

Supporting information

Insights on the polymerisation kinetics of non-isocyanate polyurethanes (NIPU) using *in situ* NMR spectroscopy

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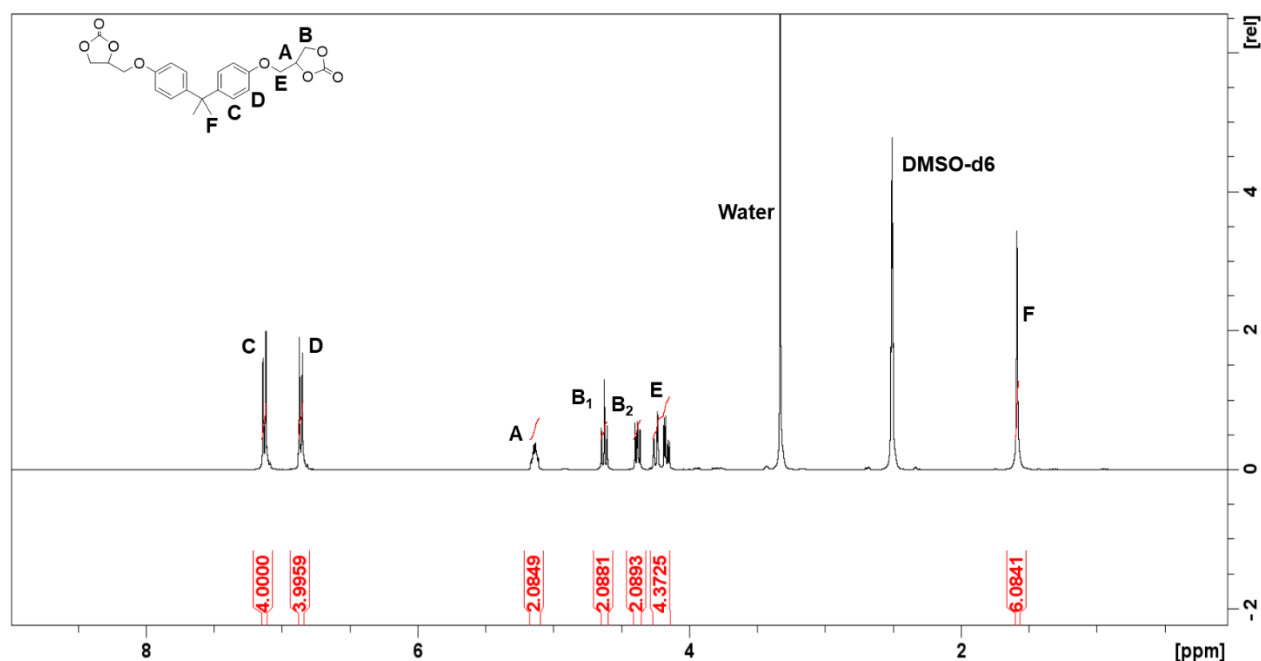


Figure S1. ¹H NMR spectrum of the 5-membered bis-cyclic carbonate of bisphenol A ether (5CC-EBA) precursor (400 MHz, non-anhydrous DMSO-d₆).

