

Supporting information for

## **DNP NMR Spectroscopy of Cross-linked Organic Polymers: Rational Guidelines towards Optimal Sample Preparation**

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**1. Tables for the preparation of PS-supported alkylammonium salts**

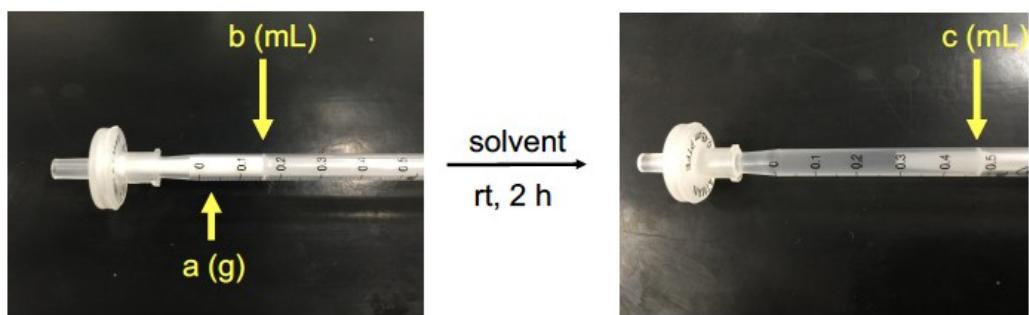
**Table S1.** C, H, N contents (%) of PS-supported alkylammonium salts

	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3c-<sup>15</sup>N</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>	<b>3g</b>	<b>3h</b>	<b>3i</b>
C	63.10	65.43	73.95	76.92	76.72	80.04	81.02	61.71	64.24	60.87
H	8.70	9.53	9.67	9.34	10.55	10.14	10.17	8.99	8.83	8.31
N	3.88	3.60	2.98	2.06	2.15	1.71	1.52	3.63	4.03	5.93

**Table S2.** Efficiencies of functionalization (%)

<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3c-<sup>15</sup>N</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>	<b>3g</b>	<b>3h</b>	<b>3i</b>
74	77	78	45	87	58	56	74	81	62

**2. Figure and table for syringe method for swelling test**



**Figure S1.** Syringe method for determination of swelling property

**Table S3.** Swelling volume for polymers

		<b>1</b>	<b>2</b>	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>	<b>3g</b>	<b>3h</b>	<b>3i</b>
Swelling volume (mL/g)	TCE	2.7	1.4	0.2	0.3	1.6	1.8	1.0	1.0	0.2	<0.1	<0.1
	DMSO	<0.1	0.5	0.9	1.1	1.4	0.4	0.2	0.3	1.2	1.0	0.4

