Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Stabilization of the hindered urea bond through de-*tert*-butylation

Yingfeng Yang[a], Hanze Ying[a], Yunchao Jia[b], Yingying Chen[a], Jianjun Cheng[a, c-g]*

*Email: jianjunc@illinois.edu

[a] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States.

[b] School of Materials Science and Engineering, Henan University of Technology, 100 Lianhua St, Zhongyuan District, Zhengzhou, Henan, China.

[c] Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States.

[d] Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States.

[e] Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States.

[f] Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801, United States.

[g] Carl R. Woese Institute for Genomic Biology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States.

1. Materials and instrumentation

1.1. Materials

All reagents were purchased from Sigma-Aldrich or TCI and used as received unless otherwise noted. Deuterated chloroform ($CDCl_3$) and deuterated water (D_2O) was purchase from Cambridge Isotope Laboratory. Tetrahydrofuran (THF) were dried with a column packed with alumina. HPLC grade 0.1% TFA-H_2O and acetonitrile were purchased from Fisher Scientific Company LLC (Hanover Park, IL, USA).

1.2. Instrumentation

1.2.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian U500, VXR500, UI500NB or a Bruker Carver B500 spectrometer, with shifts reported in parts per million downfield from tetramethylsilane and referenced to the residual solvent peak. MestReNova 11.0.1 was used to analyze all spectra.

1.2.2. Fourier-transform infrared spectroscopy (FTIR)

Fourier transform infrared (FT-IR) spectra were performed using a Spectrum 100 spectrometer (Perkin Elmer) on a KBr salt plate.

1.2.3. Electrospray ionization mass spectrometry (ESI-MS)

Electrospray ionization (ESI) mass spectrometry was performed on a Waters Quattro Ultima II. Solvent media was 50% Methanol solution with 0.2% formic acid.

1.2.4. High-performance liquid chromatography (HPLC)

HPLC analysis was conducted by Shimadzu LC system (LC-20AT) connected with PDA detector (SPD-M20A). Phenomenex Kinetex Ph-hexyl column (5 µm, 100 mm × 4.6 mm) was used for analysis. Gradient method was adopted using 0.1% TFA-H_2O and acetonitrile as mobile phase.

1.2.5. Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) was performed in chloroform at a flow rate of 1.0 mL/min on a system equipped with a Model1260 Infinity isocratic pump (Agilent Technology) in series with a 717 Autosampler (Waters) and size exclusion columns (50 Å, 100 Å Phenogel columns, 5 µm, 300 × 7.8 mm, Phenomenex) connected in series. An Optilab rEX refractive index detector

(Wyatt Technology) operating at a wavelength of 658 nm were used as detector. Samples were filtered through a 0.45 μm PTFE filter before analysis.

1.2.6. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS)

MALDI-TOF spectra were obtained on a Bruker Daltonics UltrafleXtreme MALDI TOFTOF equipped with a nitrogen laser of 337 nm. The sample was dissolved in chloroform at a concentration of 10 mg/mL. The cationization agent CF_3COONa was dissolved in THF at a concentration of 10 mg/mL. The matrix used was α-Cyano-4-hydroxycinnamic acid (CHCA, Sigma-Aldrich) and was dissolved in THF at a concentration of 10 mg/mL. Solutions of matrix, sample and cationization agent were mixed in a volume ratio of 4/1/1. The mixed solution was spotted (1μL) on the MALDI sample plate and air-dried. All spectra were recorded in reflectron mode.

1.2.7. Dynamic mechanical analysis (DMA)

The stress-strain curve, creep behavior and stress relaxation were performed using dynamic mechanical analyzer (DMA Q800, TA instruments).

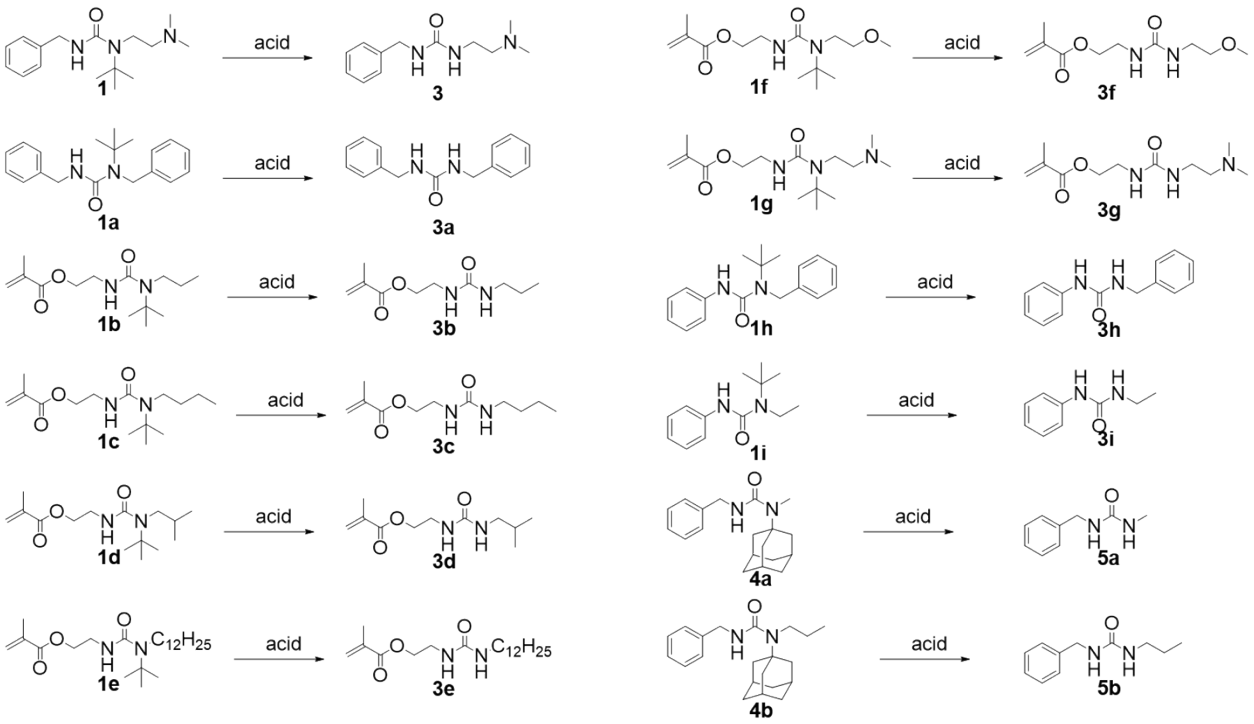
The stress relaxation: First, a 10 × 5 × 1mm specimen was heated up and equilibrated at the desired temperature. The specimen was then stretched to a constant strain of 10% with the relative stress being monitored.

The stress-strain curve was obtained via DMA under a controlled-force mode in which the force was ramped from 0 to 18 N with a rate of 3 N/min. The specimen size was 10 × 5 × 1mm.

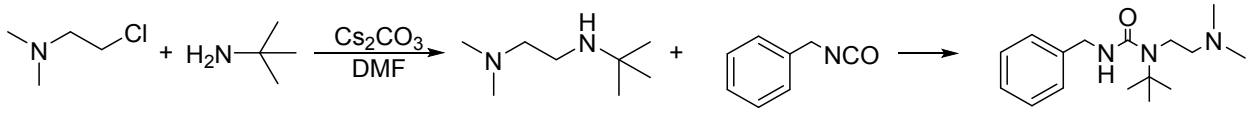
The creep behavior was tested under a constant force of 0.5N under controlled force DMA mode.

2. Experimental procedures

2.1. Preparation of the model compounds, polymers and organogels



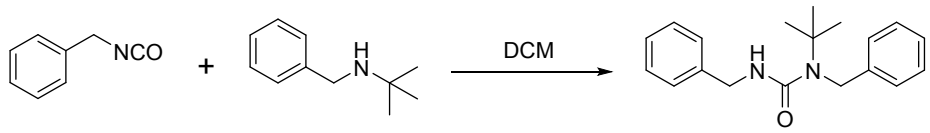
Scheme S1: The model compounds synthesized and tested for the feasibility of the de-*tert*-butylation reaction by acid.



Scheme S2: Synthesis of compound **1**

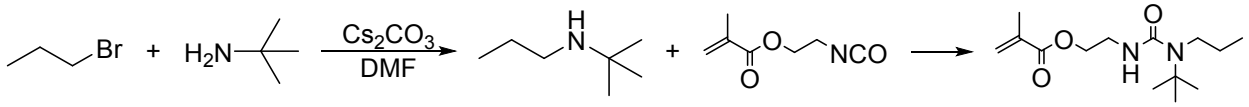
Compound 1: 2-Chloro-*N,N*-dimethylethan-1-amine (215.2 mg, 2 mmol) was dissolved in 3 mL DMF in a 7-mL vial. Then *tert*-butyl amine (160.8 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. Then benzyl isocyanate (293.0 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was then quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. Final product was purified by column chromatography.^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.33 – 7.27 (m, 4H), 7.25 – 7.19 (m,

1H), 4.28 (d, *J* = 5.0 Hz, 2H), 3.26 – 3.18 (m, 2H), 2.44 – 2.34 (m, 2H), 2.01 (s, 6H), 1.38 (d, *J* = 0.8 Hz, 9H).



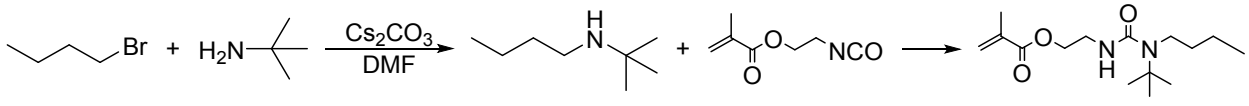
Scheme S3: Synthesis of compound **1a**

Benzyl isocyanate (133.2 mg, 1 mmol) and *N*-benzyl-*tert*-butylamine (163.3 mg, 1 mmol) were mixed in 10 mL DCM. The mixture was stirred at room temperature for 30 min followed by removal of the solvent under vacuum. The product was obtained as white powder and used without purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11~7.36 (m, 10H), 4.53 (b, 1H), 4.52 (s, 2H), 4.33 (d, 2H), 1.49 (s, 9H).



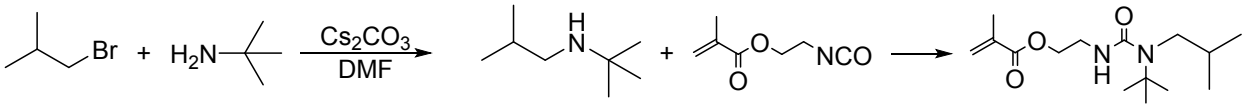
Scheme S4: Synthesis of compound **1b**

1-Bromopropane (246.0 mg, 2 mmol) was dissolved in 3 mL DMF in a 7-mL vial. *tert*-Butyl amine (160.82 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. 2-Isocyanatoethyl methacrylate (341.4 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. The final product was purified by column chromatography. ^{1}H NMR ((400 MHz, Deuterium Oxide): δ 5.93 (s, 1H), 5.51 (s, 1H), 4.06 (t, *J* = 5.1 Hz, 2H), 3.26 (t, *J* = 5.2 Hz, 2H), 2.99 – 2.91 (m, 2H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.31 (d, *J* = 8.5 Hz, 2H), 1.17 (d, *J* = 1.4 Hz, 9H), 0.67 – 0.56 (m, 3H).



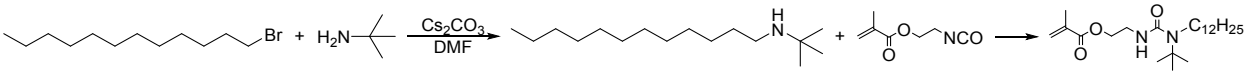
Scheme S5: Synthesis of compound **1c**

1-Bromobutane (274.0 mg, 2 mmol) was dissolved in 3 mL DMF in a 7-mL ml vial. *tert*-Butyl amine (160.82 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. 2-Isocyanatoethyl methacrylate (341.4 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. The final product was purified by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.12 (s, 1H), 5.67 – 5.53 (m, 1H), 4.71 (s, 1H), 4.38 – 4.22 (m, 2H), 3.52 (q, *J* = 5.3 Hz, 2H), 3.17 – 3.05 (m, 2H), 1.95 (d, *J* = 1.3 Hz, 3H), 1.51 (p, *J* = 7.9 Hz, 2H), 1.41 (s, 9H), 1.35 – 1.21 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).



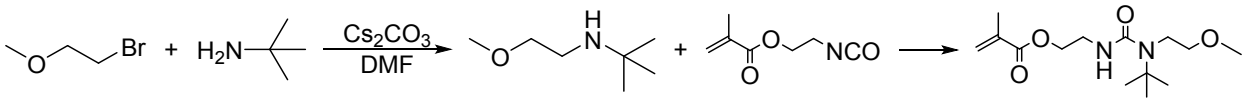
Scheme S6: Synthesis of compound **1d**

1-Bromo-2-methylpropane (274.0 mg, 2 mmol) was dissolved in 3 mL DMF in a 7-mL vial. *tert*-Butyl amine (160.82 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. 2-Isocyanatoethyl methacrylate (341.4 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. The final product was purified by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.17 – 6.08 (m, 1H), 5.58 (q, *J* = 1.6 Hz, 1H), 4.74 (s, 1H), 4.28 – 4.24 (m, 2H), 3.51 (q, *J* = 5.3 Hz, 2H), 2.97 (d, *J* = 7.6 Hz, 2H), 1.94 (q, *J* = 2.8, 2.0 Hz, 3H), 1.90 – 1.80 (m, 1H), 1.41 (s, 9H), 0.90 (d, *J* = 6.7 Hz, 6H).



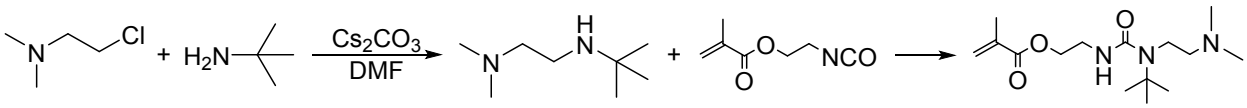
Scheme S7: Synthesis of compound **1e**

1-Bromododecane (498.4 mg, 2 mmol) was dissolved in 3 mL DMF in a 7-mL vial. *tert*-Butyl amine (160.82 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. 2-Isocyanatoethyl methacrylate (341.4 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. The final product was purified by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.11 (dt, *J* = 2.2, 1.0 Hz, 1H), 5.58 (p, *J* = 1.6 Hz, 1H), 4.71 (t, *J* = 5.5 Hz, 1H), 4.32 – 4.24 (m, 2H), 3.51 (q, *J* = 5.3 Hz, 2H), 3.16 – 3.05 (m, 2H), 1.94 (t, *J* = 1.3 Hz, 3H), 1.56 – 1.47 (m, 2H), 1.41 (s, 9H), 1.34 – 1.18 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H).



Scheme S8: Synthesis of compound **1f**

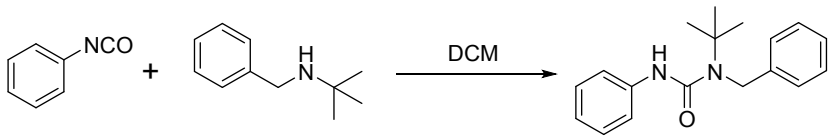
1-Bromo-2-methoxyethane (278.0 mg, 2 mmol) was dissolved in DMF (3 mL) in a 7-mL vial. *tert*-Butyl amine (160.82 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. 2-Isocyanatoethyl methacrylate (341.4 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. The final product was purified by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (s, 1H), 6.13 (dt, *J* = 1.9, 0.9 Hz, 1H), 5.57 (q, *J* = 1.7 Hz, 1H), 4.20 (t, *J* = 5.4 Hz, 2H), 3.49 – 3.46 (m, 2H), 3.46 – 3.43 (m, 2H), 3.36 – 3.34 (m, 3H), 1.95 (p, *J* = 0.8 Hz, 3H), 1.37 (s, 9H).



Scheme S9: Synthesis of compound **1g**

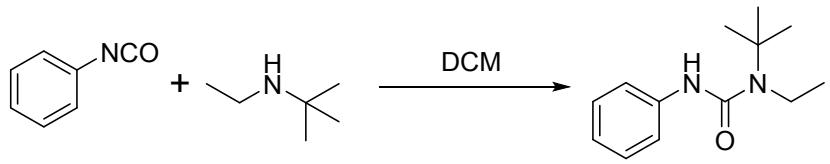
2-Chloro-*N,N*-dimethylethan-1-amine (215.2 mg, 2 mmol) was dissolved in DMF(3 mL) in a 7-mL vial. *tert*-Butyl amine (160.82 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the

solution. The suspension was stirred at room temperature for about three days. 2-Isocyanatoethyl methacrylate (341.4 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. The final product was purified by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H), 6.15 – 6.06 (m, 1H), 5.55 (t, *J* = 1.8 Hz, 1H), 4.22 (t, *J* = 5.6 Hz, 2H), 3.45 (q, *J* = 5.5 Hz, 2H), 3.33 – 3.18 (m, 2H), 2.54 – 2.40 (m, 2H), 2.25 (s, 6H), 1.95 (d, *J* = 1.2 Hz, 3H), 1.37 (s, 9H).



