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Effect of Backbone and End-group Regioisomerism on Thermomechanical Properties of Vanillin-based Polyurethane Networks

Adithya Rangamani,[a] and Christopher A. Alabi* [a]

[a]Robert Frederick Smith School of Chemical & Biomolecular Engineering, 120 Olin Hall, Cornell University, Ithaca, NY 14853, USA

Contents

Characterization:

NMR Spectroscopy: 1D NMR spectroscopy was conducted on a Bruker 500 MHz NMR spectrometer equipped with a cryoprobe. VT-NMR, 2D ROESY and 2D HSQC spectra was collected using a Varian INOVA 600 MHz spectrometer. 2D ROESY spectra were collected at 0 ms and 200 ms mixing times for each oligomer and exchange rate constants were calculated using EXSY CALC by Mestrelab research NMR solutions. The ^{1}H-^{13}C HSQC spectra for the ApAG macromer was a standard 2D HSQC and for the AmAG macromer it was a band selective 2D HSQC with an 8 ppm ^{13}C spectral width around the peaks of interest (50 ppm).

Liquid chromatography – mass spectroscopy: All LC-MS experiments were carried out on an Agilent 1100 Series LC/MSD equipped with a C4 LC column and a UV detector monitoring 210 nm, 230 nm, 260 nm and 360 nm wavelengths.

Flash chromatography: Purification of the SD-PUMs was carried out via column chromatography using a Teledyne CombiFlash Rf200i automated flash chromatography system using hexanes and ethyl acetate.

Viscosity measurements using a Rheometer: A TA Instruments DHR3 Rheometer with a 40mm parallel plate geometry was heated to 45^{o}C using a Peltier Plate. The samples were loaded on to the plate and the samples were trimmed, to keep the liquid surface as close as possible to a cylindrical shape. The experiment was carried out using the Flow Peak Hold method at a constant shear rate of 0.1 s^{-1}.

Differential Scanning Calorimetry: A TA Instruments Q1000 Modulated Differential Scanning Calorimeter was used to obtain the glass transition temperature of the crosslinked networks. Samples were prepared in aluminum pans using 2-4 mg of the crosslinked networks and analyzed with 2 cooling cycles and 2 heating cycles (10 °C/min ramp rates). The cycles were (1) cool to -30°C and equilibrate for 5 minutes, (2) heat from -30°C to 150°C, (3) cool from 150°C to -30°C and equilibrate for 5 minutes, and (4) heat from -30 °C to 150 °C. Glass transition temperatures were obtained from the second heating cycle.

Dynamic Mechanical Analysis : A TA Instruments Q800 Dynamic Mechanical Analyzer instrument was used to obtain the storage and loss modulus (E' and E'') of the crosslinked networks. Thin strips of films of dimension 20mm x 5 mm x 1 mm were clamped down and sealed in a furnace and the experiment consists of a frequency sweep between 16 Hz (approx. 100 rad s^{-1}) and 0.02 Hz (approx. 0.01 rad s^{-1}) at 150^{o}C. Temperature sweeps at a constant frequency (6.28 rad s^{-1}) were started at 110 °C and the sample was cooled at a rate of 5 °C min^{-1} to 0°C or lower depending on the network's T_g.

Fluorescence and Excitation Spectra of Macromers: Using a Tecan plate reader, we obtained the fluorescence intensities of the oligomers at 0.1 mg/mL in acetonitrile and a 90:10 solution of milliQ water and acetonitrile.

Thiol-ene kinetics: To investigate the kinetics of the thiol-ene reaction or rate of crosslinking of the SD-PUM, a monothiol, 3-mercaptopropionic acid (3-MPA) was reacted with the SD-PUM under similar conditions to cross-linking (10 mol% excess thiol, 20 mol% DMPA, [SD-PUM]= 720

mM in acetonitrile). The conversion of each reaction was determined at various timepoints, t=0, 15, 30, 60, 120, 180, 300, 600, 900 and 1200 seconds by monitoring the disappearance of the methine peak of the allyl group centered 5.8 ppm with respect to unchanging oligomer peaks centered at 4.5 ppm via ^{1}H NMR spectroscopy.

Gel fraction analysis: All films were prepared according to the protocol in the curing of films section. After 60 minutes of irradiating with UV-light, each of the films were swelled with 5 mL of acetonitrile. After 48 hours of swell time, the acetonitrile mixture was removed, and the solvent was dried under vacuum and the mass of the residual oligomer and thiol mixture was obtained. The residual mass was subtracted from the total mass of all starting materials to determine the gel fraction gravimetrically.

Density Measurements for FFV: All films were cooled to -10 ^{o}C in the DMA furnace and the film dimensions were measured using vernier calipers. The mass was obtained using a weighing balance.

Materials and Methods:

Materials: All solvents were obtained from Fisher Scientific and used as received. The following reagents were also used as received: vanillin (99%, Alfa Aesar), isovanillin (98%, TCI), triethylamine (Aldrich), 4-nitrophenyl chloroformate (Oakwood), guaiacol (TCI), pentanol (TCI), 2,2-dimethyl-1-propanol (TCI), 2,2- dimethoxy-2-phenylacetophenone (DMPA, Aldrich), allylamine (Aldrich), 3-mercaptopropionic acid (3-MPA, Aldrich), trimethylolpropane tris(3-mercaptopropionate) (TCI), pentaerythritol tetrakis(3-mercaptopropionate) (TCI), chloroform-d (Cambridge Isotopes), dimethyl sulfoxide-d6 (Cambridge Isotopes).

Synthesis of Divanillin Carbonate: Vanillin (5 equiv) and triethylamine (1.5 equiv) were dissolved in of dichloromethane and cooled to 0 °C. Then, 4-nitrophenyl chloroformate (1.0 equiv) was dissolved in dichloromethane and added dropwise. The reaction was conducted for 16 hours. Finally, the reaction mixture was extracted twice with 1 M HCl and twice with saturated $NaHCO_3$ solution . The organic layer was dried over anhydrous Na_2SO4. The solvent was removed by rotary evaporation and the powder that was collected was triturated with diethyl ether. Divanillin carbonate was obtained as a white powder (84.6%, ^{1}H and ^{13}C NMR spectra shown in Supplementary Figure 18-19).

Synthesis of 3,4-Dimethoxy-N-allylbenzylamine (Figure 1, i): 3,4-Dimethoxybenzaldehyde (1 equiv) was dissolved in methanol followed by the addition of allylamine (2.5 equiv). The reaction was stirred at room temperature for 2-3 h then cooled using an ice bath. Sodium borohydride (0.6 equiv) was then added and the reaction was vented release hydrogen gas produced during the reduction. The reaction was stirred at room temperature for 1 h and quenched with water. The product was extracted from the aqueous layer with three times with dichloromethane. The organic layers were combined and dried over anhydrous Na_2SO_4 before the solvent was removed by rotary evaporation. The product was obtained as a clear liquid (88%, ^{1}H and ^{13}C NMR spectra shown in Supplementary Figure 20-21).

General Method for Synthesis of Ap or Am Carbamates (Figure 1, ii): 3,4-Dimethoxy-N-allylbenzylamine (1 equiv) and triethylamine (1.1 equiv) were dissolved in acetonitrile and the

reaction was heated to 50 °C. Divanillin carbonate (1.1 equiv, Ap carbamate) or 4-nitrophenyl-activated isovanillin (1.1 equiv, Am carbamate) was then added and the reaction was stirred for 6 h. Upon reaction completion, the acetonitrile was removed by rotary evaporation and the reaction mixture was redissolved in dichloromethane. Ammonium hydroxide (50 mL) was added to the solution to degrade any residual divanillin carbonate and the mixture was extracted three times with dichloromethane. The organic layer was combined and washed twice with HCl (1M), twice with saturated $NaHCO_3$ solution, and once with brine. The organic layer was dried over anhydrous Na_2SO_4 and the dichloromethane was removed by rotary evaporation. The product was obtained as a yellow oil (Ap carbamate ^1H NMR spectra shown in Supplementary Figure 30, Am carbamate ^1H NMR spectrum shown in Supplementary Figure 32).

General Method for Synthesis of ApA and AmA amines (Figure 1, i second reductive amination): Ap or Am carbamate (1 equiv) was dissolved in methanol and allylamine (2.5 equiv) was added. The reaction was stirred at room temperature for 2-3 hours and then cooled 0 °C before adding sodium borohydride (0.6 equiv). The reaction was vented during this step to prevent buildup of hydrogen gas and stirred for 1 h at room temperature. Upon completion, the reaction was quenched with water and the product was extracted three times from the aqueous layer with dichloromethane. The organic layers were collected and dried over anhydrous Na_2SO_4 before the dichloromethane was removed by a rotary evaporation. The ApA and AmA amines were obtained as yellow oils (ApA amine ^1H NMR spectra shown in Supplementary Figure 31, AmA amine ^1H NMR spectrum shown in Supplementary Figure 33).

General Method for Macromer Capping Step: ApA or AmA amine (1.1 equiv) and triethylamine (1.1 equiv) were dissolved in acetonitrile and 4-nitrophenyl-activated carbonate (1 equiv, end groups: guaiacol (G)-ApAG, AmA; neopentanol (N)- ApAN; pentanol (P)- ApAP). The reaction was conducted for 6 hours at 50 °C. Upon completion, the acetonitrile was removed and the reaction mixture was redissolved in dichloromethane. Ammonium hydroxide (50 mL) was added to degrade any excess carbonate and the product was extracted three times with dichloromethane. The combined organic layers were then washed with twice with 1 M and three times with a saturated $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 before the dichloromethane was removed by rotary evaporation. Finally, the product was loaded onto silica gel and further purified using Flash chromatography with a gradient of ethyl acetate in hexanes to obtain the capped macromer. The product was characterized using NMR spectroscopy and LCMS (Supplementary Figures 1-8).

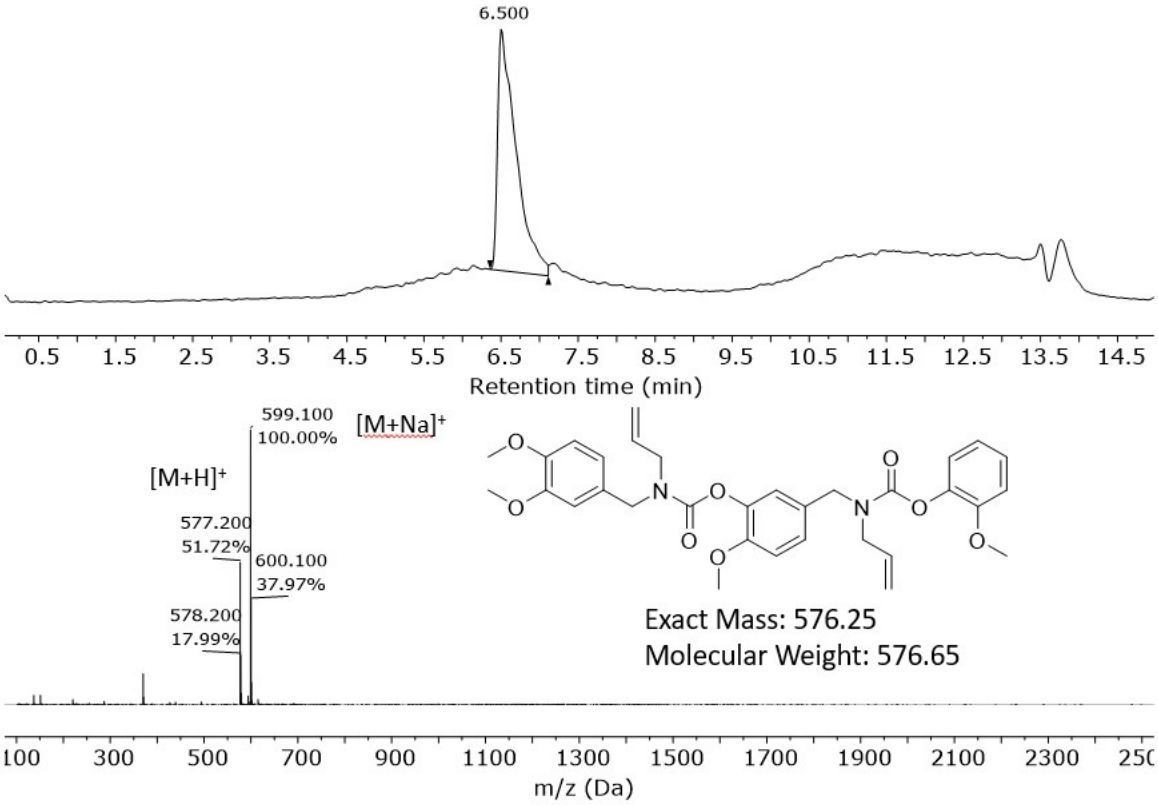
Synthesis of 4-Nitrophenyl-Activated Guaiacol Capping Group: Guaiacol (1 equiv) and triethylamine (1.5 equiv) were dissolved in dichloromethane and the reaction mixture was cooled to 0 °C. 4-Nitrophenyl chloroformate (1.0 equiv), dissolved in dichloromethane, was then added dropwise. The reaction was stirred at room temperature for 6 hours. Finally, the reaction mixture was purified by extraction twice with 1 M HCl and twice with a saturated $NaHCO_3$ solution. The organic layer was collected and dried over anhydrous Na_2SO_4 before the dichloromethane was removed by rotary evaporation. The resulting powder was then triturated with diethyl ether. 4-Nitrophenyl-activated guaiacol was obtained as a white powder (93%, ^1H and ^{13}C NMR spectra shown in Supplementary Figure 22-23).

