Determining Relative Proton-Proton Proximities from the Build-up of Two-Dimensional Correlation Peaks in ^{1}H Double-Quantum MAS NMR: Insight from Multi-Spin Density-Matrix Simulations: *Supplementary Information*

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S1 Representative SPINEVOLUTION files

Main input file

```
****** The System *********************
spectrometer(MHz)  500
spinning_freq(kHz) 12.5
channels           H1
nuclei             H1 H1 H1 H1 H1 H1 H1 H1
atomic_coords      dipeptide_8spin_h6.cor
cs_isotropic       12.9 7.5 7.5 7.5 7.5 4.1 2.7 2.2 ppm
csa_parameters     chasp.csa
j_coupling         *
quadrupole         *
dip_switchboard    on_8.dsw on_8.dsw off_8.dsw on_8.dsw on_8.dsw
csa_switchboard    *
exchange_nuclei    (2 3 5)
bond_len_nuclei    *
bond_ang_nuclei    *
tors_ang_nuclei    *
groups_nuclei      *
******* Pulse Sequence *****************************
CHN 1
timing(usec)       (1element.seq)  0  (80)1024  (1element.seq)  0.25
power(kHz)         *               0  0         *               1000
phase(deg)         *               0  0         *               270
freq_offs(kHz)     *               0  0         *               0
*************************VARIABLES**********************
select_2 = rowmatrix("-2")
******* Options etc ************************************
rho0               F1z
observables        I6p
EulerAngles        zcw34
n_gamma            16
line_broaden(Hz)   10
zerofill           *
FFT_dimensions     *
```

dipeptide_8spin_h6.cor

```
6.26943  2.54043  16.62039  H1 (molecule B)
3.74518  1.59953  16.10280  H2 (molecule A)
4.31689  0.72449  15.08679  H3 (molecule A)
5.37310  5.42899  13.66821  H3 (molecule C)
2.91184  1.00676  15.02928  H4 (molecule A)
4.92252  2.84152  14.55003  H6 (Observe)
2.86824  2.06057  12.78639  H7 (molecule A)
4.26844  1.39253  12.76722  H8 (molecule A)
```

chasp.csa

```
1     24.4  0.2   28    171   252
2     20.4  0.2   351   59    48
3     20.4  0.2   99    140   178
4     20.4  0.2   303   10    282
5     20.4  0.2   241   23    325
6     -8.0  0.9   243   83    277
7     -5.8  0.8   201   119   177
8     5.7   0.7   13    20    23
```

NB: Randomly chosen arbitrary orientations of the CSA tensors were considered in the simulations.

on.dsw

```
*
1 *
1 1 *
1 1 1 *
1 1 1 1 *
1 1 1 1 1 *
1 1 1 1 1 1 *
1 1 1 1 1 1 1 *
```

off.dsw

```
*
0 *
0 0 *
0 0 0 *
0 0 0 0 *
0 0 0 0 0 *
0 0 0 0 0 0 *
0 0 0 0 0 0 0 *
```

1element.seq

```
2.857  87.5 51.43  0
11.429 87.5 231.43 0
8.571  87.5 51.43  0
```

S2 Simulated ^{1}H DQ build-up curves showing the effect of not including the ^{1}H CSAs

