

Experimental:

Conventional ^1H NMR spectra were measured at 600.13 MHz on a Bruker DRX-600 spectrometer at 300 K using a broad band probe, chemical shifts are given on a δ scale, in ppm, and referenced to the residual solvent signals with resonance at δ ^1H 3.31 and δ ^{13}C 49.15 (CD_3OD). Each compound (*ca* 15 mg) was dissolved in 0.6ml of CD_3OD .

Initial assignments were carried out with the help of ^1H spectra and regular ^{13}C NMR spectra with a ^1H spectral width of 5500 Hz and a ^{13}C spectral width of 24 000 Hz, using 32 K data points (zero filled to 64 K) in each case.

2D ^1H - ^1H COSY spectra were acquired using the following parameters: acquisition time 0.41 s, spectral width 4921 Hz, time domain points 4096, number of transients per increment 08, 256 increments in t1, zero-filling by factors of two and four in t2 and t1 respectively.

The TOCSY (total correlation spectroscopy) data were collected with a sweep width of 4921.2 Hz. The spin-locking field was generated with a 39 μs pulse at a power of 9 dB. A matrix of 4K x 256 was obtained with a mixing time of 50 ms using a MLEV sequence and the data were zero-filled to 4K x 1024. 48 scans were obtained per increment. TPPI phase cycling was used to generate phase sensitive data. The data were processed in both dimensions with a sine bell squared function prior to FT.

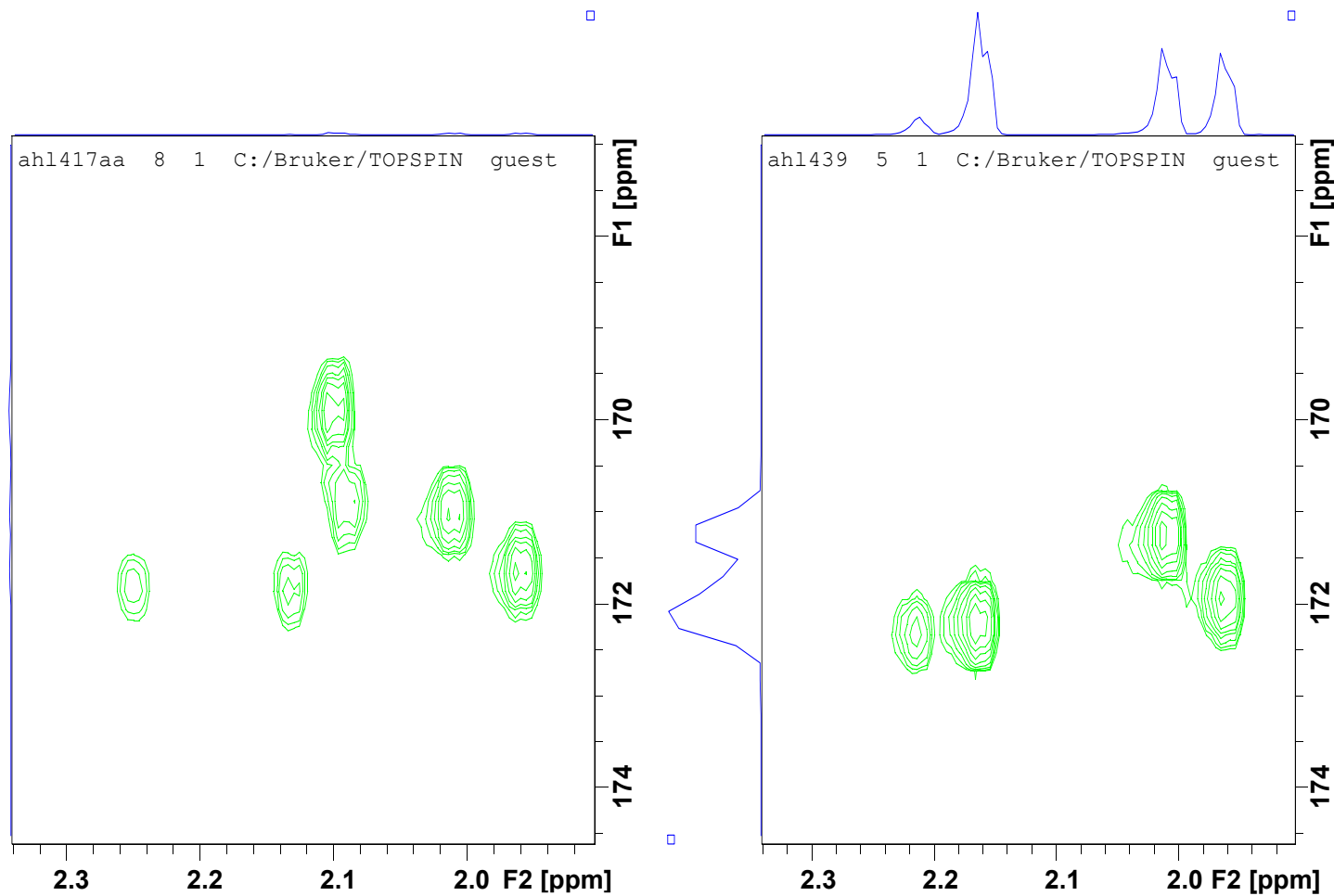
Two-dimensional inverse-detected ^1H - ^{13}C heteronuclear correlation (HSQC) (heteronuclear single quantum correlation) NMR spectra were obtained using 48 transients per increment for 256 increments into 4096 data points covering spectral widths of 4921.2 Hz and 30302 Hz on the ^1H and ^{13}C axes respectively. The HMBC (heteronuclear multiple bond correlation) data were collected with the same sweep width as the HSQC, 96 scans per increment were collected. The $^1\text{J}_{\text{CH}}$ filter was set to 3.44 ms, and the delay for the evolution of the long-range coupling was set to 70 ms. A 3-sine gradient pulse program was employed for the duration of 1 ms each and amplitude of 50%, 30% and 40%.