Synthesis of 4-Nitrophenyl-Activated Pentanol Capping Group: Pentanol (1 equiv) and triethylamine (1.5 equiv) were dissolved in dichloromethane and the reaction mixture was cooled to 0 °C. 4-Nitrophenyl chloroformate (1.0 equiv), dissolved in dichloromethane, was then added dropwise. The reaction was stirred at room temperature for 6 hours. Finally, the reaction mixture was purified by extraction twice with 1 M HCl and twice with a saturated $NaHCO_3$ solution. The organic layer was collected and dried over anhydrous Na_2SO_4 before the dichloromethane was removed by rotary evaporation. 4-Nitrophenyl-activated pentanol was obtained as an oil (78%, ^1H and ^{13}C NMR spectra shown in Supplementary Figure 24-25).

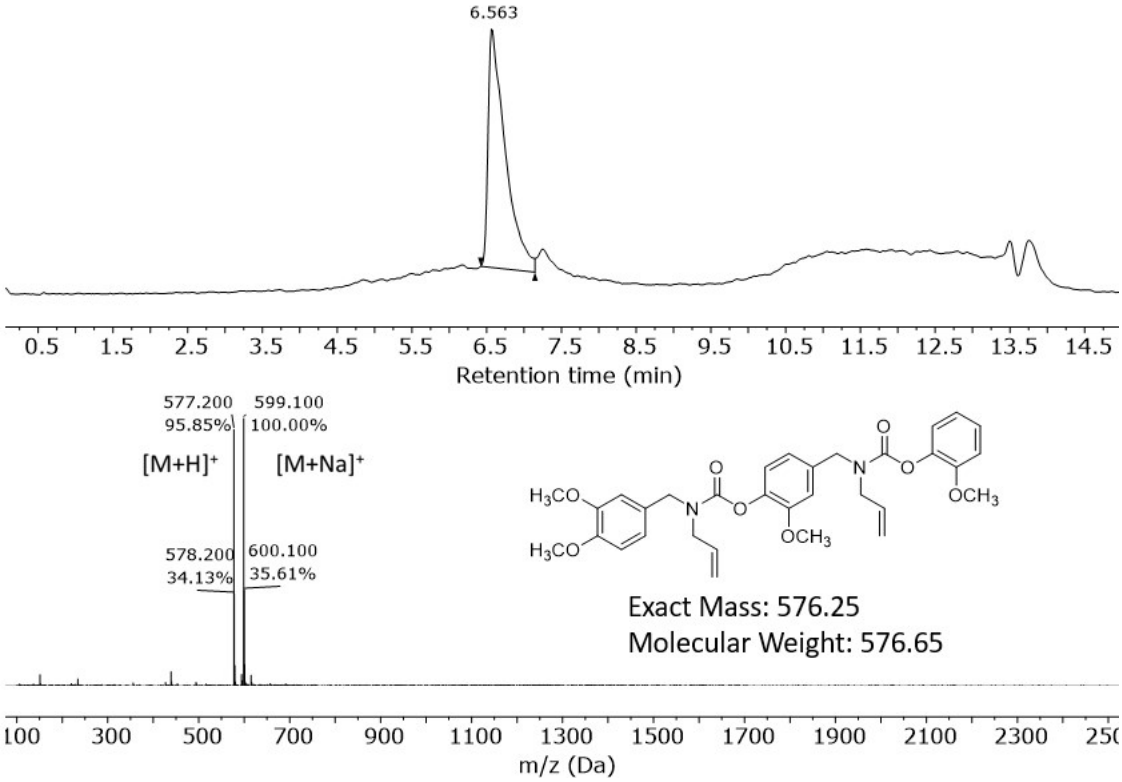
Synthesis of 4-Nitrophenyl-Activated Neopentanol Capping Group: 2,2-Dimethyl-1-propanol (1 equiv) and triethylamine (1.5 equiv) were dissolved in dichloromethane and the reaction mixture was cooled to 0 °C. 4-Nitrophenyl chloroformate (1.0 equiv), dissolved in dichloromethane, was then added dropwise. The reaction was stirred at room temperature for 6 hours. Finally, the reaction mixture was purified by extraction twice with 1 M HCl and twice with a saturated $NaHCO_3$ solution. The organic layer was collected and dried over anhydrous Na_2SO_4 before the dichloromethane was removed by rotary evaporation. 4-Nitrophenyl-activated neopentanol was obtained as an oil (91%, and %, ^1H and ^{13}C NMR spectra shown in Supplementary Figure 26-27).

Synthesis of 4-Nitrophenyl-Activated Isovanillin: Isovanillin (1 equiv) and triethylamine (1.5 equiv) were dissolved in dichloromethane and the reaction mixture was cooled to 0 °C. 4-Nitrophenyl chloroformate (1.0 equiv), dissolved in dichloromethane, was then added dropwise. The reaction was stirred at room temperature for 6 hours. Finally, the reaction mixture was purified by extraction twice with 1 M HCl and twice with a saturated $NaHCO_3$ solution. The organic layer was collected and dried over anhydrous Na_2SO_4 before the dichloromethane was removed by rotary evaporation. The resulting powder was then triturated with diethyl ether. 4-Nitrophenyl-activated isovanillin was obtained as a white powder (56%, ^1H and ^{13}C NMR spectra shown in Supplementary Figure 28-29).

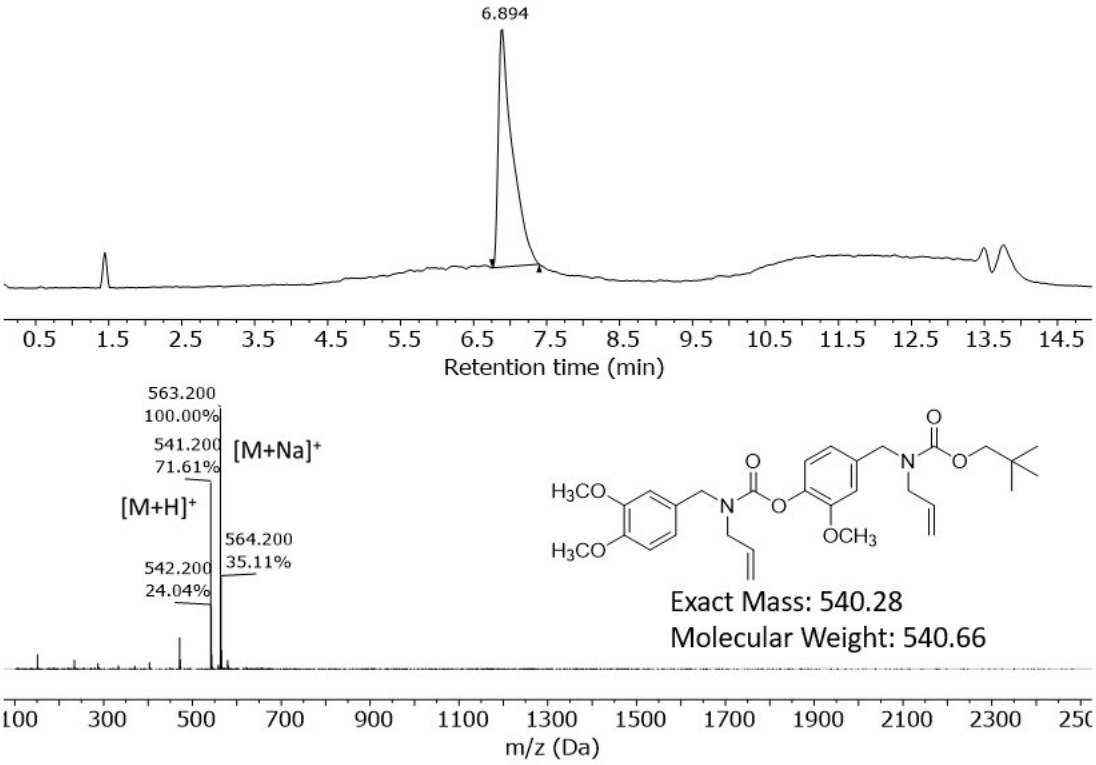
Curing of Films: Crosslinked networks were prepared by dissolving oligomer (191 mg, 0.331 mmol of Guaiacol capped oligomers or 179.1 mg, 0.331 mmol of the aliphatic capped oligomers), thiol (97.1 mg, 0.198 mmol of pentaerythritol tetra(3-mercaptopropionate) or 96.8 mg, 0.243 mmol of trimethylolpropane tris(3-mercaptopropionate)) and 2,2-dimethoxy-2-phenylacetophenone photoinitiator (33.9 mg, 0.132 mmol) in acetonitrile (300 µL). The solution was transferred to a PTFE mold with dimensions 20mm x 15mm x 1mm and then irradiated with UV light (365 nm, 20 mW/cm^2) for 60 minutes. After curing, each film was swelled in acetonitrile (5mL) for 48 h and then the films were removed from the solvent and dried in a vacuum oven at 105^o C for 12 h to ensure complete removal of the acetonitrile.



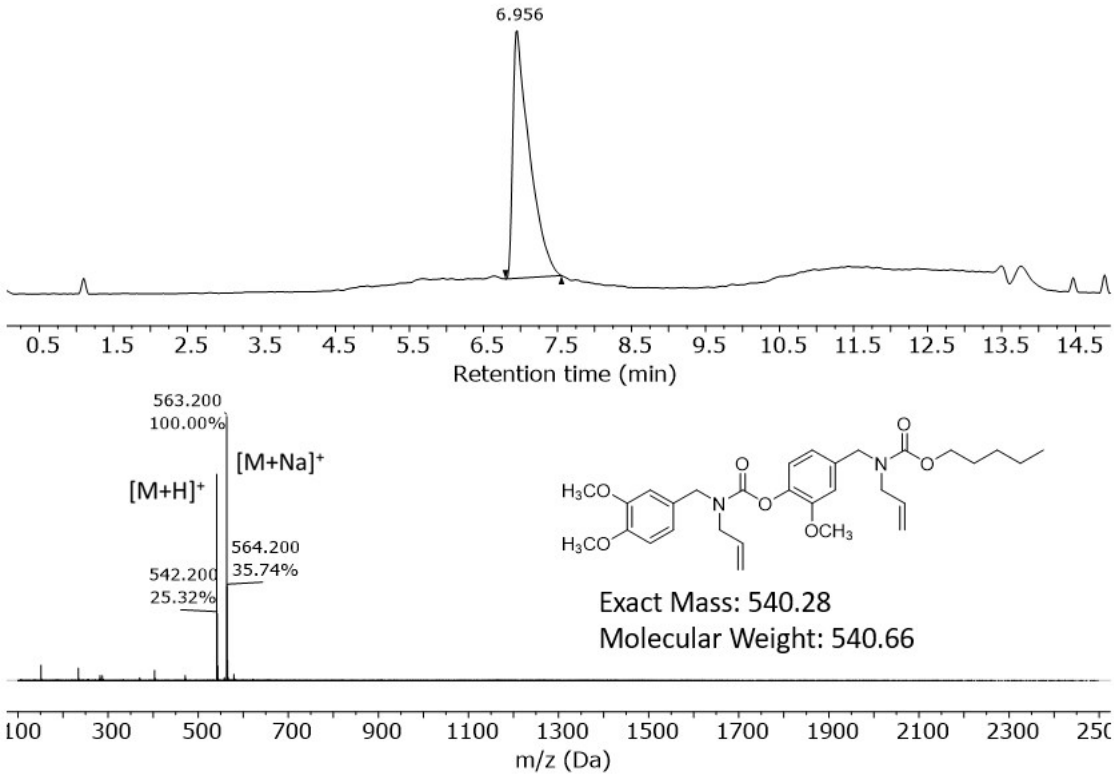
Supplementary Figure 1: LC-MS analysis of AmAG showing the TIC (top) and mass spectrum of the peak at 6.50 min (bottom).