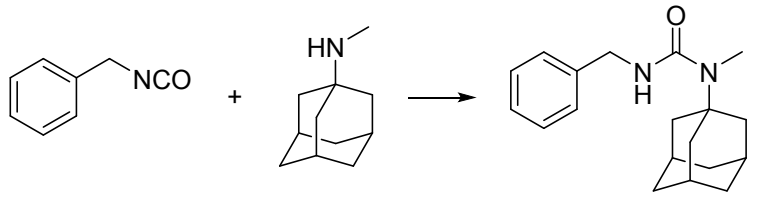
Scheme S10: Synthesis of compound **1h**

Phenyl isocyanate (119.1 mg, 1 mmol) and *N*-Benzyl-*tert*-butylamine (163.3 mg, 1 mmol) were mixed in 10 mL DCM. The mixture was stirred at room temperature for 30 min and then solvent was removed. Product was obtained as white powder and used without purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.13 – 7.08 (m, 2H), 6.95 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.19 (s, 1H), 4.63 (s, 2H), 1.53 (s, 9H).



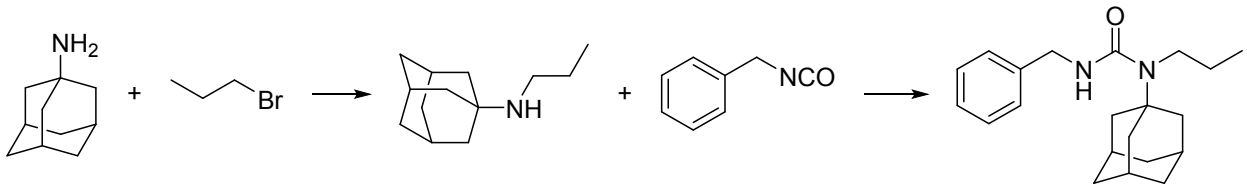
Scheme S11: Synthesis of compound **1i**

Phenyl isocyanate (119.1 mg, 1 mmol) and N-ethyl-2-methylpropan-2-amine (101.2 mg, 1 mmol) were mixed in 10 mL DCM. The mixture was stirred at room temperature for 30 min and then solvent was removed. Product was obtained as white powder and used without purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.05 – 6.98 (m, 1H), 6.31 (s, 1H), 3.40 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).



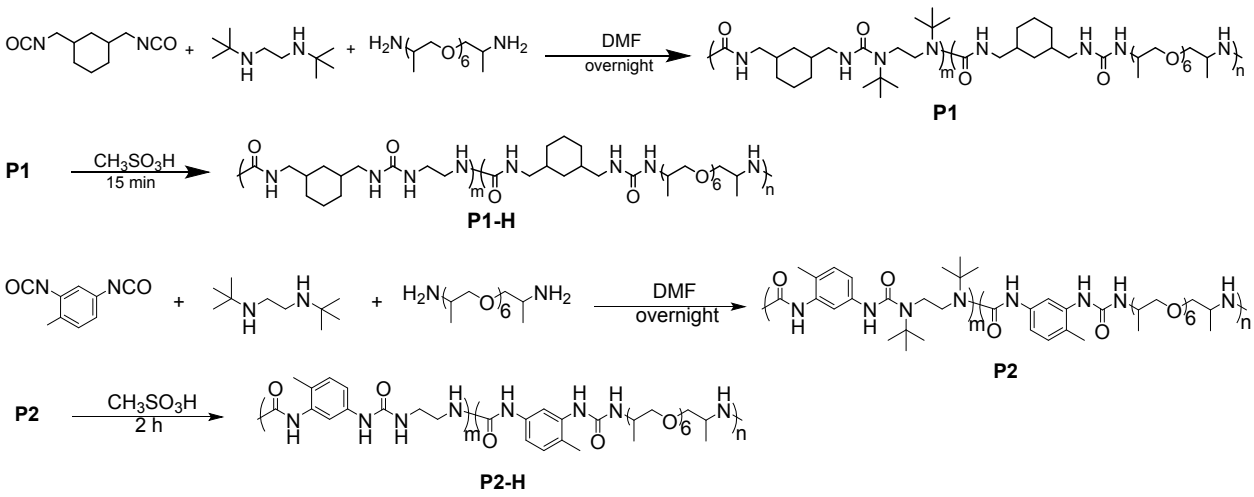
Scheme S12: Synthesis of compound **4a**

Benzyl isocyanate (133.2 mg, 1 mmol) and N-Methyl-1-adamantanamine (165.3 mg, 1 mmol) were mixed in DCM (10 mL). The mixture was stirred at room temperature for 30 min and then solvent was removed. Product was obtained as white powder and used without purification. ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (499 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 5H), 4.53 (s, 1H), 4.39 (d, *J* = 5.4 Hz, 2H), 2.82 (s, 3H), 2.16 (d, *J* = 2.9 Hz, 6H), 2.10 (s, 3H), 1.76 – 1.60 (m, 6H).



Scheme S13: Synthesis of compound **4b**

1-Bromopropane (246.0 mg, 2 mmol) was dissolved in DMF (3 mL) in a 7-mL vial. 1-Adamantanamine (332.8 mg, 2.2 mmol) and Cs_2CO_3 (325.8 mg, 1 mmol) were added to the solution. The suspension was stirred at room temperature for about three days. Then benzyl isocyanate (293.0 mg, 2.2 mmol) was added to the suspension and stirred for another 30 min. The reaction was then quenched with water (20 mL) and extracted with DCM (30 mL × 3). The organic layer was combined, washed twice with brine and then dried with anhydrous Na_2SO_4. DCM was removed by rotary evaporator. Final product was purified by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.18 (m, 5H), 4.59 (s, 1H), 4.38 (d, *J* = 5.4 Hz, 2H), 3.17 – 3.02 (m, 2H), 2.17 (d, *J* = 2.9 Hz, 6H), 2.07 (s, 3H), 1.78 – 1.58 (m, 6H), 1.53 (dq, *J* = 10.4, 7.5 Hz, 2H), 0.82 (dd, *J* = 7.8, 6.9 Hz, 3H).



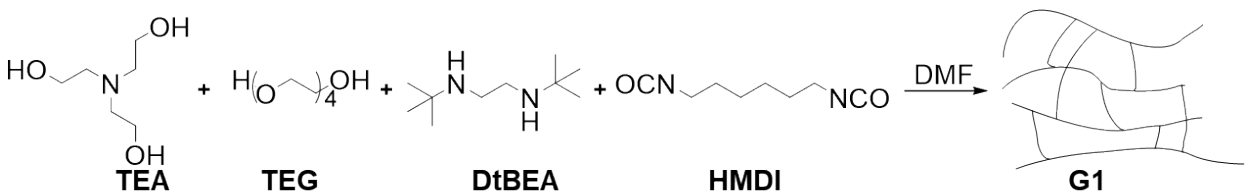
Scheme S14: Synthesis of polymer **P1** and **P2**

Synthesis of **P1** and **P2:** the corresponding diisocyanates and di-*tert*-butylethylenediamine (DtBEA) afforded the dynamic bond. The poly (propylene glycol)diamine (PPGDA) was added to increase the solubility of the de-*tert*-butylated polymer. The mixture (diisocyanate:DtBEA:PPGDA=2:1:1) was incubated at 50 ^{o}C in DMF overnight until reaction was complete as evidenced by the complete disappearance of the isocyanate peak in FTIR. The polymer was then precipitated in ether as white solid.

Procedure of de-*tert*-butylation: **P1-H** was obtained by dissolving 125 mg **P1** in $CHCl_3$ (1 mL), adding 100 µL methanesulfonic acid. After 15 min, the mixture was washed and precipitated again to remove extra acid and fractures.

Procedure of the amine treatment: **P1** or **P1-H** (10 mg) was dissolved in DMF (1 mL). *tert*-Butylamine (100 µL) was added and the mixture was stirred at 60^{o}C for 4h. Excessive amount of amine was removed under vacuum and the treated solution was analyzed directly by GPC.

Treatment of **P2-H** is similar.



Scheme S15: Synthesis of organogel **G1**

Synthetic procedures: **G1** was synthesized from hexmethylenediisocyanate (HMDI), di-*tert*-butylethylenediamine (DtBEA) which afforded the dynamic bond, triethanolamine (TEA) which function as the crosslinker, and the chain extender tetraethylene glycol (TEG). The mixture (TEA:TEG:DtBEA:HMDI=1:6.5:4:12 with 30 wt% DMF) was incubated at 50 ^{o}C for 2 days until complete reaction as evidenced by the complete disappearance of the isocyanate stretching in FTIR.

Preparation of the thin films from **G1**: After mixing the components as mentions above (TEA:TEG:DtBEA:HMDI=1:6.5:4:12 with 30 wt% DMF), the mixture was quickly poured into a big flat PTFE disc. The gel was allowed to cure at 50 ^{o}C for 2 days until complete reaction as evidenced by the complete disappearance of the isocyanate stretching in FTIR. After that the film was incubated in vacuum oven (75 ^{o}C) for three days to remove the residue solvent as much as possible. The films were then cut into specimens with desired dimensions.

De-*tert*-butylation of the thin films: The specimens were first immersed in 3 mL chloroform in a covered shallow disc to allow for full swelling (2 h). TFA (3 mL) was then added and the mixture was set aside for another 2 h. After that, the acid treated specimens were carefully brought out from the solvent and rinsed three times with chloroform, followed by three-day's incubation in vacuum oven (75 ^{o}C) to remove the residue solvent and acid. These specimens were then used for mechanical tests.

