Supporting information

Solvent-Free Dynamic Nuclear Polarization of Amorphous and Crystalline Ortho-Terphenyl

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Synthesis of bis-TEMPO terephthalate (bTtereph)

bis-TEMPO terephthalate (bTtereph) was synthesized by the dropwise addition of a solution of terephthaloyl chloride (2 mM in dichloromethane (DCM)) to a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine-l-oxyl (5.8 mM) and pyridine (6 mM) in DCM at 0 °C. The solution was then stirred at that temperature for one hour before being warmed to room temperature where it was stirred for an additional twelve hours. After washing with acidic water (pH 4) the organic phase was concentrated and purified via column chromatography (cyclohexane/ethyl acetate). The orange-red, crystalline powder was obtained with an overall yield of 40%.

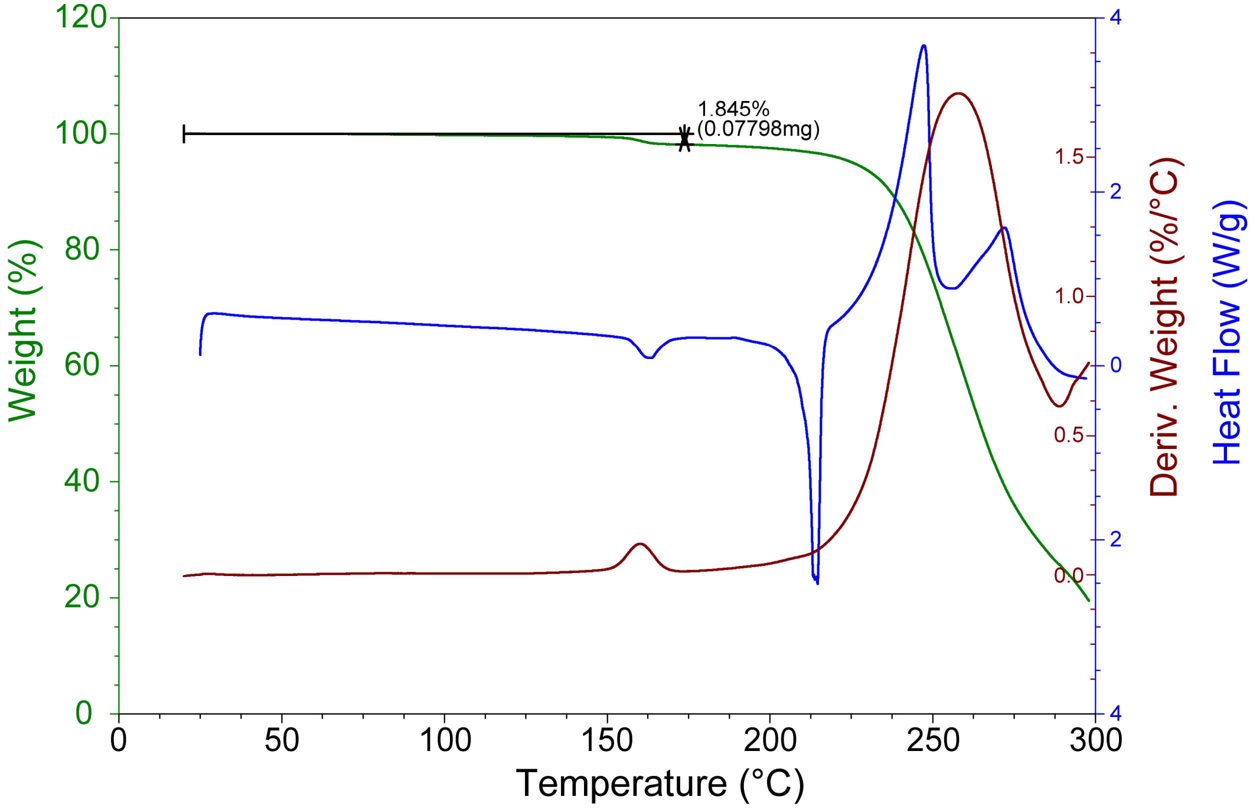

Figure S1. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) plots of bTtereph. Measurements of bTtereph weight (green) and change in weight (maroon) show decomposition starting at ~160 °C. DSC thermogram (blue) shows two endothermic events at 160 and 210 °C, followed by two exothermic events at higher temperatures.

