

Supporting information

Unusual Radical 6-*endo* Cyclization to the Carbocyclic-ENA and Elucidation of its Solution Conformation by 600 MHz NMR and *ab initio* Calculations

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Contents:

General experimental methods.	3
Figure S1. ¹ H NMR spectrum of mixture of 8 and 9.	4
Figure S2. ¹³ C NMR spectrum of mixture of 8 and 9.	5
Figure S3. DEPT NMR spectra of mixture of 8 and 9.	6
Figure S4. COSY spectrum of mixture of 8 and 9.	7
Figure S5. COSY spectrum of mixture of 8 and 9.	8
Figure S6. COSY spectrum of mixture of 8 and 9.	9
Figure S7. HMQC spectrum of mixture of 8 and 9.	10
Figure S8. Expansion of HMQC spectrum of mixture of 8 and 9.	10
Figure S9. ¹ H NMR spectrum of compound 7.	11
Figure S10. ¹³ C NMR spectrum of compound 7.	12
Figure S11. COSY spectrum of compound 7.	13
Figure S12. HMQC spectrum of compound 7.	14
Figure S13. HMBC spectrum of compound 7.	15
Figure S14. 1D nOe NMR spectrum of compound 7.	16
Figure S15. 1D nOe NMR spectrum of compound 8.	17
Figure S16. ¹ H NMR spectrum of compound 10.	18
Figure S17. ¹³ C NMR spectrum of compound 10.	19
Figure S18. ¹ H NMR spectrum of compound 11.	20
Figure S19. ¹³ C NMR spectrum of compound 11.	21
Figure S20. ¹ H NMR spectrum of compound 12.	22
Figure S21. ¹³ C NMR spectrum of compound 12.	23
Figure S22. ¹ H NMR spectrum of compound 13.	24
Figure S23. ¹³ C NMR spectrum of compound 13.	25
Figure S24. ¹ H NMR spectrum of compound 14.	26
Figure S25. ¹³ C NMR spectrum of compound 14.	27
Figure S26. ¹ H NMR spectrum of compound 1.	28
Figure S27. ¹ H NMR spectrum of compound 1.	29

Figure S28. DEPT spectrum of compound 1.	30
Figure S29. HMQC spectrum of compound 1.	31
Figure S30. HMBC spectrum of compound 1.....	32
Figure S31. DQF-COSY spectrum of compound 1.	33
Figure S32. 1D-nOe spectrum of compound 1.	34
Figure S33. Homodecoupling NMR spectra of compound 1.	35
Table S1. Sugar moiety conformation parameters ^a of compound 1.	39

General experimental methods.

Chromatographic separations were performed on Merck G60 silica gel. Thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F₂₅₄ glass-backed plates. ¹H NMR spectra were recorded at 600 MHz and 500 MHz respectively, using TMS (0.0 ppm) as internal standards. ¹³C NMR spectra were recorded at 125.7 MHz and 150.9 MHz respectively. Chemical shifts are reported in ppm (δ scale). MALDI-TOF mass spectra were recorded in positive ion mode. The mass spectrometer was externally calibrated with a peptide mixture using alpha-cyano-4-hydroxycinnamic acids as matrix.

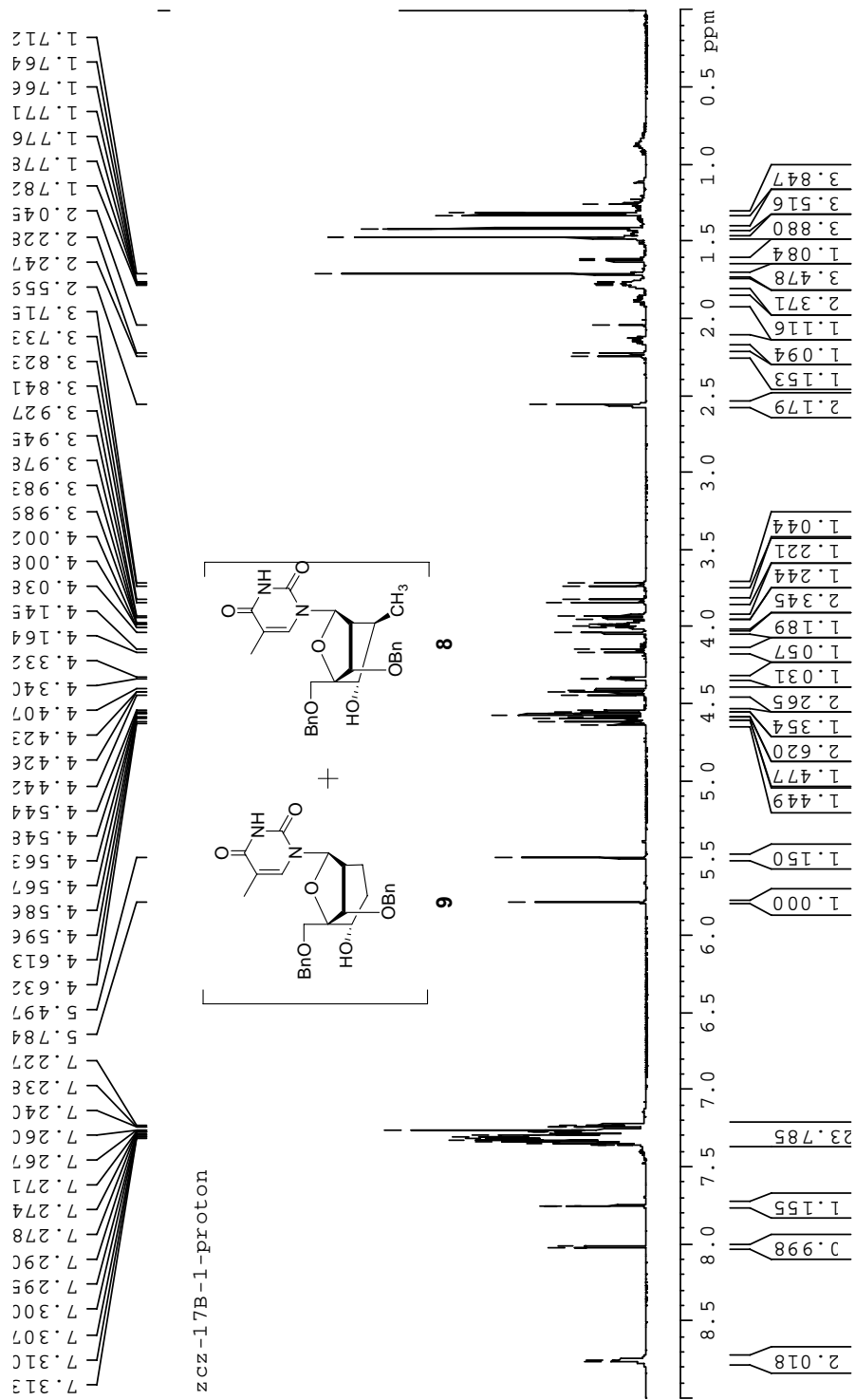


Figure S1. ¹H NMR spectrum of mixture of 8 and 9.

zcZ-17B-2-C13

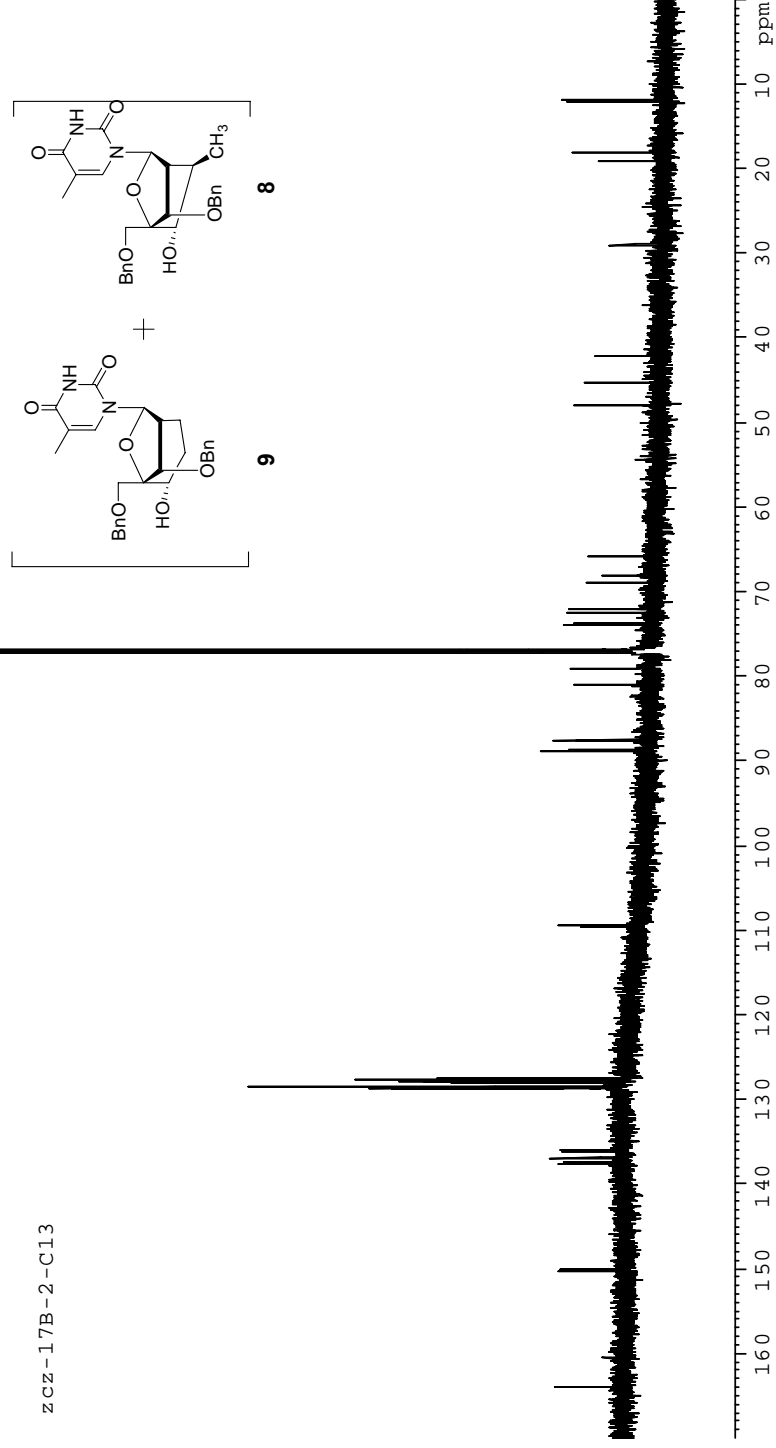


Figure S2. ^{13}C NMR spectrum of mixture of 8 and 9.

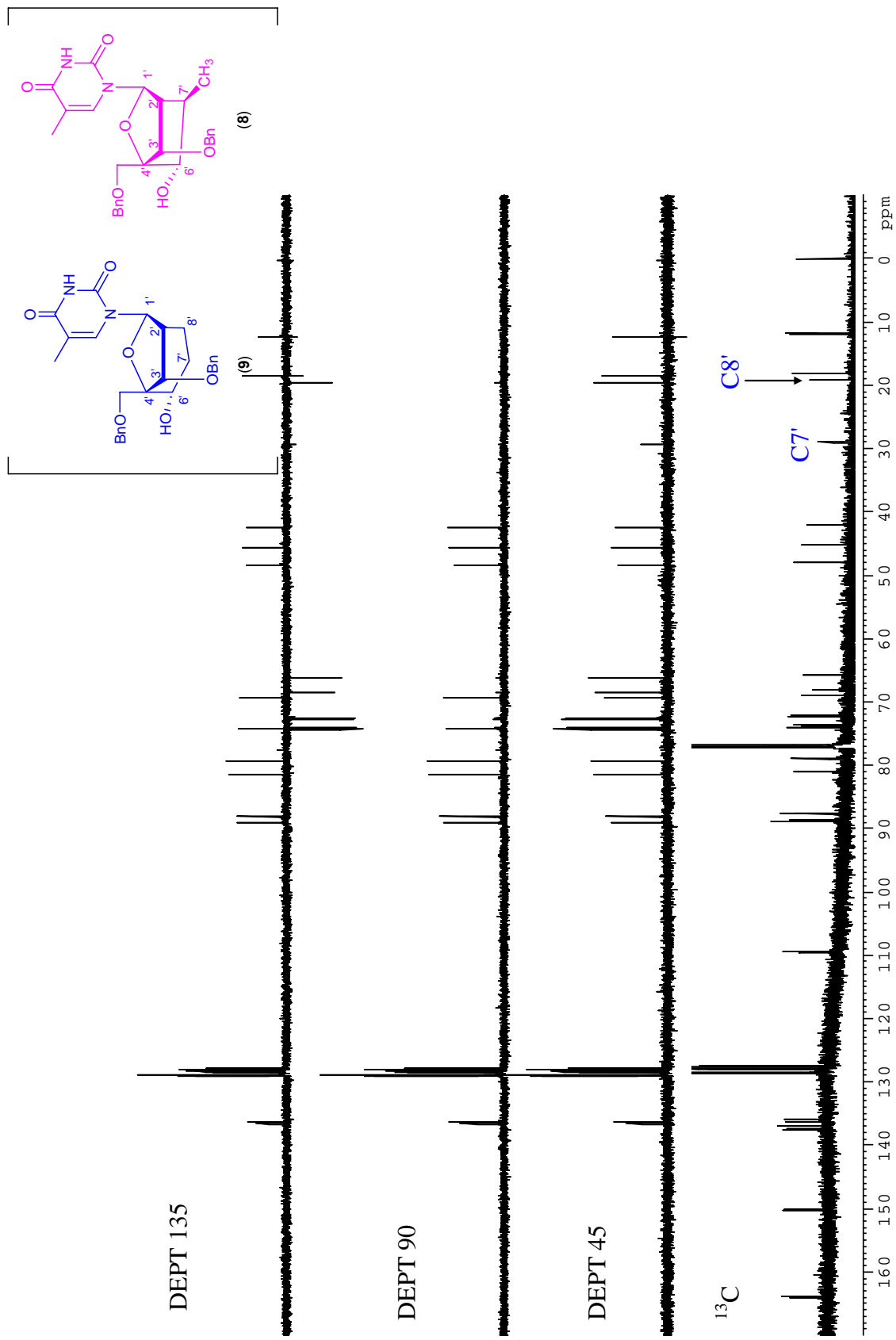


Figure S3. DEPT NMR spectra of mixture of 8 and 9.

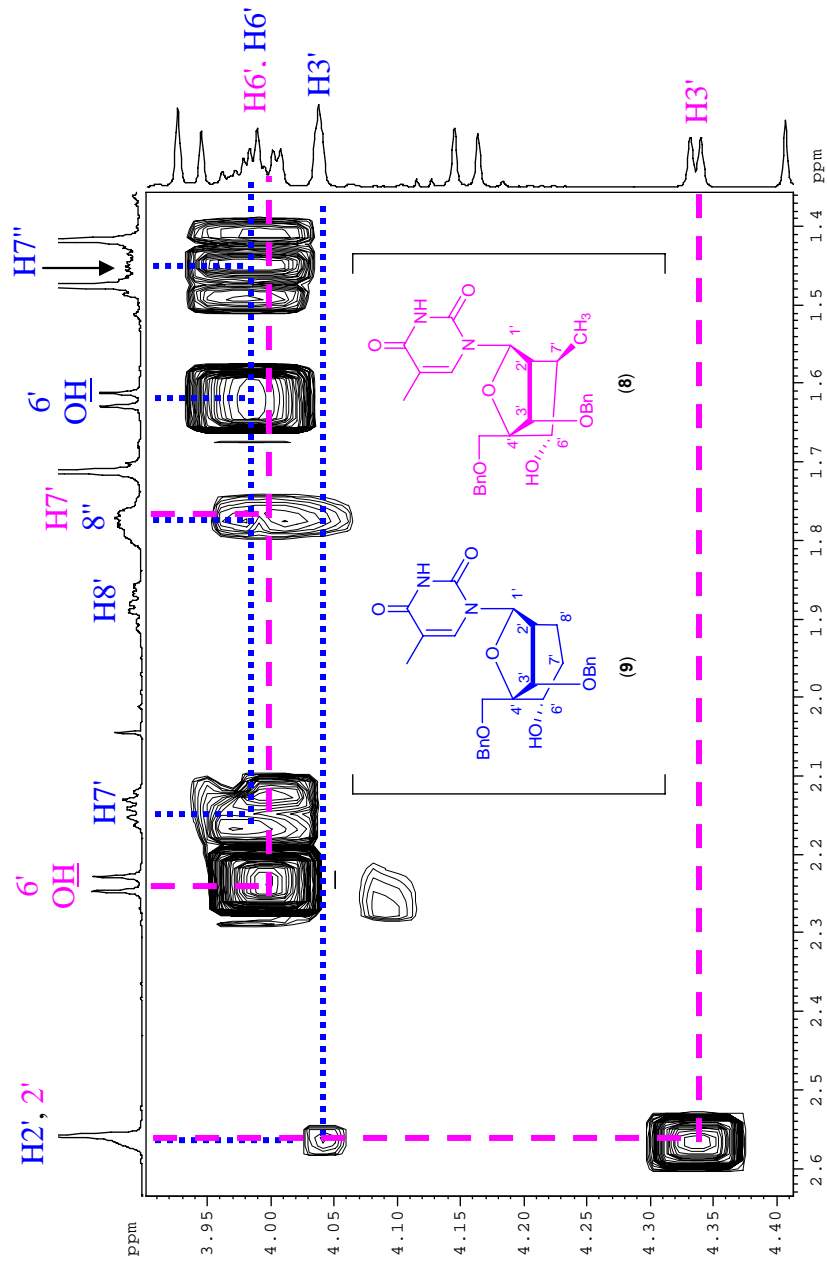


Figure S4. COSY spectrum of mixture of 8 and 9.