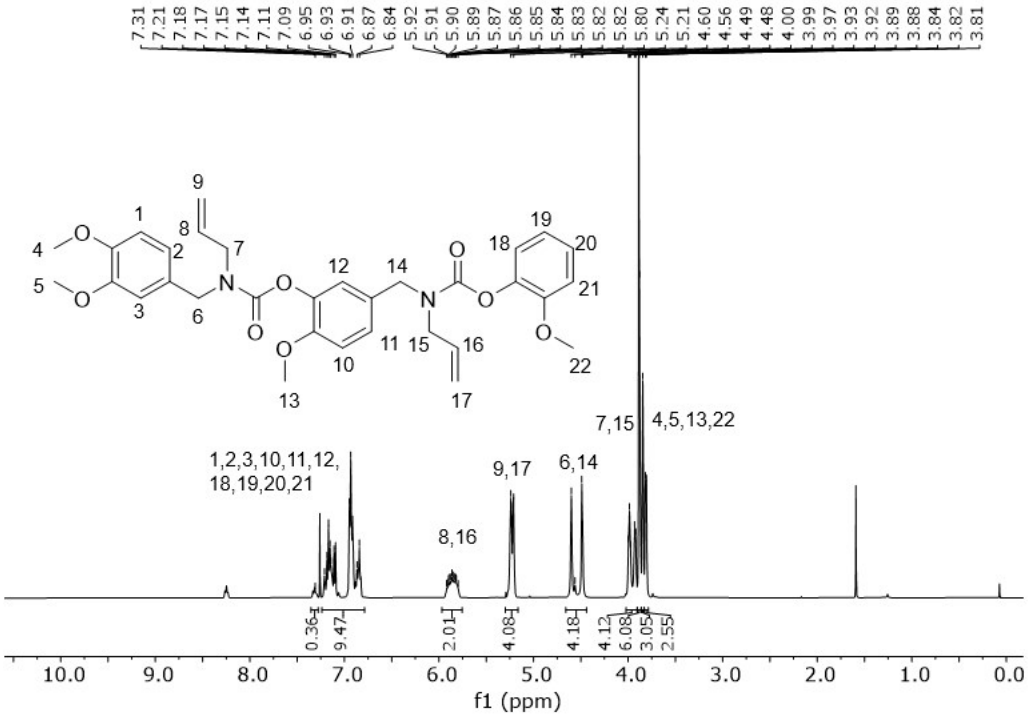
Supplementary Figure 2: LC-MS analysis of ApAG showing the TIC (top) and mass spectrum of the peak at 6.56 min (bottom).



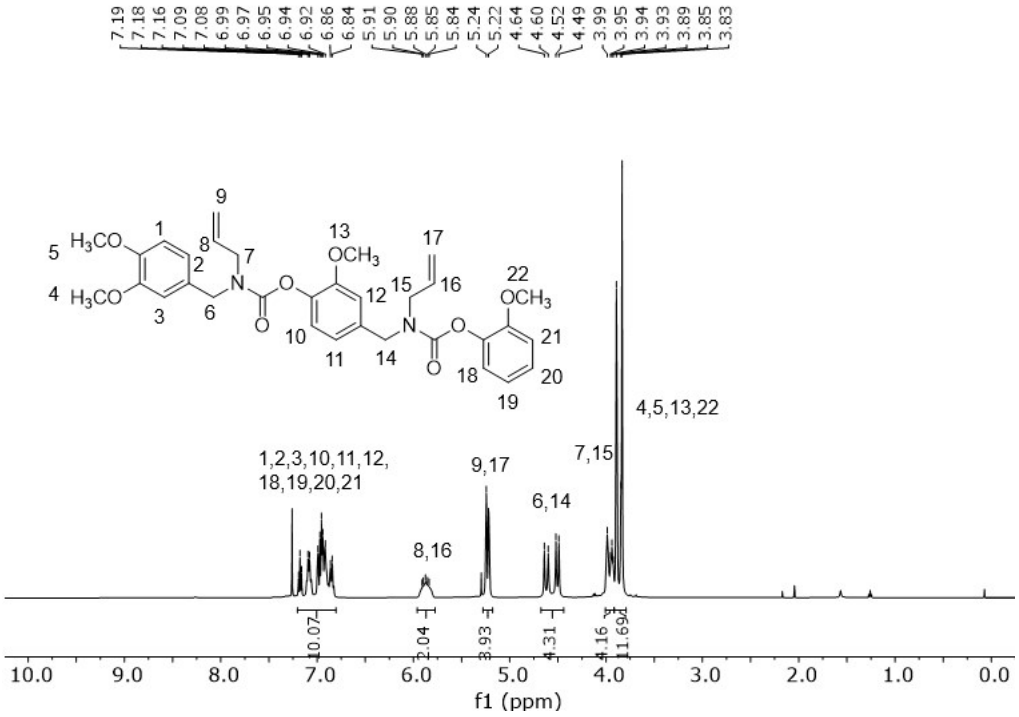
Supplementary Figure 3: LC-MS analysis of ApAN showing the TIC (top) and mass spectrum of the peak at 6.89 min (bottom).



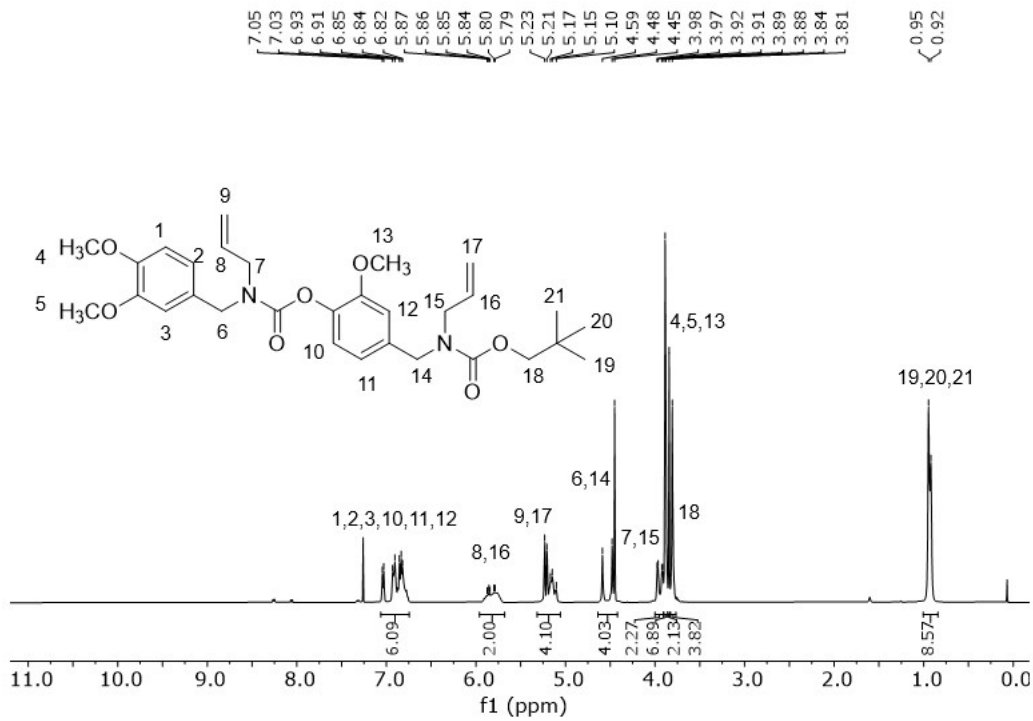
Supplementary Figure 4: LC-MS analysis of ApAP showing the TIC (top) and mass spectrum of the peak at 6.95 min (bottom).



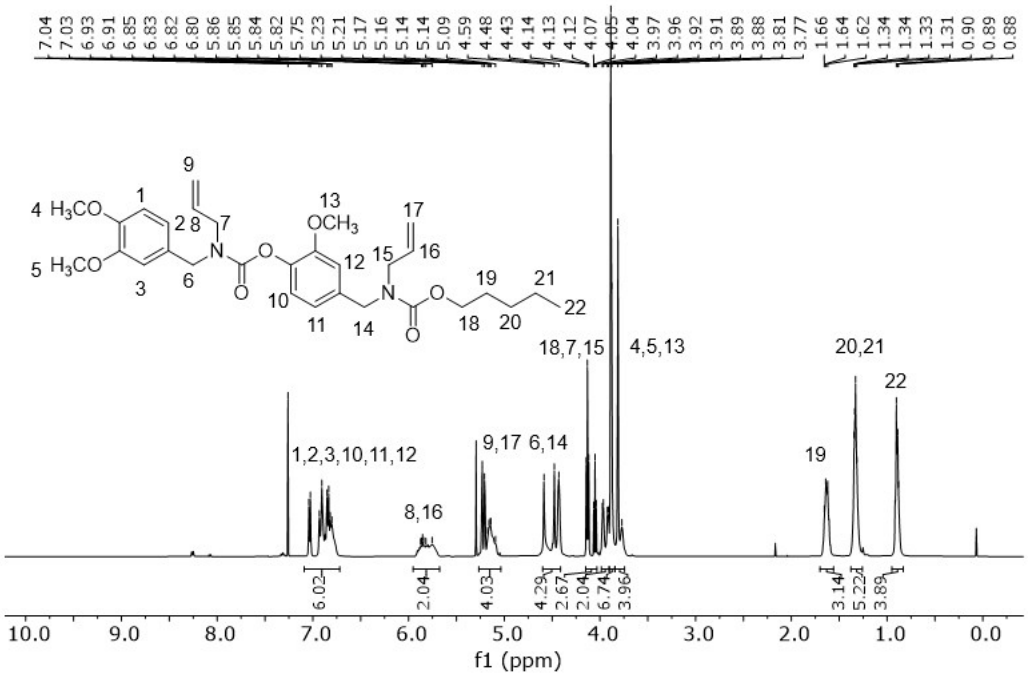
Supplementary Figure 5: ^{1}H NMR spectrum of AmAG in $CDCl_3$



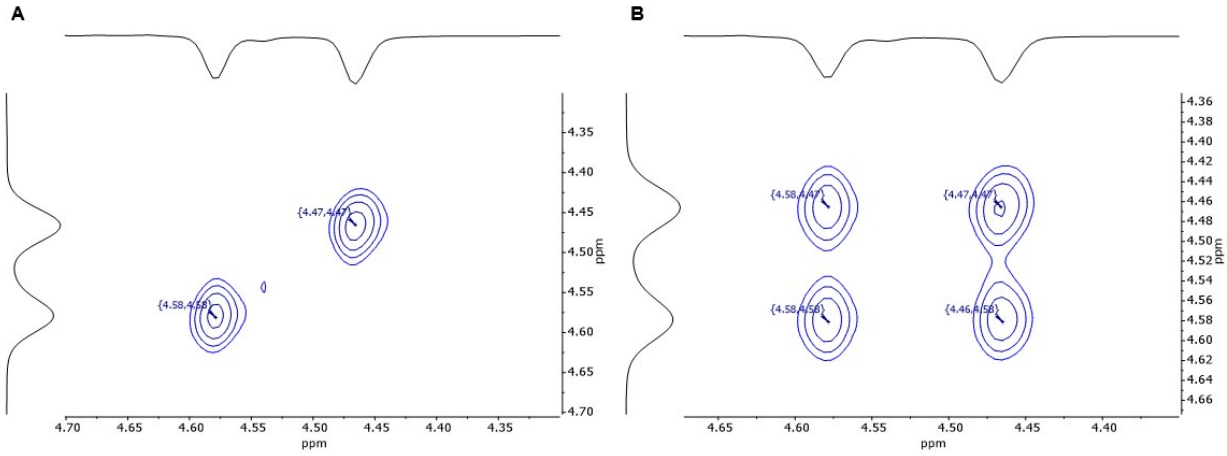
Supplementary Figure 6: ^{1}H NMR spectrum of ApAG in $CDCl_3$