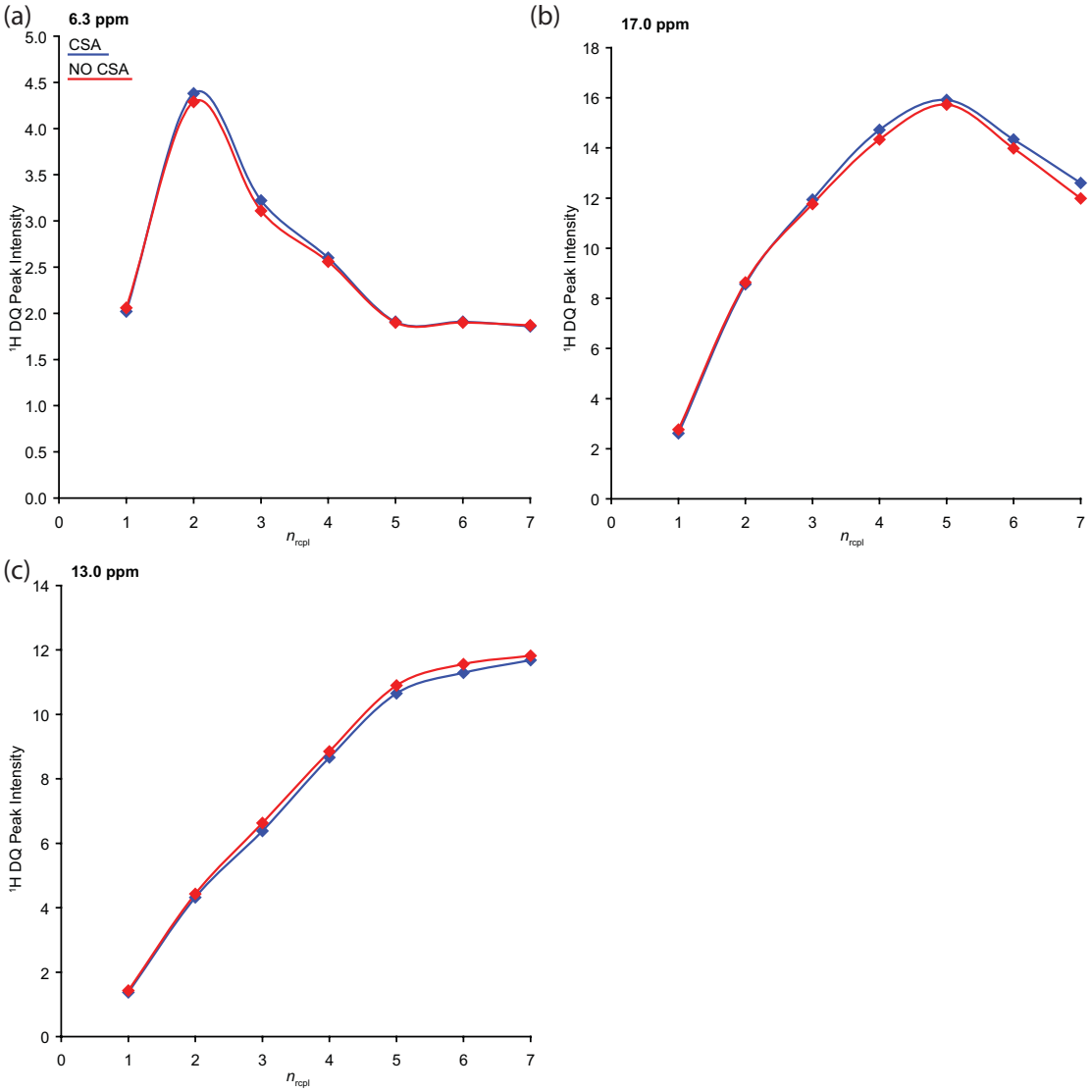

Fig. S2 Simulated ^{1}H DQ build-up curves of (a) the CH(Asp) – CH_2(a) peak at δ_{DQ} = 4.1 + 2.2 = 6.3 ppm, (b) the CH(Asp) – OH peak at δ_{DQ} = 4.1 + 12.9 = 17.0 ppm and (c) the NH – CH(Ala) peak at δ_{DQ} = 8.0 + 5.0 = 13.0 ppm. The blue and red curves correspond to eight-spin SPINEVOLUTION simulations in which the CSA interactions are and are not considered, respectively. Lines linking the diamonds corresponding to simulated DQ peak intensities are included as guides for the eye. The DQ peak intensities are in arbitrary units.

S3 Simulated ^{1}H DQ build-up curves showing the effect of decreasing the minimum time interval