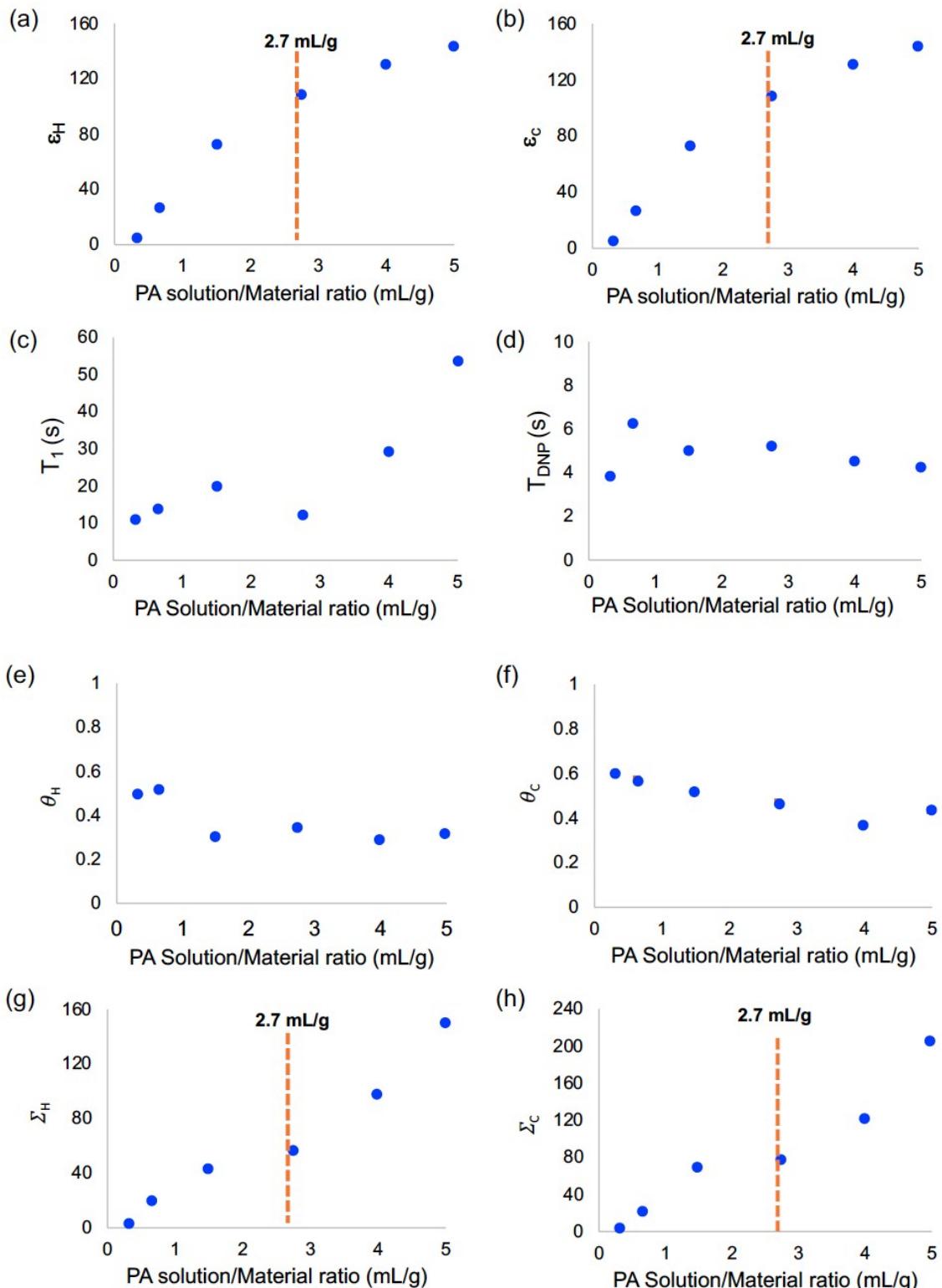
### 3. Table for the results of DNP solid-state NMR measurement

**Table S4.**  $\varepsilon_H$ ,  $\varepsilon_C$ ,  $T_{DNP}$ ,  $T_1$ ,  $\theta_H$ ,  $\theta_C$ ,  $\Sigma_H$ , and  $\Sigma_C$  for polymers

