

Supporting information for

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

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Contents

1.	Tables for Preparation of PS-supported alkylammonium salts	S2
2.	Figure and table for Syringe method for swelling test	S3
3.	Table for result of DNP solid-state NMR measurements	S4
4.	Optimization of PA solution/material ratio and impregnation time	S5
5.	Relation of swelling property and DNP enhancement for ¹ H nuclei (ϵ_H)	S6
6.	Relation of swelling property and longitudinal relaxation time with solution (T_1) and DNP build-up time (T_{DNP})	S8
7.	Spin counting experiment by EPR spectroscopy	S9
8.	Effect of partial deuteration of solvent on DNP experiment	S10
9.	¹⁵ N signal enhancement using ¹⁵ N-enriched sample	S11
10.	DNP enhanced ¹⁵ N NMR of 4b	S11
11.	¹⁵ N NMR of 3c-¹⁵N at 297K	S12

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

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

	3a	3b	3c	3c-¹⁵N	3d	3e	3f	3g	3h	3i
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 (%)

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

2. Figure and table for syringe method for swelling test

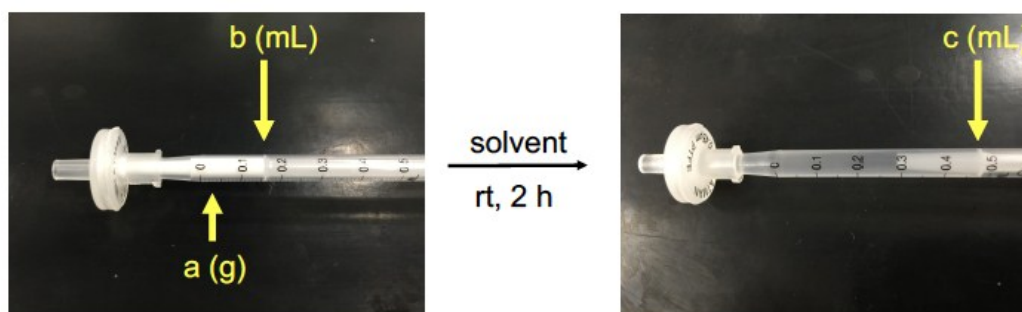


Figure S1. Syringe method for determination of swelling property

Table S3. Swelling volume for polymers

		1	2	3a	3b	3c	3d	3e	3f	3g	3h	3i
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. ε_H , ε_C , T_{DNP} , T_1 , θ_H , θ_C , Σ_H , and Σ_C for polymers

		1	2	3a	3b	3c	3d	3e	3f
ε_H^a	TEKPol/TCE	108	86	4	1	36	29	29	21
	AMUPol/DMSO	1	37	128	74	100	39	7	7
ε_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) ^b	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) ^c	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
θ_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
θ_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
Σ_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
Σ_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

^aDNP enhancement defined as equation 1. ^bDNP build-up time. ^c¹H longitudinal relaxation time of sample swollen in solvent. ^dcontribution factor defined as equation 2. ^eoverall sensitivity gain defined as equation 3.

