Supporting Information:

Proton Assisted Recoupling at High Spinning Frequencies

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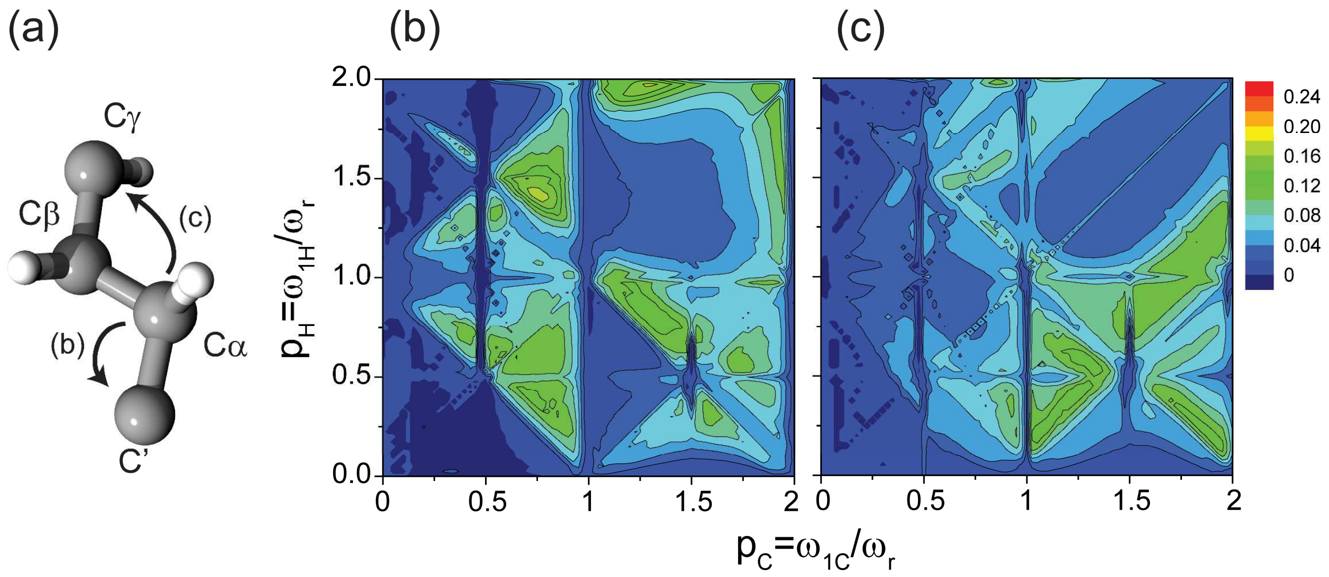

Figure SI1. Numerical simulation of the ^{13}C-^{13}C PAR polarization transfer optimization map performed on the spin system shown in (a). The contour plots represent polarization transfer between the C_α and C' in (b), and C_α and C_γ in (c) as a function of ^{13}C and ^{1}H irradiation strength in units of spinning frequency. Simulations were performed using 5 ms PAR mixing time at $\omega_r/2\pi$=65 kHz MAS and $\omega_{0H}/2\pi$=500 MHz and include chemical shift. The details of the spin system are listed in Table SI1.

Atom	X	Y	Z	δ_{iso} (ppm)	δ_{anis} (ppm)	η
LCA	0.297	0.449	0.95	41.2	25.1	0
LC	-0.263	1.661	0.227	-77.2	-76	0.99
LCB	1.831	0.463	0.896	57.3	23.8	0.92
LCG	2.514	-0.743	1.538	73	-19.8	0
LHA	-0.045	0.454	2.017	0	5	0.6
LHB2	2.192	1.389	1.412	0	5	0.6
LHG	2.235	-1.667	0.969	0	5	0.6

Table SI1. Spin system used in simulation in the Figure 2 in the main text and Figure SI1. The coordinates were taken from the SSNMR structure of N-*f*-MLF-OH[1] (PDB ID 1Q7O). The CH bond lengths were set to 1.12 Å.