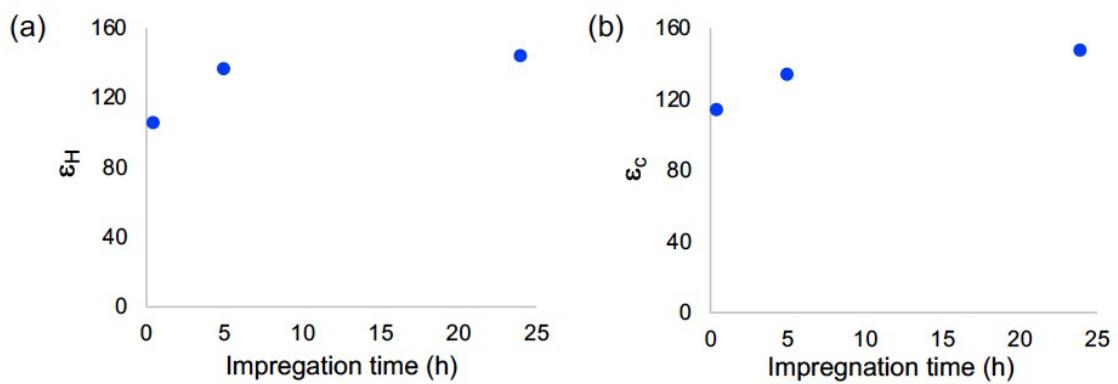
		<b>1</b>	<b>2</b>	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>3d</b>	<b>3e</b>	<b>3f</b>
$\varepsilon_H^a$	TEKPol/TCE	108	86	4	1	36	29	29	21
	AMUPol/DMSO	1	37	128	74	100	39	7	7
$\varepsilon_c^a$	TEKPol/TCE	107	88	1	1	37	28	29	21
	AMUPol/DMSO	1	16	41	35	45	15	4	4
$T_{DNP}$ (s) <sup>b</sup>	TEKPol/TCE	5.2	6.7	30	5.3	11	12	7.6	13
	AMUPol/DMSO	21	3.8	3.2	2.7	2.9	3.8	4.9	10
$T_1$ (s) <sup>c</sup>	TCE	12.3	27.6	30.6	9.65	17	11.8	20.3	10.7
	DMSO	11.4	19.2	27.3	12.5	23.3	8.22	11.6	10.2
$\theta_H^d$	TEKPol/TCE	0.34	0.68	0.71	0.87	0.78	0.62	0.84	0.64
	AMUPol/DMSO	0.78	0.71	0.52	0.40	0.48	0.48	0.61	0.70
$\theta_C^d$	TEKPol/TCE	0.47	0.63	0.99	0.97	0.97	1.0	1.0	0.98
	AMUPol/DMSO	0.87	0.86	0.57	0.57	0.49	0.59	0.77	0.79
$\Sigma_H^e$	TEKPol/TCE	57	113	2.9	1.2	35	18	40	12
	AMUPol/DMSO	0.57	59	195	63	135	28	6.6	4.9
$\Sigma_C^e$	TEKPol/TCE	77	119	1	1.3	44	28	48	19
	AMUPol/DMSO	0.64	31	69	43	63	13	4.7	3.2

<sup>a</sup>DNP enhancement defined as equation 1. <sup>b</sup>DNP build-up time. <sup>c</sup><sup>1</sup>H longitudinal relaxation time of sample swollen in solvent. <sup>d</sup>contribution factor defined as equation 2. <sup>e</sup>overall sensitivity gain defined as equation 3.