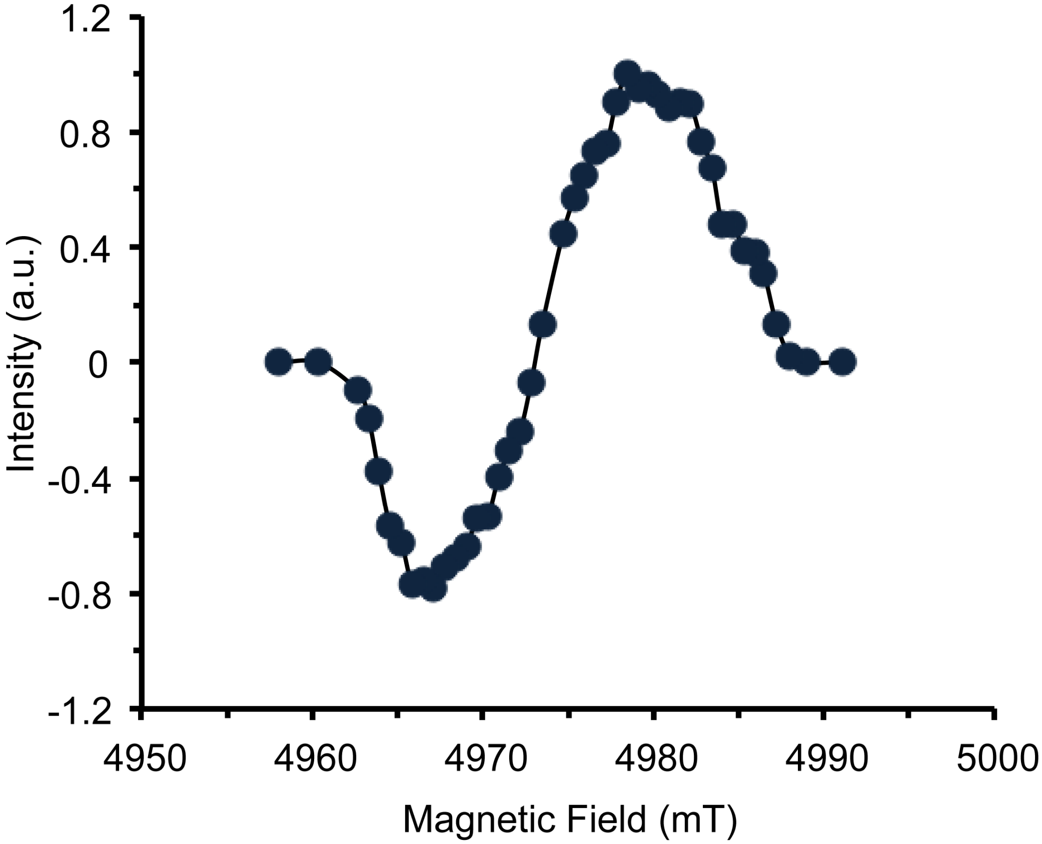

Figure S2. NMR field dependent ^{1}H enhancement (ε) profile of bTtereph in 95% deuterated amorphous OTP, taken at 5 T using 8 W of microwave power and MAS frequency of 4.5 kHz. A line is drawn connecting the data points as a guide.

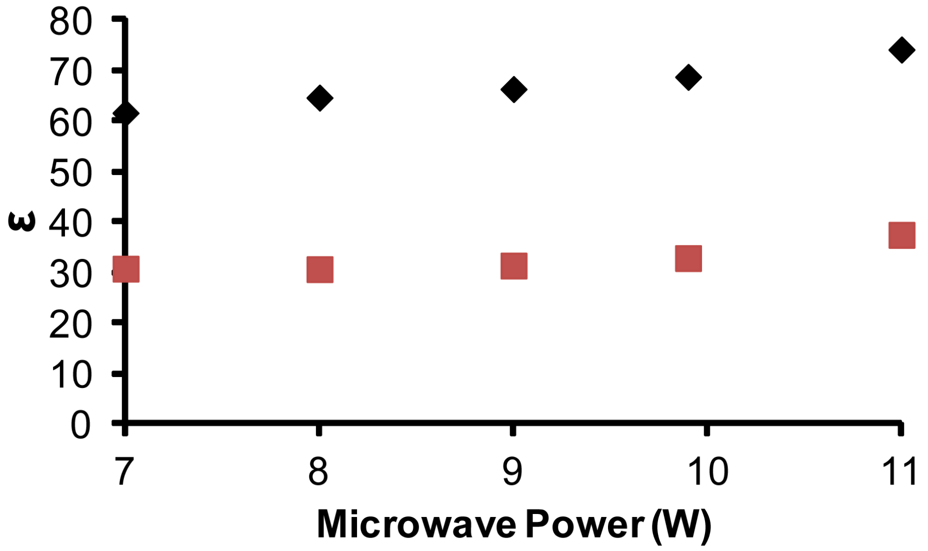

Figure S3. DNP enhancement (ε) as a function of gyrotron microwave power from 7 to 11 W. A small increase (~ 10%) in enhancement was observed for the amorphous (♦) and the crystalline (■) 95% deuterated OTP with 0.5 mol% bTtereph.