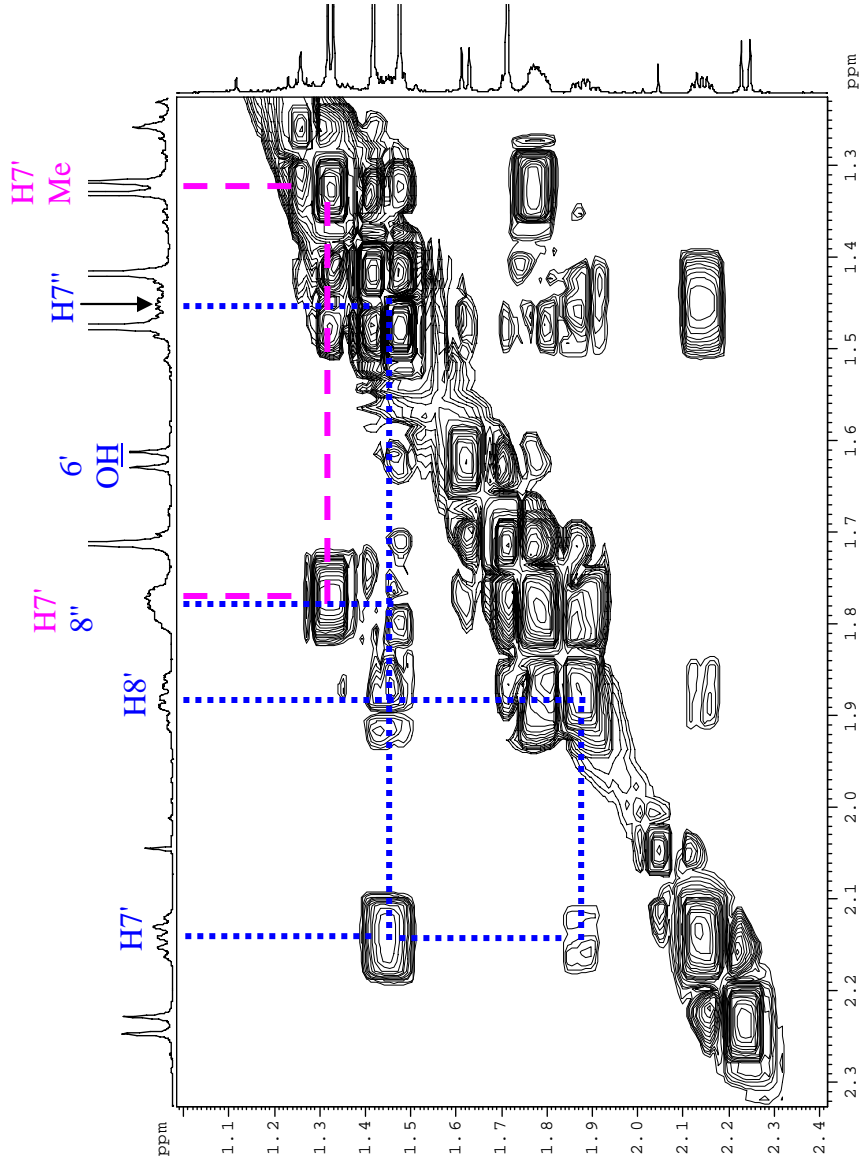


Figure S5. COSY spectrum of mixture of 8 and 9.

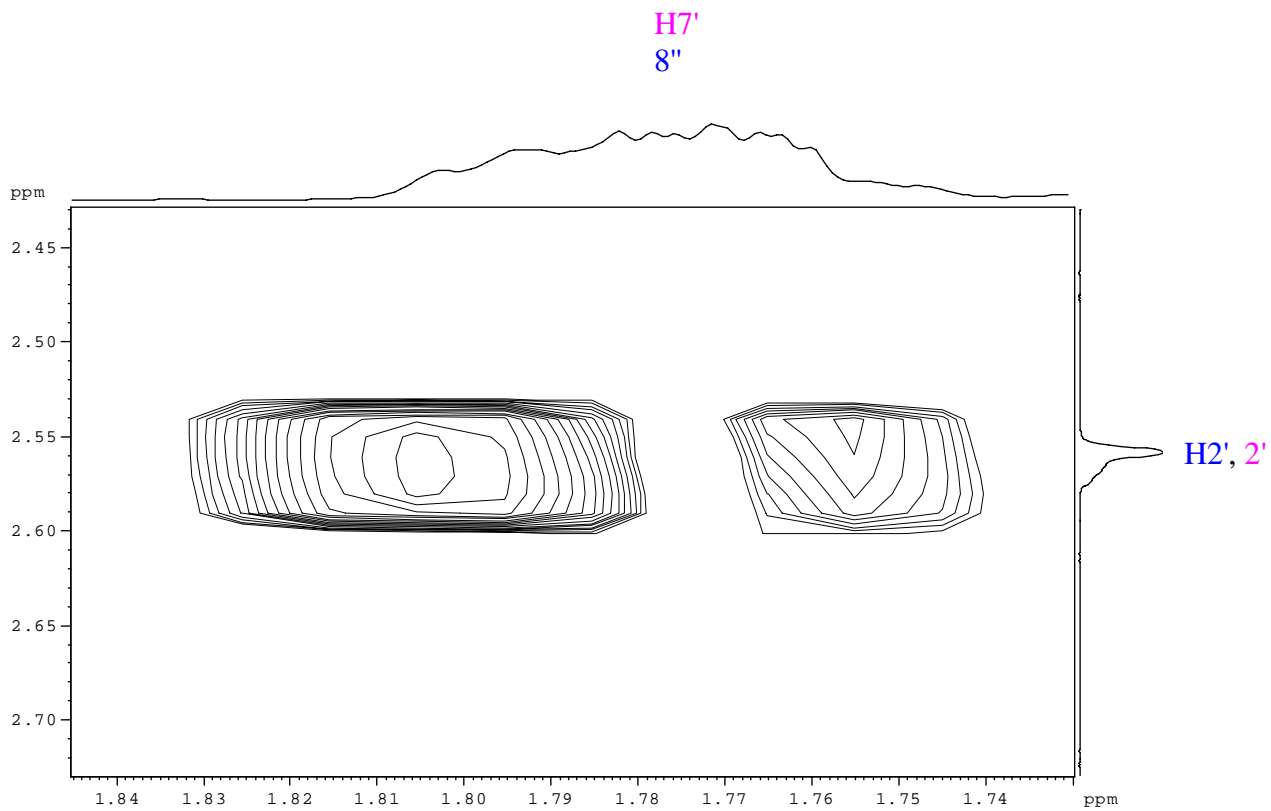
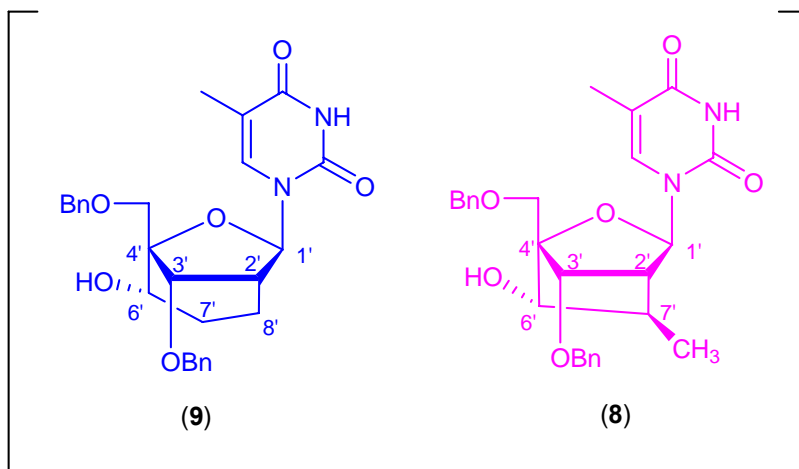


Figure S6. COSY spectrum of mixture of 8 and 9.



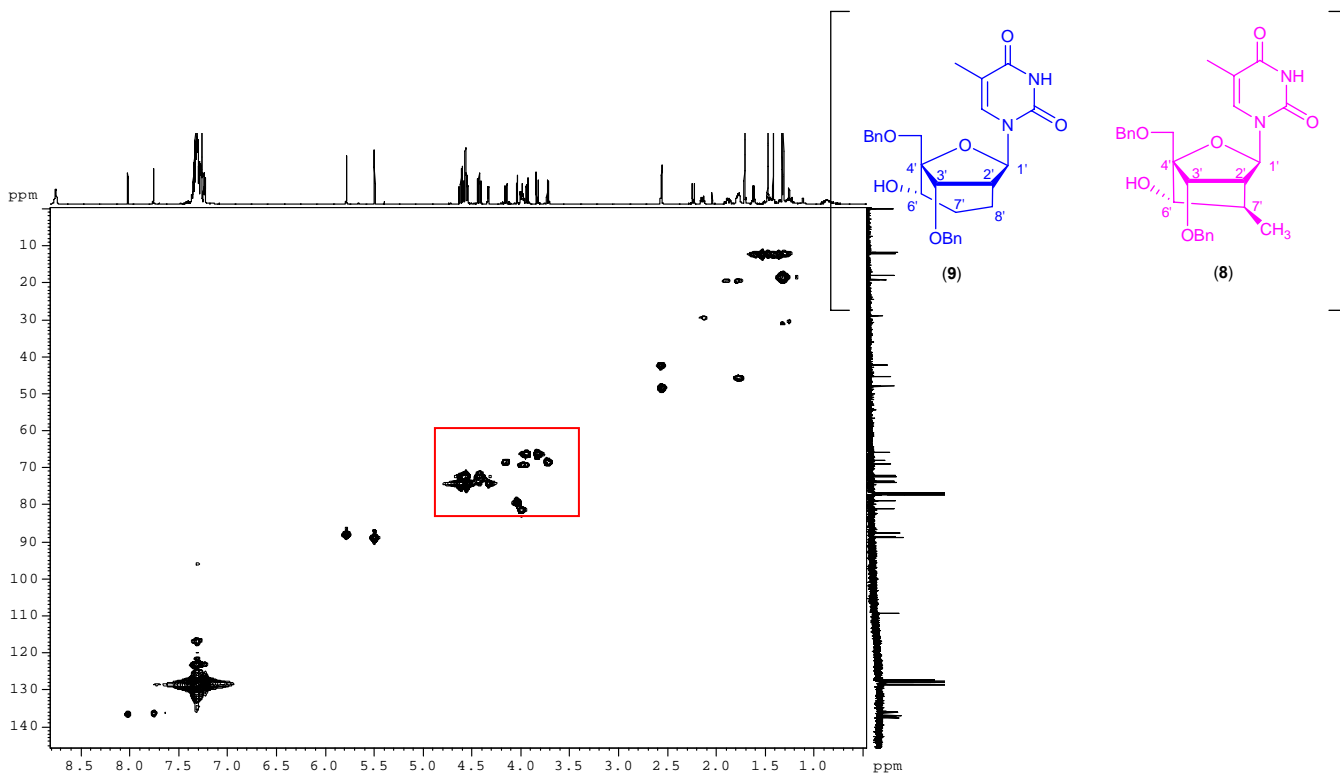


Figure S7. HMQC spectrum of mixture of 8 and 9.

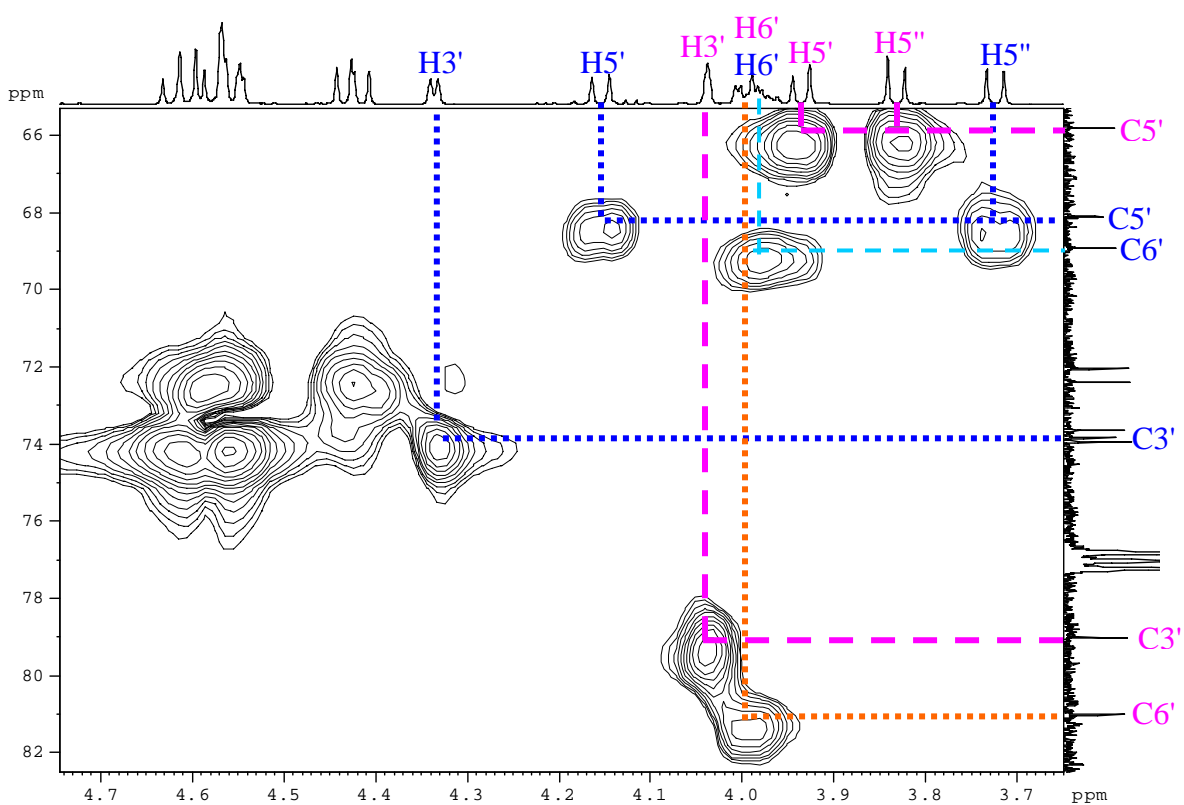


Figure S8. Expansion of HMQC spectrum of mixture of 8 and 9.

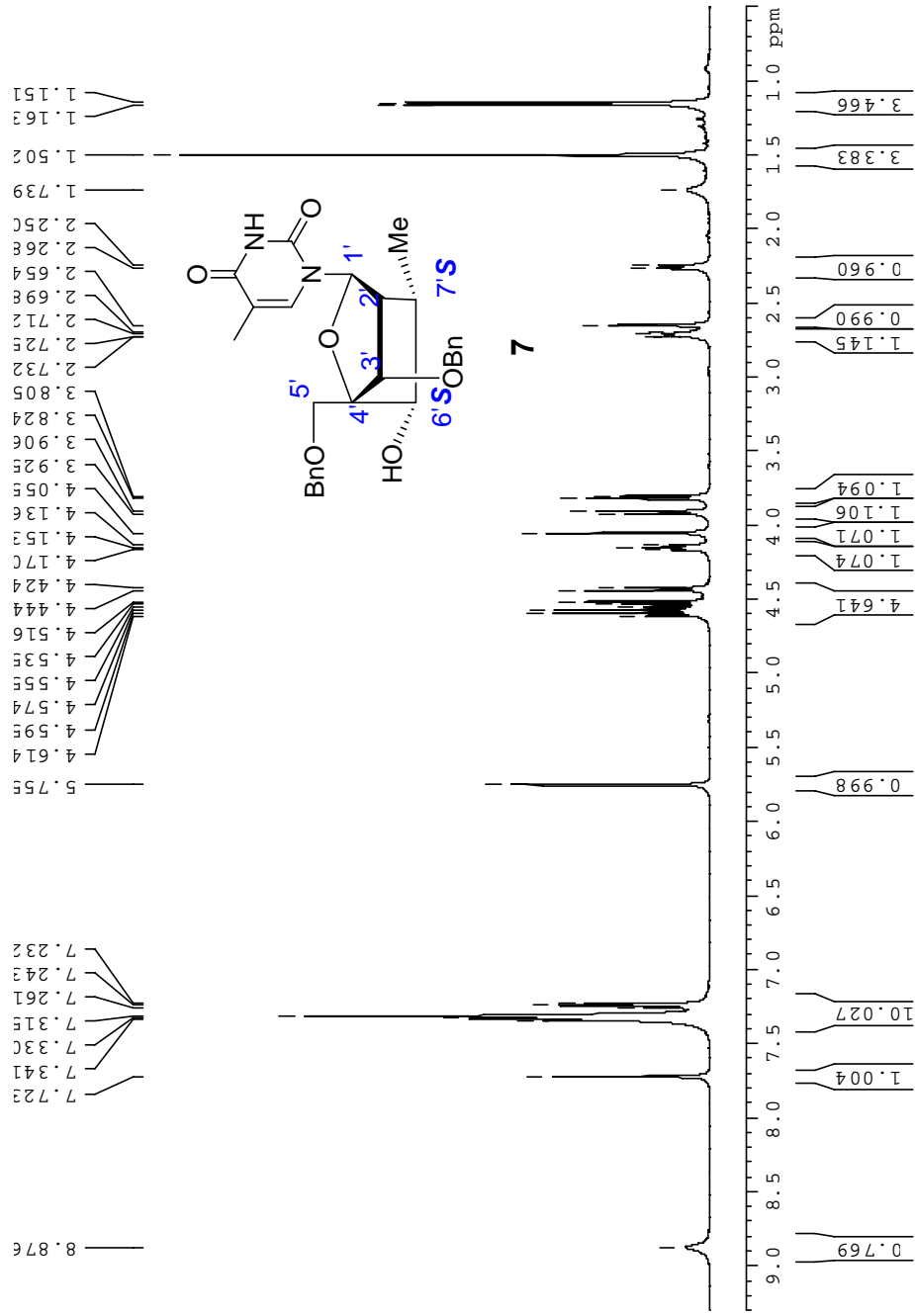


Figure S9. ^1H NMR spectrum of compound 7.