#### 4. Optimization of PA solution/material ratio and impregnation time

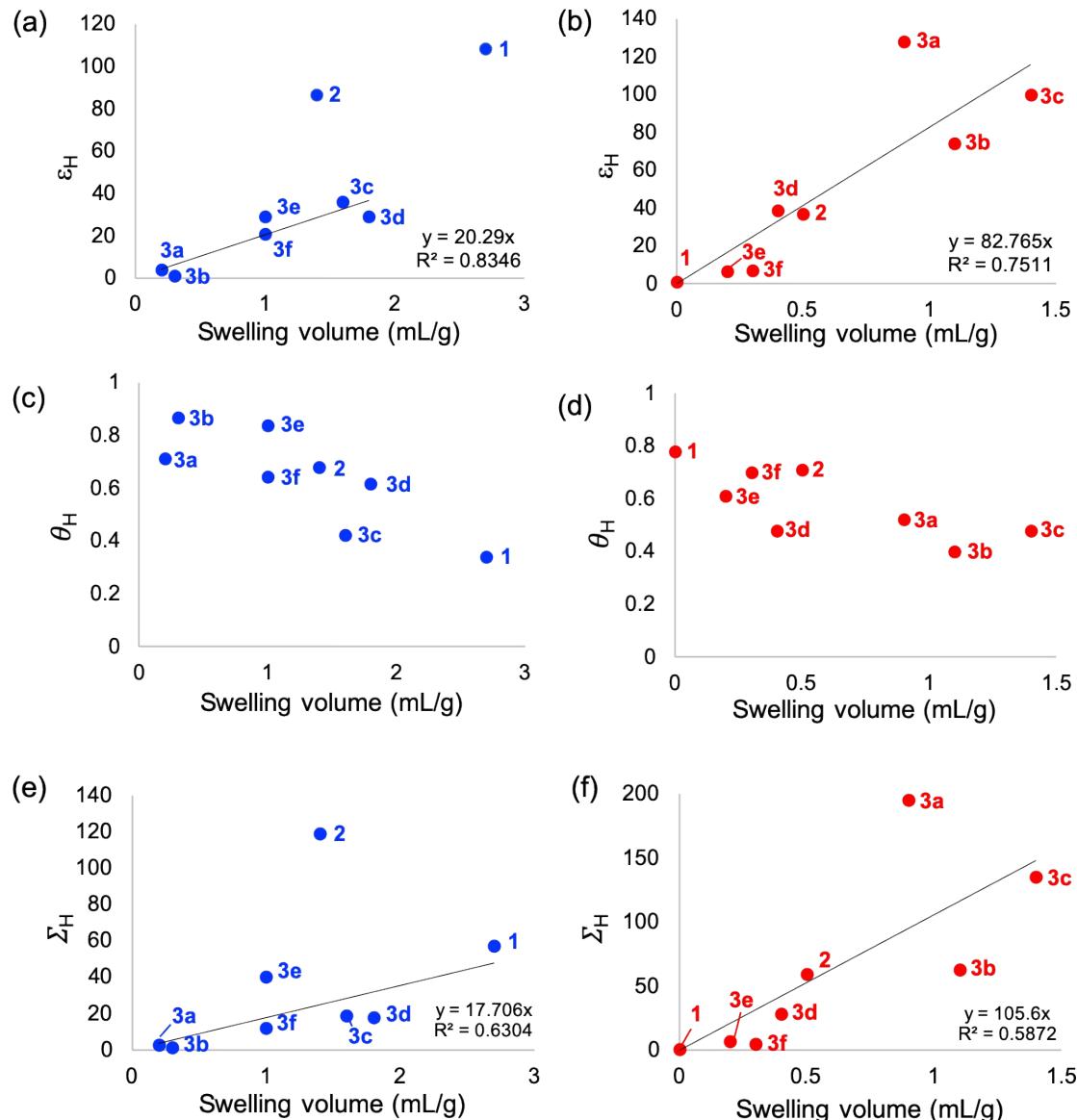


**Figure S2.** Plot of PA solution/material ratio (mL/g) for the sample of **1** with TEKPol/TCE solution versus  $\varepsilon_H$  (a),  $\varepsilon_C$  (b),  $T_1$  (c),  $T_{DNP}$  (d),  $\theta_H$  (e),  $\theta_C$  (f),  $\Sigma_H$  (g), and  $\Sigma_C$  (h)



