

Recycling polyurethanes through transcarbamoylation

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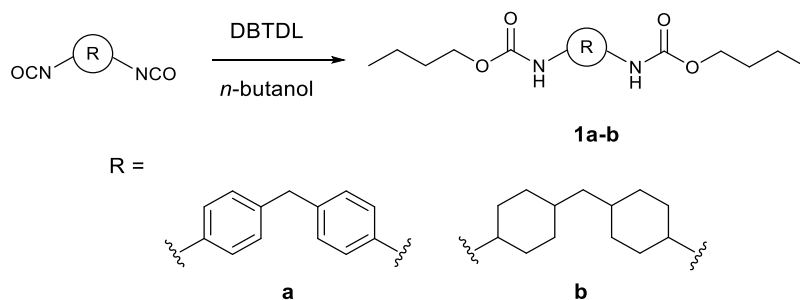


Figure S1. Synthesis of model dicarbamates **1a** and **1b**.

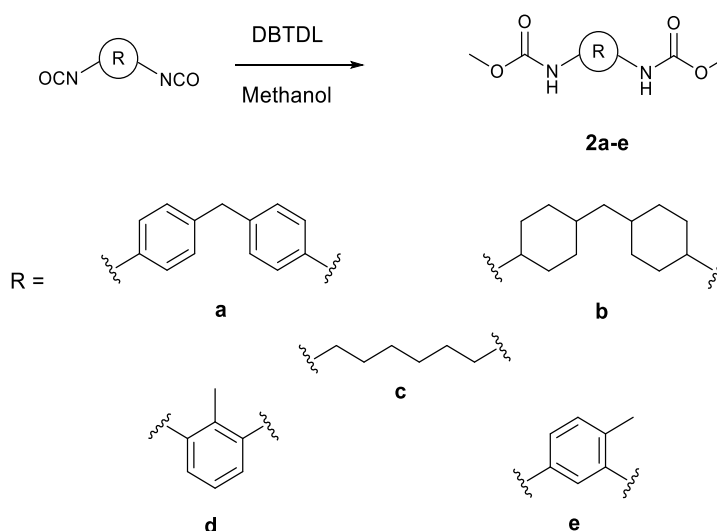


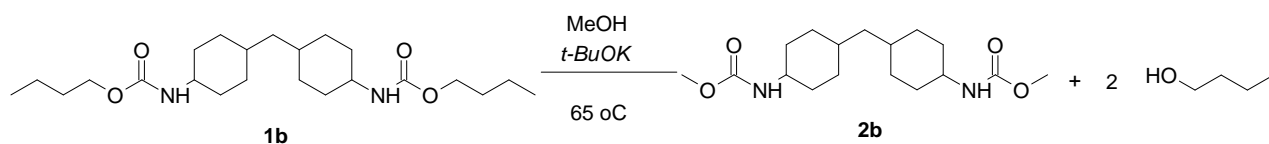
Figure S2. Synthesis of model dicarbamates **2a** – **2e**.

Methanolysis optimization of aliphatic dicarbamate **1b**.

In order to optimize the methanolysis of *O*-dibutylcarbamate **1b**, several conditions were used in the investigation and are summarized in Table S1. The optimized conditions are : *O*-dibutylcarbamate **1b** (100 mg, 0.24 mmol) reacted in the presence of methanol (2 mL) and *t*-BuOK (0.96 mmol) at 65°C during 20 h to afford **2b**. The conversion of the reaction was estimated from the ¹H NMR by integrating the signal of proton ‘a’ (*O*-butylcarbamate) and the signal of proton ‘b’ (*O*-methylcarbamate) depicted in Figure S3.

Table S1. Optimization of the transcarbamoylation reaction conditions (aliphatic urethanes)

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Entry	equiv. of <i>t</i> -BuOK ^a	Reaction time (h)	Conversion (%) ^b
1	2	20	93
2	2.5	20	91
3	2	24	93

