Experimental section:

All measurements performed with a Bruker AV-750 spectrometer equipped with a double channel CP-MAS probe head and using a ^{13}C radio frequency of 188 MHz, a MAS rate of 12 kHz and sample temperatures of 253K. 2D CHHC/CP^3 spectra were recorded at ^1H diffusion times of 200 μs and 325 μs for the U-LH2 sample and at 250 μs and 325 μs for the 2.3-LH2 sample.[1,2] The ^1H π/2 pulse was set to 3.1μs, corresponding with a nutation frequency of 80.6 kHz. The initial CP contact time was set to 256μs. Short CP contact times of 128μs enclosing the ^1H-^1H spin diffusion step were used in order to ensure that the polarization transfer was restricted to directly bonded ^1H-^{13}C spin pairs. Two-pulse phase modulation (TPPM) proton decoupling was applied during the evolution and detection periods.[3] The total acquisition time for each 2D dataset was between 20-24 h. All spectra were processed using QSINE window functions in F1 and F2 and analyzed using the program SPARKY (T. D. Goddard & D. G. Kneller, University of California).

1D CHHC/CP^3 spectrum of the U-LH2 sample

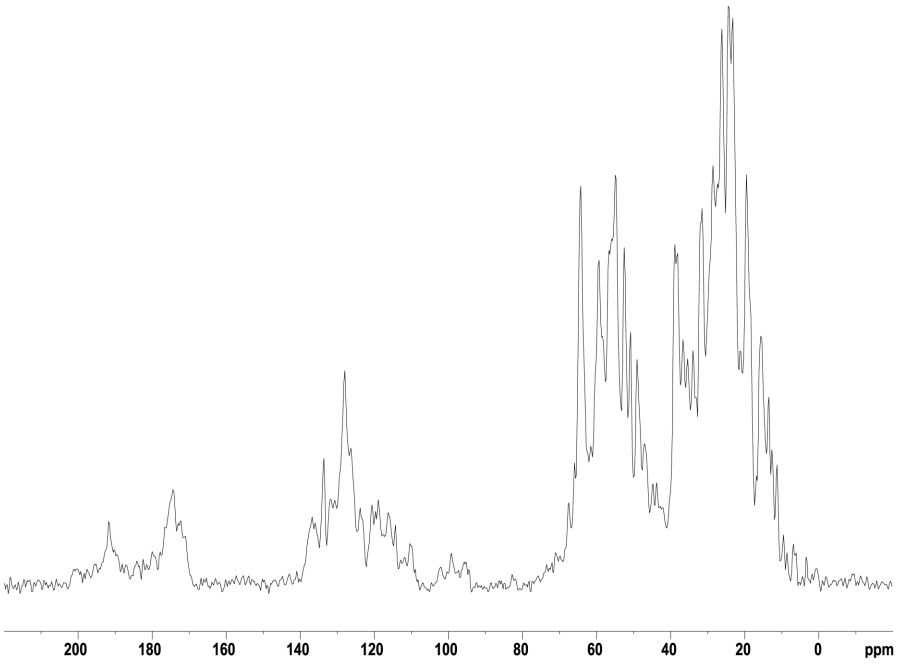

Figure S1: 1D CHHC/CP^3 spectrum of the U-LH2 sample recorded at $\omega_r/2\pi$=12000 Hz in 512 scans.

2D CHHC/CP^3 dataset of the 2.3-LH2 sample

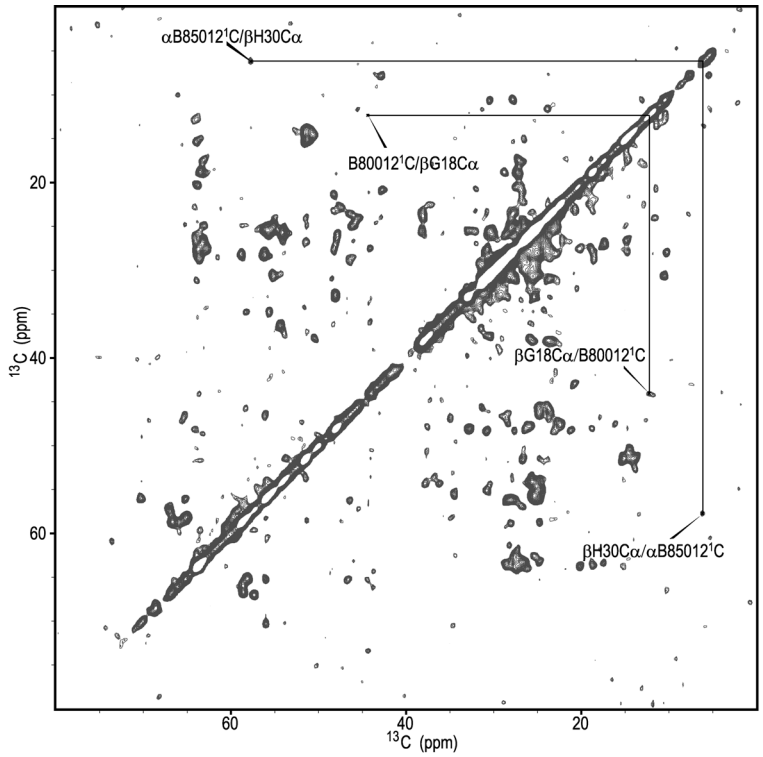

Figure S2. Aliphatic region of a CHHC/CP^3 dataset collected from the 2.3-LH2 sample at $\omega_r/2\pi$=12000 Hz and with 250μs ^{1}H-^{1}H spin diffusion mixing time. The solid lines indicate correlations between cofactors and protein side chains indicated with orange arrows in Figure 1.

References

(1) de Boer, I.; Bosman, L.; Raap, J.; Oschkinat, H.; de Groot, H. J. M. *J. Magn. Reson.* 2002, *157*, 286-291.

(2) Lange, A.; Luca, S.; Baldus, M. *J. Am. Chem. Soc.* 2002, *124*, 9704-9705.

(3) Bennett, A. E.; Rienstra, C. M.; Auger, M.; Lakshmi, K. V.; Griffin, R. G. *J. Chem. Phys.* 1995, *103*, 6951-6958.