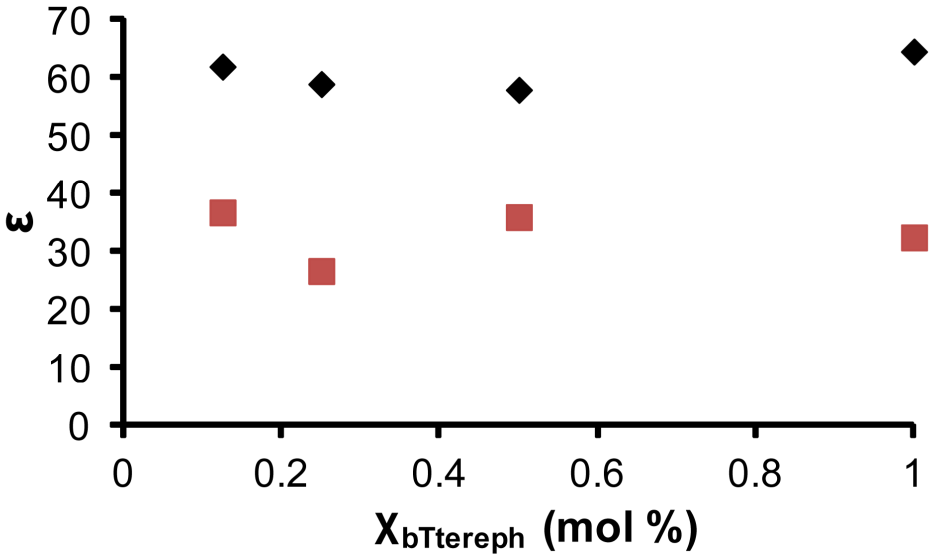

Figure S4. DNP enhancement (ε) as a function of bTtereph concentration up to 1 mol% for the amorphous (♦) and the crystalline (■) 95% deuterated OTP using 8 W microwave power and MAS frequency of 4.5 kHz.

Simulations of EPR spectra

EPR spectra have been simulated (Figure S5) using the EasySpin package.[1] In the case of the amorphous samples the spectra recorded at 9 GHz (X-Band) and 140 GHz have been simulated with a single set of parameters. The first derivative of the 140 GHz spectrum has been obtained using EasySpin's "fieldmod" function with 0.3 mT pseudo-modulation amplitude. Two $S = 1/2$ electron spins each hyperfine coupled to a ^{14}N nucleus were assumed with the following set of interaction tensors: $g_{xx} = 2.00221$; $g_{yy} = 2.00636$; $g_{zz} = 2.01016$; $A_{xx} = 97.5$ MHz; $A_{yy} = 18.0$ MHz; $A_{zz} = 19.0$ MHz; $D_{xx} = -7.5$ MHz; $D_{yy} = -7.5$ MHz; $D_{zz} = 15.0$ MHz. The g and hyperfine coupling (A) tensors were assumed to be identical and collinear for both electrons. The electron–electron interaction (described by D) was assumed to be purely dipolar in nature; no exchange interaction was considered. Line broadening has been applied independently for each frequency. For 9 GHz, orientation dependent broadening ("HStrain") has been applied with 21, 28, and 17 MHz in the x, y, and z orientation, respectively; for 140 GHz, 16, 28, and 34 MHz have been used. General Gaussian line broadening (*via* the "lw" parameter) of 0.1 mT (full width at half maximum, FWHM) has been applied for both frequencies while for 9 GHz an additional Lorentzian broadening of 0.16 mT (FWHM) was used (also *via* the "lw" parameter).