^a equiv. per urethane group

^b estimated by ¹H NMR

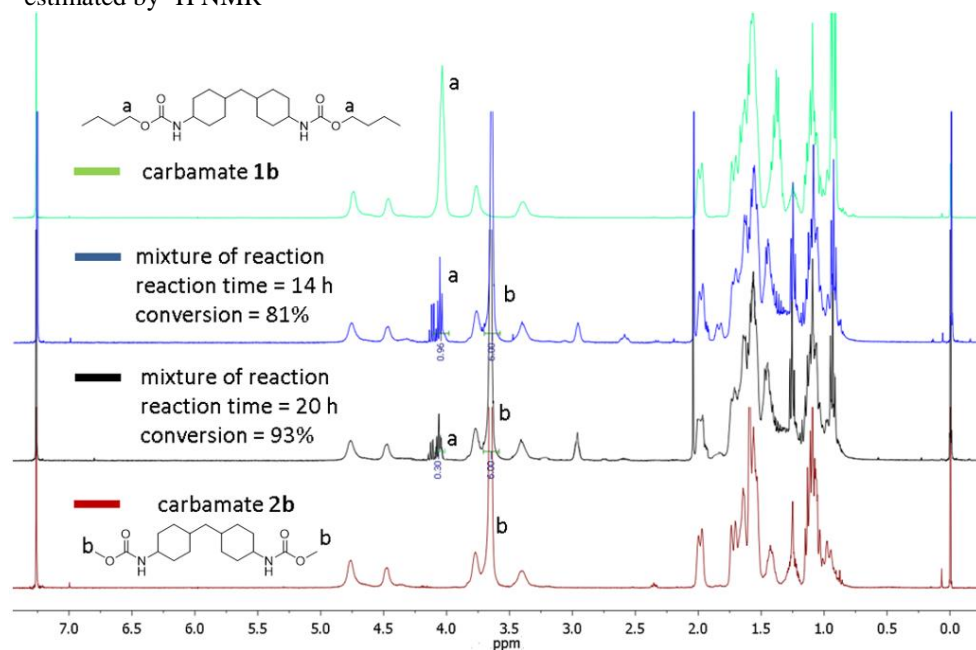


Figure S3. Methanolysis reaction of aliphatic carbamate **1b**.

General procedure for the synthesis of model polyurethanes **4a** – **4e**

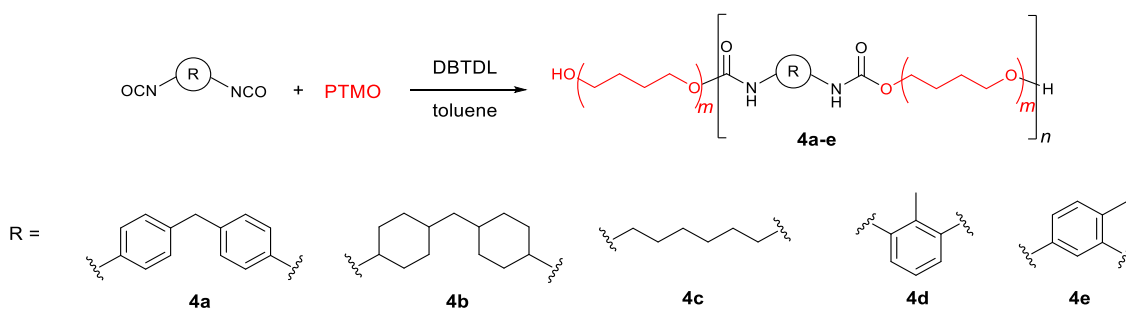


Figure S4. Synthesis of model polyurethanes **4a** – **4e**.

Diisocyanate (methylene diphenyl 4,4'-diisocyanate, hexamethylene diisocyanate, 1,6-Diisocyanatohexane, 2,6-tolylene diisocyanate, or 2,4-tolylene diisocyanate) (5 mmol) and polytetrahydrofuran (5 mmol, molecule weight is 1000, 2000, or 3000) were added to 50 mL of dry toluene at ambient temperature slowly. Dibutyltin dilaurate (5 μL , 0.008 mmol) was added and the reaction mixture was stirred at 65°C for 1 – 5 h (see Table S2) and a nitrogen inlet. Finally, after it was cooled to room

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temperature, the obtained PU was solubilized in tetrahydrofuran, precipitated in cooled methanol, and then analyzed by GPC.

Table S2. Synthesis of model polyurethanes

Entry	4	Reaction time (h)	M _w of PTMO (g/mol)	M _w of PU (g/mol) ^a
1	4a	1	1000	6500
2	4a	3	2000	20000
3	4a	4	2000	28000
4	4a	4	3000	33600
5	4b	1	1000	5250
6	4b	4	2000	28000
7	4c	2	1000	8200
8	4c	4	2000	22000
9	4d	1	1000	4700
10	4d	4	2000	14000
11	4e	2	1000	5900
12	4e	5	2000	20000

^a Determined by GPC

General procedure for the depolymerization reaction (from PU foam to monomer and oligomer). Achieve the mixture and repolymerize the mixture to new PU method or achieve pure monomer **2**.

