Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Chemical Separation of Polyurethane *via* Acidolysis – Combining Acidolysis with Hydrolysis for Valorisation of Aromatic Amines

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SI-1. General Information

Unless otherwise stated, all hydrogenation reactions were set-up in a glovebox under an atmosphere of argon in a PTFE inlay placed inside a 45 mL dry autoclave cell. Autoclaves were pressurised with hydrogen (99.999% purity, Air Liquide) using a 5000 Multi Reactor System (Parr®). The pressure vessels were heated in an aluminium block designed to fit the vessels. For the hydrogenation reactions, solvents were purchased from Sigma-Aldrich, degassed with argon, and stored over 3Å molecular sieves inside the glovebox. For other reactions, purchased chemicals were used without further purification. The Virgin 3000 M_w propoxylated glycerol was acquired from Dow Chemicals. Mn-(BiPy-^{Ph}PNN)-$(CO)_2$Br was synthesised according to a known literature procedure.[1] Ru-(Py-^{tBu}PNN*H*(*t*Bu))-(CO)HCl was synthesised according to a known literature procedure.[2]

Flash column chromatography was conducted using the Interchim Puriflash XS520plus automated column system, employing Interchim Puriflash prepacked 25 g columns with 30 µm spherical silica (PF-30SIHP-F0025).

Nuclear magnetic resonance (NMR) experiments were carried out using a Bruker Ascend 400 spectrometer, with ^{1}H-NMR and ^{13}C-NMR spectra recorded at 400 MHz and 101 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal of the deuterated solvent. Multiplicity patterns in NMR spectra are abbreviated as follows: s = singlet, bs = broad singlet, d = doublet, m = multiplet.

High-resolution mass spectrometry (HRMS) spectra were acquired using a Bruker Maxis Impact Spectrometer (TOF, ESI). FT-IR spectra were recorded at room temperature in ATR mode on an Alpha II spectrophotometer with a monolithic diamond crystal (Alpha II, Bruker, USA). Background (n = 24) and sample measurements (n = 24) were measured with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}. Wavelength-dependent penetration depth and baseline were corrected using built-in functions in OPUS software (v. 8.7.41., Bruker, USA).

Matrix assisted laser desorption/absorption ionization time-of-flight (MALDI-TOF) mass spectrometry experiments were performed using a Bruker Daltonics Autoflex spectrometer, an AnchorChip target plate, and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) in MeCN as matrix.

SI-2. Description of Pressure Vessels

In all hydrogenation experiments, 45 mL pressure vessels were employed. The head consists of a single inlet/outlet valve fitted for the 5000 Multi Reactor System (Parr®), a thermowell for thermocouple insertion, a removable PTFE gasket and six stainless steel bolts for sealing the reaction contents. Unless otherwise stated, the hydrogenation reactions were carried out using a 30 mL PTFE inlay along with a PTFE coated magnet (Figure S1). All connections were sealed using PTFE tape.

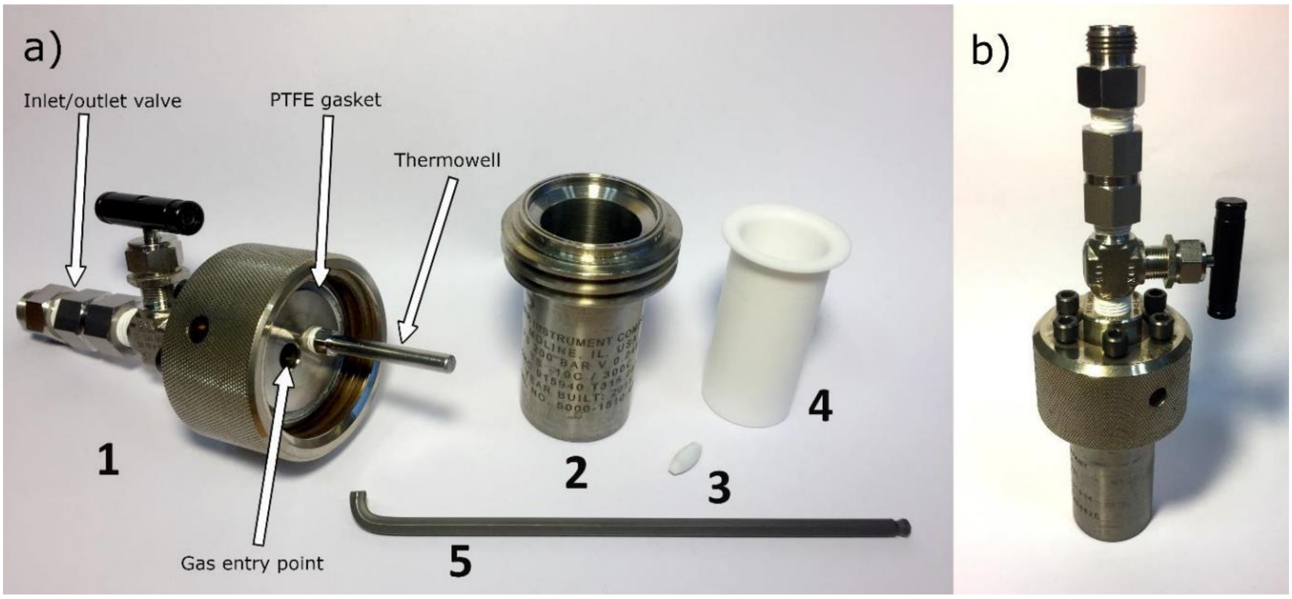
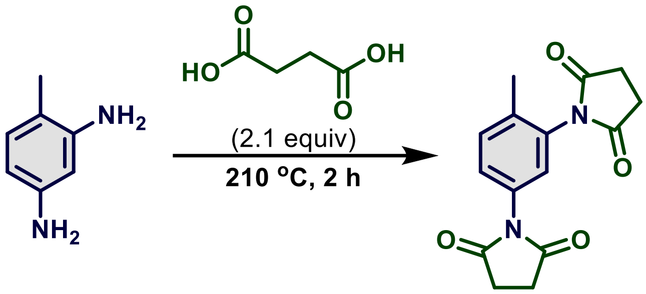


Figure S1. a) Parts of a pressure vessel: 1: vessel head, 2: 45 mL reaction well, 3: magnetic stirring bar, 4: 30 mL PTFE inlay, 5: hex key for fastening bolts. b) Assembled pressure vessel.

SI-3. Preparation of Model Substrates

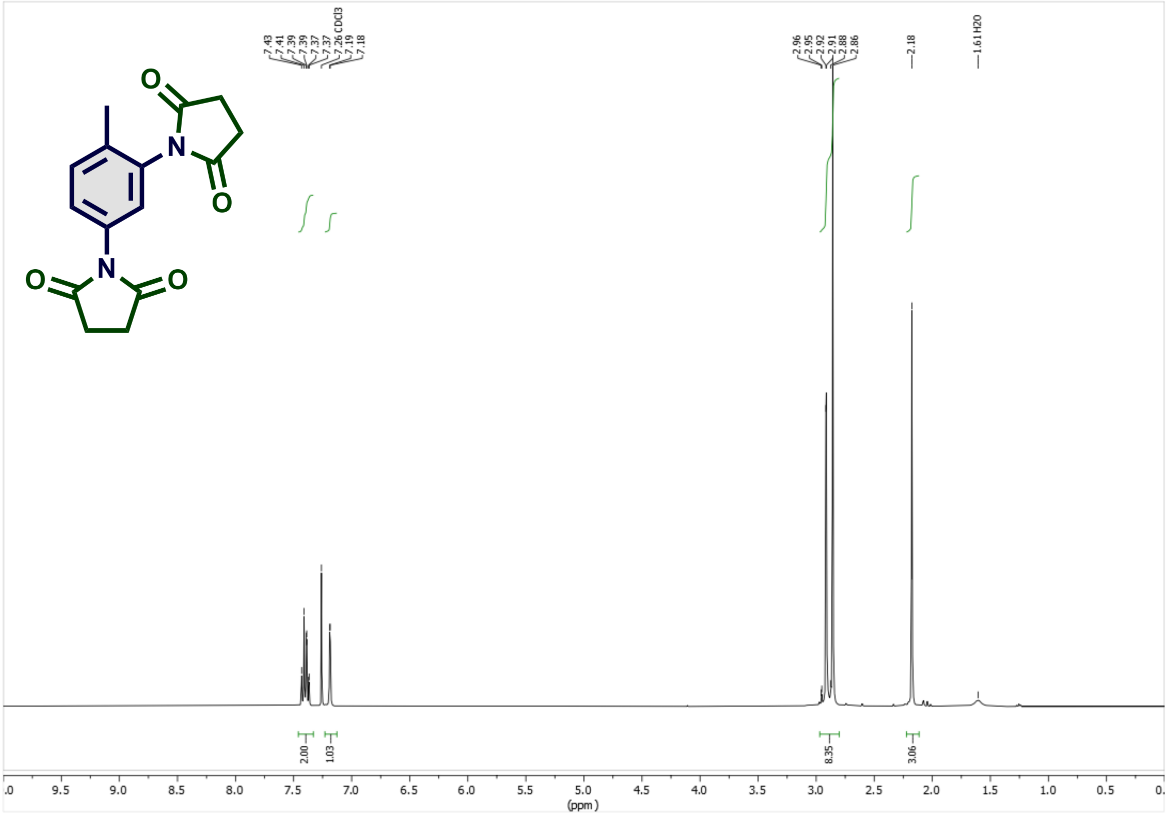
1,1’-(4-Methyl-1,3-phenylene)bis(pyrrolidine-2,5-dione) (Model 1)

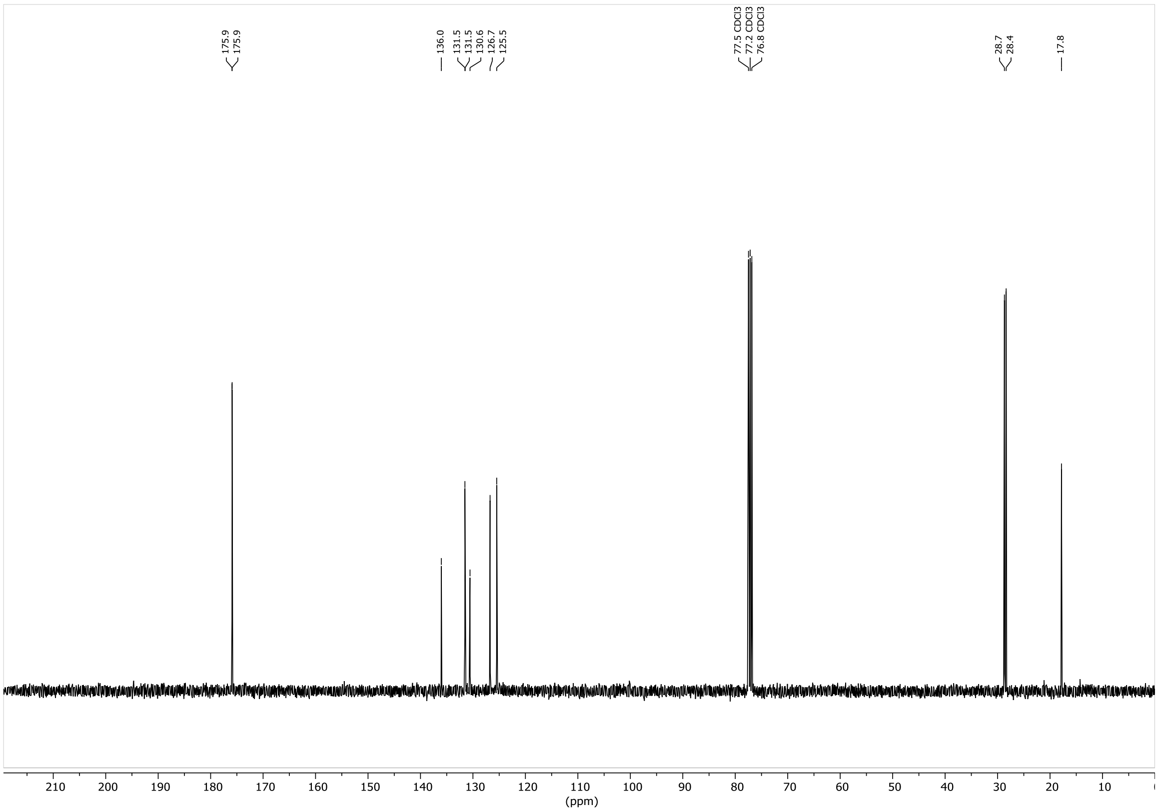


Toluene-2,4-diamine (2.13 g, 17.5 mmol, 1.0 equiv.) and succinic acid (4.35 g, 36.9 mmol, 2.1 equiv.) were added to a dry 25 mL round-bottom flask equipped with a magnet. The flask was sealed with a septum and fitted with a needle as output. The mixture was heated to 210 °C and stirred for 2 h, resulting in a brown solid. The solids were chopped into smaller pieces, placed in a 25 mL round-bottom flask along with a magnet, and left to stir in EtOAc overnight. The residue was filtered, washed with EtOAc, and dried under reduced pressure, resulting in **Model 1** as an off-white solid (1.07 g, 3.74 mmol, 21%).

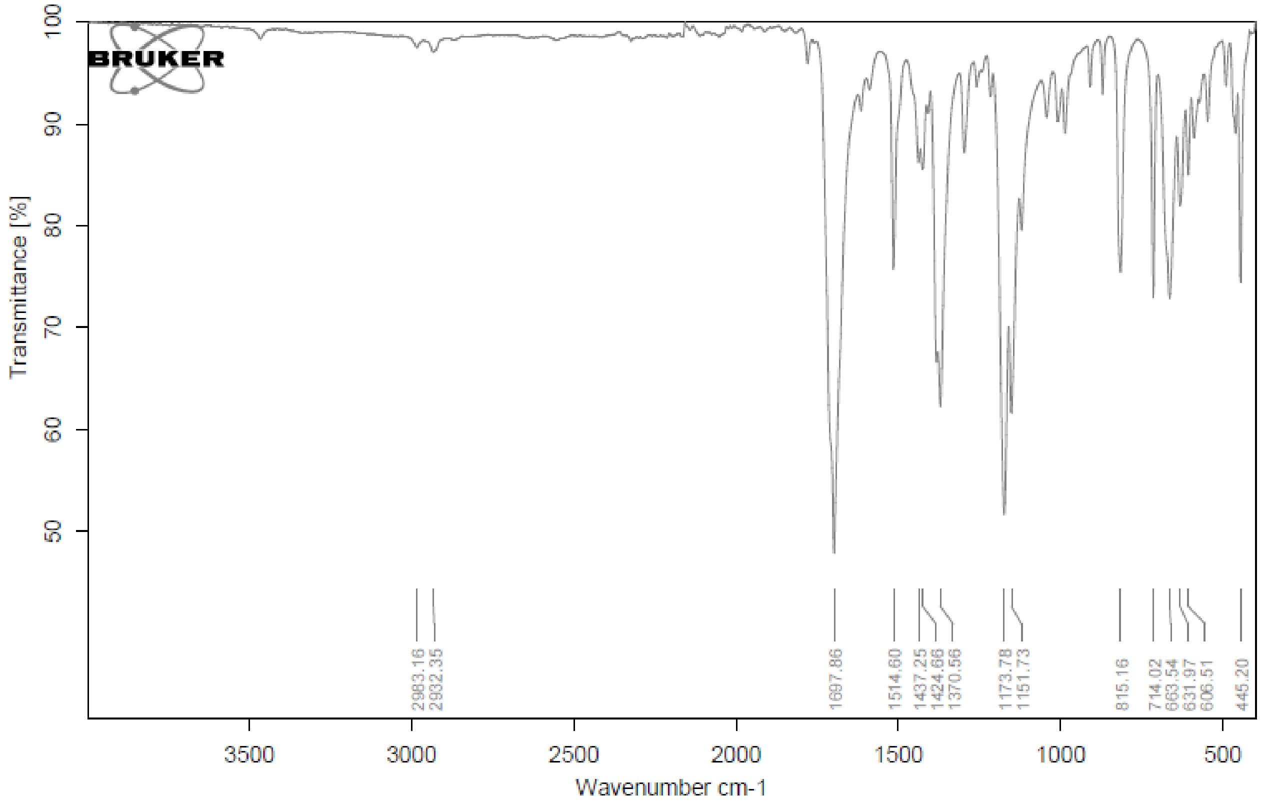
^{1}H-NMR (400 MHz, CDCl$_3$) δ_H 7.45–7.34 (m, 2H), 7.18 (d, *J* = 1.7 Hz, 1H), 2.94–2.88 (m, 4H), 2.85 (s, 4H), 2.17 (s, 3H). **^{13}C-NMR (101 MHz, CDCl$_3$)** δ_C 175.9 (2C), 175.9 (2C), 136.0, 131.5, 131.5, 130.6, 126.7, 125.5, 28.7 (2C), 28.4 (2C), 17.8. **HRMS (ESI+)**: m/z calcd. for $C_{15}H_{14}N_2O_4$ $[M+Na]^+$: 309.0846, found 309.0845.

