Supplementary Information for

Optimal Control-Based Nuclear Spin Cross-Polarization in the Presence of Complicating Anisotropic Interactions

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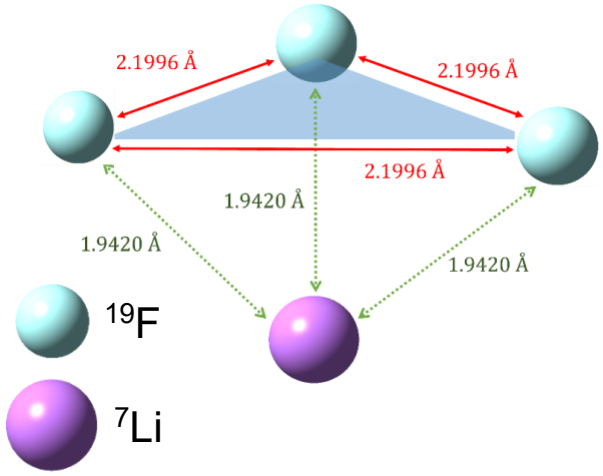
Table: Table of Contents



Simulation Parameters

- ^{19}F – ^{19}F Dipolar Coupling: 10 kHz
- ^{19}F – ^{7}Li Dipolar Coupling: 6 kHz
- ^{19}F Chemical Shift Anisotropy: 210 ppm
- ^{7}Li Quadrupolar Coupling: 250 kHz.
- Magic Angle Spinning Frequency: 42 kHz.
- ^{1}H Larmor Frequency: 400 MHz
- Pulse Digitization: 0.3 μs

Figure S1. Schematic representation of the spin system and the interaction strengths used in the simulations. Right Side data shows amount of anisotropic interactions (dipolar coupling, CSA and QC), and optimizing conditions of MAS and spectrometer field.

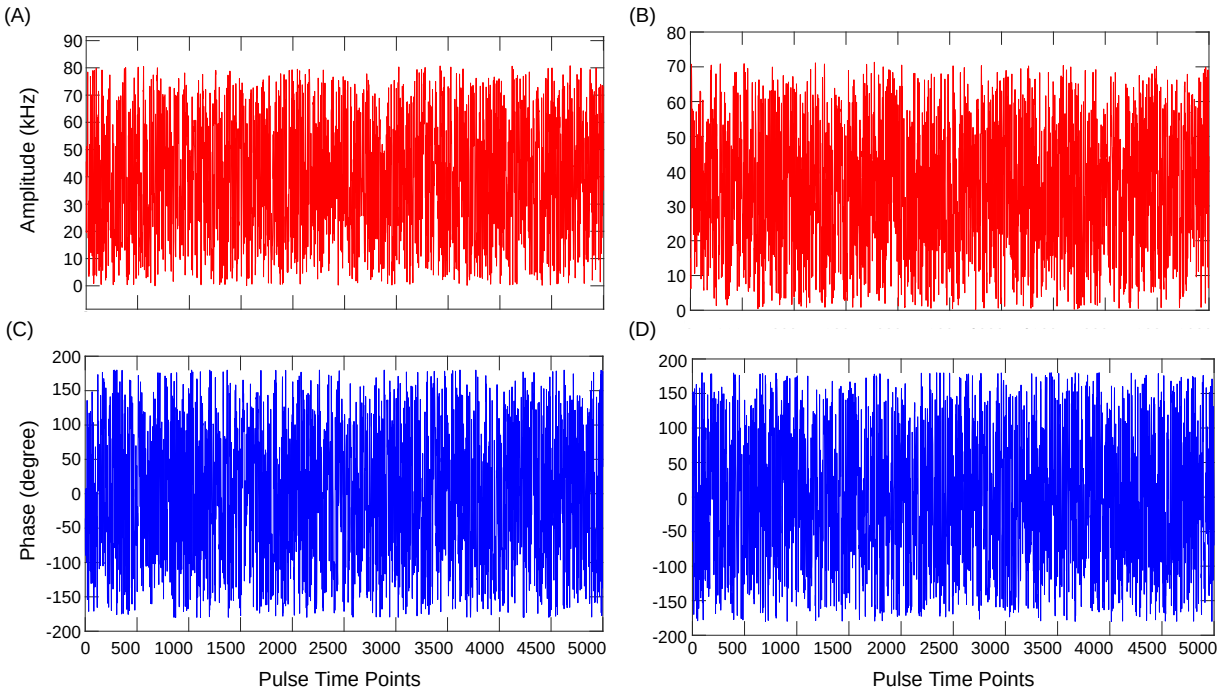


Figure S2. Optimized RF Shapes. Amplitude and phase profiles of OTPIANS for ^{19}F channel (A and C) and ^{7}Li channel (B and D), respectively. The digitization is 300 ns. The parameters used in the simulations to generate the shapes are provided in the methods section.