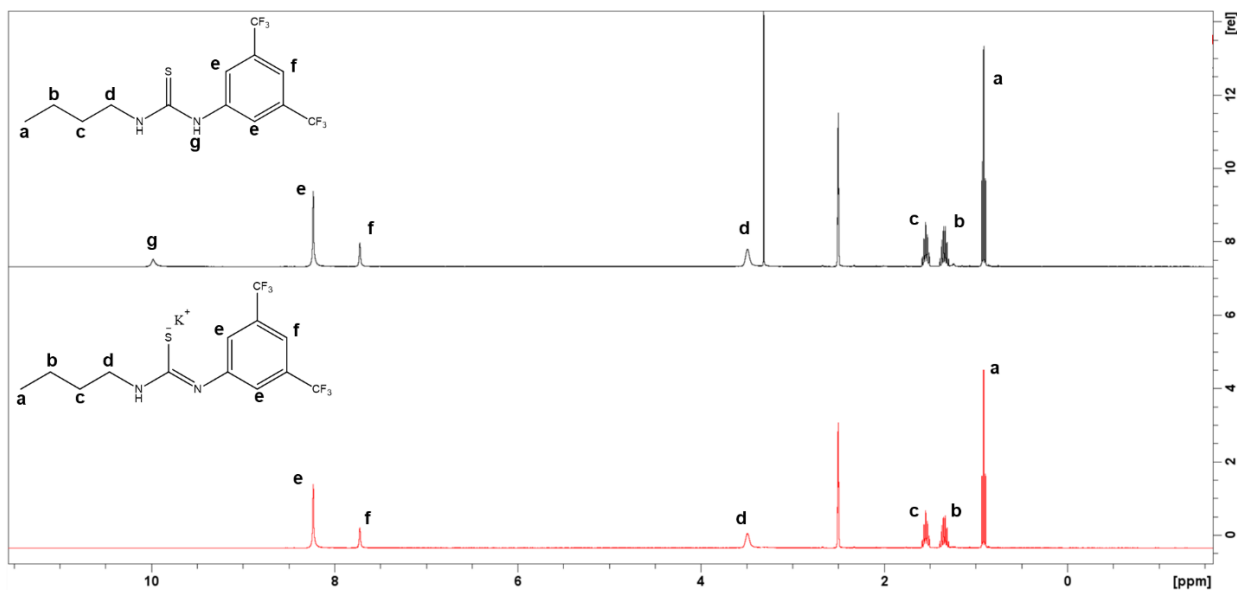
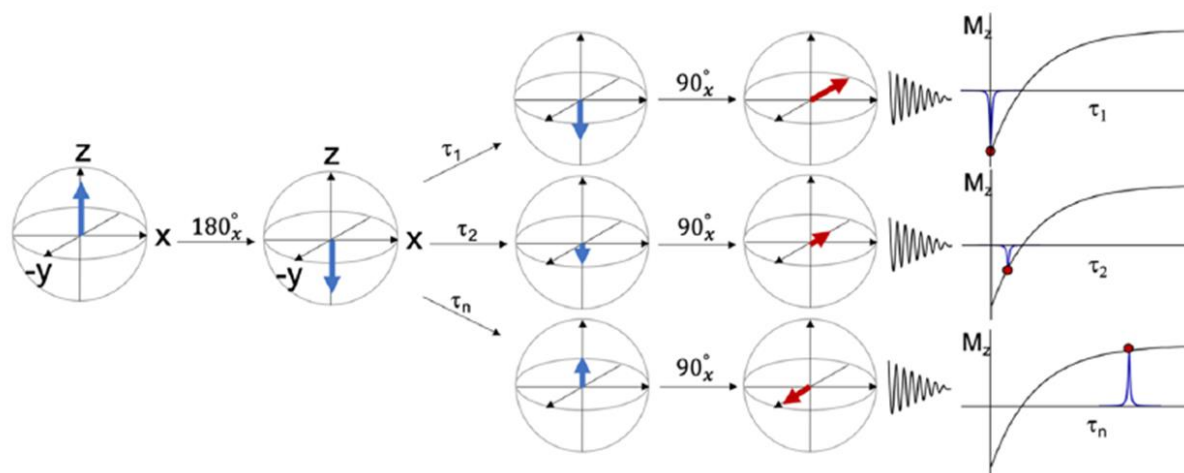


Figure S2. ^1H NMR spectrum of 1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea (TU) and its potassium thiomidate form (TU⁻) (400 MHz, DMSO-d₆).



Inversion recovery sequence

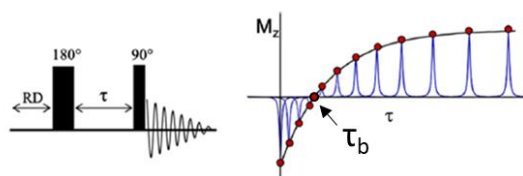


Figure S3. Diagram of the pulse sequence and example of an inversion recovery experiment used for relaxation time (T_1) measurements. Modified from [1]

Table S1. Details of the NMR sequence developed for the *in situ* monitoring of the aminolysis of 5CC-EBA with 1,4-diaminobutane (DMSO-d₆, 400 MHz).

Spectrum	Sequence	NS (scans)	D1 (s)
1	¹ H	16	3
2	4 min delay		
3	¹ H	16	3
4	4 min delay		
[5-94]
95	¹ H	16	3
96	4 min delay		
97	¹ H	16	3
98	19 min delay		
99	¹ H	16	3
100	19 min delay		
[101-106]
107	¹ H	16	3
108	19 min delay		
109	¹ H	16	10
110	HSQC ¹ H- ¹³ C	24	1.5
111	DEPT-135°	1024	2
112	¹³ C	2048	4
113	¹ H	32	15
114	COSY	8	2

Table S2. Evolution of the NMR signal of C and L protons (7.07-7.19 ppm) during the kinetic experiments.