NMR Spectra of Model 1

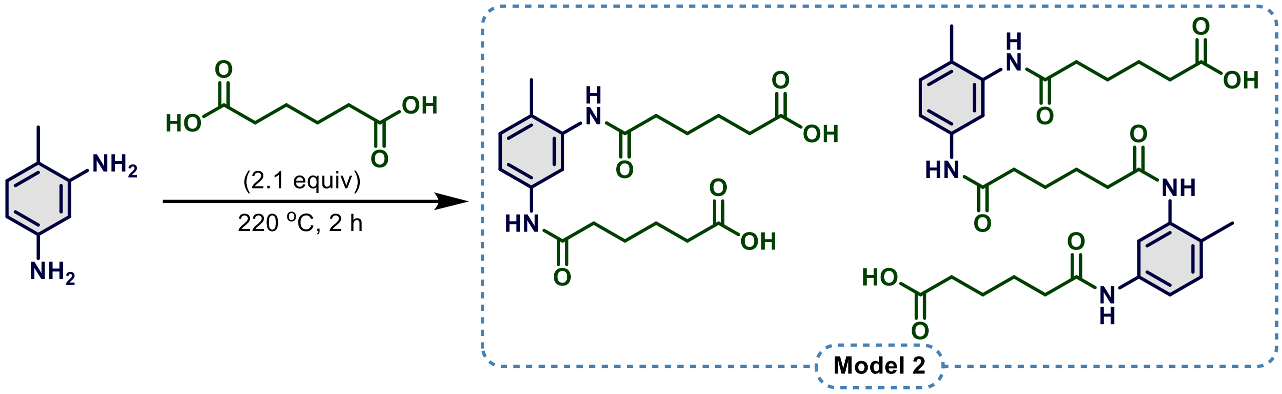




ATR-IR Spectrum of Model 1



Model 2: Mixture of 6,6'-((4-Methyl-1,3-phenylene)bis(azanediyl))bis(6-oxohexanoic acid) (2’) and 6-((5-(6-((5-(5-carboxypentanamido)-2-methylphenyl)amino)-6-oxohexanamido)-2-methylphenyl)amino)-6-oxohexanoic acid (2’’)



Toluene-2,4-diamine (2.14 g, 17.5 mmol, 1.0 equiv.) and adipic acid (5.38 g, 36.8 mmol, 2.1 equiv.) were added to a dry 25 mL round-bottom flask equipped with a magnet. The flask was sealed with a septum and fitted with a needle as output. The mixture was heated to 220 °C and stirred for 2 h, resulting in a brown solid. The solids were chopped into smaller pieces, placed in a 25 mL round-bottom flask along with a magnet, and left to stir in EtOAc overnight. The residue was filtered, washed with EtOAc, and concentrated under reduced pressure, resulting in **Model 2** as an off-white solid (3.71 g, 40%, based on a 0.35:0.65 ratio of **2’**:**2’’**).

^{1}H-NMR (400 MHz, DMSO-d$_6$) δ_H 12.03 (bs, 1H), 9.82 (s, 1H), 9.23 (s, 1H), 7.60 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 2.40–2.17 (m), 2.11 (s, 3H), 1.70–1.47 (m). **^{13}C-NMR (101 MHz, DMSO-d$_6$)** δ_C 174.4, 170.9, 137.2, 136.4, 130.1, 116.0, 36.2, 36.1, 35.7, 35.5, 33.5, 33.4, 25.2, 24.9, 24.7, 24.2, 24.0, 17.4. **HRMS (ESI+)**: m/z calcd. for $C_{19}H_{26}N_2O_6$ [M+H]$^+$: 379.1864, found 379.1864 and $C_{32}H_{42}N_4O_8$ [M+H]$^+$: 611.3075, found 611.3081.

Calculation of ratio between 2’ and 2’’:

$$x: 2', \qquad y: 2''$$

$$\text{ratio Aliphatic: Aromatic:} \qquad \text{x}\ (16:3), \qquad \text{y}\ (12:3)$$