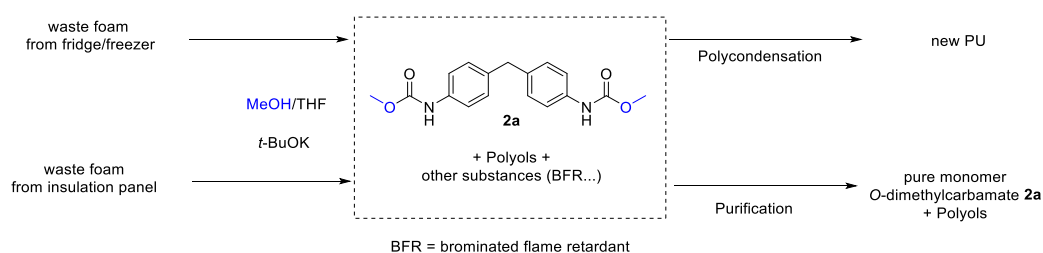


Figure S5. Recycling of PU foams waste.

Polyurethane foam (foam from fridge/freezer and foam from insulation panel) (10 g) was suspended in THF (100 mL) and methanol (100 mL), 3 g *t*-BuOK was added to the suspension, with continuous stirring at 65 °C for 20 h. Then the solvent was evaporated, to get brown mixture, and the residue were washed by acetone, filtered to remove insoluble fraction. solvent was evaporated to get brown residue, (foam from fridge/freezer, 9.8 g; foam from insulation panel, 11 g).

For foam from fridge/freezer: the residue (2.0 g, 20.4 % of total residue) was dissolved in toluene (50 mL), with nitrogen inlet, TBD (50 mg, 0.35 mmol) added to the solution, the temperature was progressively increased to 130 °C under nitrogen flow (to remove MeOH) and stirring. Then, the polymerization reaction was conducted over 16 h. Finally, after it was cooled to room temperature, the obtained PU was solubilized in THF, precipitated in methanol. (0.9 g, yield = 0.9/(10*20.4%) = 44 %)

For foam from insulation panel residue (2.0 g, 18.2 % of total residue), water (50 mL) was added to the residue. Extracted with EtOAc (3x). The combined organic layers were washed with brine, dried on magnesium sulfate and the solvent was evaporated. The residue was purified by silica column

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chromatography with hexane/ethyl acetate (75/25). The fractions were concentrated under reduced pressure to give the **2a**. (291 mg, yield = $0.291/(10 \times 18.2\%) = 16\%$)