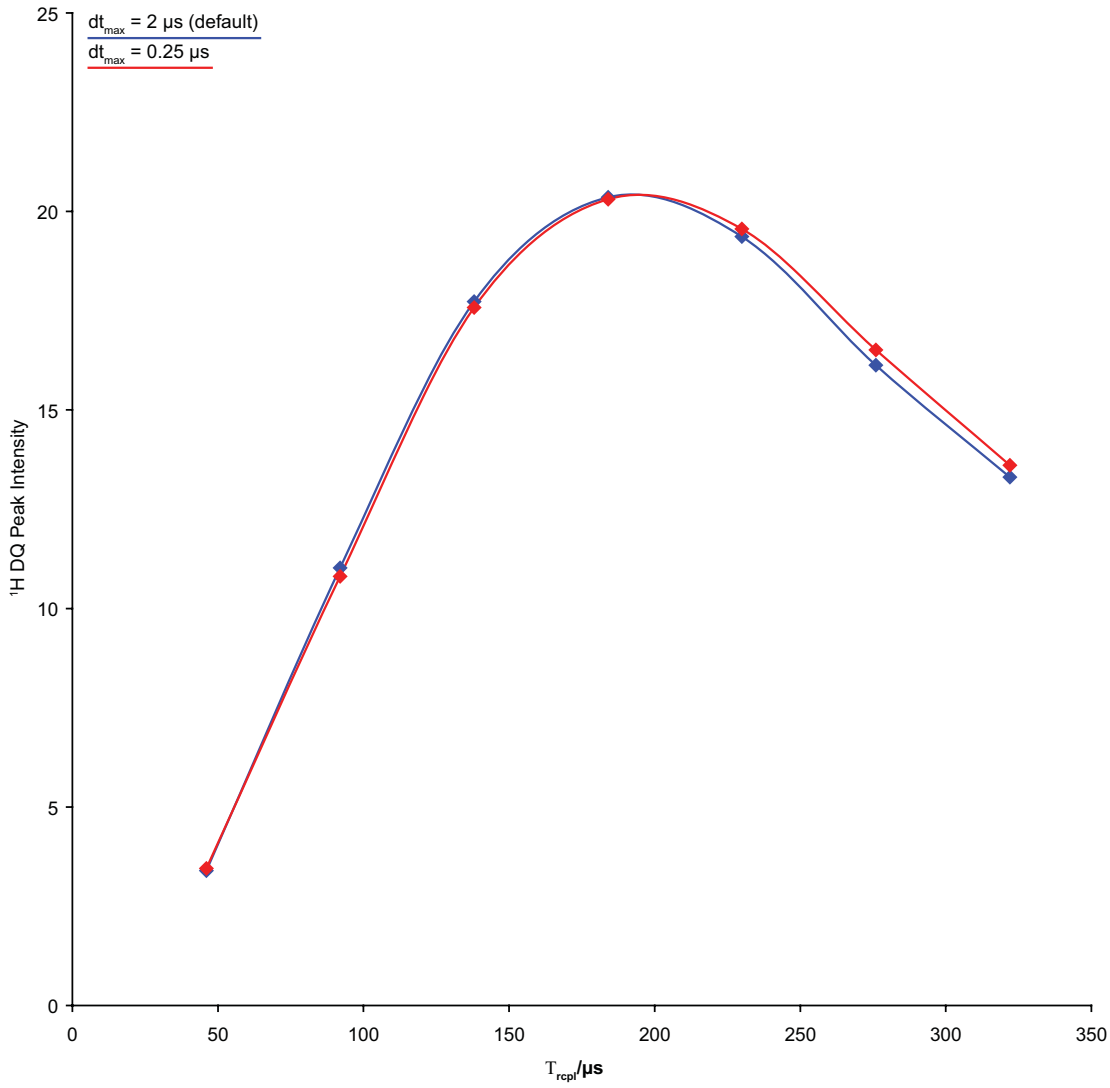

Fig. S3 Simulated ^{1}H DQ build-up curves of the CH(Asp) – OH peak at δ_{DQ} = 4.1 + 12.9 = 17.0 ppm. The blue and red curves correspond to eight-spin SPINEVOLUTION simulations for an MAS frequency, ν_R = 125 kHz, and *rf* nutation frequency, ν_1 = 875 kHz setting the parameter dt_{max} (this is stated as the time interval used in the integration of the equation of motion) equal to 2 and 0.25 µs, respectively. Lines linking the diamonds corresponding to simulated DQ peak intensities are included as guides for the eye. The DQ peak intensities are in arbitrary units.

S4 Simulated ^{1}H DQ build-up curves showing the effect of increasing the number of powder averaging angles