Table 1: NMR Spectral data for compound **8** at 600 MHz (^1H) and 150 MHz (^{13}C) in CD_3OD

| Position | ^1H | ^{13}C | ^1H - ^1H COSY | HMBC |
|--------------------------|-------------------|-----------------|----------------------------------|-----------------------------|
| Ring I | | | | |
| 1 | 3.61 | 50.60 | 2 (ax, eq) | 3 |
| 2eq | 1.90 | 35.01 | 2ax | 3 |
| 2 ax | 1.57 | | | 1, 3 |
| 3 | 3.60 | 50.23 | 2 (ax, eq) | 1, 154.12 |
| 4 | | 79.77 | 3 | |
| 5 | 3.88 | 83.46 | 4 | 1'', 4, 6 |
| 6 | 4.79 | 76.85 | 1, 5 | 1, 5, 172.4 |
| Ring II | | | | |
| 1' | 5.67 | 98.54 | 2' | |
| 2' | 3.90 | 53.76 | | 5', 4', 2', 171.8 |
| 3' | 5.05 | 73.80 | 2', 4' | |
| 4' | 4.88 | 70.52 | 5' | |
| 5' | 4.08 | 69.76 | 6'ab | |
| 6'a/b | 3.40/3.32 | 41.20 | 6'a/b | |
| Ring III | | | | |
| 1'' | 5.23 | 110.15 | | 5, 3'', 4'' |
| 2'' | 5.14 | 74.98 | 3'' | 4'' |
| 3'' | 4.10 | 76.98 | 4'' | |
| 4'' | 4.00 | 79.77 | 5'' (3.61) | |
| 5'' a/b | 4.29/3.61 | 53.27 | 5'' (3.61) | |
| Ring IV | | | | |
| 1''' | 4.31 | 99.51 | 2''' | 2''', 3'' |
| 2''' | 3.90 | 46.20 | 3''' | 157 |
| 3''' | 3.15 | 52.78 | | 5''', 3''', 157 |
| 4''' | 3.35 | 52.04 | 3''' | 3''', 5''', 2''', 158.94 |
| 5''' | 4.00 | 73.04 | 4''', 6''' | 6''', 4''', 1''' |
| 6''' a/b | 3.35 | 43.42 | | 4''', 5''', 158.94 |
| Thymine moiety | | | | |
| 2 | | 151.37 | | |
| 4 | | 165.50 | | |
| 5 | | 111.27 | | |
| 6 | 7.35 | 143.57 | | 2, 4, C-5Me |
| C-5 Methyl | 2.08 | 13.40 | | 5, 6, 4 |
| Protecting groups | | | | |
| Benzoyl | | | | |
| | | 170.46 (s) | | |
| | | 133.20 (s) | | |
| | 8.06 | 131.73 (d) | | |
| | 7.57 | 130.43 (d) | | |
| | 7.73 | 136.26 (d) | | |
| NHBoc | | | | |
| CH3 | (1.44-1.5) | 29.00 | | (80-81), CH3 |
| C=O | 6 C=O | (150-160) | | |
| C-O | | (80-81) | | |
| Acetyl | | | | |
| CH3 | 4 CH3 (2.21-1.95) | 21.00 | | C=O |
| C=O | 4 C=O | (172.2-172.8) | | |