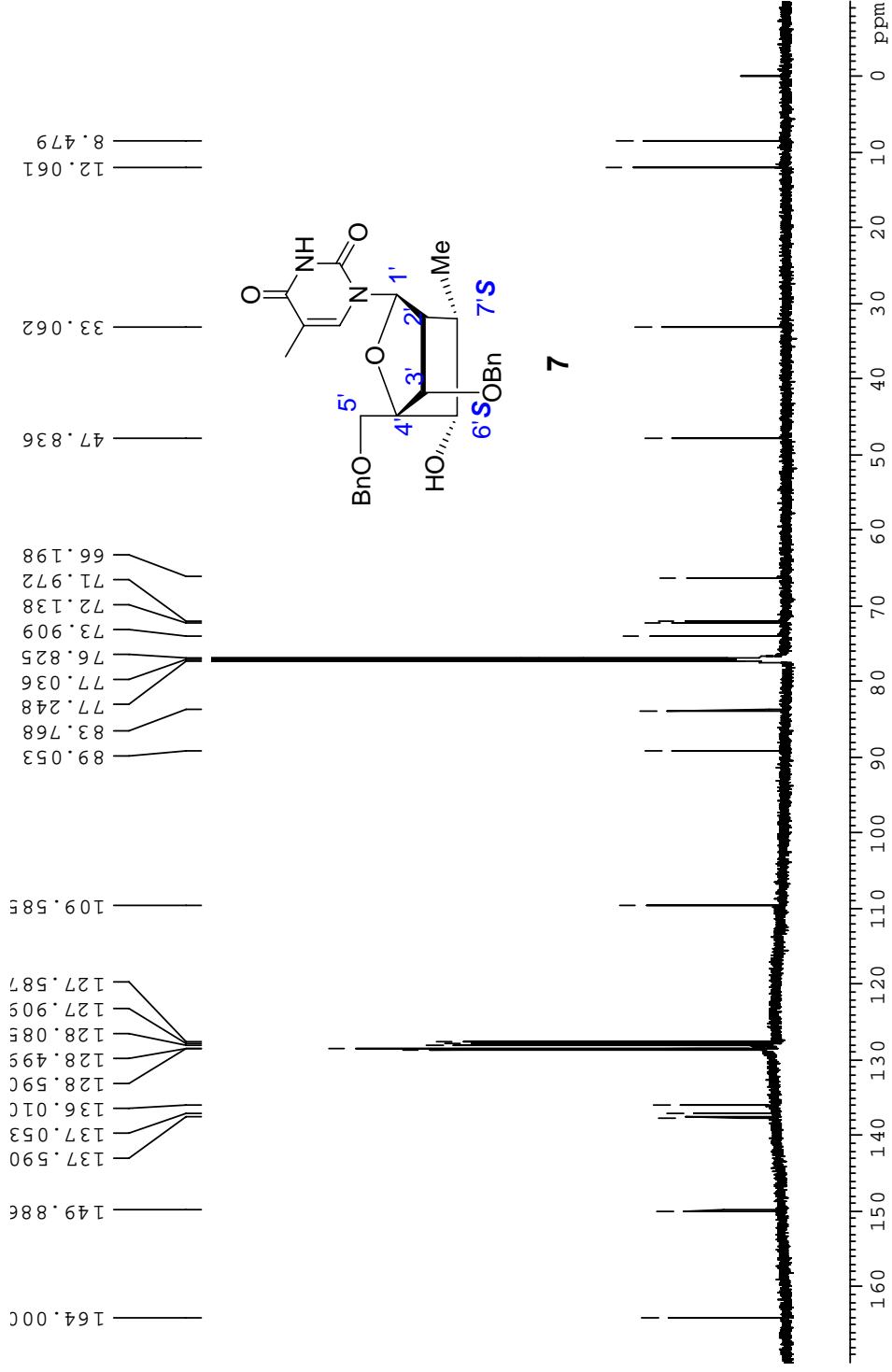


Figure S10. ^{13}C NMR spectrum of compound 7.

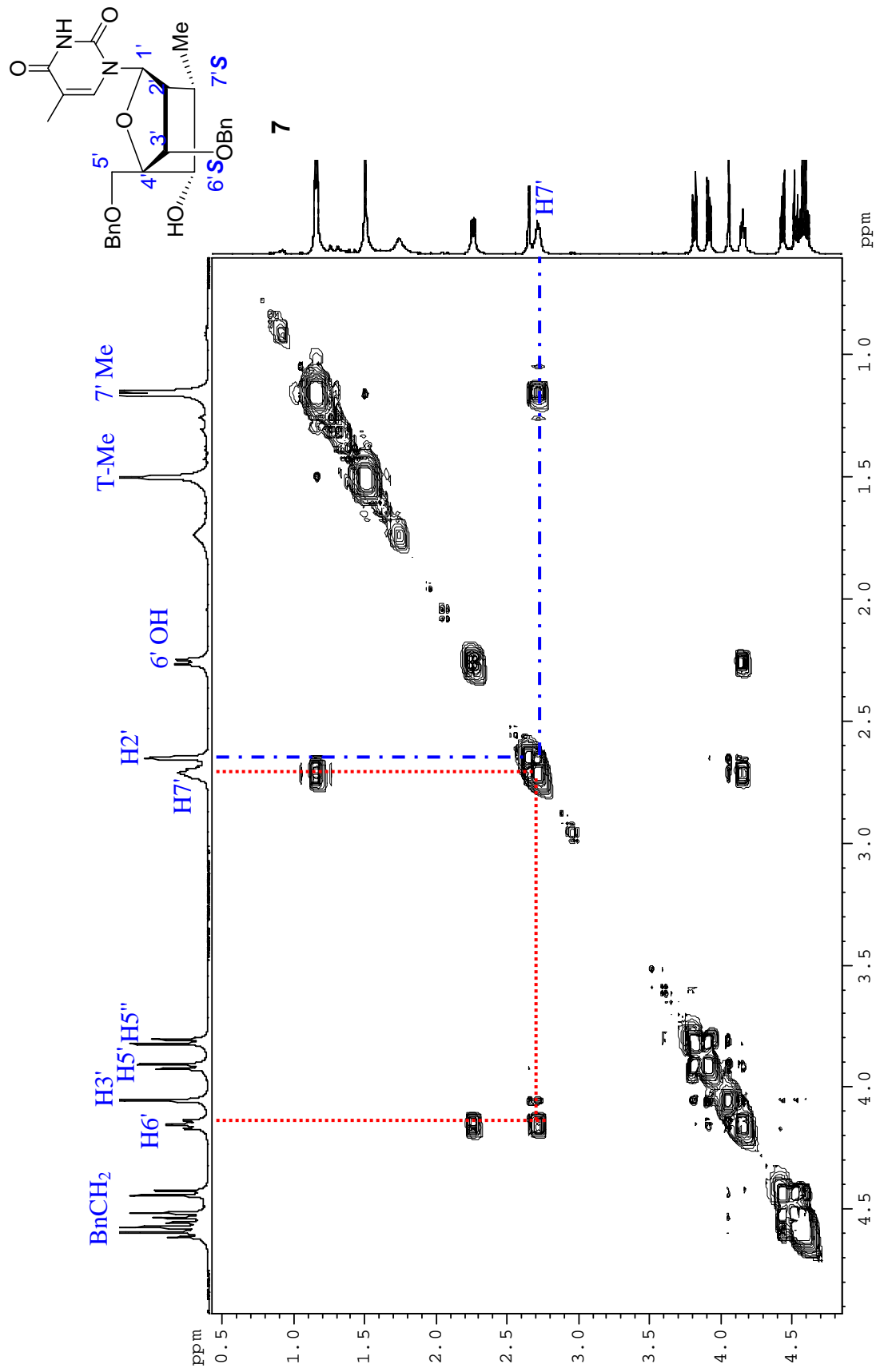


Figure S11. COSY spectrum of compound 7.

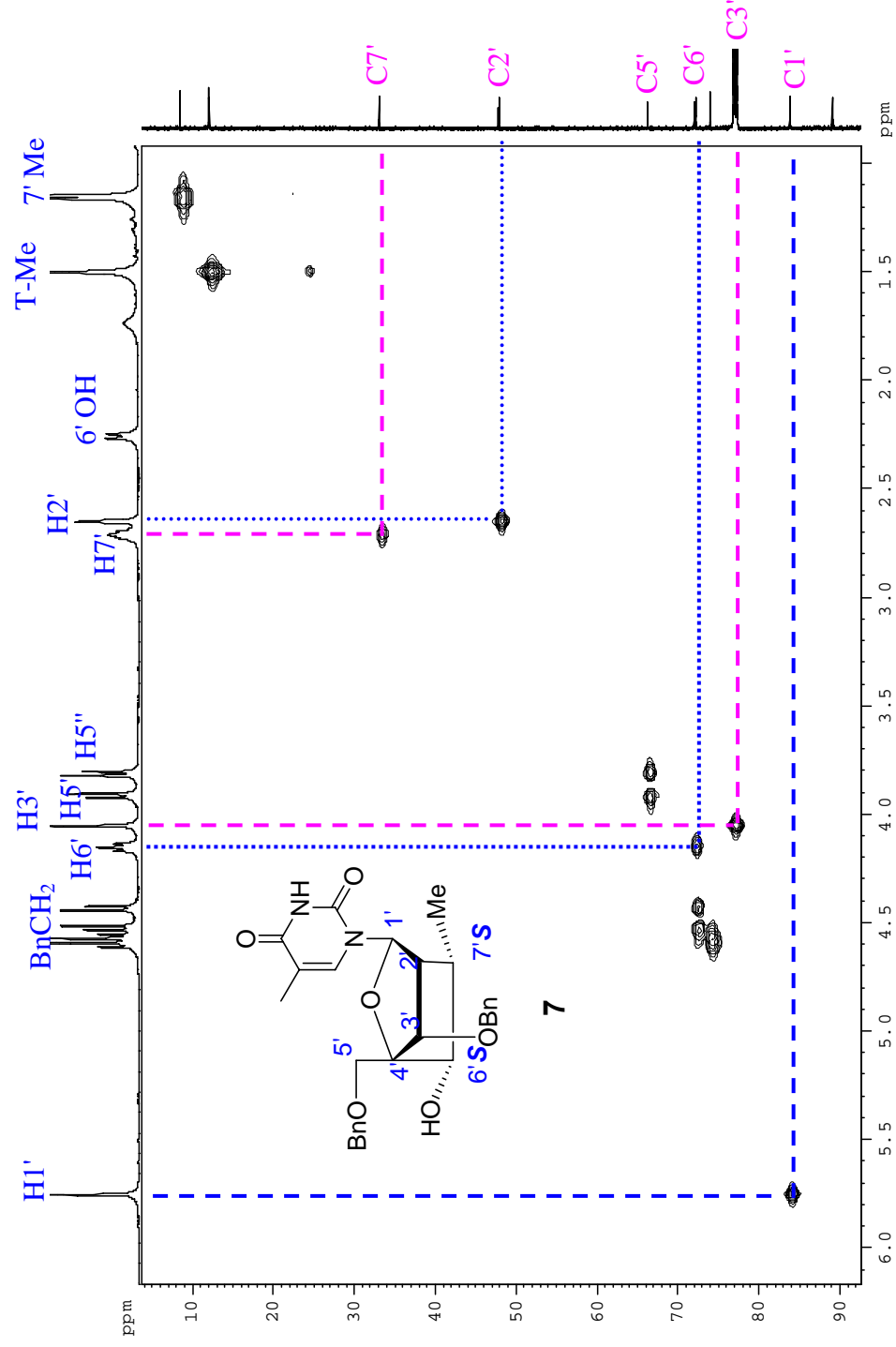


Figure S12. HMBC spectrum of compound 7.

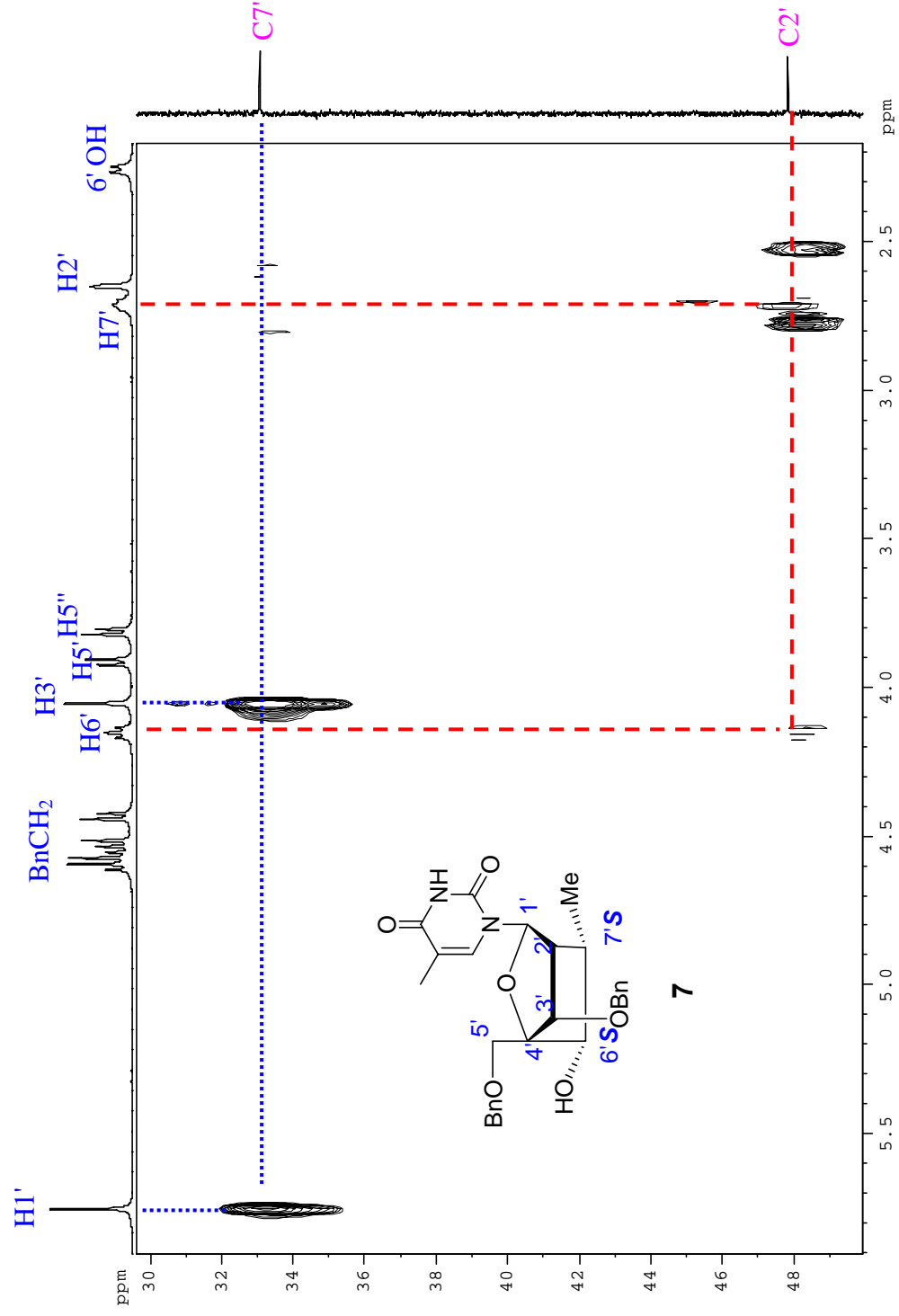


Figure S13. HMBC spectrum of compound 7.

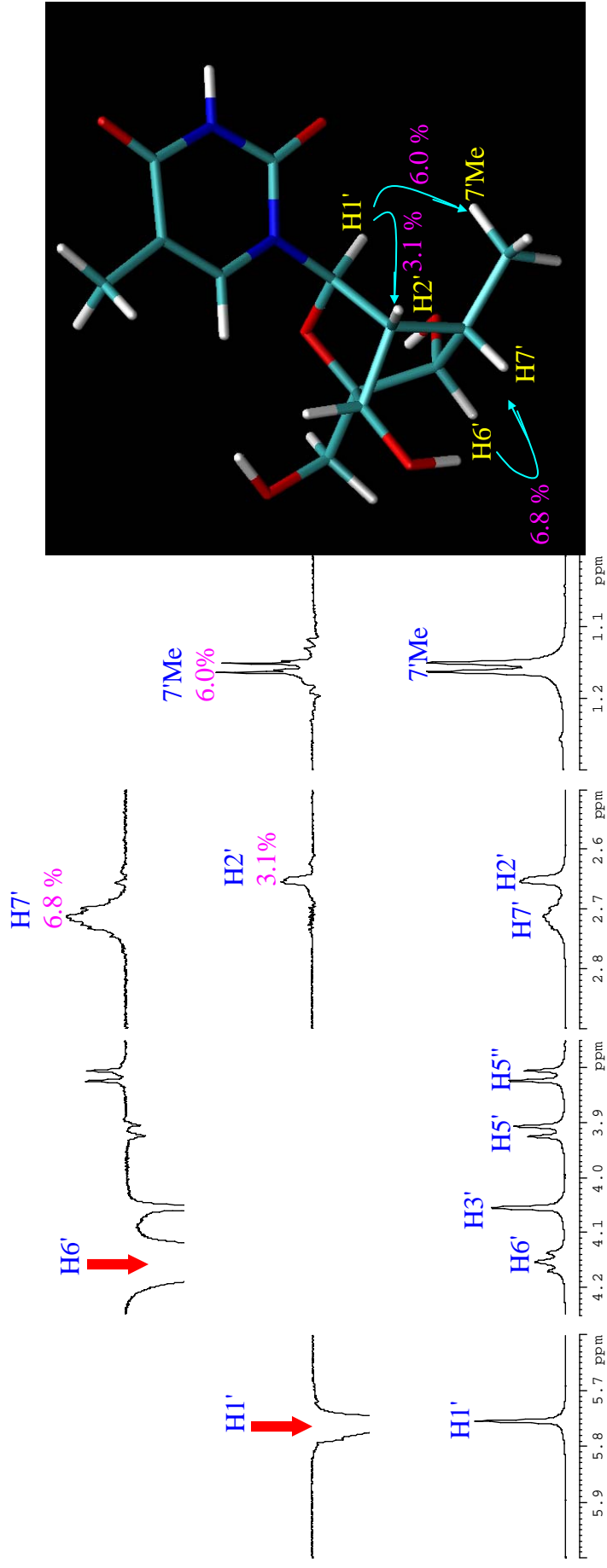


Figure S14. 1D nOe NMR spectrum of compound 7.

