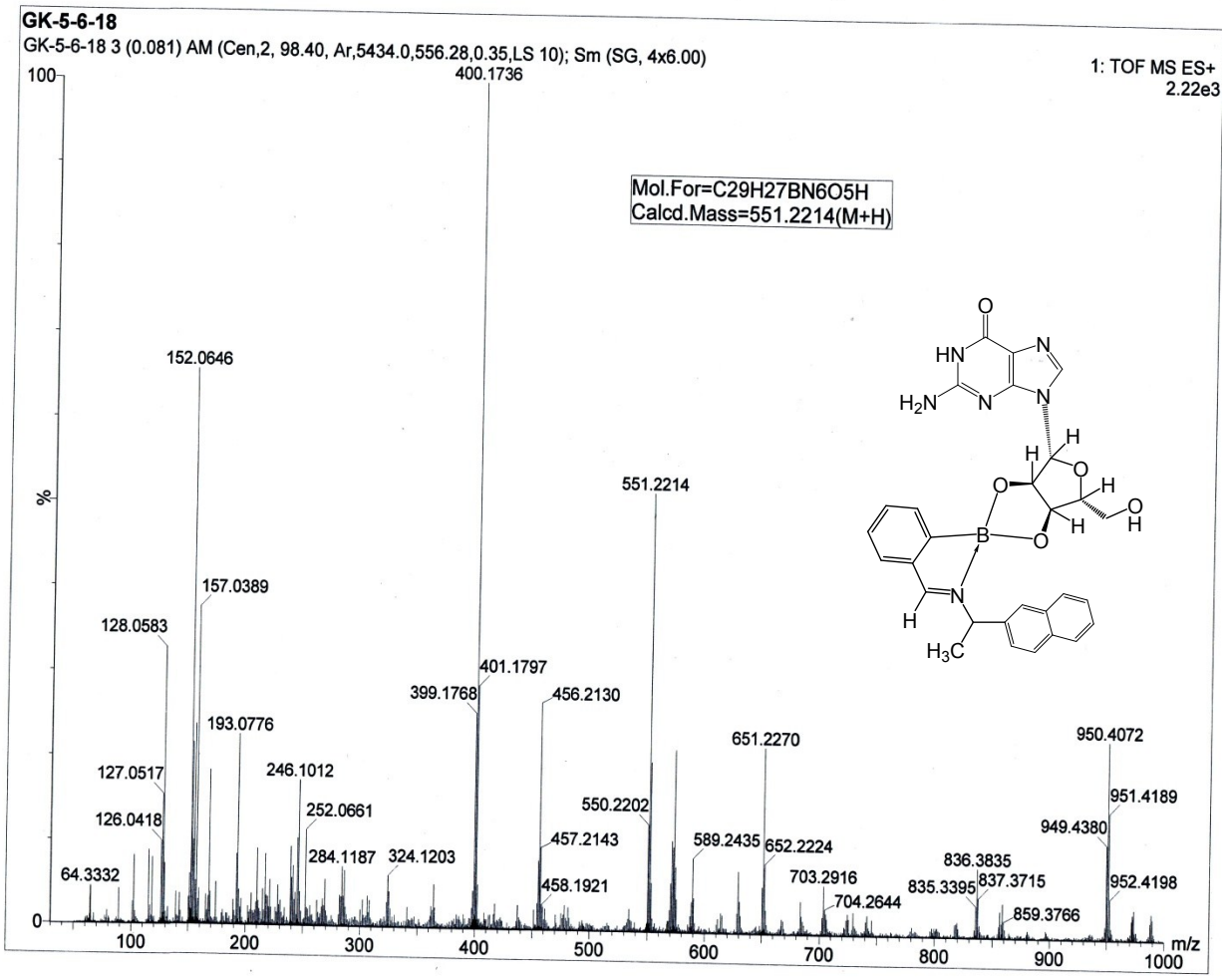


Figure S20: HR-MS spectrum of guanosine:2-formylphenylboronic acid: 1-(2-naphthyl)ethanamine diastreomeric complex

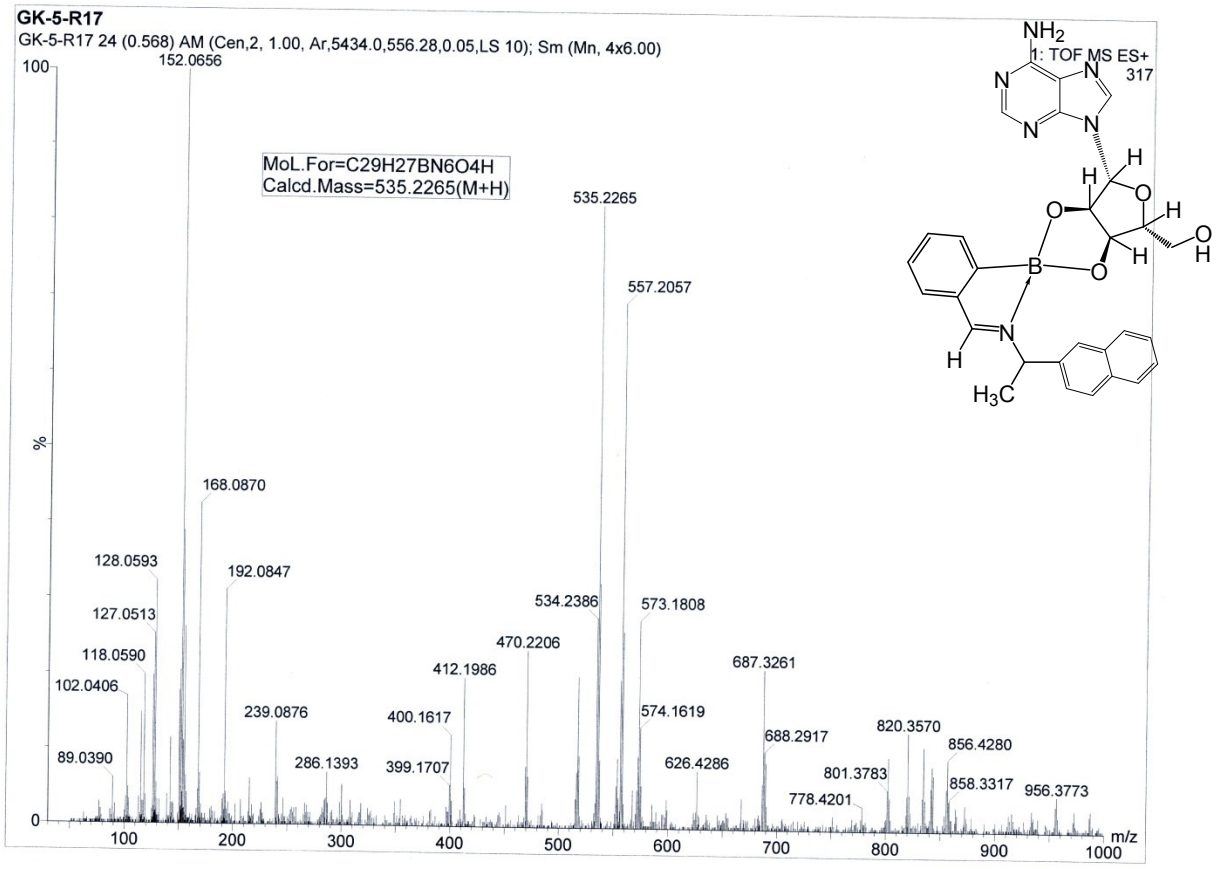


Figure S21: HR-MS spectrum of adenosine:2-formylphenylboronic acid: 1-(2-naphthyl)ethanamine diastreomeric complex

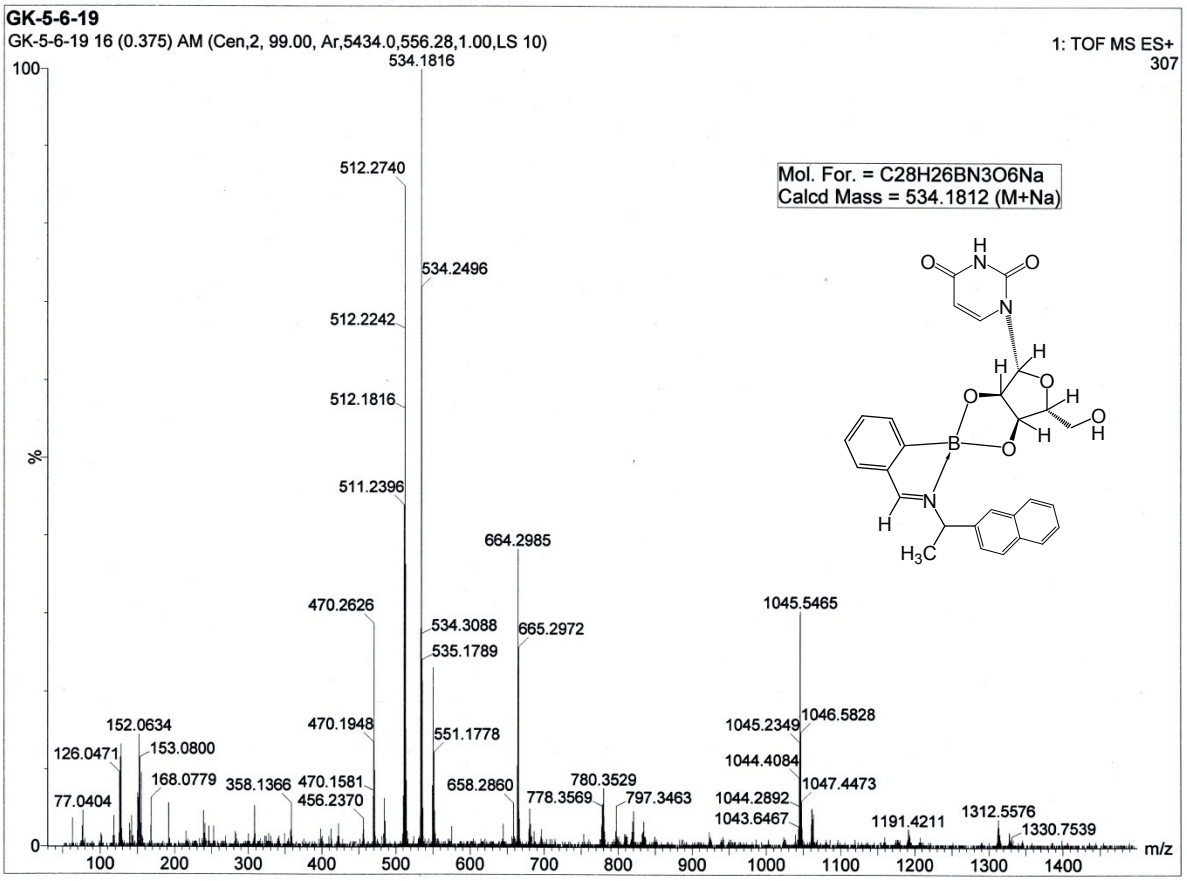


Figure S22: HR-MS spectrum of uridine:2-formylphenylboronic acid: 1-(2-naphthyl)ethanamine diastreomeric complex

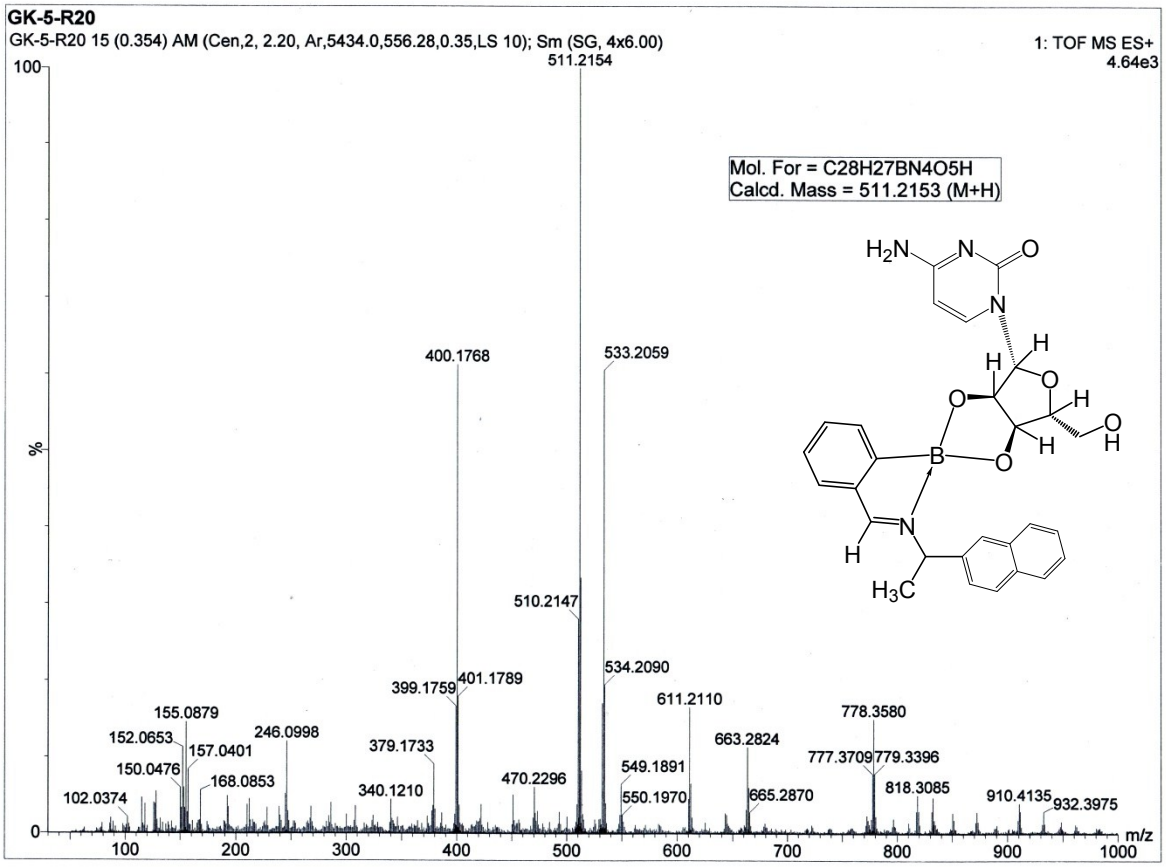


Figure S23: HR-MS spectrum of cytidine:2-formylphenylboronic acid: 1-(2-naphthyl)ethanamine diastreomeric complex