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

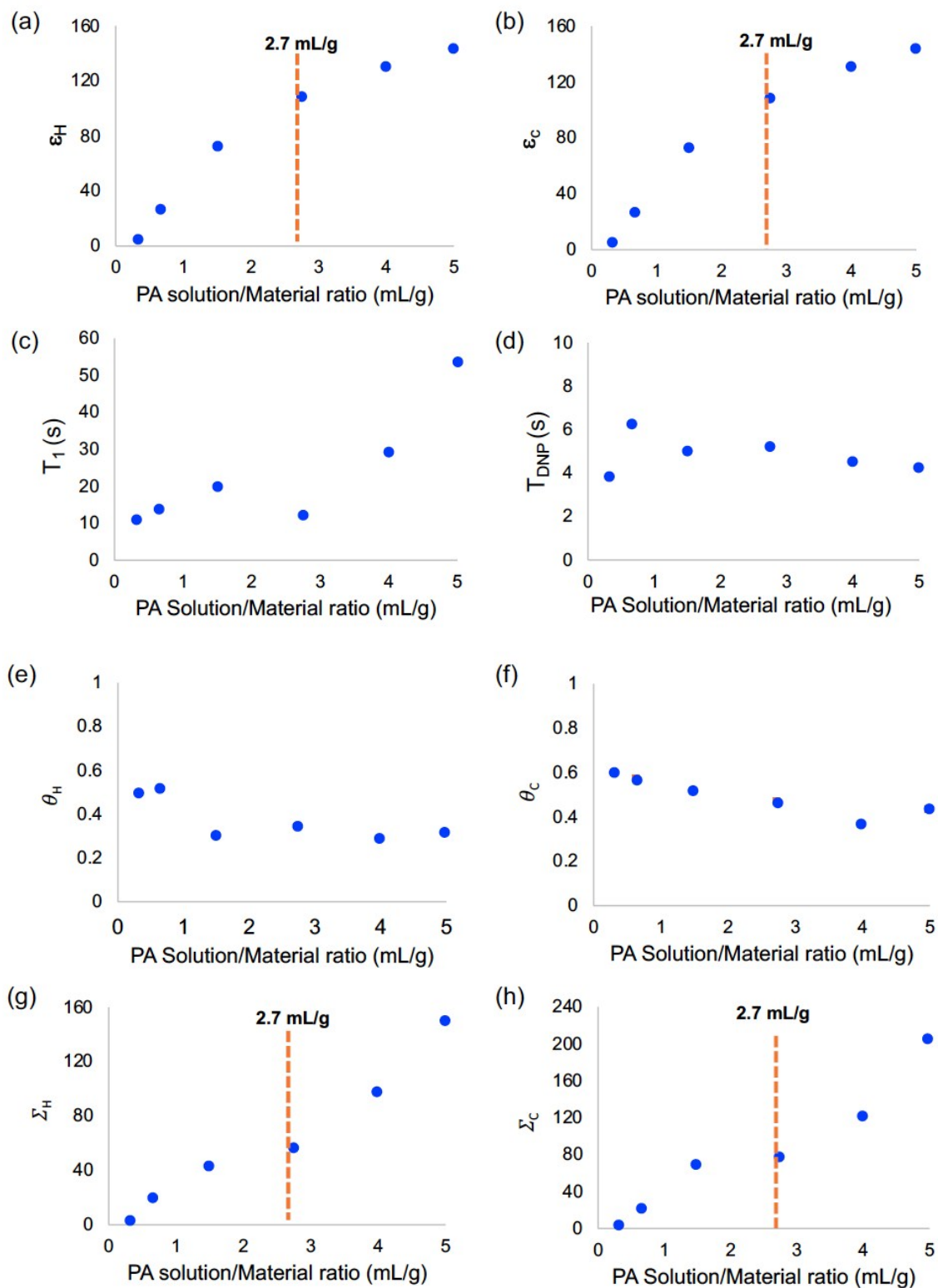


Figure S2. Plot of PA solution/material ratio (mL/g) for the sample of **1** with TEKPol/TCE solution versus ϵ_H (a), ϵ_C (b), T_1 (c), T_{DNP} (d), θ_H (e), θ_C (f), Σ_H (g), and Σ_C (h)