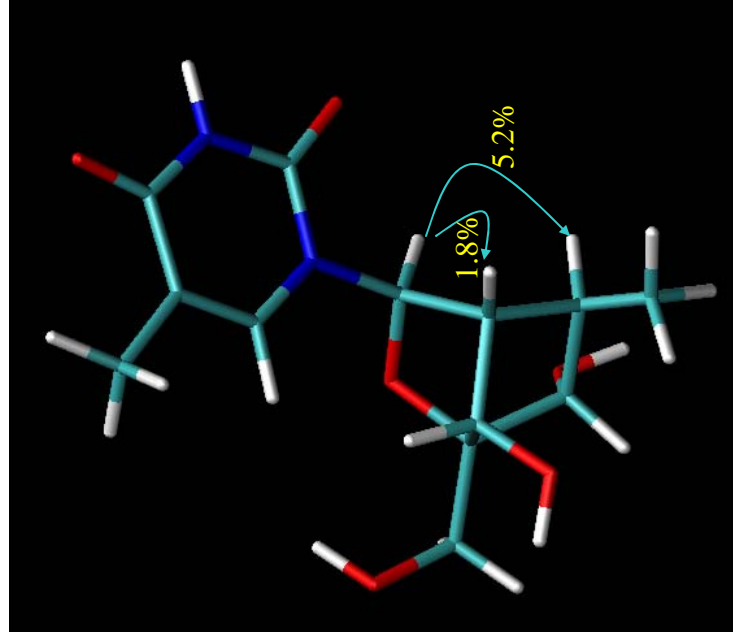
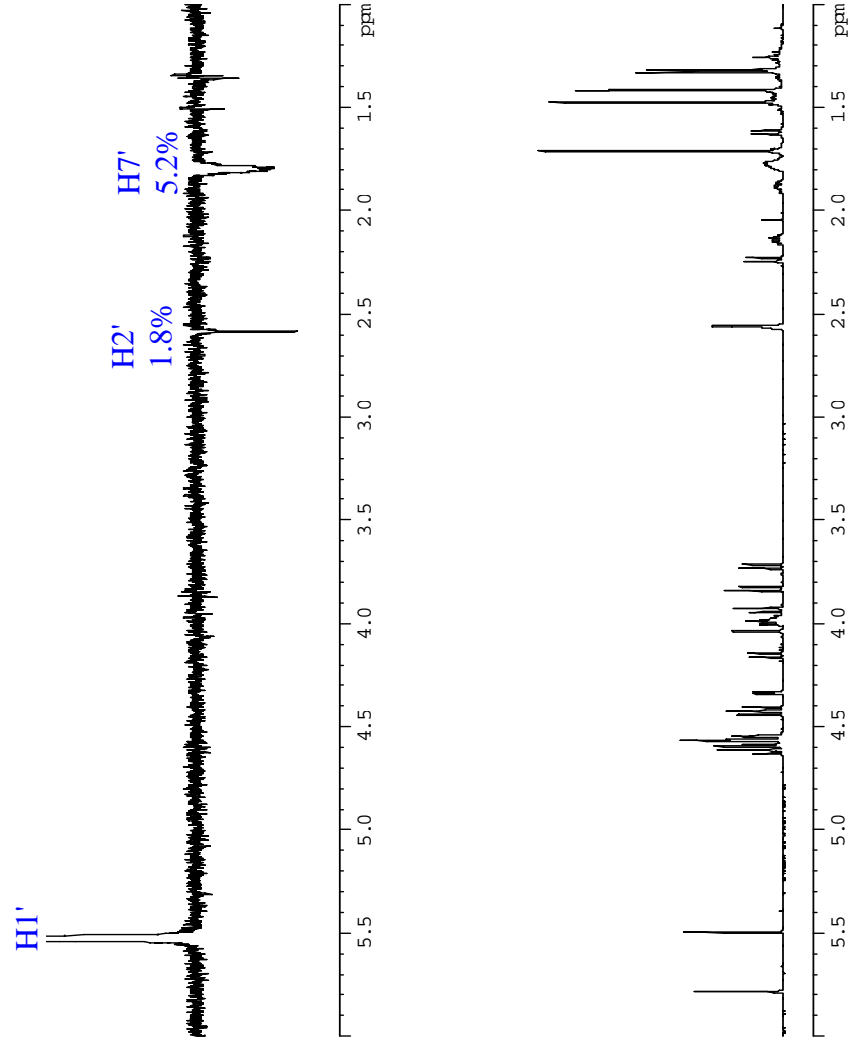


Figure S15. 1D nOe NMR spectrum of compound 8.

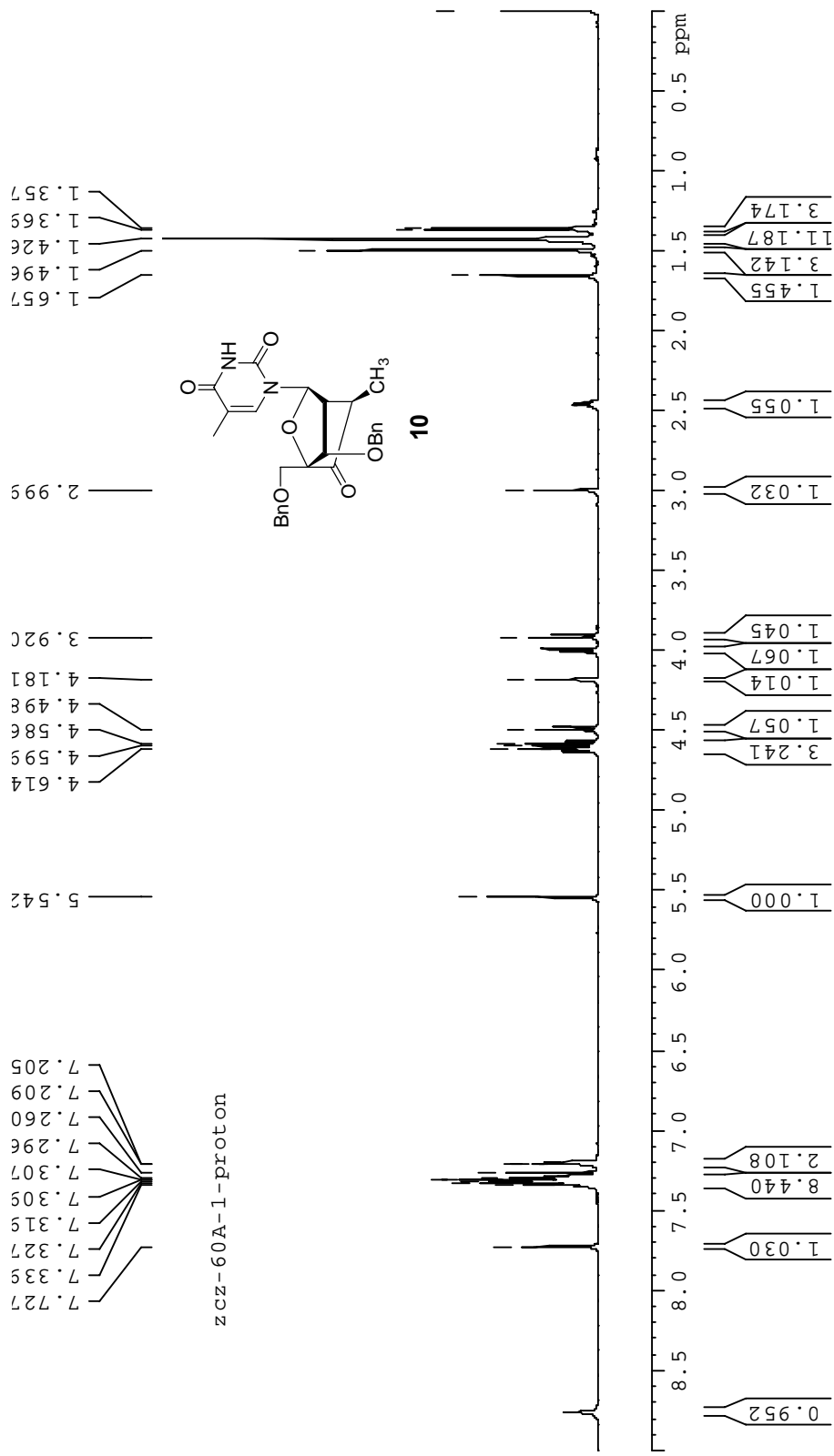


Figure S16. ¹H NMR spectrum of compound 10.

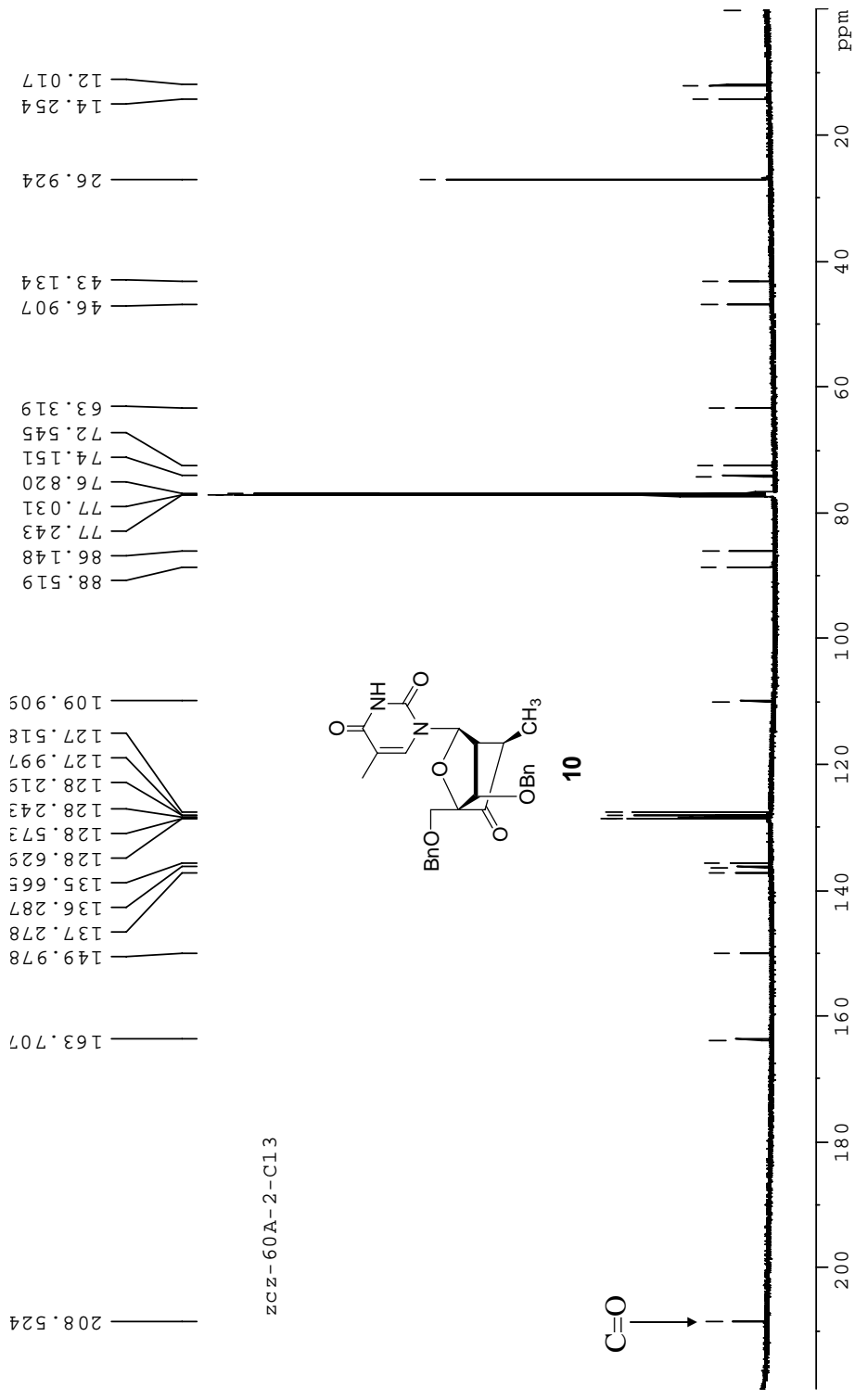
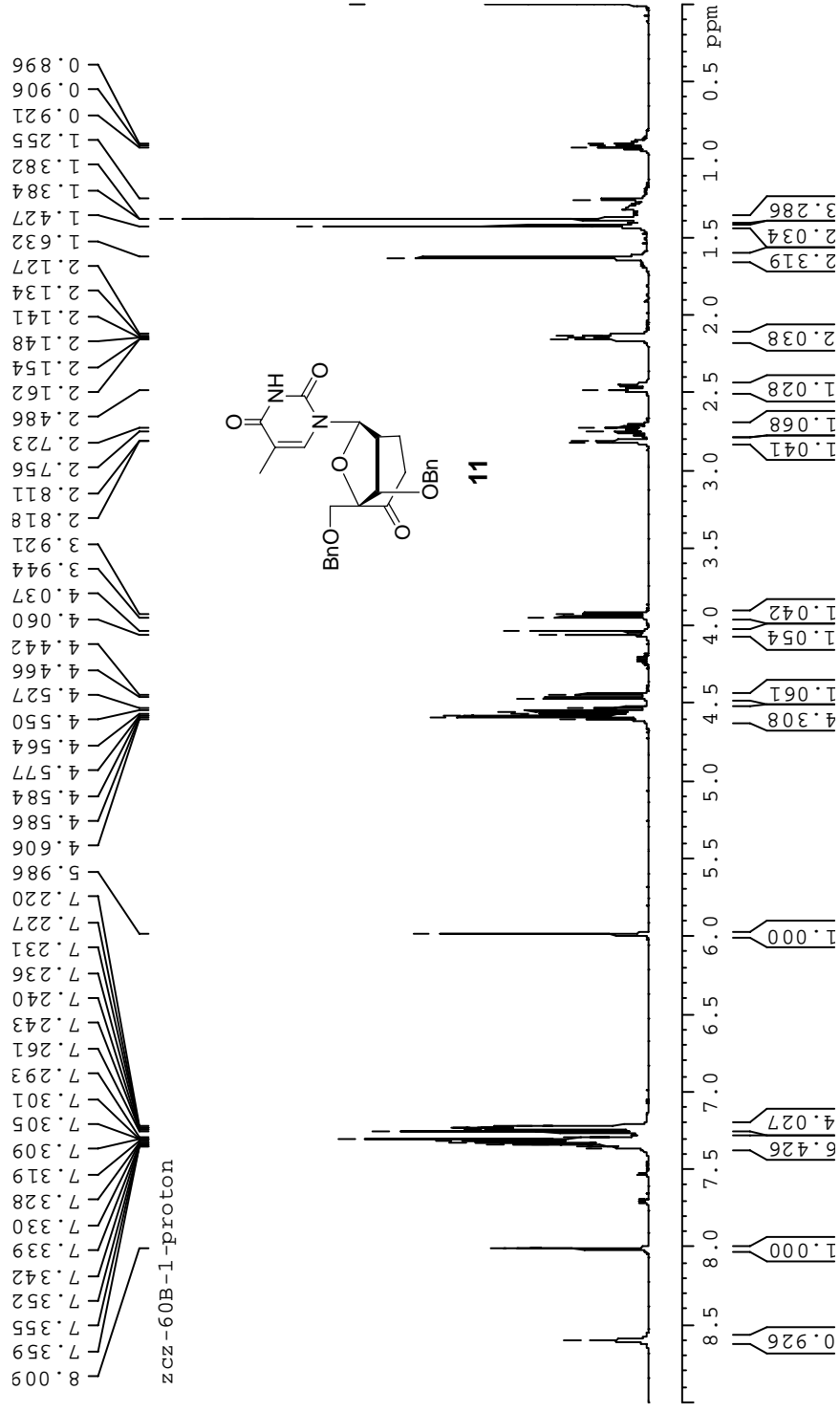


Figure S17. ¹³C NMR spectrum of compound 10.