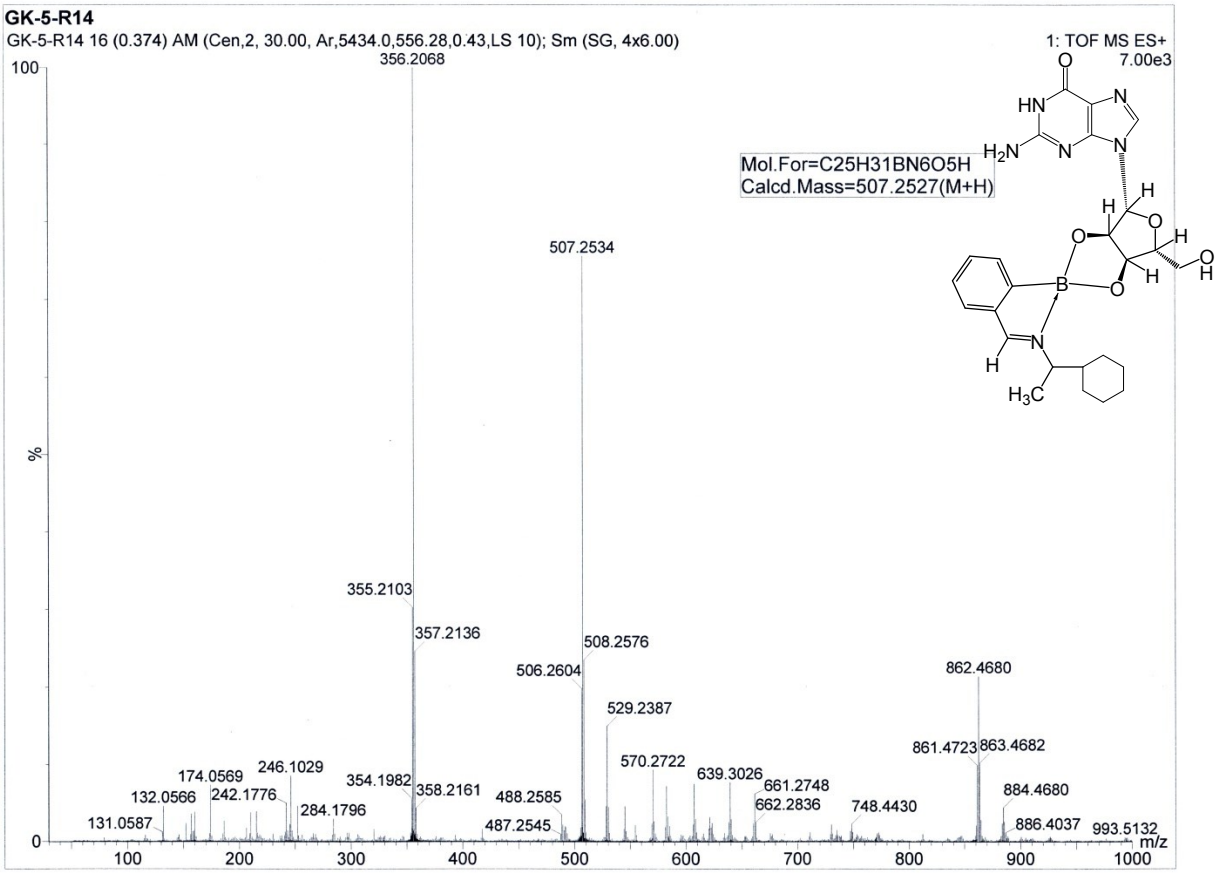


Figure S24: HR-MS spectrum of guanosine:2-formylphenylboronic acid: 1-cyclohexylethylamine diastreomeric complex

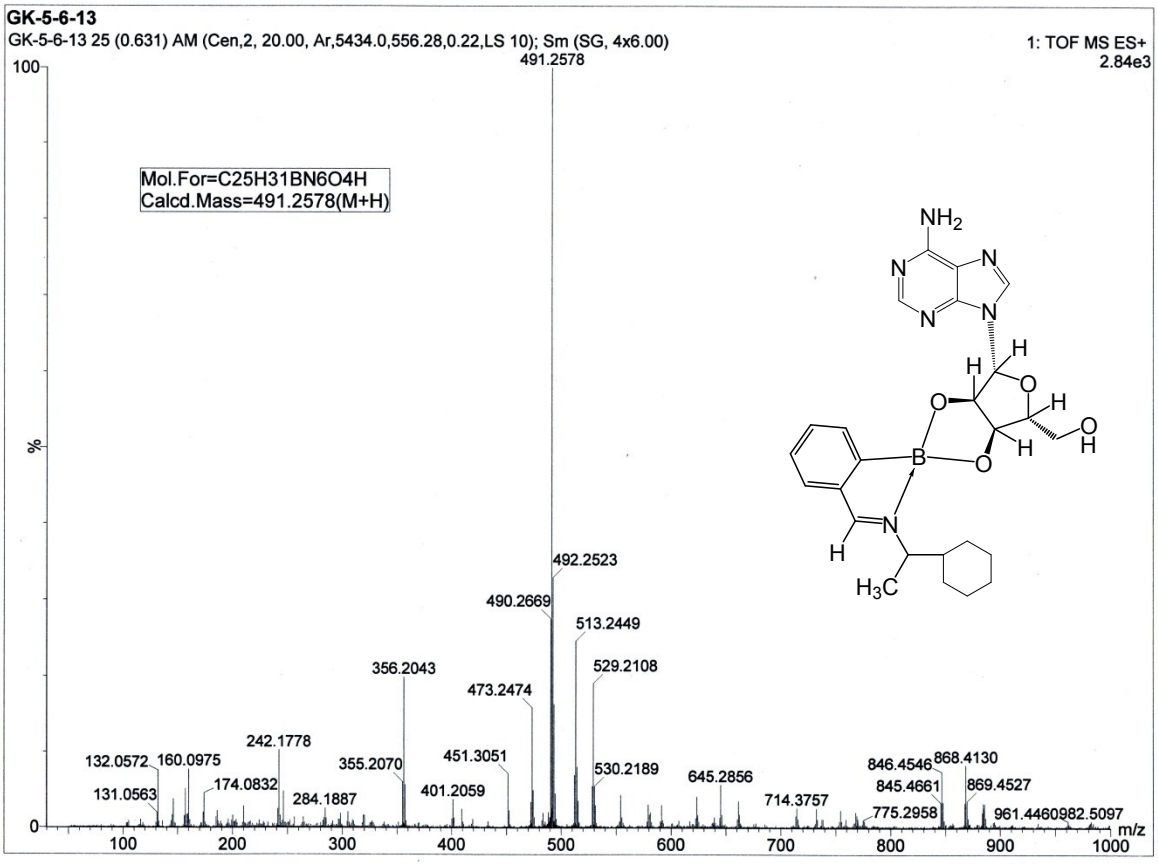


Figure S25: HR-MS spectrum of adenosine:2-formylphenylboronic acid: 1-cyclohexylethylamine diastreomeric complex

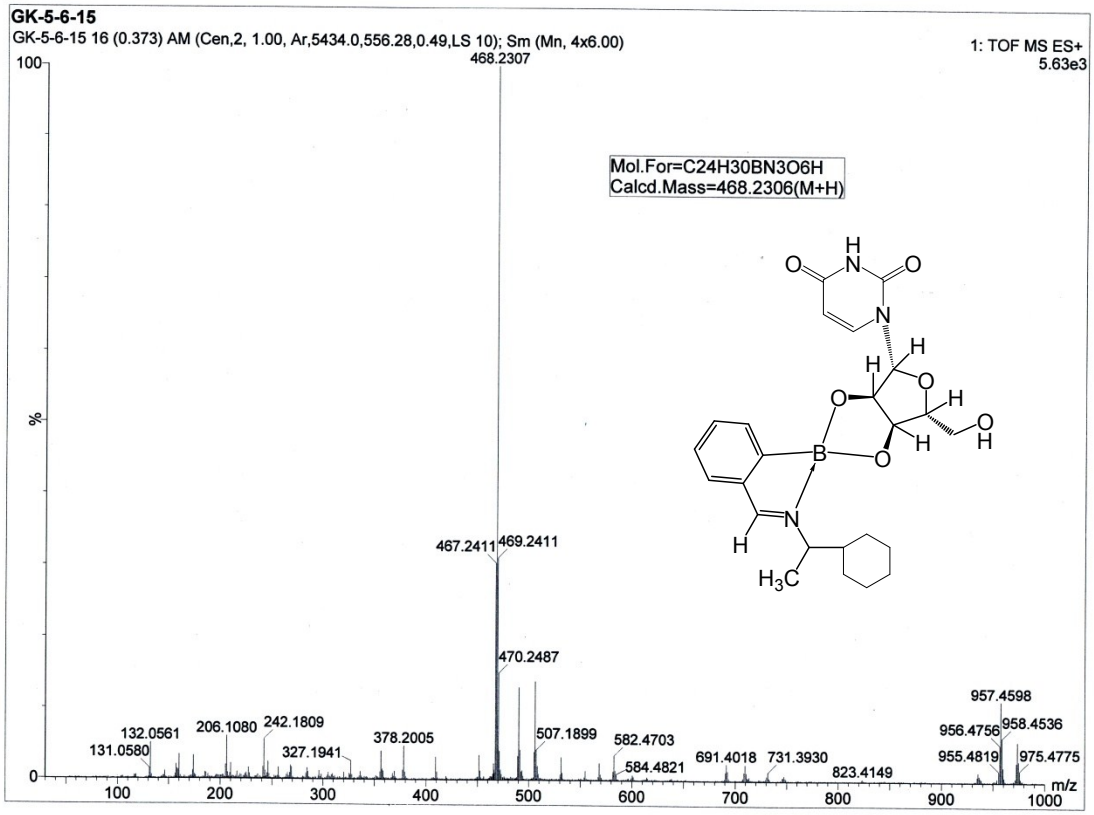


Figure S26: HR-MS spectrum of uridine:2-formylphenylboronic acid: 1-cyclohexylethylamine diastreomeric complex

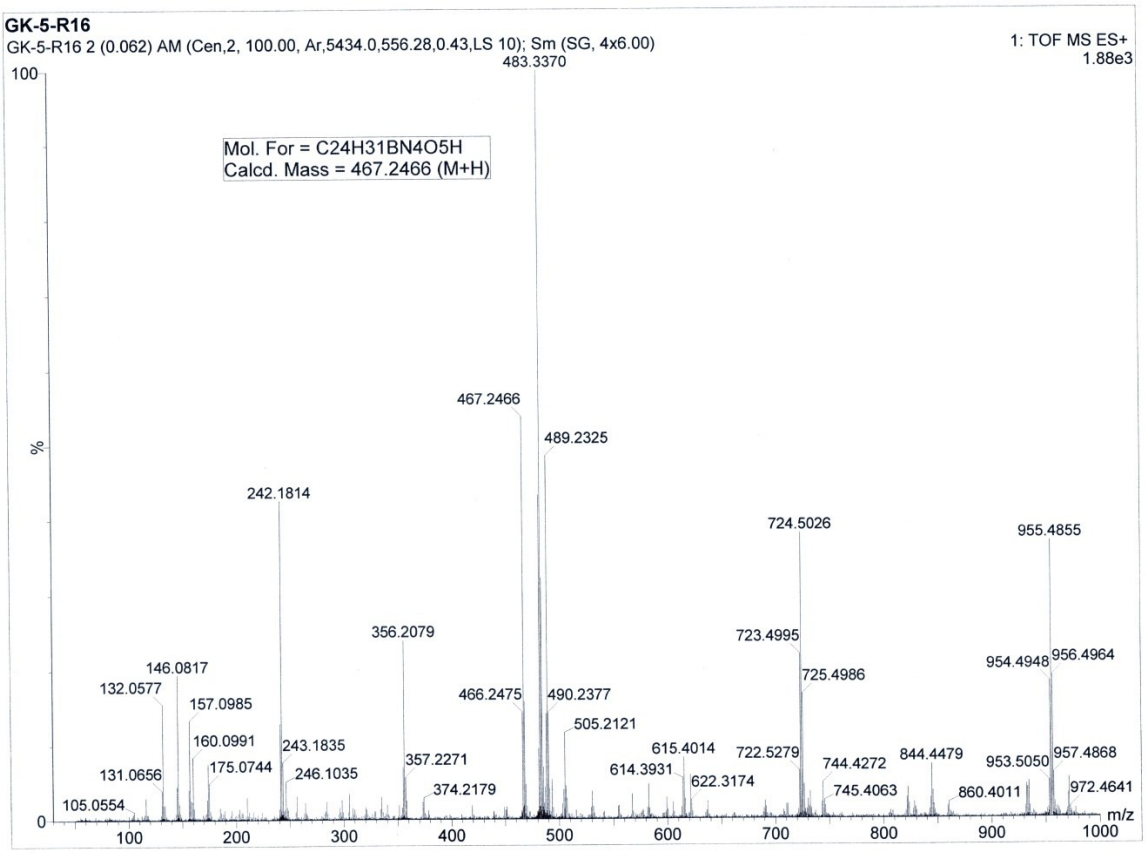


Figure S27: HR-MS spectrum of cytidine:2-formylphenylboronic acid: 1-cyclohexylethylamine diastreomeric complex