Spectra	Proton	D1 (s)	Pulse angle (°)	Chemical shift (ppm)	Signal absolute area given by the Topspin software	Normalized area
1	C+L	3	67	7.13	1.66485E+12	4
113	C+L	15	67	7.13	1.67169E+12	4

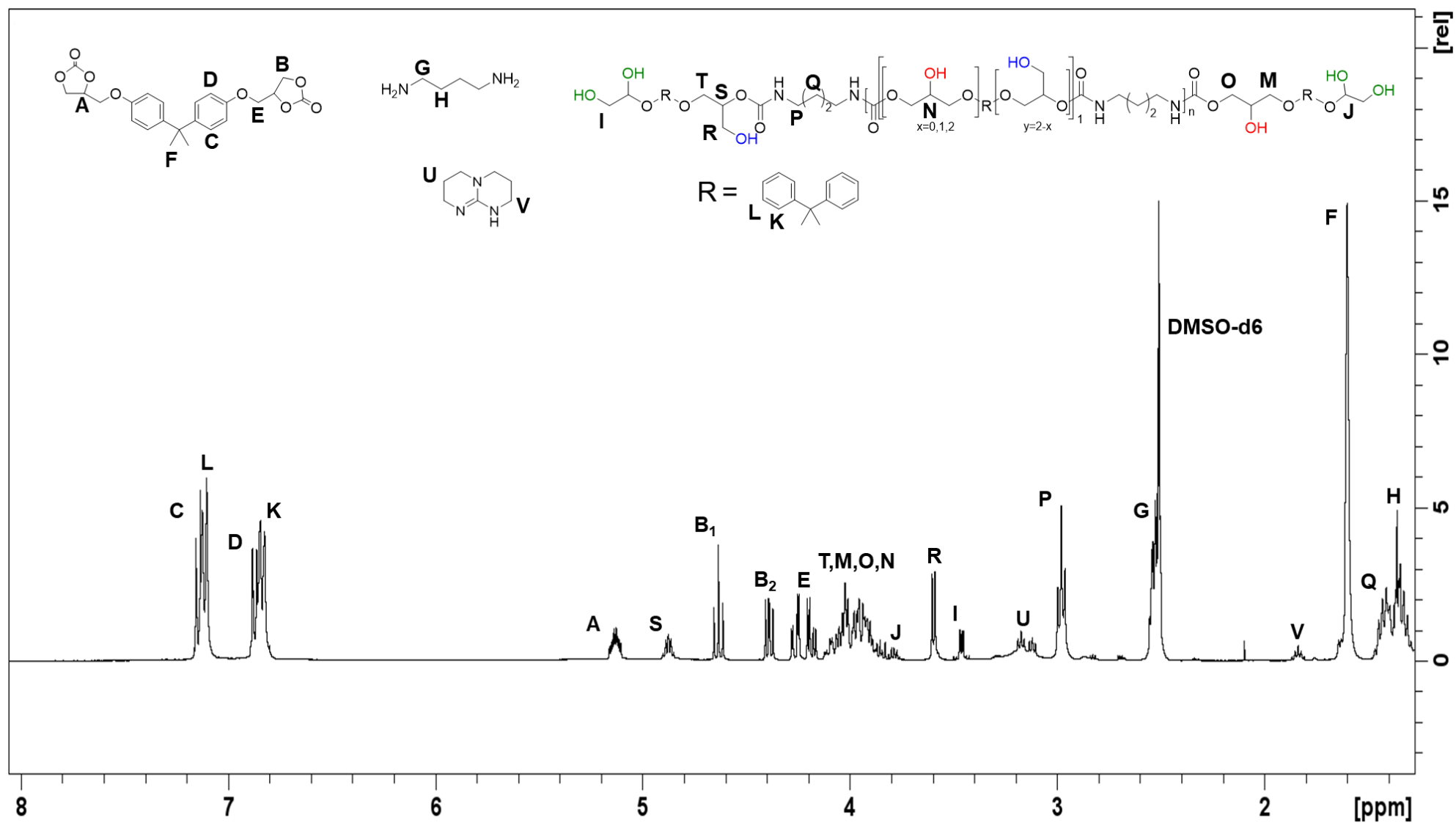


Figure S4. ¹H NMR spectrum measured *in situ* after 6h of reaction between the 5-membered bis-cyclic carbonate of bisphenol A ether (5CC-EBA) precursor and 1,4-diaminobutane in stoichiometric conditions, catalysed with TBD (0.05 eq_{5CC}) at 353 K (400 MHz, DMSO-d₆).