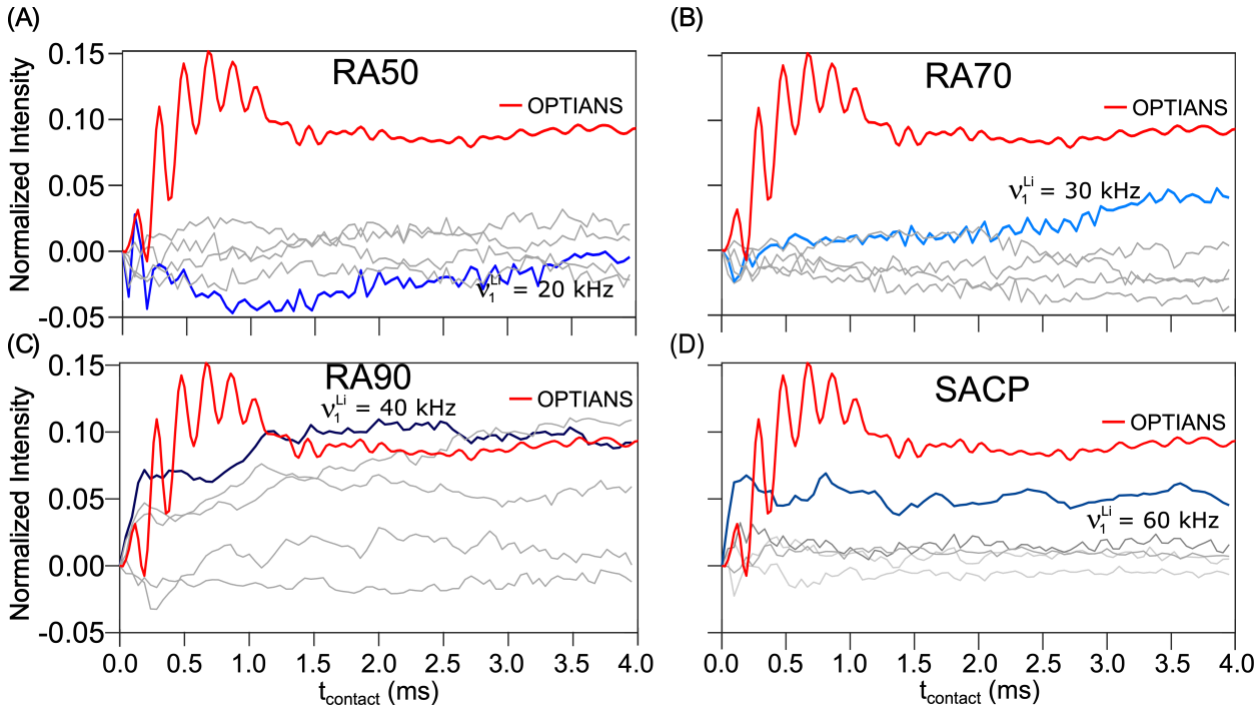


Figure S3. Comparison of (A) Ramp50-100 (RA50), (B) Ramp70-100 (RA70), (C) Ramp90-100 (RA90), and (D) Single Amplitude CP (SACP) with OPTIANS simulated at 9.4T field with fixed $\boldsymbol{\nu_r}$ = 42 kHz, $\boldsymbol{\delta_{CSA}^F}$ = 210 ppm, $\boldsymbol{C_Q^{Li}}$ =250 kHz, and for RACP $\boldsymbol{\nu_1^F}$ = **100 kHz**, and varied $\boldsymbol{\nu_1^{Li}}$ in the range of 20 to 60 kHz. The colors curves are the ones used in Figure 1A while the gray curves indicate remaining simulations with varying $\boldsymbol{\nu_1^{Li}}$ values.

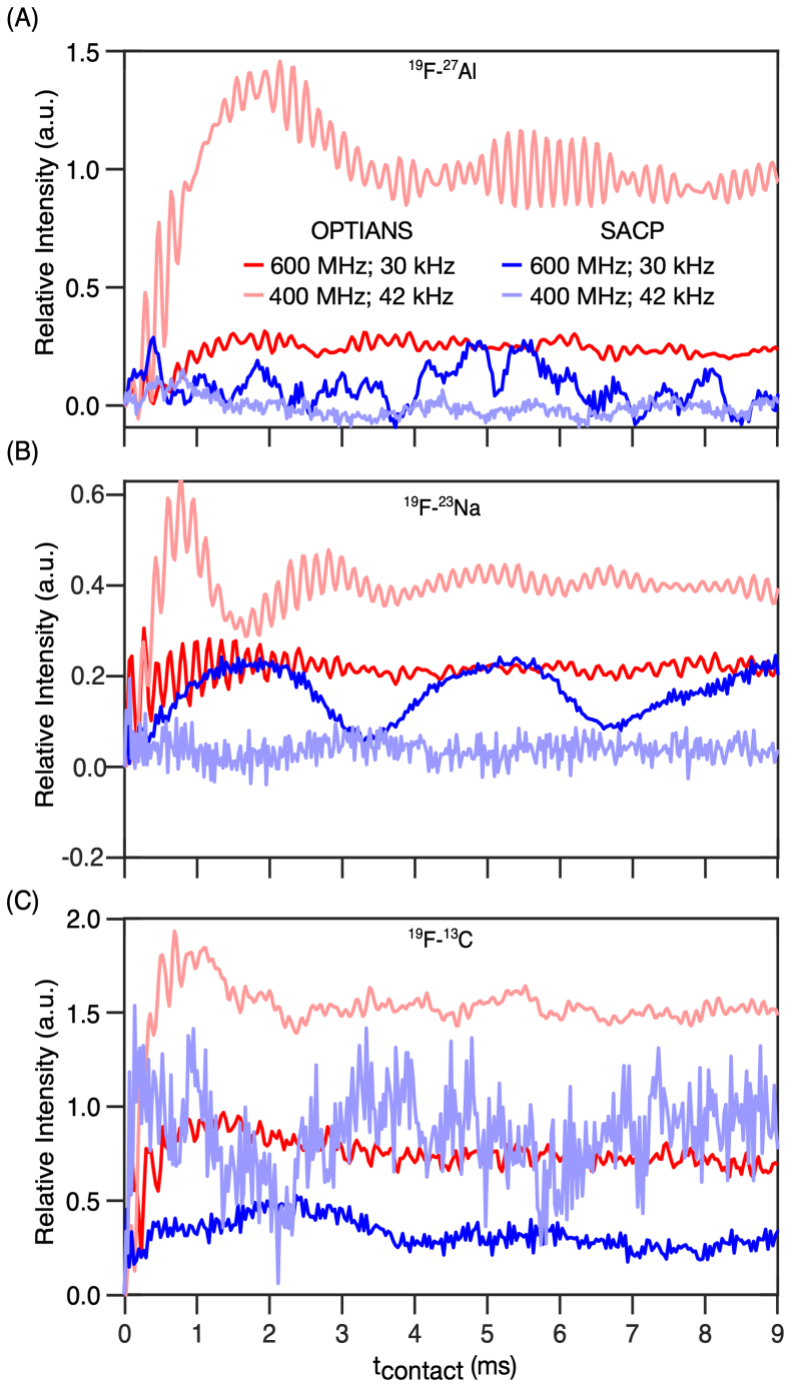


Figure S4. The simulated polarization transfer curves for SACP (Blue) and OPTIANS (Red) to compare the polarization transfer efficiency for various spins systems (A) ^{19}F-^{27}Al, (B) ^{19}F-^{23}Na, and (C) ^{19}F-^{13}C as labeled on the plots. The dark colors represent 600 MHz spectrometer and 30 kHz MAS, and the faded colors are for 400 MHz spectrometer and 42 kHz MAS. The intensities on y-axis are taken from the direct output of SIMPSON simulations without any further normalization.