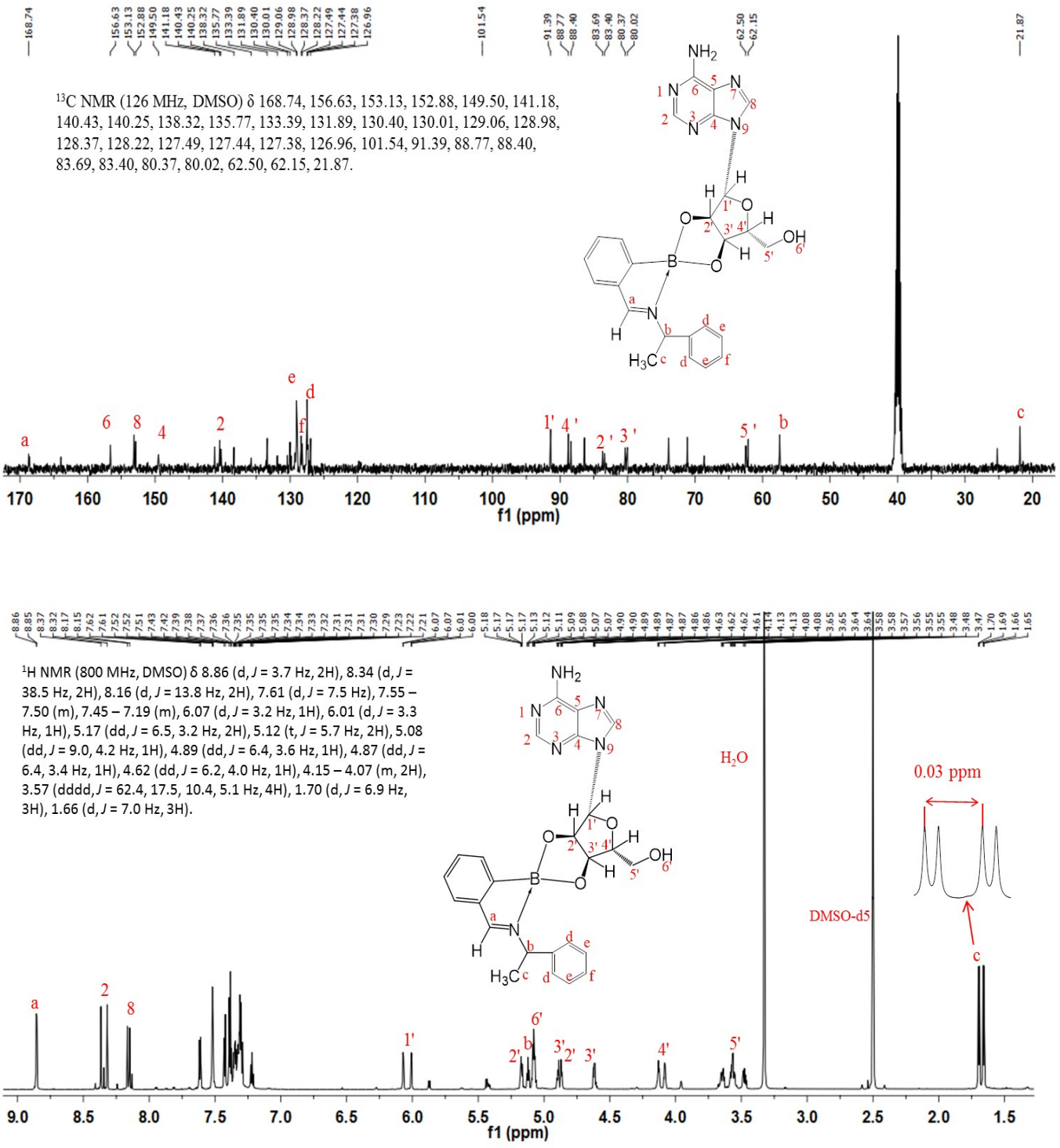


Figure S28. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of α-methylbenzylamine : adenosine : 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown in expanded region ($\Delta\delta^{R,S}$ = 0.03 ppm) given as an inset.

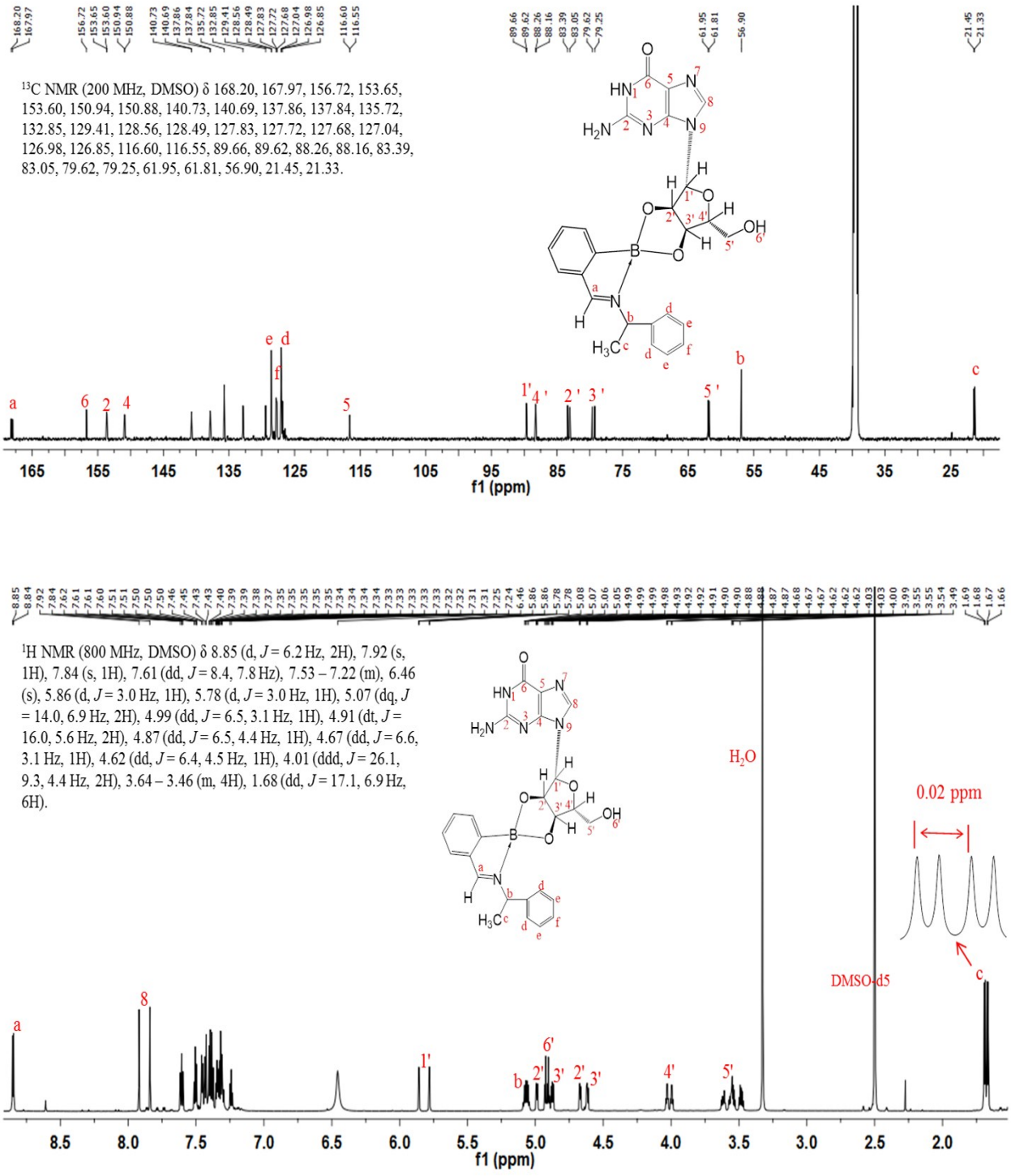


Figure S29. 800 MHz ^{1}H (bottom) and 200 MHz ^{13}C (top) NMR spectra of α-methylbenzylamine : guanosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown in expanded region ($\Delta\delta^{R,S}$ = 0.02 ppm) is given as an inset

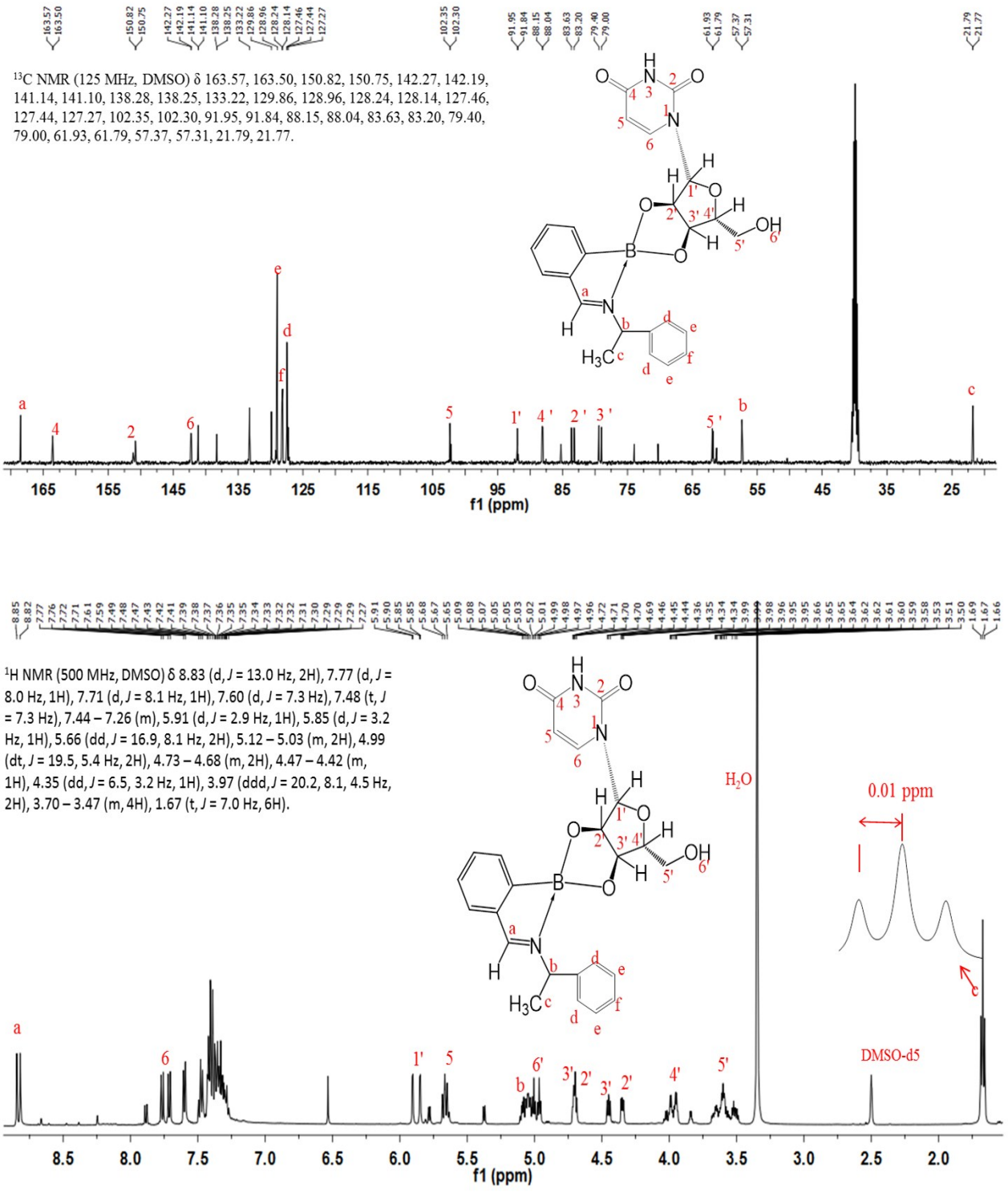


Figure S30. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of α-methylbenzylamine : uridine : 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown in expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm).

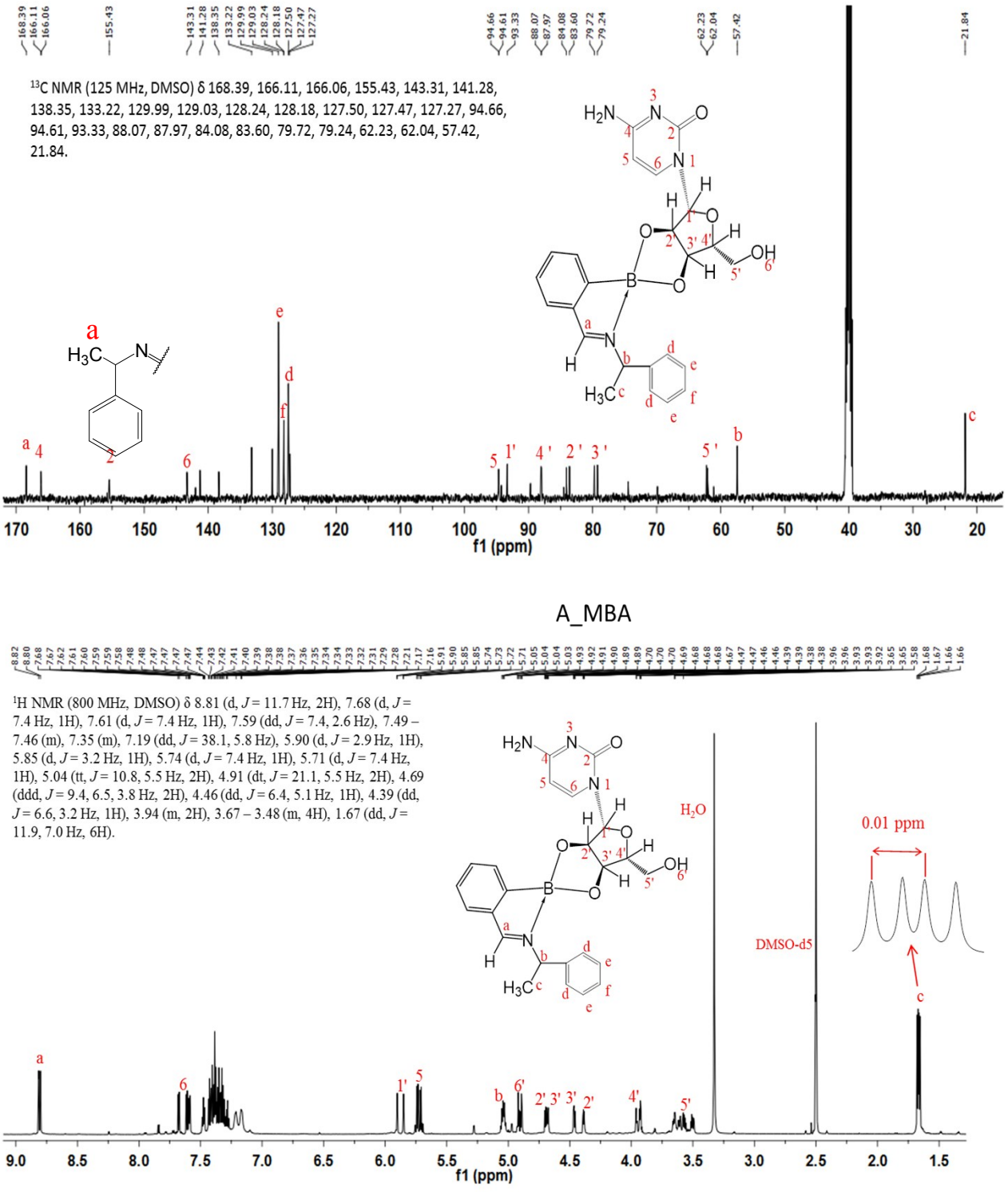


Figure S31. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of α-methylbenzylamine:cytidine: 2-formylphenylboronic acid diastreomeric complex, methyl protons and corpessponding peaks are labeled as c. Proton chemical shift is shown in the expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm).