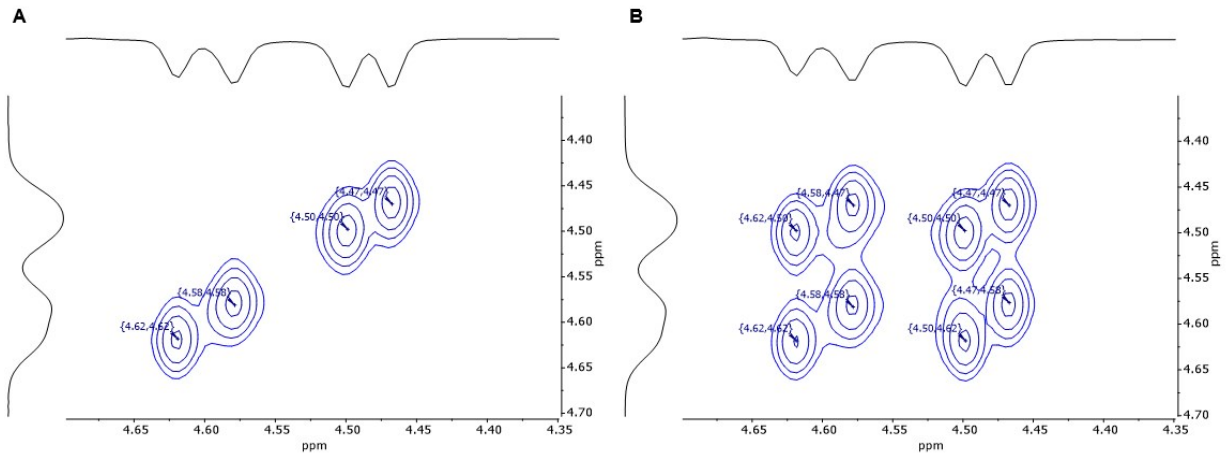
Supplementary Figure 7: ^{1}H NMR spectrum of ApAN in $CDCl_3$



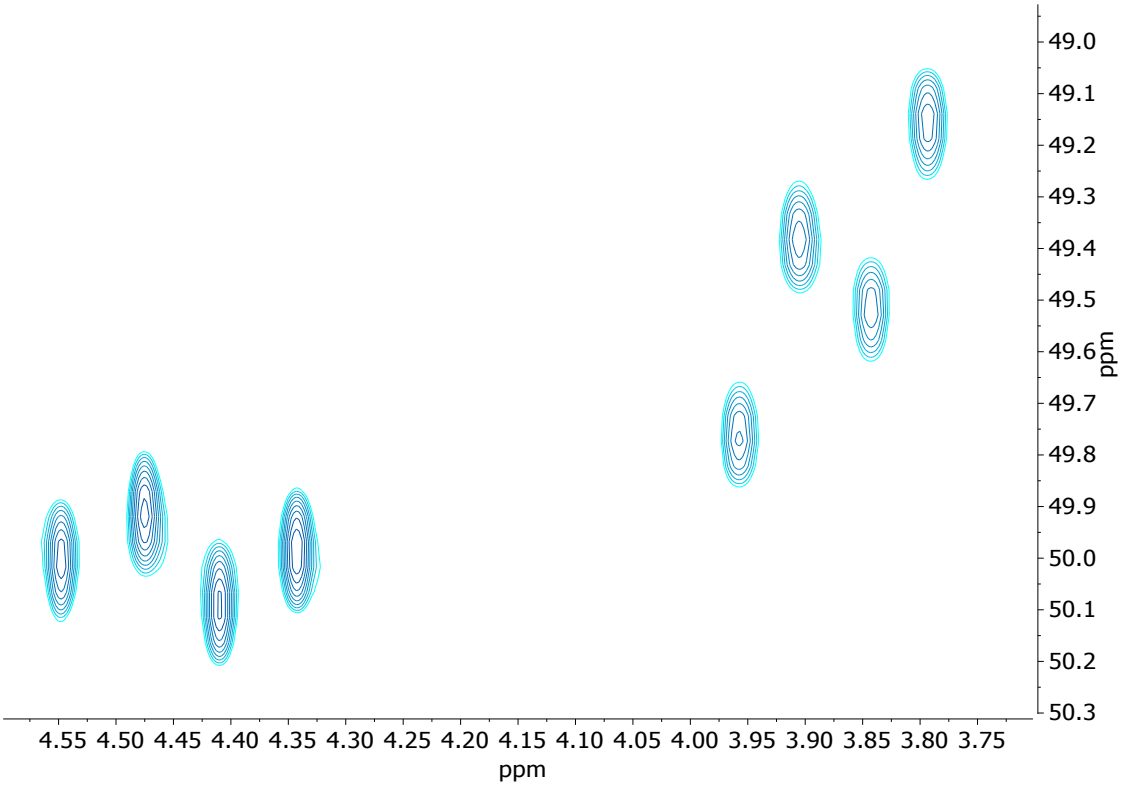
Supplementary Figure 8: ^{1}H NMR spectrum of ApAP in $CDCl_3$



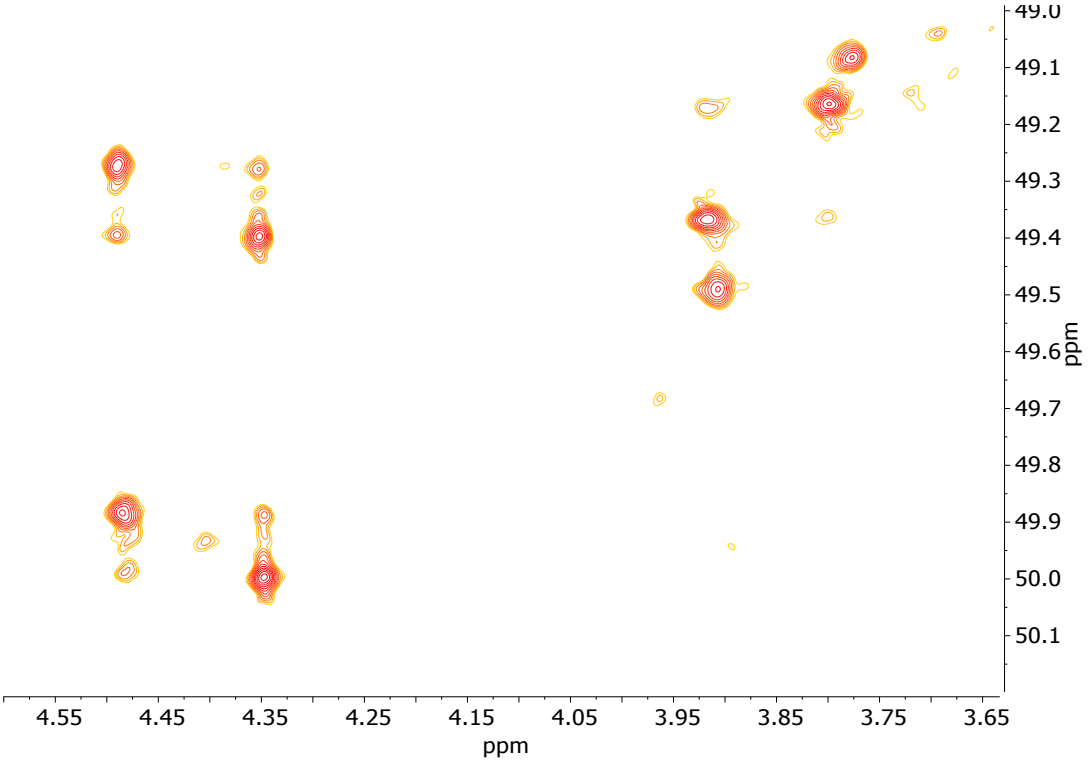
Supplementary Figure 9: ROESY 2D ^{1}H NMR Spectra of AmAG in $CDCl_3$ at (A) 0 ms and (B) 200 ms mixing times.



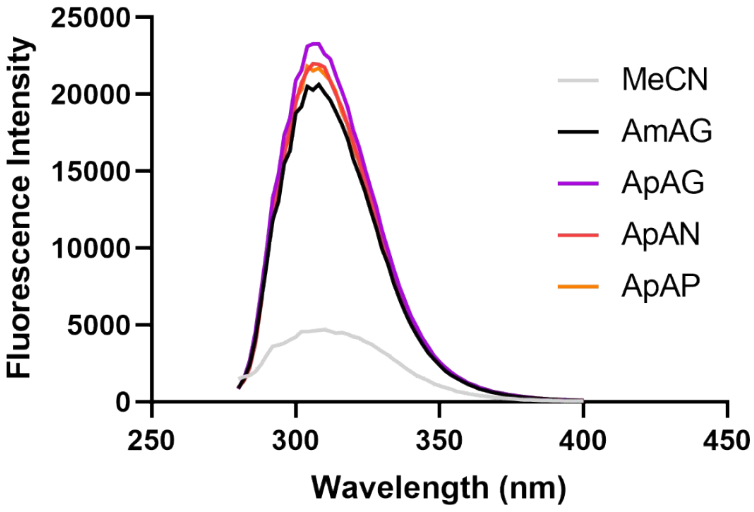
Supplementary Figure 10: ROESY 2D ^{1}H NMR Spectra of ApAG in $CDCl_3$ at (A) 0 ms and (B) 200 ms mixing times.



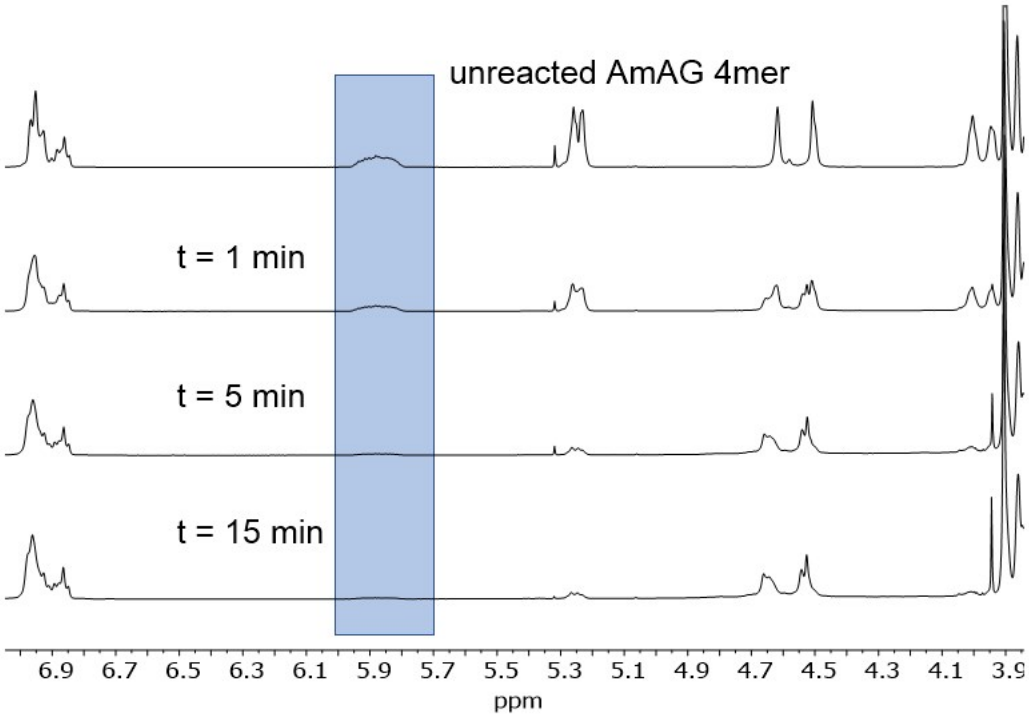
Supplementary Figure 11: HSQC ^{1}H-^{13}C NMR Spectra of ApAG in $CDCl_3$.