$$\text{Ratio NMR: } (13.4:3)$$

$$\text{eq 1: x}\frac{12}{3} + \text{y}\frac{16}{3} = \frac{13.4}{3}$$

$$\text{eq 2: x} + \text{y} = 1$$

$$12\text{x} + 16(1 - \text{x}) = 13.4$$

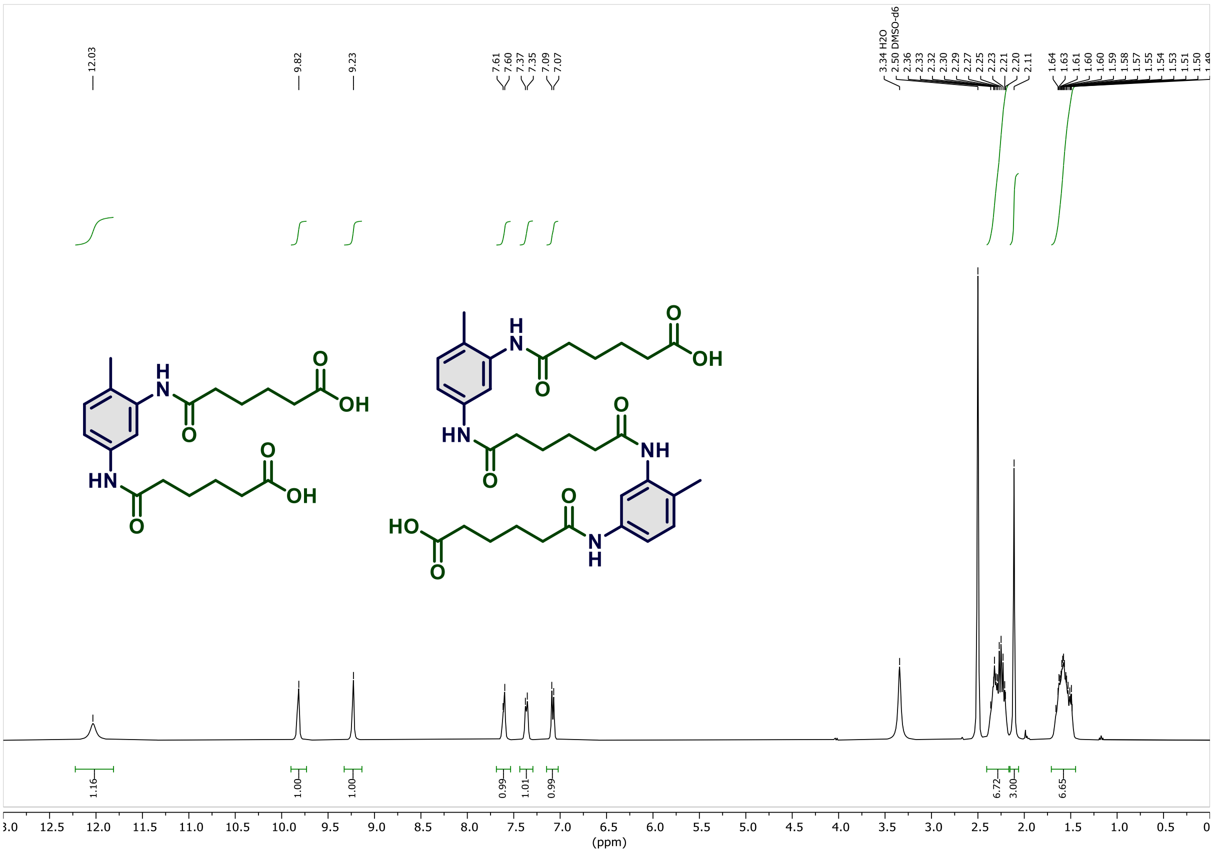
$$12\text{x} + 16 - 16\text{x} = 13.4$$

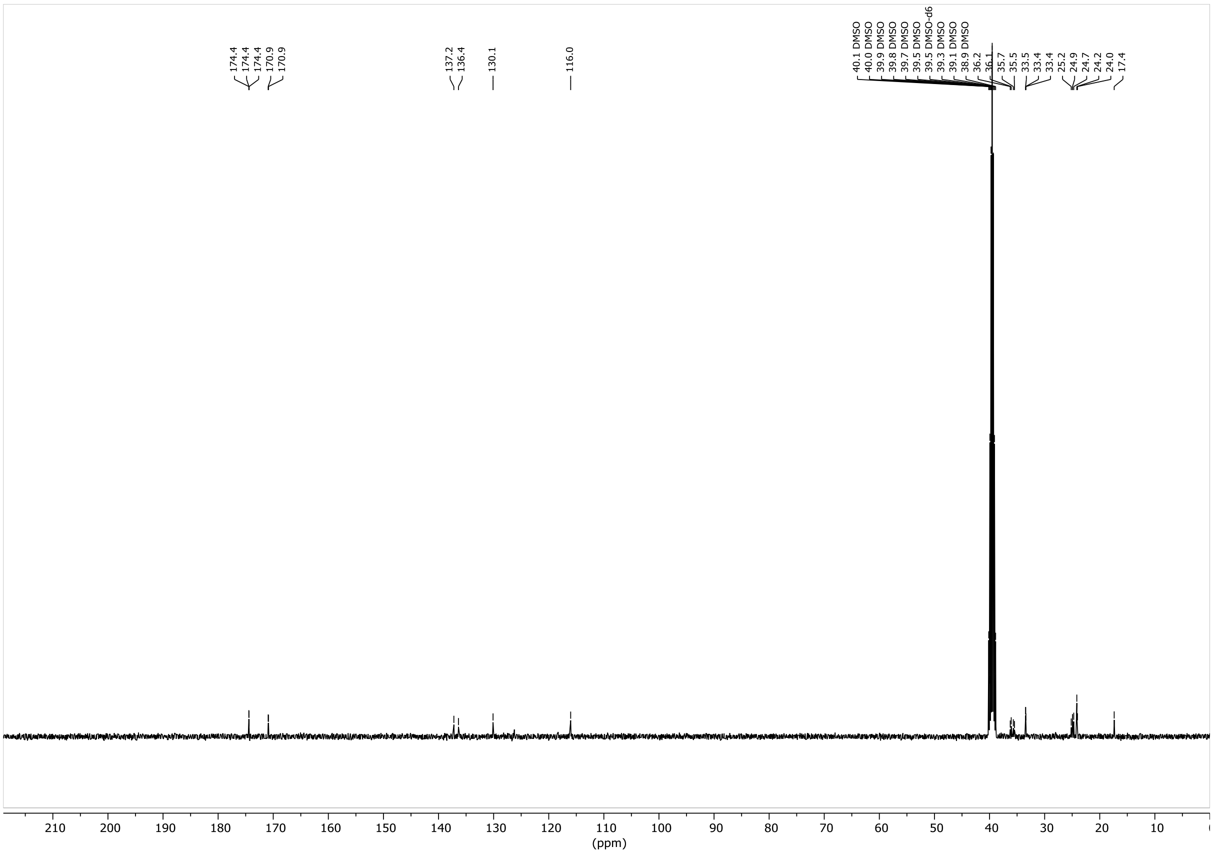
$$-4\mathrm{x} = -2.6$$

$$\mathrm{x} = \frac{2.6}{4} = 0.65$$

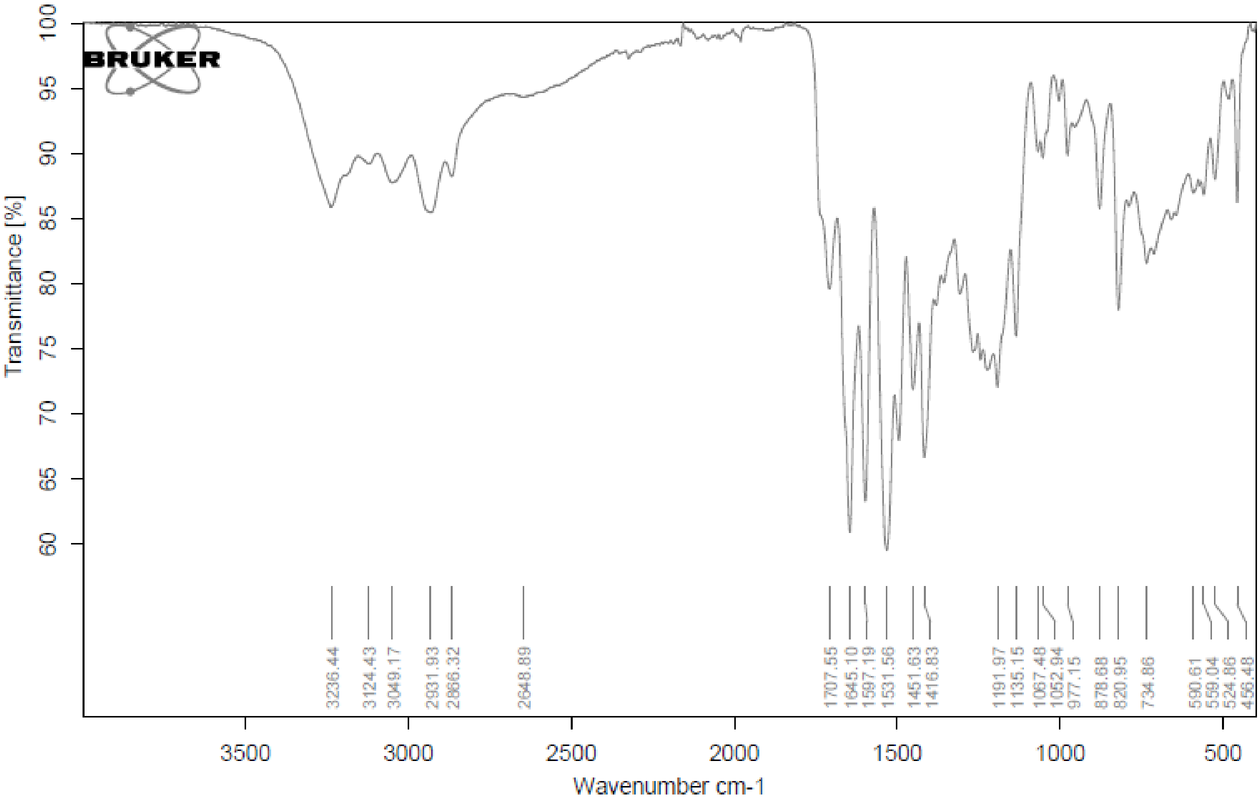
$$\mathrm{y} = 1 - \mathrm{x} = 0.35$$

NMR Spectra of Model 2

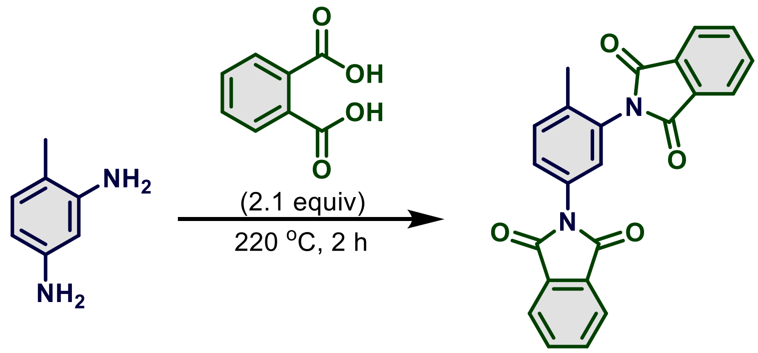




ATR-IR Spectrum of Model 2



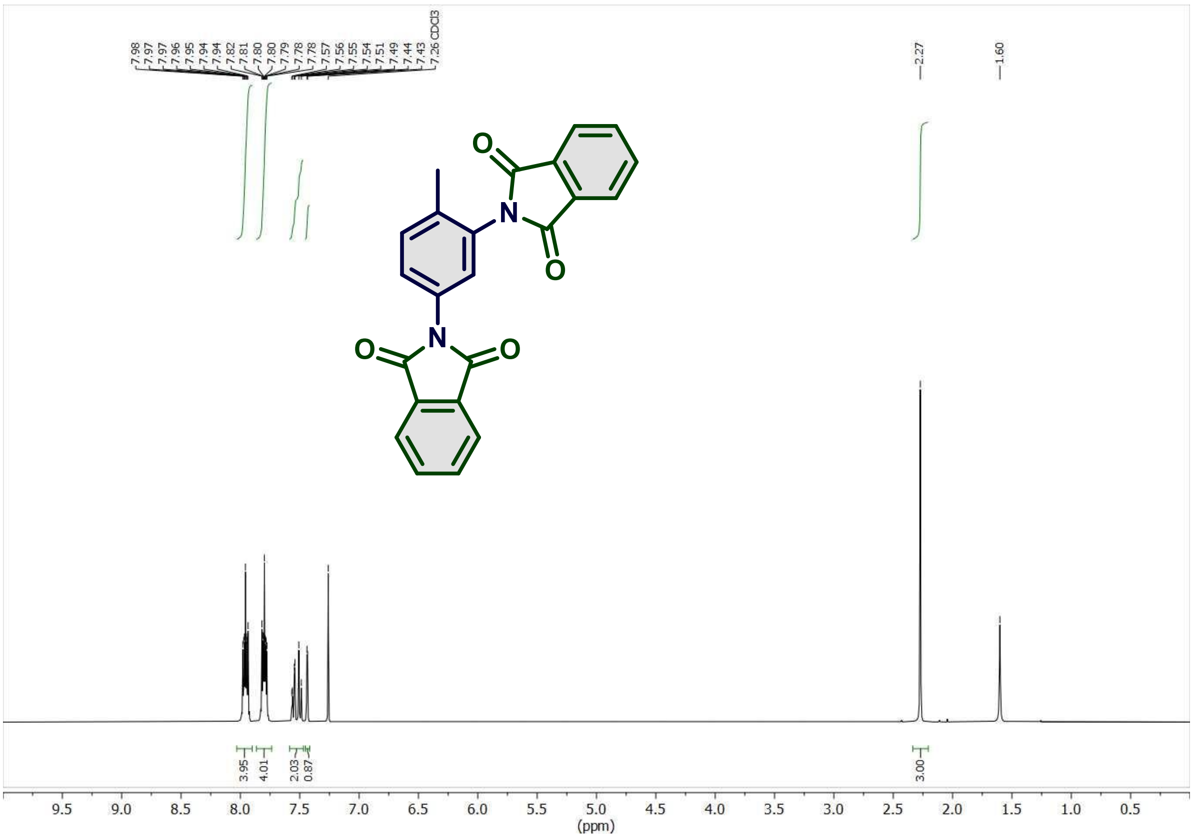
***N*,*N*'-(4-Methyl-*m*-phenylene)-bis-phthalimide (Model 3)**

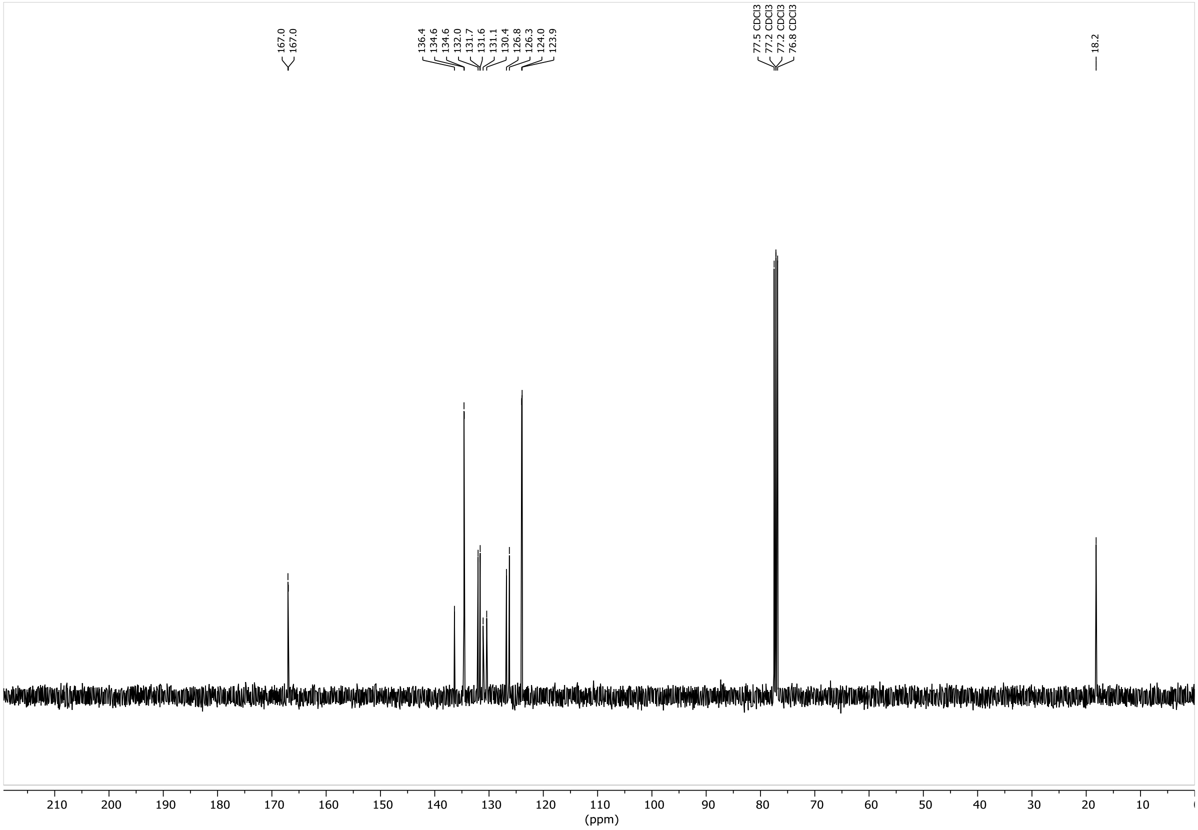


Toluene-2,4-diamine (2.24 g, 18.4 mmol, 1.0 equiv.) and phthalic acid (6.41 g, 38.6 mmol, 2.1 equiv.) were added to a dry 25 mL round-bottom flask equipped with a magnet. The flask was sealed with a septum and fitted with a needle as output. The mixture was heated to 220 °C and stirred for 2 h, resulting in a brown solid. The solids were chopped into smaller pieces, placed in a 25 mL round-bottom flask along with a magnet, and left to stir in EtOAc overnight. The residue was filtered, washed with EtOAc, and dried under reduced pressure, resulting in **Model 3** as a white solid (4.53 g, 11.8 mmol, 65%).

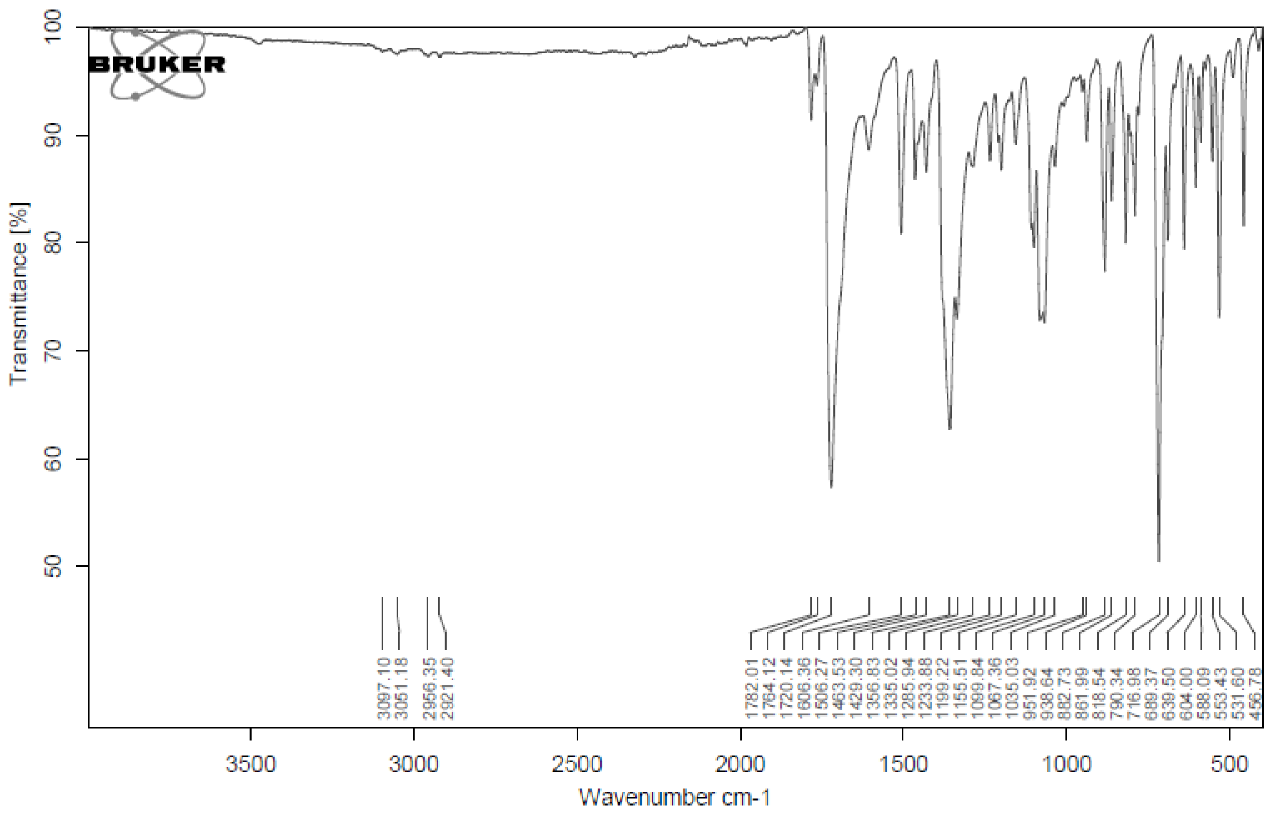
^{1}H-NMR (400 MHz, $CDCl_3$) δ_H 7.98–7.78 (m, 8H), 7.57–7.49 (m, 2H), 7.44 (d, *J* = 2.2 Hz, 1H), 2.27 (s, 3H). **^{13}C-NMR (101 MHz, $CDCl_3$)** δ_C 167.0, 167.0, 136.4, 134.6, 134.6, 132.0, 131.7, 131.6, 131.1, 130.4, 126.8, 126.3, 124.0, 123.9, 18.2. **HRMS (ESI+)**: m/z calcd. for $C_{23}H_{14}N_2O_4$ $[M+Na]^+$: 405.0846, found 405.0852.

NMR Spectra of Model 3





ATR-IR Spectrum of Model 3



SI-4. General Procedures

General Procedure A: Acidic Hydrolysis of Model Substrates

To an 8 mL vial fitted with a magnet, model substrate (50.0 mg) and a solution of 2M H_2SO_4 (4 mL, aq.) were added. The vial was sealed with a screw cap and left to stir for 3 h in an aluminium block at 100 ^oC. Following this, the solution was basified with 4M NaOH (aq.) (pH=10–12) and extracted with EtOAc (4x10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording TDA as a yellow solid.

General Procedure B: Alkaline Hydrolysis of Model Substrates

To an 8 mL vial fitted with a magnet, model substrate (50.0 mg) and a solution of 2M NaOH (4 mL, aq.) were added. The vial was sealed with a screw cap and left to stir for 3 h in an aluminium block at 100 ^oC. Following this, the aqueous phase was extracted with EtOAc (4x10 mL), the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording TDA as a yellow solid.

General Procedure C: Catalytic Hydrogenation of Model Substrates

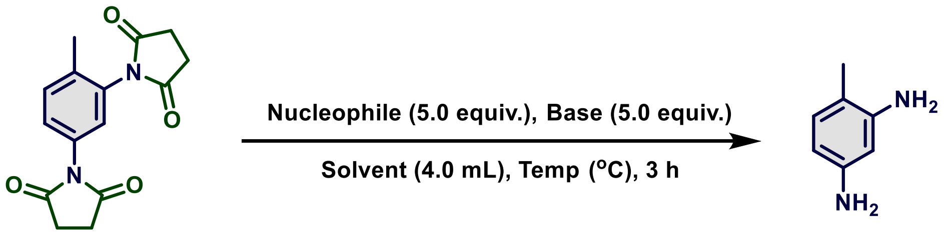
Ruthenium Catalysed Hydrogenation

In an argon filled glovebox, model substrate (0.25 mmol, 1.0 equiv.) was added to a PTFE inlay equipped with a stir bar and placed in an autoclave reactor. To a 4 mL vial, RuP*t*BuNNH complex (2.4 mg, 0.005 mmol, 0.02 equiv.) and KO*t*Bu (1.7 mg, 0.015 mmol, 0.06 equiv.) were mixed with 1,4-dioxane (1 mL) resulting a deep blue/purple solution. The mixture was transferred to the PTFE inlay and rinsed with 1,4-dioxane (1 mL). The autoclave was sealed, removed from the glovebox, connected to a 5000 Multi Reactor System, pressurised with H_2 (40 bar), disconnected from the system, and finally heated at the specified temperature for 24 h at 800 rpm in an aluminium block. Afterwards, the reactor was cooled in an ice bath for 15 min and the pressure was carefully released on the 5000 Multi Reactor System. The reaction mixture was transferred to a 25 mL round-bottom flask and the solvent was removed under reduced pressure. To the crude, water (10 mL) was added, the mixture was acidified with 2M HCl (aq.) (pH=1–2), EtOAc (10 mL) was added, and the organic phase was separated from the aqueous phase. The aqueous phase was washed with EtOAc (3x10 mL) before it was basified using 2M NaOH (aq.) (pH=10–12). The basic aqueous solution was extracted with EtOAc (4x10 mL) and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording TDA as a yellow solid.

Manganese Catalysed Hydrogenation

In an argon filled glovebox, model substrate (0.25 mmol, 1.0 equiv.) was added to a PTFE inlay equipped with a stir bar and placed in an autoclave reactor. To a 4 mL vial, Mn-(BiPy-^{Ph}PNN)-$(CO)_2Br$ (5.5 mg, 0.010 mmol, 0.04 equiv.) and KO*t*Bu (1.7 mg, 0.015 mmol, 0.06 equiv.) were mixed with THF (1 mL). The mixture was transferred to the PTFE inlay and rinsed with THF (1 mL). The autoclave was sealed, removed from the glovebox, connected to a 5000 Multi Reactor System, pressurised with H_2 (40 bar), disconnected from the system, and finally heated at the specified temperature for 24 h at 800 rpm in an aluminium block. Afterwards, the reactor was cooled in an ice bath for 15 min and the pressure was carefully released on the 5000 Multi Reactor System. The reaction mixture was transferred to a 25 mL round-bottom flask, the solvent was removed under reduced pressure and the remaining crude was analysed by ^{1}H-NMR.

General Procedure D: Nucleophilic Substitution for Dianiline Recovery from Model 1



Model 1

Entry	Nucleophile	Solvent	Base	Temp (°C)	2,4-TDA [%]
1[a]	$NH_2OH·HCl$	MeOH	Et_3N	70	traces
2	$NH_2OH·HCl$	MeOH	Et_3N	70	0
3	NH_2NH_2	MeOH	-	70	0
4	$MeNH_2$	*i*PrOH	-	90	0
5[b]	$NH_2OH·HCl$	EtOH	Et_3N	90	0
6[b]	$NH_2OH·HCl$	Toluene	Et_3N	150	0
7[b]	NH_2NH_2	Toluene	-	150	0
8[b]	$NH_2OH·HCl$	MeOH	Et_3N	150	0

[a]Reaction time extended to o/n. [b]Reaction performed in a sealed 10 mL tube.