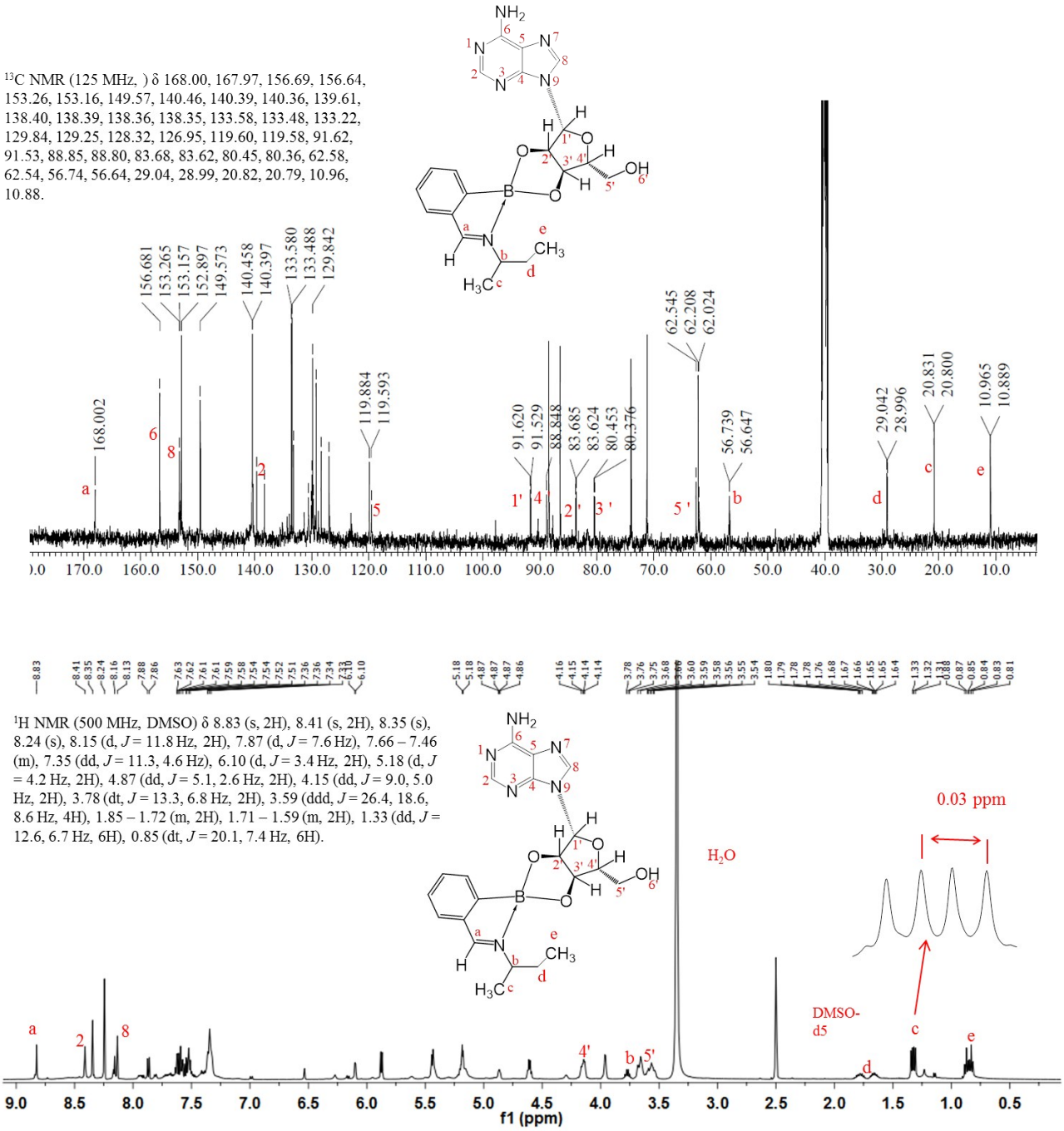


Figure S32. 500 MHz ^{1}H (bottom)) and 125 MHz 13C (top) NMR spectra of sec-butylamine: adenosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on the expanded region ($\Delta\delta^{R,S}$ = 0.03 ppm for c).

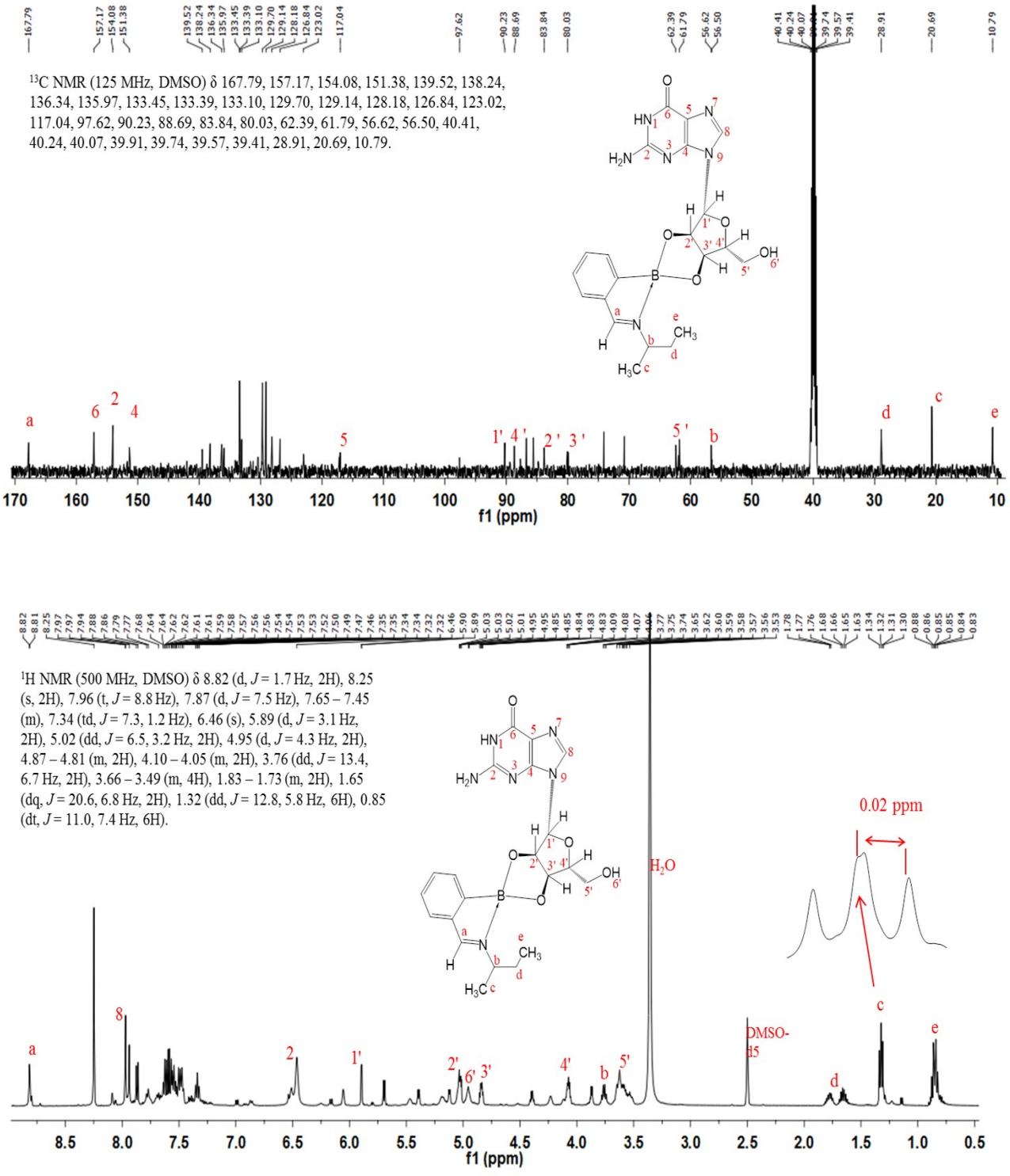


Figure S33. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of sec-butylamine: guanosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.02 ppm for c).

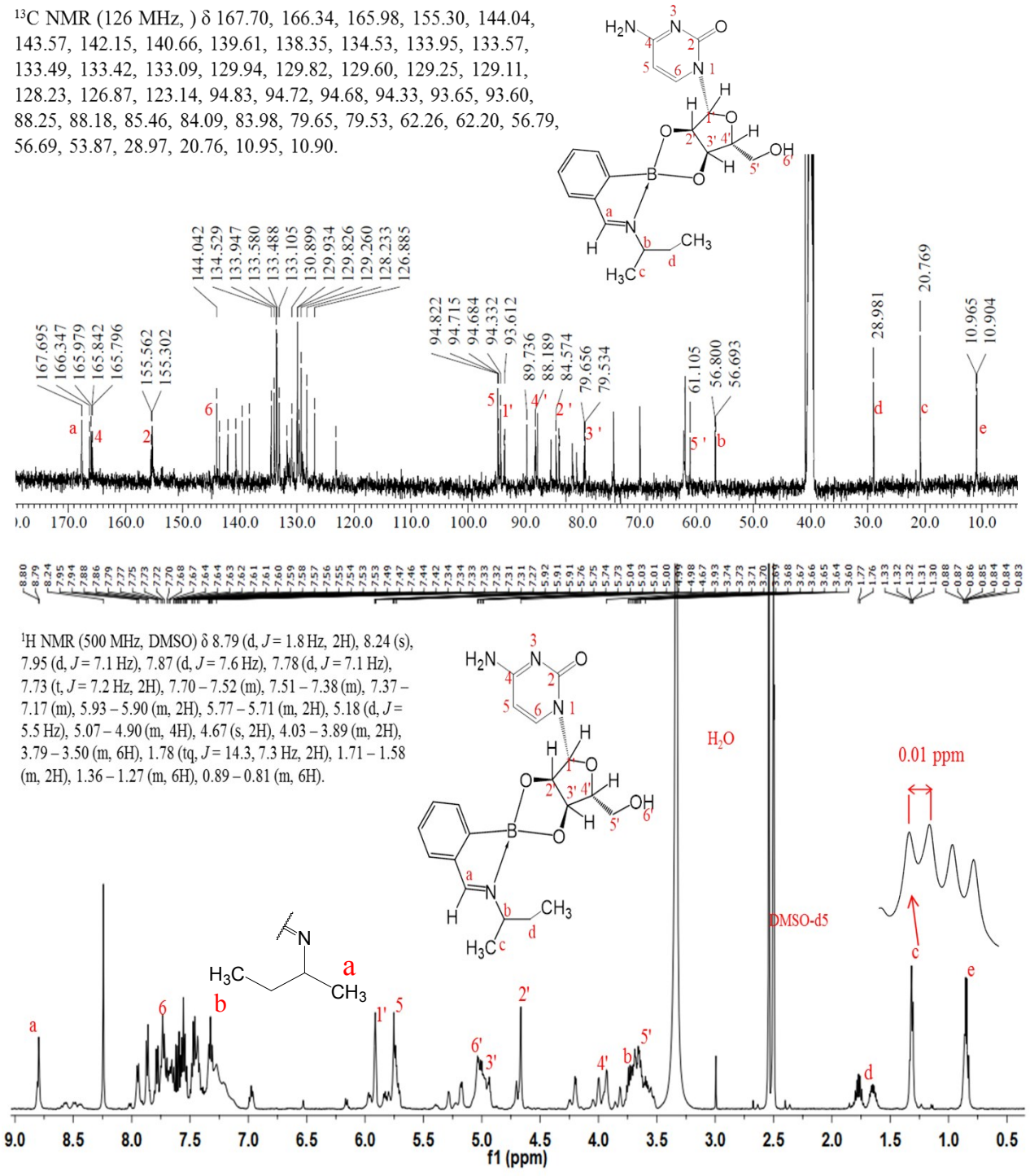


Figure S34. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of sec-butylamine:cytidine: 2-formylphenylboronic acid diastereomeric complex, methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm for c)