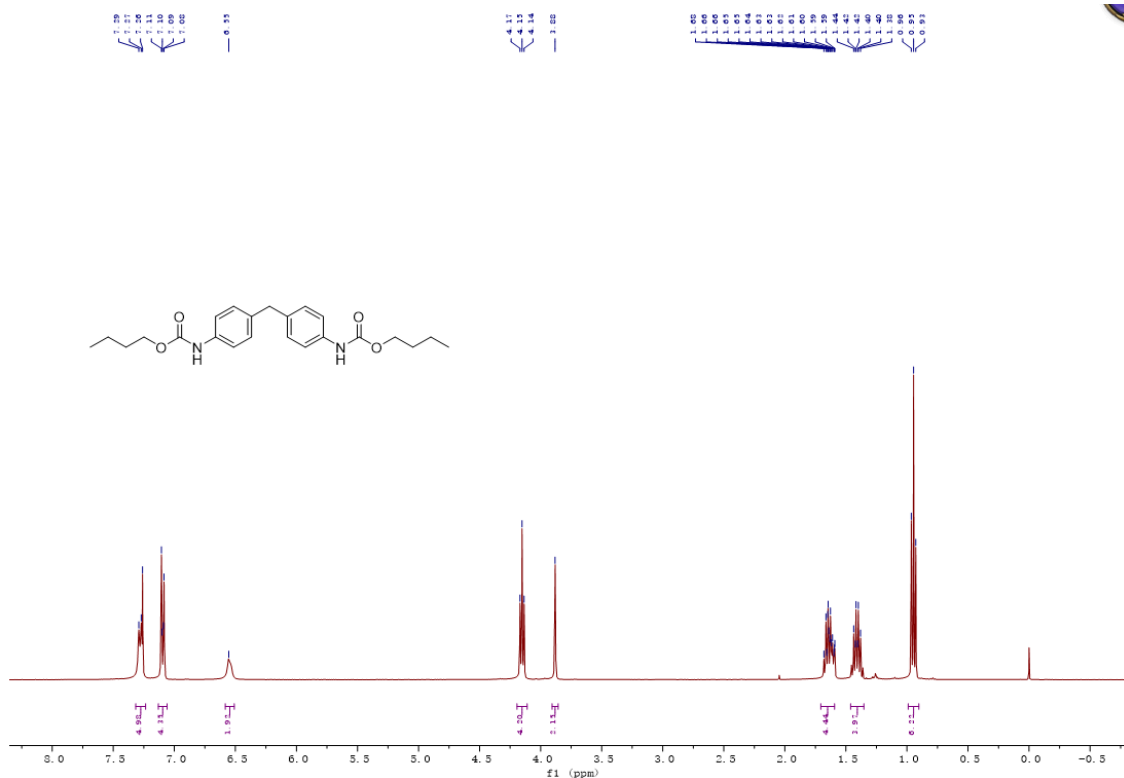


Figure S6. ¹H NMR (CDCl₃, 400 MHz) spectrum of compound **1a**

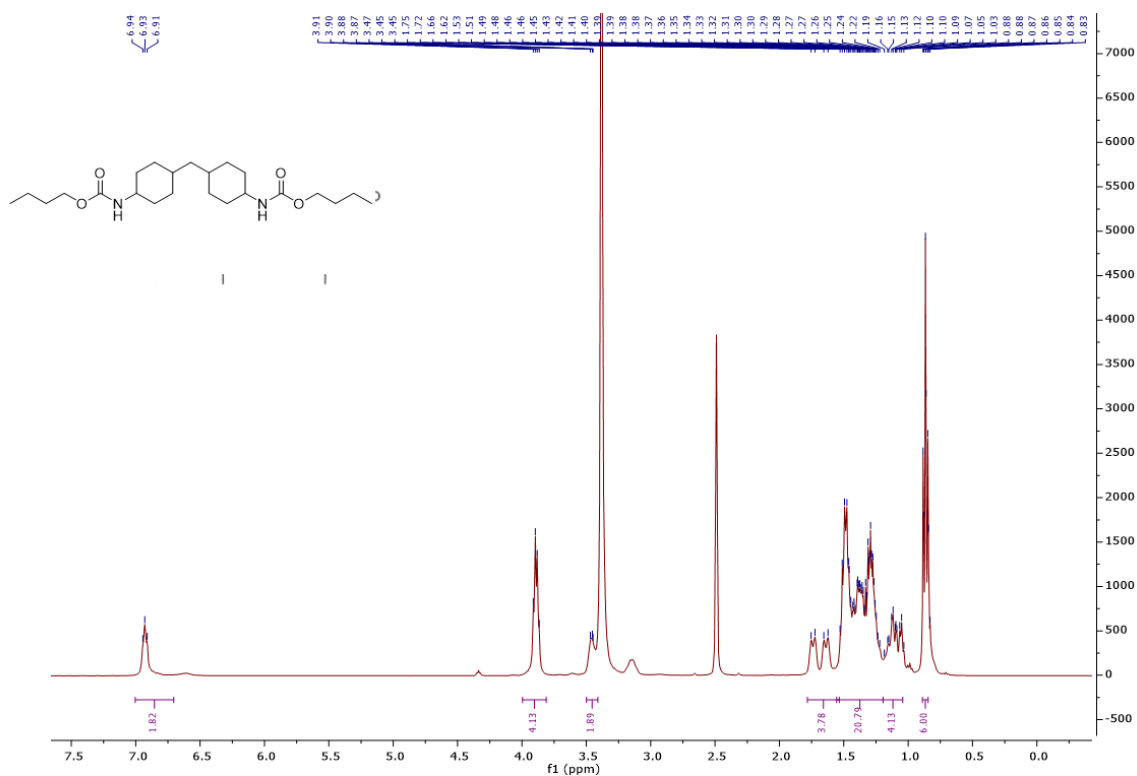