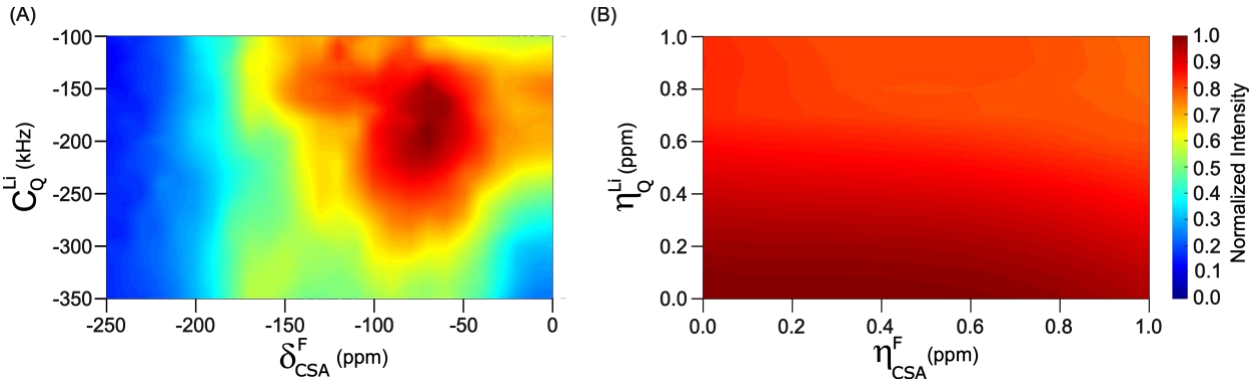


Figure S5. Simulated profiles of (A) Polarization transfer efficiency of OPTIANS as a function of negative values of CSA, and QC to demonstrate the biaxiality of OPTIANS; (B) $\boldsymbol{\eta_{CSA}^{F}}$ and $\boldsymbol{\eta_{Q}^{Li}}$ variation for visualizing the powder dependency of OPTIANS.

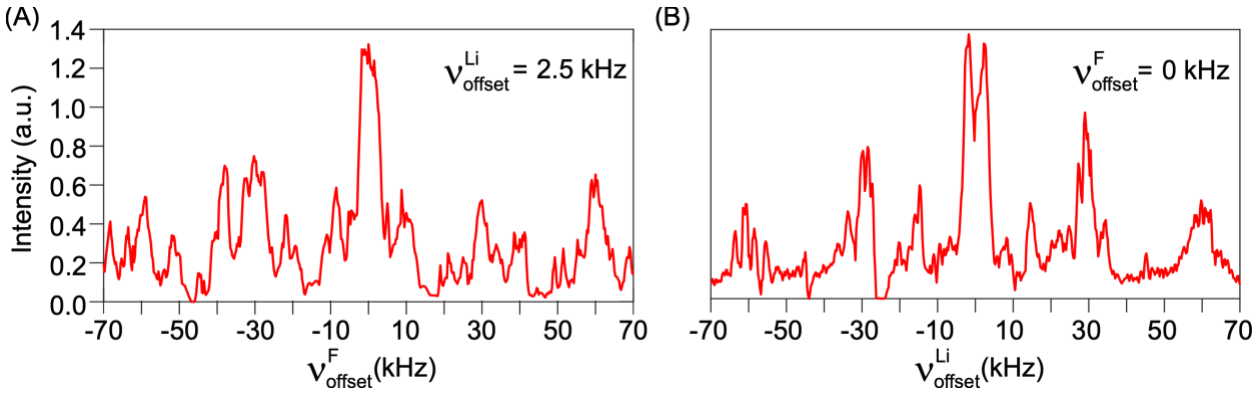


Figure S6. Simulated 1D offset profiles of OPTIANS on ^{19}F and ^{7}Li channels. (A) Offset profile for ^{19}F channel with keeping ^{7}Li offset fixed to 2.5 kHz, the most intense peak coming in Figure 3(B) along ^{7}Li channel; (B) Offset profile for ^{7}Li channel with keeping ^{19}F offset fixed to 0 kHz, the most intense peak coming in Figure 3(B), along ^{19}F channel. Rest parameters are same as Figure 3B OPTIANS simulation.

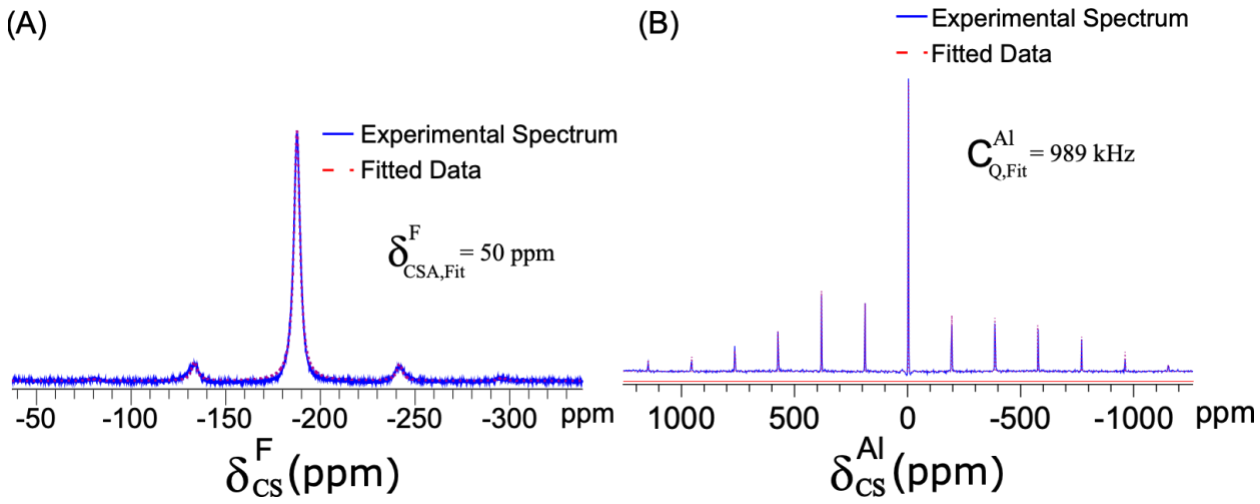


Figure S7. Experimental data and simulated fits of (A)^{19}F Hahn-echo; (B) ^{27}Al spectra. The fitted values are $\boldsymbol{\delta^{F}_{CSA} = 50}$ ppm**,** and $\boldsymbol{C^{Al}_{Q} = 989}$ **kHz**, resepctively.