2.2. Materials characterizations

2.2.1. The ^{1}H NMR of the model compounds

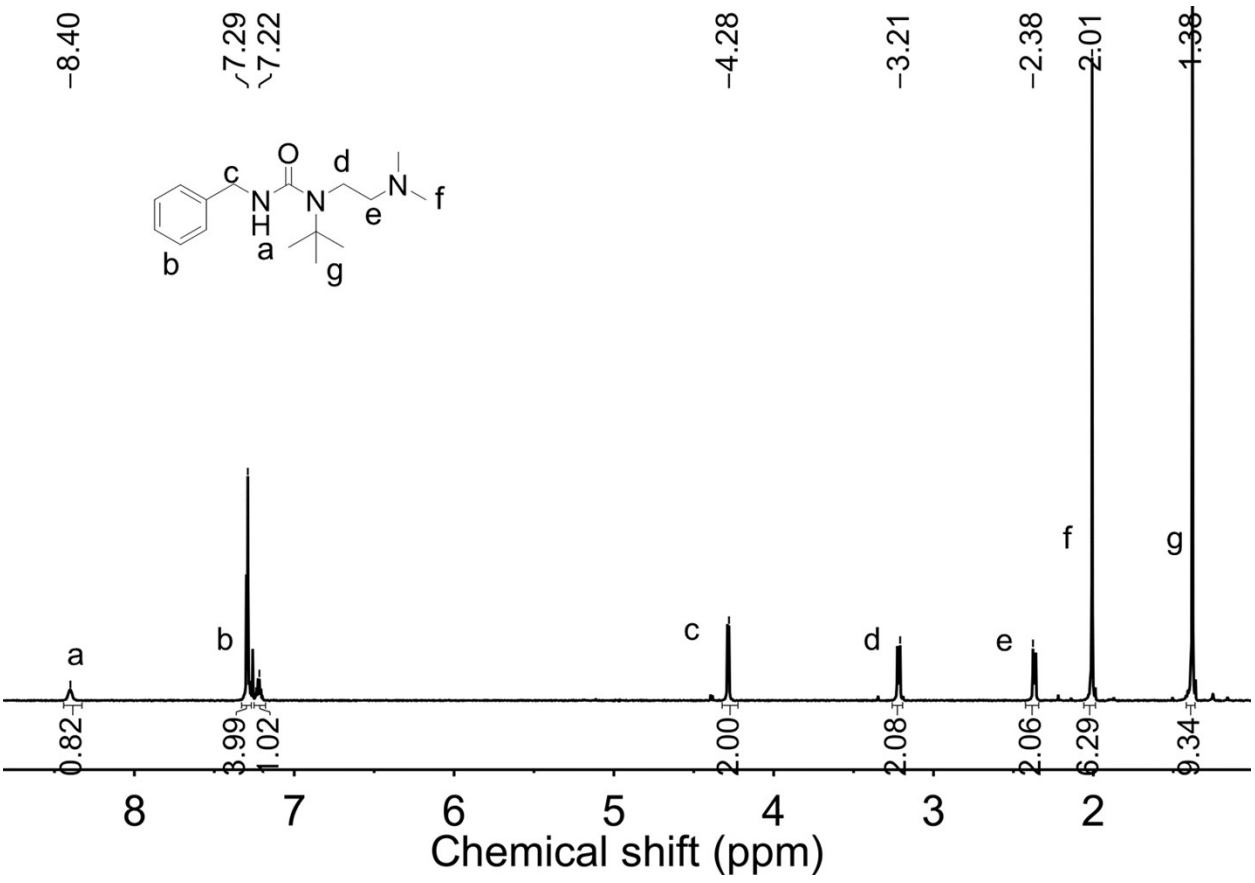


Figure S1: ^{1}H NMR of compound **1**

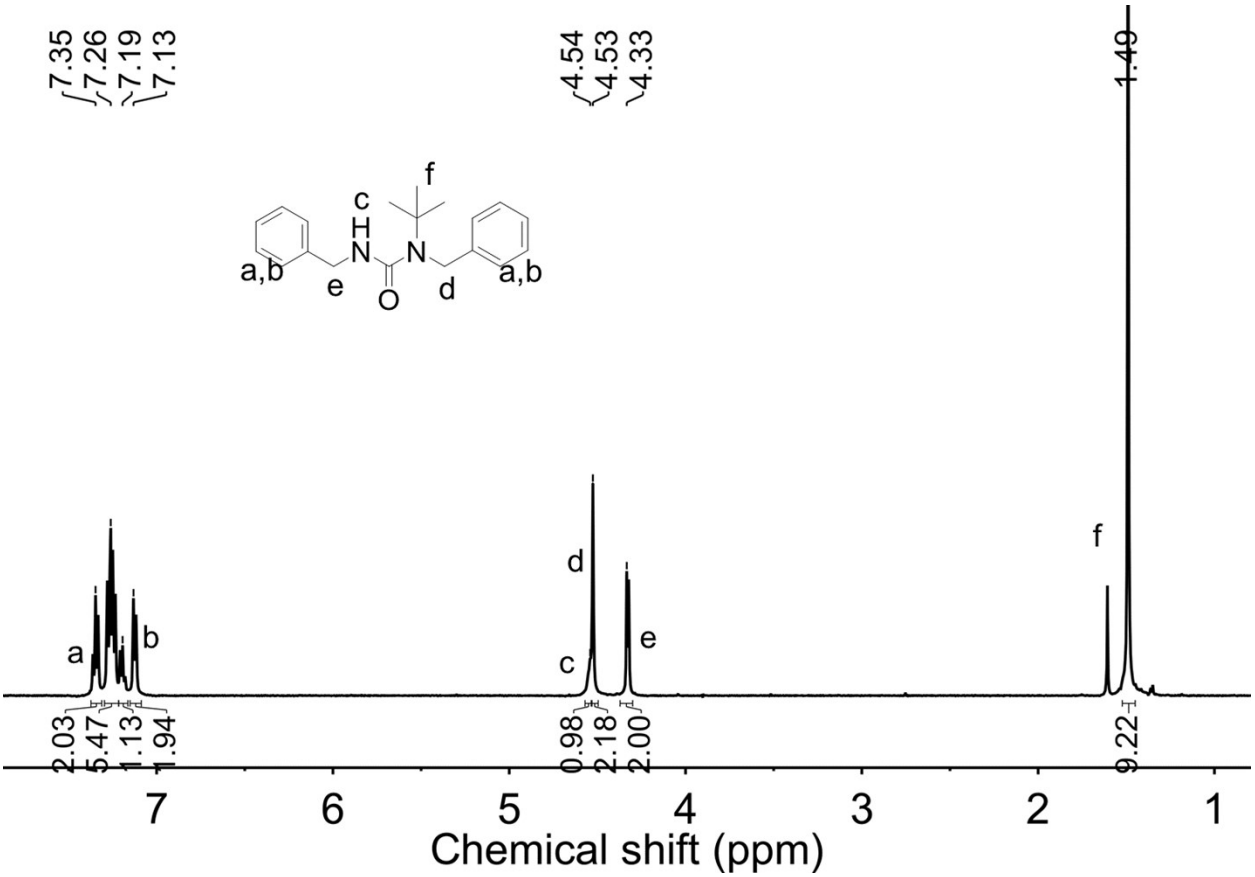


Figure S2: ^{1}H NMR of compound **1a**

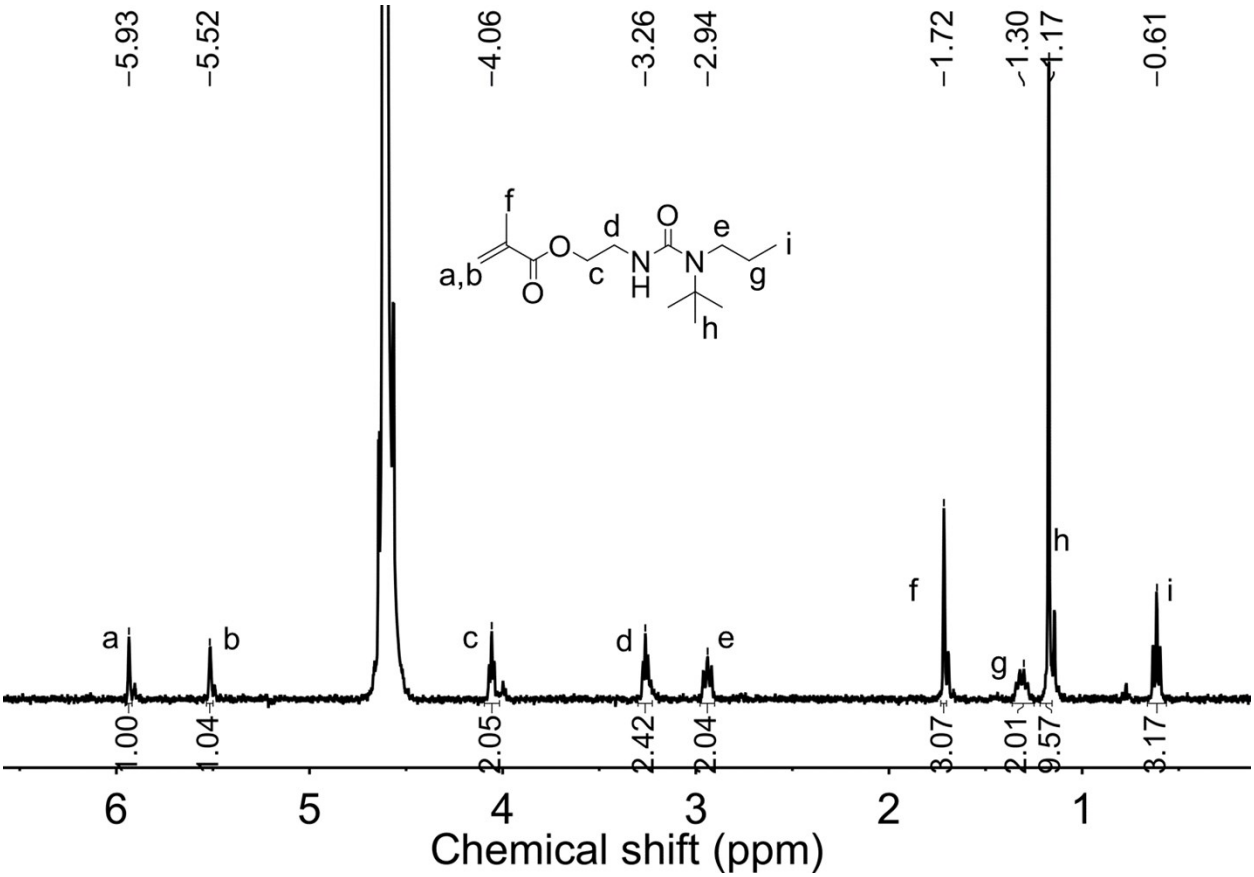


Figure S3: ^{1}H NMR of compound **1b**

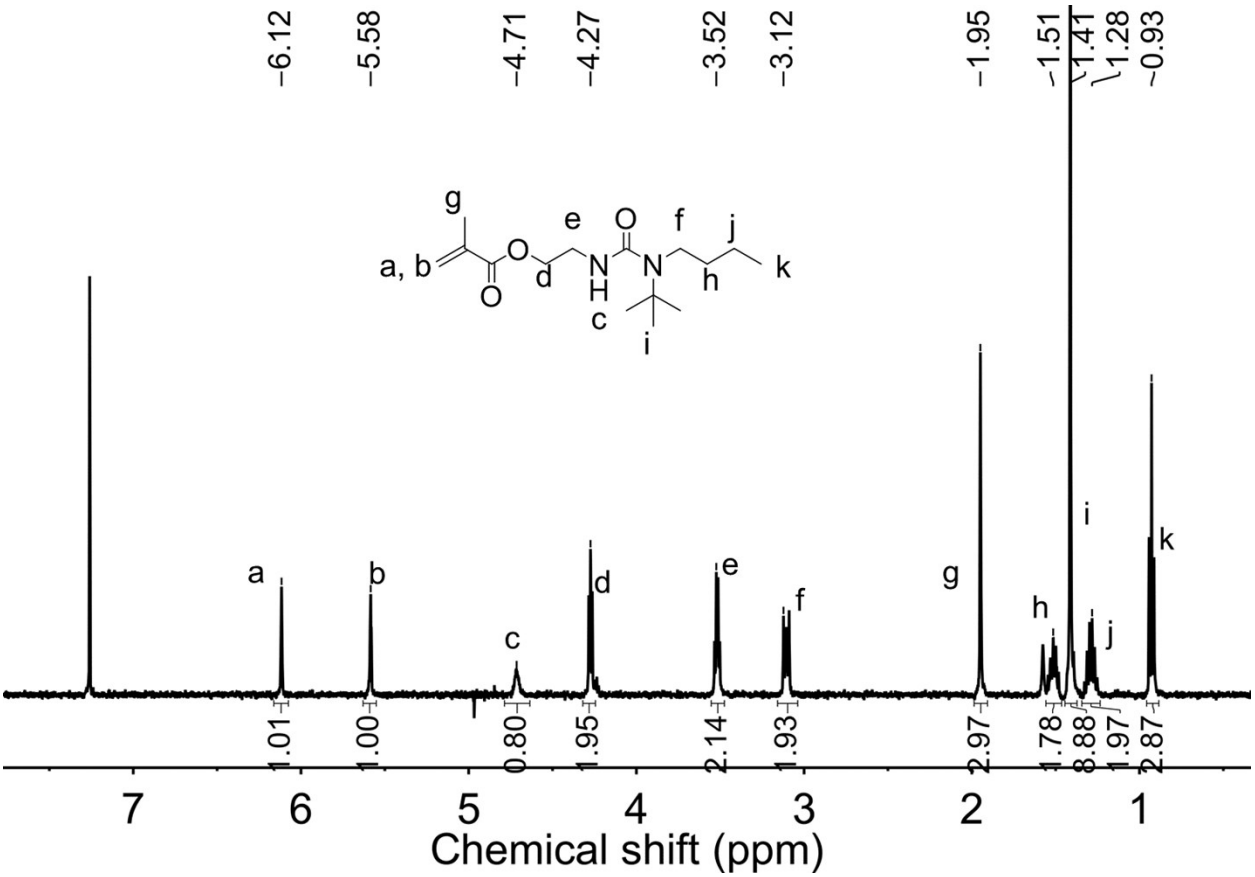


Figure S4: ^{1}H NMR of compound **1c**

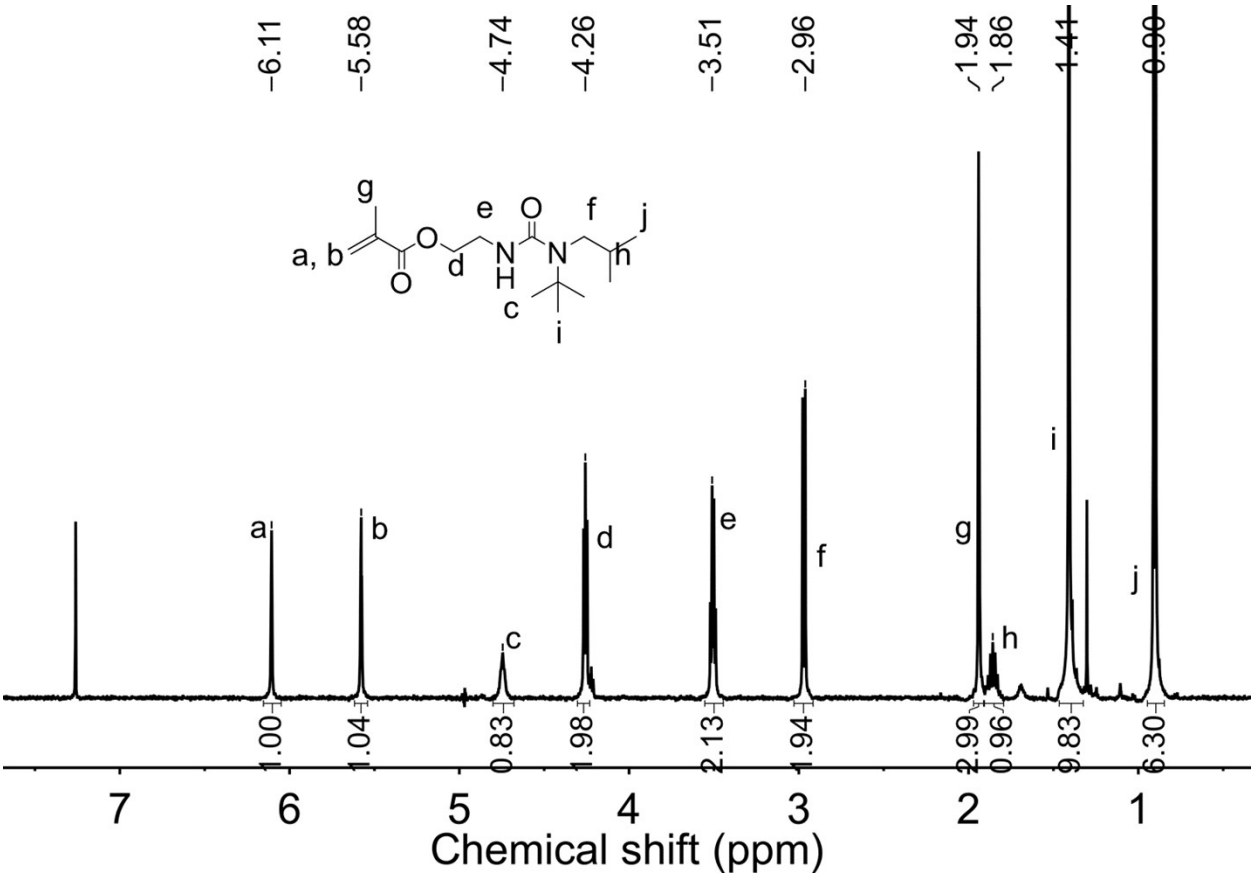


Figure S5: ^{1}H NMR of compound **1d**

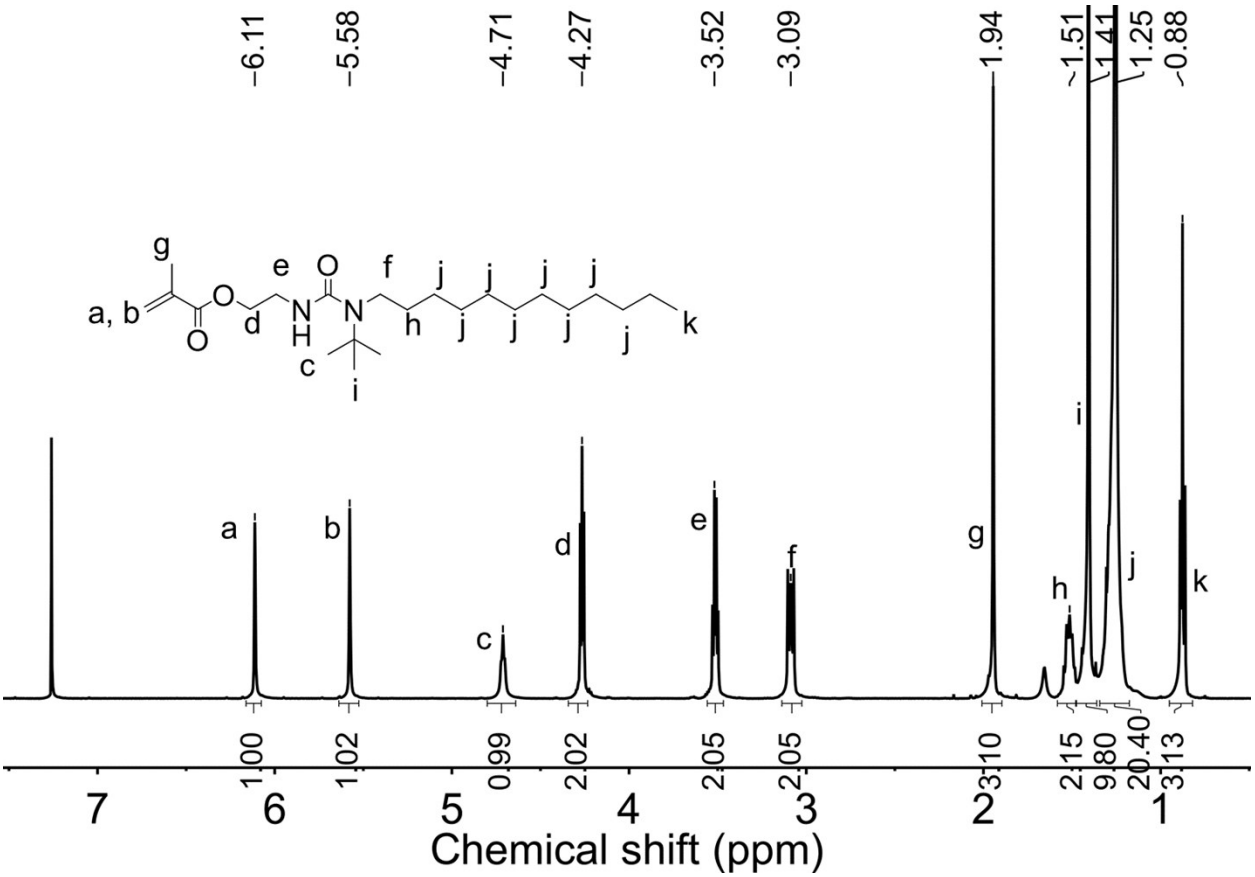


Figure S6: ^{1}H NMR of compound **1e**

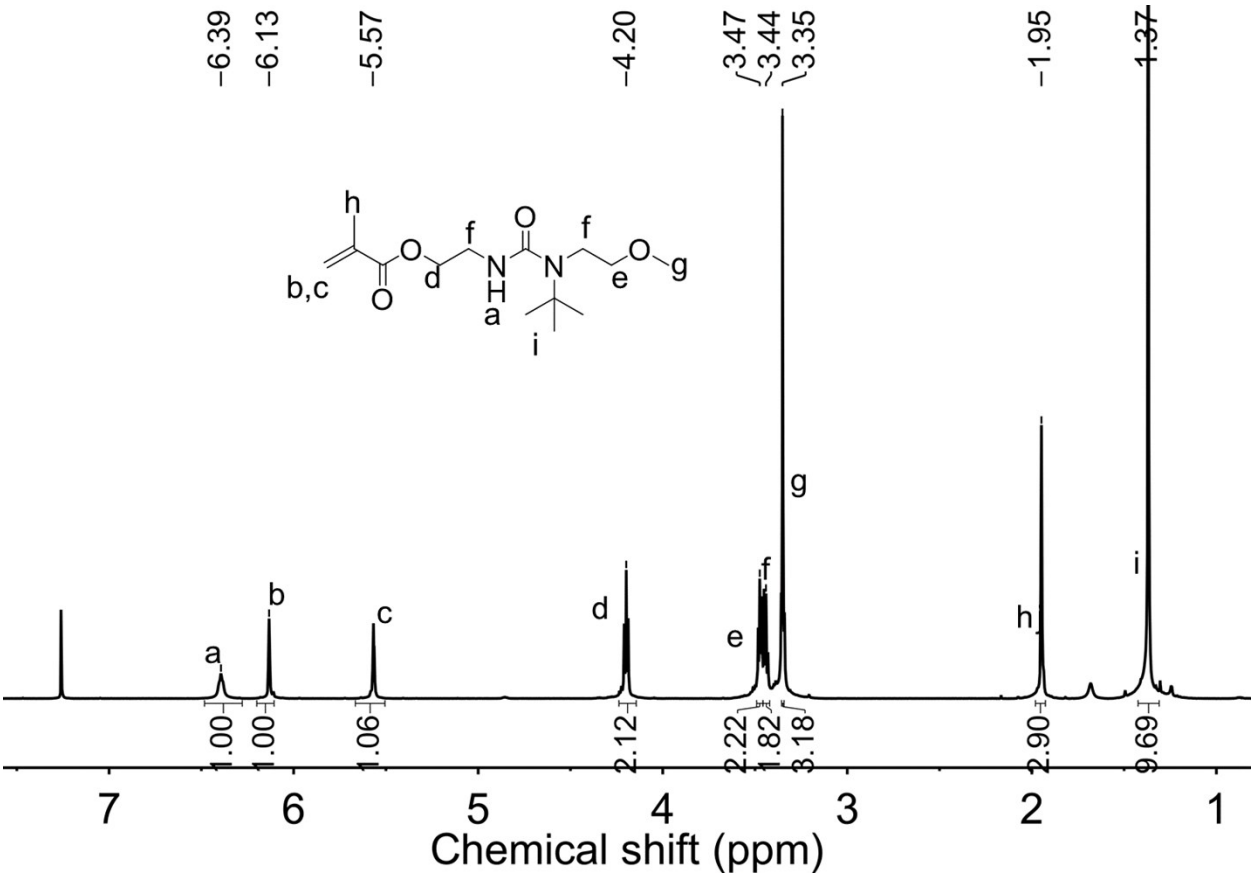