The spectra of bTtereph in crystalline OTP can be simulated by weighted summation of the spectrum of bTtereph in amorphous OTP and a featureless line with $g = 2.0064$. In order to mimic the shape of this homogeneous line, a distribution of Lorentzian lines with widths between 0.1 and 10 mT (FWHM) had to be assumed. For the simulation, a probability distribution with

$$p(\delta) \propto \delta^4 e^{-\frac{\delta}{0.7}} \tag{0.1}$$

reproduced the line shape adequately. The distribution probability is shown in Figure S6. Note that this function was chosen solely to reproduce the line shape and is not based on physical models regarding cluster size distribution, for example. The relative intensity (double integral) of the resolved bTtereph signal is ~8 %.

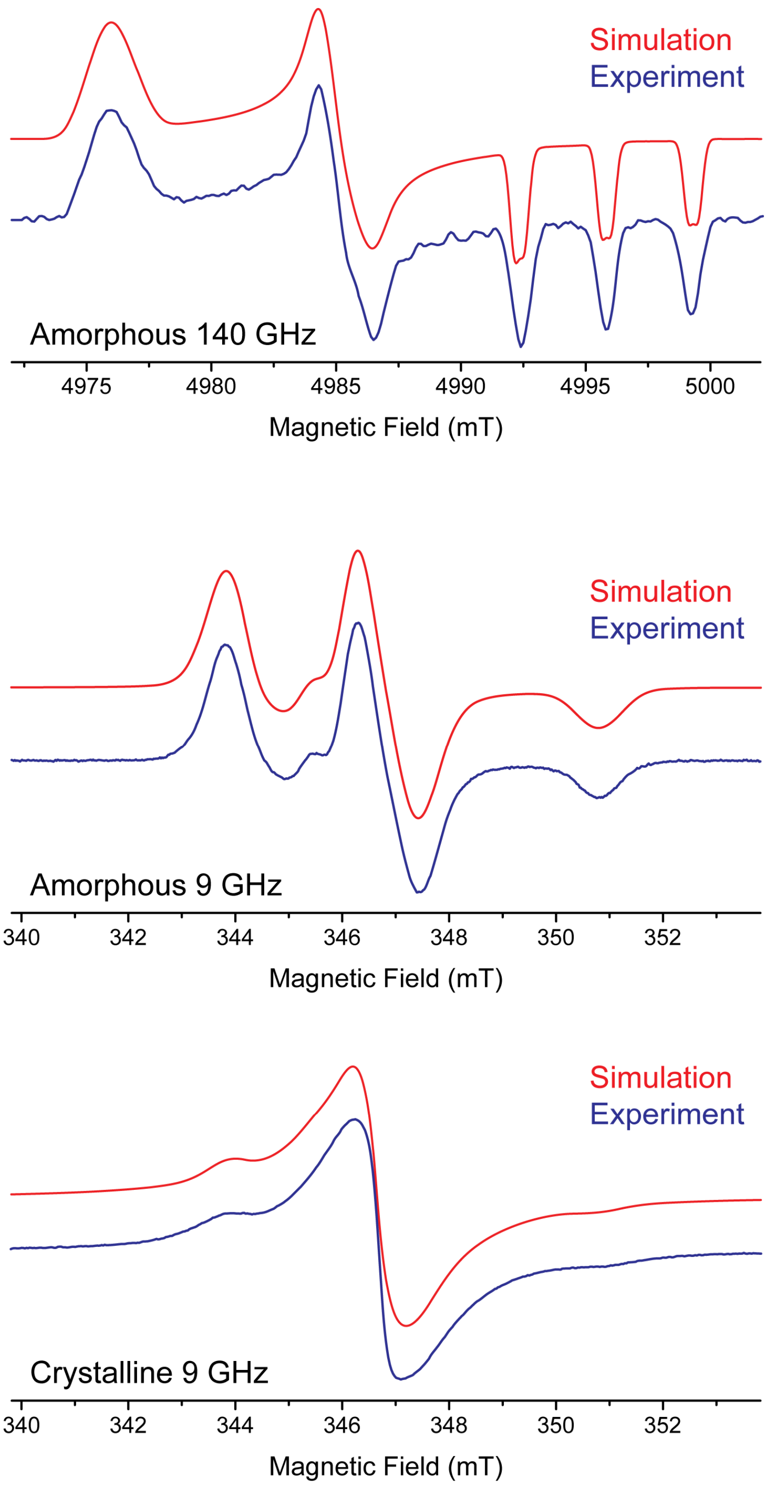

Figure S5. Experimental and simulated EPR spectra of bTtereph in amorphous or crystalline OTP at 9 or 140 GHz.