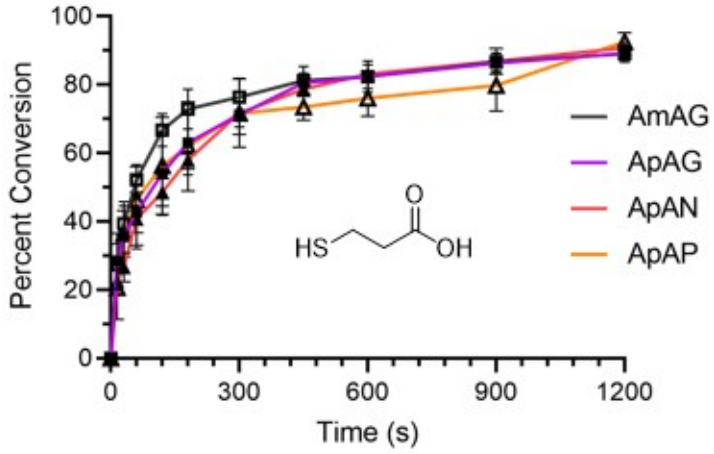
Supplementary Figure 12: HSQC ^{1}H-^{13}C NMR Spectra of AmAG in $CDCl_3$.



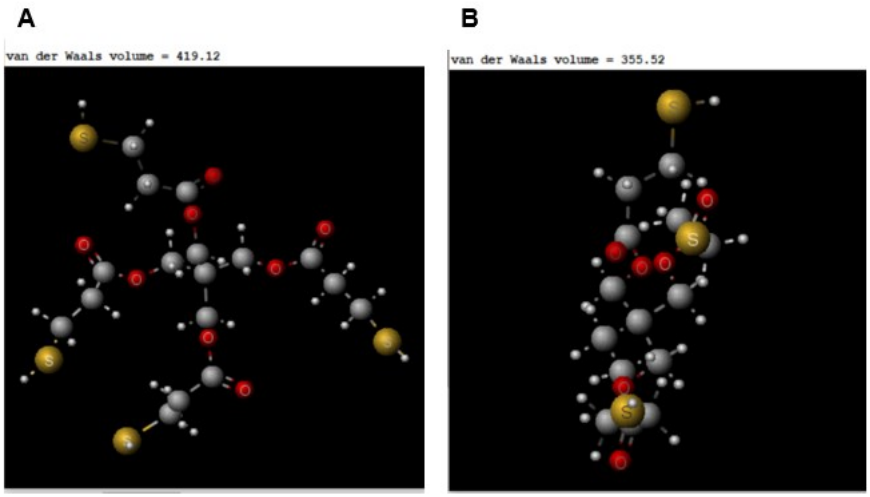
Supplementary figure 13: Fluorescence spectra for the SD-PUMs with the peak intensity observed at a wavelength of 306 nm.



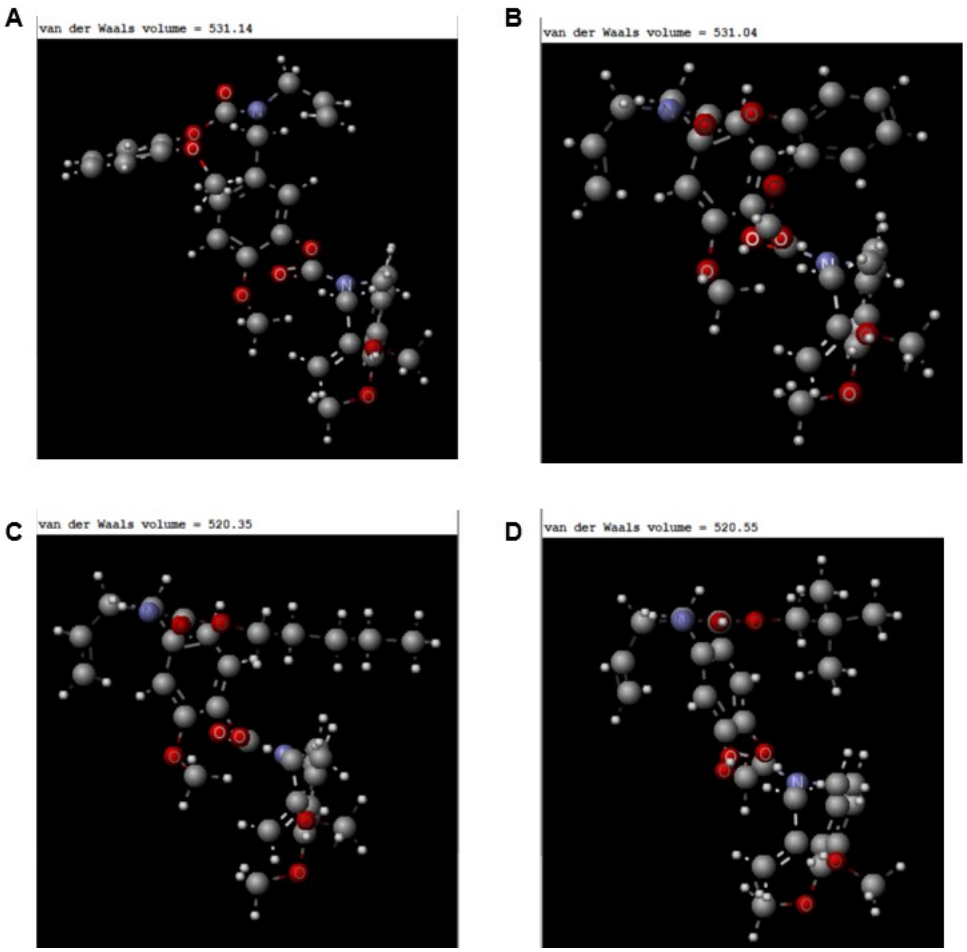
Supplementary figure 14: ^{1}H NMR spectra for the thiol-ene reaction monitoring disappearance of the methine peak of the allyl group in the AmAG.



Supplementary figure 15: Solution phase thiol-ene kinetics of all macromers with 3-mercaptopropionic acid determined by monitoring the disappearance of methine peak of the allyl group at 5.88 ppm by ^{1}H NMR spectroscopy.



Supplementary Figure 16: van der Waals volumes of the (A) tetravalent thiol and (b) trivalent thiol cross-linkers estimated using the MarvinSketch software.



Supplementary Figure 17: van der Waals volumes of the(A) AmAG, (B) ApAG, (C) ApAP, and (D) ApAN estimated using the MarvinSketch software.

	V_{vdw}* (Å^3)	V_{vdw} (cm^3/mol)	Specific volume (cm^3/g)
AmAG 4mer	531.14	319.853	0.554
ApAG 4mer	531.04	319.792	0.554
ApAN 4mer	520.55	313.475	0.579
ApAP 4mer	520.35	313.355	0.579
Trithiol	355.52	214.094	0.537
Tetrathiol	419.12	252.394	0.516

*Calculated by using MarvinSketch software

Supplementary Table 1. Fractional free volumes of all macromers and multivalent thiols.

Tetrathiol Crosslinker	Measured specific volume (cm^3/g)	Specific volume* (cm^3/g)	Fractional free volume ($1 - 1.3\times V_w/V$)
AmAG 4mer	1.194	0.543	0.399 ± 0.019
ApAG 4mer	1.105	0.543	0.367 ± 0.018
ApAN 4mer	1.131	0.560	0.359 ± 0.006
ApAP 4mer	1.133	0.560	0.354 ± 0.009

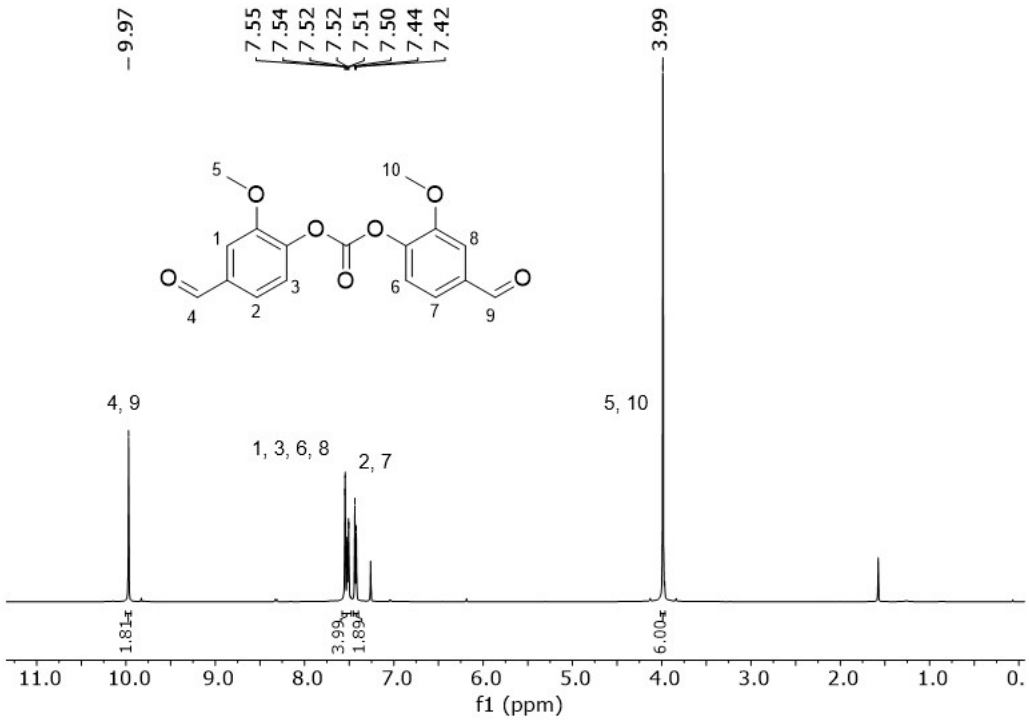
*Calculated by using MarvinSketch software

Supplementary Table 2. Fractional free volumes of all macromer networks crosslinked with a tetravalent thiol

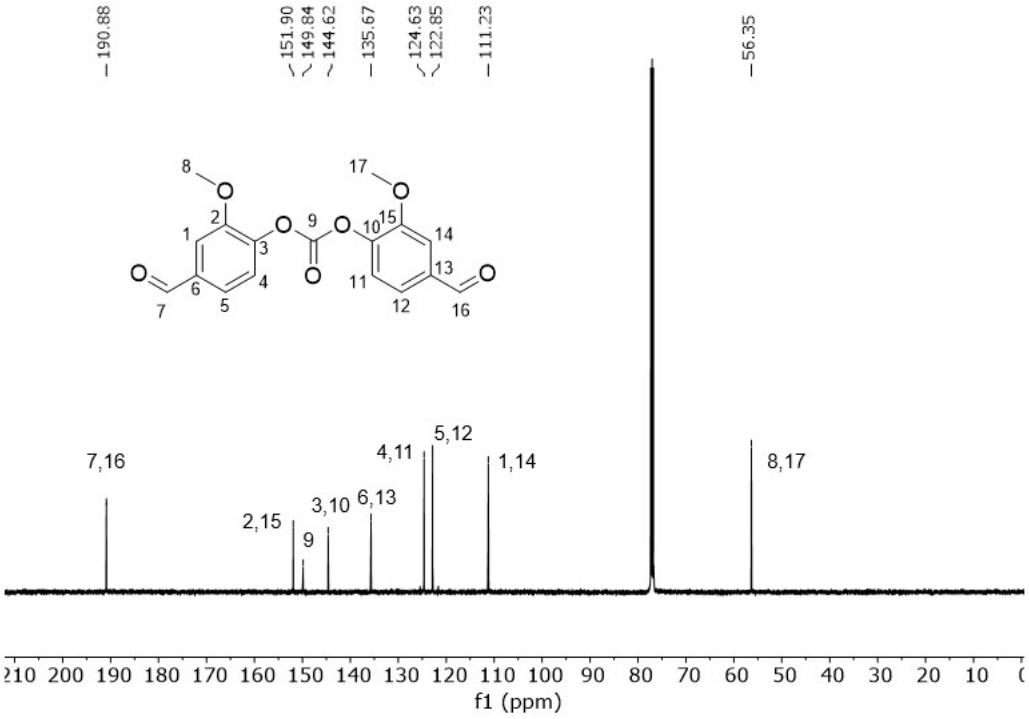
Trithiol Crosslinker	Measured specific volume (cm^3/g)	Specific volume* (cm^3/g)	Fractional free volume ($1 - 1.3\times V_w/V_o$)
AmAG 4mer	1.216	0.549	0.409 ± 0.011
ApAG 4mer	1.164	0.549	0.394 ± 0.011
ApAN 4mer	1.178	0.566	0.366 ± 0.018
ApAP 4mer	1.074	0.566	0.278 ± 0.028