Table 2: NMR Spectral data for compound **12** at 600 MHz (^1H) and 150 MHz (^{13}C) in CD_3OD

| Position | ^1H | ^{13}C | ^1H - ^1H COSY | HMBC |
|--------------------------|-------------------|-----------------|----------------------------------|-------------------|
| Ring I | | | | |
| 1 | 3.63 | 50.30 | 2 (ax, eq) | 3 |
| 2eq | 1.92 | 35.17 | 2ax | 1 |
| 2 ax | 1.60 | | | |
| 3 | 3.63 | 50.06 | 2 (ax, eq) | |
| 4 | 3.61 | 79.52 | 3 | 3 |
| 5 | 3.89 | 83.02 | 4 | 1'', 4, 6 |
| 6 | 4.82 | 76.89 | 5, 1 | 1, 5, 171.85 |
| Ring II | | | | |
| 1' | 5.67 | 98.43 | 2' | |
| 2' | 3.90 | 53.94 | | 157.25 |
| 3' | 5.06 | 73.66 | 4', 2' | 171.66, 4', 2' |
| 4' | 4.90 | 70.48 | 5' | |
| 5' | 4.08 | 69.8 | 6'ab | |
| 6'a/b | 3.40/3.33 | 41.20 | 6'a, 6'b | |
| Ring III | | | | |
| 1'' | 5.27 | 109.89 | | 5, 3'', 4'' |
| 2'' | 5.23 | 74.94 | 3'' | |
| 3'' | 4.22 | 78.36 | 4'' | |
| 4'' | 4.08 | 79.52 | 5'' (3.71) | |
| 5'' a/b | 4.28/3.71 | 53.20 | 5''a, 5''b, 4'' | |
| Ring IV | | | | |
| 1''' | 4.74 | 99.19 | 2''' | 3'', 2''' |
| 2''' | 3.71 | 49.90 | | |
| 3''' | 4.90 | 70.48 | | |
| 4''' | 4.72 | 67.65 | 5''' | 3'', 170.83 |
| 5''' | 4.01 | 74.02 | 6''' a/b | 4'', 6''' |
| 6''' a/b | 3.31/3.20 | 41.20 | 6''' a/b | 5'', 4'', 158 |
| Thymine moiety | | | | |
| 2 | | 151.50 | | |
| 4 | | 165.54 | | |
| 5 | | 111.51 | | |
| 6 | 7.38 | 143.73 | | 2, 4, C-5 Me, 5'' |
| C-5 Methyl | 2.08 | 13.30 | | 4, 5, 6 |
| Protecting groups | | | | |
| Benzoyl | | | | |
| | | 170.45 (s) | | |
| | | 133.31 (s) | | |
| | 8.05 | 131.76 (d) | | |
| | 7.57 | 130.42 (d) | | |
| | 7.73 | 136.27 (d) | | |
| NHBoc | | | | |
| CH3 | (1.44-1.50) | 29.24 | | (80-81), CH3 |
| C=O | | (150-160) | | |
| C-O | | (80-81) | | |
| Acetyl | | | | |
| CH3 | 6 CH3 (2.25-1.96) | 21.00 | | C=O |
| C=O | 6 C=O | (170.00-171.87) | | |



Portion of the 2D HMBC spectrum of 8 and 12 : Correlations between the acetate methyl groups with their corresponding carbonyls (C=O) indicate the presence of 6 acetate groups for 12 and 4 for 8, respectively.