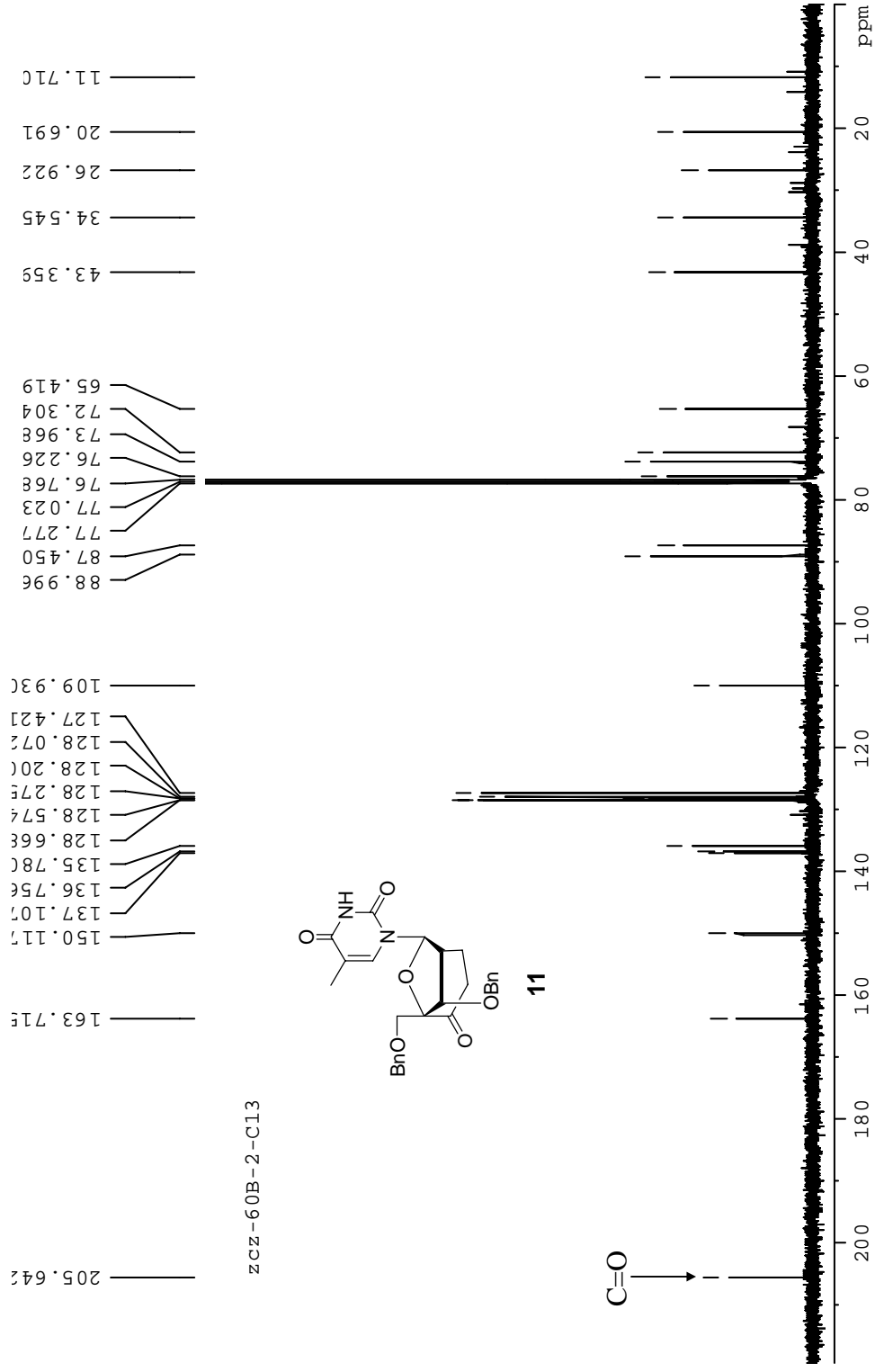


Figure S19. ^{13}C NMR spectrum of compound 11.

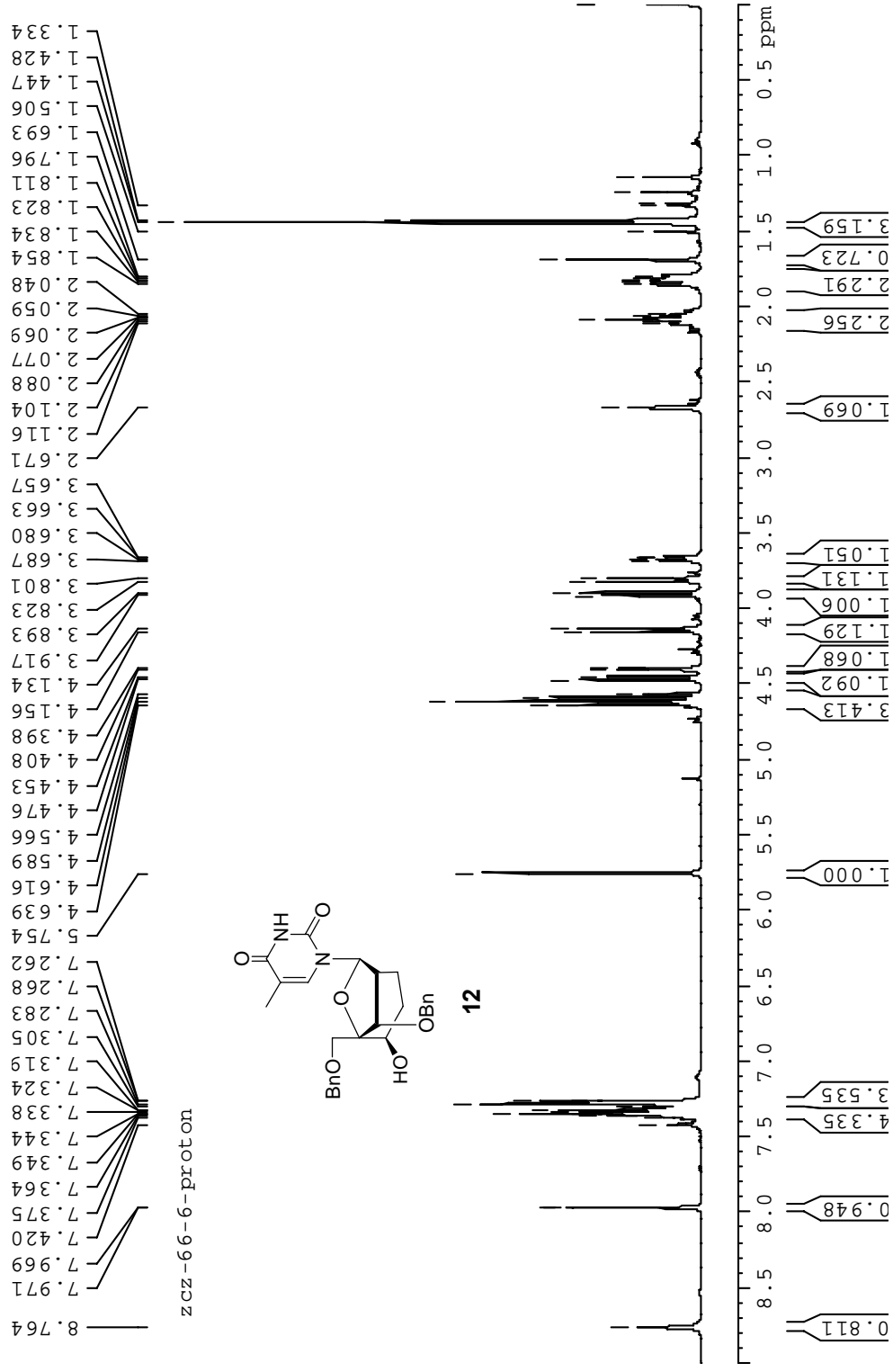


Figure S20. ¹H NMR spectrum of compound 12.

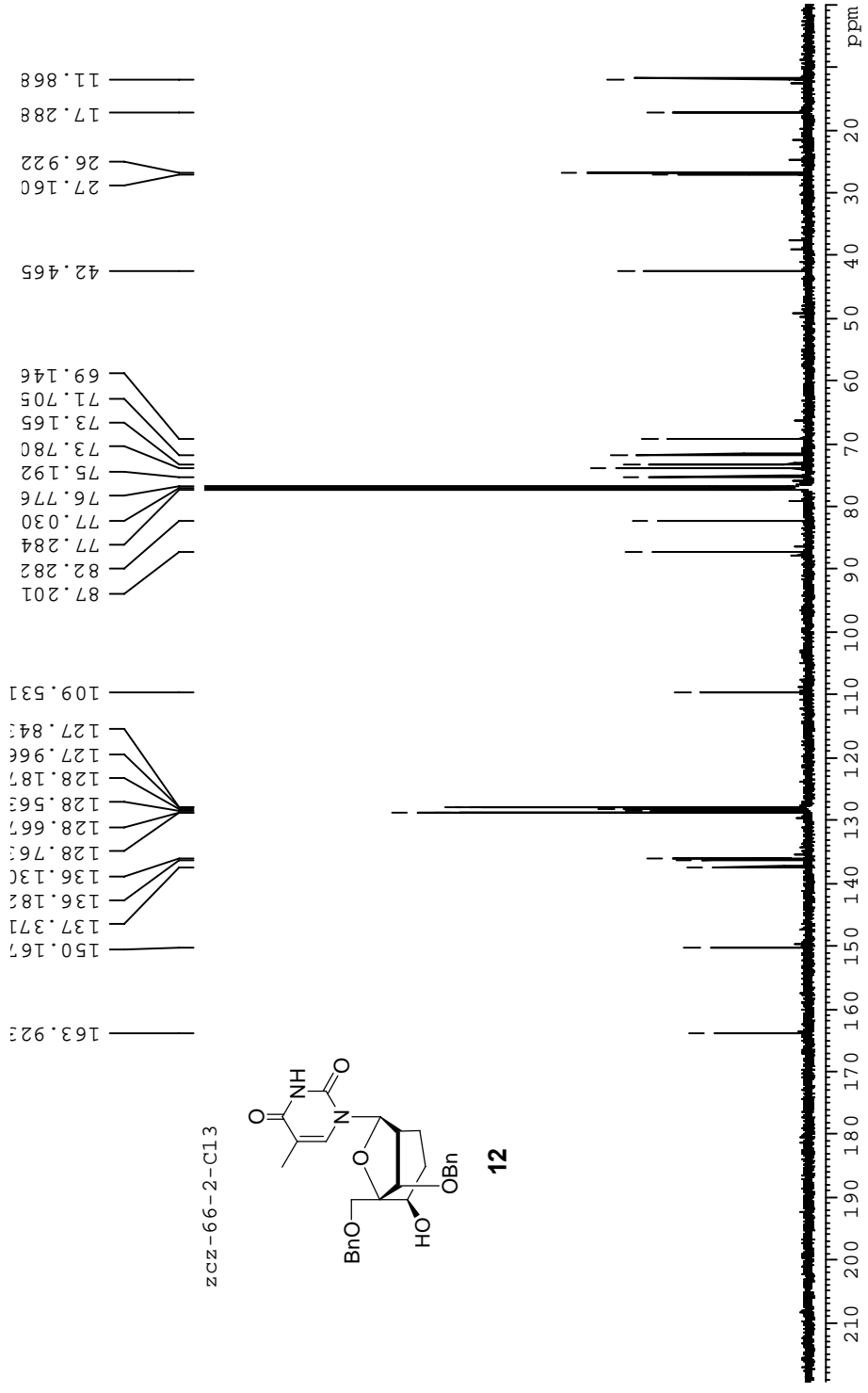


Figure S21. ¹³C NMR spectrum of compound 12.

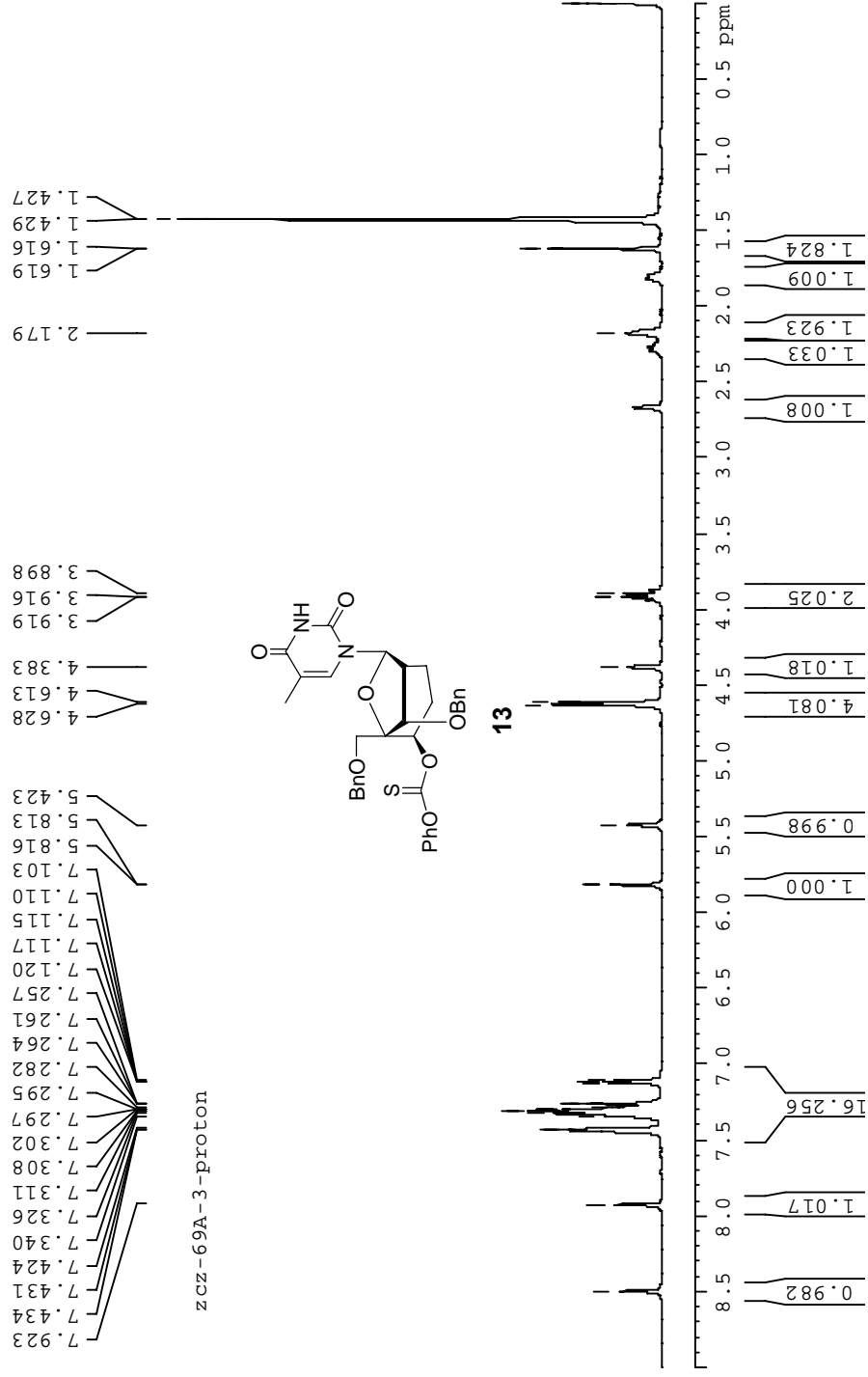


Figure S22. ¹H NMR spectrum of compound 13.

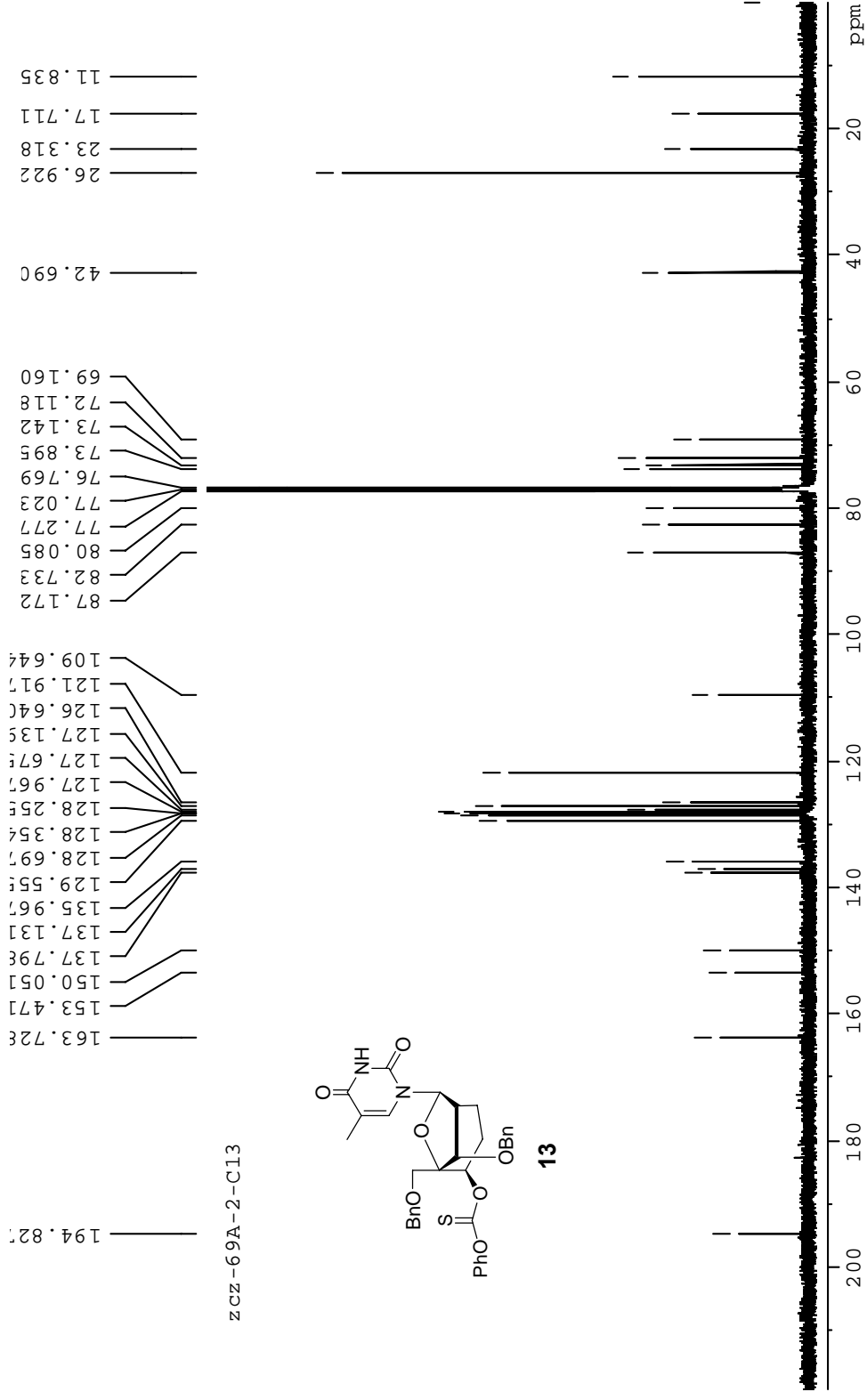


Figure S23. ¹³C NMR spectrum of compound 13.