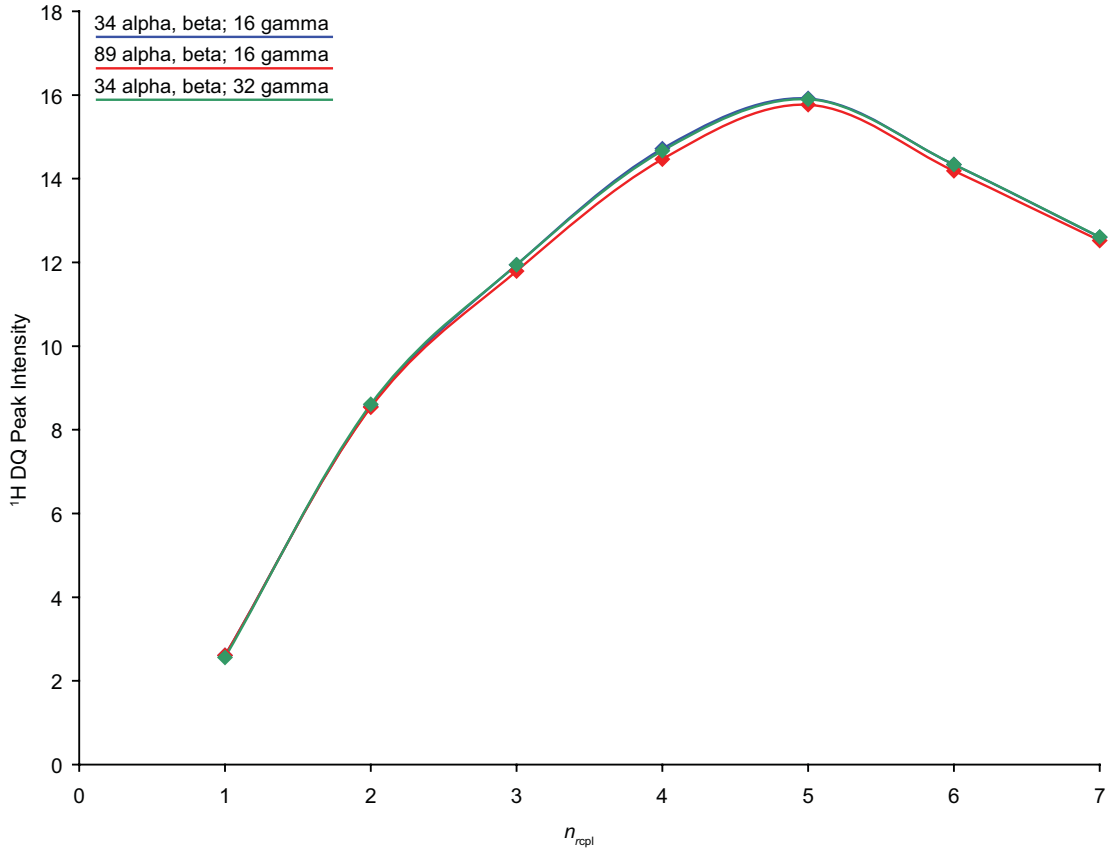

Fig. S4 Simulated (SPINEVOLUTION) ^{1}H DQ build-up curves of the CH(Asp) – OH peak at δ_{DQ} = 4.1 + 12.9 = 17.0 ppm for an eight-spin cluster. The blue curve shows the standard number (34 alpha and beta angles, 16 gamma angles) used in all other simulations, while the red and green curves show the effect of increasing the number of alpha and beta, and gamma angles, respectively. Lines linking the diamonds corresponding to simulated DQ peak intensities are included as guides for the eye. The DQ peak intensities are in arbitrary units.

S5 A comparison of the simulated ^{1}H DQ build-up curves (as in Figure 4 of main text)