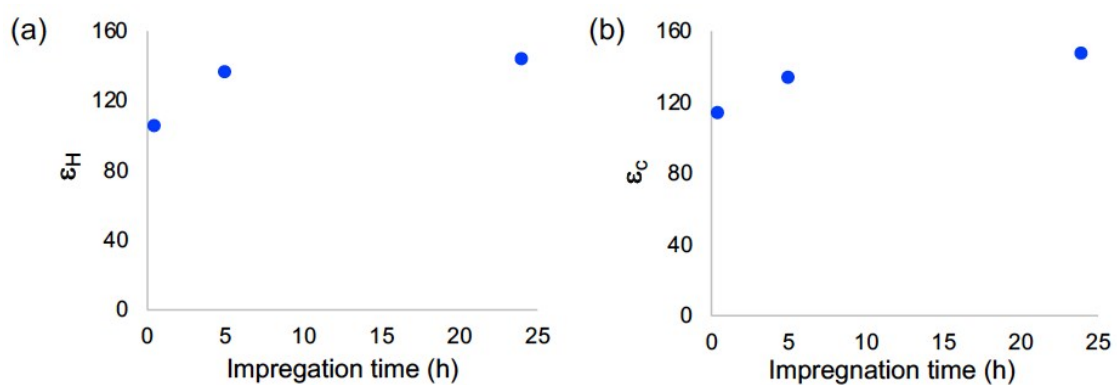


Figure S3. Plot of impregnation time for **1** with TEKPol/TCE solution (PA solution/material (mL/g): 5) versus ϵ_H (a) and ϵ_C (b)