Reaction with $MeNH_2$ or NH_2NH_2

To an 8 mL vial fitted with a magnet, **Model 1** (50.0 mg, 0.17 mmol, 1 equiv.), nucleophile (0.87 mmol, 5 equiv.), and solvent (4 mL) were added. The vial was sealed and left to stir for 3 h in an aluminium block at 100 ^{o}C. Following this, solvent was evaporated and crude NMR analysis was performed.

Reactions with $NH_2OH\cdot HCl$:

To an 8 mL vial fitted with a magnet, **Model 1** (50.0 mg, 0.17 mmol, 1 equiv.), $NH_2OH\cdot HCl$ (60.3 mg, 0.87 mmol, 5 equiv.), Et_3N (0.122 mL, 0.87 mmol, 5 equiv.), and solvent (4 mL) were added. The vial was sealed and left to stir for 3 h in an aluminium block at 100 ^{o}C. Following this, solvent was evaporated and crude NMR analysis was performed.

General Procedure E: Acidic Hydrolysis of PU-HS

To an 8 mL vial fitted with a magnet, PU-HS (50.0 mg) and a solution of 2M H_2SO_4 (4 mL, aq.) were added. The vial was sealed with a screw cap and left to stir for 3 h in an aluminium block at 100 ^{o}C. Following this, the solution was basified with 4M NaOH (aq.) (pH=10–12), and extracted with EtOAc (4x10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The mixture was dissolved in EtOAc and filtered through a small silica-plug before solvent was removed under reduced pressure, affording TDA as a yellow solid.

General Procedure F: Alkaline Hydrolysis of PU-HS

To an 8 mL vial fitted with a magnet, PU-HS (50.0 mg) and a solution of 2M NaOH (4 mL, aq.) were added. The vial was sealed with a screw cap and left to stir for 3 h in an aluminium block at 100 ^{o}C. Following this, the aqueous phase was extracted with EtOAc (4x10 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in EtOAc and filtered through a small silica-plug before solvent was removed under reduced pressure, affording TDA as a yellow solid.

General Procedure G: Catalytic Hydrogenation of PU-HS

In an argon filled glovebox, PU-HS (0.25 mmol, 1.0 equiv.) was added to a PTFE inlay equipped with a stir bar and placed in an autoclave reactor. To a 4 mL vial, RuP*t*BuNNH complex (2.4 mg, 0.005 mmol, 0.02 equiv.) and KO*t*Bu (1.7 mg, 0.015 mmol, 0.06 equiv.) were mixed with 1,4-dioxane (1 mL) resulting in a deep blue/purple solution. The mixture was transferred to the inlay and the vial was rinsed with 1,4-dioxane (1 mL). The autoclave was sealed, taken out of the glovebox, connected to a 5000 Multi Reactor System, pressurised with H_2 (40 bar), disconnected from the system, and finally heated at 180 ^{o}C for 24 h at 800 rpm in an aluminium block. Afterwards, the reactor was cooled in an ice bath for 15 min and the pressure was carefully released on the 5000 Multi Reactor System. The reaction mixture was transferred to a 25 mL round-bottom flask and the solvent was removed under reduced pressure. To the crude, water (10 mL) was added and acidified with 2M HCl (aq.) (pH=1–2) before the aqueous phase was washed with EtOAc (4x10 mL). The aqueous phase was basified with 2M NaOH (aq.) (pH=10–12) and extracted with EtOAc (4x10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The mixture was dissolved in EtOAc and filtered through a small silica-plug. The mixture was concentrated onto celite, and TDA was isolated by flash column chromatography as a yellow solid.

SI-5. Acidolysis of Flexible Polyurethane FoamSI-5.1. Flexible PU Foam Recipe and Calculation of Acid Equivalents for Acidolysis

The flexible foam was formulated from the following recipe:

Flexible PU Foam (Mattress)	wt%
TDI 4:1 (2,4-:2,6-TDI)	51.6
3000 M_W propoxylated glycerol	100
Water	4
TEGOSTAB® BF2370 Surfactant	1
Stannous octoate (tin T9)	0.2
DABCO 33 LV: 33% triethylenediamine, 67% dipropylene glycol	0.2

The foam was shredded on a modified twin screw extruder (Xinda, 65 mm twin screw extruder with 2000 mm barrel length) before being subjected to chemical depolymerisation via the acidolysis process with either succinic-, adipic- or phthalic acid. Calculations for amount of acid used are shown below.

$$\mathrm{wt\%_{TDI}} = \frac{51.6}{51.6 + 100 + 4 + 1 + 0.2 + 0.2} = 32.9\%$$

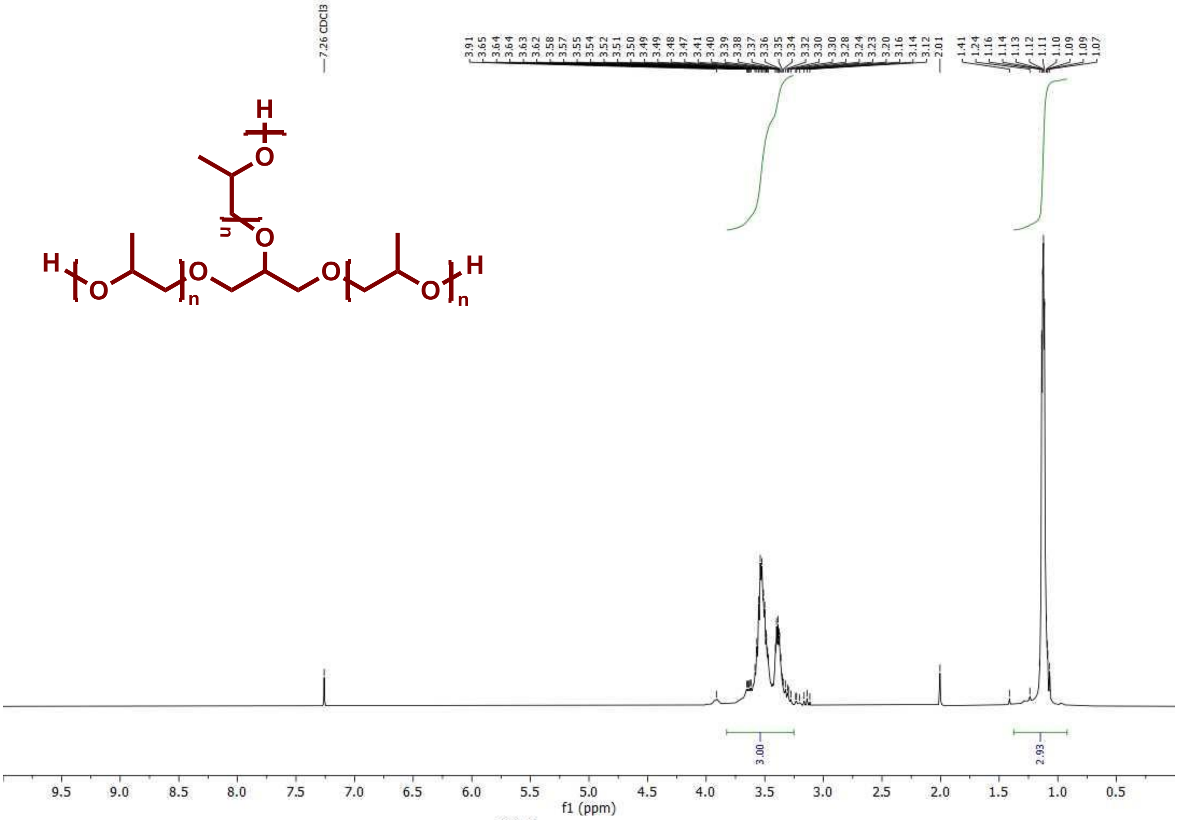
$$\mathrm{m_{TDI}} = \mathrm{m_{PU}} \cdot \mathrm{wt\%_{TDI}}$$

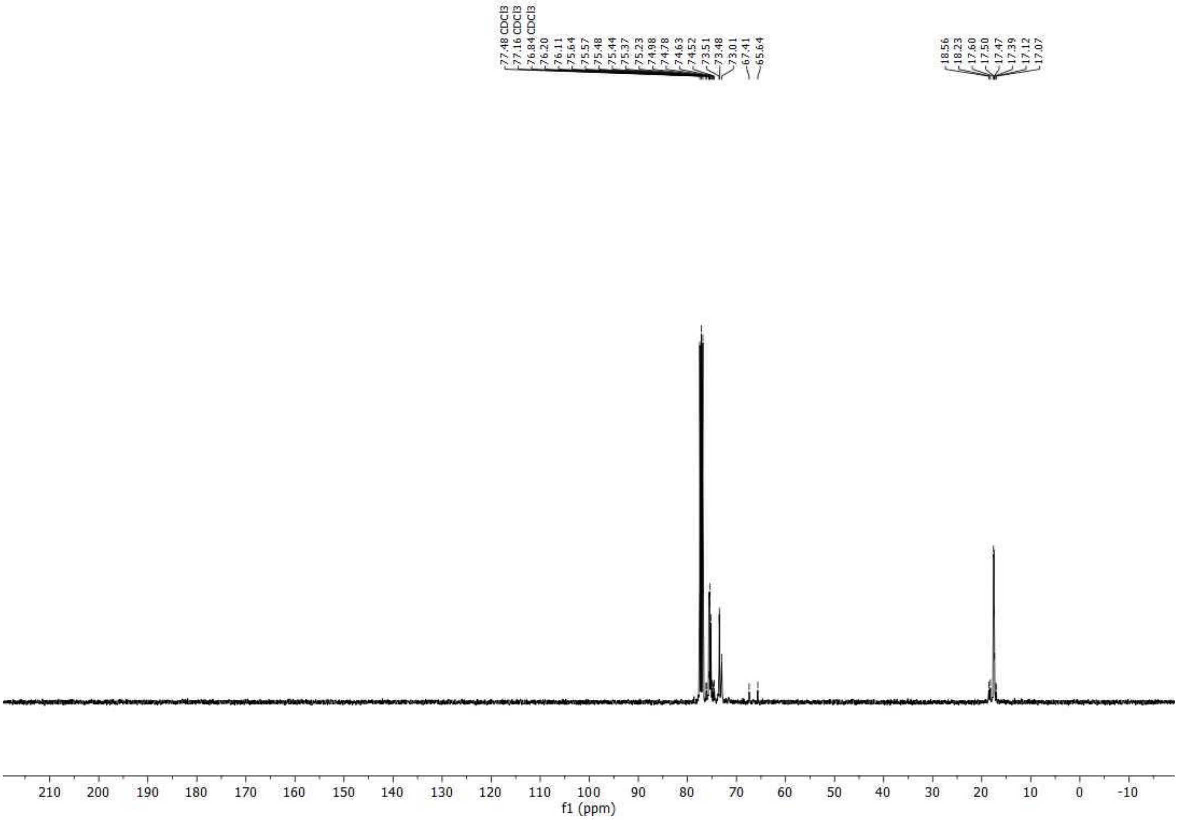
$$\mathrm{n_{TDI/TDA}} = \frac{\mathrm{m_{TDI}}}{\mathrm{M_{TDI}}}$$

$$\mathrm{n_{acid}} = 2.1 \cdot \mathrm{n_{TDA}}$$

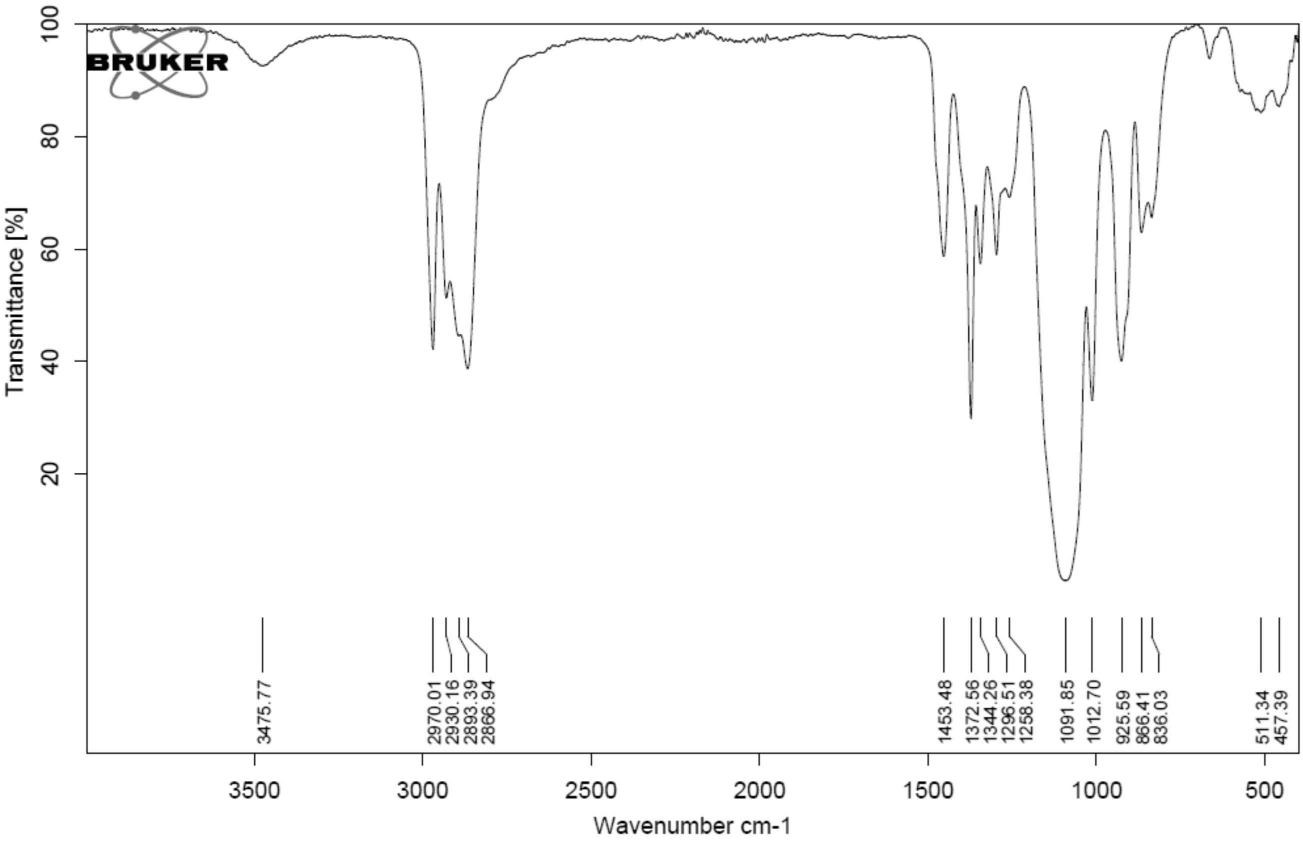
SI-5.2. Characterisation of Virgin Polyol