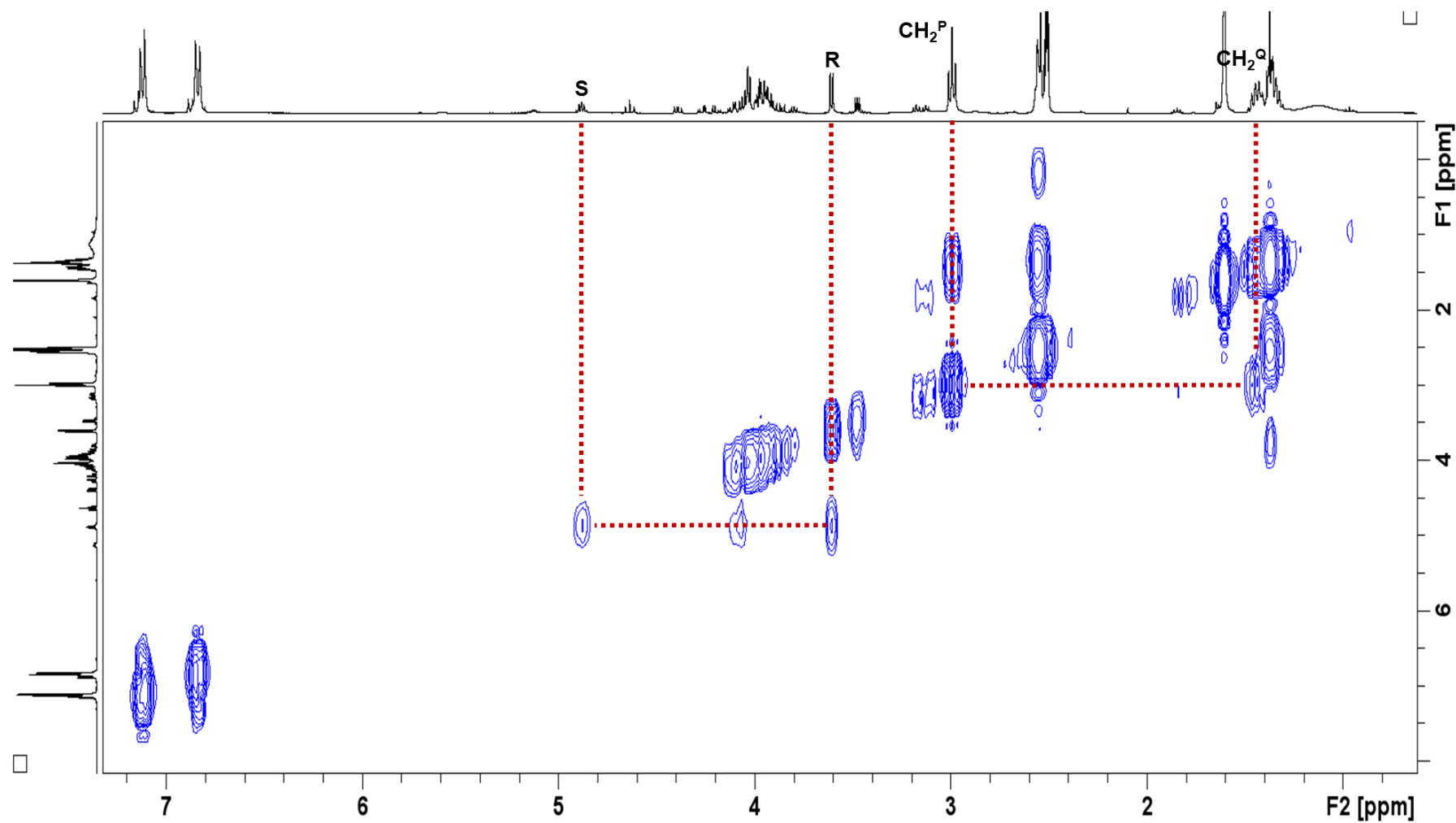


Figure S5. COSY spectrum measured *in situ* after 6h of reaction between the 5-membered bis-cyclic carbonate of bisphenol A ether (5CC-EBA) precursor and 1,4-diaminobutane in stoichiometric conditions, catalysed with TBD (0.05 eq_{5CC}) at 353 K (400 MHz, DMSO-d₆).