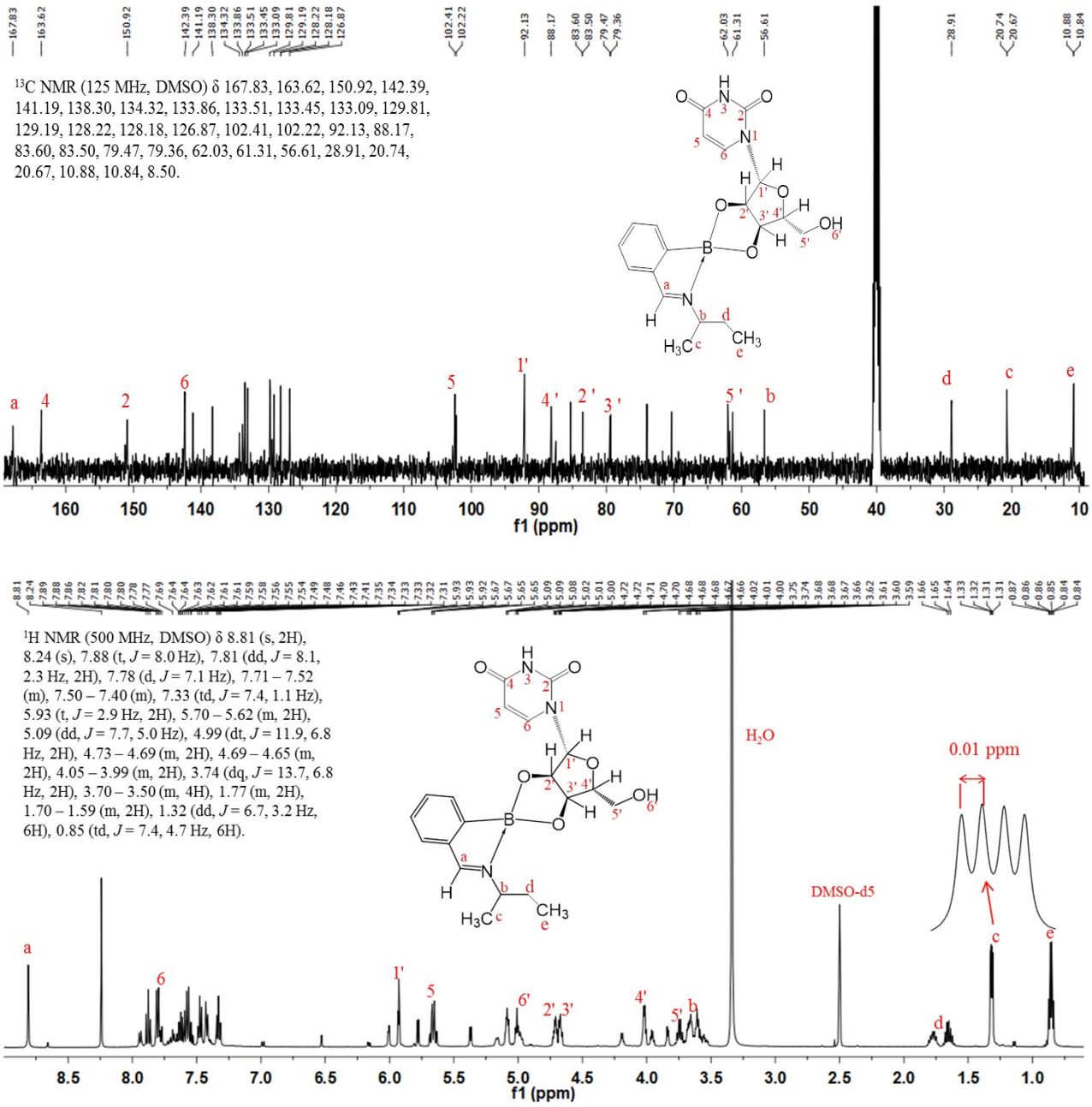


Figure S35. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of sec-butylamine: uridine: 2-formylphenylboronic acid diastereomeric complex, methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm for c).

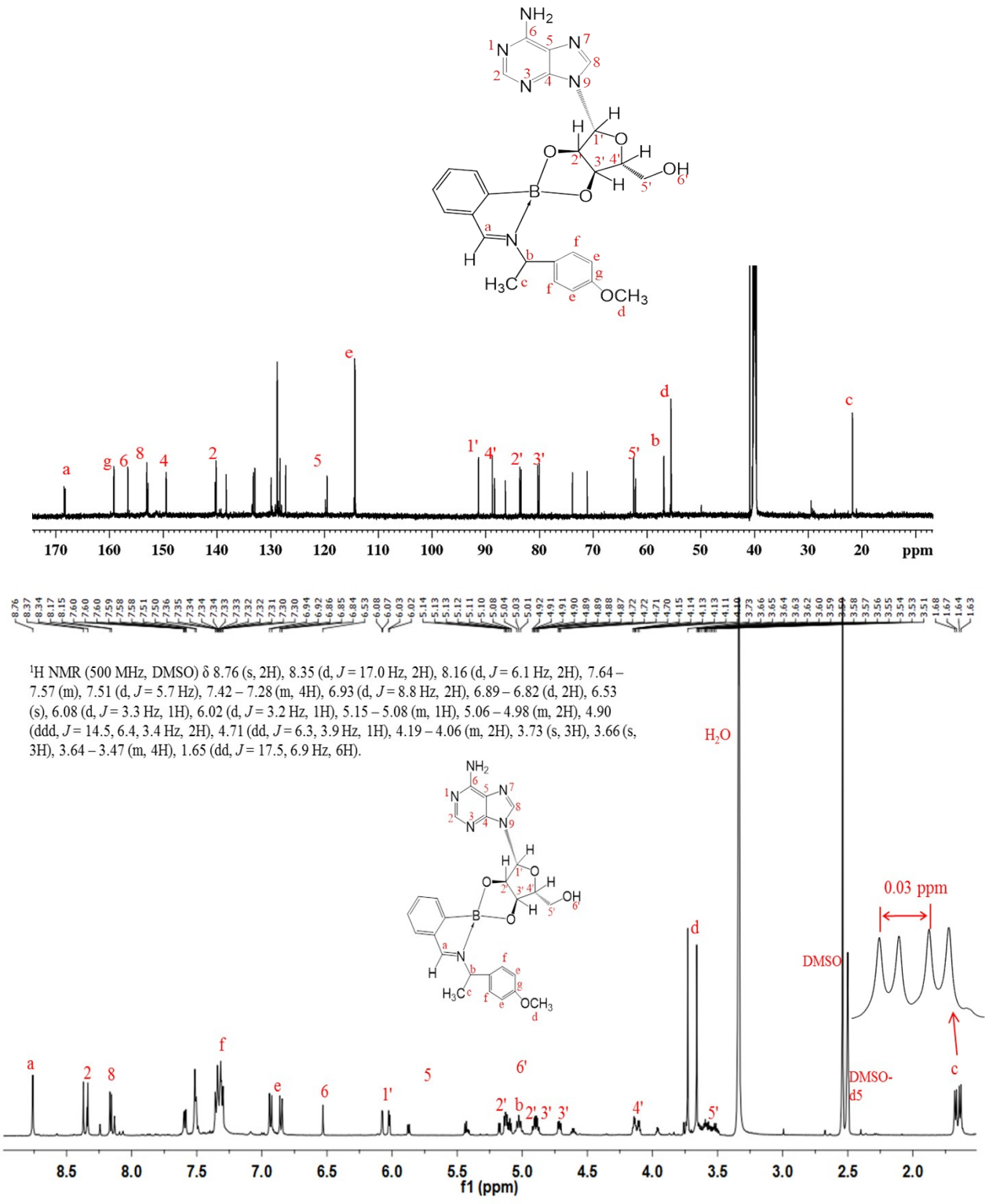


Figure S36. 500 MHz ^{1}H (bottom) and 200 MHz ^{13}C (top) NMR spectra of 4-methoxy-α-methylbenzylamine: adenosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.03 ppm for c).

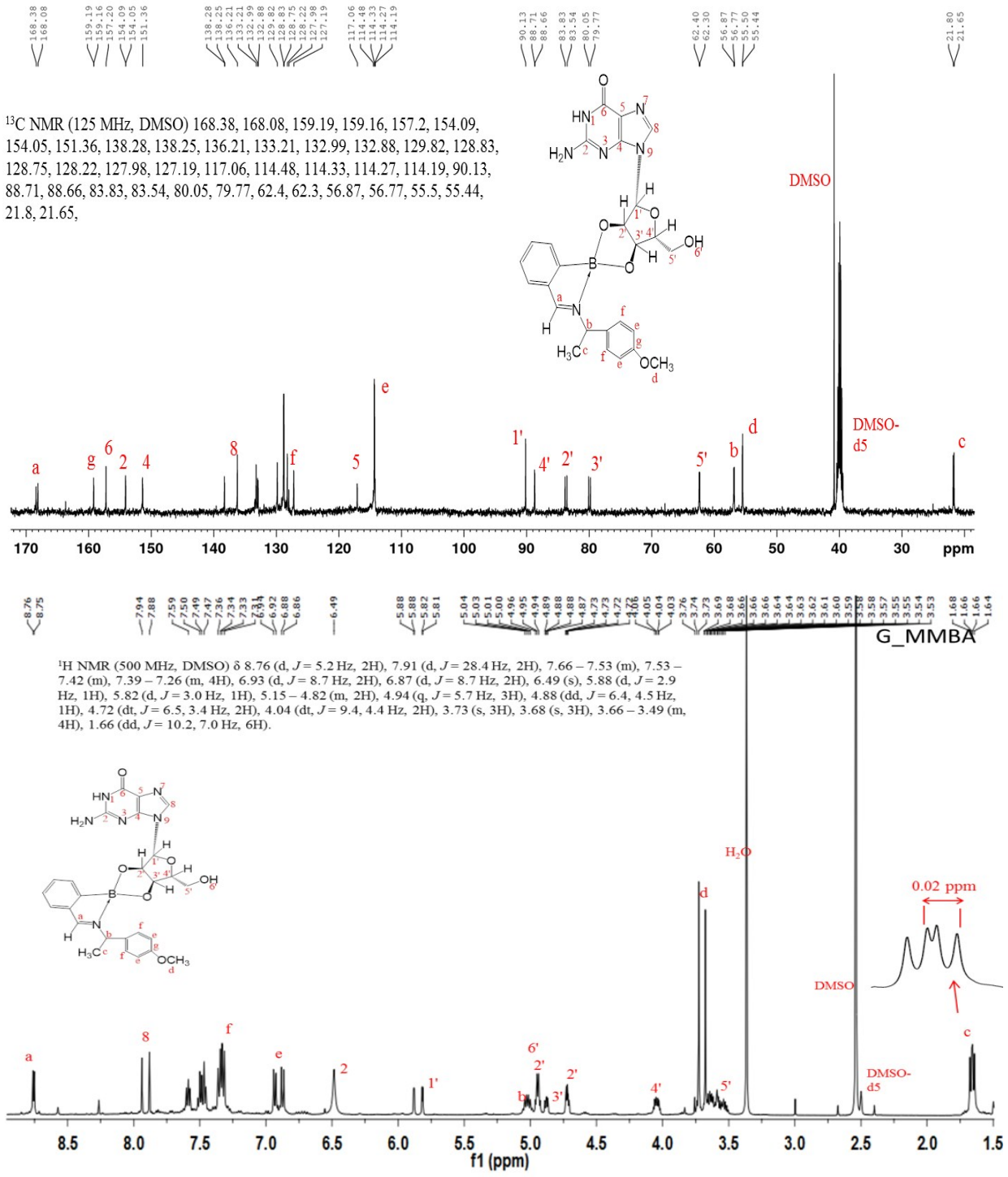


Figure S37. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 4-methoxy-α-methylbenzylamine: guanosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.02 ppm for c).

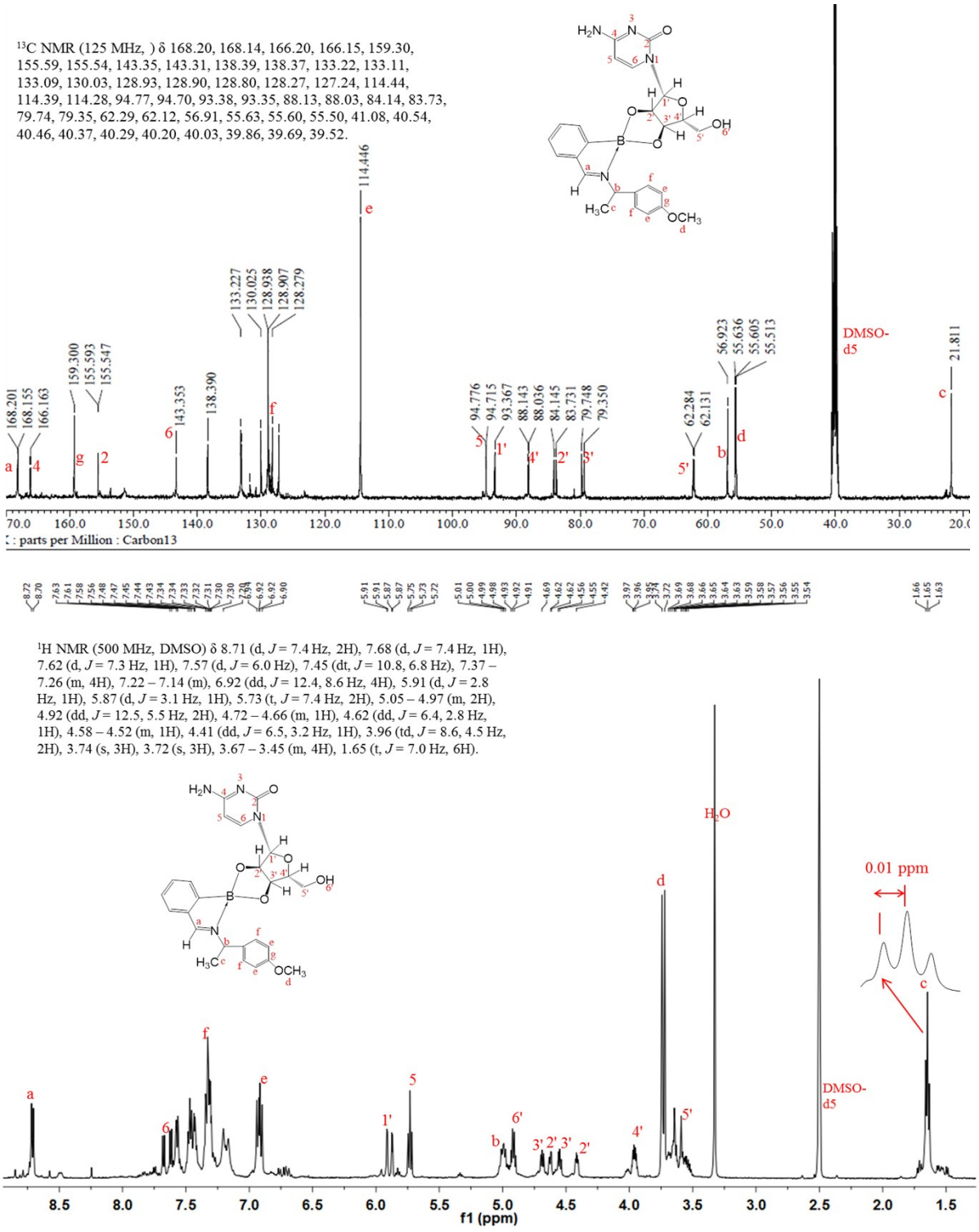


Figure S38. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 4-methoxy-α-methylbenzylamine: cytidine: 2-formylphenylboronic acid diastereomeric complex. M protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm for c).