*Calculated by using MarvinSketch software

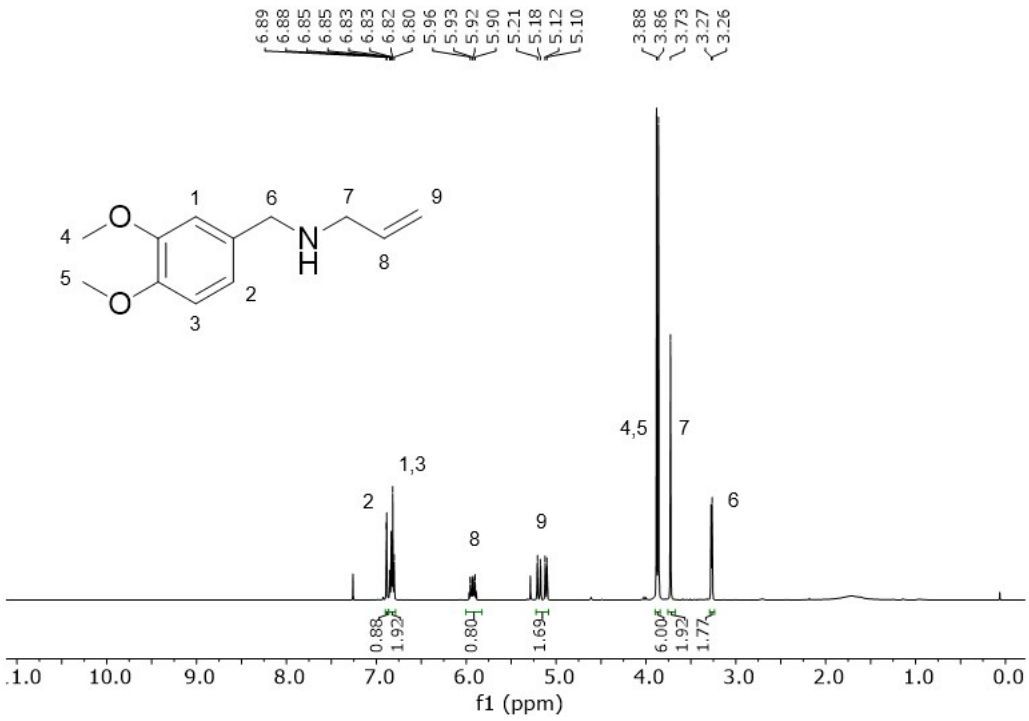
Supplementary Table 3. Fractional free volumes of all macromer networks crosslinked with a trivalent thiol



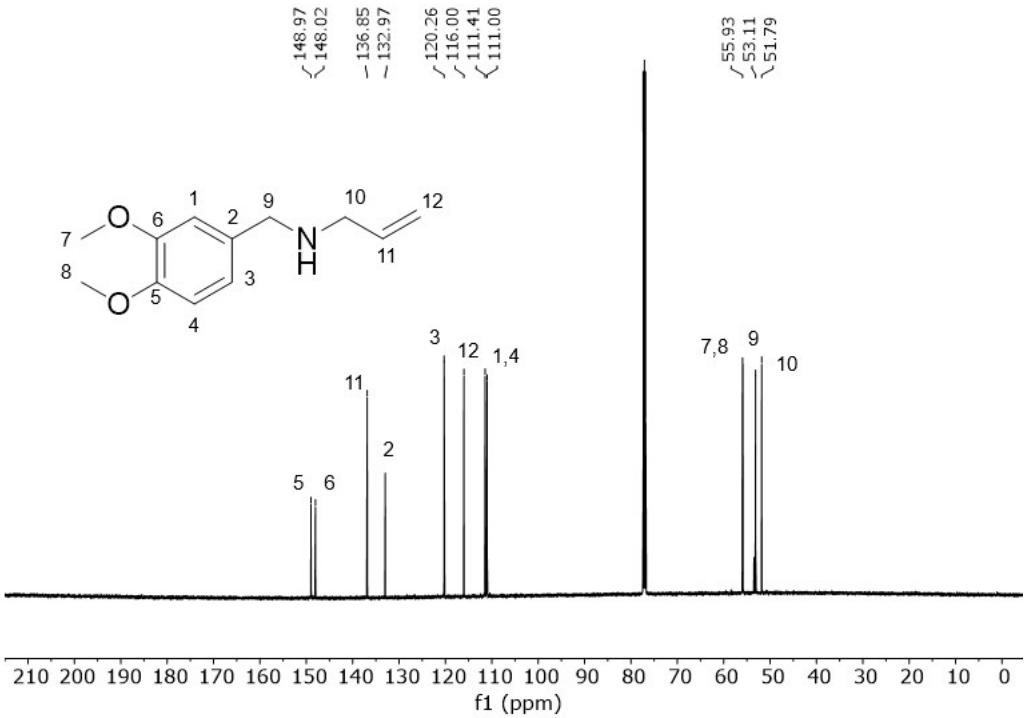
Supplementary Figure 18: ^{1}H NMR spectrum of divanillin carbonate (DVC) in $CDCl_3$



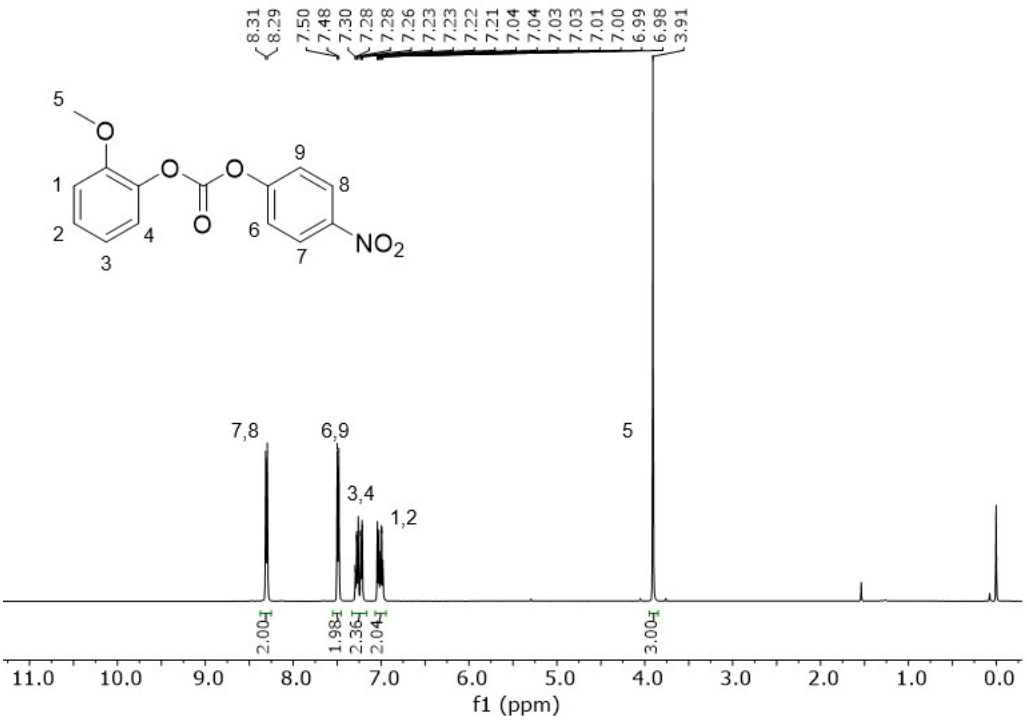
Supplementary figure 19: ^{13}C NMR spectrum of divanillin carbonate (DVC) in $CDCl_3$



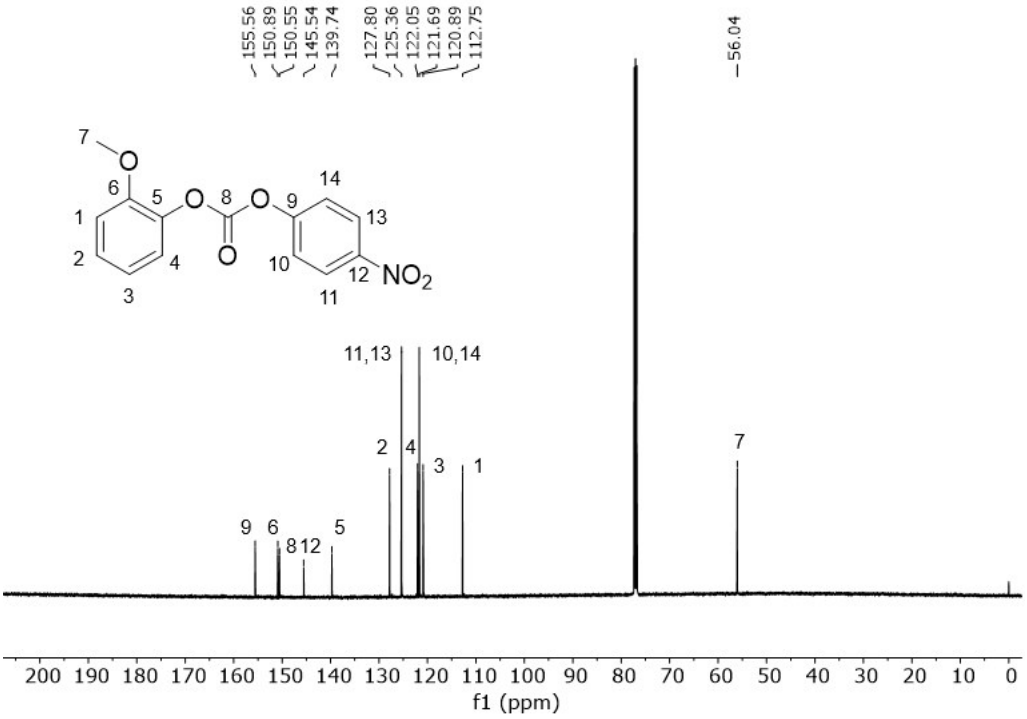
Supplementary figure 20: ^{1}H NMR spectrum of 3,4-dimethoxy-N-allylbenzylamine (DMABA) in $CDCl_3$