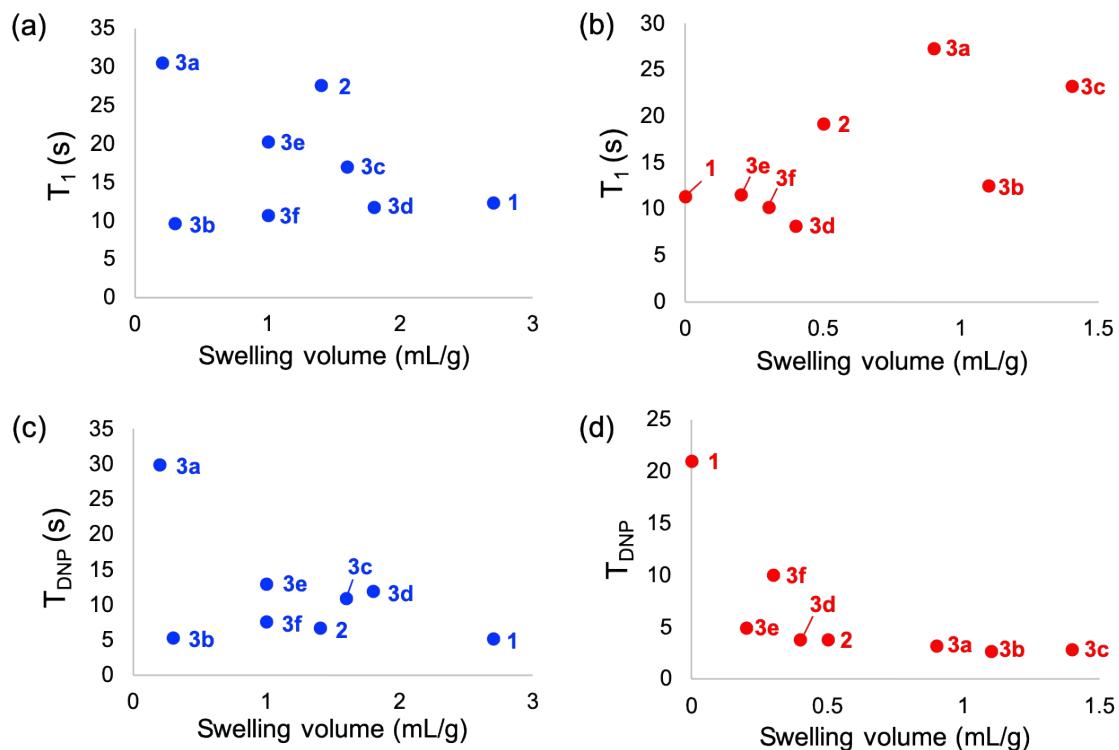
**Figure S3.** Plot of impregnation time for **1** with TEKPol/TCE solution (PA solution/material (mL/g): 5) versus  $\epsilon_H$  (a) and  $\epsilon_C$  (b)

## 5. Relation of swelling property and DNP enhancement for $^1\text{H}$ nuclei ( $\varepsilon_{\text{H}}$ )



**Figure S4.** The plot of swelling volume for TCE (blue circle) and DMSO (red circle) versus  $\varepsilon_{\text{H}}$  (a, b),  $\theta_{\text{H}}$  (c, d), and  $\Sigma_{\text{H}}$  (e, f)

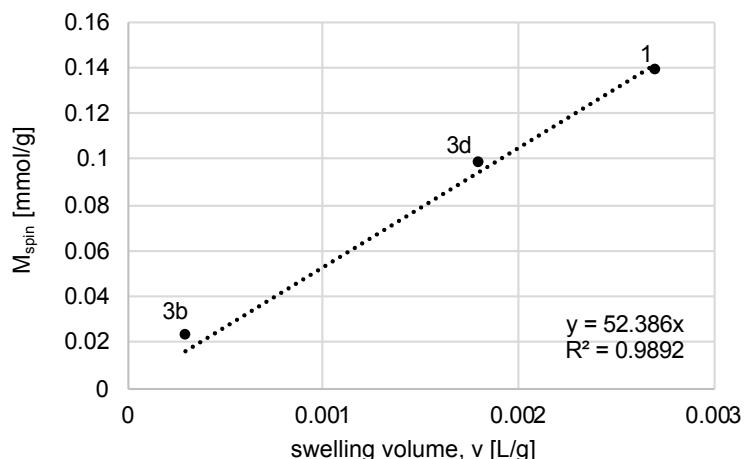
**6. Relation of swelling property and longitudinal relaxation time with solution ( $T_1$ ) and DNP build-up time ( $T_{DNP}$ )**



**Figure S5.** The plot of  $T_1$  versus swelling volume for TCE (a) and DMSO (b) and  $T_{DNP}$  versus swelling volume for TCE (c) and DMSO (d)