NMR Spectra of Virgin Polyol

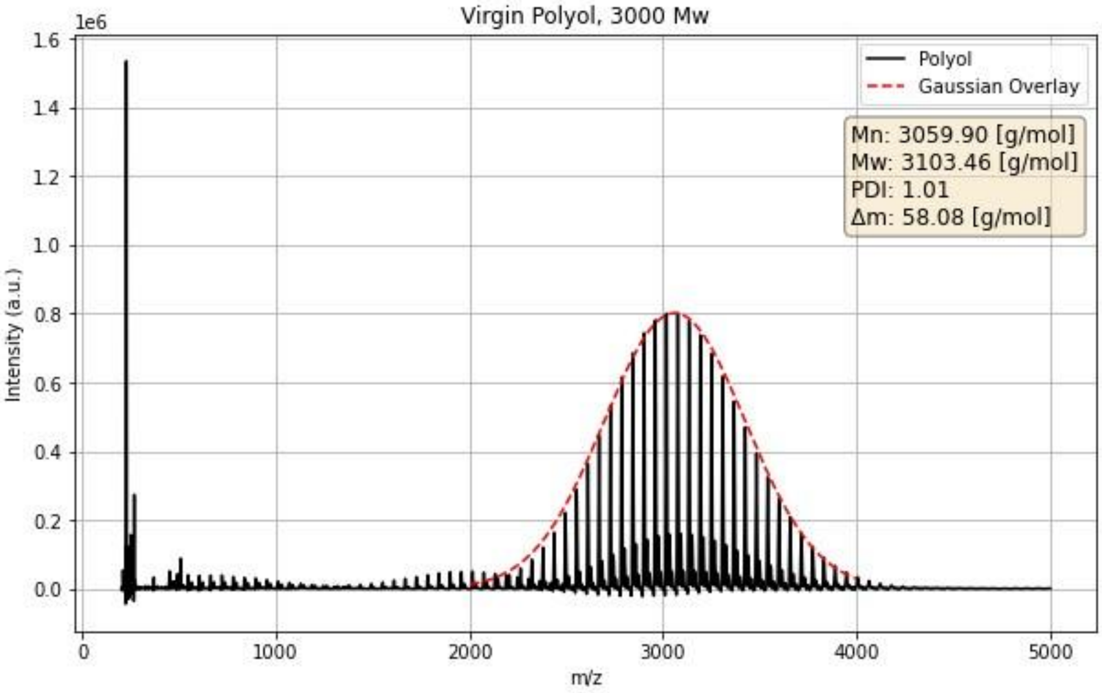




FT-IR Spectrum of Virgin Polyol

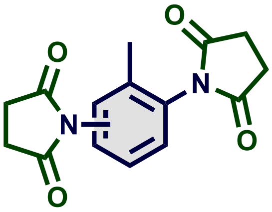


MALDI-TOF Spectrum of Virgin Polyol



SI-5.3. Acidolysis Using Succininc Acid

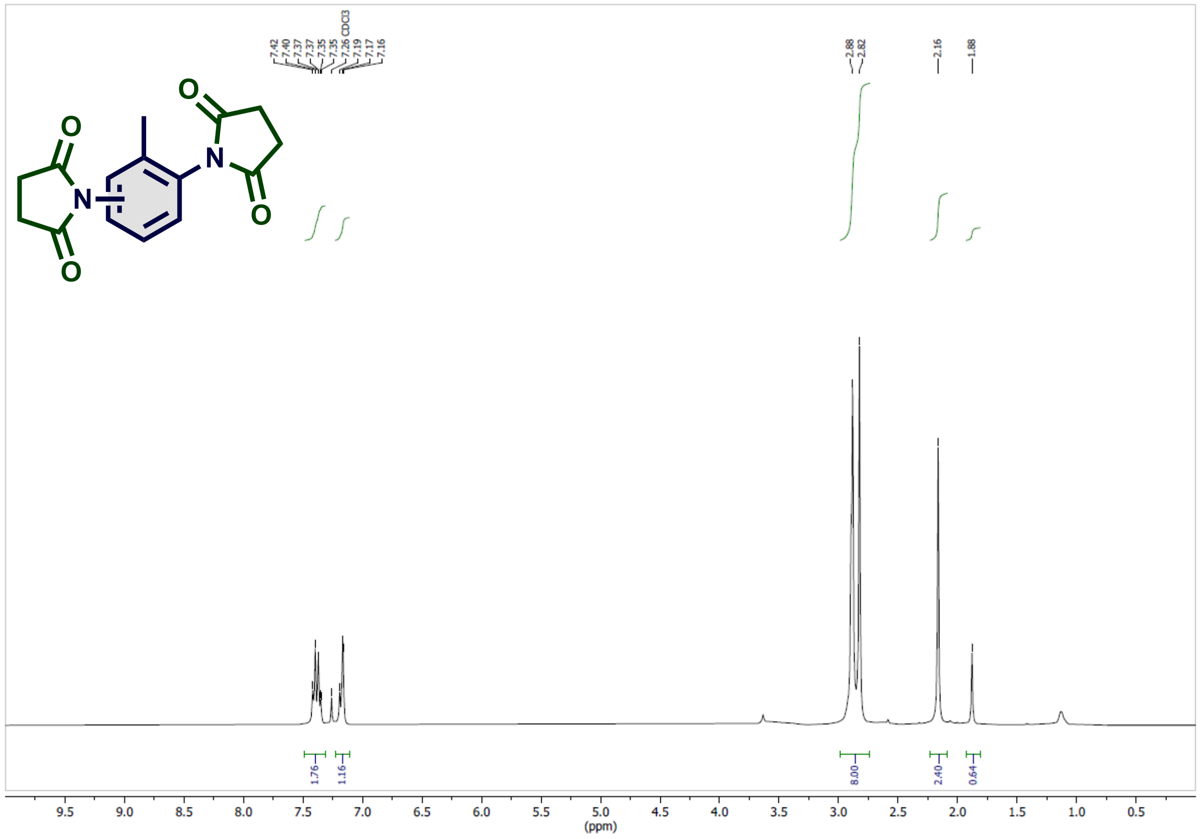
SI-5.3.1. Synthesis of PU-HS1 – Acidolysis Using Succinic Acid

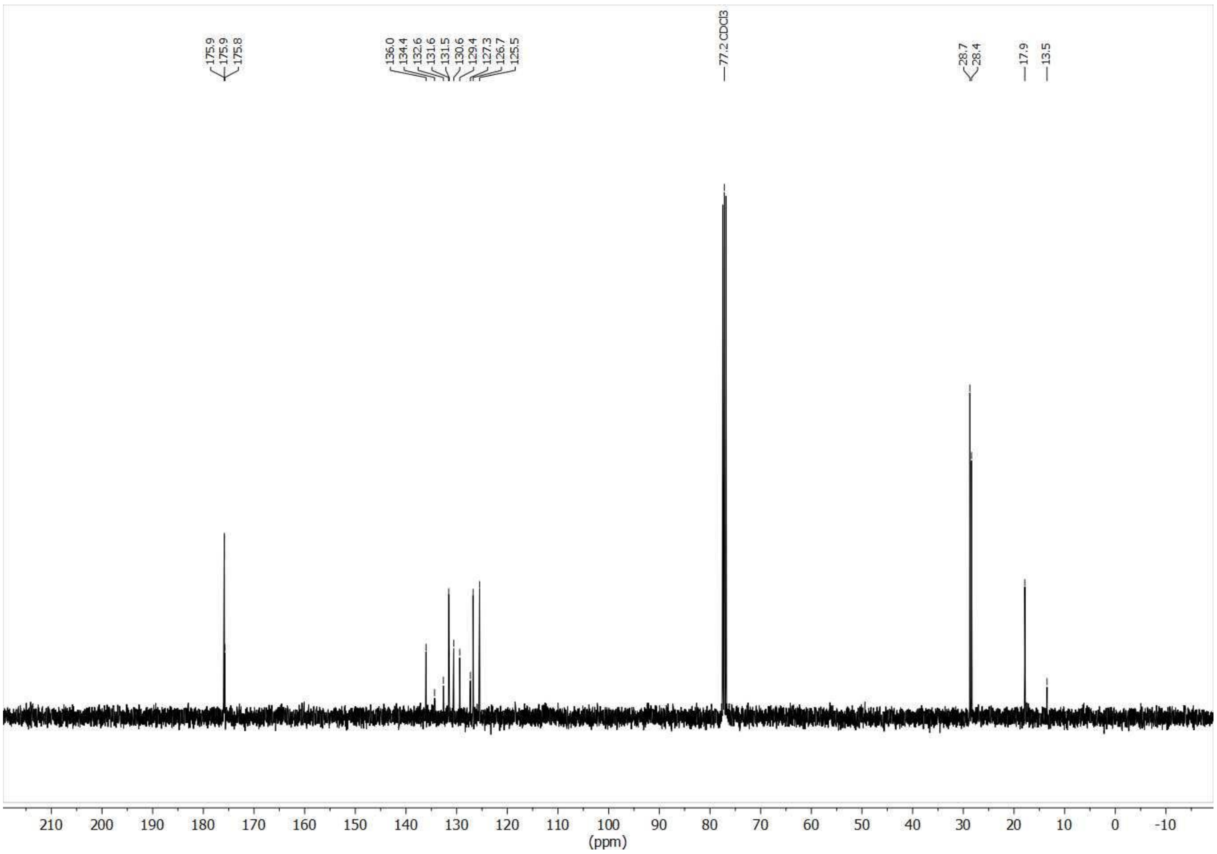


Flexible PU foam (10.0 g) and succinic acid (4.90 g, 41.5 mmol, 2.1 equiv.) were added to a 250 mL three necked round-bottom flask equipped with a magnet. The flask was sealed with septa and heated to 220 °C for 4 h under a continuous N_2 stream. After cooling to room temperature, a brown hard solid was obtained. Cyclohexane (150 mL) was added and the suspension was stirred overnight. The resulting solids were filtered, washed thoroughly with cyclohexane, crushed to a fine powder in a mortar followed by another wash with cyclohexane, and finally dried under reduced pressure, resulting in **PU-HS1** (5.36 g, 18.7 mmol, 99%) as a pale brown solid. The filtrate was transferred to a round-bottom flask and concentrated under reduced pressure, affording the polyol (6.28 g, 98%) as a light brown liquid.

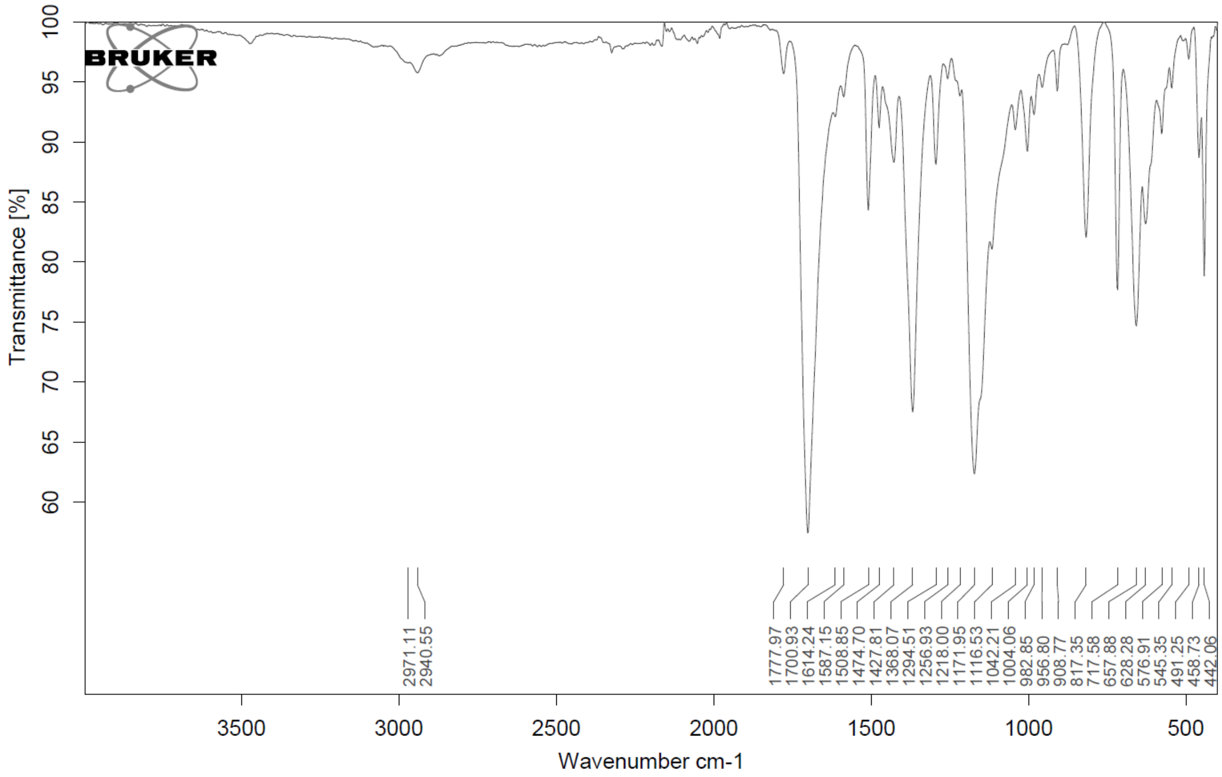
PU-HS1: ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H 7.43–7.36 (m, 2H), 7.20–7.18 (m, 1H), 2.91–2.84 (m, 8H), 2.17 (s), 1.89 (s). **^{13}C-NMR (101 MHz, $CDCl_3$)** δ_C 175.8, 175.8, 175.7, 136.0, 134.3, 132.6, 131.6, 131.5, 130.6, 129.4, 127.3, 126.7, 125.5, 28.7, 28.4, 17.9, 13.5. **IR (ATR)** ν (cm^{-1}): 2971–2941 (sp^3 C–H, stretch), 1701 (C=O, stretch). **HRMS (ESI+)**: m/z calcd. for $C_{15}H_{14}N_2O_4$ $[M+H]^+$: 287.1026, found 287.1030.

NMR Spectra of PU-HS1 (Succinic Acid)