Figure S7. ¹H NMR (DMSO-*d*₆, 400 MHz) spectrum of compound **1b**

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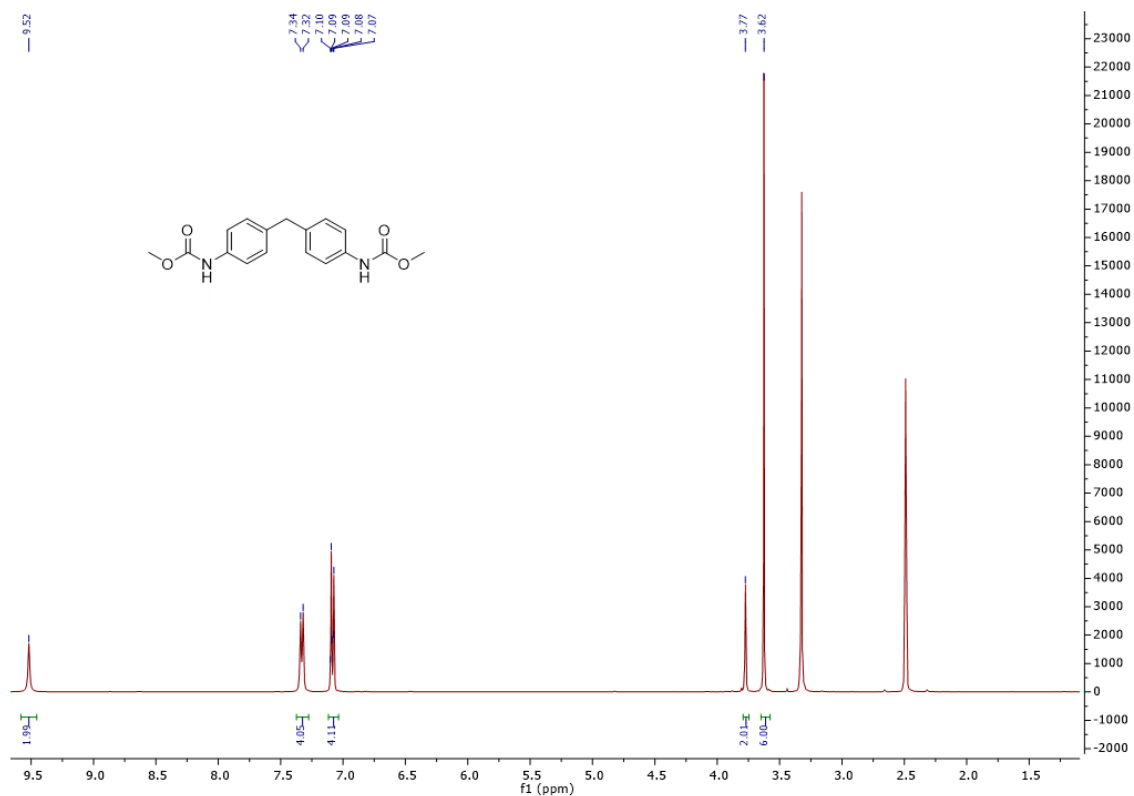