5. Relation of swelling property and DNP enhancement for ^1H nuclei (ϵ_{H})

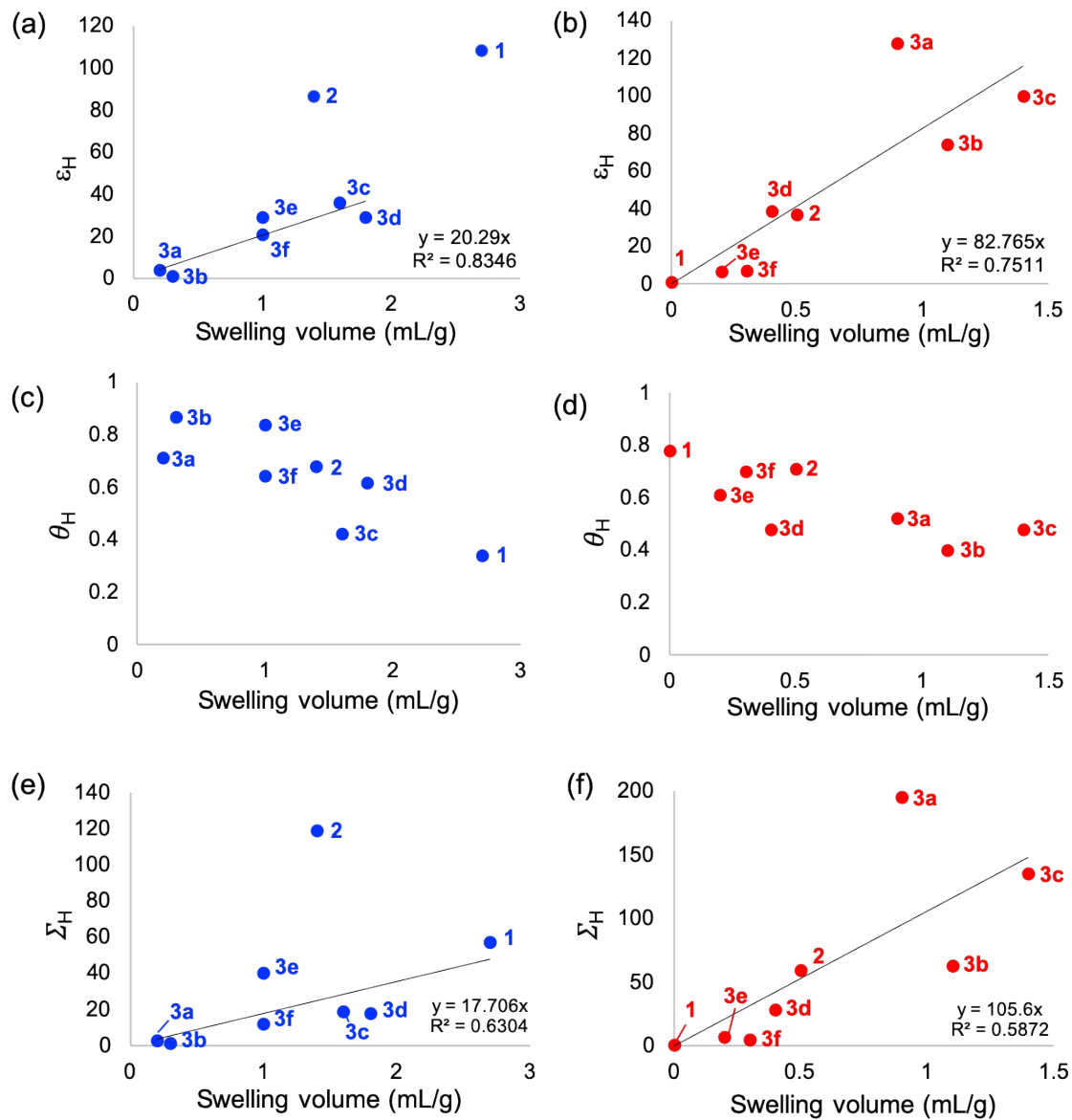


Figure S4. The plot of swelling volume for TCE (blue circle) and DMSO (red circle) versus ϵ_{H} (a, b), θ_{H} (c, d), and Σ_{H} (e, f)

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

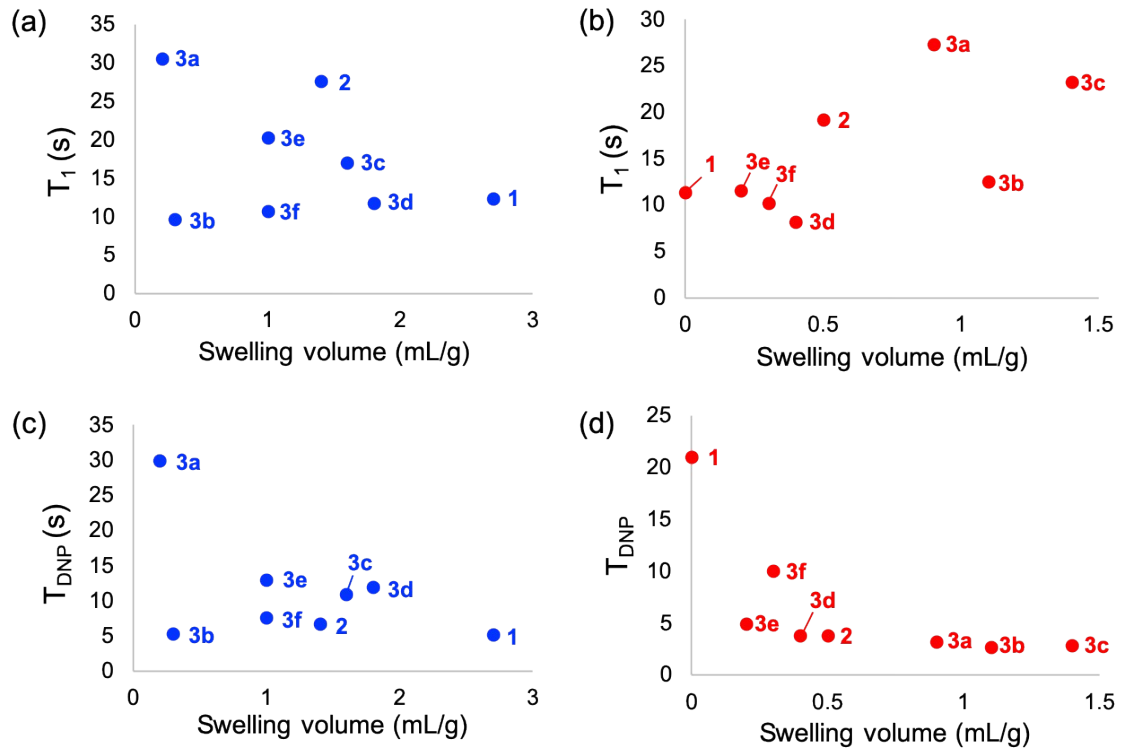


Figure S5. The plot of T_1 versus swelling volume for TCE (a) and DMSO (b) and T_{DNP} versus swelling volume for TCE (c) and DMSO (d)

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_{spin} (mmol/g) were determined. The following figure displays the linear correlation between M_{spin} and swelling volume, ν (L/g) (Figure S6).