Table S3. Relaxation times (T_1) of the protons of the 5CC-EBA and diamine precursors and of the corresponding NIPU, measured by NMR spectroscopy with an inversion recovery sequence, at different temperatures (298 K, 333 K and 353 K).

Peaks	Chemical shift (ppm)	Relaxation time T_1 (s)		
		298 K	333 K	353 K
A	5.12	3.15	2.37	3.04
B1	4.63	1.44	1.10	1.38
B2	4.39	1.41	1.05	1.25
C	6.85	1.98	1.61	1.92
D	7.13	1.86	1.49	1.77
E	4.20	1.27	0.31	0.40
F	1.59	0.17	0.25	0.34
G	2.54	3.37	2.54	3.01
H	1.37	3.24	2.63	3.14
I	3.48	0.50	0.95	1.40
K	6.83	1.01	1.26	1.50
L	7.11	0.85	1.14	1.41
T,M,O,N,J	3.76-4.14	0.42	0.55	0.71
P	2.98	0.52	0.84	1.17
Q	1.43	1.87	3.56	5.04
R	3.60	0.37	0.52	0.70
S	4.88	0.88	1.22	1.50
U	3.12	0.82	1.65	2.34
V	1.82	0.83	1.60	2.24

T_1 values of precursors follow a U-shaped curve. Actually, proton relaxation in NMR experiments is influenced by local fluctuations in the magnetic field. For relaxation to be effective, the frequency of the fluctuations must be close to the Larmor frequency of the protons. The relaxation time is therefore strongly dependent on temperature changes. At low temperatures (298 K), conditions are less favourable because the viscosity of the solvent slows down the movement of the molecules, so the spins take longer to return to equilibrium. A temperature of 333 K seems to be the ideal temperature for spin relaxation. Above 353 K, the spins tend to rotate faster, disturbing the fluctuation fields and the relaxation of the protons. This explains why the T_1 values at 333 K of some protons are lower as compared with those at 298 K and 353 K.