Figure S8. ¹H NMR (DMSO-*d*₆, 400 MHz) spectrum of compound **2a**

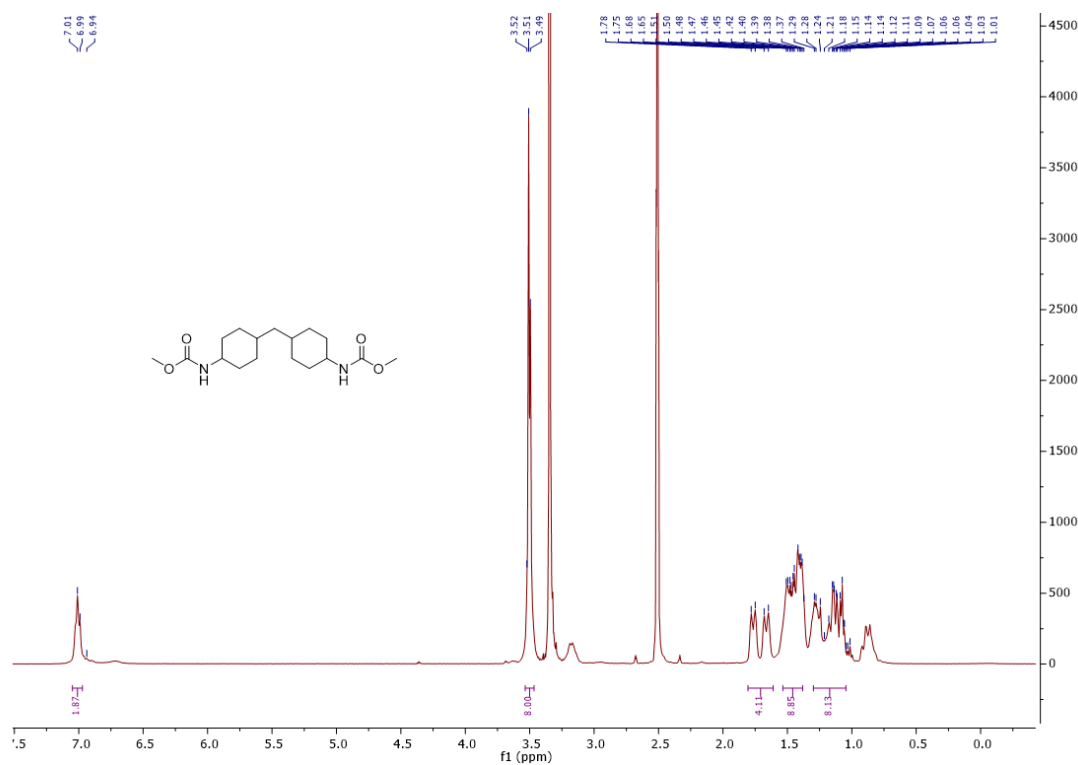