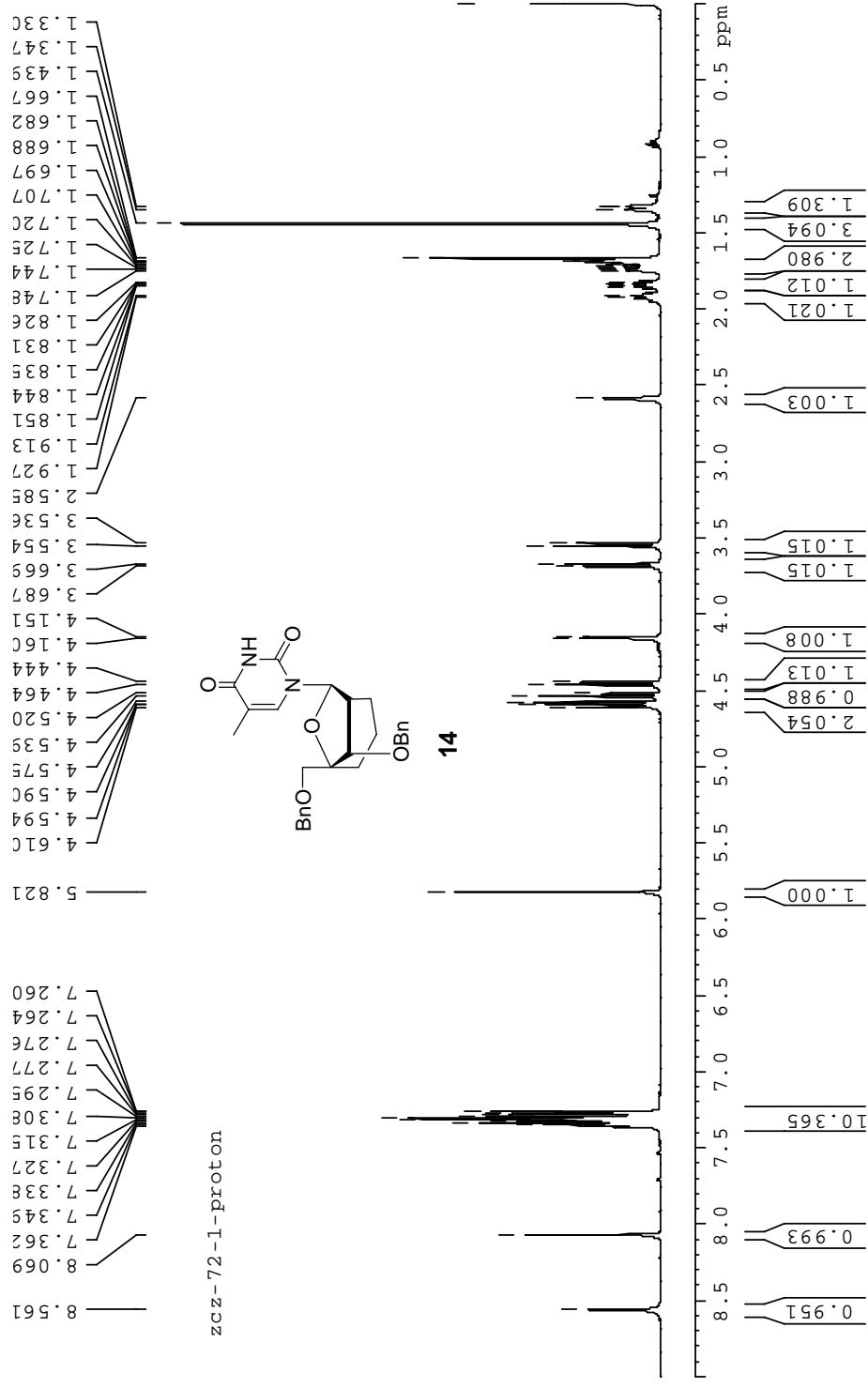


Figure S24. ¹H NMR spectrum of compound 14.

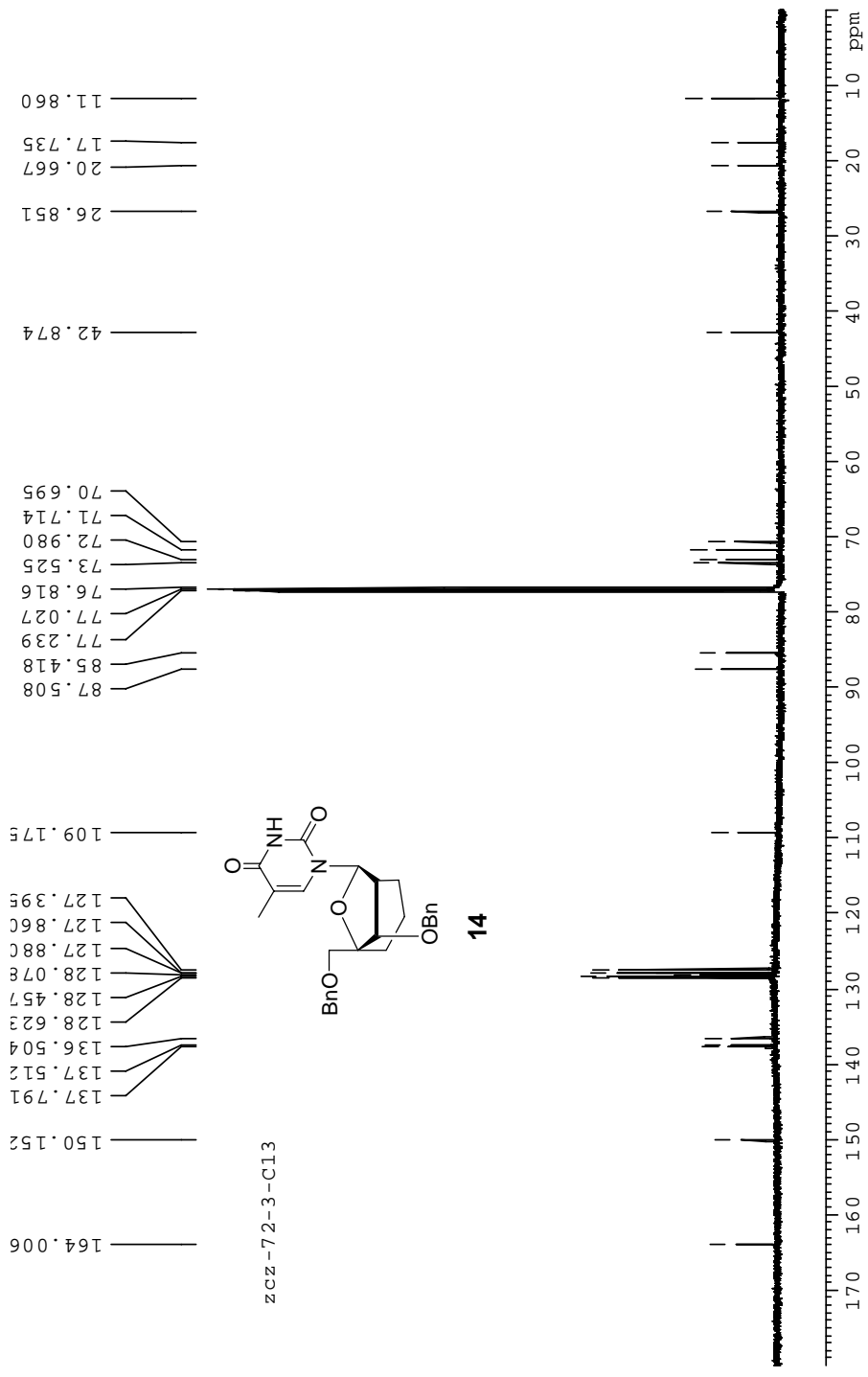


Figure S25. ¹³C NMR spectrum of compound 14.

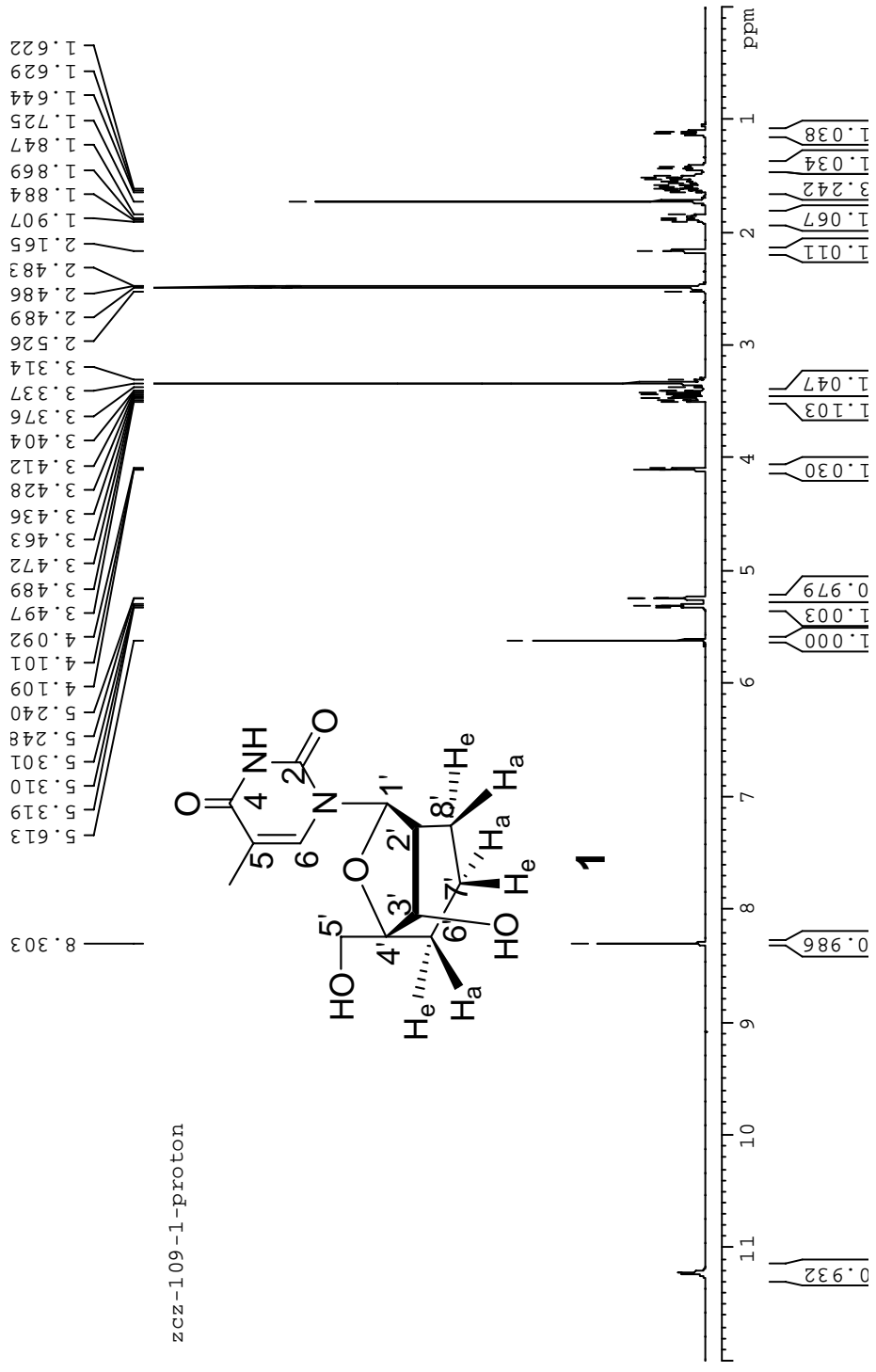


Figure S26. 1H NMR spectrum of compound 1.

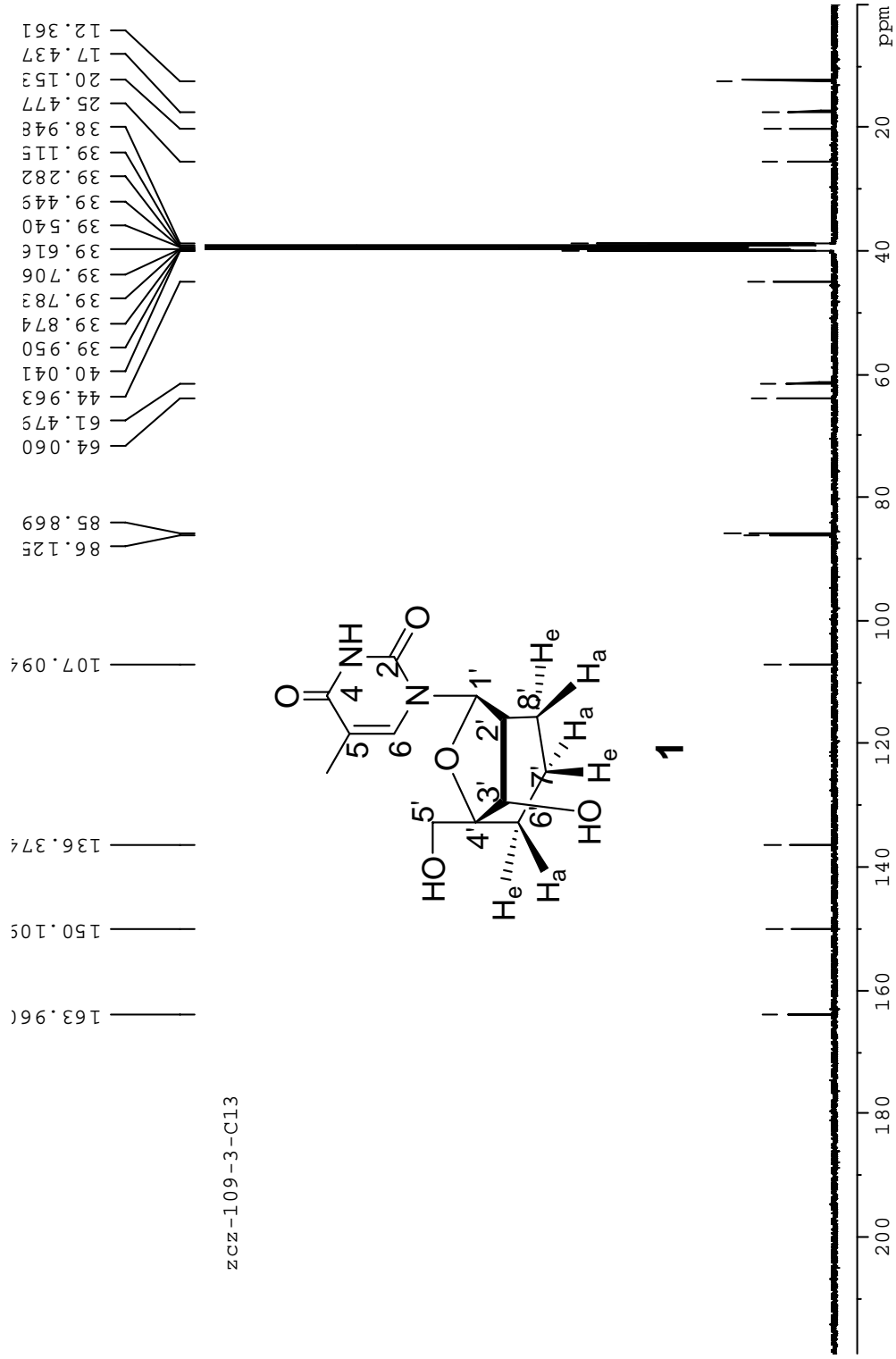


Figure S27. ¹H NMR spectrum of compound 1.