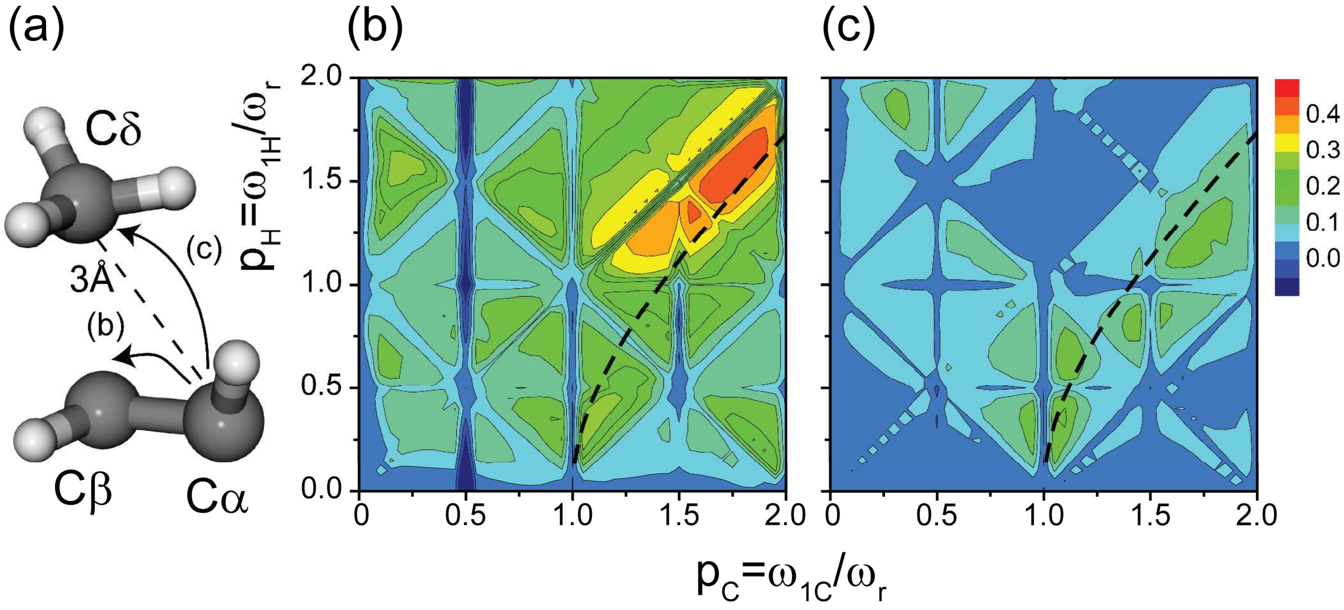

Figure SI2. Numerical simulations of the ^{13}C-^{13}C PAR optimization maps on the aliphatic region. (a) spin system used in simulation taken from the SSNMR structure of N-*f*-MLF-OH[1] (see Table SI2). The contour plots represent polarization transfer between the carbons (indicated by black arrow – Cα-Cβ in (b) and Cα-Cδ in (c)) as a function of ^{13}C and ^{1}H irradiation strength in units of spinning frequency. Simulations were performed using 5 ms PAR mixing time at $\omega_r/2\pi$=65 kHz MAS and $\omega_{0H}/2\pi$=500 MHz and include chemical shift. Simulation accounts for the threefold methyl group hop. For the settings indicated by the black dashed lines the CH auto-cross term is zero.

Atom	**X**	**Y**	**Z**	**δ_{iso} (ppm)**	**δ_{anis} (ppm)**	**η**
LCα	0.288	0.419	0.932	-15	25.1	0
LCβ	1.822	0.433	0.878	10	23.8	0.92
LCδ2	2.051	-0.907	2.978	17	-19.8	0
LHα	-0.054	0.425	1.999	0	5	0.6
Hβ2	2.183	1.36	1.394	0	5	0.6
L1Hδ2	2.149	0.071	3.515	0	5	0.6
L2Hδ2	2.686	-1.677	3.486	0	5	0.6
L3Hδ2	0.981	-1.236	2.988	0	5	0.6

Table SI2. Spin system used in simulation in the Figure SI2. The coordinates were taken from the SSNMR structure of N-*f*-MLF-OH[1] (PDB ID 1Q7O). The CH bond lengths were set to 1.12 Å.