Figure S7: ^{1}H NMR of compound **1f**

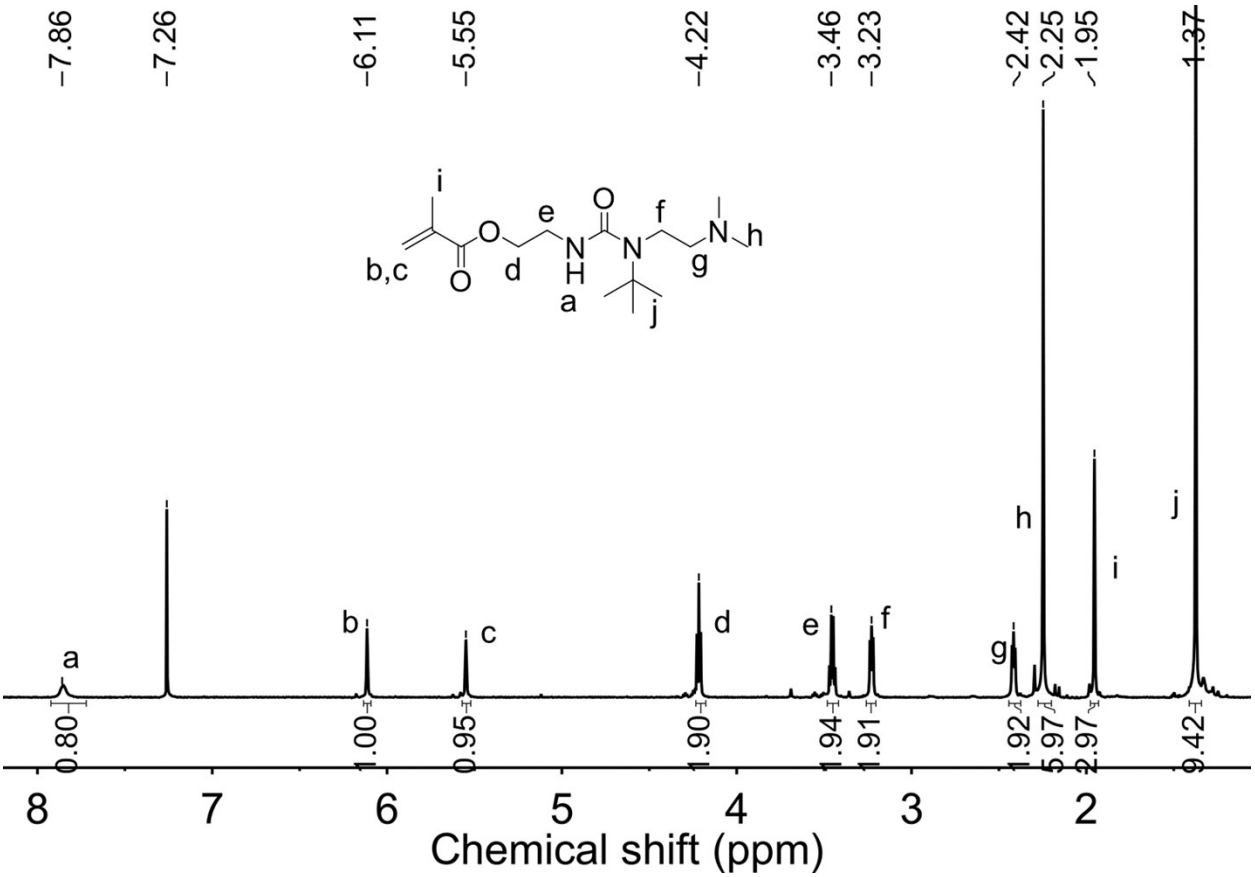


Figure S8: ^{1}H NMR of compound **1g**

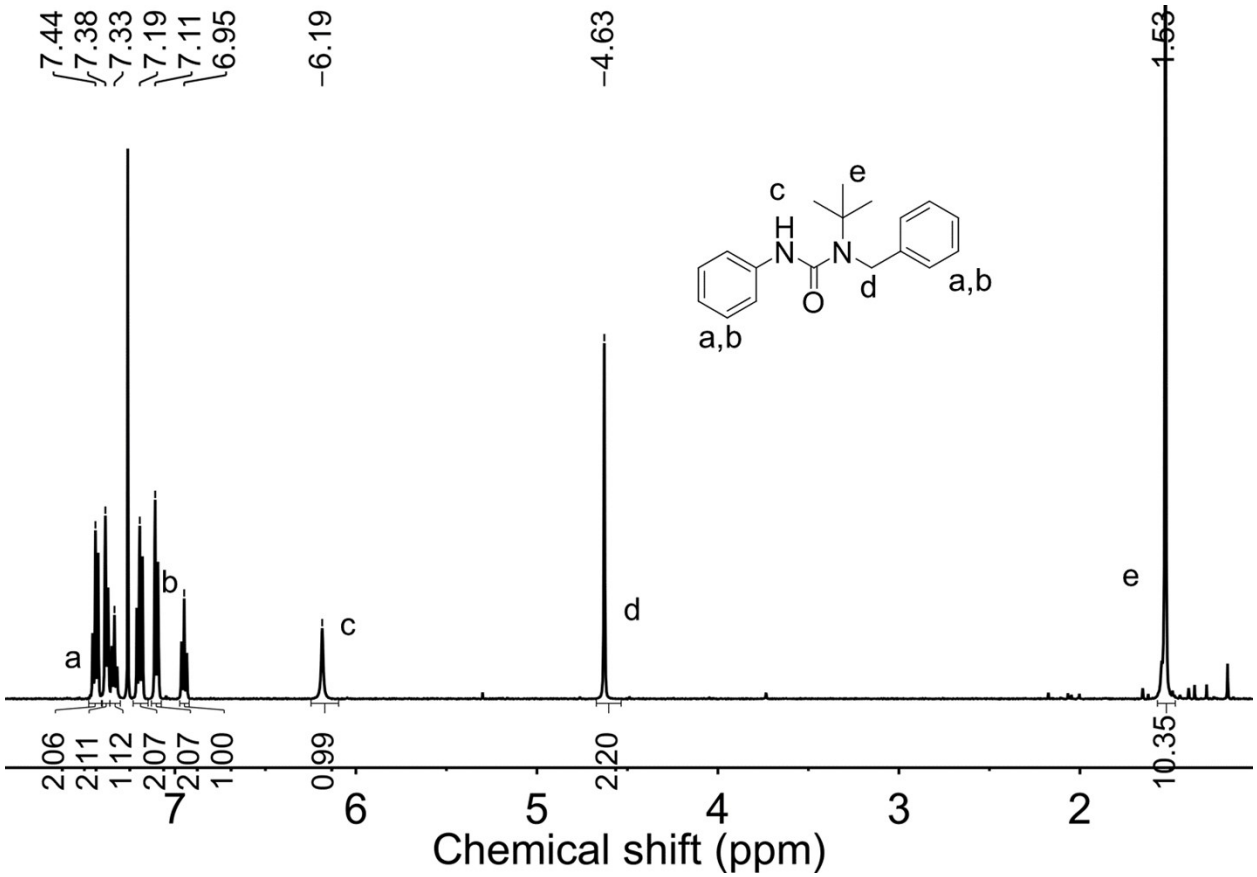


Figure S9: ^{1}H NMR of compound **1h**

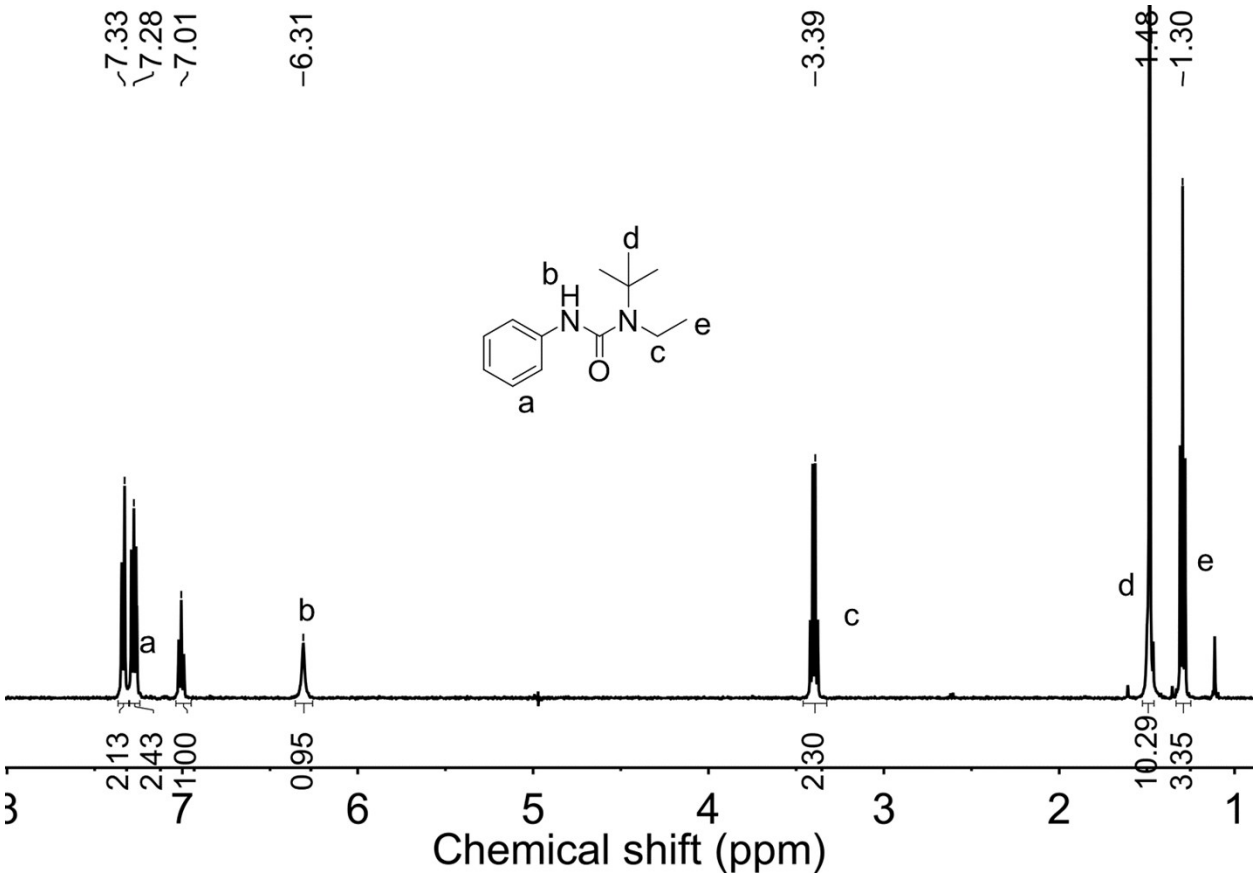


Figure S10: ^{1}H NMR of compound **1i**

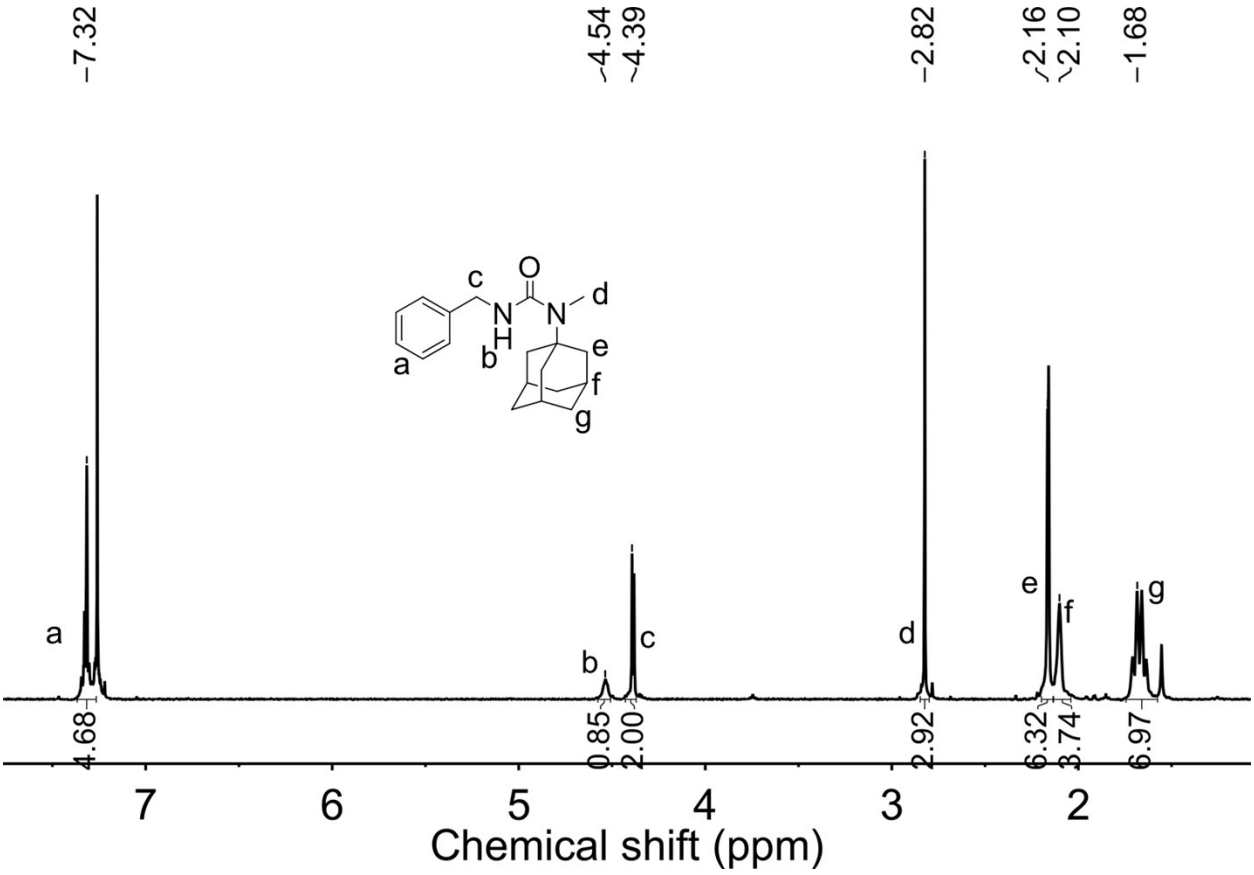


Figure S11: ^{1}H NMR of compound **4a**

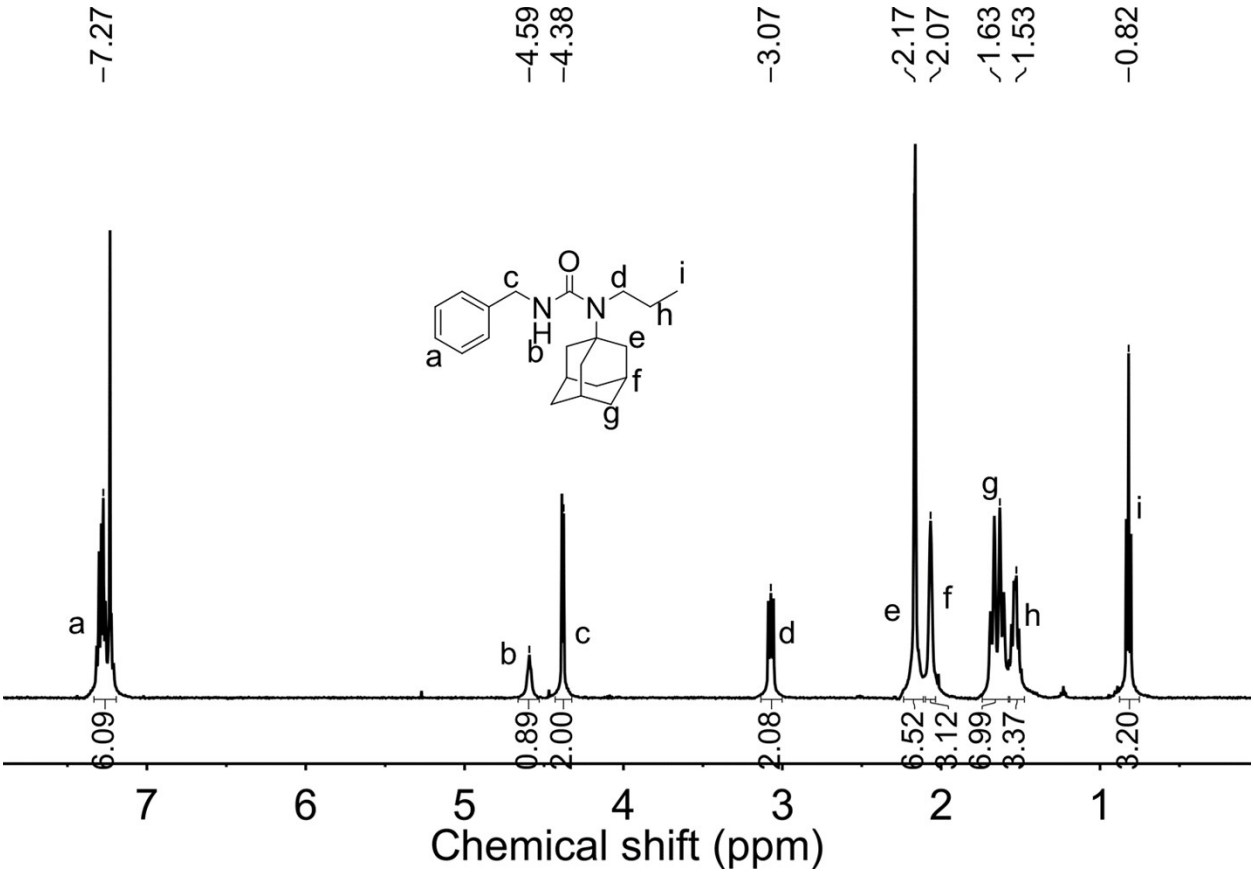


Figure S12: ^{1}H NMR of compound **4b**

2.2.2. De-*tert*-butylation of the model compounds

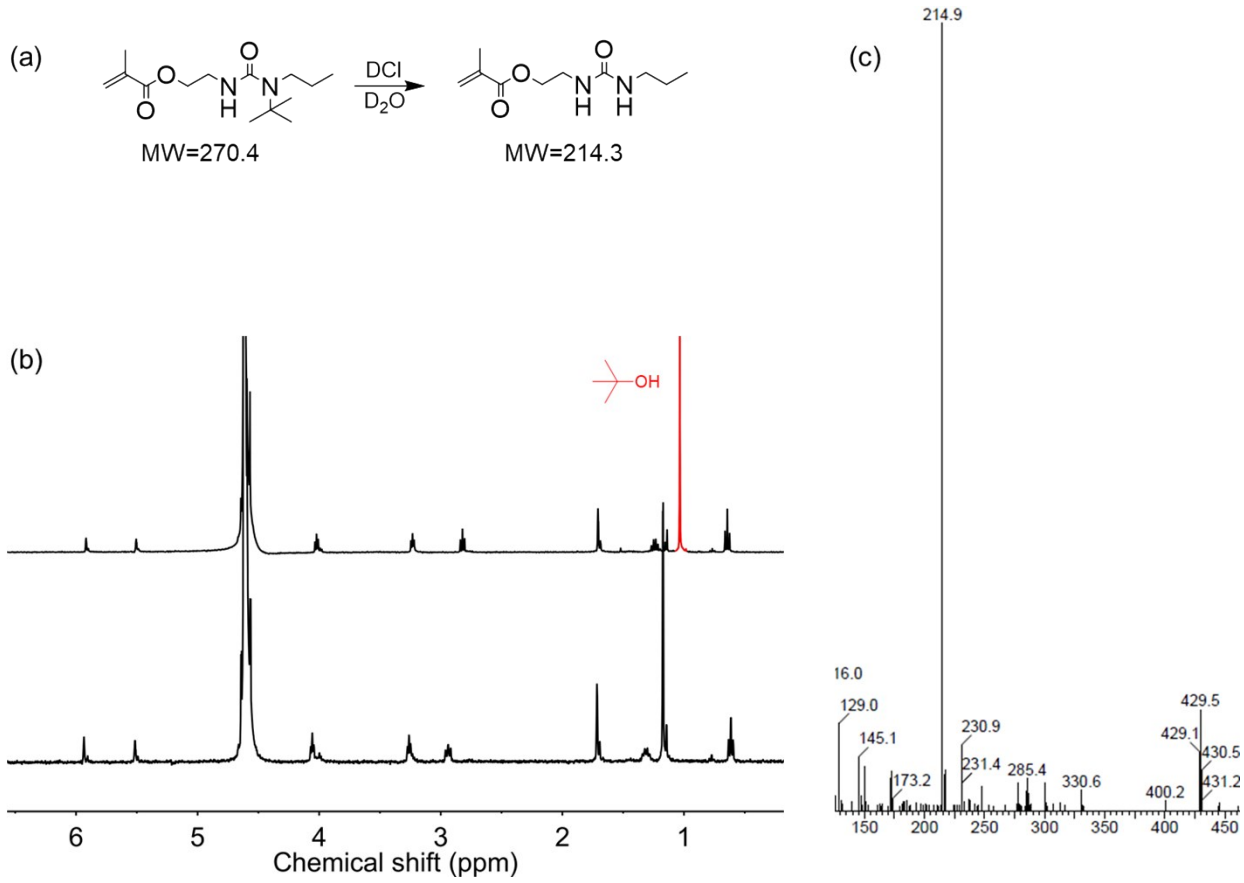


Figure S13: De-*tert*-butylation of **1b** in D_2O with DCl added as the acid (5 µL in 600 µL D_2O)