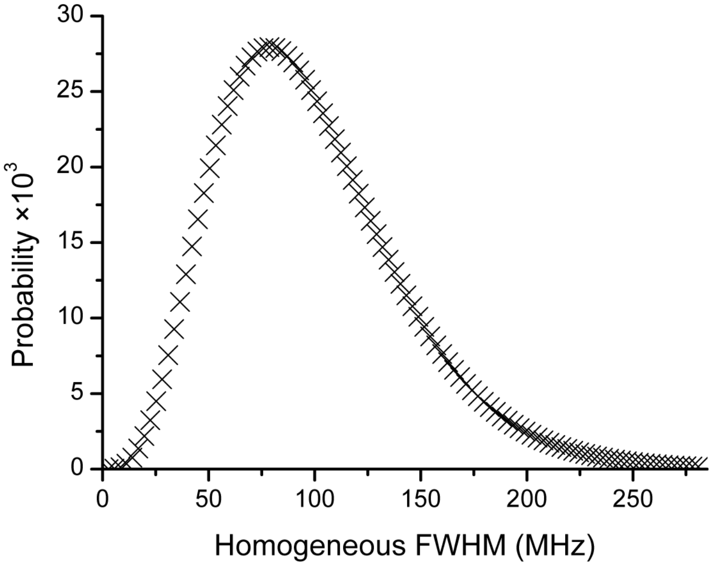

Figure S6. Probablity distribution of Lorentzian linewidth used to simulate the 9 GHz EPR spectrum of bTtereph in crystalline OTP. The linewidth distribution peaks at 79 MHz.

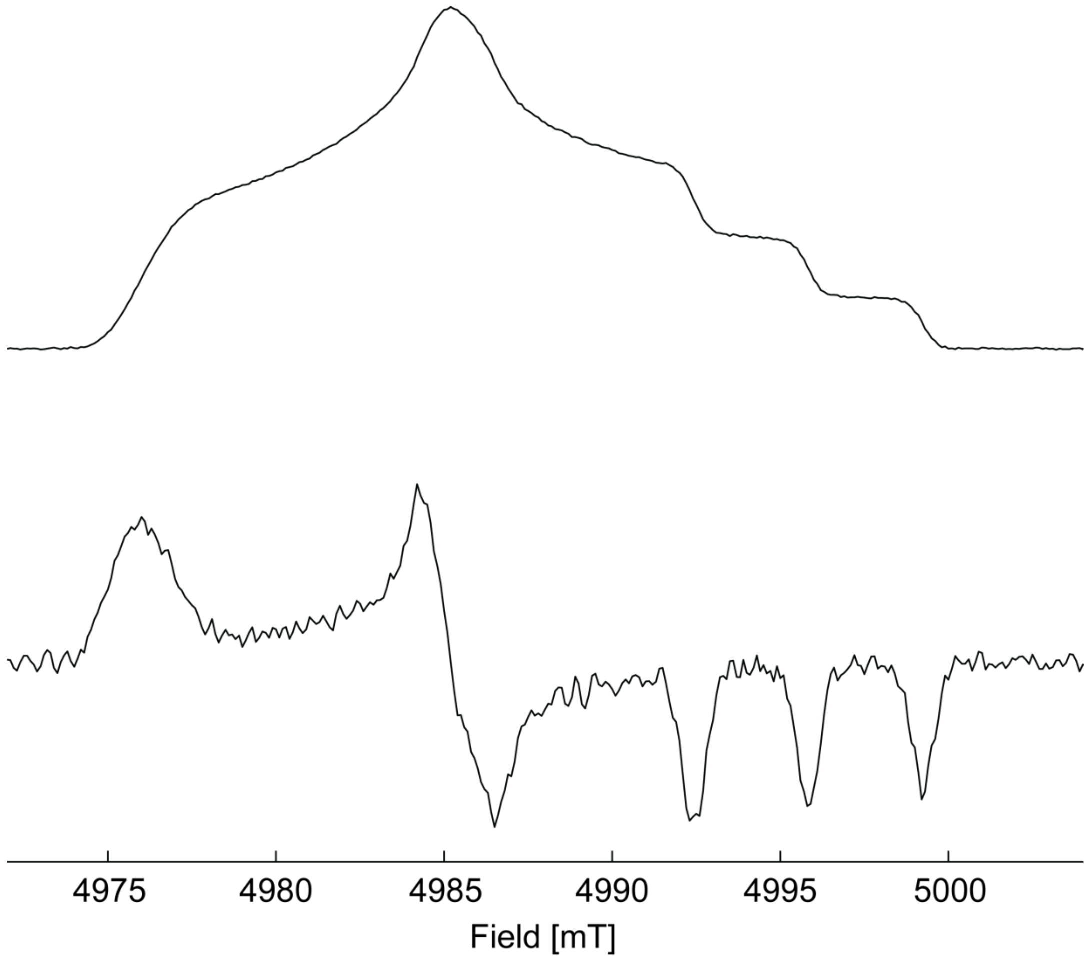

Figure S7. Pulsed 140 GHz EPR spectra of bTtereph in fully deuterated amorphous OTP at 80 K.