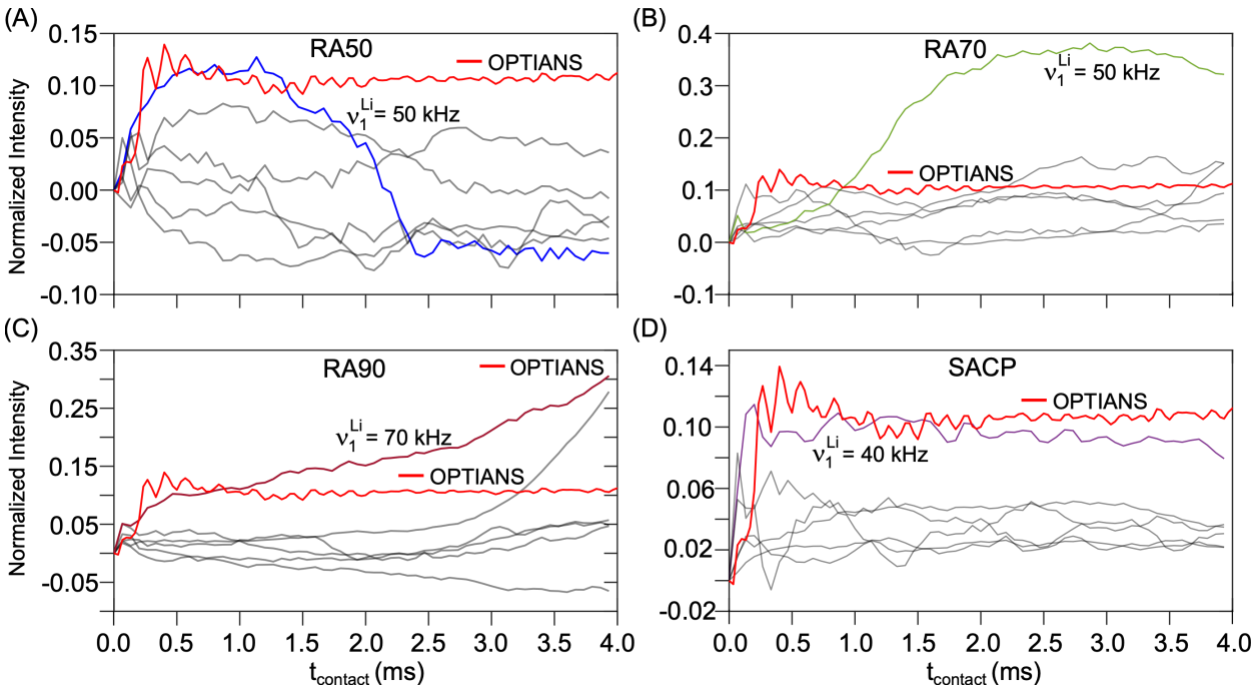


Figure S8. Various RACP and OPTIANS simulations at 14.1 T field with $\boldsymbol{\nu_r} = 30$ kHz, $\boldsymbol{\delta_{CSA}^F}$ = 50 ppm, $\boldsymbol{C_Q^{Li}}$ =250 kHz, and for RACP $\boldsymbol{\nu_1^F} = \mathbf{100\ kHz}$ and varied $\boldsymbol{\nu_1^{Li}}$ in the range of 20 to 60 kHz. The colors curves are the ones used in Figure 1A while the gray curves indicate remaining simulations with varying $\boldsymbol{\nu_1^{Li}}$ values.

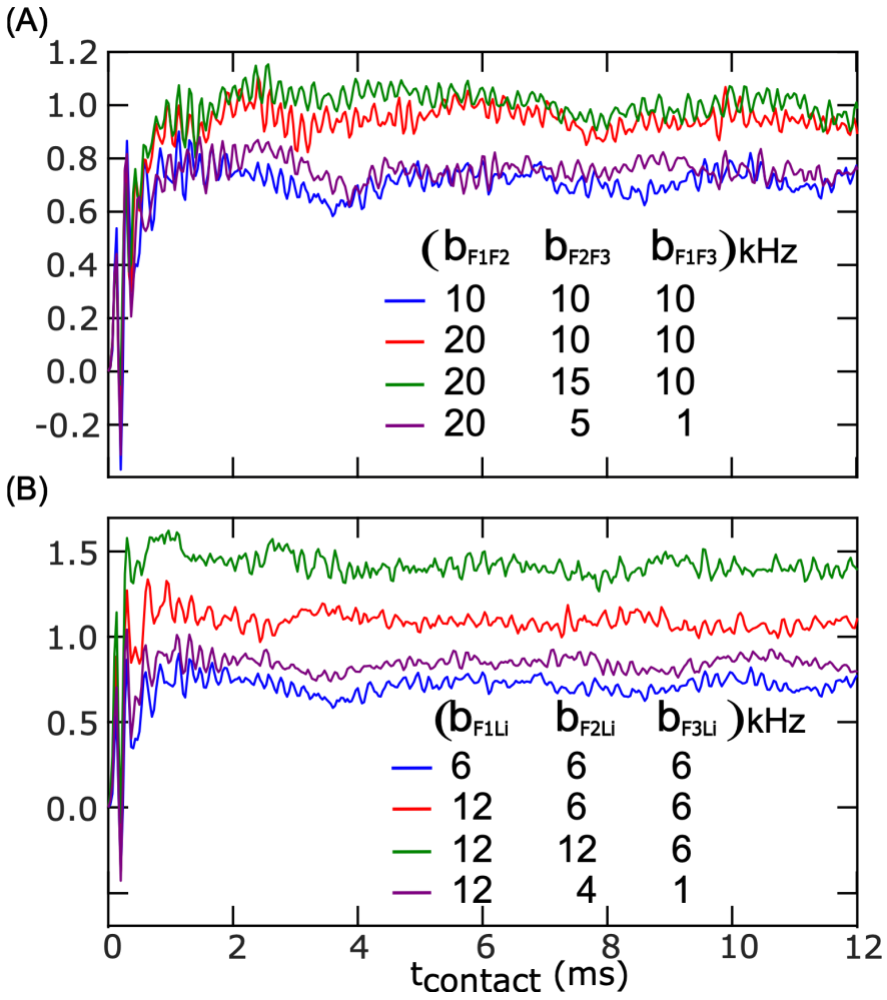


Figure S9. ^{19}F-^{7}Li polarization transfer curves using OPTIANS simulated at 14.1 T with 30 kHz MAS. The plot (A) was obtained varying three $\boldsymbol{b_{F-F}}$ and plot (B) was obtained by varying the three $\boldsymbol{b_{F-Li}}$. The efficiencies and the oscillations are affected by the strength of the dipolar couplings as well as the distribution of dipolar coupling present in the spin system. All the polarization transfer curves are produced with relative intensity in arbitrary unit.