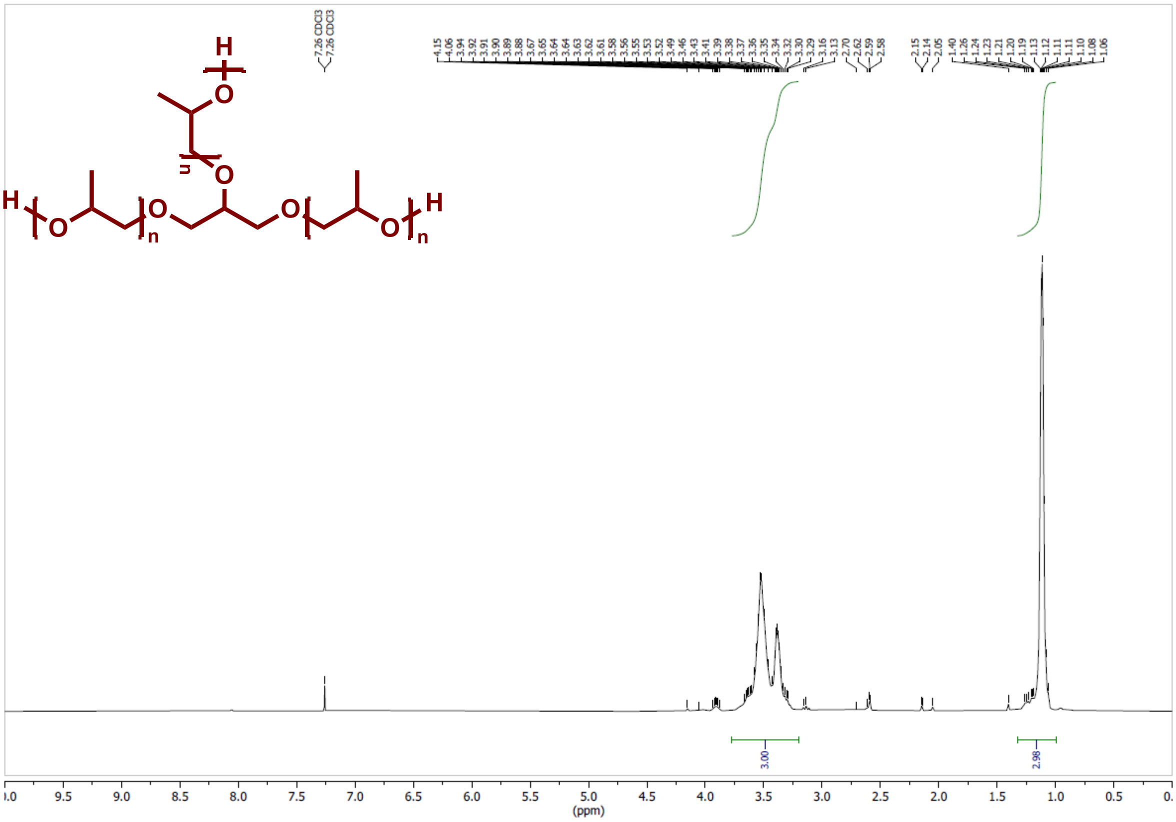


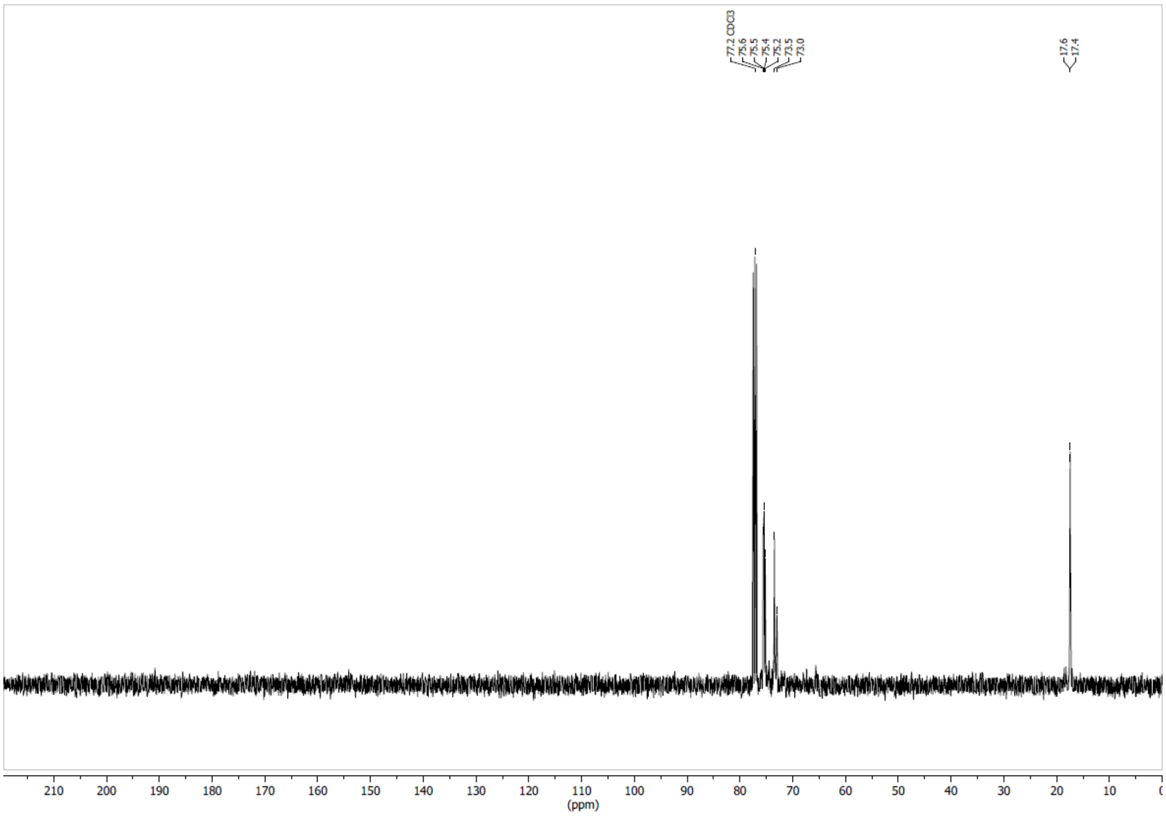


FT-IR Spectrum of PU-HS1 (Succinic Acid)

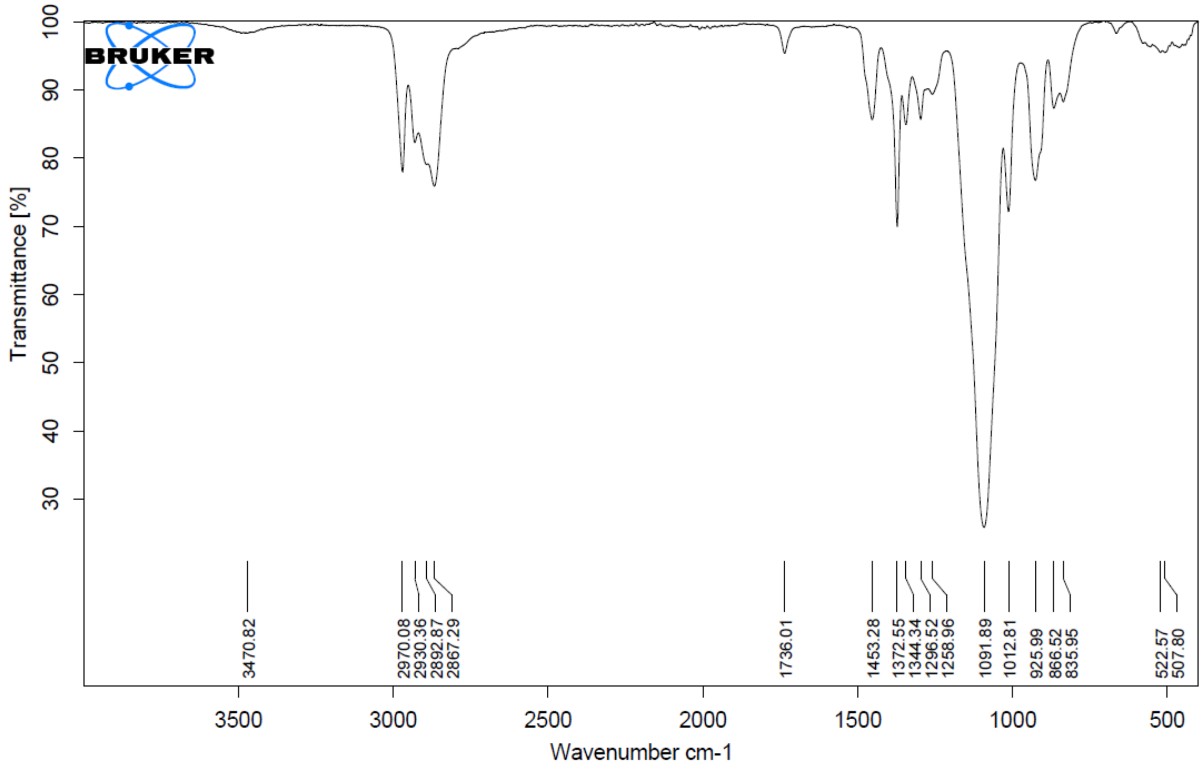


NMR Spectra of Polyol (Succinic Acid)

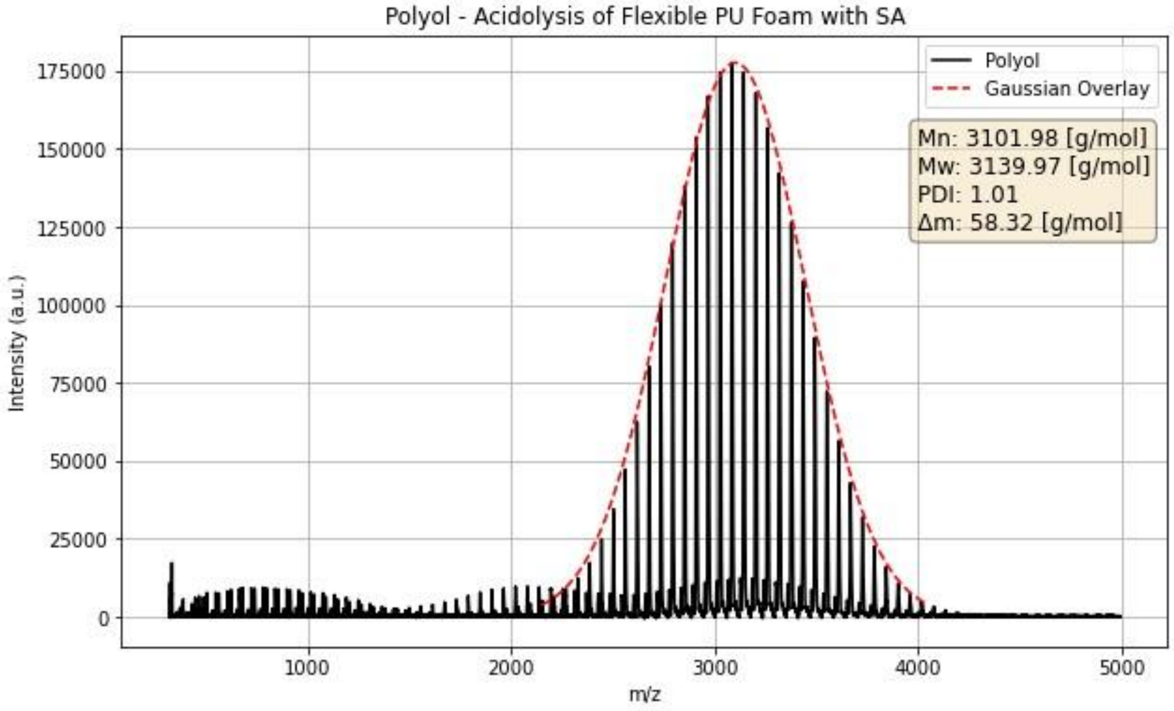




FT-IR Spectrum of Polyol (Succinic Acid)



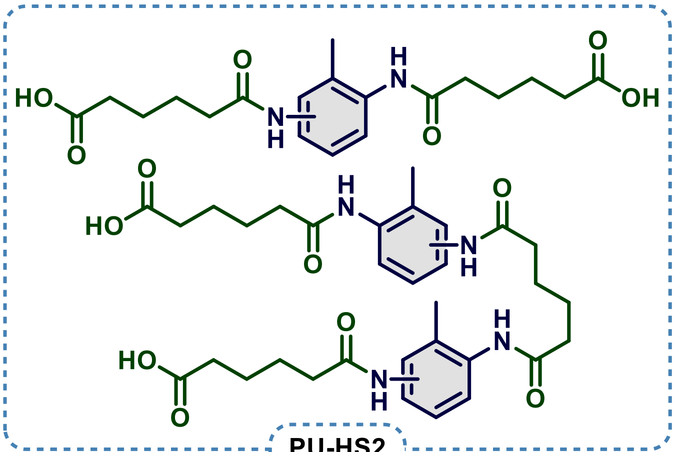
MALDI-TOF Spectrum of Polyol (Succinic Acid)



SI-5.3.2. Acidolysis Using Succinic Acid for Water and Succinic Acid Determination

The hard segment was prepared as described in **SI-5.3.1.** where the acidolysis setup was equipped with a collection flask, which resulted in a mixture of water (0.66 g, 92%) and succinic acid (10.5 mg, determined by ^{1}H-NMR with MeCN as internal standard). The obtained hard segment was further analysed for traces of succinic acid by washing with water, however, no succinic acid was observed.

SI-5.4. Synthesis of PU-HS2 – Acidolysis Using Adipic Acid

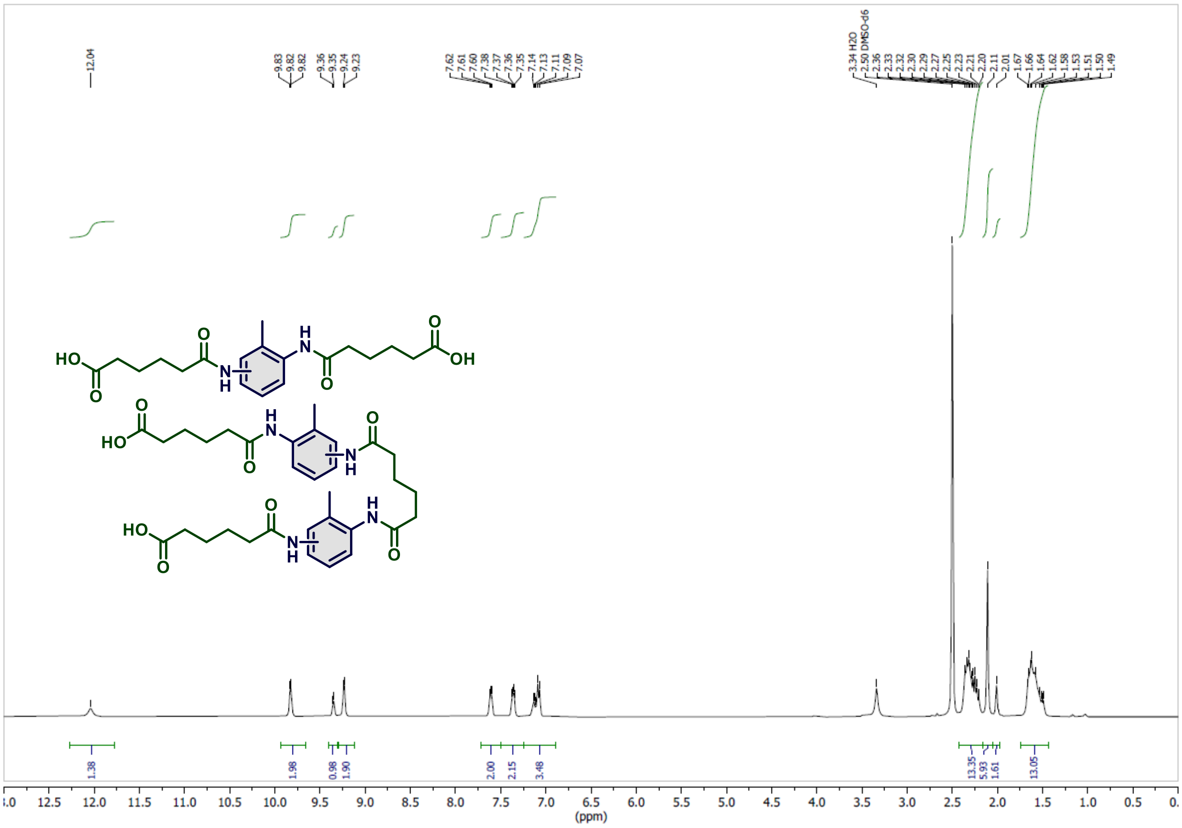

PU-HS2

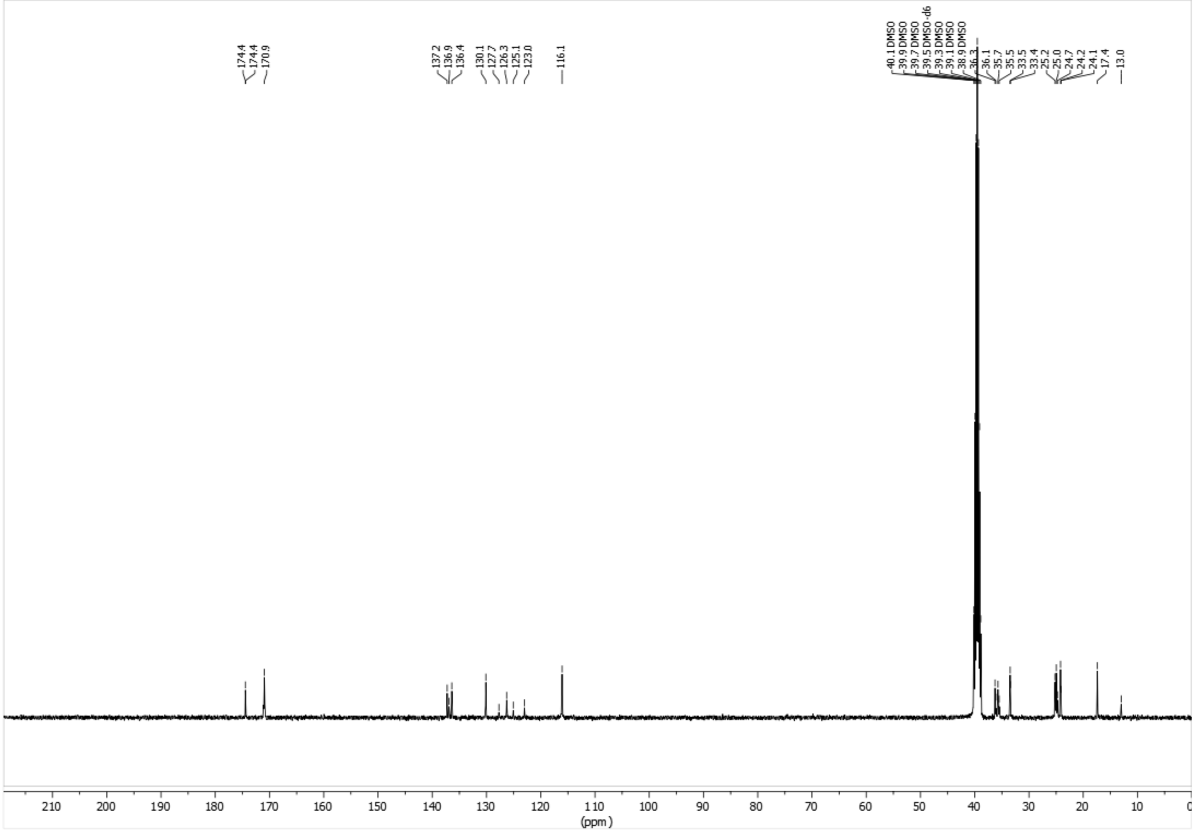
Flexible PU foam (10.0 g) and adipic acid (6.10 g, 41.8 mmol, 2.1 equiv.) were added to a 250 mL three necked round-bottom flask equipped with a magnet. The flask was sealed with septa and heated to 220 °C for 4 h, under a continuous N_2 stream. After cooling to room temperature, a brown hard solid was obtained, which was mixed with EtOAc (150 mL) and left to stir overnight. The resulting solids were filtered, washed thoroughly with EtOAc, crushed to a fine powder in a mortar followed by another wash with EtOAc, and finally dried under reduced pressure, resulting in **PU-HS2** (5.78 g, 92%*) as an off-white solid. The filtrate was transferred to a round-bottom flask and concentrated under reduced pressure, affording the polyol (8.56 g) as an opaque white liquid.