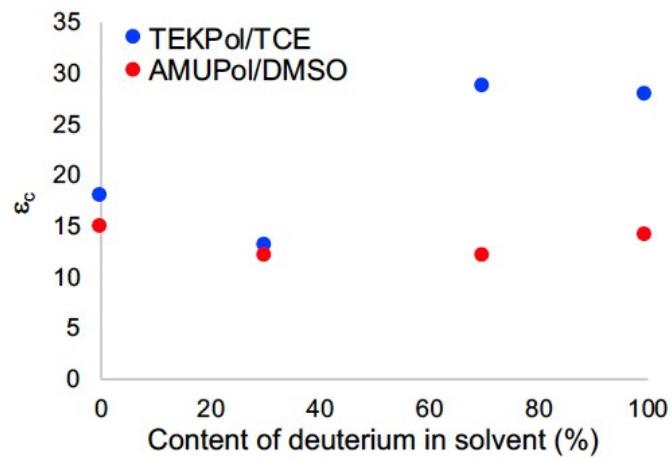
## 7. Spin counting experiment by EPR spectroscopy

Continuous Wave (CW) EPR spectra were recorded on a Bruker EMXNano X-band spectrometer (9.5 GHz microwave frequency). The conversion time was set to 15 ms and the time constant to 1.28 ms. 2000 data points were recorded. The modulation frequency was 100 kHz and the modulation amplitude was 1 G. For spin counting experiment, the NMR sample rotor packed with swollen polymers prepared by same procedure as DNP-NMR measurement was directly charged in quartz tube. Polymers **1**, **3b**, and **3d** with TEKPol/TCE (16 mM) solution was used. The spectra were recorded at room temperature with a sweep width of 200 G and an attenuation of 25 dB. Quantitative spin concentrations were directly obtained via the built-in EMXnano reference-free spin counting module (Xenon software, Bruker). Molar amounts of spin per weight of dry polymer,  $M_{\text{spin}}$  (mmol/g) were determined. The following figure displays the linear correlation between  $M_{\text{spin}}$  and swelling volume,  $v$  (L/g) (Figure S6).

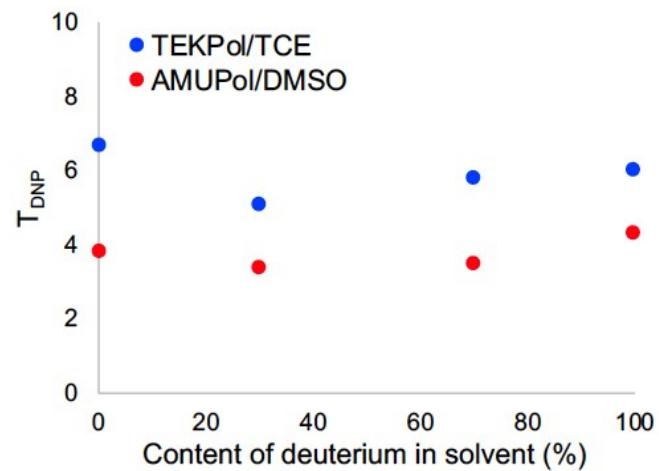


**Figure S6.** The plot of  $M_{\text{spin}}$  versus swelling volume,  $v$

## 8. Effect of partial deuteration of solvent on DNP experiment

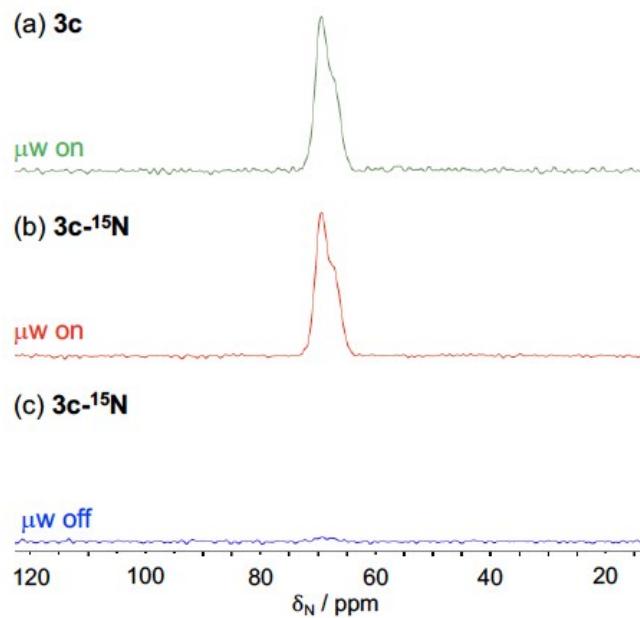


**Figure S7.** Plot of  $\varepsilon_c$  versus content of deuterium in solvent for TCE (blue circle) and DMSO (red circle)