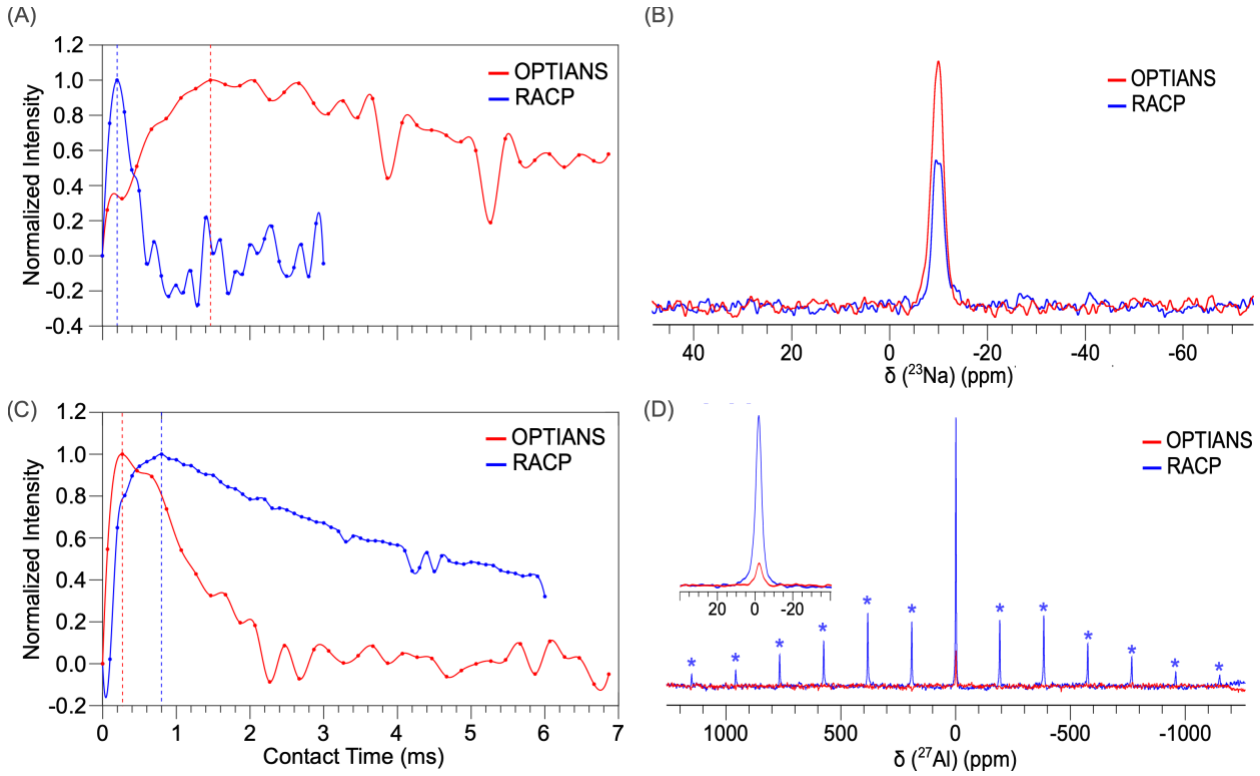


Figure S10. Experimental Polarization Transfer Curves and 1D Spectra of ^{23}Na and ^{27}Al Using OPTIANS and RACP. (A) ^{19}F-^{23}Na PT curves recorded using RACP (blue) and OPTIANS (red). Red and blue dotted lines represent the optimal contact times for OPTIANS (1.4 ms) and RACP (200 $\boldsymbol{\mu}$s), respectively. (B) Comparison of ^{23}Na MAS NMR signal recorded using RACP (blue) and OPTIANS (red) with optimal contact time (dotted lines). (C) ^{19}F-^{27}Al polarization transfer curves recorded using RACP (blue) and OPTIANS (red). Red and blue dotted lines represent the optimal contact times for OPTIANS (233 $\boldsymbol{\mu}$s) and CPMAS (800 $\boldsymbol{\mu}$s), respectively. (D) Comparison of ^{27}Al MAS NMR signal recorded using CPMAS (blue) and OPTIANS (red) with optimal contact time (dotted lines). The time steps for recording polarization transfer curves were 100 $\boldsymbol{\mu s}$ in RACP and 200.1 $\boldsymbol{\mu}$s in case of OPTIANS.

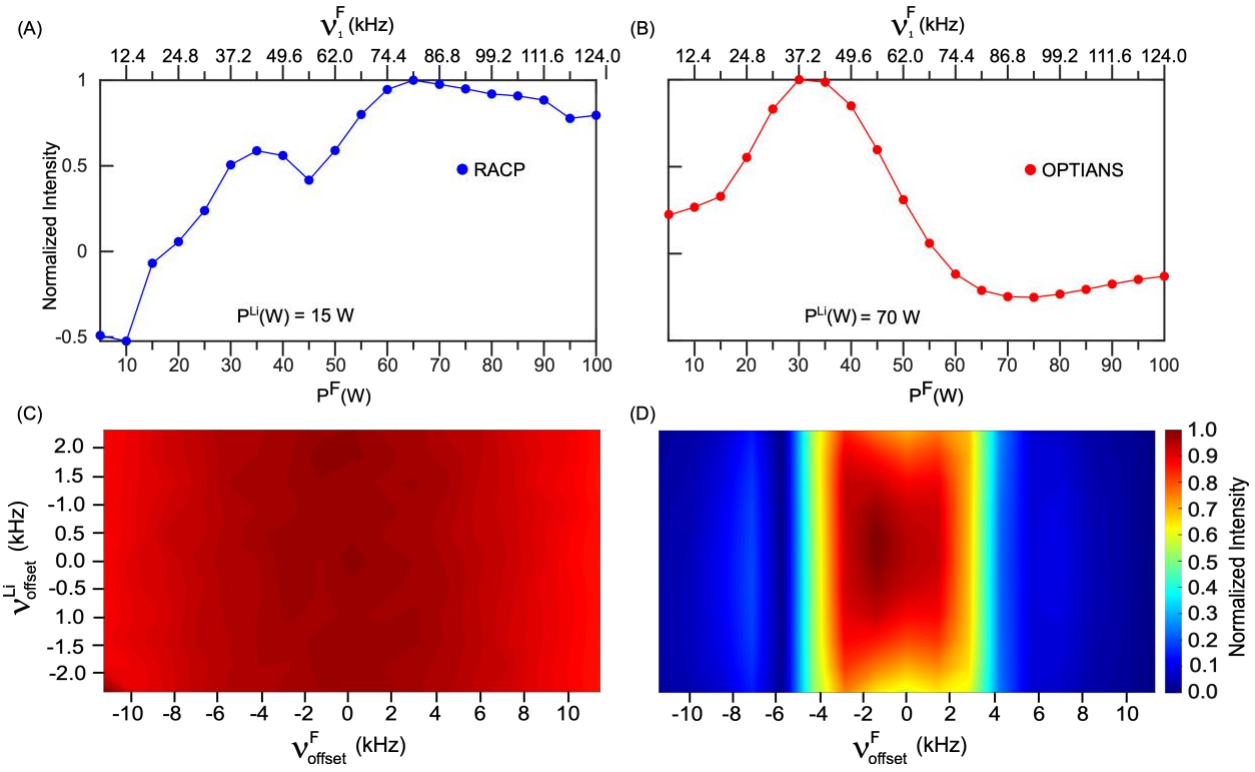


Figure S11. Experimental optimization of the contact pulse and power levels on ^{19}F channel for (A) RACP (blue) and (B) OPTIANS (red). During this optimization, ^{7}Li power level was set to 15 W (30.9 kHz) and 70 W (66.8 kHz) for CPMAS and OPTIANS, respectively. Experimental Offset Profiles of (C) SACP and (D) OPTIANS recorded by variation of offset in both ^{19}F and ^{7}Li channels in an array.