PU-HS2: IR (ATR) ν (cm^{-1}): 3255 (broad, O–H, stretch), 3152–3034 (sp^2 C–H, stretch) 2932–2866 (sp^3 C–H, stretch), 1652 (C=O, stretch). **HRMS (ESI+)**: m/z calcd. for $C_{19}H_{26}N_2O_6$ [M+H]$^+$: 379.1864, found 379.1863 and $C_{32}H_{42}N_4O_8$ [M+H]$^+$: 611.3075, found 611.3074.

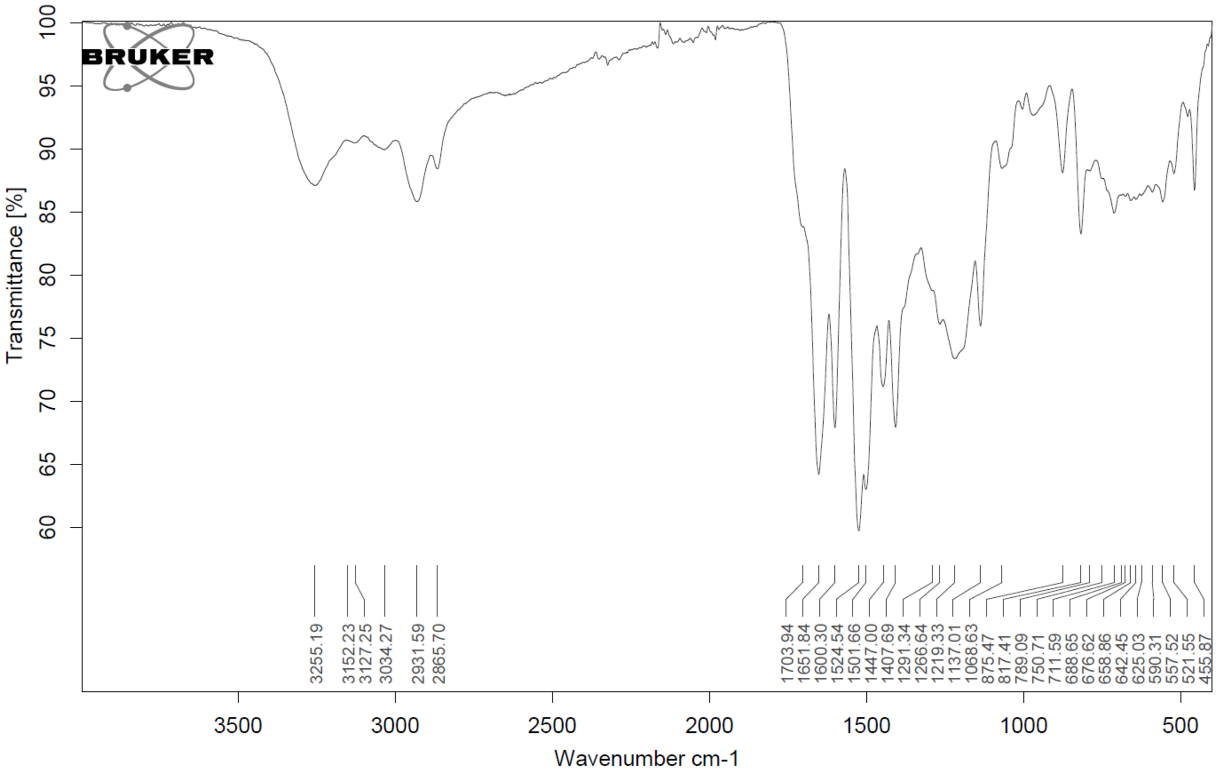
*The 92% yield was based on the ratio obtained from **Model 2** (0.35:0.65) between the constituents of **PU-HS2**. This assumption was made due to overlapping signals in the ^{1}H-NMR spectrum of **PU-HS2**.

NMR Spectra of PU-HS2 (Adipic Acid)

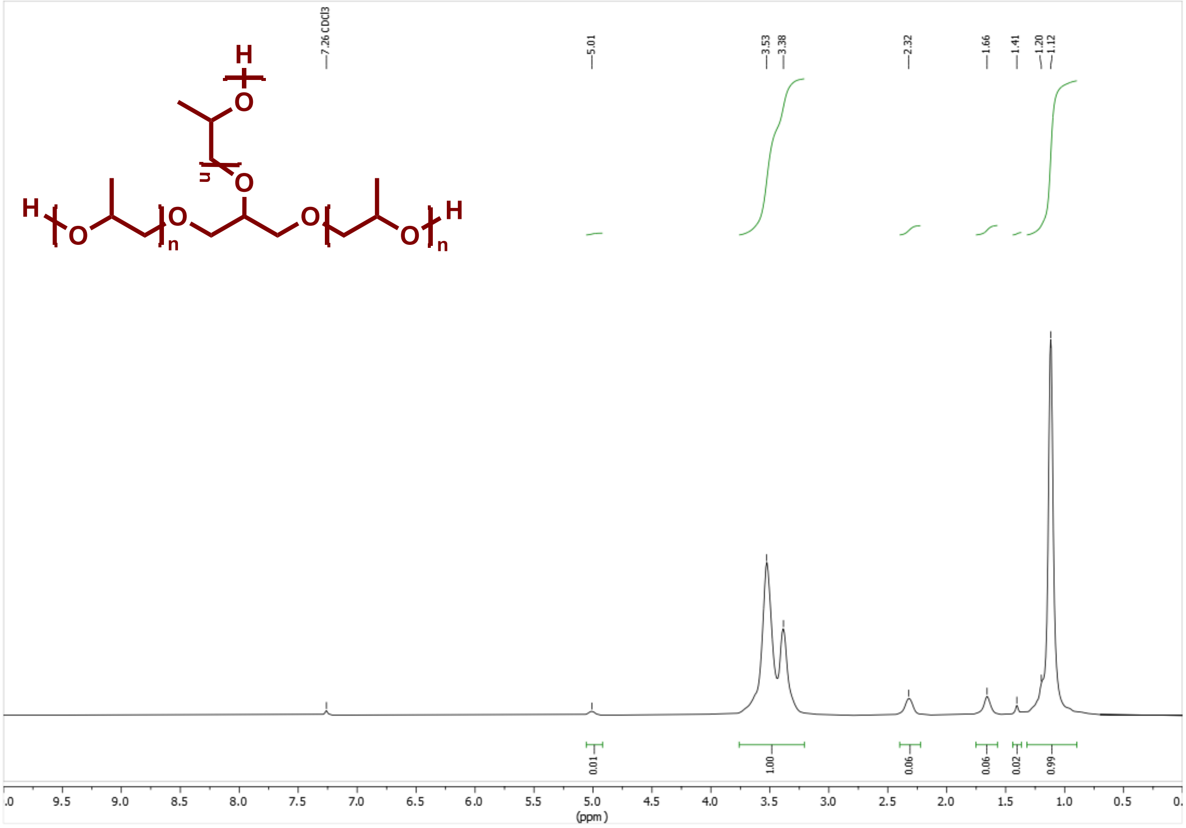


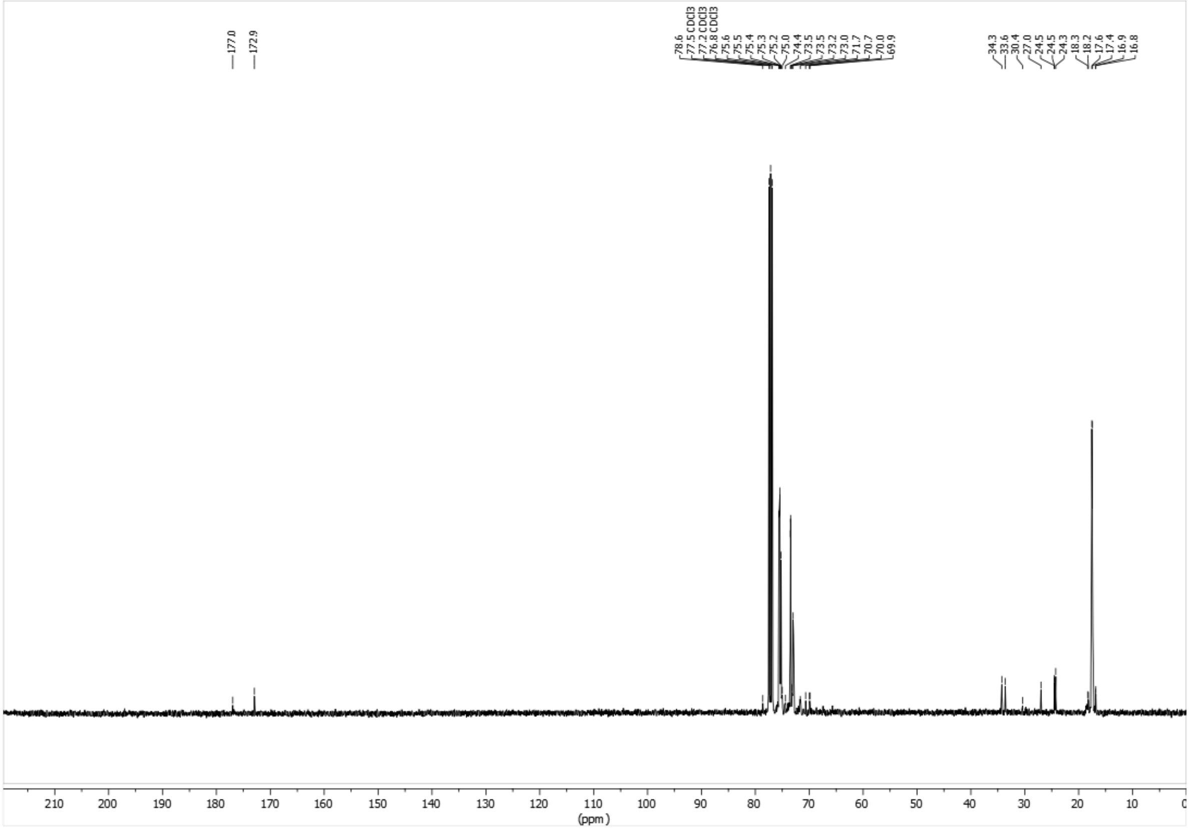


FT-IR Spectrum of PU-HS2 (Adipic Acid)

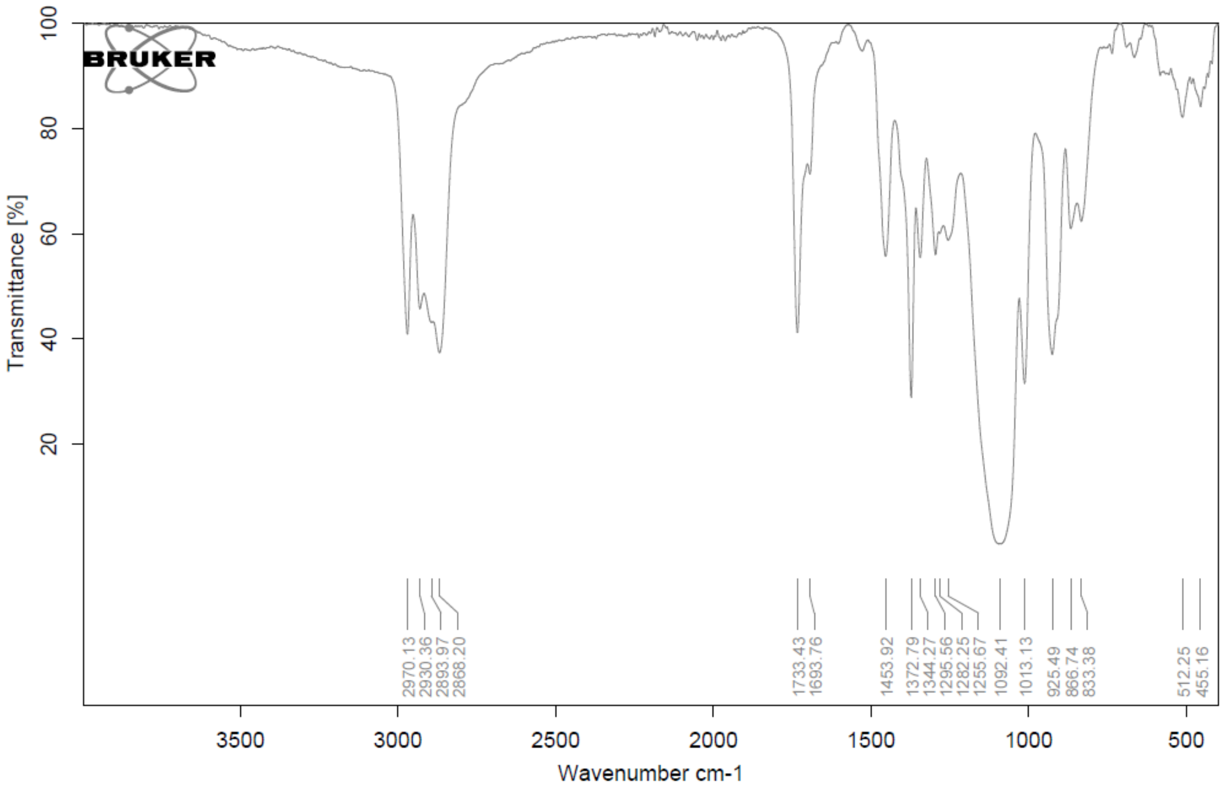


NMR Spectra of Polyol (Adipic Acid)