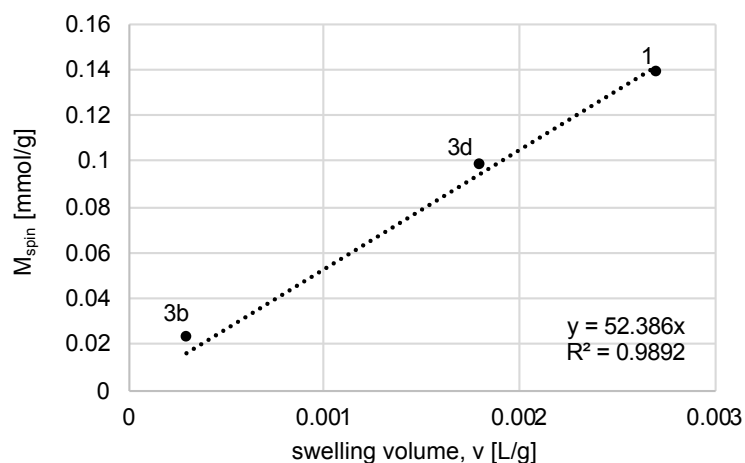


Figure S6. The plot of M_{spin} versus swelling volume, ν

8. Effect of partial deuteration of solvent on DNP experiment

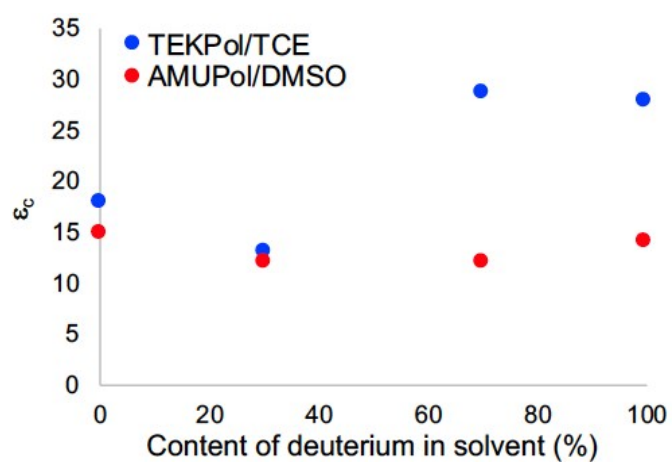


Figure S7. Plot of ϵ_C versus content of deuterium in solvent for TCE (blue circle) and DMSO (red circle)

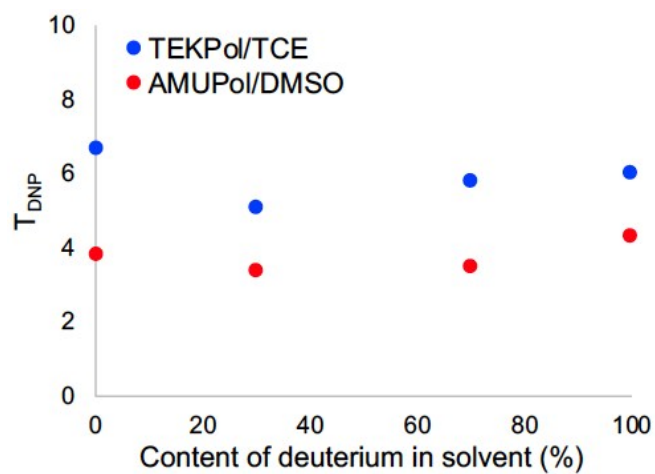


Figure S8. Plot of T_{DNP} versus content of deuterium in solvent for TCE (blue circle) and DMSO (red circle)