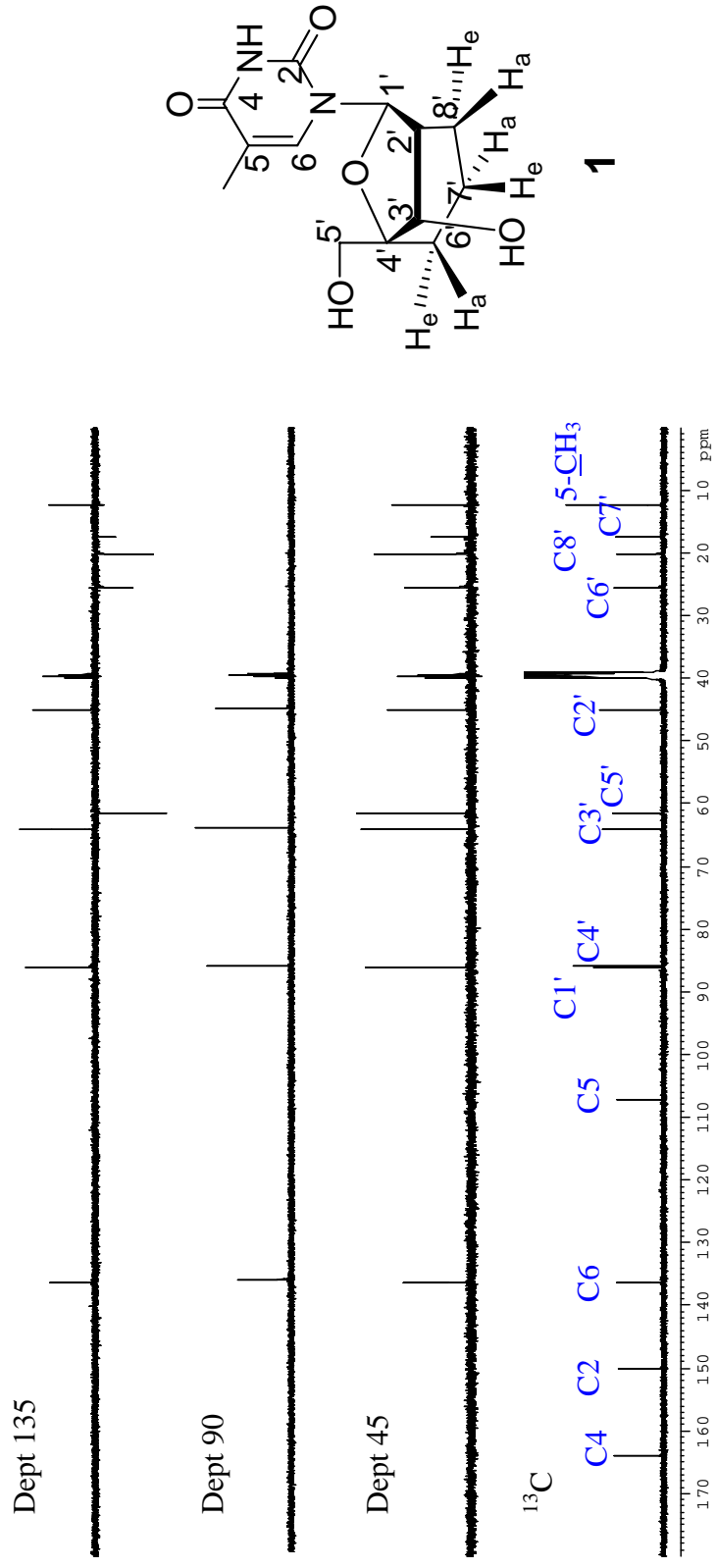


Figure S28. DEPT spectrum of compound **1**.

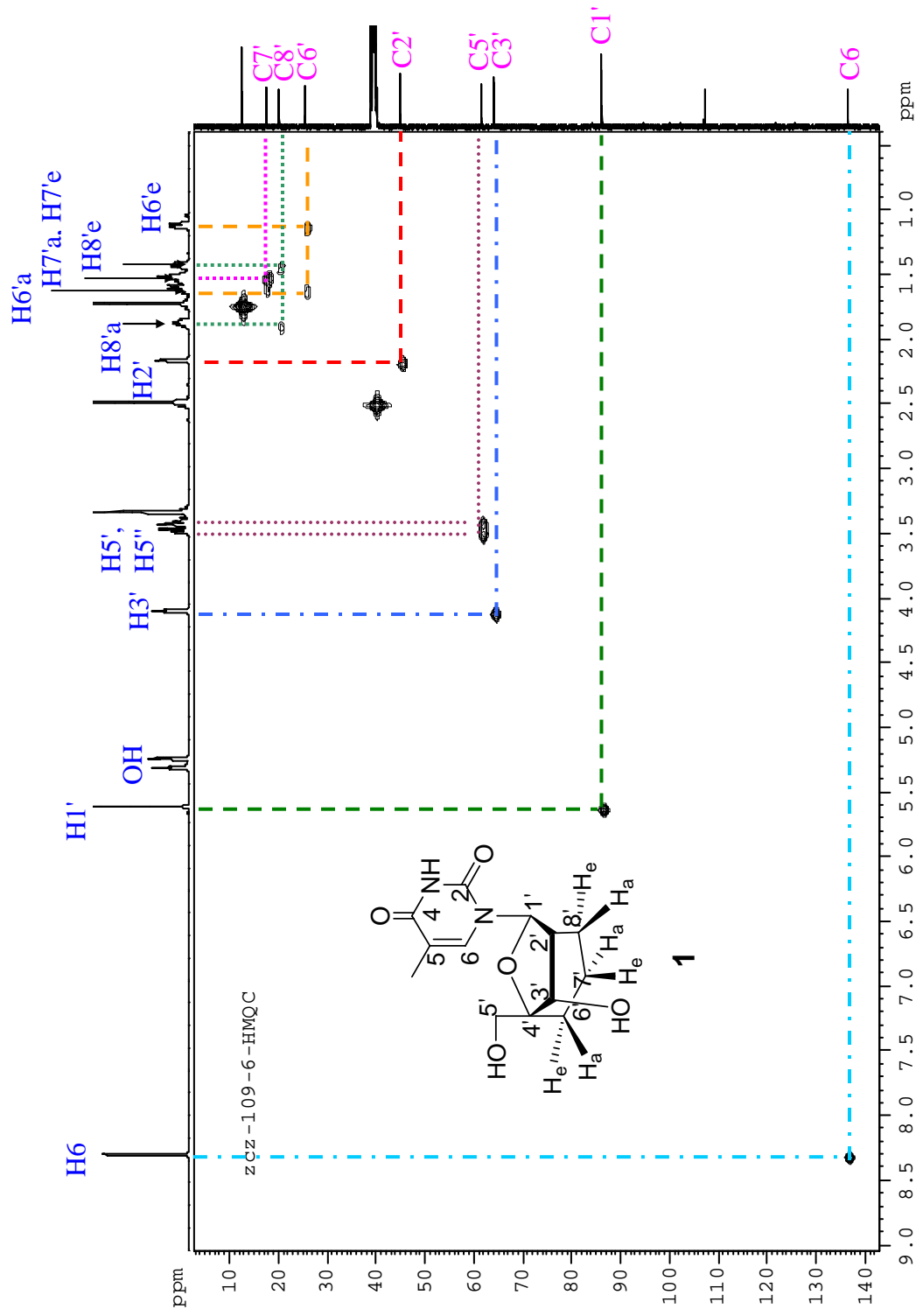


Figure S29. HMQC spectrum of compound 1.

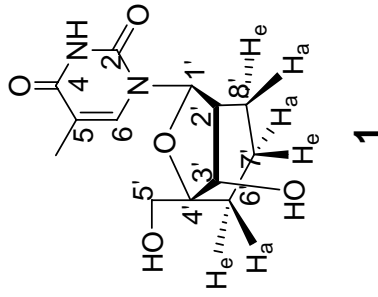
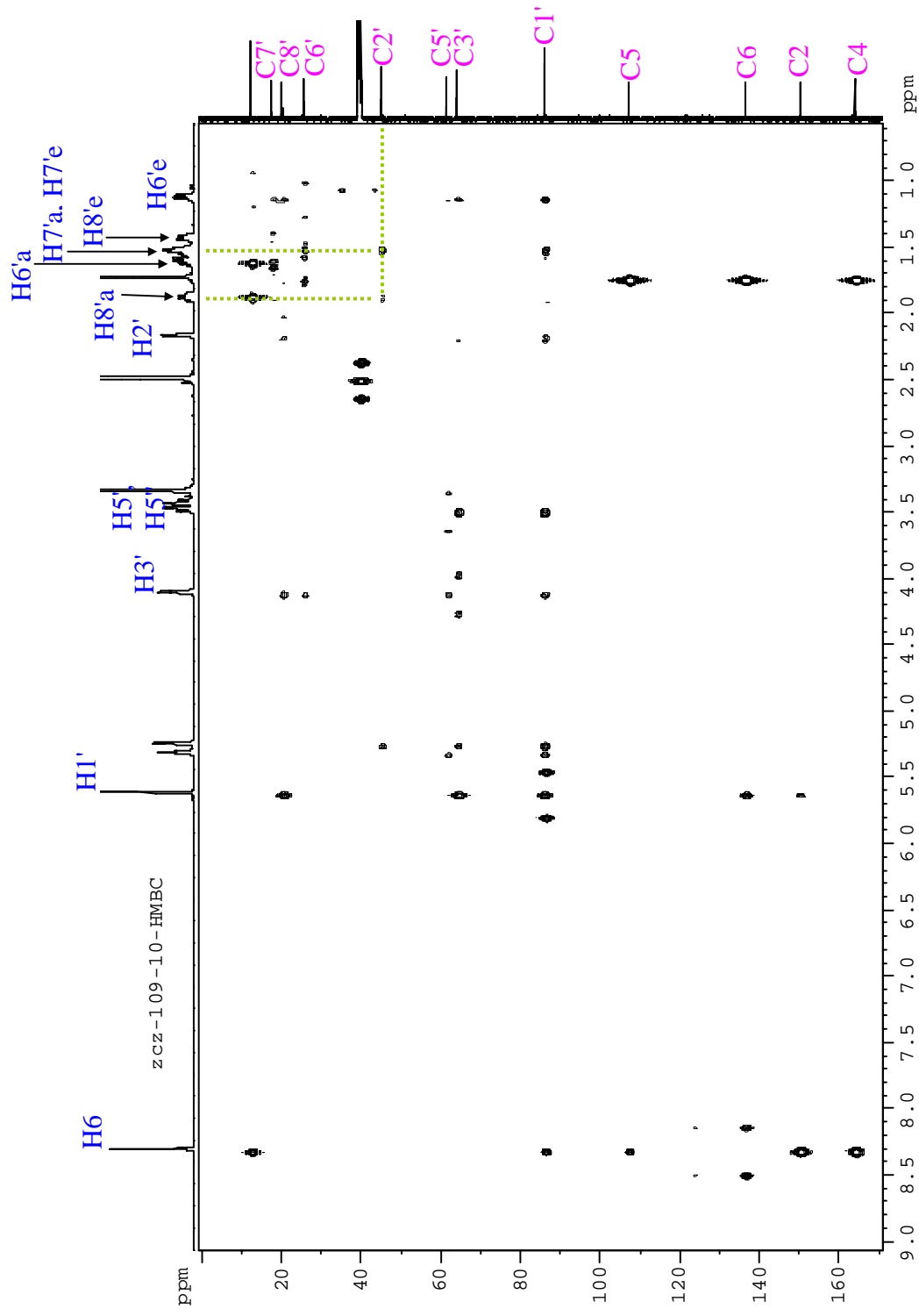


Figure S30. HMBC spectrum of compound 1.

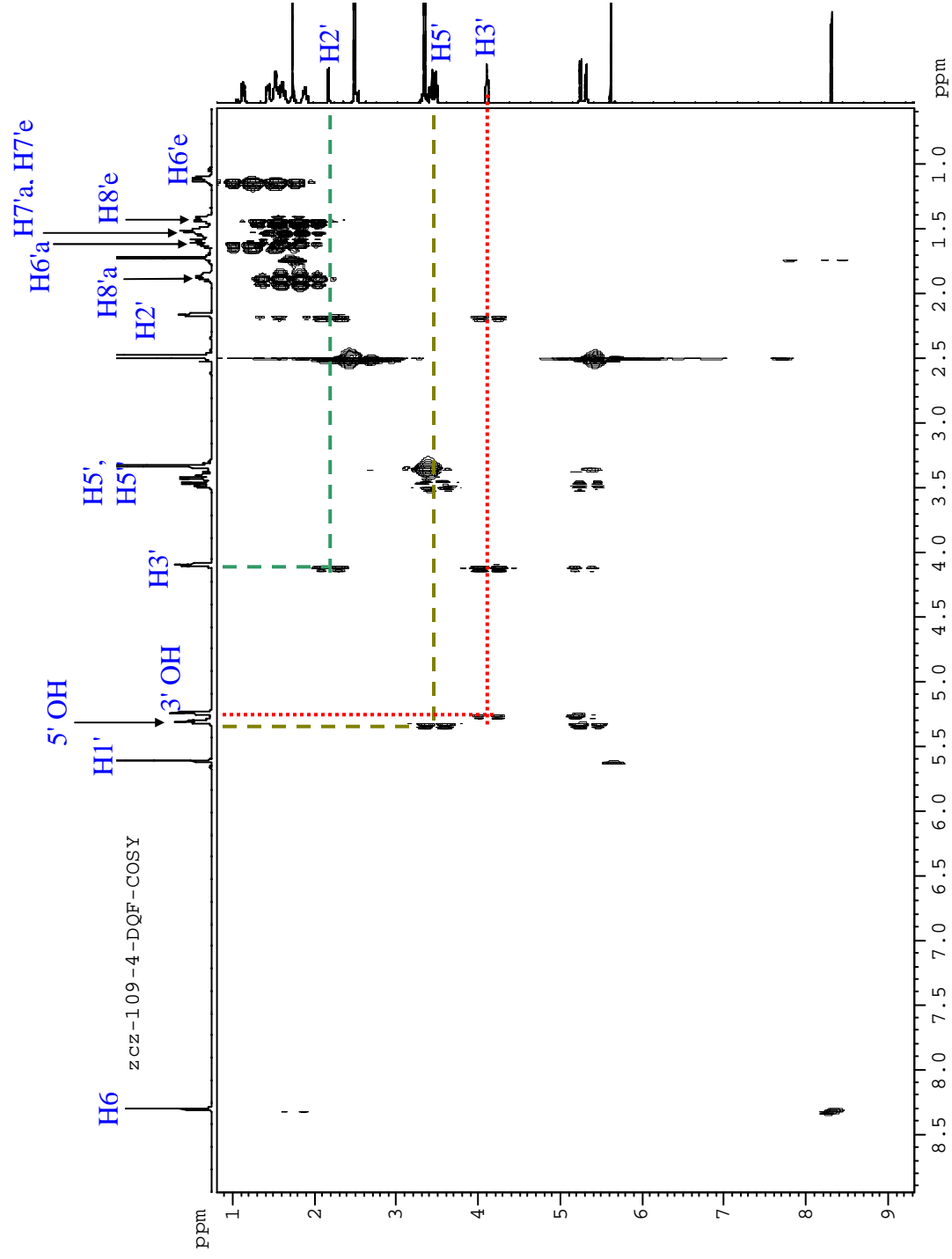


Figure S31. DQF-COSY spectrum of compound 1.