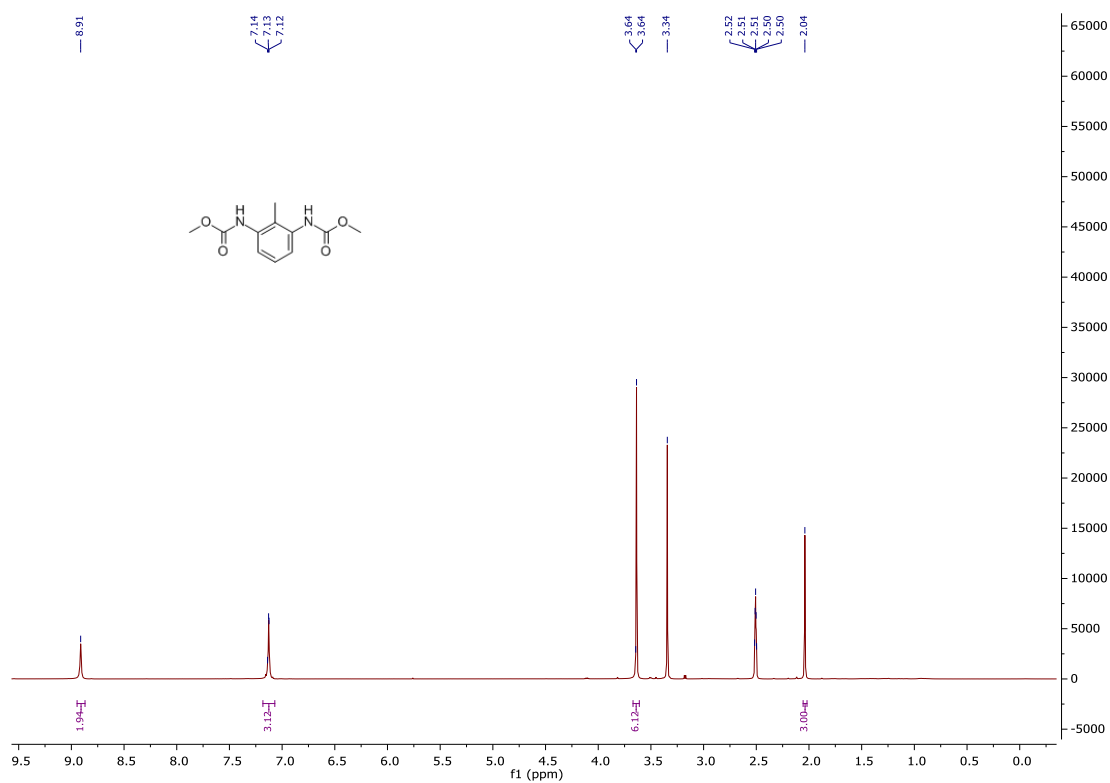
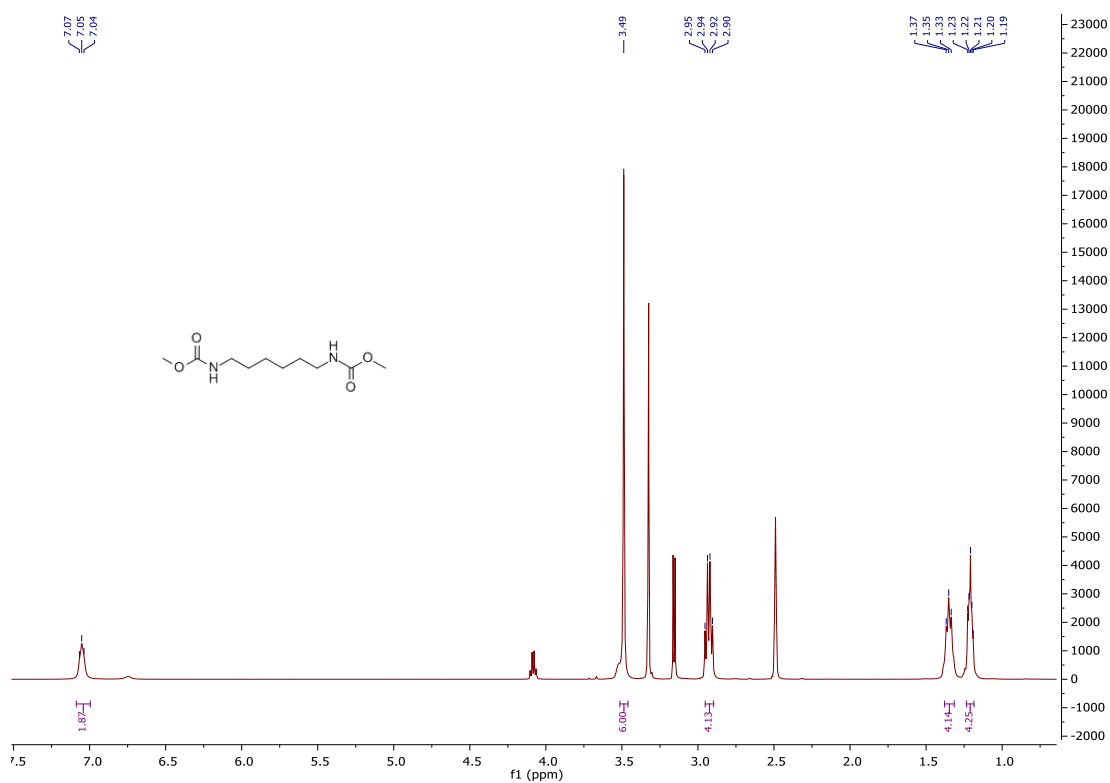