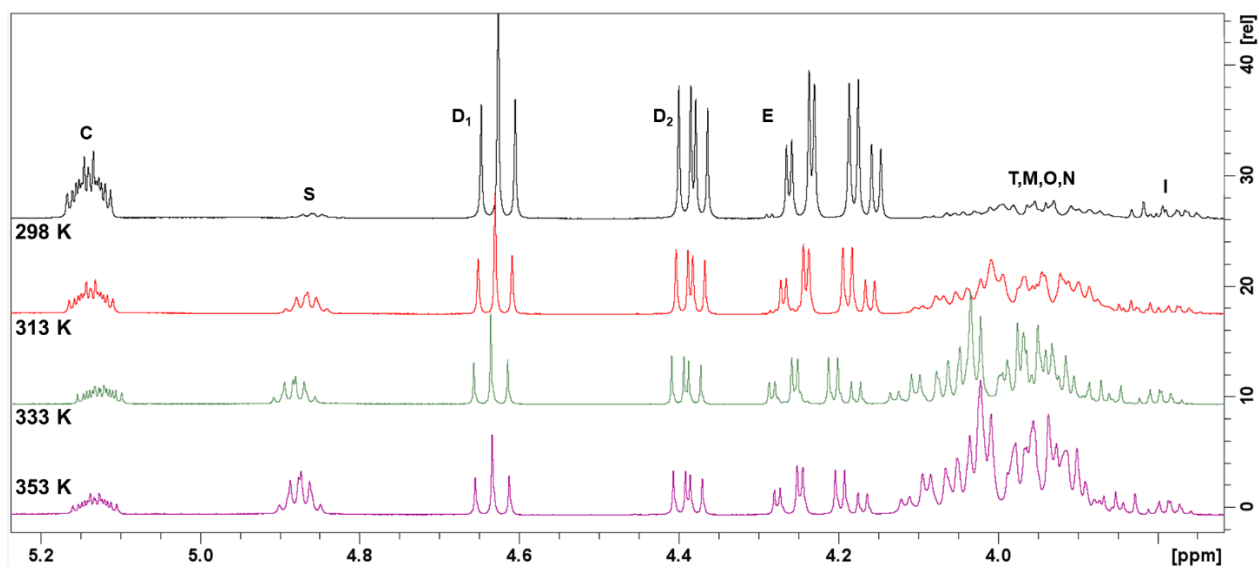


Figure S6. ¹H NMR spectra between 3.70 and 5.25 ppm measured *in situ* after 360 min of reaction between 5CC-EBA and 1,4-diaminobutane, catalysed with TBD (0.07 eq_{5CC}) at 298 K, 313 K, 333 K and 353 K (400 MHz, DMSO-d₆).

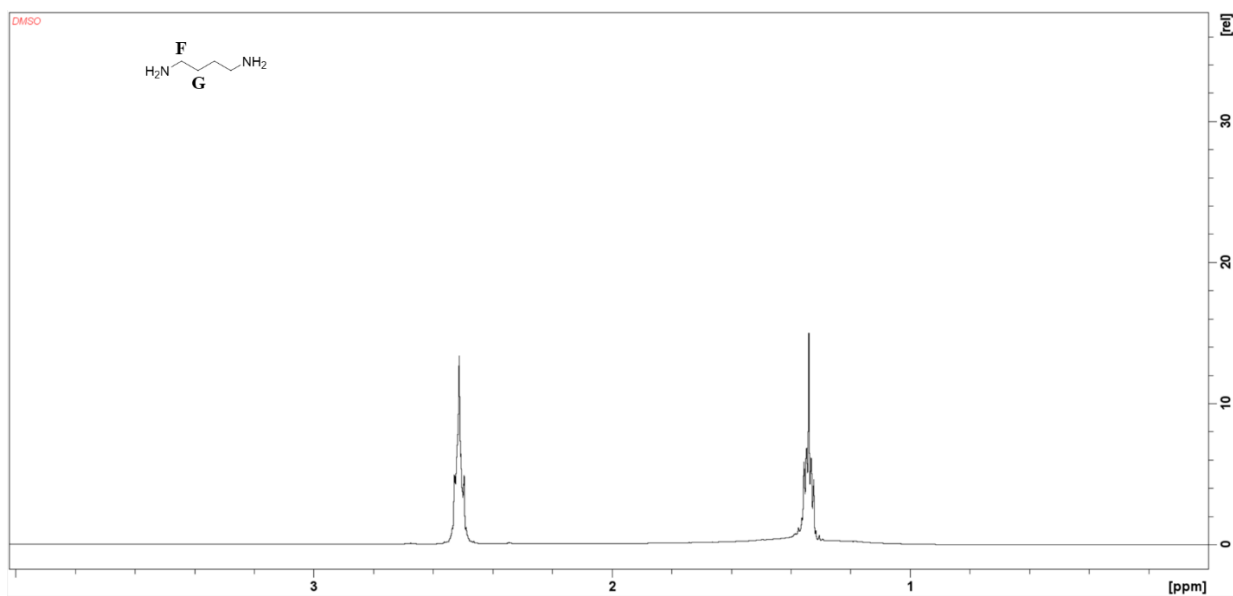


Figure S7. ^1H NMR spectrum of 1,4-diaminobutane (400 MHz, DMSO-d₆, 353 K).