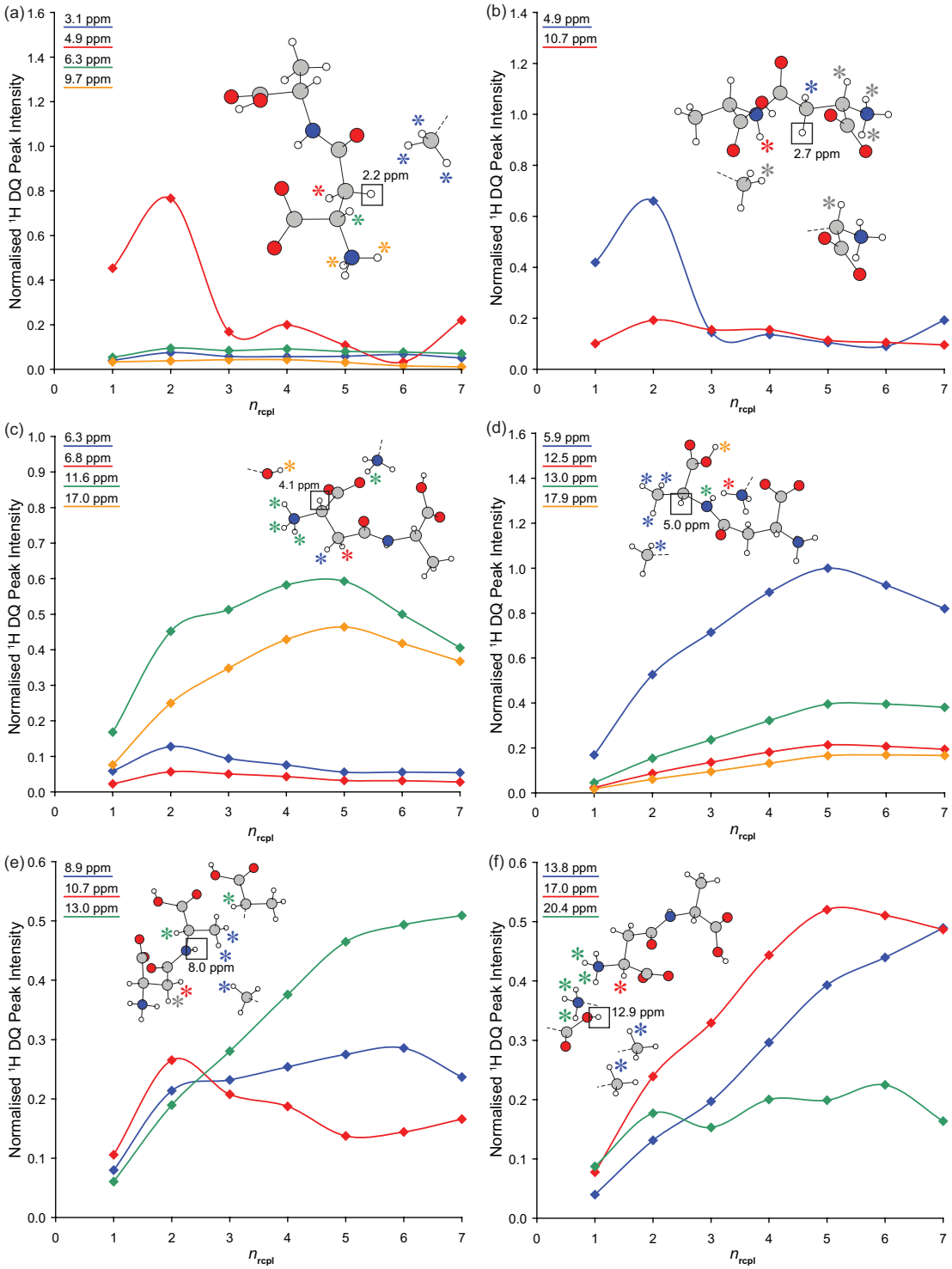

Fig. S5 Simulated ^{1}H DQ build-up curves for eight-spin clusters centred on the (a) CH_2(a), (b) CH_2(b), (c) CH(asp), (d) CH(ala), (e) NH, (f) OH protons of the dipeptide β-AspAla.

S6 A comparison of the experimental ^{1}H DQ build-up curves (as in Figure 4 of main text)

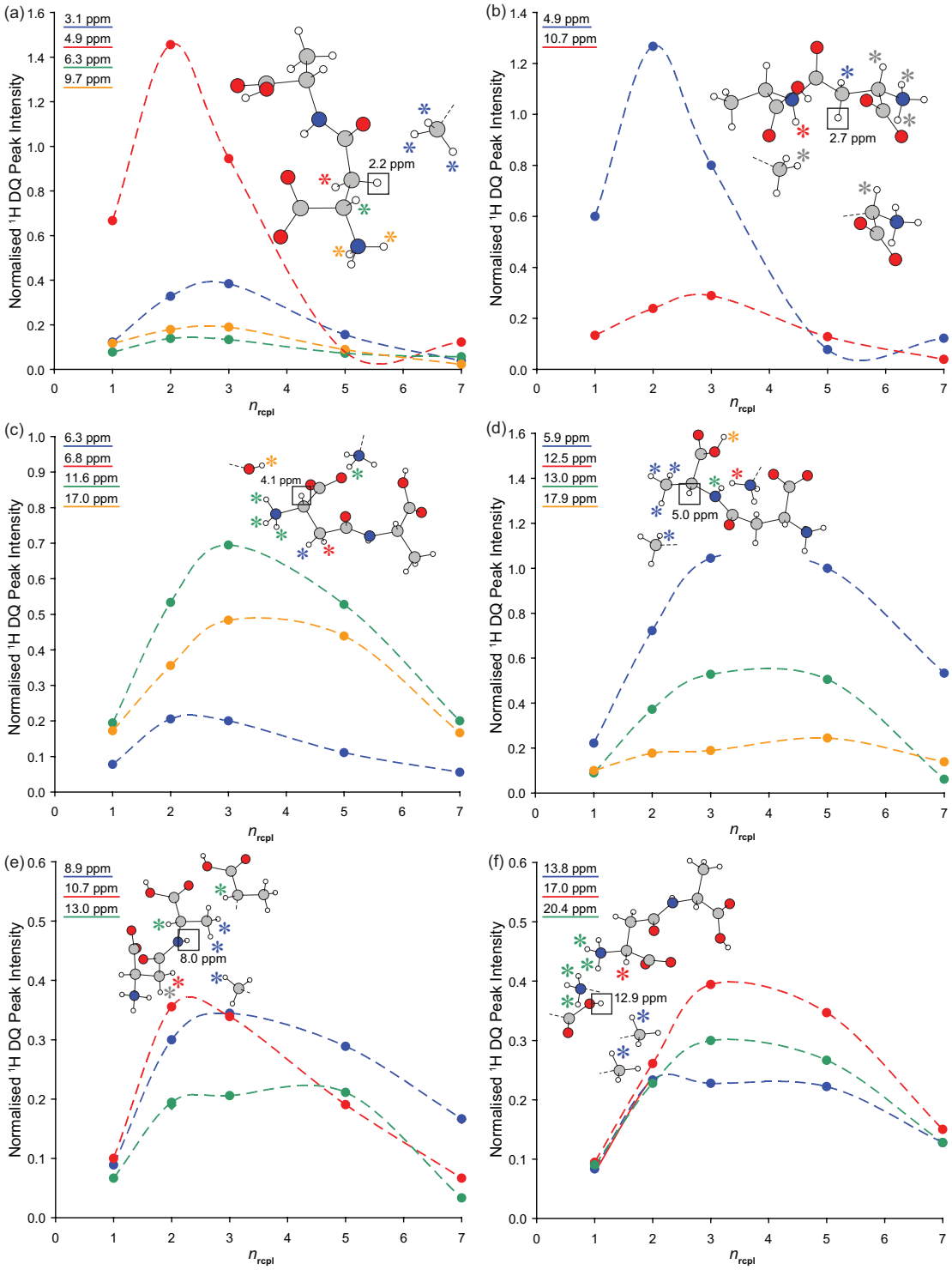

Fig. S6 Experimental ^{1}H DQ build-up curves for the (a) CH_2(a), (b) CH_2(b), (c) CH(asp), (d) CH(ala), (e) NH, (f) OH protons of the dipeptide β-AspAla.