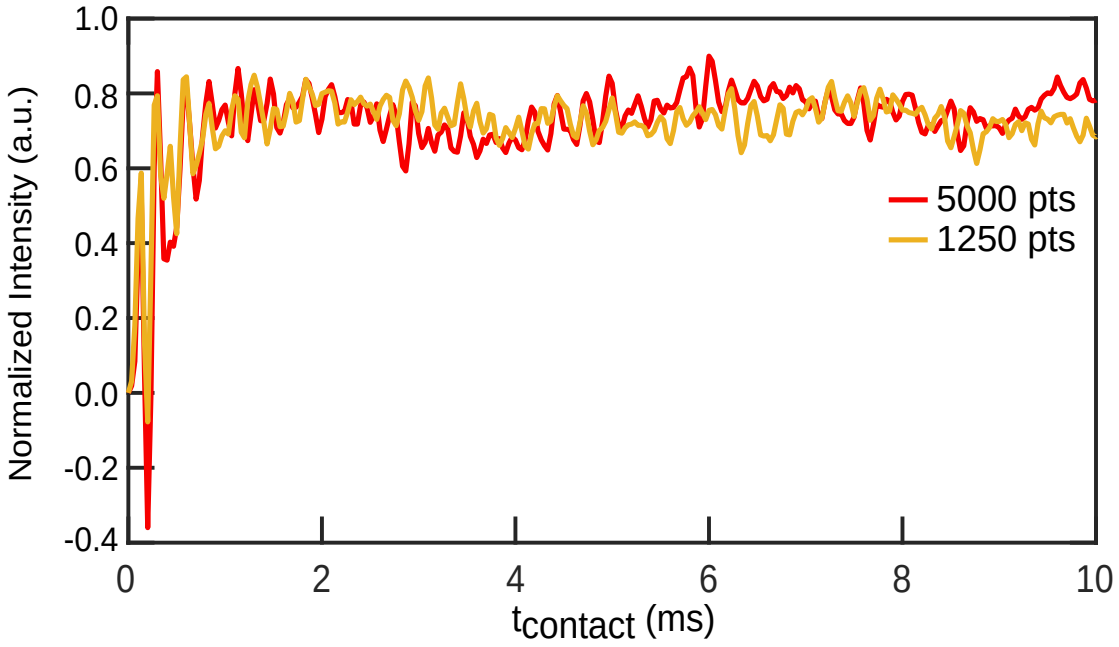


Figure S12. The simulated polarization transfer curves for optimized OPTIANS with 5000 pulse points (Red) and for a pulse which with every fourth point of the original one that is 1250 points (Yellow). The simulation was done at 600 MHz spectrometer with 30 kHz MAS frequency.

SIMPSON Script for Buildup (OPTIANS and SACP)

```
spinsys {
 channels          19F 7Li
 nuclei            19F 19F 19F 7Li
 shift             1 0p 210p 0.1 0 0 0
 shift             2 0p 210p 0.1 0 0 0
 shift             3 0p 210p 0.1 0 0 0
 shift             4 0p 10p 0.5 0 0 0
 dipole            1 2 -10000 0 0 0
 dipole            1 3 -10000 0 0 0
 dipole            2 3 -10000 0 0 0
 dipole            1 4 -6000 0 0 0
 dipole            2 4 -6000 0 0 0
 dipole            3 4 -6000 0 0 0
 quadrupole        4 1 0.25e6 0.107 0 0 0
}

par {
 proton_frequency          400e6
 spin_rate                 42000
 start_operator            I1x+I2x+I3x
 detect_operator           I4p
 crystal_file              rep20
 sw                        spin_rate
 variable duration         3000
 variable tsw              1.0e6/sw
 variable tau              1.0e6/spin_rate
 # np                      round(duration/tsw)
 np                        400
 Gamma_angles              16
 verbose                   1101
 method                    direct
 num_cores                 64
 dipole_check              false
 }

proc pulseq {} {
        global par shF shLi
        acq_block {
                #pulse $par(tsw) 86000 0 44000 0        #for  SACP
                pulse_shaped $par(tsw) $shF $shLi       #for  OPTIANS
        }
}
```

#Take the OPTIANS shapes from the data deposited in FigShare.

```
proc main {} {
        global par shF shLi

        #Load shape for 19F channel
        set shF  [load_shape ./F3Li_F_reopt_dur105ms_MAS42_LiQC250k_FCSA210p_XP_rep20.dat]

        #Load shape for 7Li channel
        set shLi [load_shape ./F3Li_Li_reopt_dur105ms_MAS42_LiQC250k_FCSA210p_XP_rep20.dat]

         set f [fsimpson]
```

```
        fsave $f ./buildup_file_name.txt
        fzerofill $f 16000
        faddlb $f 100 0
        fft $f
        fsave $f ./Fourier_Transformed_buildup_file_name.txt
}
```

SIMPSON Script for Buildup using RACP (ramped-CP)

```
spinsys {

 channels       19F 7Li
 nuclei    19F 19F 19F 7Li
 shift     1 0p 210p 0 0 0 0
 shift     2 0p 210p 0 0 0 0
 shift     3 0p 210p 0 0 0 0
 shift     4 0p 10p 0 0 0 0
 dipole    1 2 -10000 0 0 0
 dipole    1 3 -10000 0 0 0
 dipole    2 3 -10000 0 0 0
 dipole    1 4 -6000 0 0 0
 dipole    2 4 -6000 0 0 0
 dipole    3 4 -6000 0 0 0
 quadrupole   4 1 0.25e6 0.107 0 0 0
}

par {
 proton_frequency   400e6
 spin_rate          42000
 start_operator     I1x+I2x+I3x
 detect_operator    I4x

 crystal_file       rep100
 gamma_angles       8

 sw                 spin_rate/2
 variable tsw       1.0e6/sw
 variable aq_time   0.004
 np                 int(sw*aq_time)
 num_cores          32
 verbose            0
 method             direct
 dipole_check       false
}


proc pulseq {} {
 global par

 acq
 for {set j 1} {$j<$par(np)} {incr j} {

#Preparation of Ramp
   set rf_ch1 [expr $par(rf_ch1_Min)+($j-1)*($par(rf_ch1_Max)-$par(rf_ch1_Min))/($par(np)-1)]
   #set rf_ch2 [expr $par(rf_ch2_Min)+($j-1)*($par(rf_ch2_Max)-$par(rf_ch2_Min))/($par(np)-1)]

   pulse $par(tsw) $rf_ch1 0.0 $par(rf_ch2) 0.0
            acq

 }
}
```

```
proc main {} {
        global par

 for {set k 1} {$k<6} {incr k} {
 for {set i 1} {$i<7} {incr i} {

   set par(rf_ch1_Max)    100000.0

   set par(rf_ch2)    [expr 10000.0+$k*10000.0]
   set par(ramp_mid)    [expr 70+5*$i]
   set par(ramp_start)   [expr 2*$par(ramp_mid)-100]
   set par(rf_ch1_Min)    [expr $par(rf_ch1_Max)*(2*$par(ramp_mid)-100)/100]

   set name ./ RACP_600_conT_3ms_rfF_100kHz_ramp_$par(ramp_start)\_rfLi_$par(rf_ch2)

    set f [fsimpson]
    puts "$name"

        fsave $f  $name.txt
   }
}
}
```