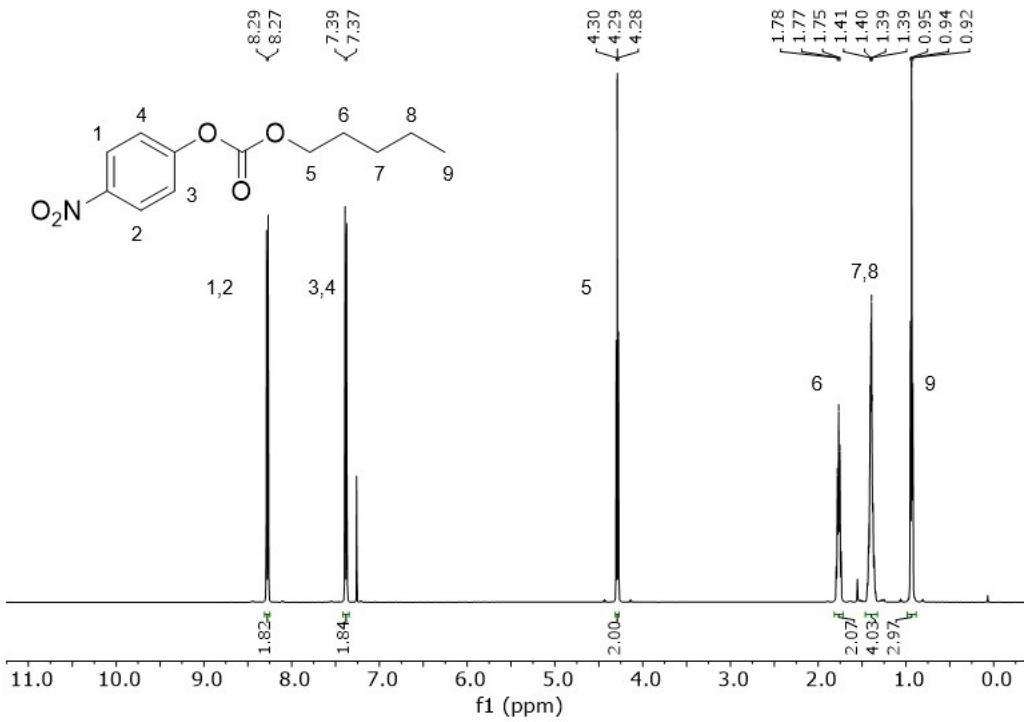
Supplementary figure 21: ^{13}C NMR spectrum of 3,4-dimethoxy-N-allylbenzyllamine (DMABA) in $CDCl_3$



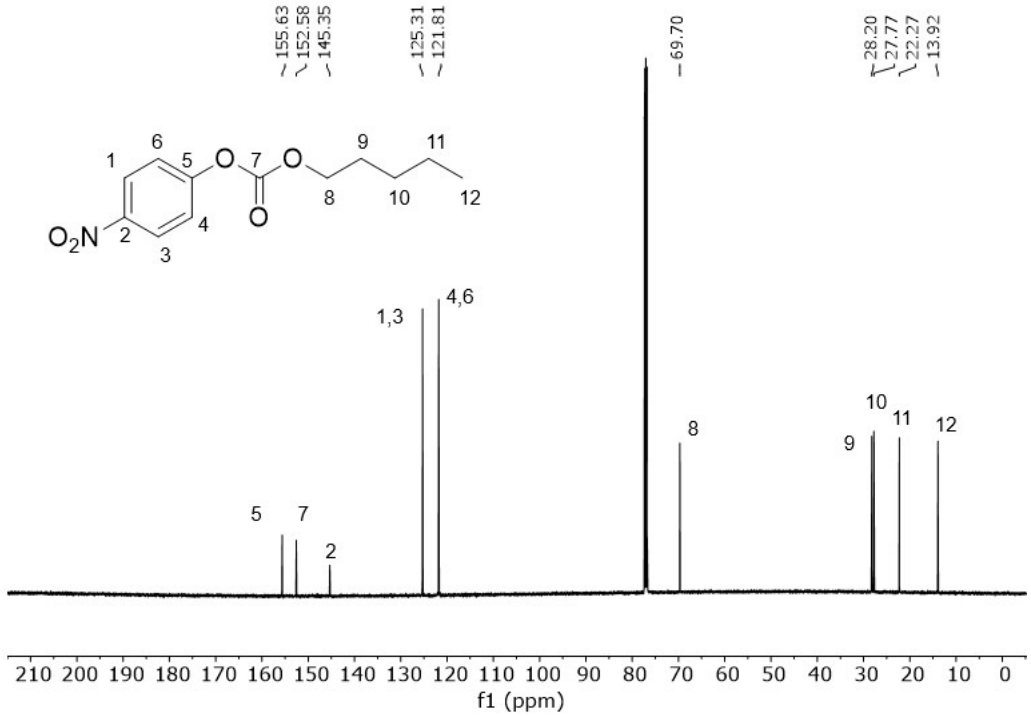
Supplementary figure 22: ^{1}H NMR spectrum of 4-nitrophenyl-activated guaiacol in $CDCl_3$



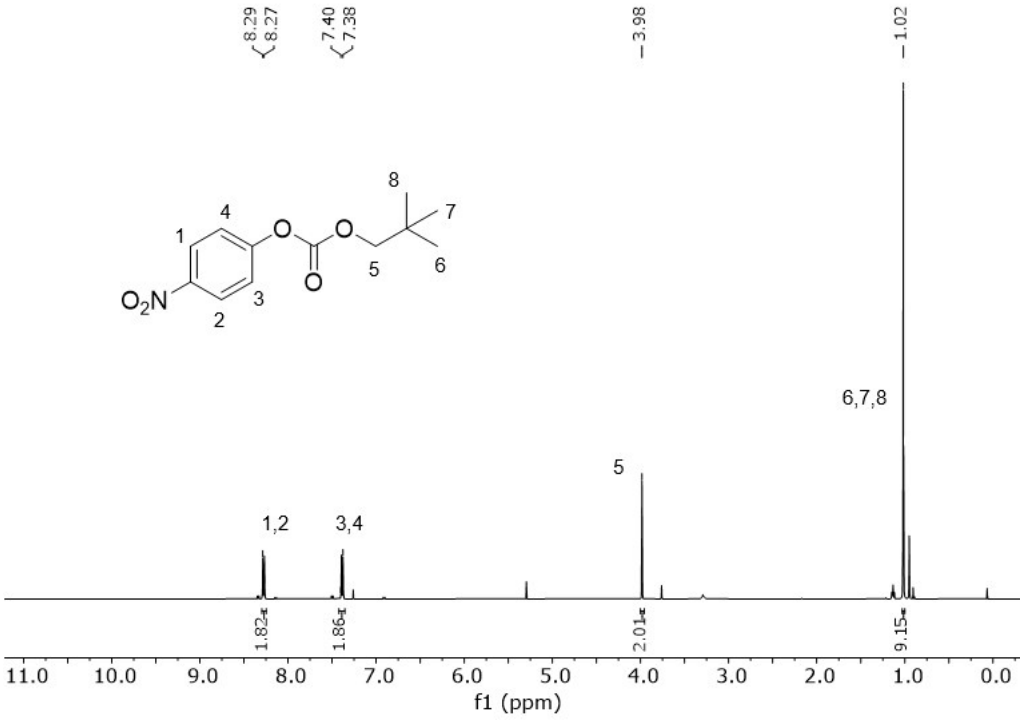
Supplementary figure 23: ^{13}C NMR spectrum of nitrophenyl guaiacol in $CDCl_3$



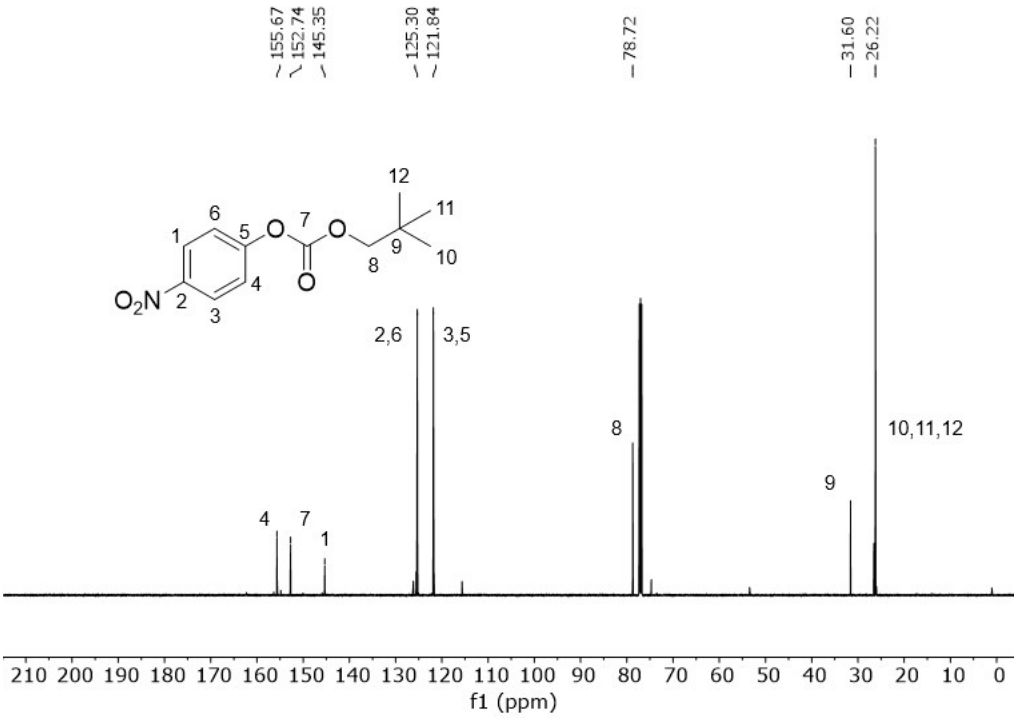
Supplementary figure 24: ^{1}H NMR spectrum of 4-nitrophenyl-activated pentanol in $CDCl_3$



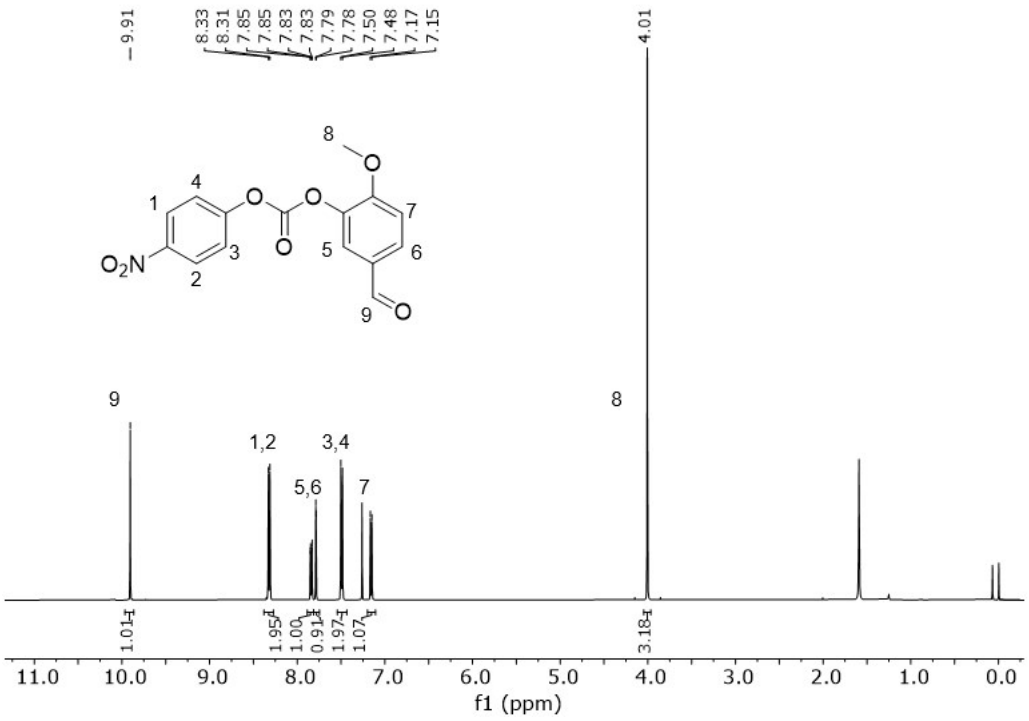
Supplementary figure 25: ^{13}C NMR spectrum of 4-nitrophenyl-activated pentanol in $CDCl_3$