S7 Simulated and experimental ^{1}H DQ build-up curves (as in Figure 4 of main text) together with rows through the experimental ^{1}H DQ CRAMPS spectra

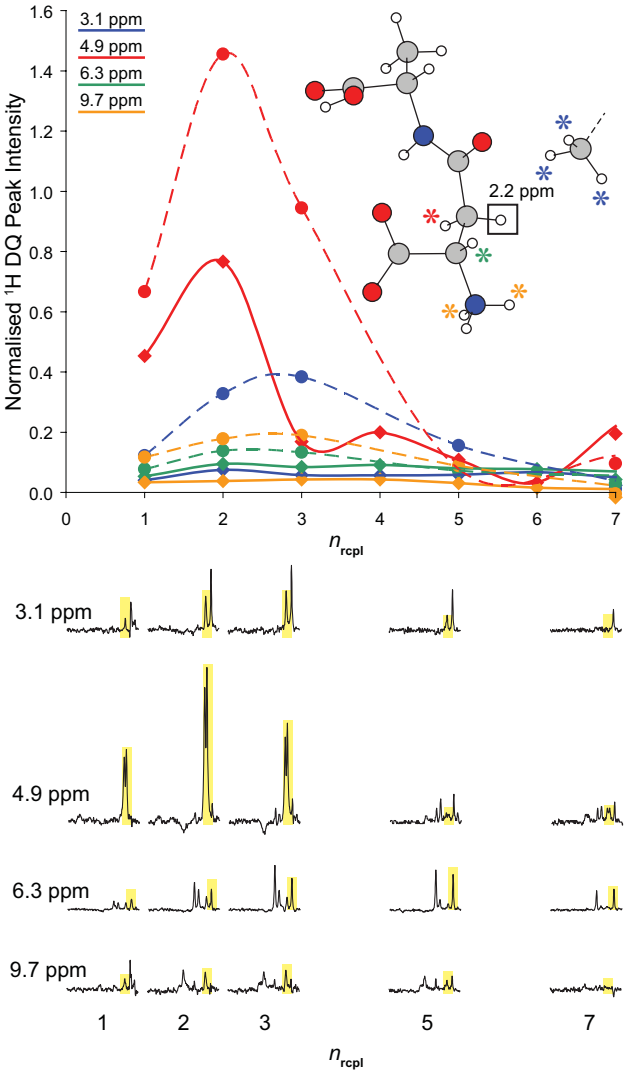

Fig. S7 A comparison of simulated (solid lines, diamonds, SPINEVOLUTION) and experimental (dashed lines, circles, 500 MHz, 12.5 kHz) ^{1}H DQ build-up curves for DQCs at the CH_2(a) SQ frequency.

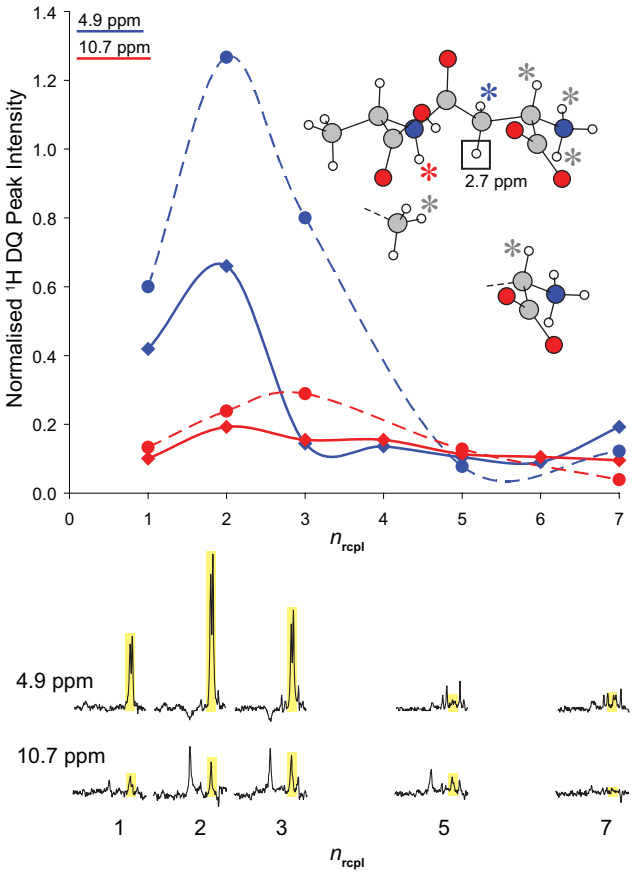

Fig. S8 A comparison of simulated (solid lines, diamonds, SPINEVOLUTION) and experimental (dashed lines, circles, 500 MHz, 12.5 kHz) ^{1}H DQ build-up curves for DQCs at the CH_2(b) SQ frequency.