SIMPSON Script for Optimal Control Optimization

```
spinsys {
 channels          19F 7Li
 nuclei            19F 19F 19F 7Li
 shift             1 0p 210p 0.5 0 0 0
 shift             2 0p 210p 0.5 0 0 0
 shift             3 0p 210p 0.5 0 0 0
 shift             4 10p 20p 0.5 0 0 0
 dipole            1 2 -10000 0 0 0
 dipole            1 3 -10000 0 0 0
 dipole            2 3 -10000 0 0 0
 dipole            1 4 -6000 0 0 0
 dipole            2 4 -6000 0 0 0
 dipole            3 4 -6000 0 0 0
 quadrupole        4 1 0.25e6 0.5 0 0 0
}


par {
 proton_frequency          400e6
 spin_rate                 42000
 gamma_angles              16
 crystal_file              rep168
 start_operator            I1x+I2x+I3x
 detect_operator           I4p
 variable NOC              2000
 variable duration         1500
 oc_tol_cg                 1e-8
 oc_tol_ls                 1e-7
 oc_mnbrak_step            5000
 oc_cutoff_iter            5000
 oc_max_brack_eval         5000
 oc_max_brent_eval         5000
 num_cores                 8
 oc_verbose                1
}

proc pulseq {} {
 global par rfshF rfshLi
 reset
 pulse_shaped $par(duration) $rfshF $rfshLi
 oc_acq_hermit
}

proc main {} {
 global par  rfshF rfshLi

  #For Re-optimization in second step
   set rfshF  [load_shape F3Li_F_reopt_dur1500us_MAS42_LiQC70k_FCSA50p_XP_rep20.dat]
   set rfshLi [load_shape F3Li_Li_reopt_dur1500us_MAS42_LiQC70k_FCSA50p_XP_rep20.dat]

   set tfopt [oc_optimize $rfshF -max 90000  $rfshLi -max 80000 ]

   save_shape $rfshF  ./F3Li_F_reopt_dur1500us_MAS42_LiQC250k_FCSA210p_XP_rep20.dat
   save_shape $rfshLi ./F3Li_Li_reopt_dur1500us_MAS42_LiQC250k_FCSA210p_XP_rep20.dat
```

```
free_all_shapes
}

proc target_function {} {
  global par
  set par(np) 1.0
  set f [fsimpson]
  set Res [findex $f 1 -re]
  return [format "%.20f" $Res]
}

proc gradient {} {
  global par rfshF rfshLi

  set par(np) [expr 2*$par(NOC)]
  set f [fsimpson]
  return $f
}
```

Bruker Pulse Program for OPTIANS 1D experiment

```
;OPTIANS_looping_with presat
;avance-version (20/11/23)
;written by Shovik Ray and Sheetal K. Jain
;
;Avance III version
;parameters:
;p3                 : f2 channel 90 at power level PLW3
;p15                : contact time at SPW1(f1) and SPW0(f2)
;pl1                : f1 channel power level during contact
;pl4                : f1 channel Power level during saturation block
;pl12               : decoupling power level (f2)
;spw0               : f2 channel power level during contact
;spw1               : f1 channel power level during contact
;cnst21             : on resonance, usually = 0
;cpdprg2  : spinal64 (at PLW12)
;d1                 : recycle delay
;pcpd2              : pulse length in decoupling sequence

;spnam0             : use F-Li_FPulse(1250) from wave folder under lists section of your current topspin version
;spnam1             : use F-Li_LiPulse(1250) from wave folder under lists section of your current topspin version

;zgoptns  : -Dfslg, -Dlacq, -Dlcp15, or blank
;;cnst31   : spinning speed
;$CLASS=Solids
;$DIM=1D
;$TYPE=optimal control cross polarisation
;$SUBTYPE=simple 1D

; Don't exceed the loop number(l1) beyond 140
prosol relations=<solids_cp>

#include <Avance.incl>

#ifdef fslg
#include <lgcalc.incl>
;cnst20 : RF field achieved at pl13
;cnst21 : on resonance, usually = 0
;cnst22 : positive LG offset
;cnst23 : negative LG offset
;cnst24 : additional LG-offset
#endif /* fslg */

"acqt0=0" ;defines t=0 for baseopt
"loccp=l1"
"p20=(2.0s/cnst31)"
"occpmix=(2.0s/cnst31)*loccp"

1 ze

2 d1 do:f2
3 d20                          ;saturation block starts. If not needed then remove till "lo to 3 times l20".
  (p1 pl4 ph4):f1
  d20*2
  (p1 pl4 ph4):f1
  d20*3
```

```
 (p1 pl4 ph4):f1
 d20*4
 (p1 pl4 ph4):f1
 lo to 3 times l20
#ifndef lcp15
#include <p15_prot.incl>
                                        ;make sure p15 does not exceed 10 msec

                                        ;more is needed
#endif
#ifndef lacq
                                        ;disable protection file for long acquisition change decoupling power !!!
                                        ;if you set the label lacq (ZGOPTNS -Dlacq), the protection is disabled

#include <aq_prot.incl>
                                        ;allows max. 50 msec acquisition time, supervisor
                                        ;may change  to max. 1s at less than 5 % duty cycle
                                        ;and reduced decoupling field
#endif

 1u fq=cnst21:f2
 1u fq=cnst22:f1
 (p3 pl3 ph1):f2
4 (p20:sp1 ph2):f1 (p20:sp0 ph10):f2            ;choose F-Li_FPulse(1250) as spnam0 and F-Li_LiPulse(1250) as ;spnam1 (see
                                                ;spnam0 and spnam 1 in comments section)
 lo to 4 times l1                               ; Don't exceed the loop number(l1) beyond 140
 1u cpds2:f2                                    ;pl12 is used here with spinal64
 go=2 ph31
 1m do:f2
 wr #0
HaltAcqu, 1m
exit

ph0= 0
ph1= 1 3
ph2= 0 0 2 2 1 1 3 3
ph4= 0
ph10= 0
ph31= 0 2 2 0 1 3 3 1

;$Id:$
```