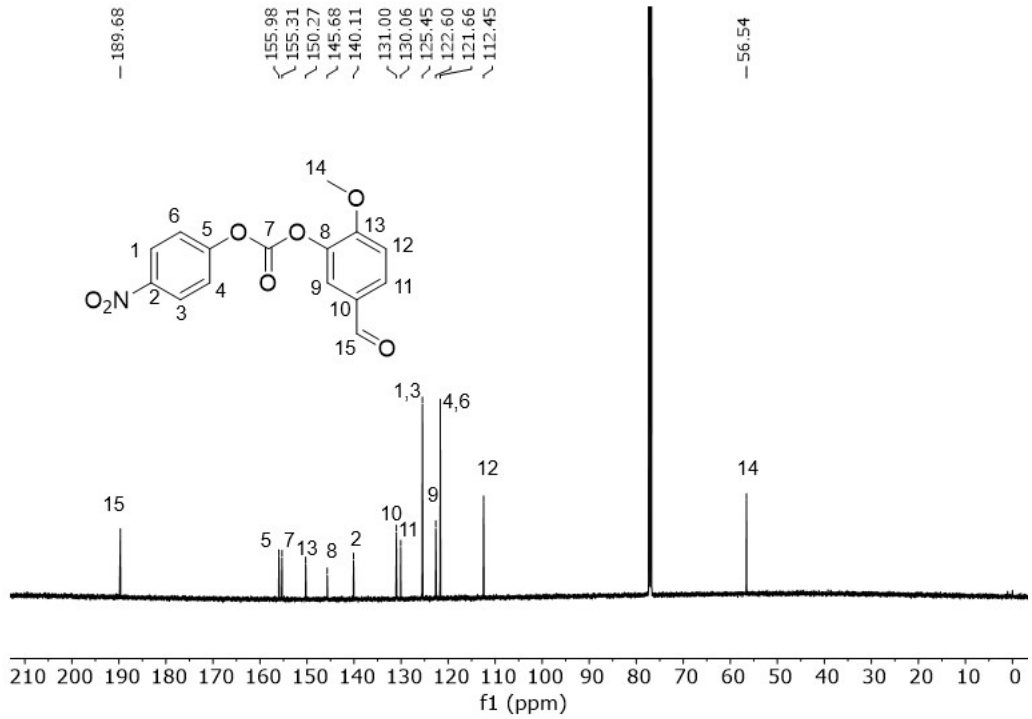
Supplementary figure 26: ^{1}H NMR spectrum of 4-nitrophenyl-activated neopentanol in $CDCl_3$



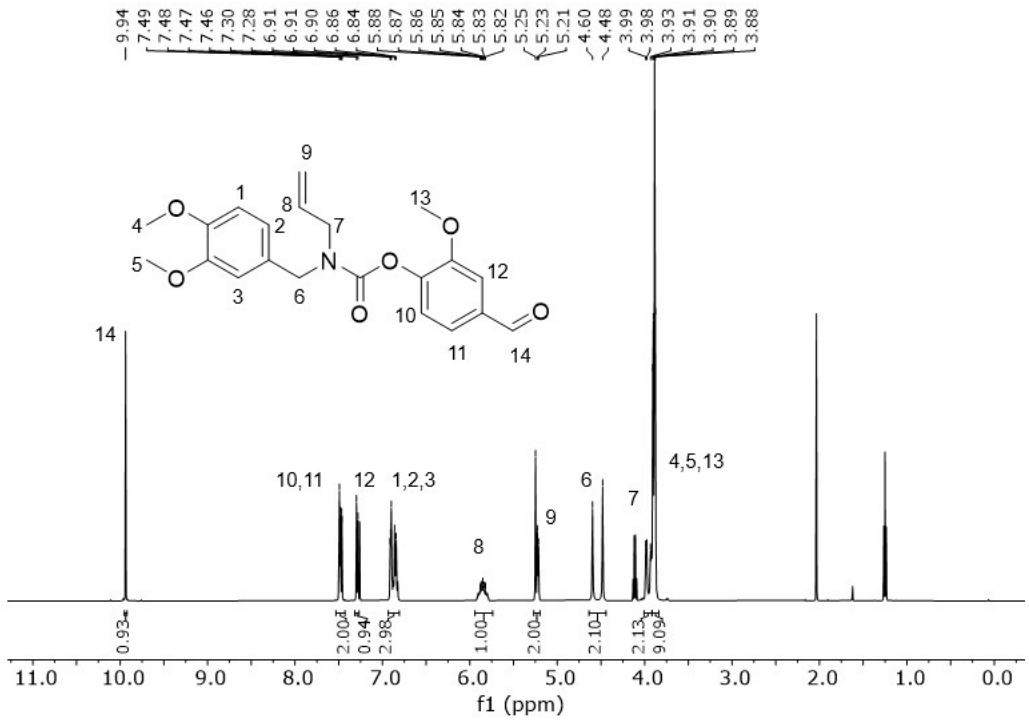
Supplementary figure 27: ^{13}C NMR spectrum of 4-nitrophenyl-activated neopentanol in $CDCl_3$



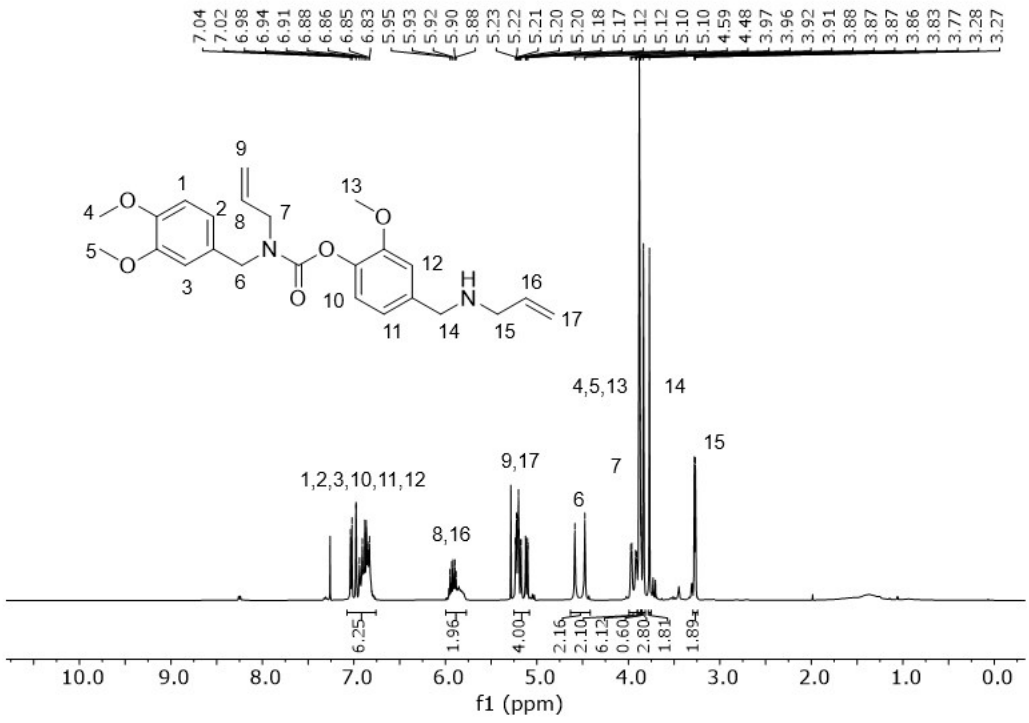
Supplementary figure 28: ^{1}H NMR spectrum of 4-nitrophenyl-activated isovanillin in $CDCl_3$



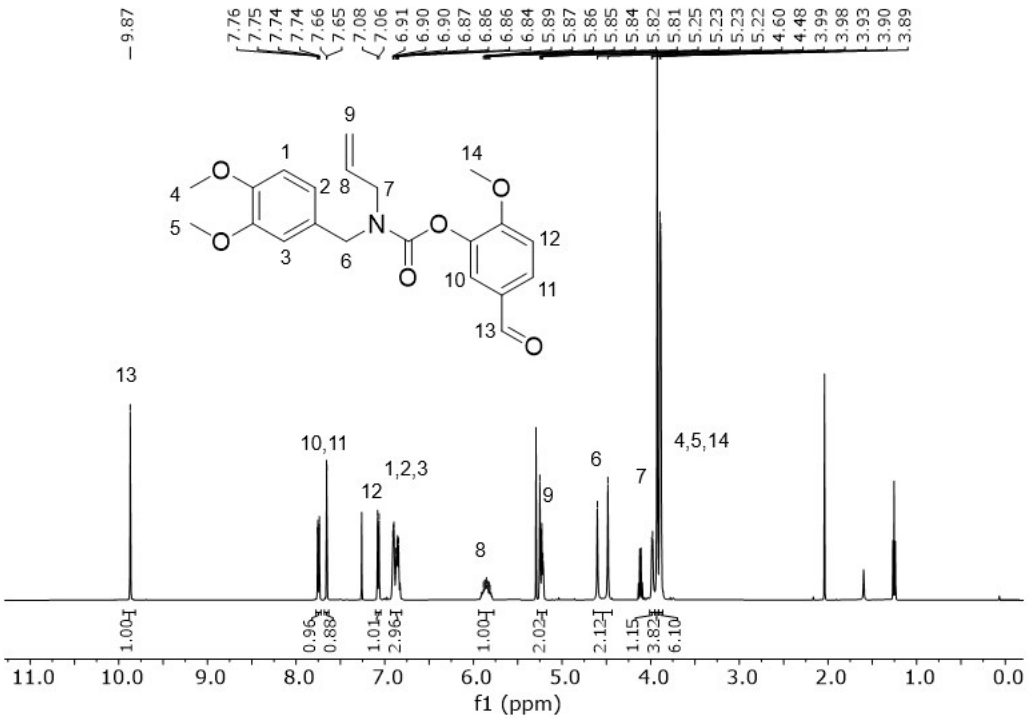
Supplementary figure 29: ^{13}C NMR spectrum of 4-nitrophenyl-activated isovanillin in $CDCl_3$



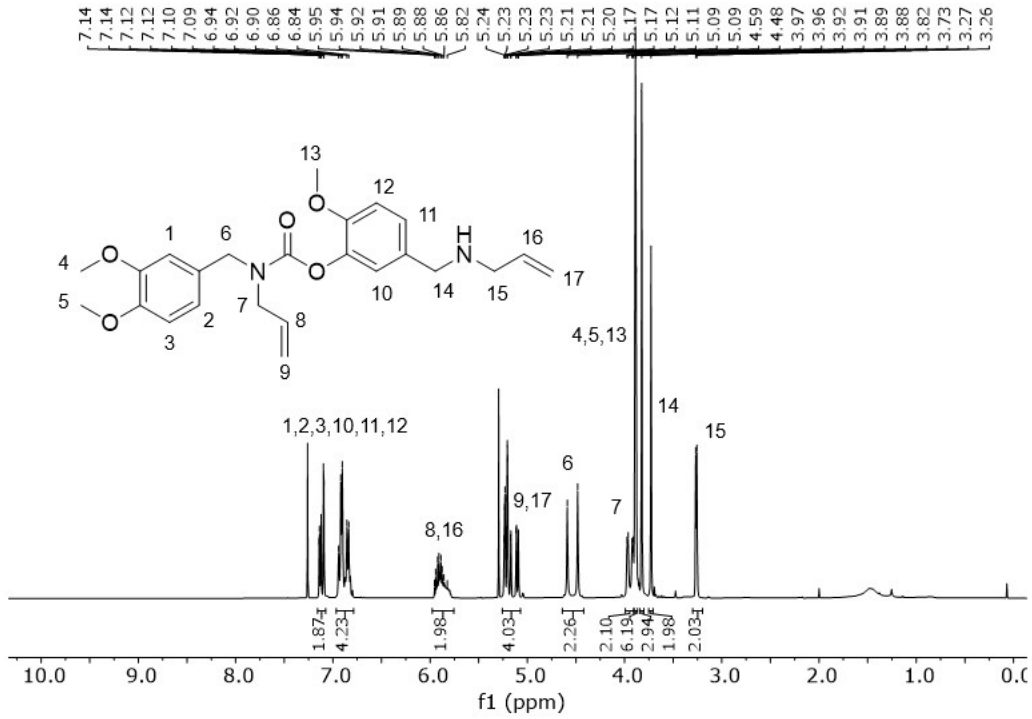
Supplementary figure 30: ^{1}H NMR spectrum of Ap carbamate in $CDCl_3$



Supplementary figure 31: ^{1}H NMR spectrum of ApA amine in $CDCl_3$



Supplementary figure 32: ^{1}H NMR spectrum of isovanillin Am carbamate in $CDCl_3$



Supplementary figure 33: ^{1}H NMR spectrum of AmA amine in $CDCl_3$