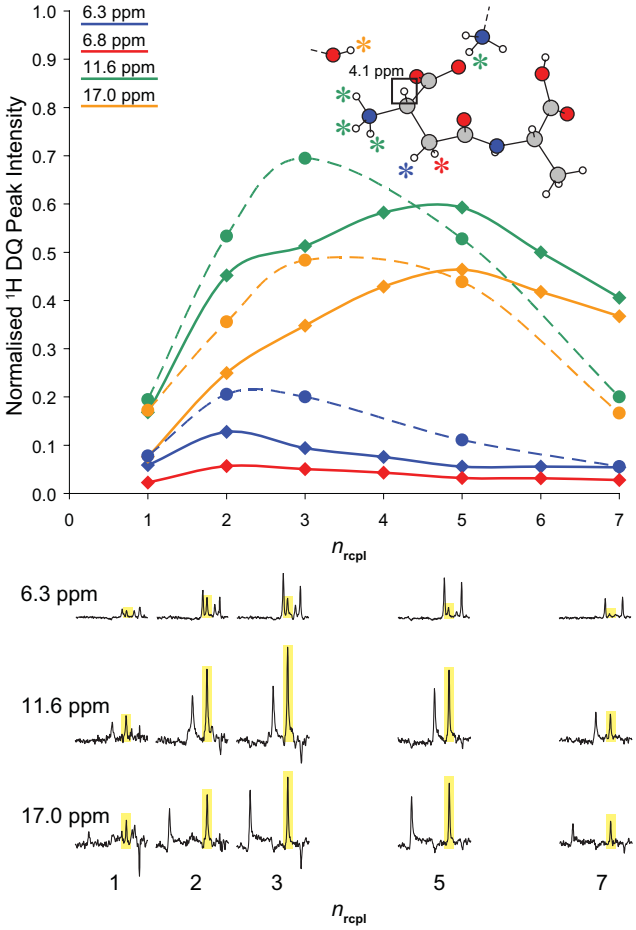

Fig. S9 A comparison of simulated (solid lines, diamonds, SPINEVOLUTION) and experimental (dashed lines, circles, 500 MHz, 12.5 kHz) ^{1}H DQ build-up curves for DQCs at the CH(Asp) SQ frequency.

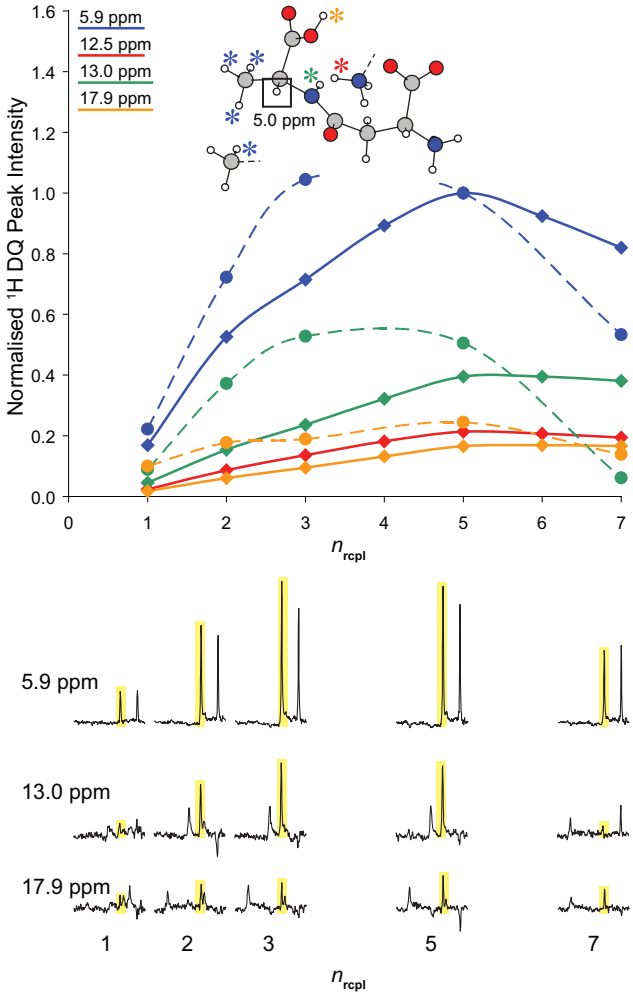

Fig. S10 A comparison of simulated (solid lines, diamonds, SPINEVOLUTION) and experimental (dashed lines, circles, 500 MHz, 12.5 kHz) ^{1}H DQ build-up curves for DQCs at the CH(Ala) SQ frequency.