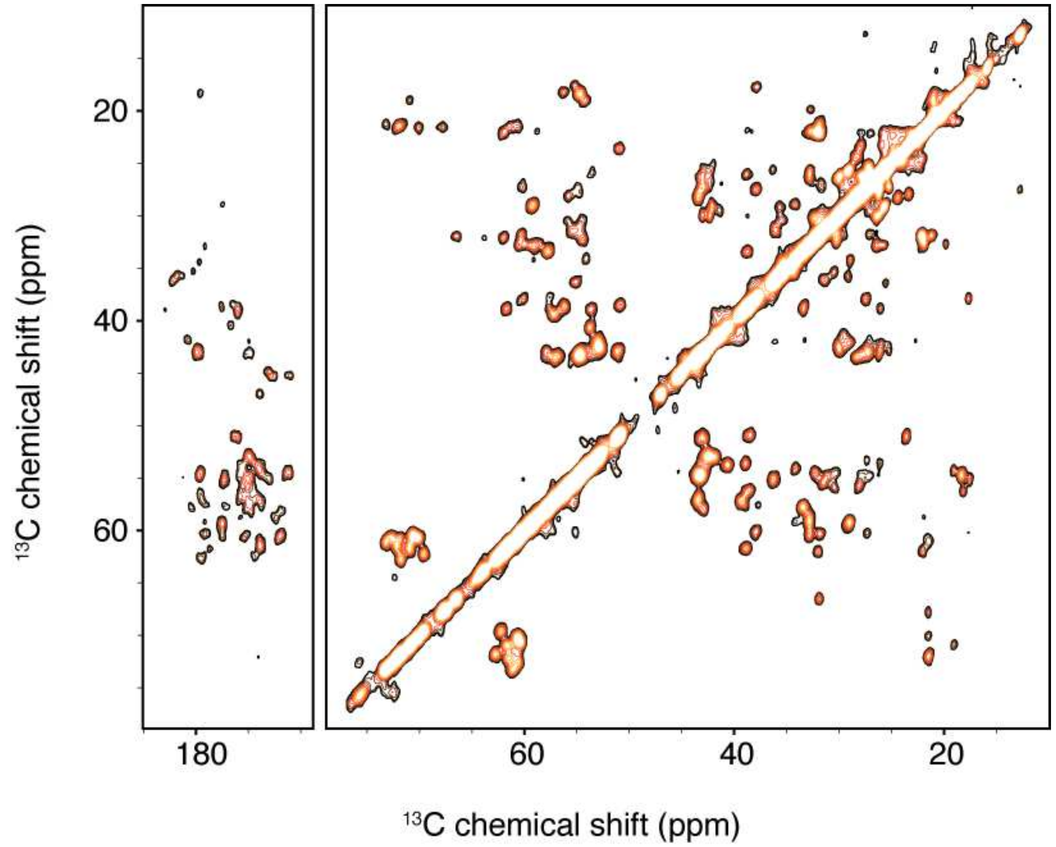

Figure SI3. 2D ^{13}C-^{13}C PAR correlation spectra on [U-^{13}C,^{15}N]-GB1 obtained at $\omega_r/2$ =65 kHz and $\omega_{0H}/2$ =500 MHz. The PAR mixing time was 2.5 ms and used ~19.5 kHz ^{13}C and ~72.8 kHz ^{1}H irradiation. 16.5 kHz low power TPPM decoupling was employed during the acquisition and t_1 evolution.