For processing the obtained data, simply use **“ef-apk-absn”**

Bruker Pulse Program for OPTIANS 2D experiment

```
;hxhetcor (TOPSPIN 4.3.0)

; heteronuclear correlation between protons and X nuclei
; with or without homonuclear decoupling during t1
; possible decoupling schemes are FSLG, PMLG, and DUMBO
; create dumbo pulse using AU program dumbo
; create pmlg pulse using AU program pmlg_shape

; written by Shovik Ray and Sheetal K. Jain

;Avance II+ version
;parameters:
;ns                 : 2, n*4
;d1                 : recycle delay
;p3                 : f2 channel 90 at power level PLW3
;p15                : contact time at SPW1(f1) and SPW0(f2)
;pl1                : f1 channel power level during contact
;pl4                : f1 channel Power level during saturation block
;pl12               : decoupling power level (f2)
;sp0                : f2 channel power level during contact
;cnst21   : on resonance, usually = 0
;cpdprg2            : spinal64 (at PLW12)
;d1                 : recycle delay
;pcpd2              : pulse length in decoupling sequence
;spnam0             : use F-Li_FPulse(1250) from wave folder under lists section of your current topspin version
;spnam1             : use F-Li_LiPulse(1250) from wave folder under lists section of your current topspin version
;pcpd2              : pulse length in decoupling sequence
;phcor3   : phase correction for optimal FSLG peformance: minimize zero frequency glitch in F1
;cpdprg2            : spinal64
;cnst20   : LG-RF field as adjusted, in Hz used to calculate cnst22 and cnst23 +and - LG frequency
;cnst21   : additional LG offset, usually =0
;cnst22   : +ve LG offset
;cnst23   : -ve LG offset
;l0                 : =0, increment for t1
;l3                 : 1, 2, or 4 for dwell in t1
;zgoptns : -Dfslg, -Ddumbo, -Dpmlg, -Dnodec
;FnMode : States-TPPI, States, or TPPI for zgoptns -Dnodec
;             undefined for all other zgoptns
;mc2                : States-TPPI, if FnMode undefined, in case of States the statement "1m rp0" must be activated
;                     by removing semicolon at the beginning of the corresponding line
;in_010   : =1/swh {f1}, calculated in program
;nd_010  : 1

;$COMMENT=HETCOR (OCCP based), with or w/o homonuclear decoupling during t1, various schemes possible
;$CLASS=Solids
;$DIM=2D
;$TYPE=cross polarisation
;$SUBTYPE=heteronuclear correlation

define loopcounter nfid
"nfid=td1/2"

;cnst11 : to adjust t=0 for acquisition, if digmod = baseopt
"acqt0=1u*cnst11"

prosol relations=<solids_cp>
```

```
"loccp=l1"
"p20=(2.0s/cnst31)"
"in0 = inf1"
"occpmix=(2.0s/cnst31)*loccp"

1 ze
2 10m do:f2
 d1                                    ;recycle delay
3 d20                                  ;saturation block starts. If not needed then remove till "lo to 3 times l20".
 (p1 pl4 ph4):f1
 d20*2
 (p1 pl4 ph4):f1
 d20*3
 (p1 pl4 ph4):f1
 d20*4
 (p1 pl4 ph4):f1
 lo to 3 times l20

 (p3 pl12 ph0):f2              ;Fluorine 90  pulse

  d0

4 (p20:sp1 ph2):f1 (p20:sp0 ph10):f2          ;choose F-Li_FPulse(1250) as spnam0 and F-Li_LiPulse(1250) as spnam1
  lo to 4 times l1                            ; (see spnam0 and spnam 1 in comments section)

 1u cpds2:f2                                  ;pl12 is used here with spinal64
 go=2  ph31
 1m do:f2
 10m mc #0 to 2 F1PH(ip0,id0)
exit

ph0= 1 3
ph4= 0
ph2= 0 0 2 2 1 1 3 3
ph10= 0
ph31= 0 2 2 0 1 3 3 1
```

For processing the obtained data, simply use **"xfb"**

Table S1: Optimized pulse parameters used in ^{19}F-^{7}Li Experiments involving OPTIANS and RACP.

Nucleus / Parameters	OPTIANS		RACP	
	^{19}F	^{7}Li	^{19}F	^{7}Li
Optimal 90° pulse length	112 W, 1.8 μs (138.9 kHz)	80 W, 3.5 μs (71.4 kHz)	112 W, 1.8 μs (138.9 kHz)	80 W, 3.5 μs (71.4 kHz)
Optimal Contact Pulse Power	30 W i.e., 71.8 kHz	70 W i.e., 66.8 kHz	65 W i.e., 101.6 kHz (50.8-101.6)	15 W i.e., 30.9 kHz
Optimal Contact Time	1.26 ms		300 μs	

Table S2: Optimized pulse parameters used in ^{19}F-^{23}Na Experiments involving OPTIANS and RACP.

Nucleus / Parameters	OPTIANS		RACP	
	^{19}F	^{23}Na	^{19}F	^{23}Na
Optimal 90° pulse length	112 W, 1.8 μs (138.9 kHz)	76.5 W, 4.5 μs (55.5 kHz)	112 W, 1.8 μs (138.9 kHz)	76.5 W, 4.5 μs (55.5 kHz)
Optimal Contact Pulse Power	80 W i.e., 117.4 kHz	15 W i.e., 24 kHz	5 W i.e., 101.6 kHz	20 W i.e., 28.41 kHz
Optimal Contact Time	2.66 ms		200 μs	

Table S3: Optimized pulse parameters used in ^{19}F-^{27}Al Experiments involving OPTIANS and RACP.

Nucleus / Parameters	OPTIANS		RACP	
	^{19}F	^{27}Al	^{19}F	^{27}Al
Optimal 90° pulse length	15 W, 2.5 μs (138.9 kHz)	20.4 W, 3.18 μs (78.6 kHz)	15 W, 2.5 μs (138.9 kHz)	20 W, 3.18 μs (78.6 kHz)
Optimal Contact Pulse Power	15 W i.e., 153.37 kHz	15 W i.e., 67.39 kHz	40 W i.e., 161.2 kHz	40 W i.e., 110.13 kHz
Optimal Contact Time	266.6 μs		800 μs	