The 140 GHz EPR spectrum of 0.0125 mol% bTtereph in OTP were acquired at 80 K, using a high-field pulsed EPR system described elsewhere.[2] A Hahn echo ($\pi/2$-τ-π) was used with a timing of 68 ns – 200 ns – 136 ns, and the echo was integrated at each field point. 4800 shots were acquired at each of 321 field points from 4972 mT to 5004 mT, using a two-step phase cycle. The derivative spectrum was calculated from the absorption spectrum using the “fieldmod” function from EasySpin[1], with a 0.3 mT modulation amplitude.

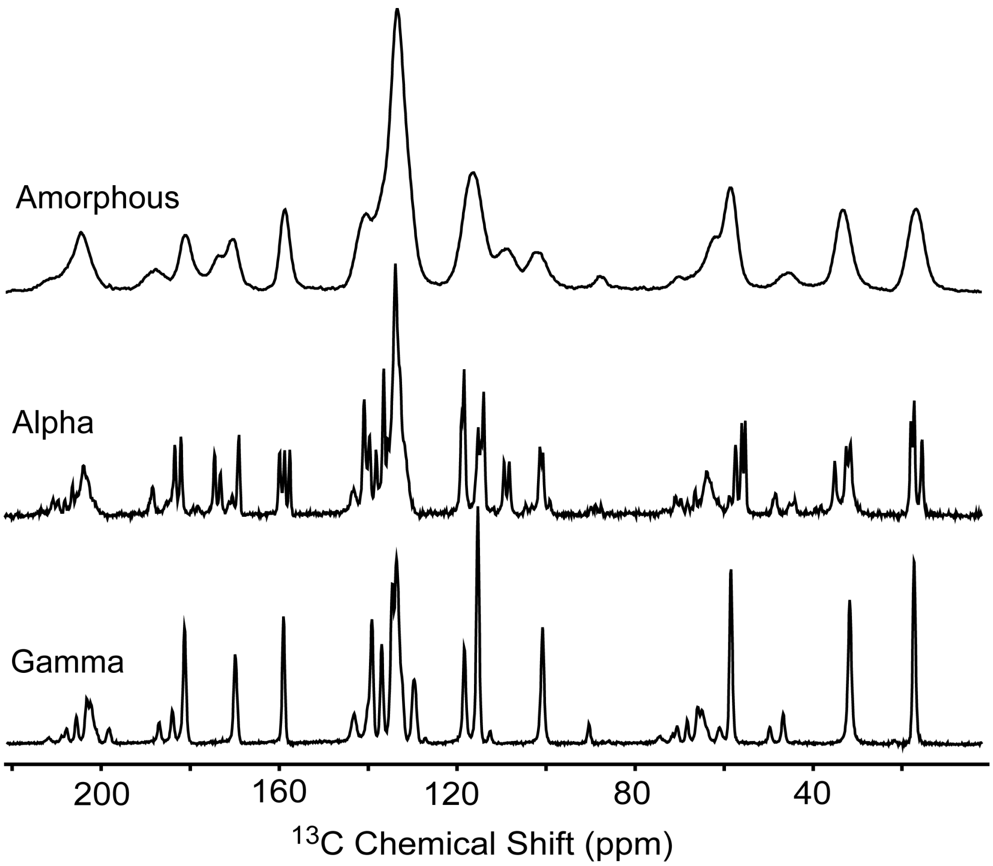

Figure S8. Room-temperature ^{13}C CPMAS NMR spectra of amorphous and crystalline (α and γ crystals) indomethacin. Data were acquired on a 11.7 T (500.7 MHz, ^{1}H) home-built spectrometer (courtesy of Dr. Dave Ruben) using a triple channel MAS probe with spinning frequency of 8 kHz. All data were acquired for 24 hours using TPPM decoupling.[3]

References

1. Stoll, S.; Schweiger, A., *J. Magn. Reson.* **2006,** *178* (1), 42-55.
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