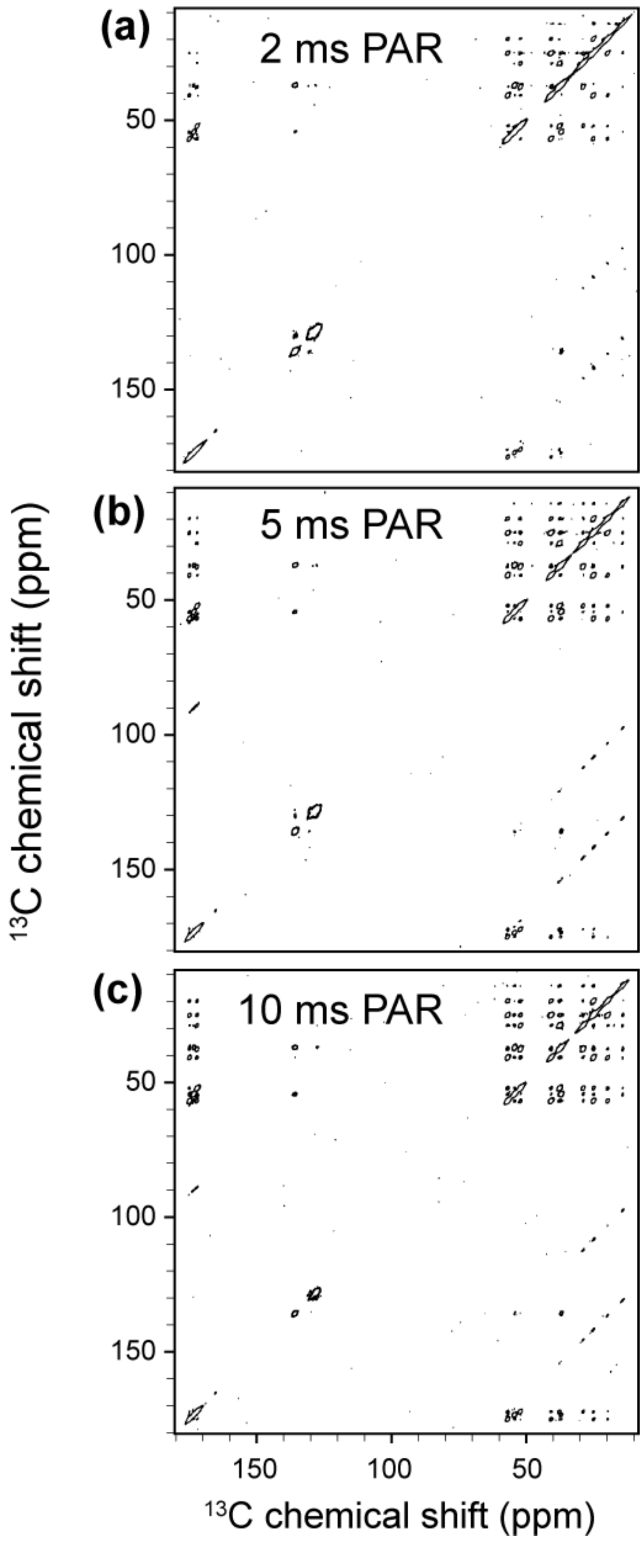

Figure SI4. 2D ^{13}C-^{13}C PAR correlation spectra on [U-^{13}C,^{15}N]-*f*-MLF-OH obtained at $\omega_r/2$ =65 kHz and $\omega_{0H}/2$ =500 MHz. The PAR mixing time was (a) 2 ms, (b) 5 ms, (c) 10 ms and used ~110 kHz ^{13}C and ~85 kHz ^{1}H irradiation. 230 kHz XiX decoupling (the XiX pulse was 60.2 μs i.e. 3.91 τ_r) was employed during the acquisition and t_1 evolution.