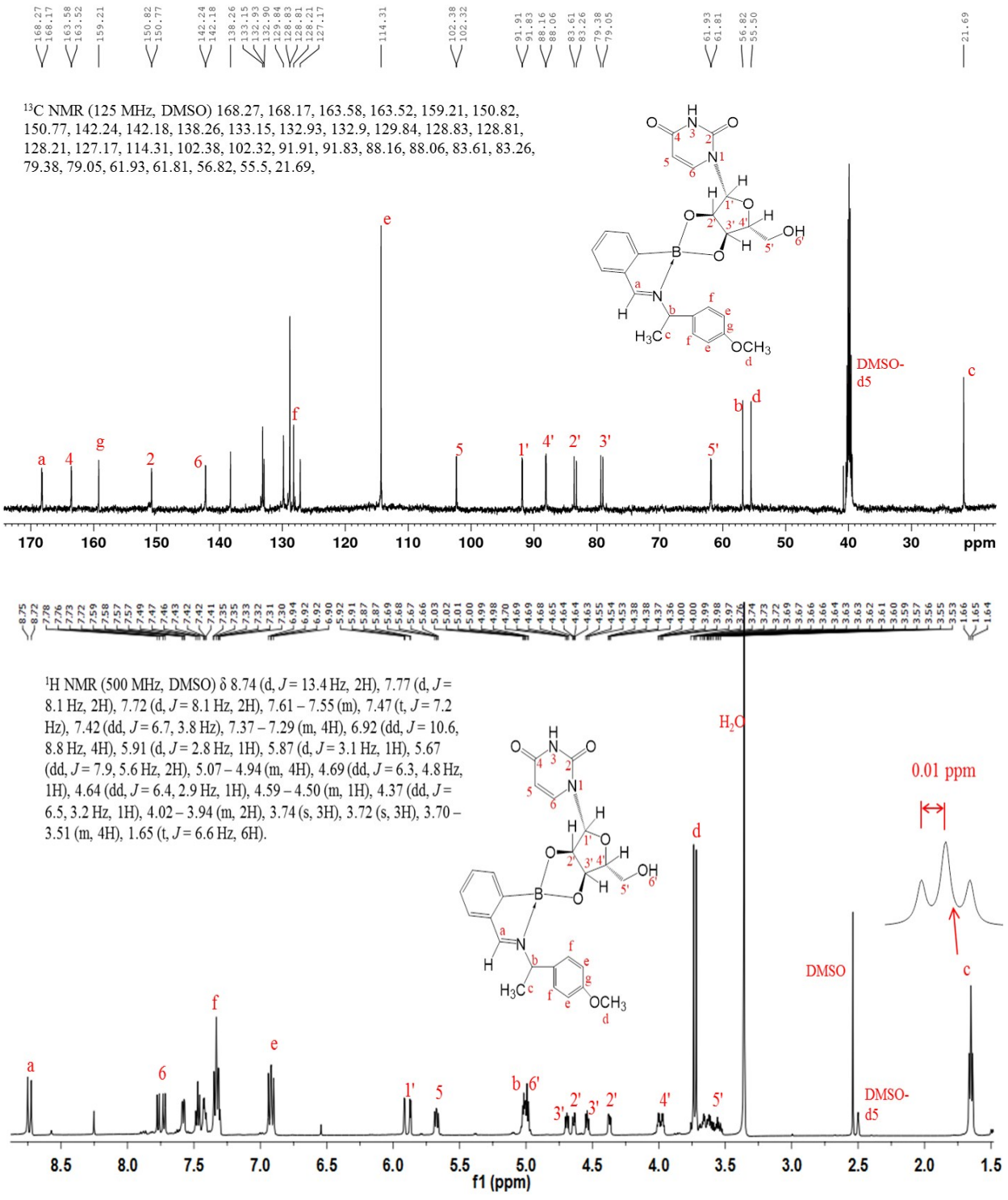


Figure S39. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 4-methoxy-α-methylbenzylamine: uridine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations are shown on expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm for c).

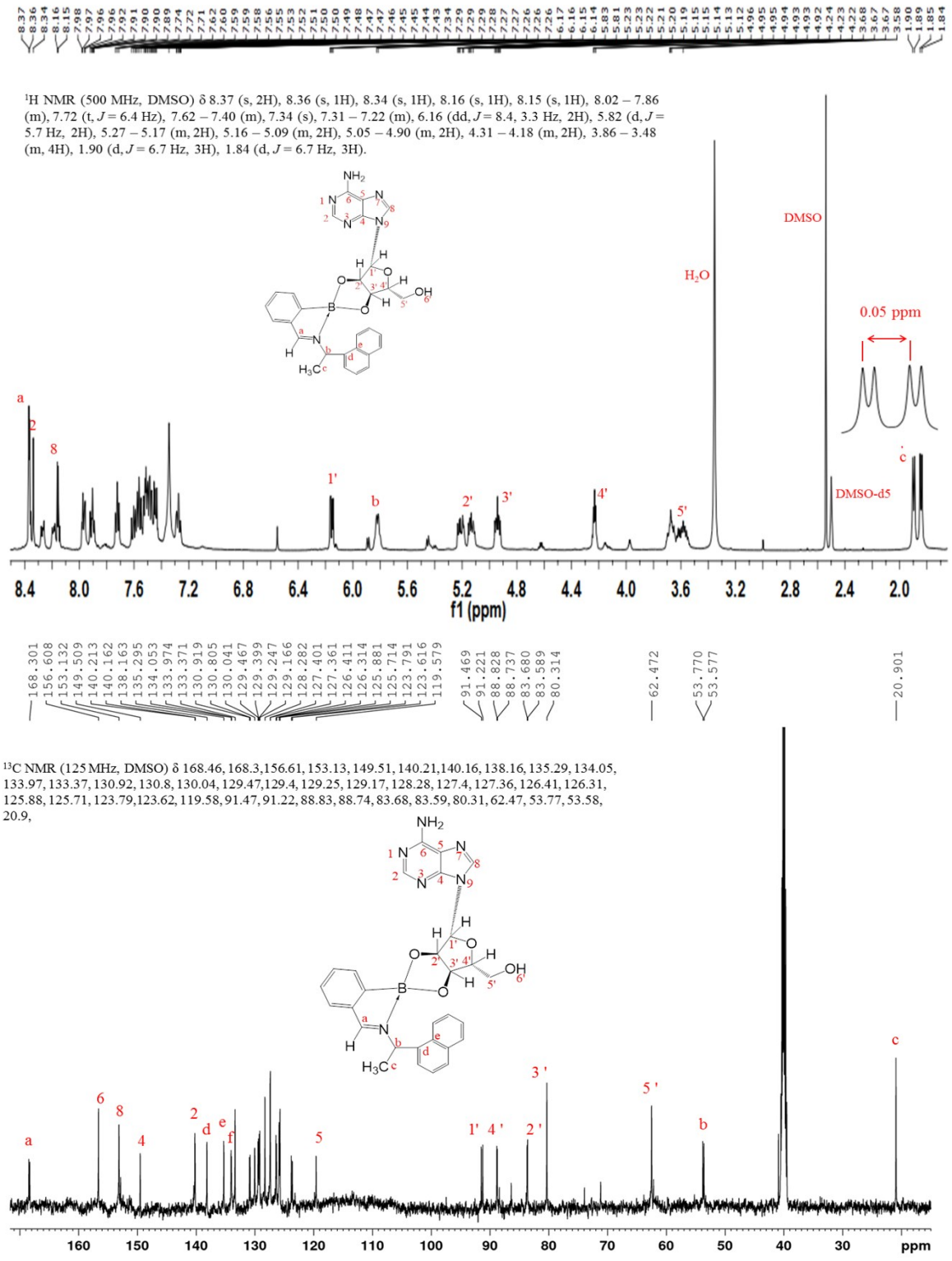


Figure S40. 500 MHz ^{1}H (top) and 125 MHz ^{13}C (bottom) NMR spectra of 1-(2-naphthyl)ethanamine: adenosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown on expanded region ($\Delta\delta^{R,S}$ = 0.05 ppm for c).

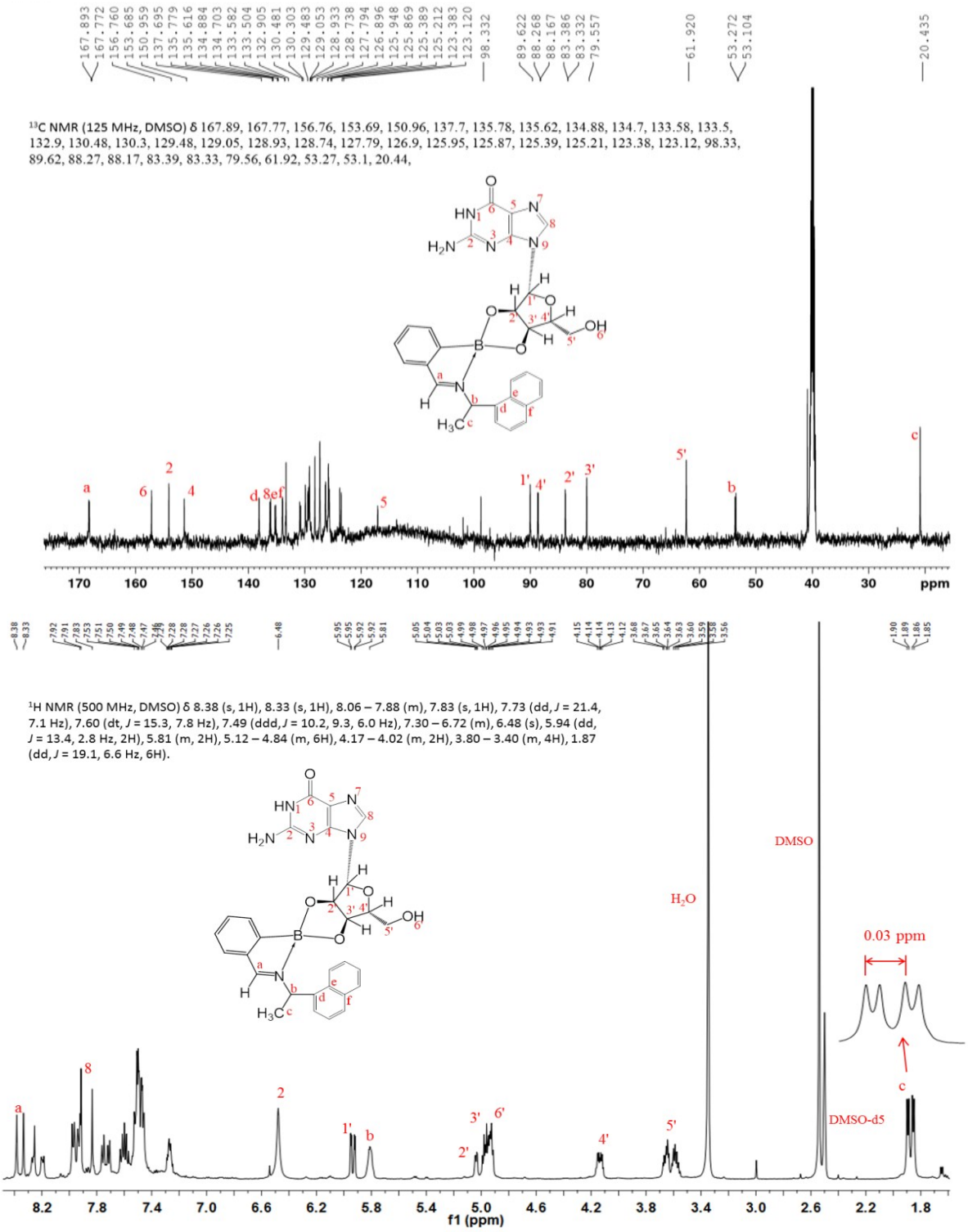


Figure S41. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 1-(2-naphthyl)ethanamine: guanosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift seperation is shown on expanded region ($\Delta\delta^{R,S}$ = 0.03 ppm for c).