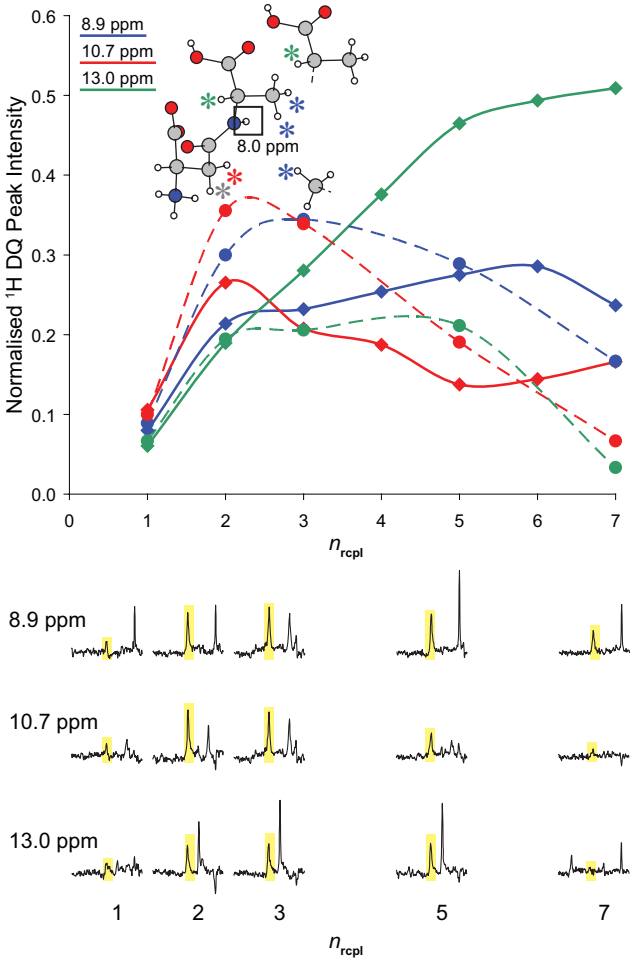

Fig. S11 A comparison of simulated (solid lines, diamonds, SPINEVOLUTION) and experimental (dashed lines, circles, 500 MHz, 12.5 kHz) ^{1}H DQ build-up curves for DQCs at the NH SQ frequency.

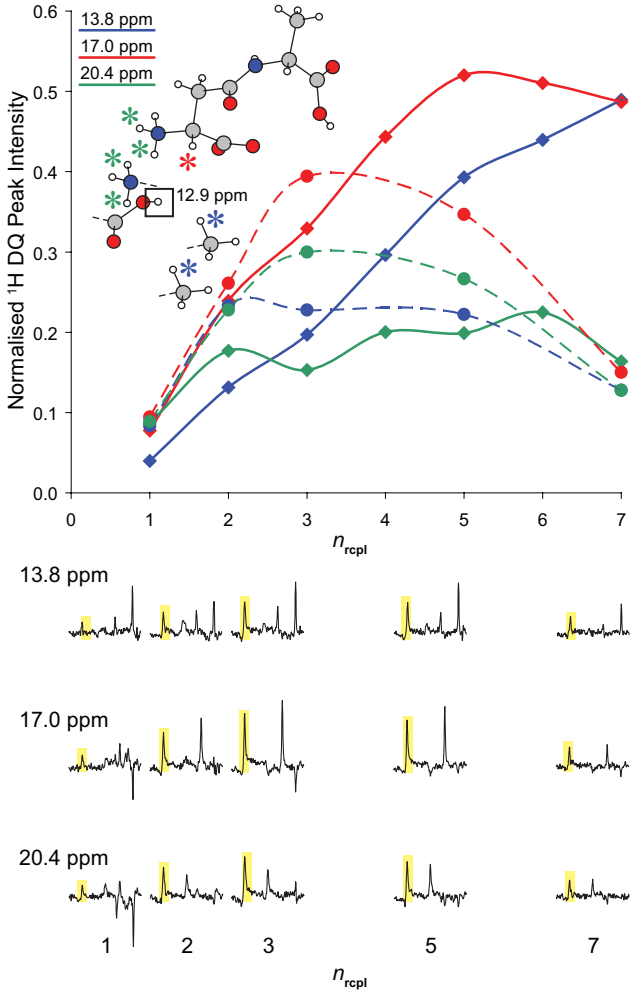

Fig. S12 A comparison of simulated (solid lines, diamonds, SPINEVOLUTION) and experimental (dashed lines, circles, 500 MHz, 12.5 kHz) ^{1}H DQ build-up curves for DQCs at the OH SQ frequency.