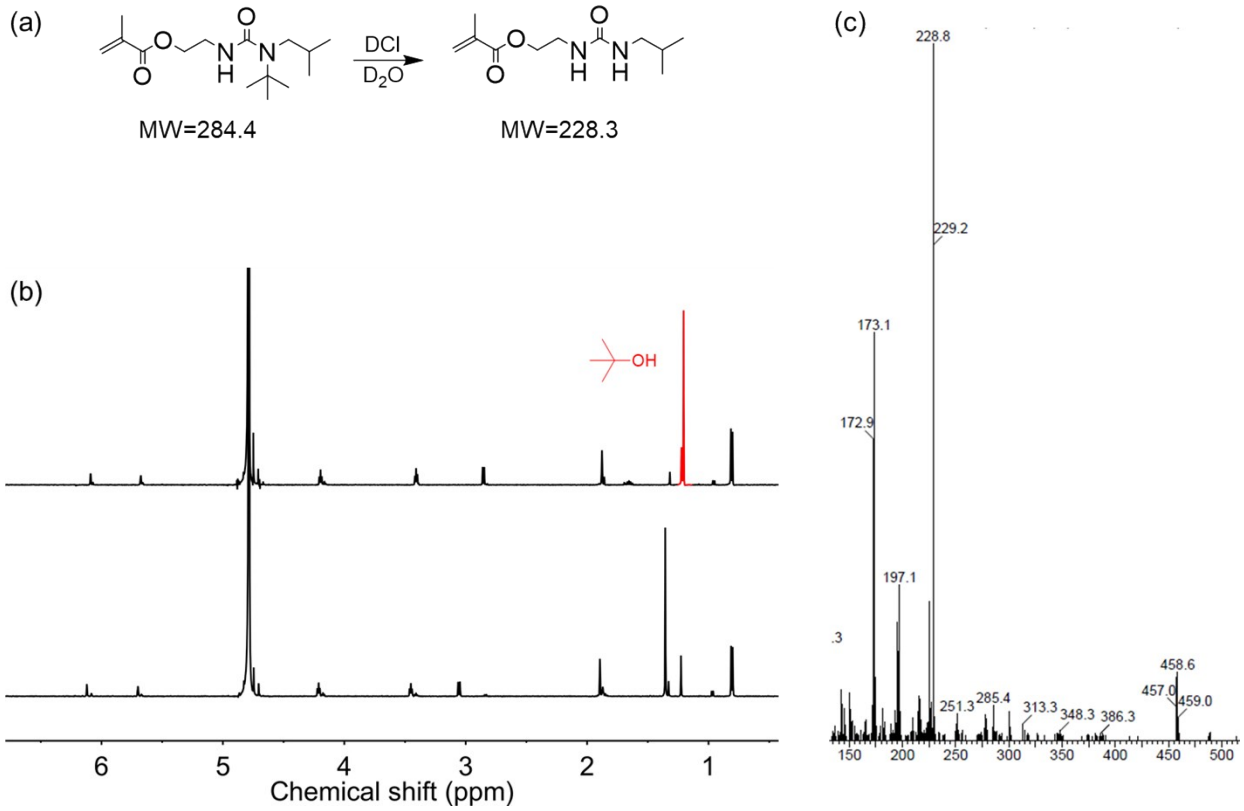


Figure S14: De-*tert*-butylation of **1d** in D_2O with DCl added as the acid (5 µL in 600 µL D_2O)

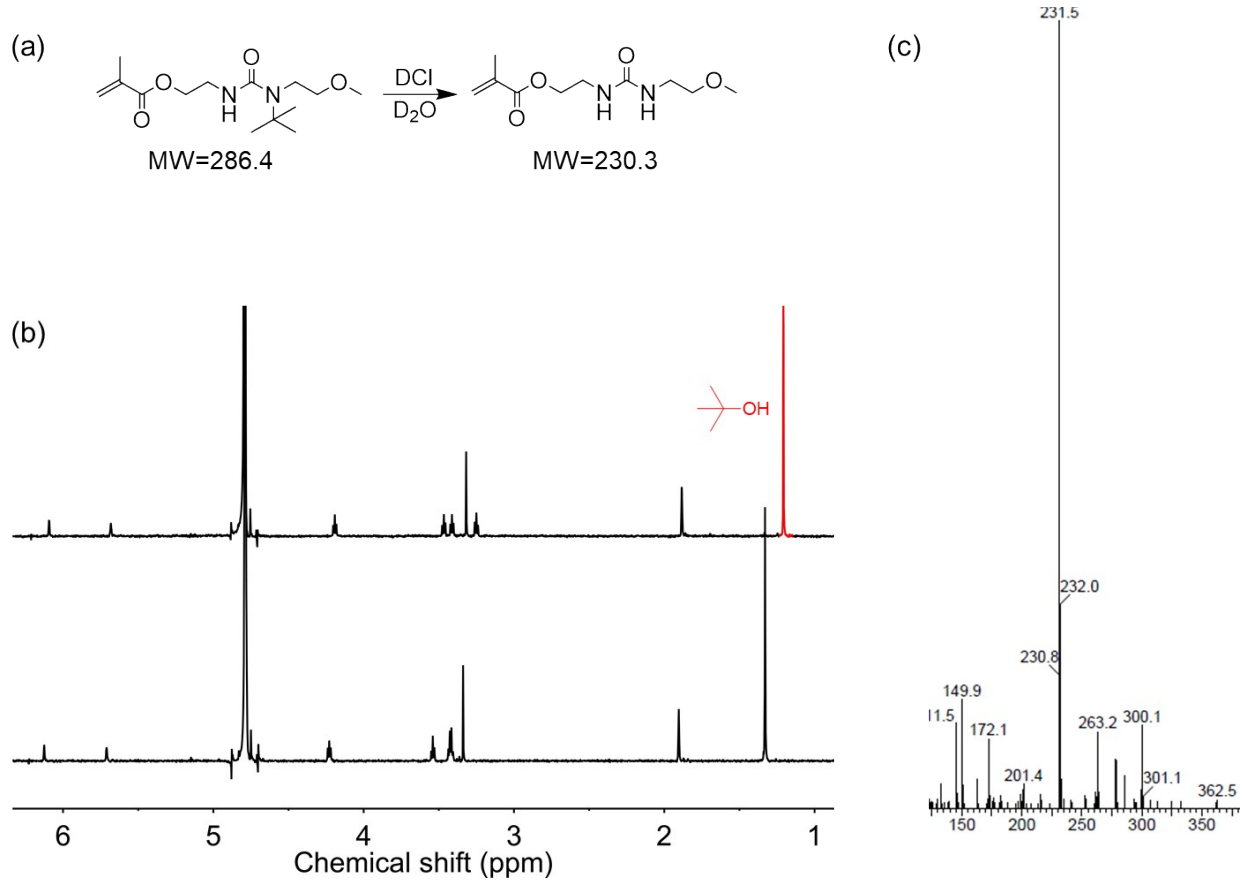


Figure S15: De-*tert*-butylation of **1f** in D_2O with DCl added as the acid (5 µL in 600 µL D_2O)

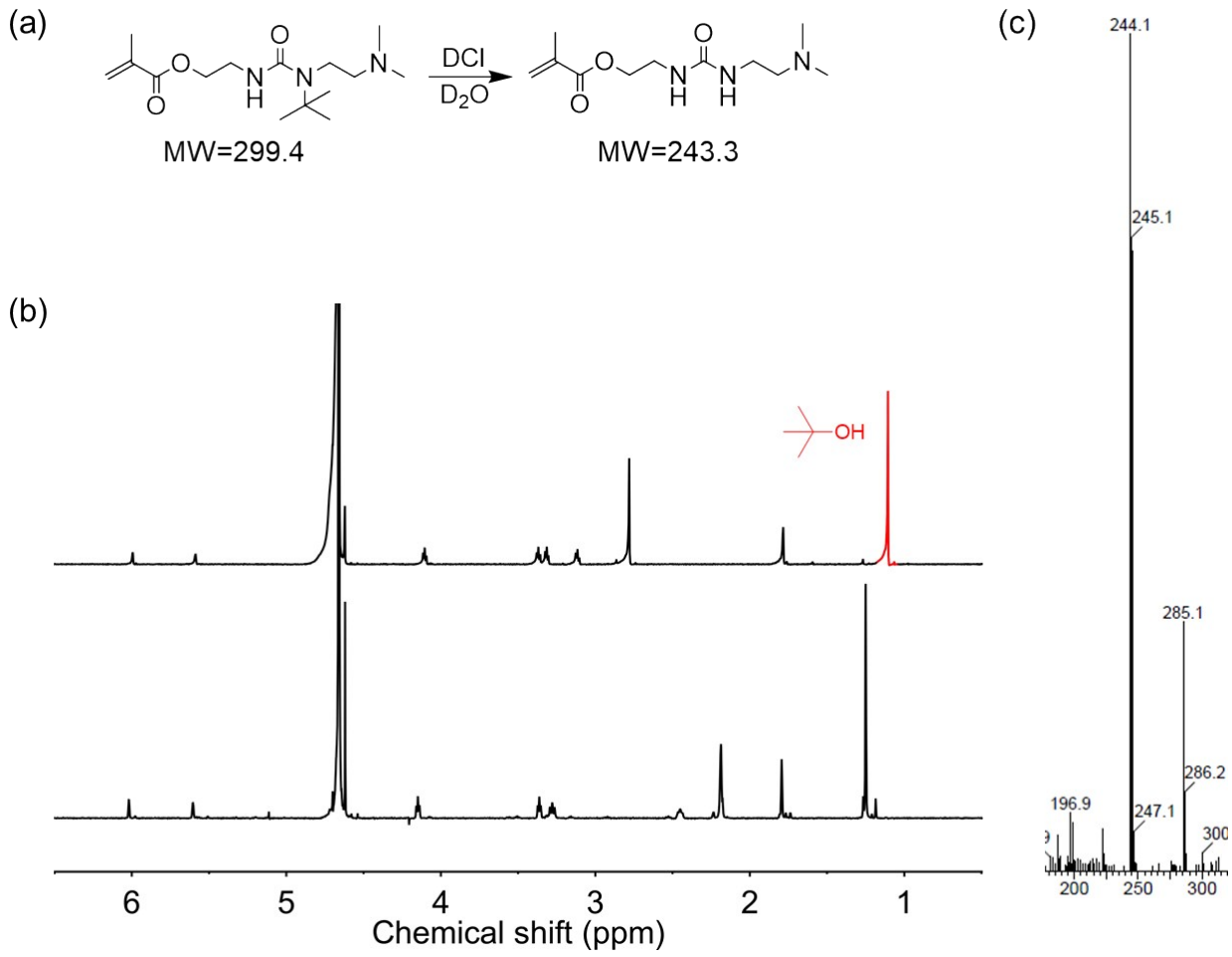


Figure S16: De-*tert*-butylation of **1g** in D_2O with DCl added as the acid (5 µL in 600 µL D_2O)

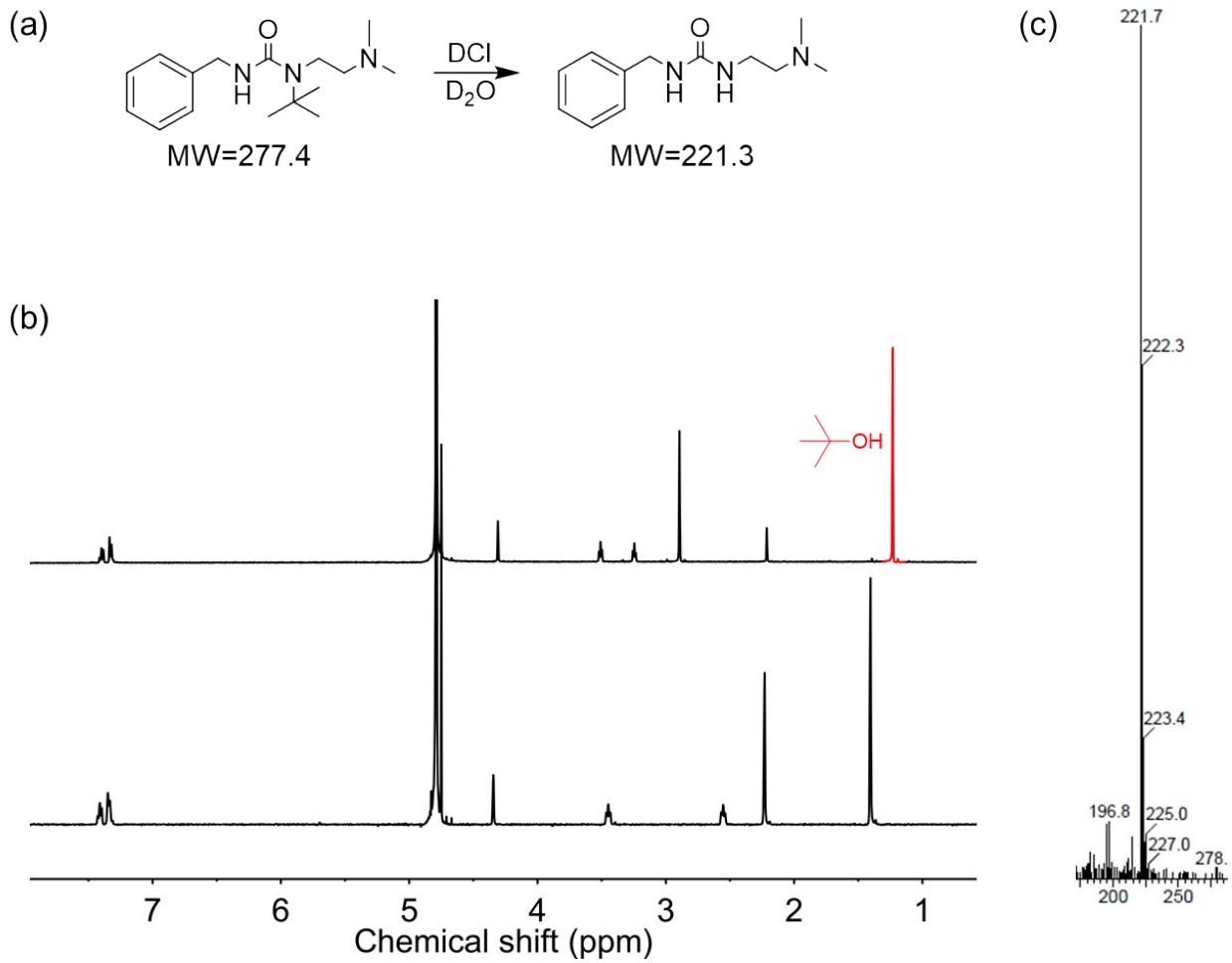


Figure S17: De-*tert*-butylation of **1** in D_2O with DCl added as the acid (5 µL in 600 µL D_2O)