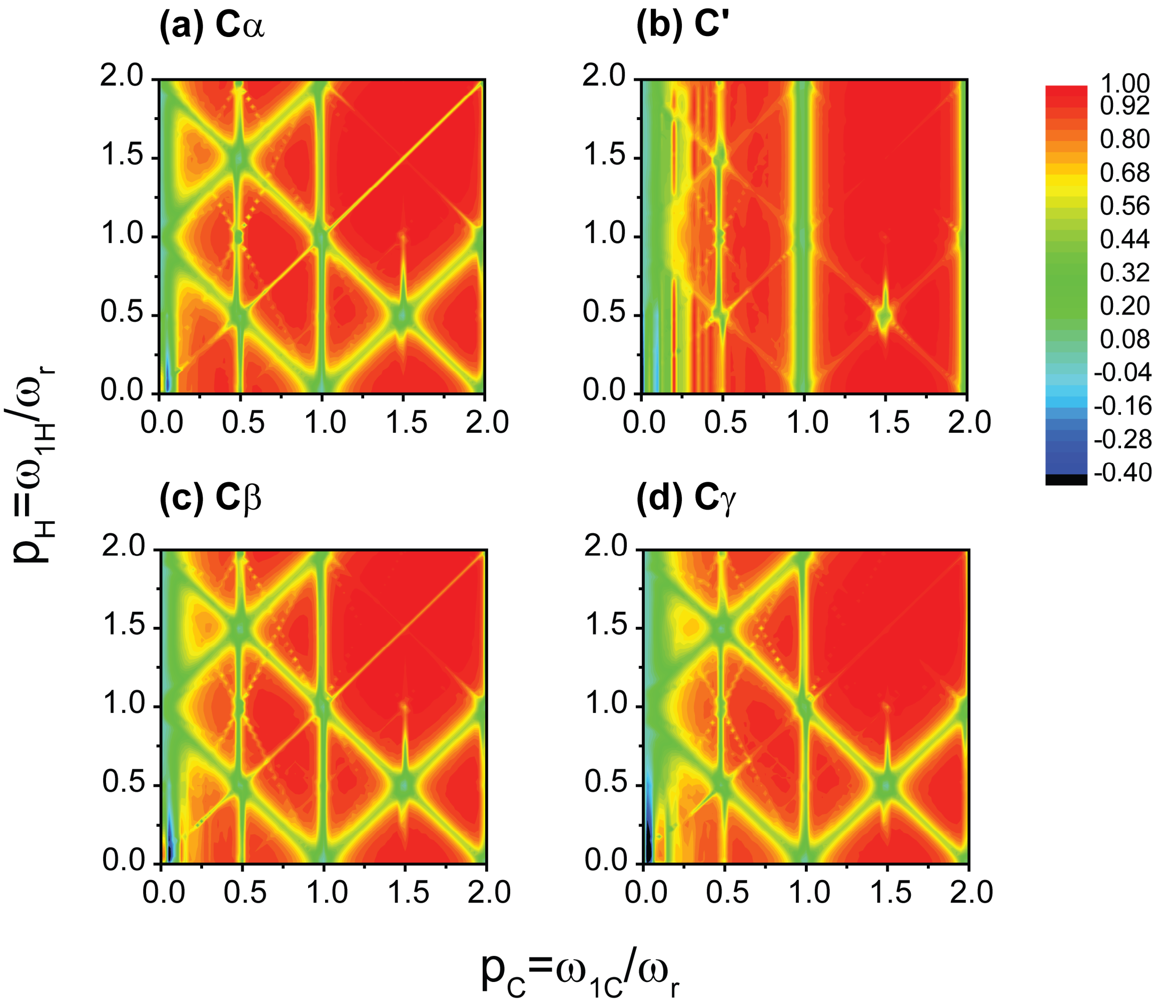

Figure SI5. Simulated "interference" map on the spin system described in Table SI1. In the interference map the decay of the magnetization on the carbons after the PAR mixing is monitored as a function of carbon (p_C) and proton (p_H) irradiation in units of spinning frequency. The initial magnetization is prepared on the x-axis on all the carbons. The settings for the simulation are identical to the settings used in Fig. SI1. The comparison between the interference maps and the polarization transfer map shown in Fig. 2 and Fig. SI1 allows one to choose the appropriate rf settings for performing PAR experiments. Note that the destructive interference features are roughly the same for the PAR polarization transfer maps and the "interference" maps (Hartmann-Hahn and Rotary Resonance conditions). These common features are used to calibrate the rf field strength and to optimize the PAR settings. It is important to keep in mind that the "interference" map is used solely for the calibration of relative ^{13}C and ^{1}H rf powers and that settings yielding high intensities in the "interference" maps do not necessarily yield efficient PAR polarization transfer.

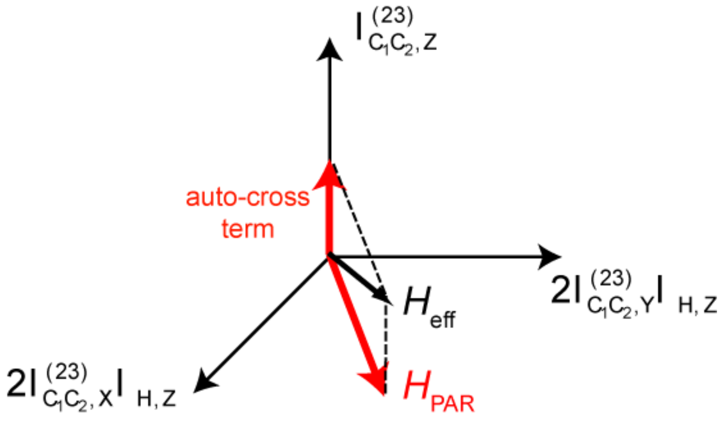

Figure SI6. Visualization of PAR spin dynamics subspace. The space can be seen as a coupled basis between a fictitious ZQ operator involving the two carbons and a proton spin. The red arrows indicate PAR recoupling axis and longitudinal tilting field resulting from auto-cross terms.