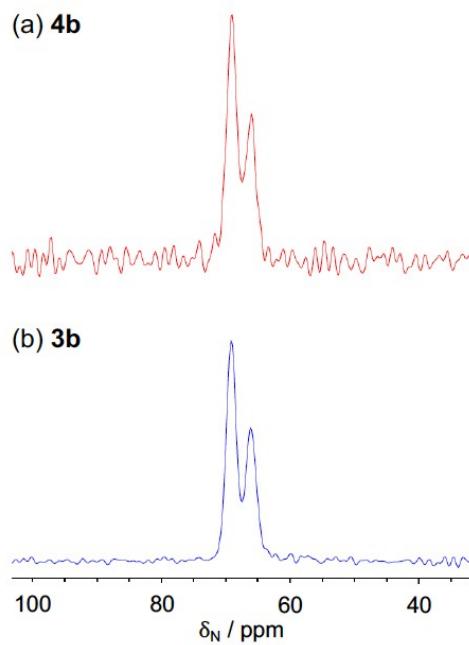
**Figure S8.** Plot of  $T_{DNP}$  versus content of deuterium in solvent for TCE (blue circle) and DMSO (red circle)

**9.  $^{15}\text{N}$  signal enhancement using  $^{15}\text{N}$ -enriched sample**



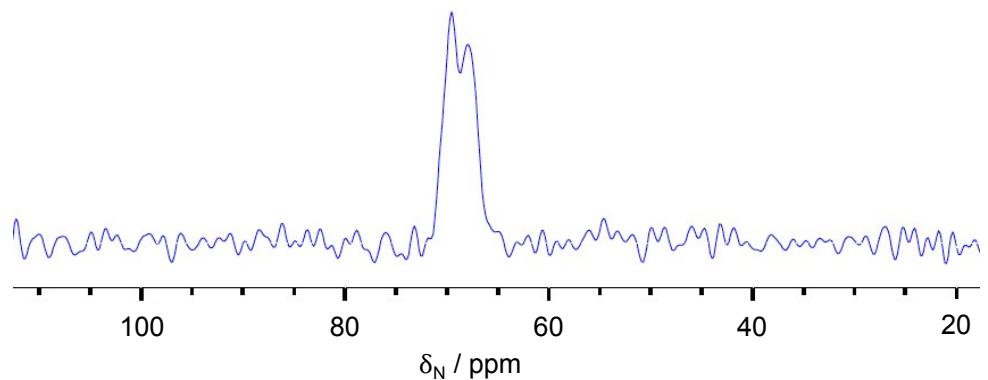
**Figure S9.** DNP  $^{15}\text{N}$  NMR spectra of **3c** (a) and **3c- $^{15}\text{N}$**  with microwave on (b) and off (c). 16 mM AMUPol/DMSO-d<sub>6</sub>/DMSO was used for sample preparation. 8660 scans were accumulated for a, and 16 scans for b and c.

**10. DNP enhanced  $^{15}\text{N}$  NMR of 4b**



**Figure S10.** DNP  $^{15}\text{N}$  NMR spectra of **4b** (a) **3b** (b). 8 mM AMUPol/DMSO-d<sub>6</sub>/DMSO (for **4b**) and 16 mM AMUPol/DMSO (for **3b**) were used for sample preparation. 1080 scans were accumulated for a, and 2770 scans for b.

**11.  $^{15}\text{N}$  NMR of 3c- $^{15}\text{N}$  at 297K**



**Figure S11.**  $^{15}\text{N}$  CPMAS NMR spectra of 3c- $^{15}\text{N}$  at 297 K. 2700 scans were accumulated.