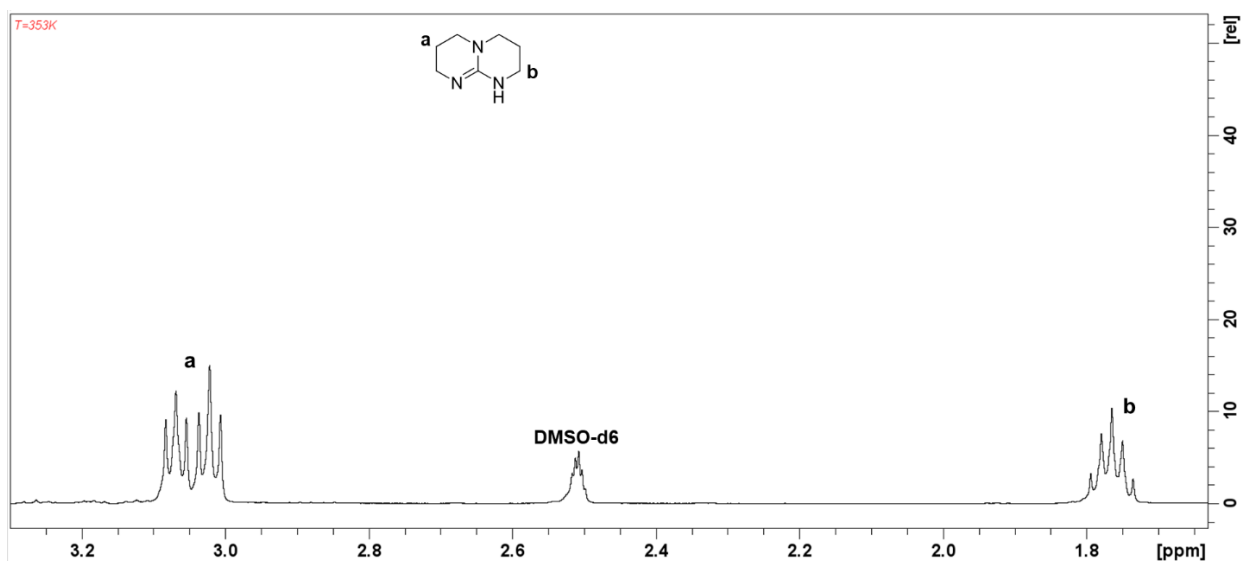


Figure S8. ^1H NMR spectrum of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (400 MHz, DMSO-d₆, 353 K).

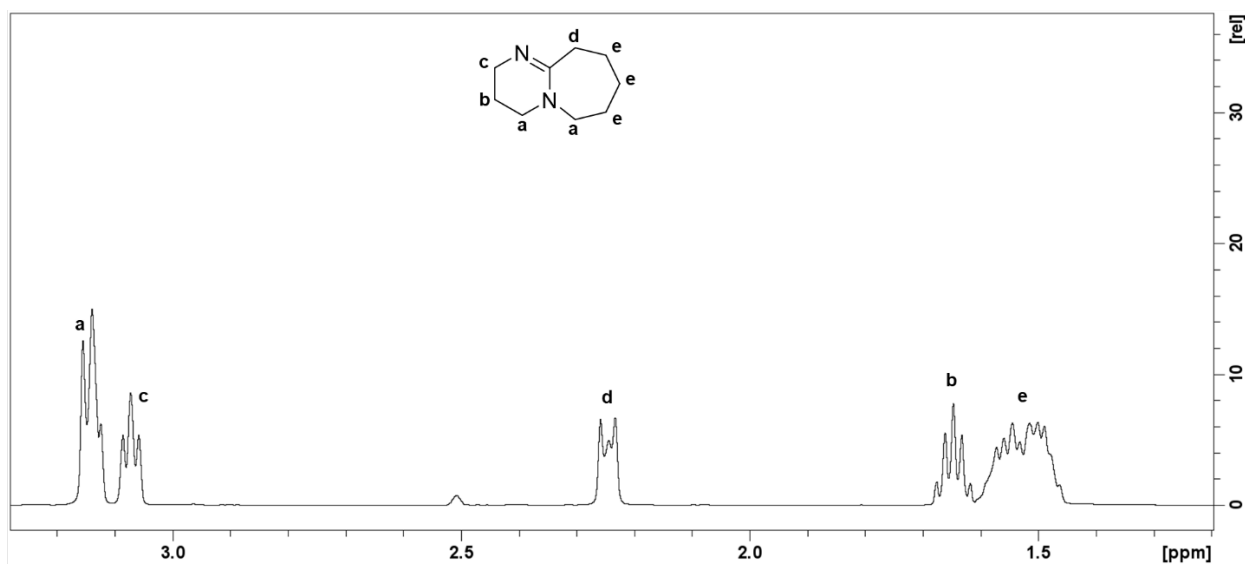


Figure S9. ¹H NMR spectrum of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (400 MHz, DMSO-d₆, 353 K).

Reference :

- [1] R. Wei, C.L. Dickson, D. Uhrín, G.C. Lloyd-Jones, Rapid Estimation of T1 for Quantitative NMR, *J. Org. Chem.* 86 (2021) 9023–9029. <https://doi.org/10.1021/acs.joc.1c01007>.