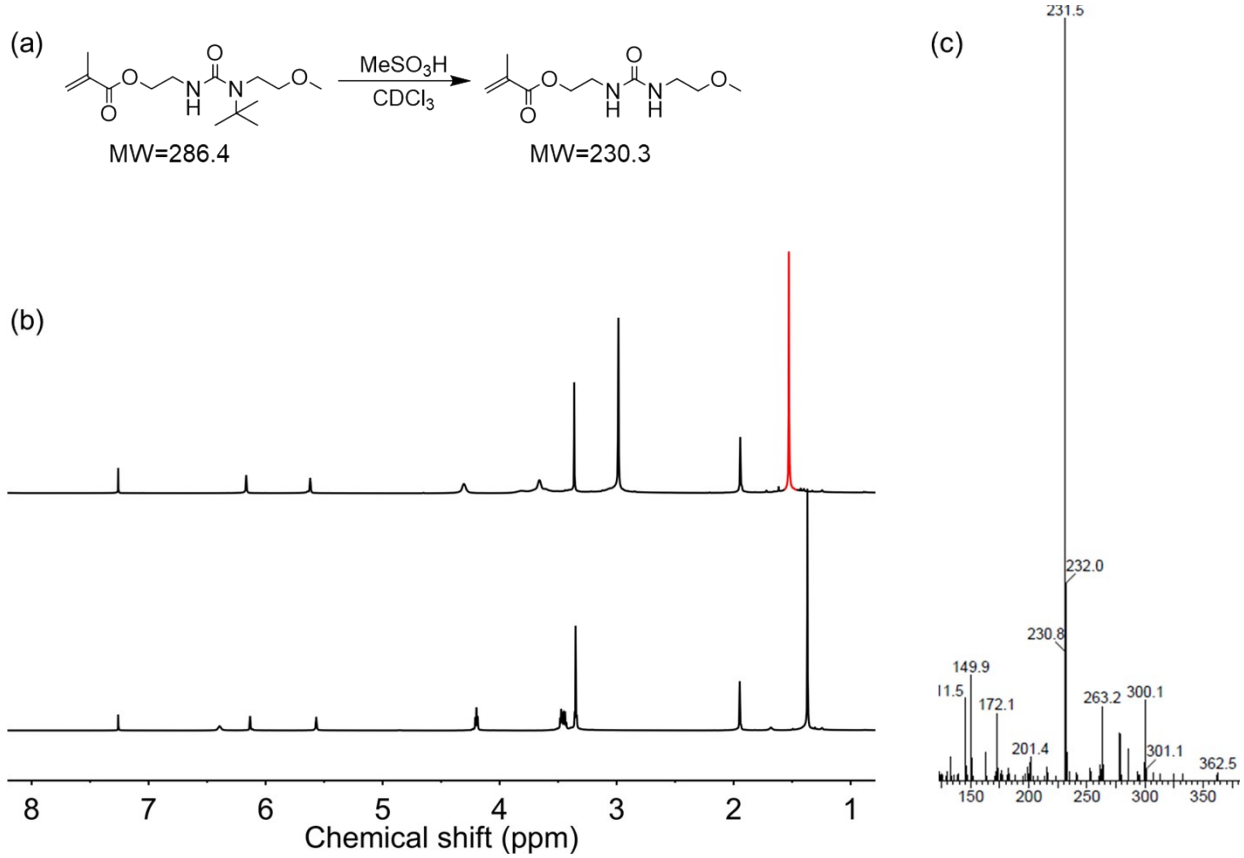


Figure S18: De-*tert*-butylation of **1f** in $CDCl_3$ with $MeSO_3H$ added as the acid (5 µL in 600 µL $CDCl_3$)

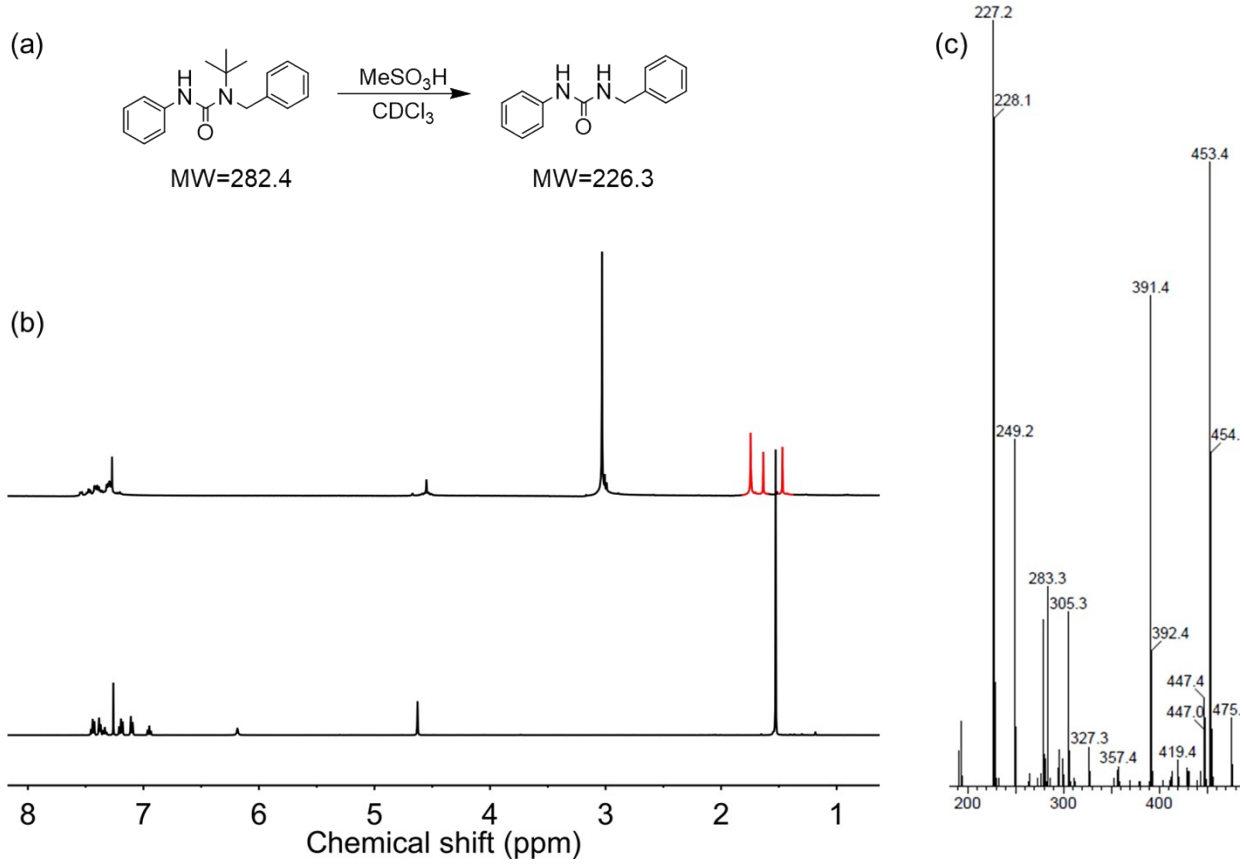


Figure S19: De-*tert*-butylation of **1h** in $CDCl_3$ with $MeSO_3H$ added as the acid (5 µL in 600 µL $CDCl_3$)

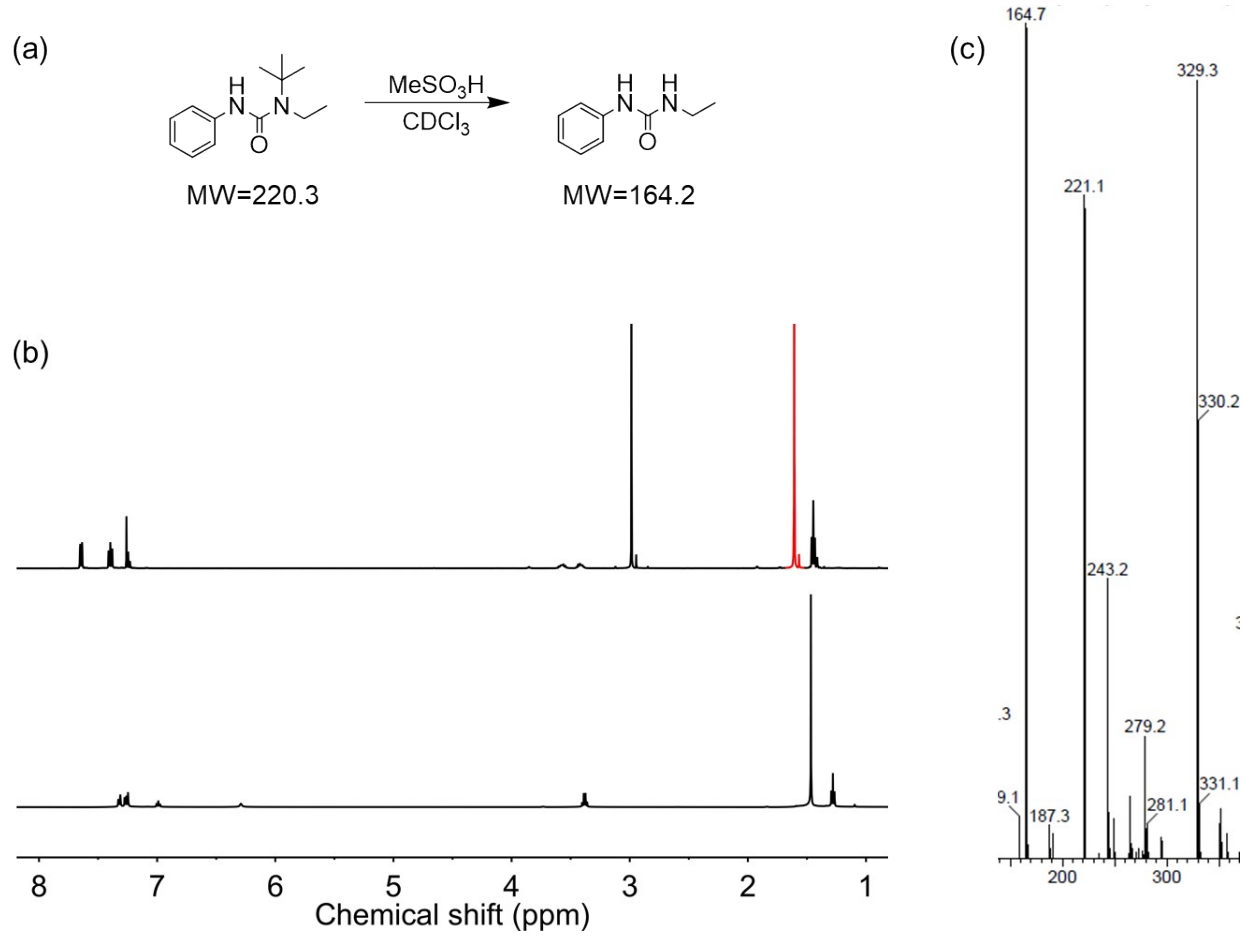


Figure S20: De-*tert*-butylation of **1i** in $CDCl_3$ with $MeSO_3H$ added as the acid (5 µL in 600 µL $CDCl_3$)

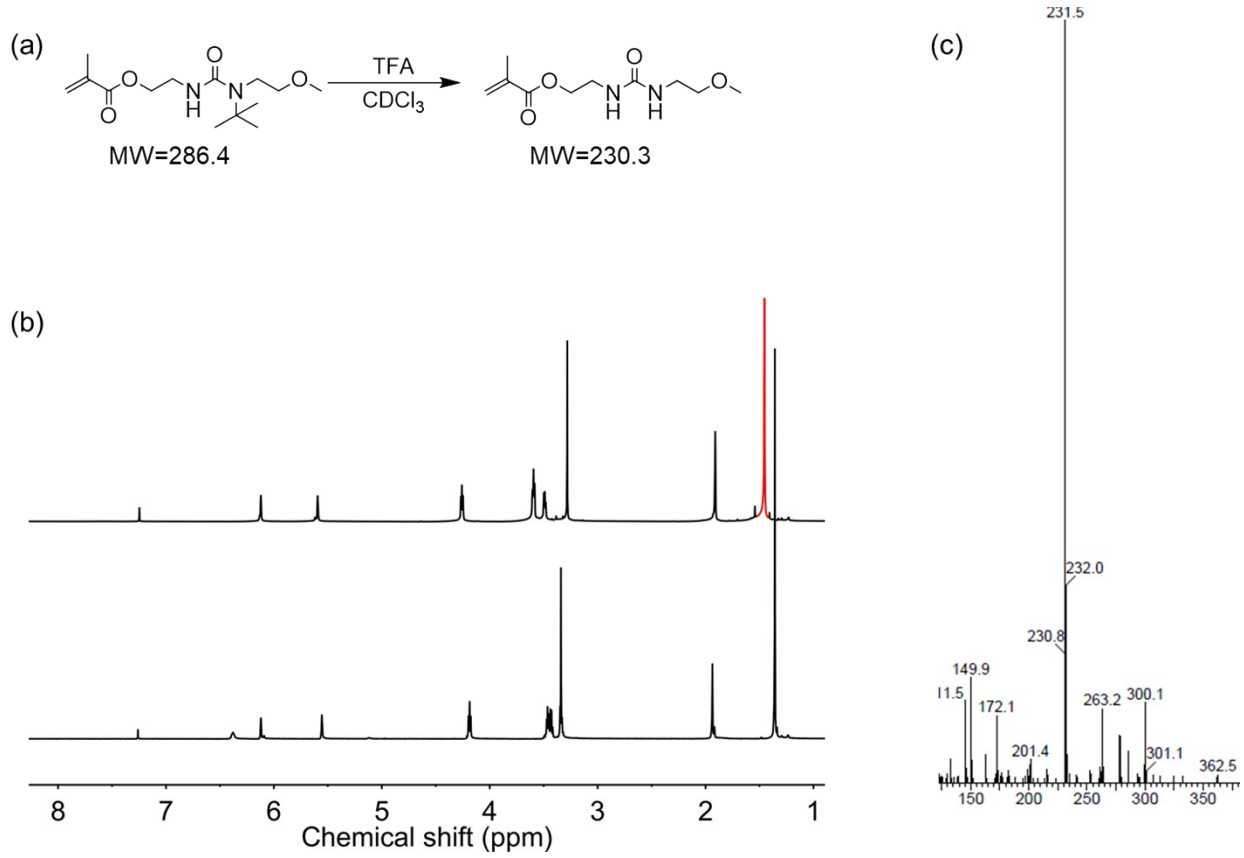


Figure S21: De-*tert*-butylation of **1f** in $CDCl_3$ with TFA added as the acid (50 v%)

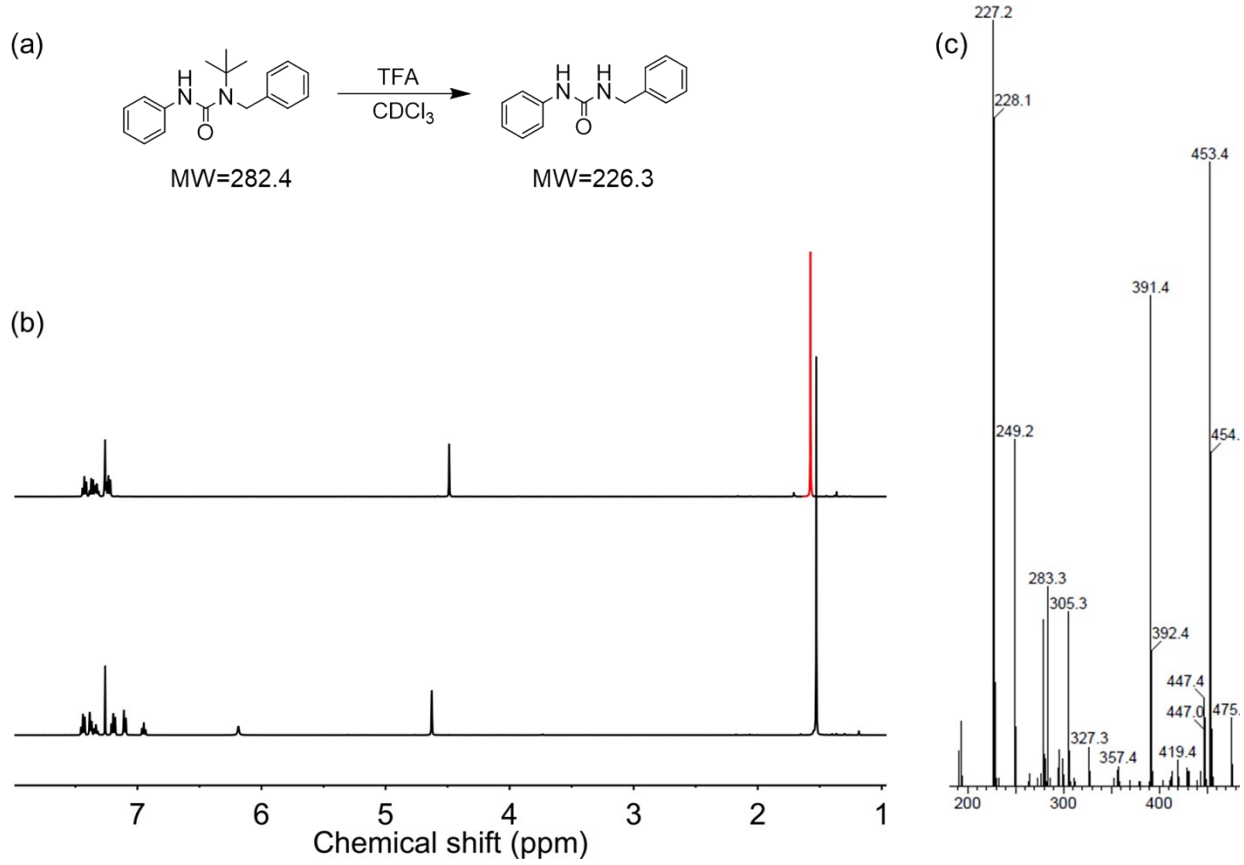


Figure S22: De-*tert*-butylation of **1h** in $CDCl_3$ with TFA added as the acid (50 v%)