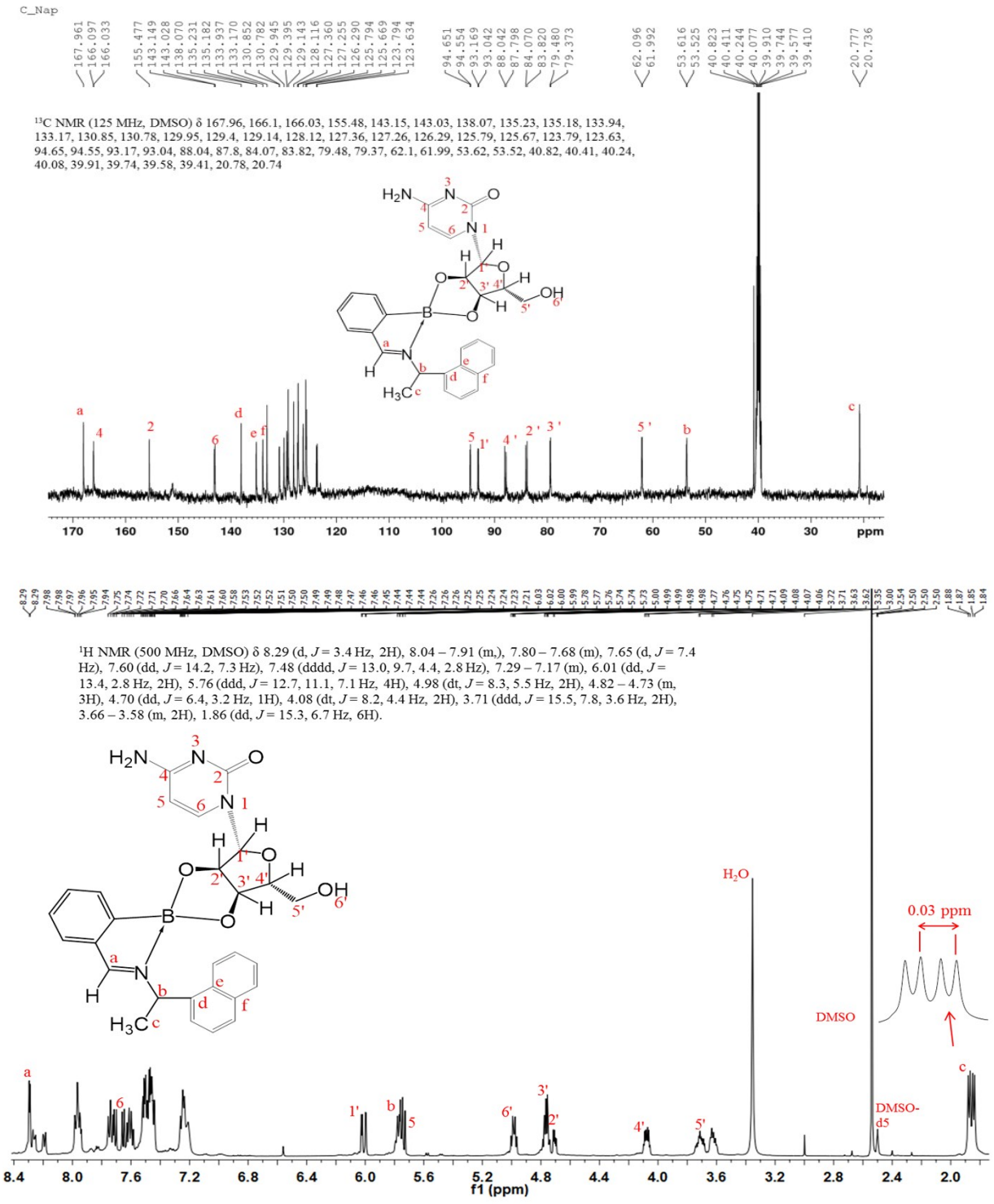


Figure S42. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 1-(2-naphthyl)ethanamine: cytidine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separations is shown on expanded region ($\Delta\delta^{R,S}$ = 0.03 ppm for c).

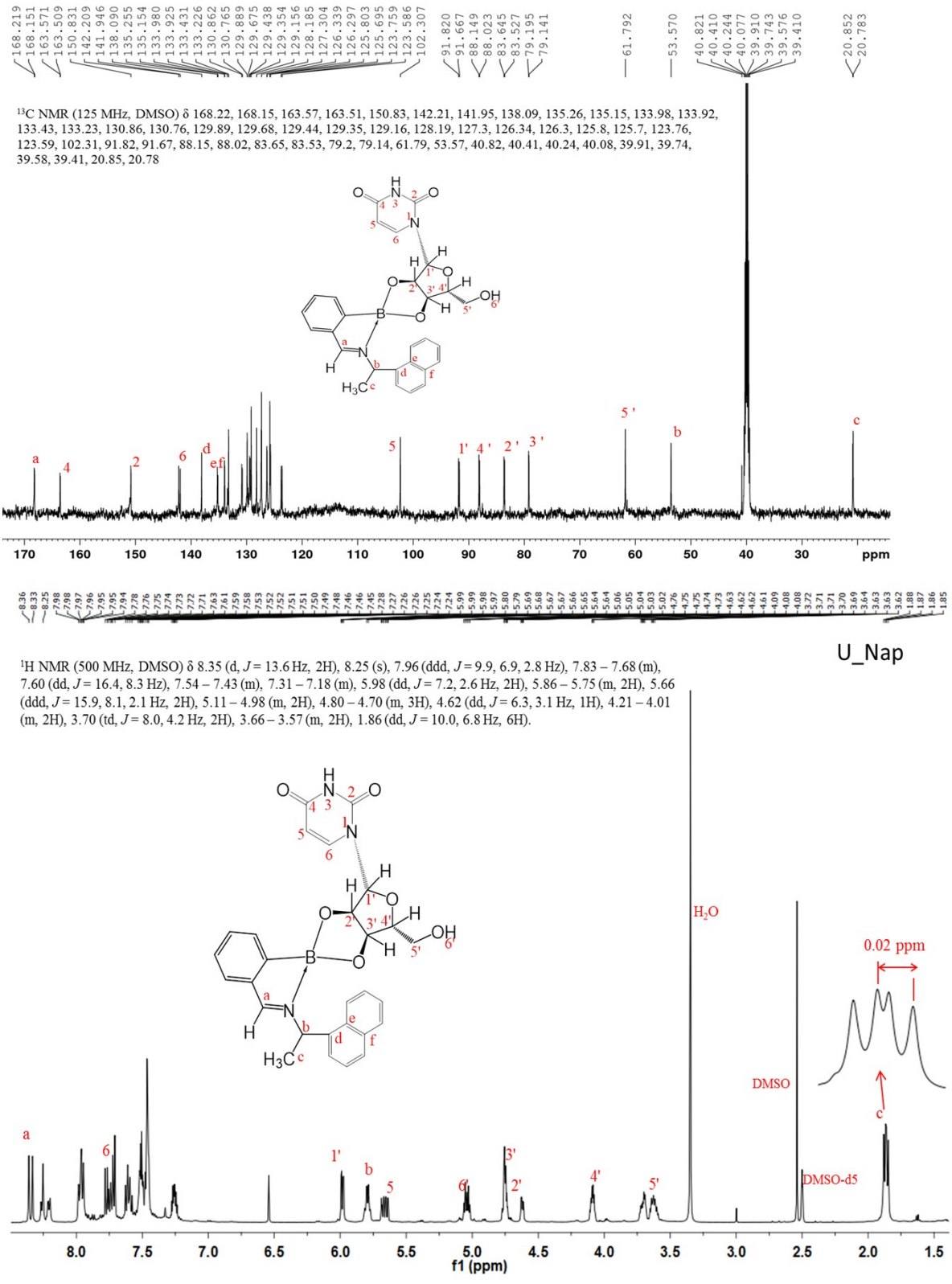


Figure S43. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 1-(2-naphthyl)ethanamine:

uridine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. proton chemical shift separations is shown on expanded region ($\Delta\delta^{R,S}$ = 0.02 ppm for c).

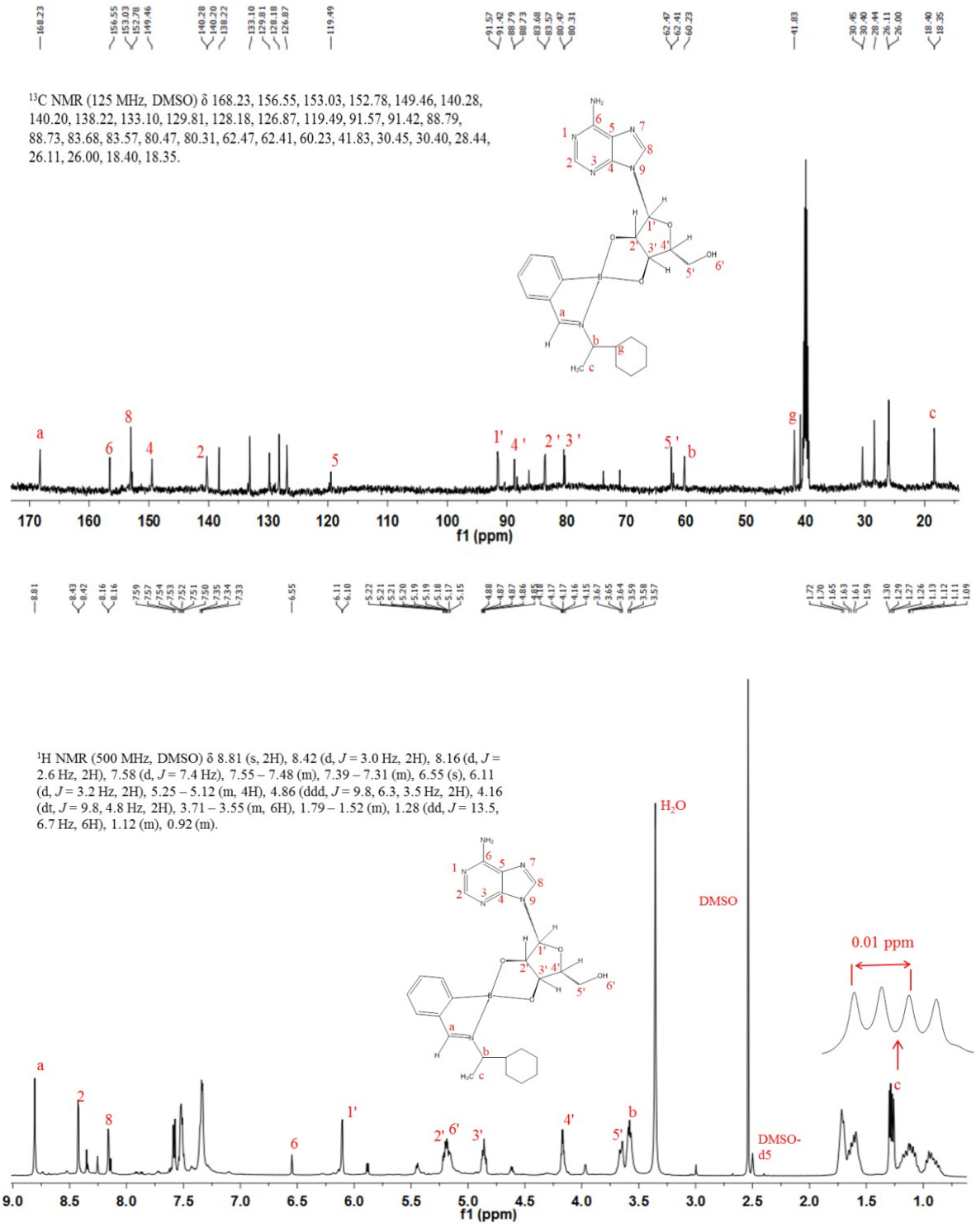
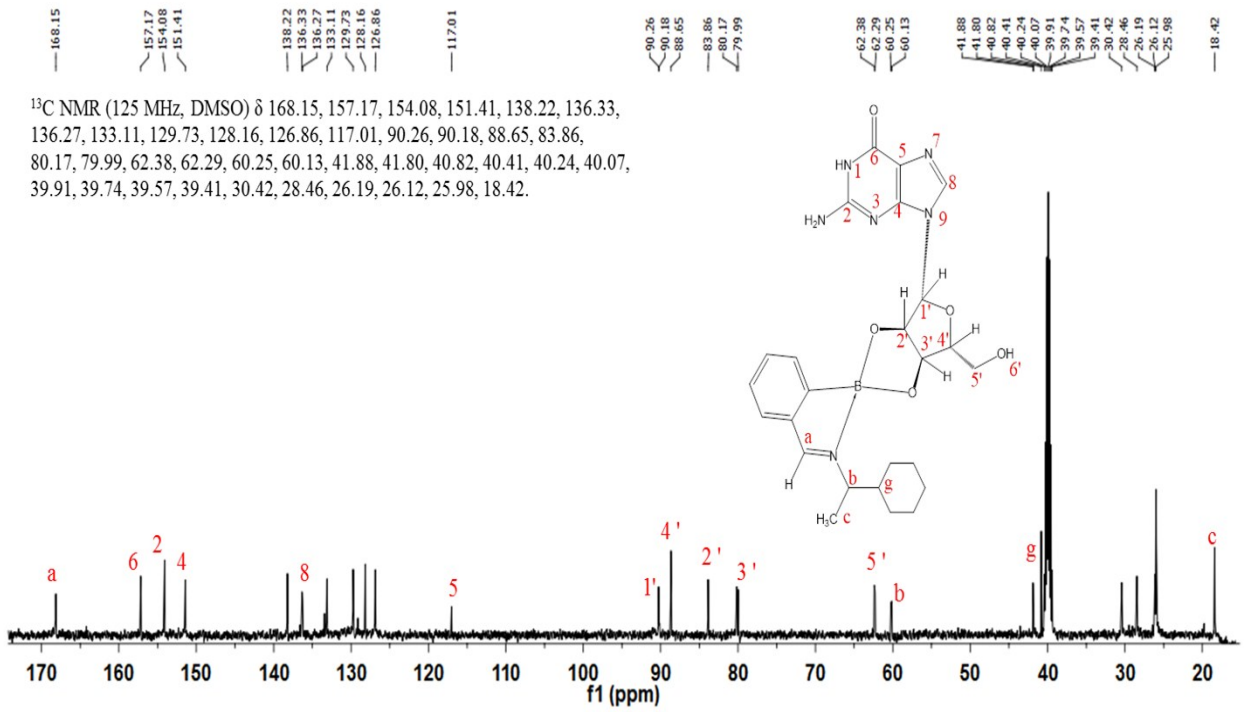


Figure S44. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 1-cyclohexylethylamine: adenosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown on expanded region ($\Delta\delta^{R,S}$ = 0.03 ppm).