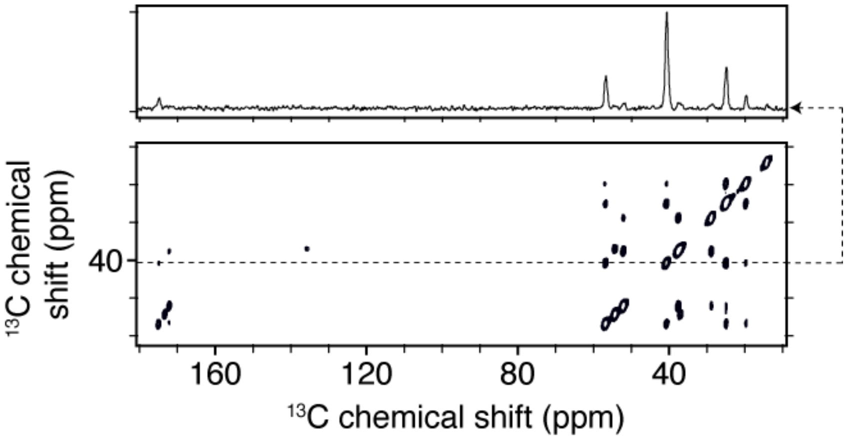

Figure SI7. Short ^{13}C-^{13}C PAR 2D spectrum of [U-^{13}C,^{15}N]-*f*-MLF-OH obtained in ~52 minutes at $\omega_r/2\pi$ =65 kHz and $\omega_{0H}/2\pi$ =500 MHz. The top panel shows a representative 1D slice to illustrate the overall SNR. The PAR mixing time was set to 5 ms and the rf field strength were respectively ~110 kHz for the ^{13}C irradiation and ~85 kHz for the ^{1}H irradiation. 230 kHz XiX decoupling was employed during the acquisition and t_1 evolution (the XiX pulse was set 60.2 μs i.e. 3.91 τ_r). The spectral width in the indirect dimension was 25.1 kHz.

SPINEVOLUTION File for generating PAR polarization transfer maps.

Example of a SPINEVOLUTION input file for simulating PAR polarization transfer (the contents of the input file are in Courier pt. 9 font):

```
****** The System ***********************************
spectrometer(MHz)  500
spinning_freq(kHz) 60
channels           C13 H1
nuclei             C13 C13 C13 H1 H1
atomic_coords      CO-Ca-Ha-Cb-Hb.cor
cs_isotropic       -65 65 75 0 0 ppm
csa_parameters     1 -76 0.9 90 90 0 ppm
csa_parameters     2 -20 0.5 99.4 146.0 138.9 ppm
csa_parameters     3 -22 0.7 0 14.0 38.9 ppm
csa_parameters     4 5.7 0.65 90 -90 90 ppm
csa_parameters     5 5.7 0.65 90 -90 90 ppm
j_coupling         *
quadrupole         *
dip_switchboard    *
csa_switchboard    *
exchange_nuclei    *
bond_len_nuclei    *
bond_ang_nuclei    *
tors_ang_nuclei    *
groups_nuclei      *
******* Pulse Sequence ******************************
CHN 1
timing(usec)       (100)40D0
power(kHz)           50
phase(deg)            0
freq_offs(kHz)        0
CHN 2
timing(usec)       (100)
power(kHz)           50
phase(deg)            0
freq_offs(kHz)        0
******* Variables ***************************************
*edit the spinning frequency in the next line
spinning_freq=20

*select the grid parameters: pc - 13C power, ph - 1H power
scan_par pc/0:0.1:5/ ph/0:0.1:5/

*the carbon and proton power levels are scanned from 0 to 5*spinning_freq=100kHz in steps of
0.1*spinning_freq=0.1*20=2kHz

power_1_1_1=pc*spinning_freq
power_2_1_1=ph*spinning_freq
******* Options **************************************
rho0               I1x
observables        I1x I2x I3x
EulerAngles        rep168
n_gamma            10
line_broaden(Hz)   *
zerofill           *
FFT_dimensions     *
options            -v1 -re
```

In this example the mixing time is 100 x 40 ms = 4 ms. The initial magnetization is prepared on the C' and observed on all three carbon. The CSA values are generic - you can update them according to your system.

The nuclear coordinates can be placed in a separate file, here *CO-Ca-Ha-Cb-Hb.cor.* An example of *CO-Ca-Ha-Cb-Hb.cor* would look as follows (the contents of the file are in Courier pt. 9 font):

```
-0.272   1.663   0.264   LC
 0.288   0.451   0.987   LCA
 1.822   0.465   0.933   LCB
-0.042   0.456   2.016   LHA
 2.171   1.360   1.431   L2HB
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References

(1) Rienstra, C. M.; Tucker-Kellogg, L.; Jaroniec, C. P.; Hohwy, M.; Reif, B.; McMahon, M. T.; Tidor, B.; Lozano-Perez, T.; Griffin, R. G. *Proceedings of the National Academy of Sciences of the United States of America* **2002**, *99*, 10260-10265.