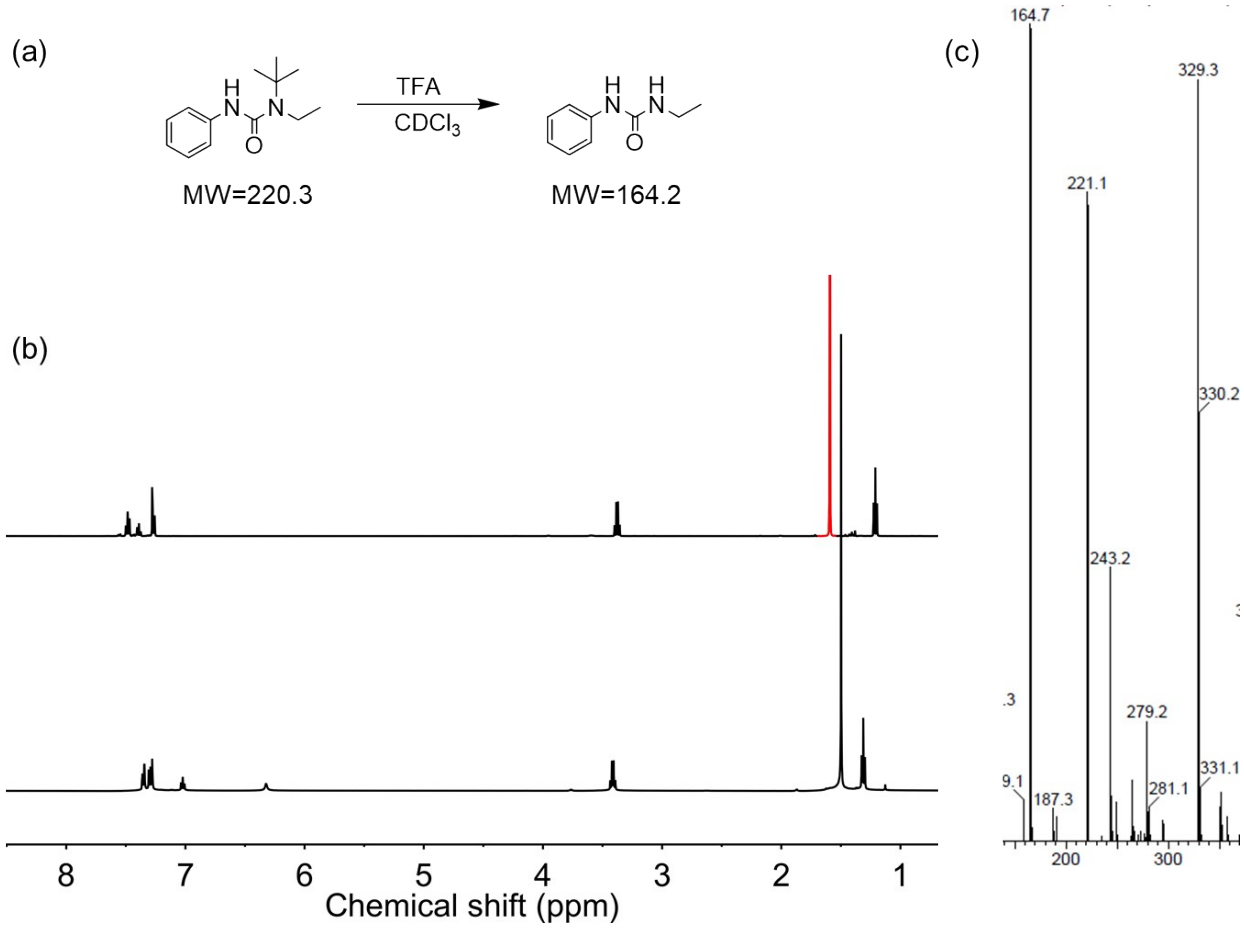


Figure S23: De-*tert*-butylation of **1i** in $CDCl_3$ with TFA added as the acid (50 v%)

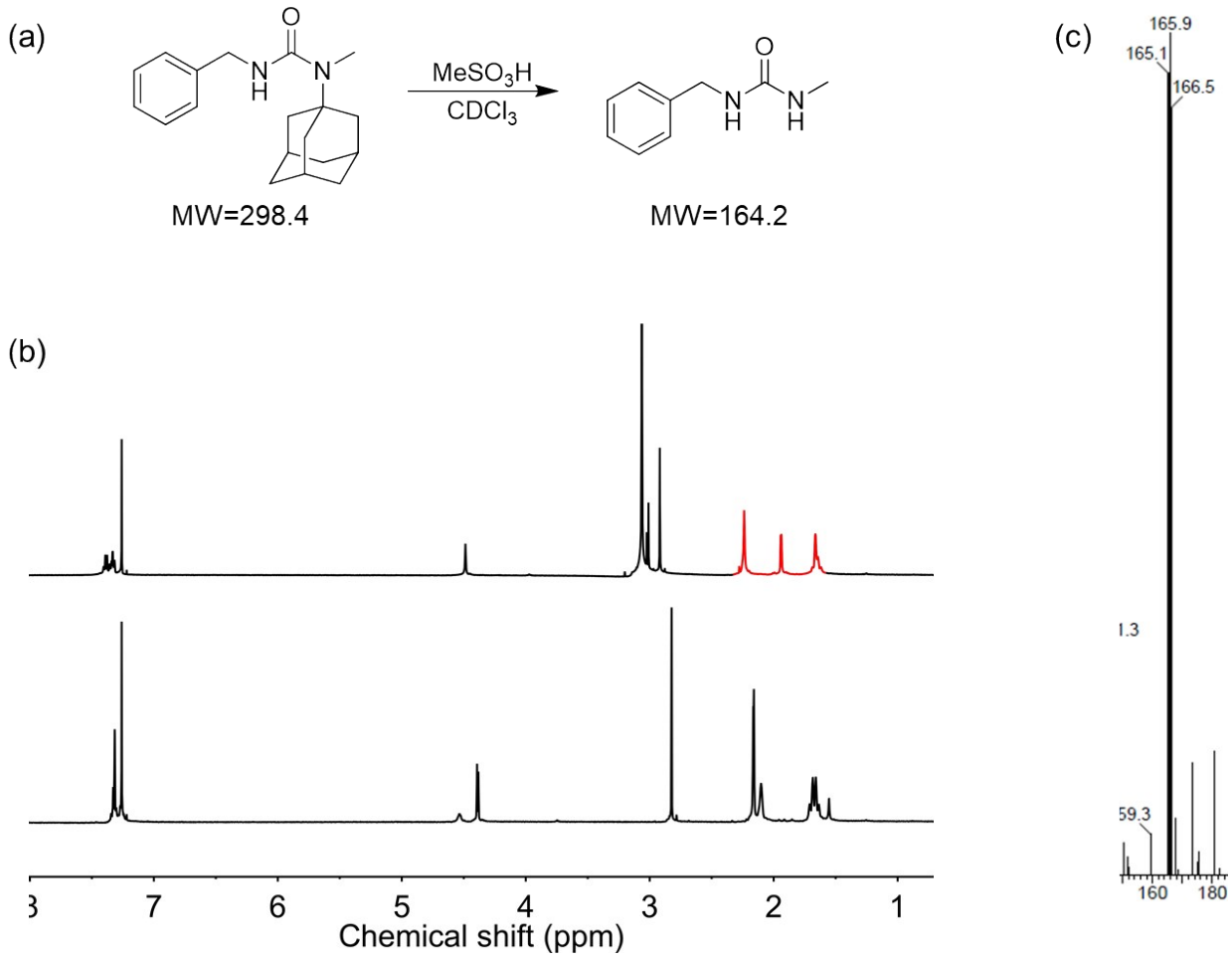


Figure S24: De-*tert*-butylation of **4a** in $CDCl_3$ with $MeSO_3H$ added as the acid (5 µL in 600 µL $CDCl_3$)

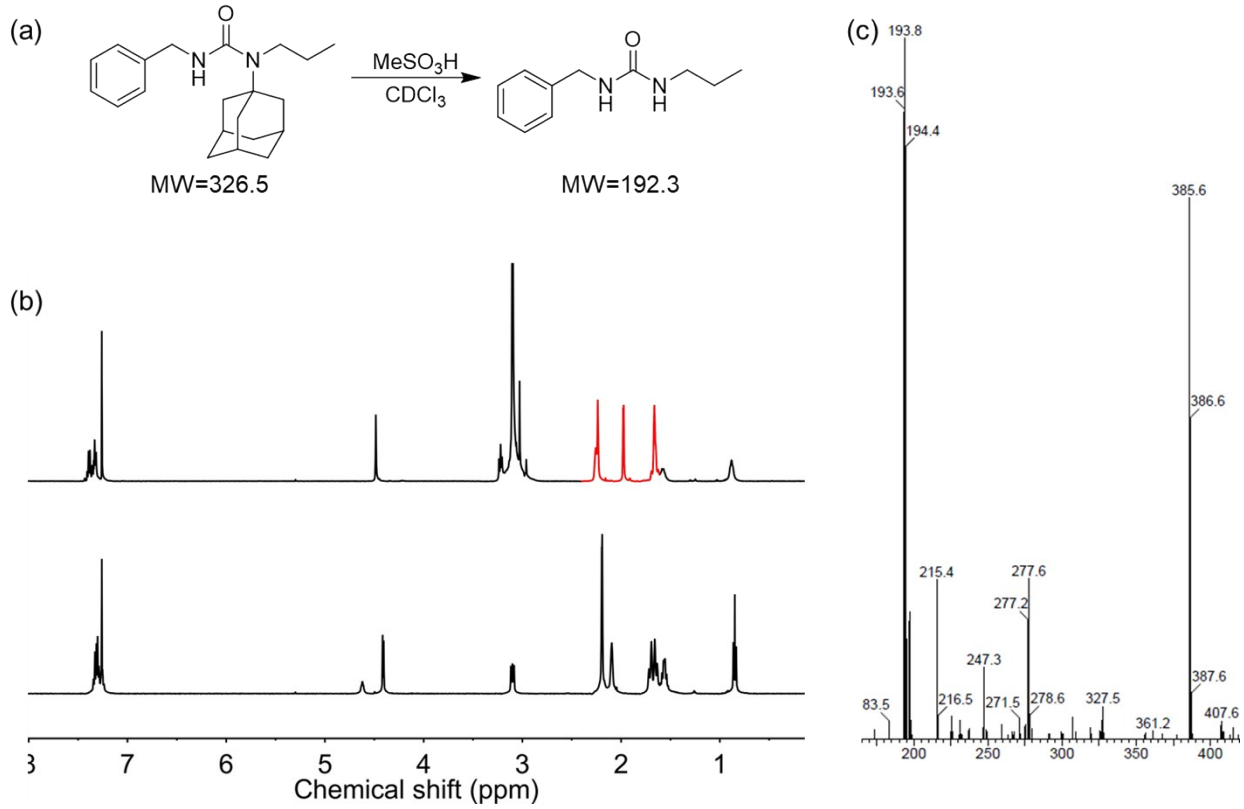


Figure S25: De-*tert*-butylation of **4b** in $CDCl_3$ with $MeSO_3H$ added as the acid (5 µL in 600 µL $CDCl_3$)

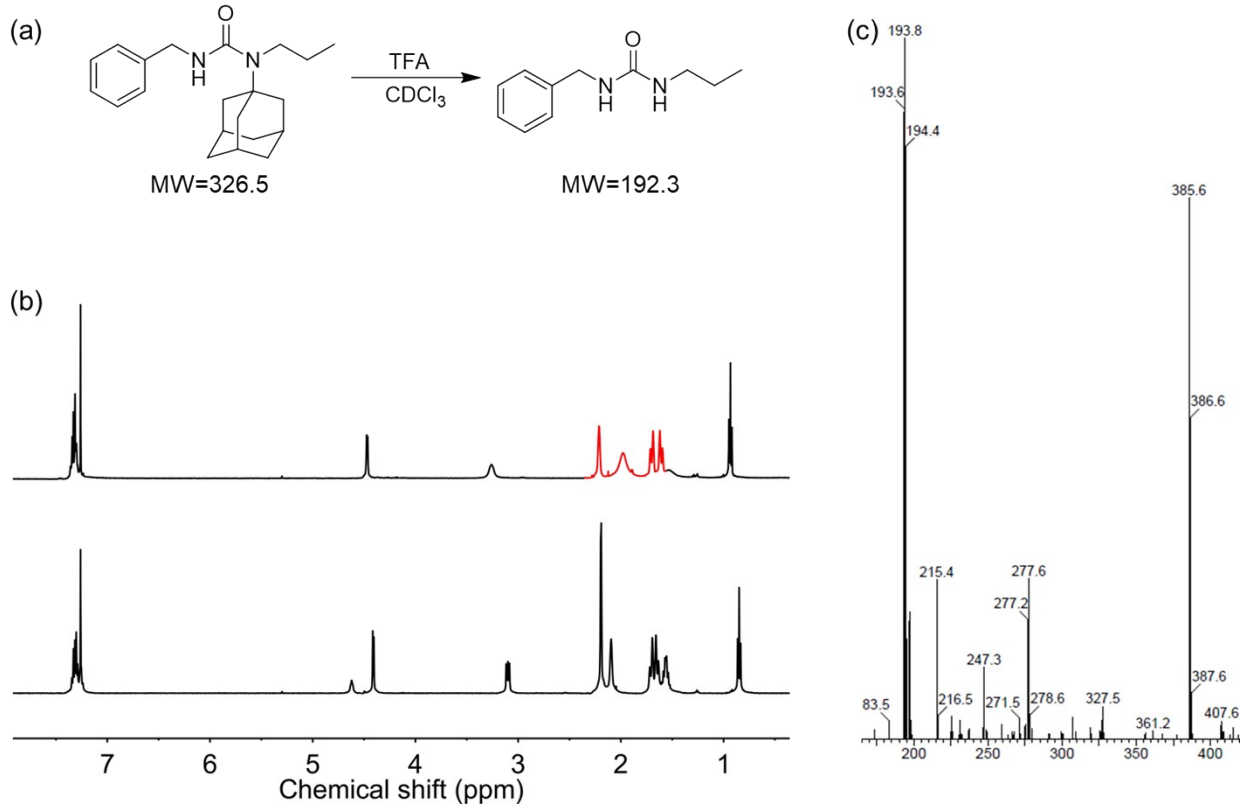


Figure S26: De-*tert*-butylation of **4b** in $CDCl_3$ with TFA added as the acid (50 v%)

2.2.3. The pH dependence and reaction kinetics of the de-*tert*-butylation reaction

Preparation of citrate buffer:

pH	Volume of 0.1 M-citric acid (mL)	Volume of 0.1 M-trisodium citrate (mL)
3.0	82	18
4.0	59	41
5.0	35	65
6.0	11.5	88.5

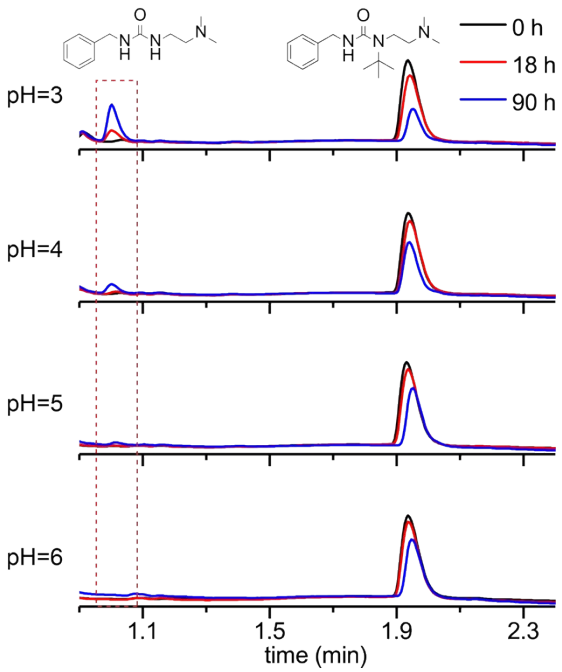


Figure S27: The pH dependence of the model reaction. At higher pH, only hydrolysis product was observed. The de-*tert*-butylated species only emerged when the pH went down to 3