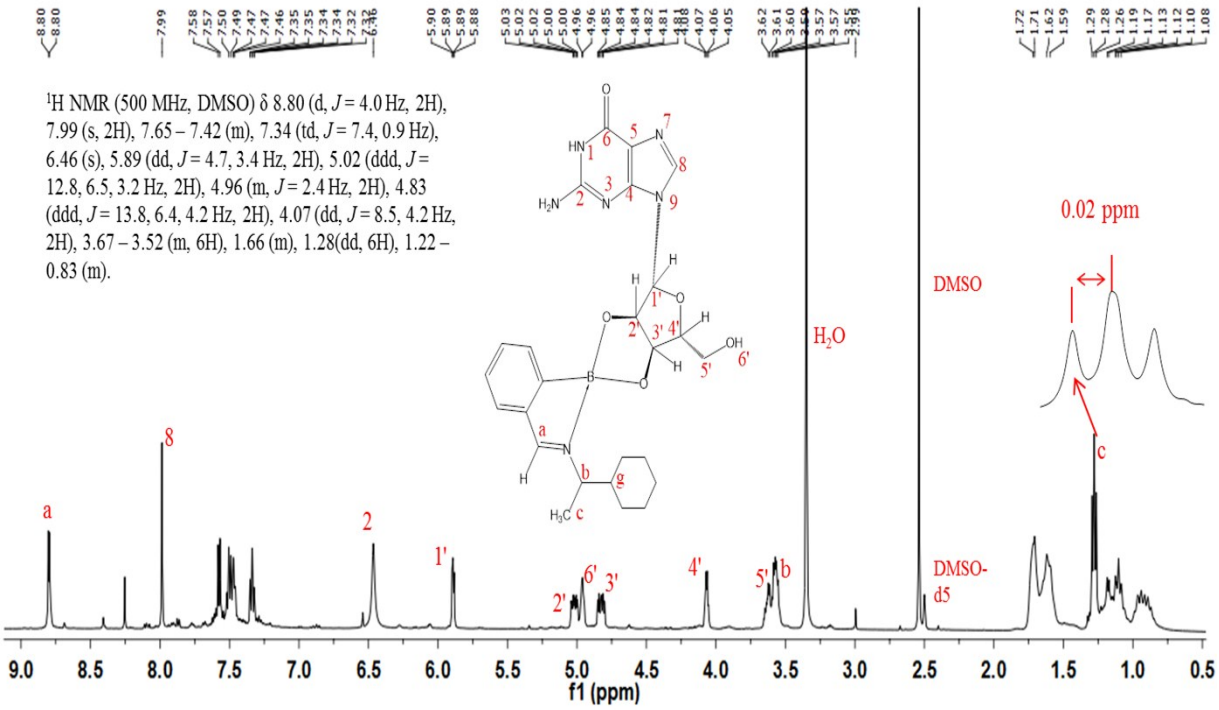
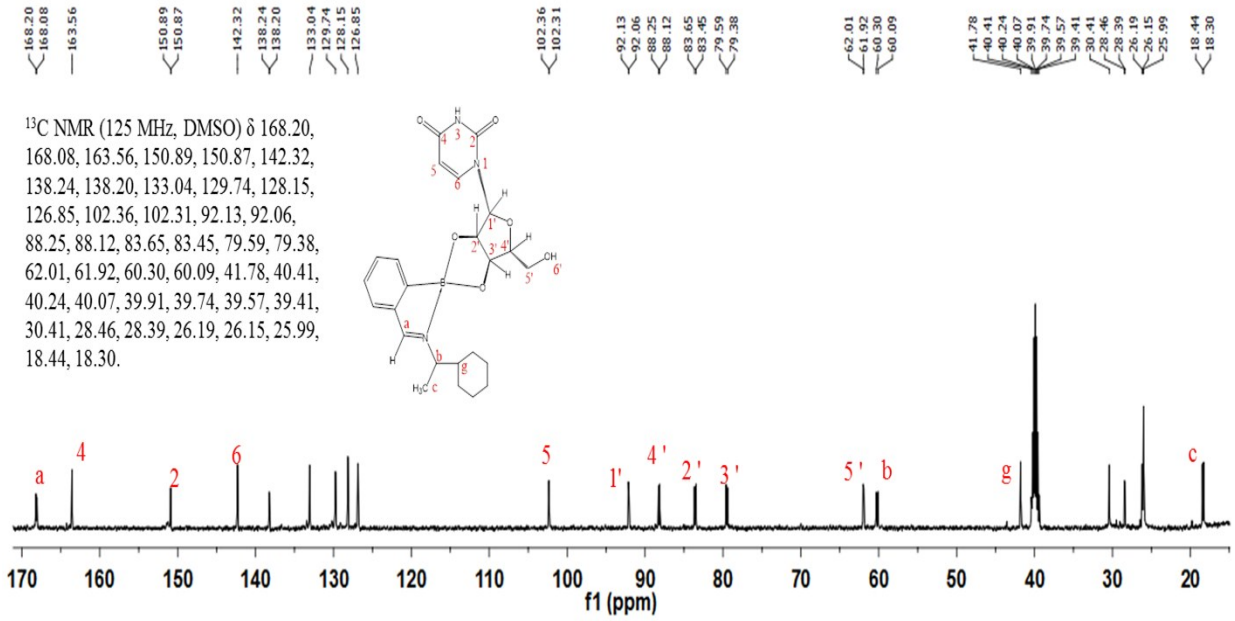


Figure S45. 500 MHz [1]H (bottom) and 125 MHz [13]C (top) NMR spectra of 1-cyclohexylethylamine: guanosine: 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown on expanded region ($\Delta\delta^{R,S}$ = 0.02 ppm).



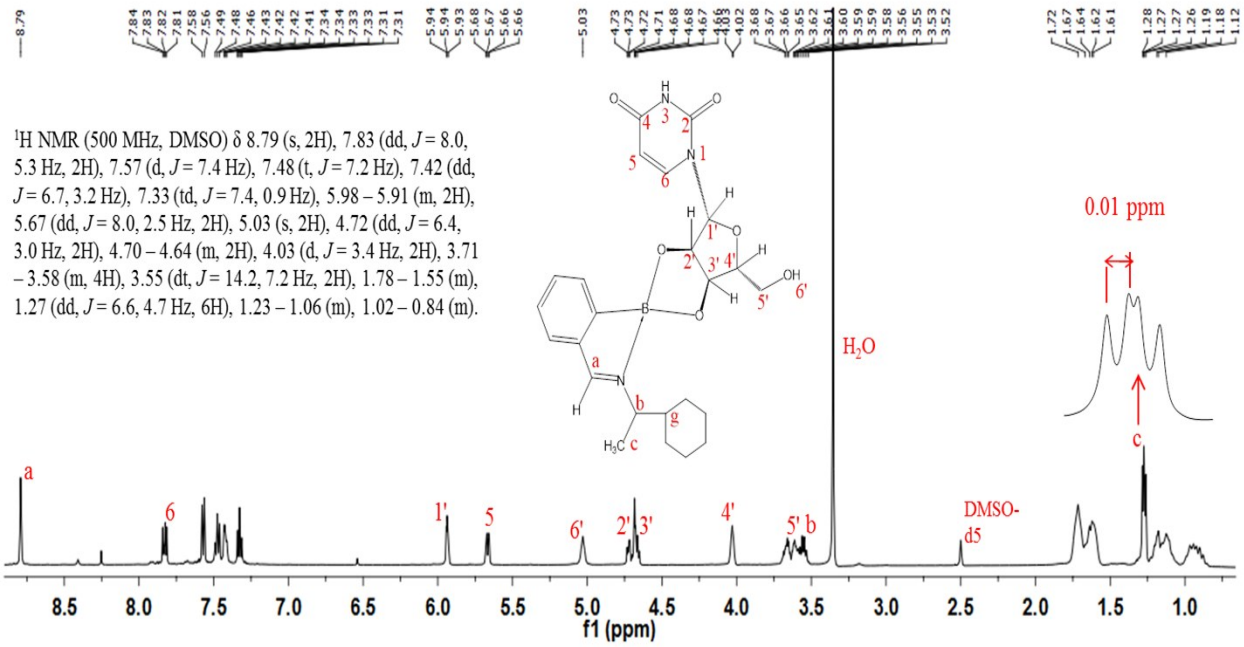


Figure S46. 500 MHz ^{1}H (top) and 125 MHz ^{13}C (bottom)NMR spectra of 1-cyclohexylethylamine : uridine : 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as c. Proton chemical shift separation is shown on expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm).

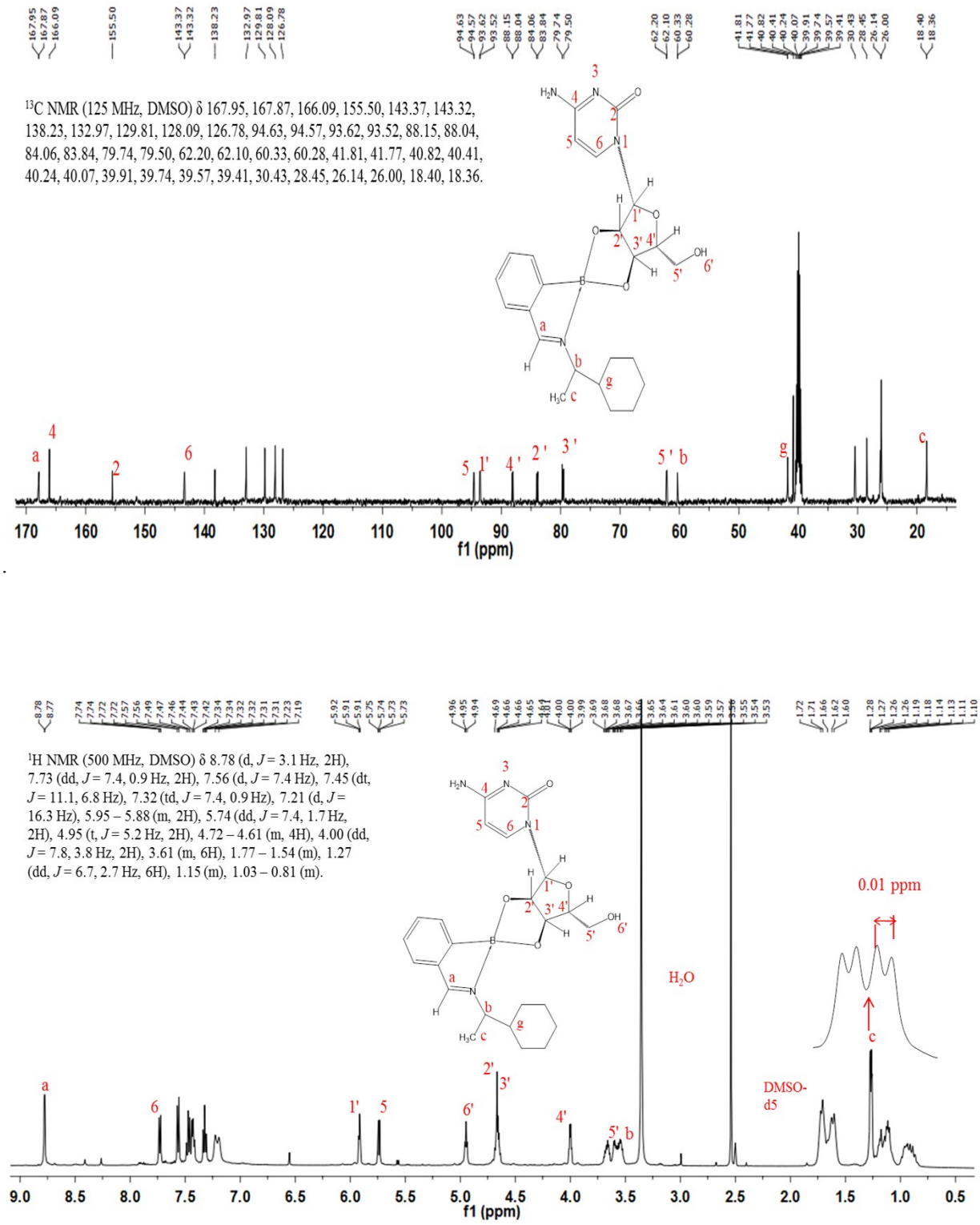


Figure S47. 500 MHz ^{1}H (bottom) and 125 MHz ^{13}C (top) NMR spectra of 1-cyclohexylethylamine : cytidine : 2-formylphenylboronic acid diastereomeric complex. Methyl protons and corpessponding peaks are labeled as a. proton chemical shift separation is shown on expanded region ($\Delta\delta^{R,S}$ = 0.01 ppm).

1. Diastereomeric excess calculations.

A series of 4-methoxy-α-methylbenzylamine : adenosine : 2-formyl phenylboronic diastreomeric complexes were prepared with varying (*R)* and (*S)* 4-methoxy-α-methylbenzylamine. The NMR experimentally determined diastereomeric excess has been compared with gravimetrically prepared ratios. In NMR, the methyl peaks are integrated to calculate diastereomeric excess(d.e.), the peaks used were shown in manuscript Figure 4. The area of peaks and the calulation are given below

Entry	**Integration** I_R:I_S	$de\ of\ R = \frac{(I_R - I_S)}{(I_R + I_S)} X100$ (NMR)	**Gravimetrically prepared ratios of diastereomeric excess (*de*)**
Sample 1	1:2.95	-49.4 %	-52.1 %
Sample 2	1:1.8	-28.5 %	-30.2 %
Sample 3	1:1.23	-10.3 %	-12 %
Sample 4	1:1.03	-1.4 %	0 %
Sample 5	1:0.69	18.3 %	20.2 %
Sample 6	1: 0.59	25.7 %	28 %
Sample 7	1: 0.43	39.8 %	42 %