Figure S9. ¹H NMR (DMSO-*d*₆, 400 MHz) spectrum of compound **2b**

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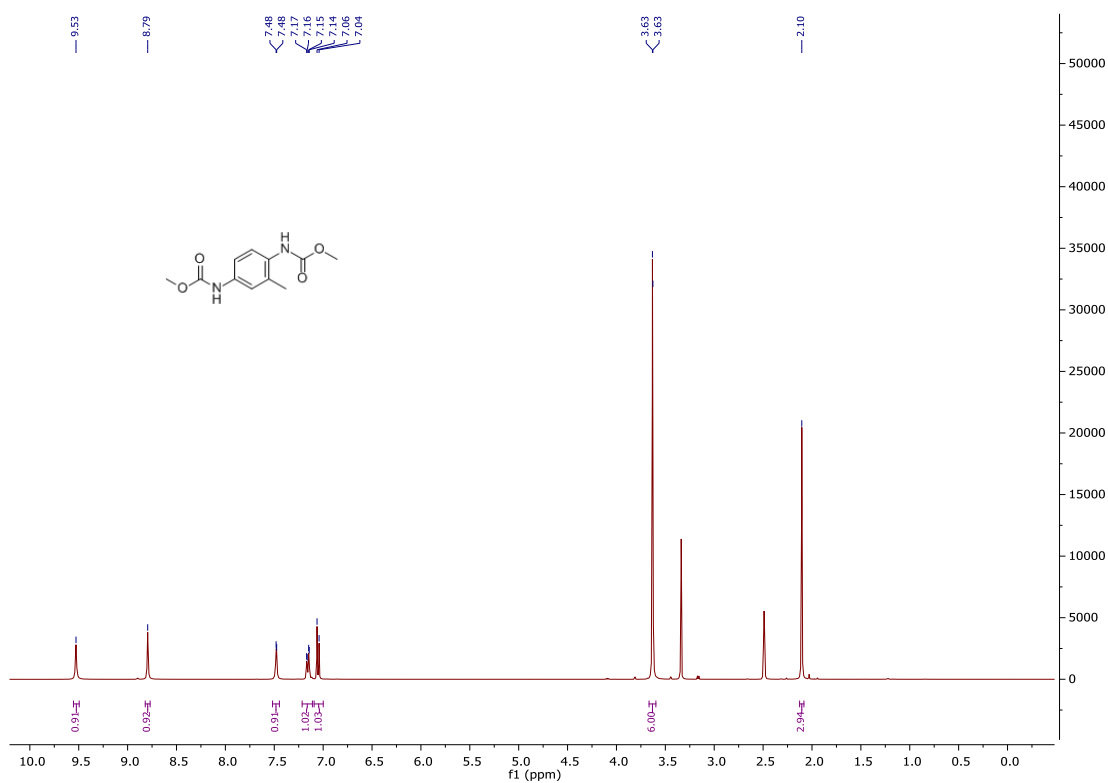


Figure S12. ^1H NMR (DMSO- d_6 , 400 MHz) spectrum of compound 2e

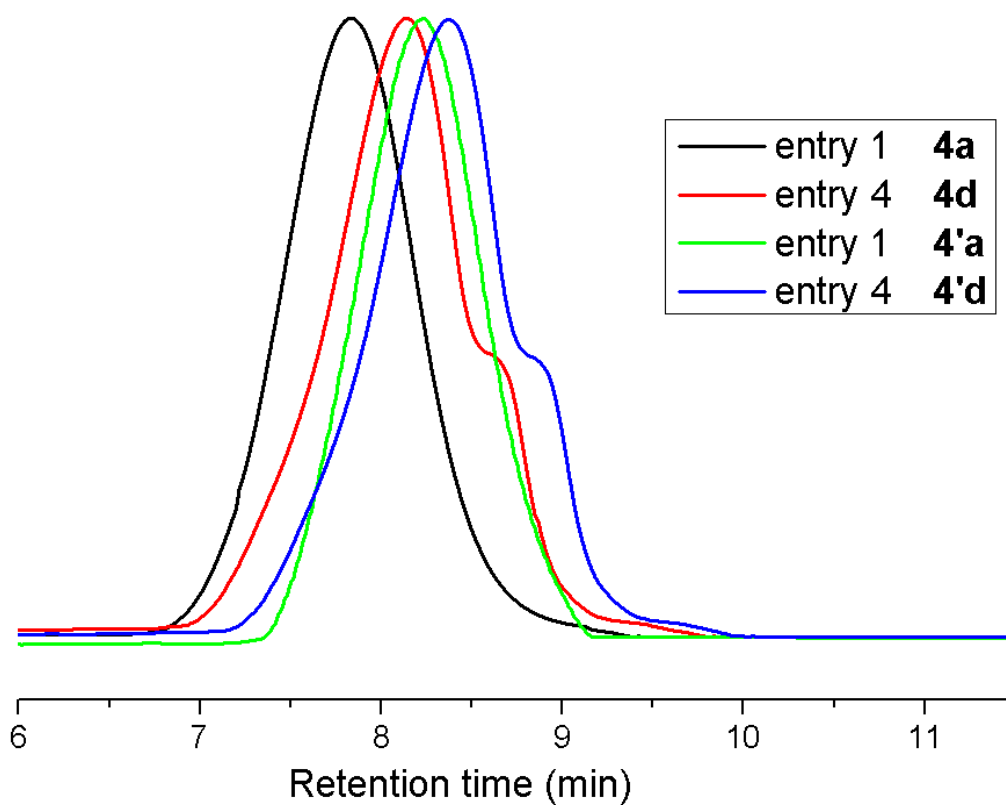


Figure S13. GPC curves of PUs from Table 4 with THF as the eluent.