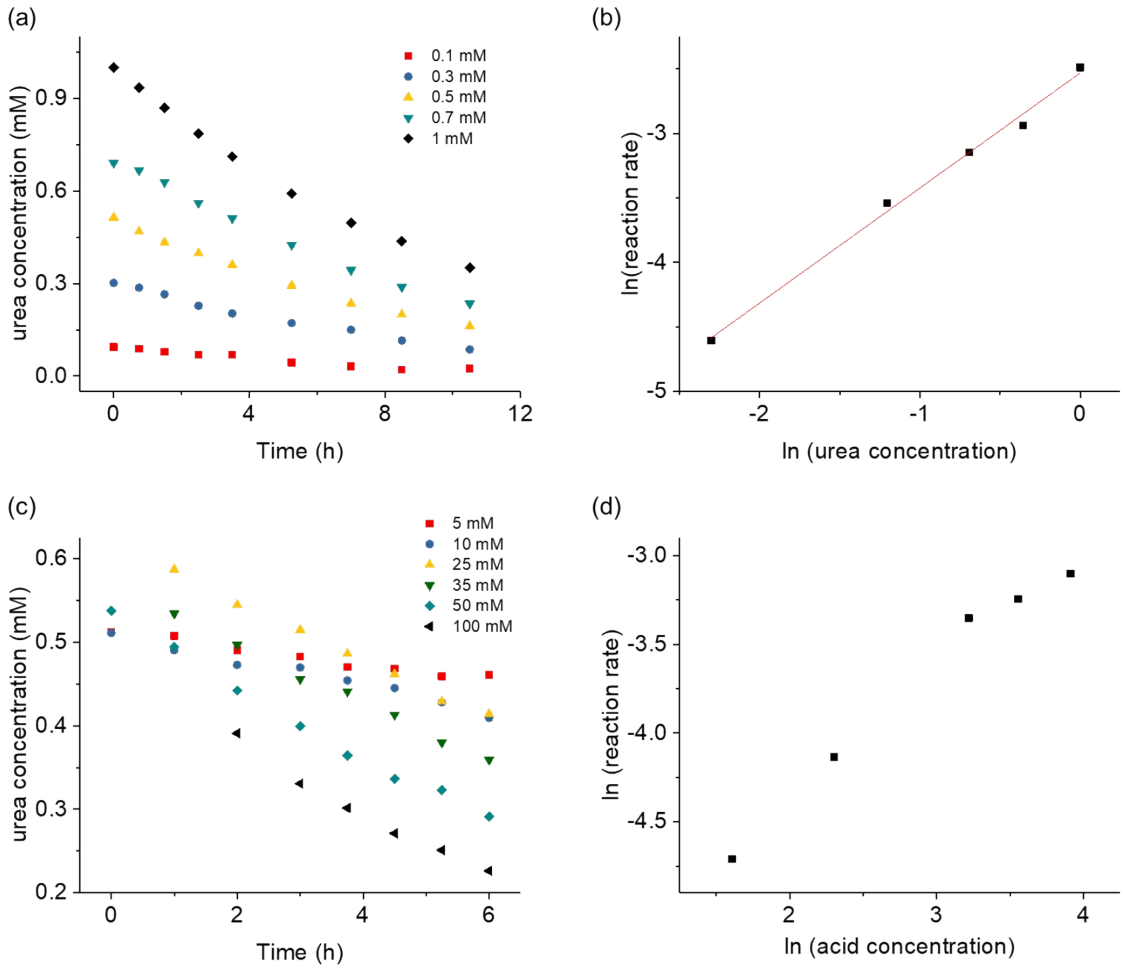
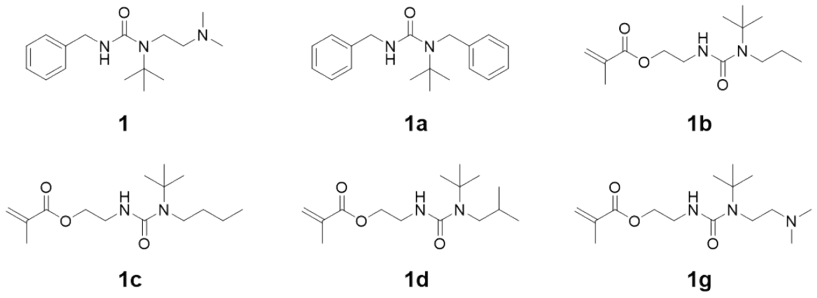


Figure S28: De-*tert*-butylation kinetics of model compound **1c**. The data was measured (water:ACN=1:1, R.T) with HPLC.



Compound	**1**	**1a**	**1b**	**1c**	**1d**	**1g**
$t_{1/2}$ (h)	7.3	15.8	6.2	6.7	1.3	8.1

Figure S29: Half-life of different hindered urea compounds. The data was measured under standard condition (0.5mM urea, 50mM acid, water:ACN=1:1, R.T) with HPLC.

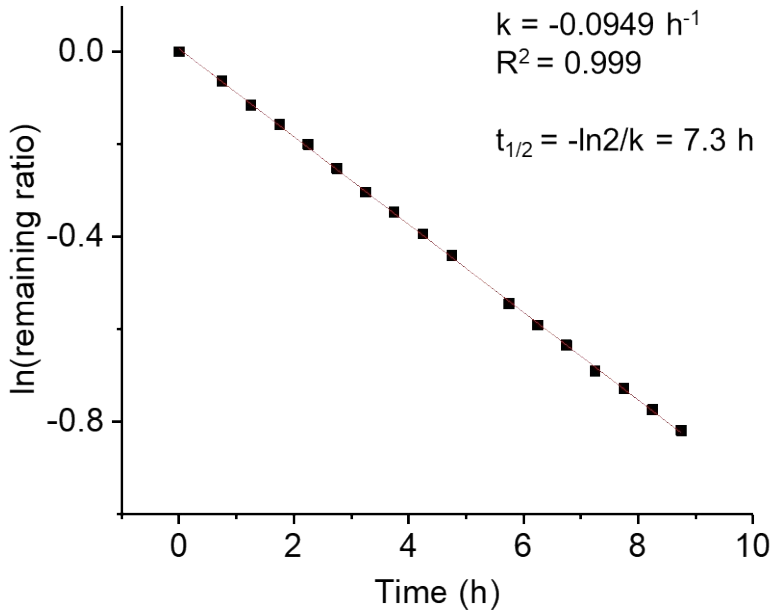


Figure S30: De-*tert*-butylation kinetics of compound **1**. The data was measured under standard condition (0.5mM urea, 50mM MeSO3H, water:ACN=1:1, R.T) with HPLC.

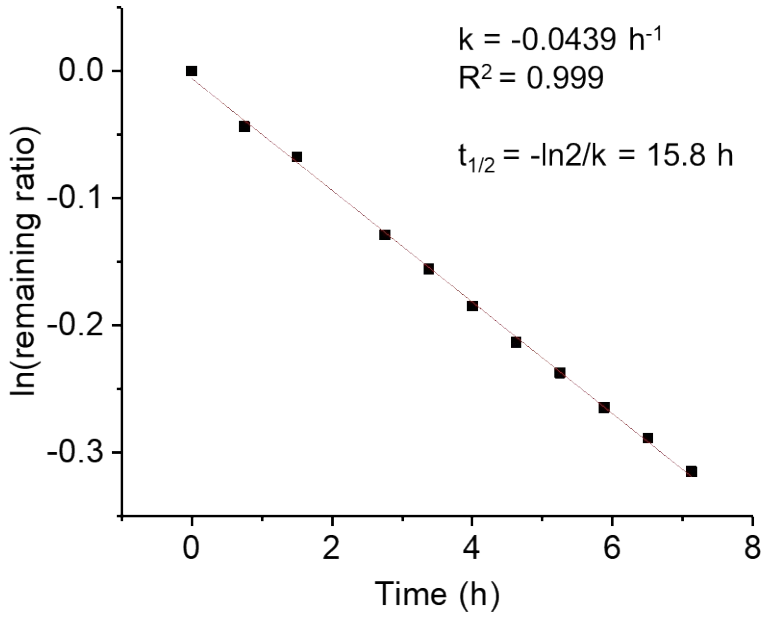


Figure S31: De-*tert*-butylation kinetics of compound **1a**. The data was measured under standard condition (0.5mM urea, 50mM MeSO3H, water:ACN=1:1, R.T) with HPLC.

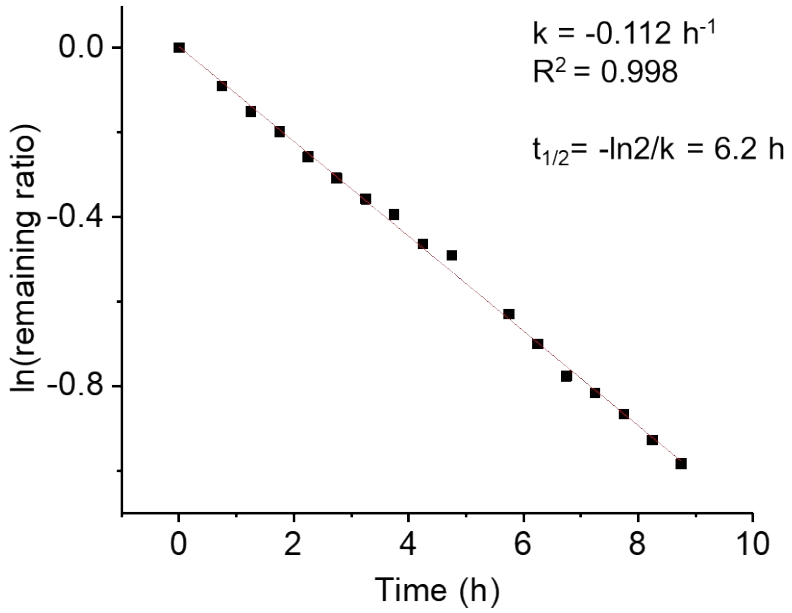


Figure S32: De-*tert*-butylation kinetics of compound **1b**. The data was measured under standard condition (0.5mM urea, 50mM MeSO3H, water:ACN=1:1, R.T) with HPLC.

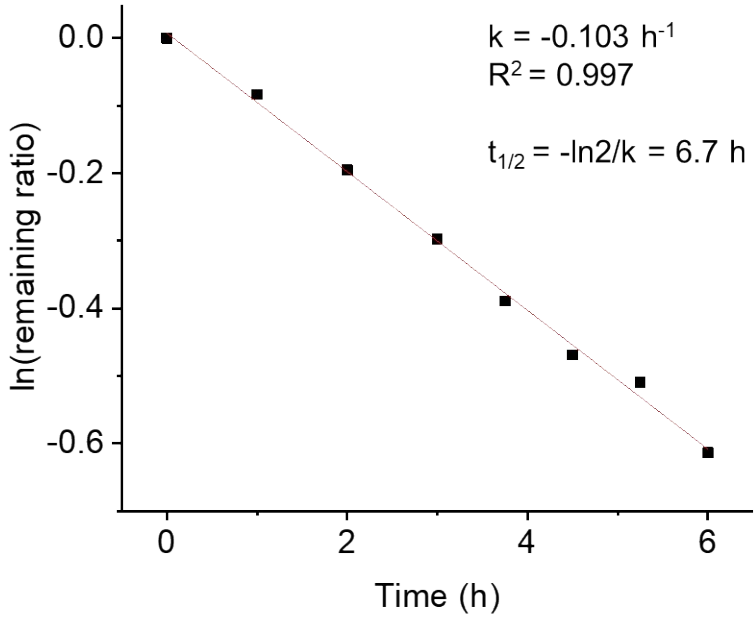


Figure S33: De-*tert*-butylation kinetics of compound **1c**. The data was measured under standard condition (0.5mM urea, 50mM MeSO3H, water:ACN=1:1, R.T) with HPLC.

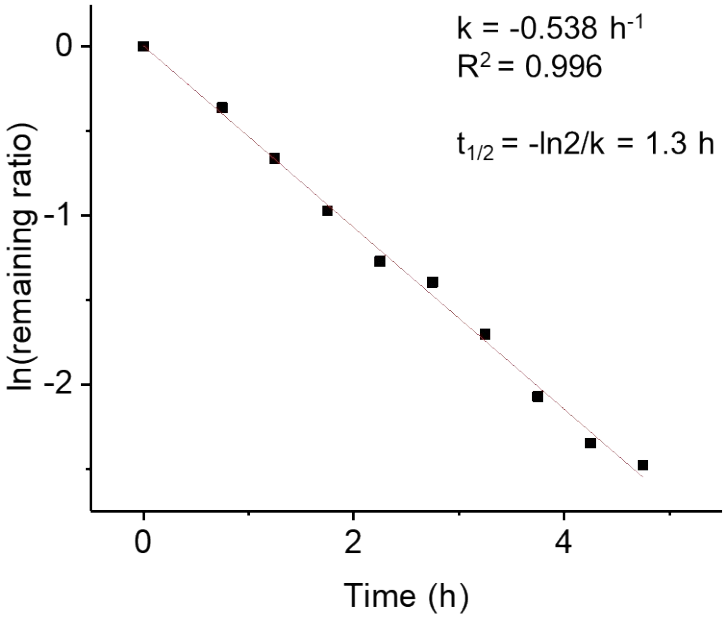


Figure S34: De-*tert*-butylation kinetics of compound **1d**. The data was measured under standard condition (0.5mM urea, 50mM MeSO3H, water:ACN=1:1, R.T) with HPLC.

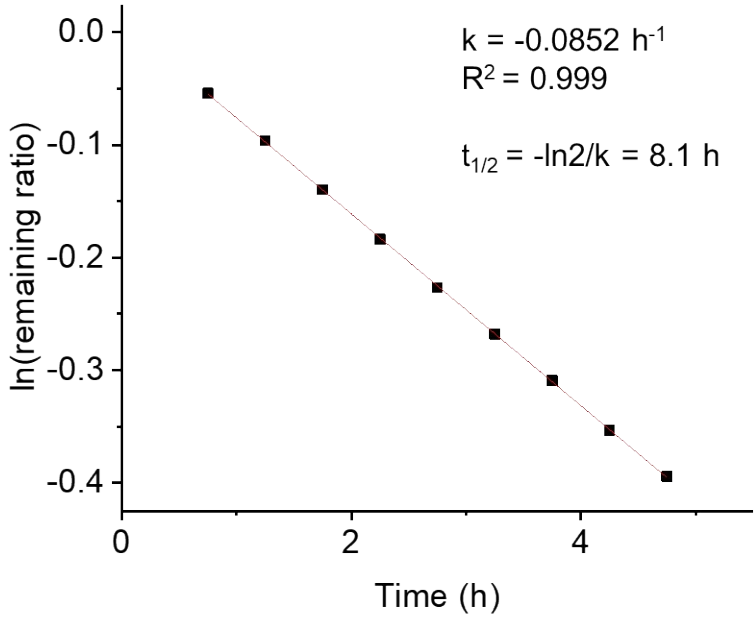


Figure S35: De-*tert*-butylation kinetics of compound **1g**. The data was measured under standard condition (0.5mM urea, 50mM MeSO3H, water:ACN=1:1, R.T) with HPLC.

2.2.4. The de-*tert*-butylation reaction in linear polymers

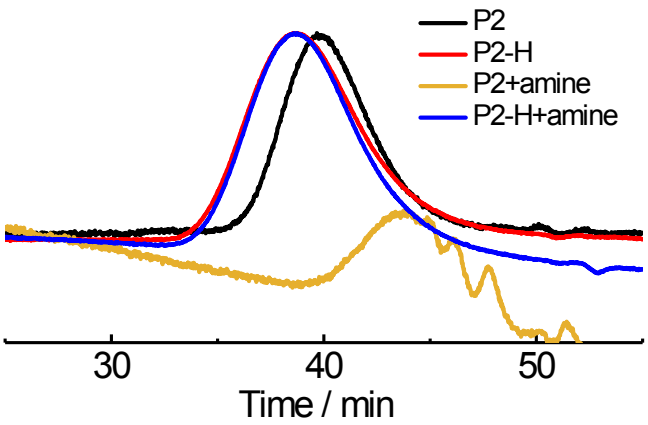


Figure S36: GPC data of the original polymer **P2**(black), the polymer after acid treatment **P2-H**(red), **P2** after incubation with amine at 60 °C for 4 hours(orange) and **P2-H** after incubation with amine at 60°C for 4 hours(blue).

From above figure, we can see after incubation with amine, **P2** showed a significant molecular weight decrease (orange curve), which was conceivable. However, for **P2-H**, the MW did not change at all after incubation with amine. The original **P2** (black curve) showed a smaller MW compared with **P2-H**. That's because aromatic hindered urea bonds are quite dynamic, so the original polymer **P2** will degrade during the process of GPC, thus the measured MW is smaller than the real MW of the polymer. But for **P2-H**, the polymer is stable, thus the actual MW is kept during the GPC process. This result showed the de-*tert*-butylation reaction was highly efficient and 100% complete.