9. ^{15}N signal enhancement using ^{15}N -enriched sample

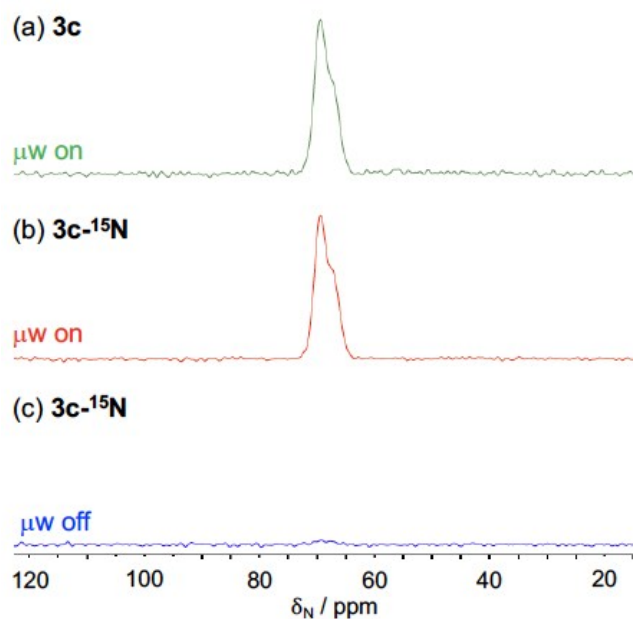


Figure S9. DNP ^{15}N NMR spectra of **3c** (a) and **3c- ^{15}N** with microwave on (b) and off (c). 16 mM AMUPol/DMSO- d_6 /DMSO was used for sample preparation. 8660 scans were accumulated for a, and 16 scans for b and c.

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

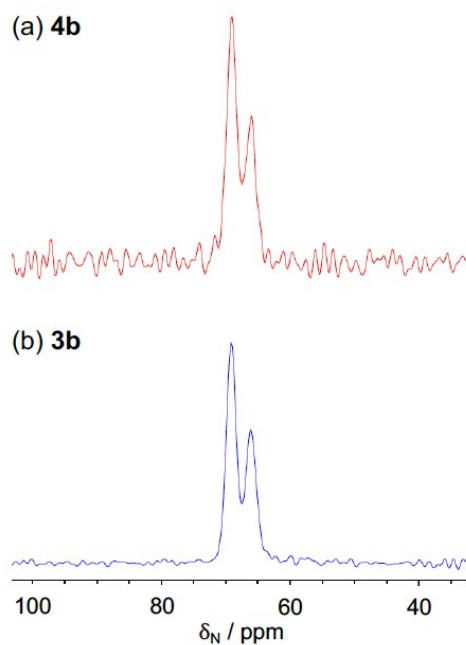


Figure S10. DNP ^{15}N NMR spectra of **4b** (a) **3b** (b). 8 mM AMUPol/DMSO- d_6 /DMSO (for **4b**) and 16 mM AMUPol/DMSO (for **3b**) were used for sample preparation. 1080 scans were accumulated for a, and 2770 scans for b.

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

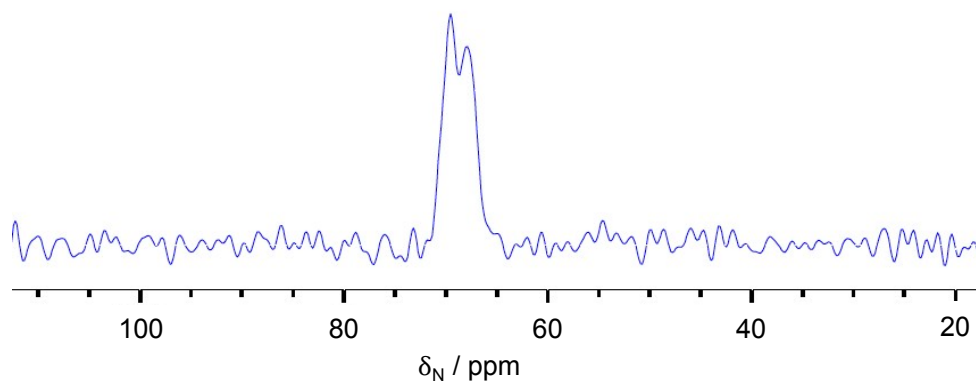


Figure S11. ^{15}N CPMAS NMR spectra of $3\text{c-}^{15}\text{N}$ at 297 K. 2700 scans were accumulated.