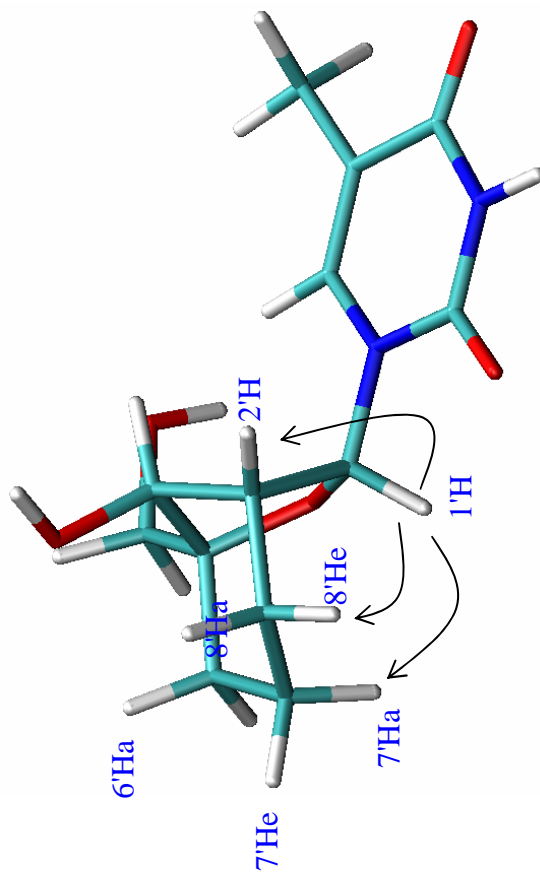
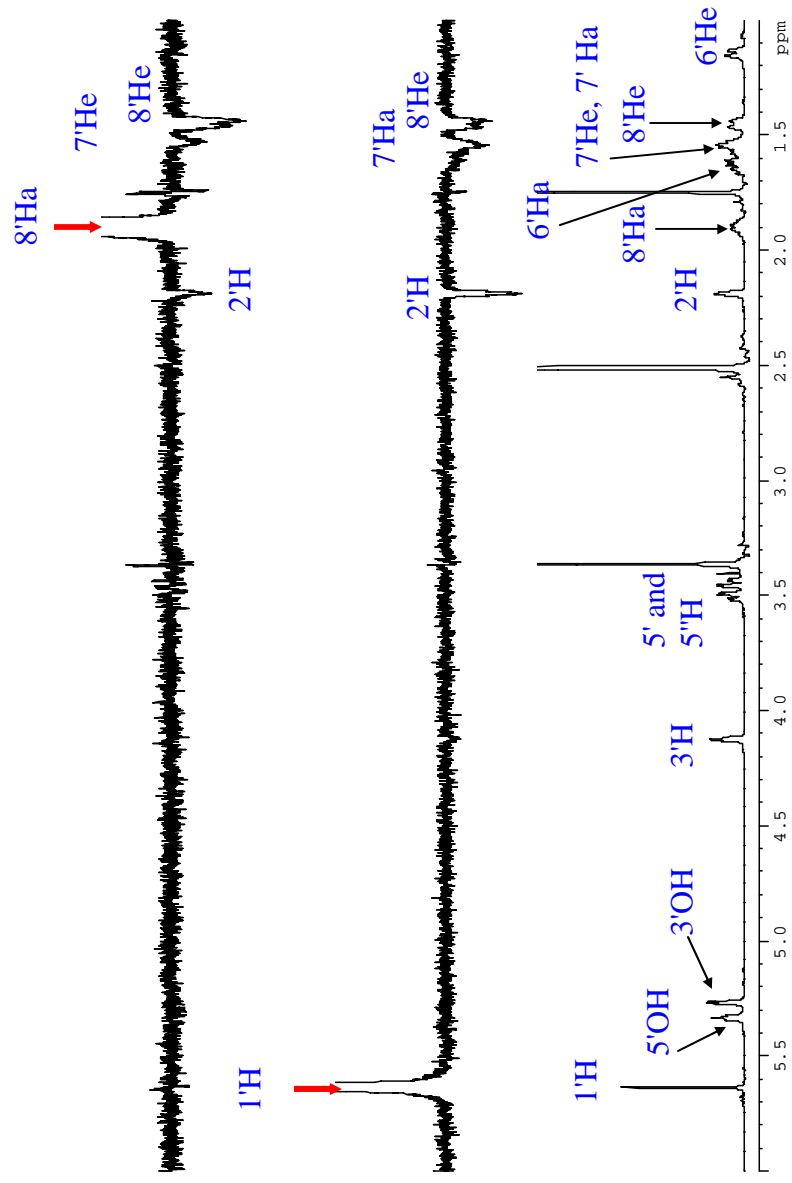
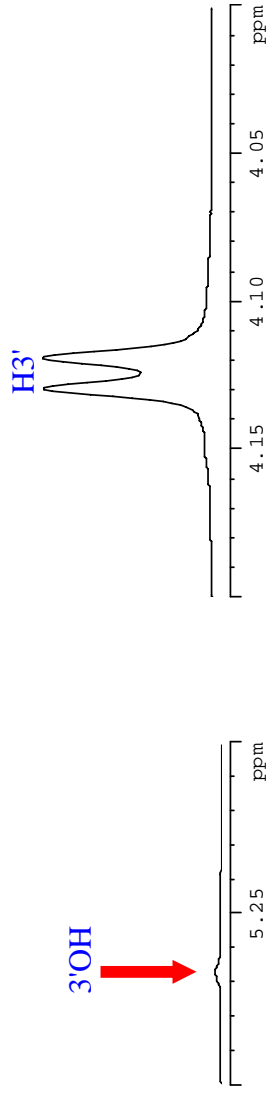
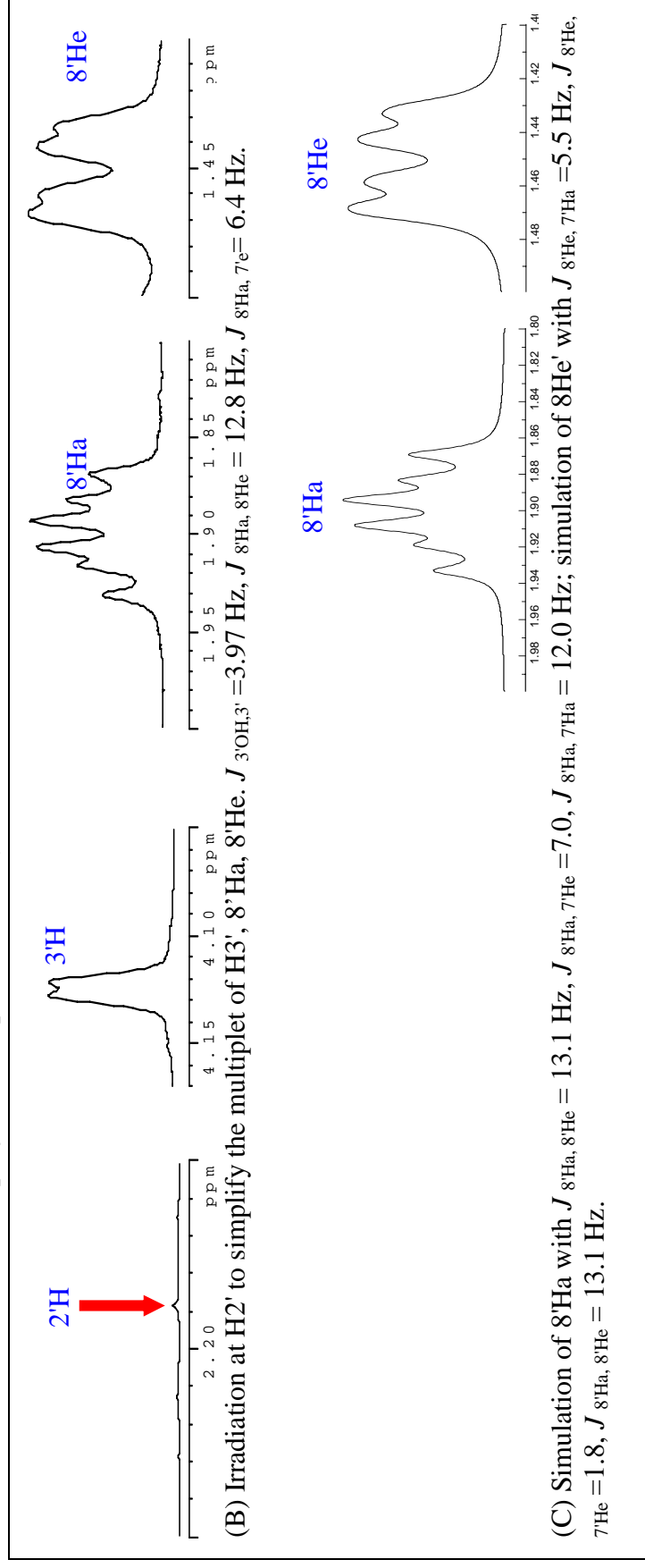


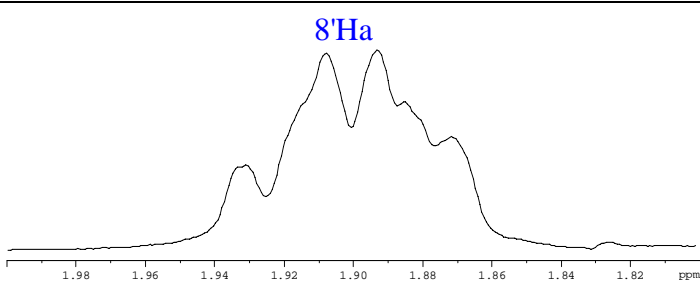
Figure S32. 1D-nOe spectrum of compound 1.

Figure S33. Homodecoupling NMR spectra of compound 1.

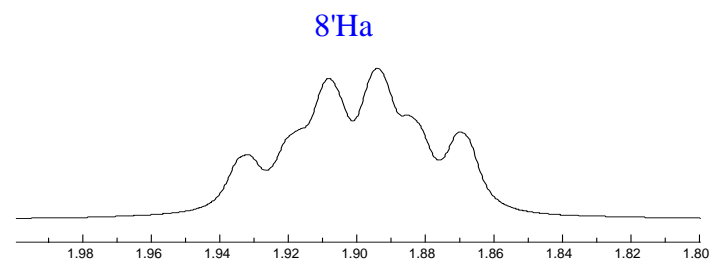


(A) Irradiation at 3'-OH to simplify the multiplet of H3'. $J_{2',3'} = 5.19$ Hz.

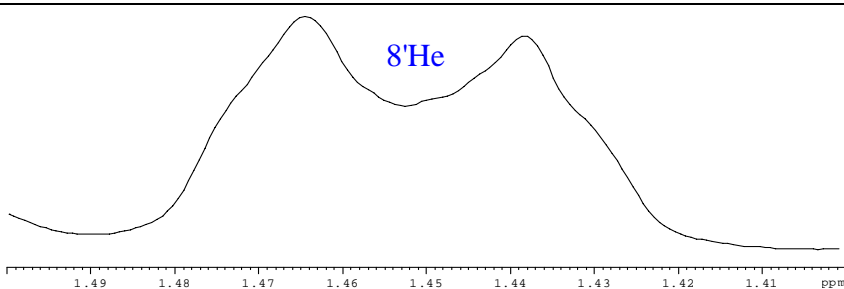




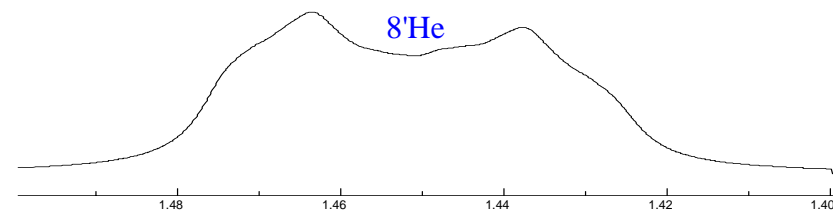
(D) Experimental spectrum of 8' H a.



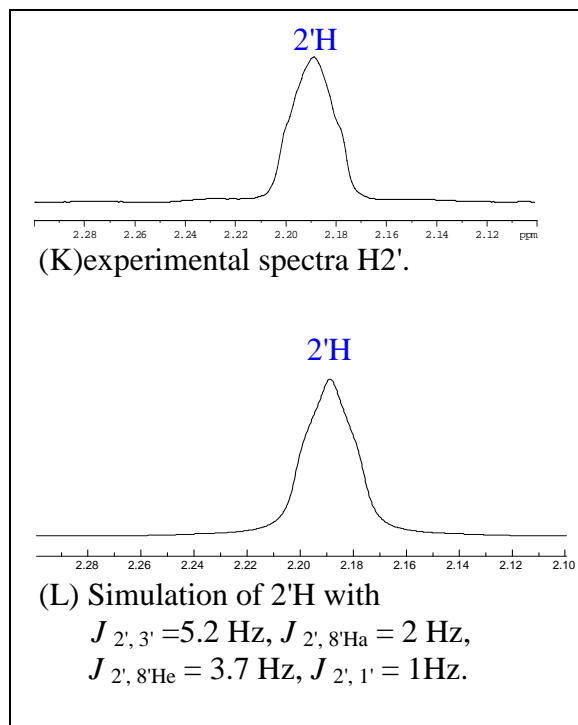
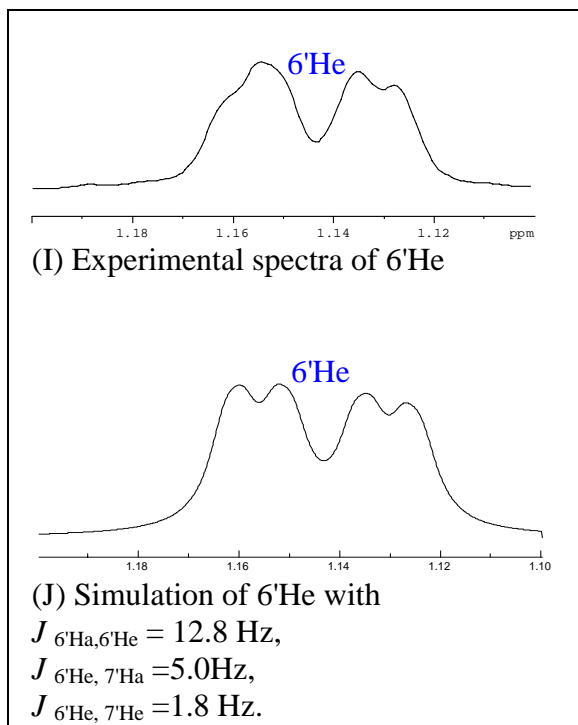
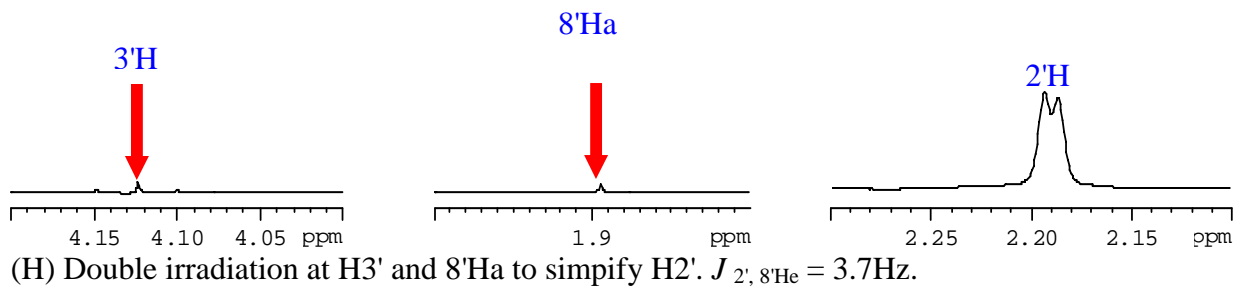
(E) Simulation of 8'H with $J_{8'H_a, 8'He} = 13.1$ Hz, $J_{8'H_a, 7'He} = 7.0$ Hz, $J_{8'H_a, 7'Ha} = 12.0$ Hz, $J_{8'H_a, 2'H} = 2.0$ Hz.

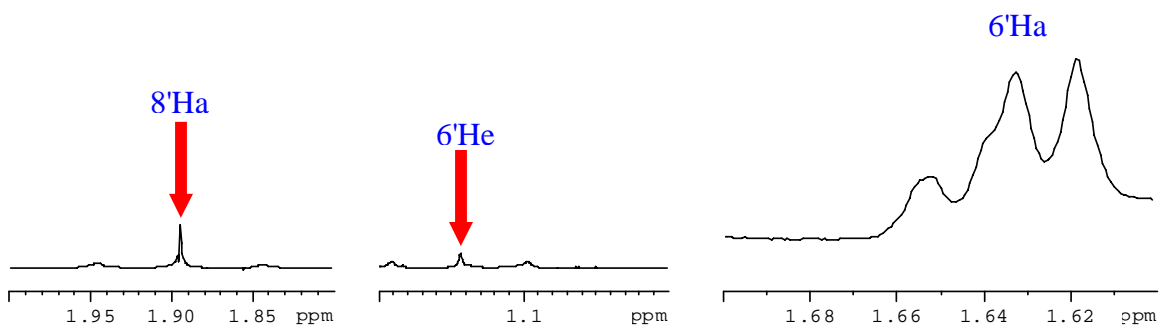


(F) Experimental spectrum of 8' He.

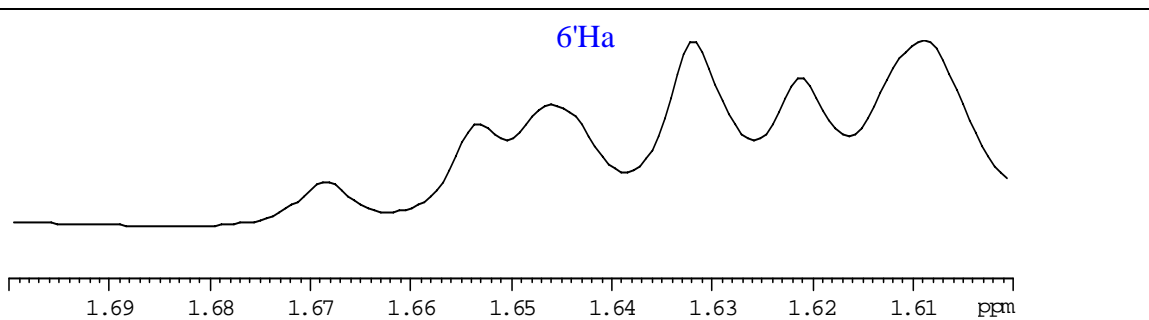


(G) Simulation of H8'Ha with $J_{8'He, 2'H} = 3.7$ Hz, $J_{8'He, 7'Ha} = 5.5$ Hz, $J_{8'Ha, 8'He} = 13.1$ Hz, $J_{8'He, 7'He} = 1.8$ Hz.

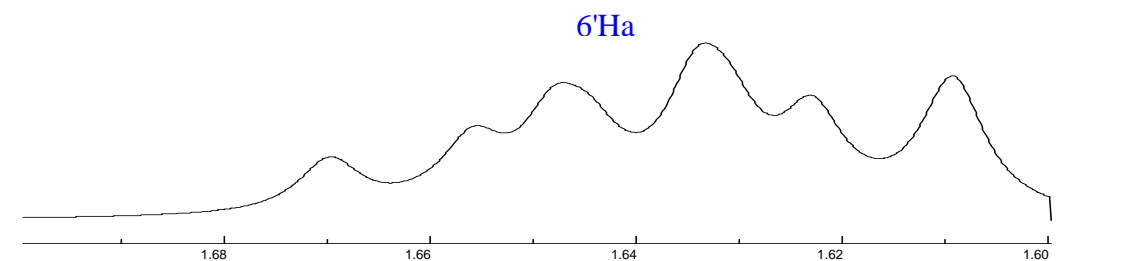




(M) Double irradiation at 8'Ha and 6'He to simplify 6'Ha. $J_{6'Ha,7'Ha} = 7.0$ Hz, $J_{6'Ha,7'He} = 11.0$ Hz.



(N) Experimental spectrum of 6'Ha.



(O) Simulation of 6'Ha with $J_{6'Ha,6'He} = 12.8$ Hz, $J_{6'Ha,7'Ha} = 11.0$ Hz, $J_{6'Ha,7'He} = 7.0$ Hz.

Table S1. Sugar moiety conformation parameters^a of compound 1.

Sugar conformational parameters	1 (carba-ENA T)	carba-ENA U	8'-Me carba-ENA	ENA	Aza-ENA
ν_0 : C4'-O4'-C1'-C2'	-0.96°		-0.7	-1.05	-0.91
ν_1 : O4'-C1'-C2'-C3'	-27.45°		-27.8	-28.10	-28.21
ν_2 : C1'-C2'-C3'-C4'	43.23°		43.5	43.70	43.87
ν_3 : C2'-C3'-C4'-O4'	-44.61°		-45.0	-44.84	-45.14
ν_4 : C3'-C4'-O4'-C1'	29.19°		29.20	28.88	29.65
Phase angle P	19.6	20°	19.4	19.1	19.4
Puckering amplitude Ψ_m:	45.9	46°	47.1	46.3	46.5

^a Obtained from the ab initio (HF/6-31G**) geometry optimization by Gaussian 98 program.