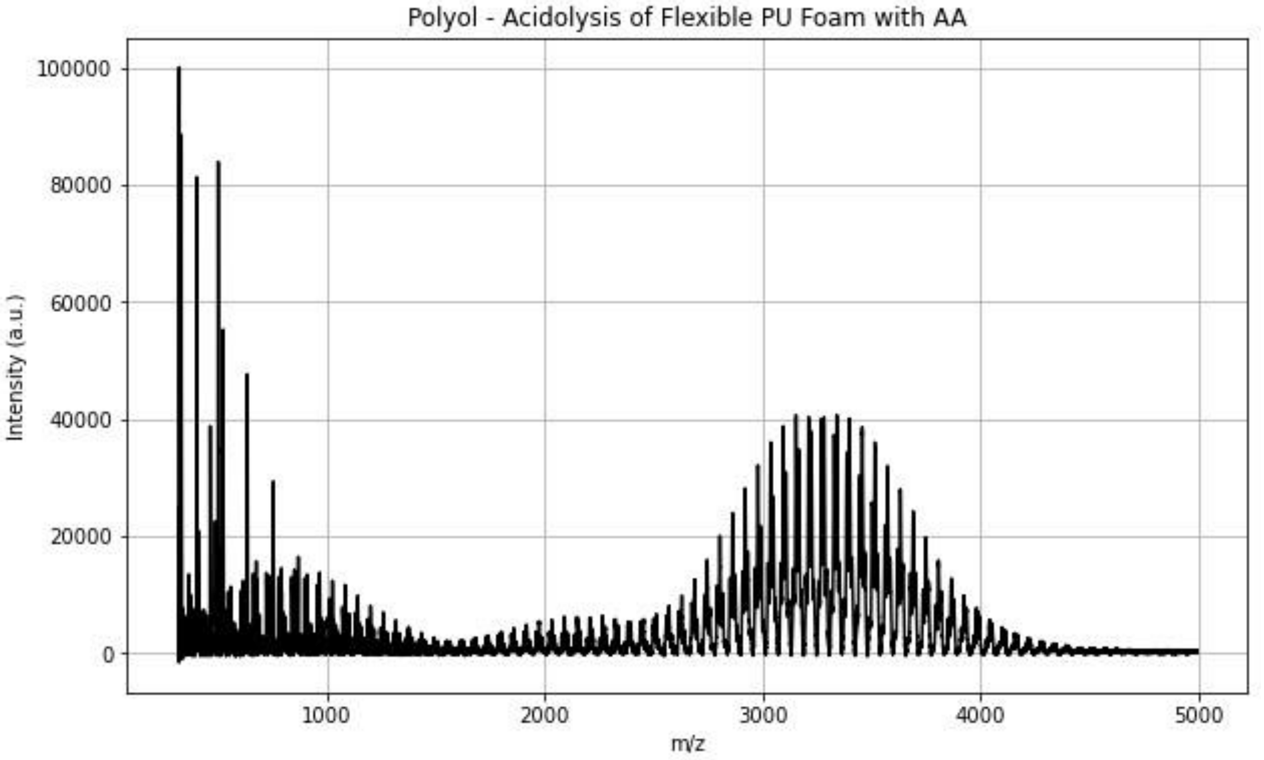




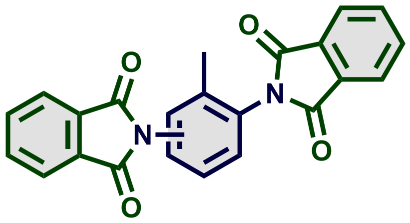
FT-IR Spectrum of Polyol PU-HS2 (Adipic Acid)



MALDI-TOF Spectrum of Polyol (Adipic Acid)



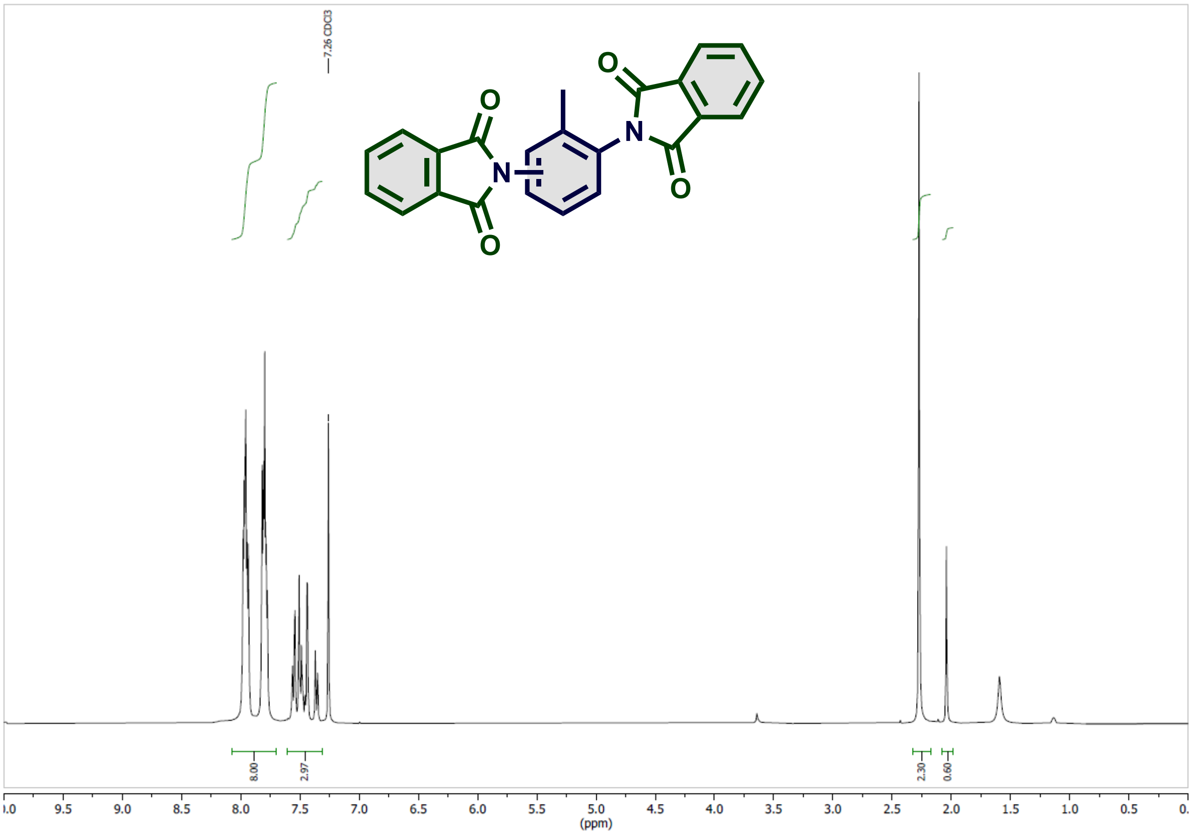
SI-5.5. Synthesis of PU-HS3 – Acidolysis Using Phthalic Acid

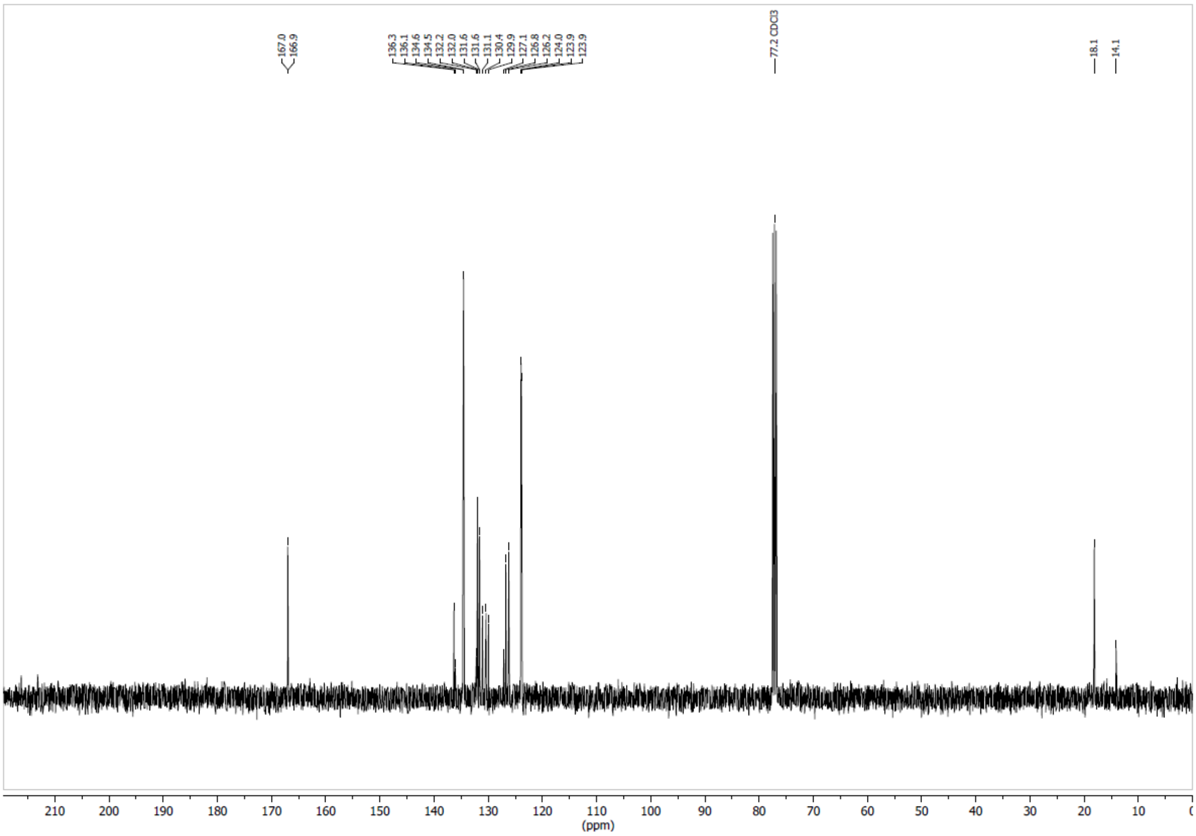


Flexible PU foam (10.0 g) and phthalic acid (6.91 g, 41.6 mmol, 2.1 equiv.) were added to a 250 mL three necked round-bottom flask equipped with a magnet. The flask was sealed with septa and heated to 220 °C for 4 h, under a continuous N_2 stream. After cooling to room temperature, a brown hard solid was obtained, which was mixed with EtOAc (150 mL) and left to stir overnight. The resulting solids were filtered and washed thoroughly with EtOAc, crushed to a fine powder in a mortar followed by another wash with EtOAc, and finally dried under reduced pressure, affording the **PU-HS3** (4.77 g, 12.5 mmol, 66%) as an off-white solid. The filtrate was transferred to a round-bottom flask and concentrated under reduced pressure, resulting in polyol (5.06 g) as a yellow liquid.

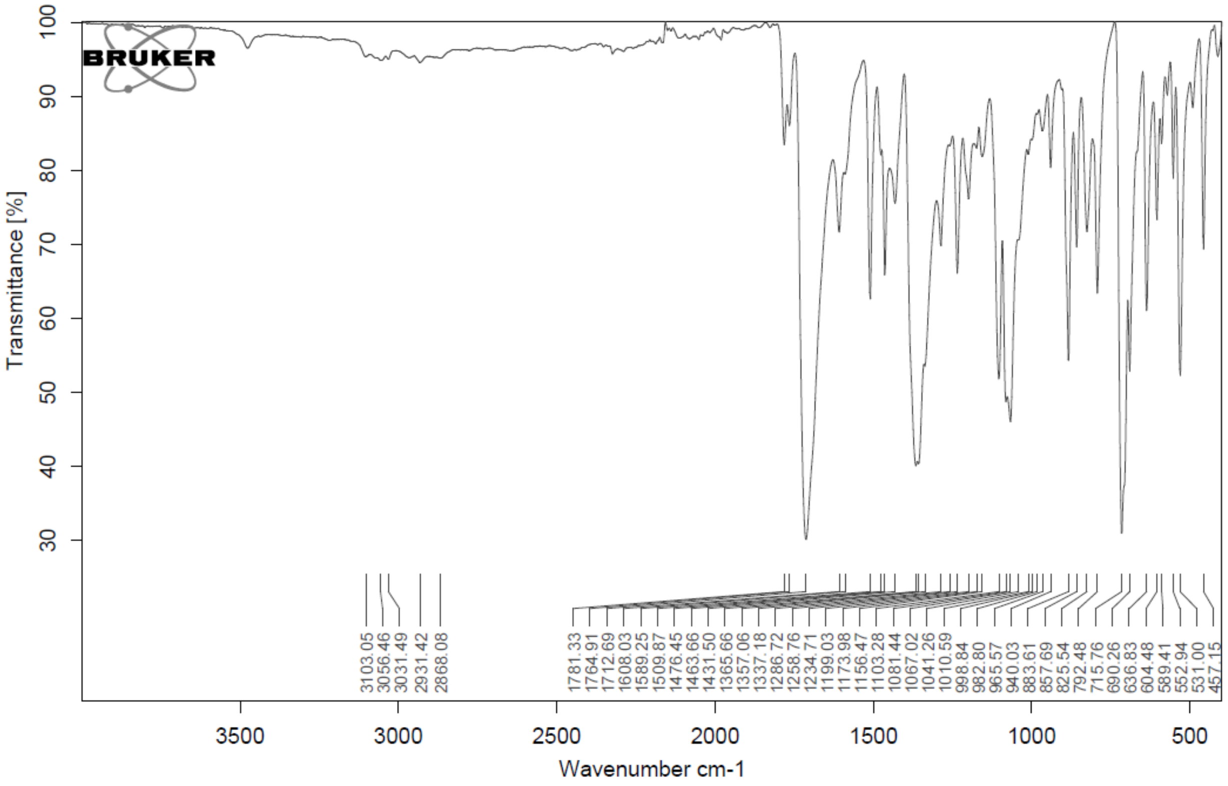
PU-HS3: ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H 7.98–7.78 (m, 8H), 7.57–7.35 (m, 3H), 2.27 (s), 2.04 (s). **^{13}C-NMR (101 MHz, $CDCl_3$)** δ_C 167.0, 166.9, 136.3, 136.1, 134.6, 134.5, 132.2, 132.0, 131.6, 131.6, 131.1, 130.4, 129.9, 127.1, 126.8, 126.2, 124.0, 123.9, 123.9, 18.1, 14.1. **IR (ATR)** ν (cm^{-1}): 3103–3031 (sp^2 C–H, stretch), 2931–2868 (sp^3 C–H, stretch), 1713 (C=O, stretch). **HRMS (ESI+)**: m/z calcd. for $C_{23}H_{14}N_2O_4$ $[M+H]^+$: 383.1026, found 383.1028.

NMR Spectra of PU-HS3 (Phthalic Acid)

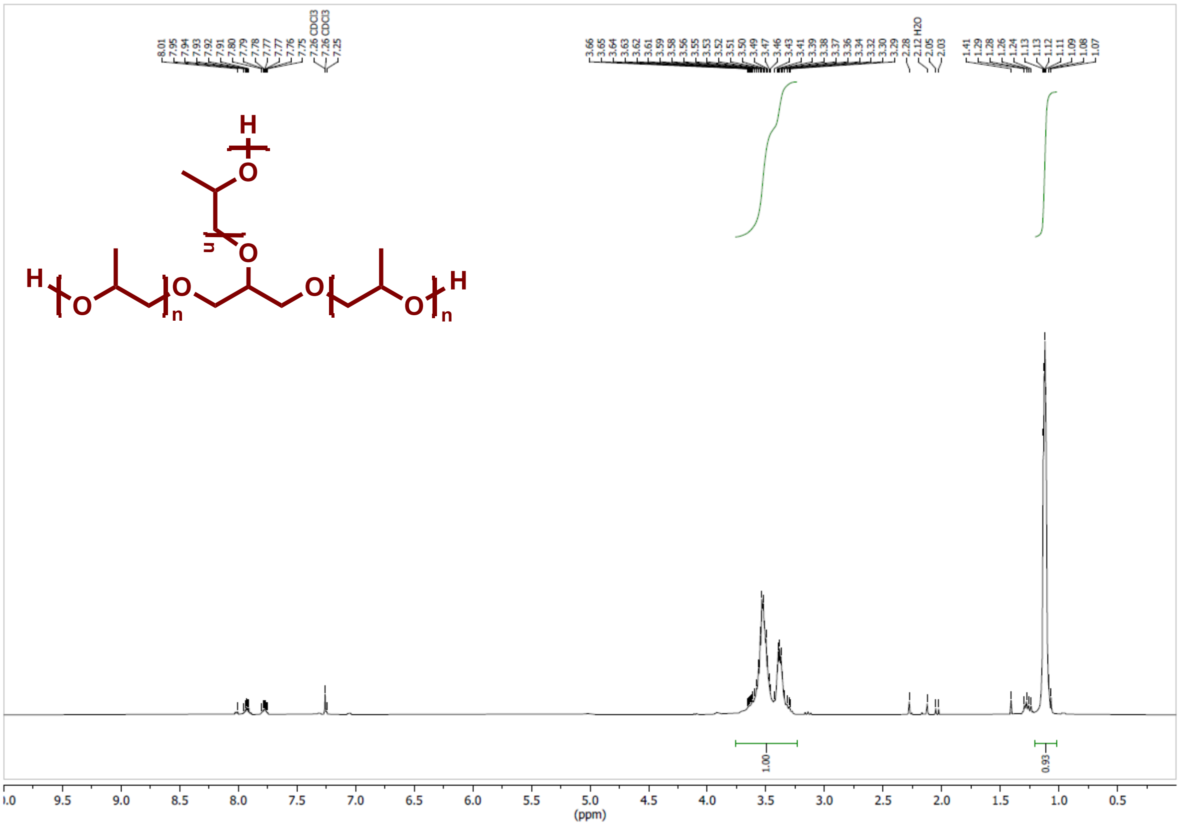


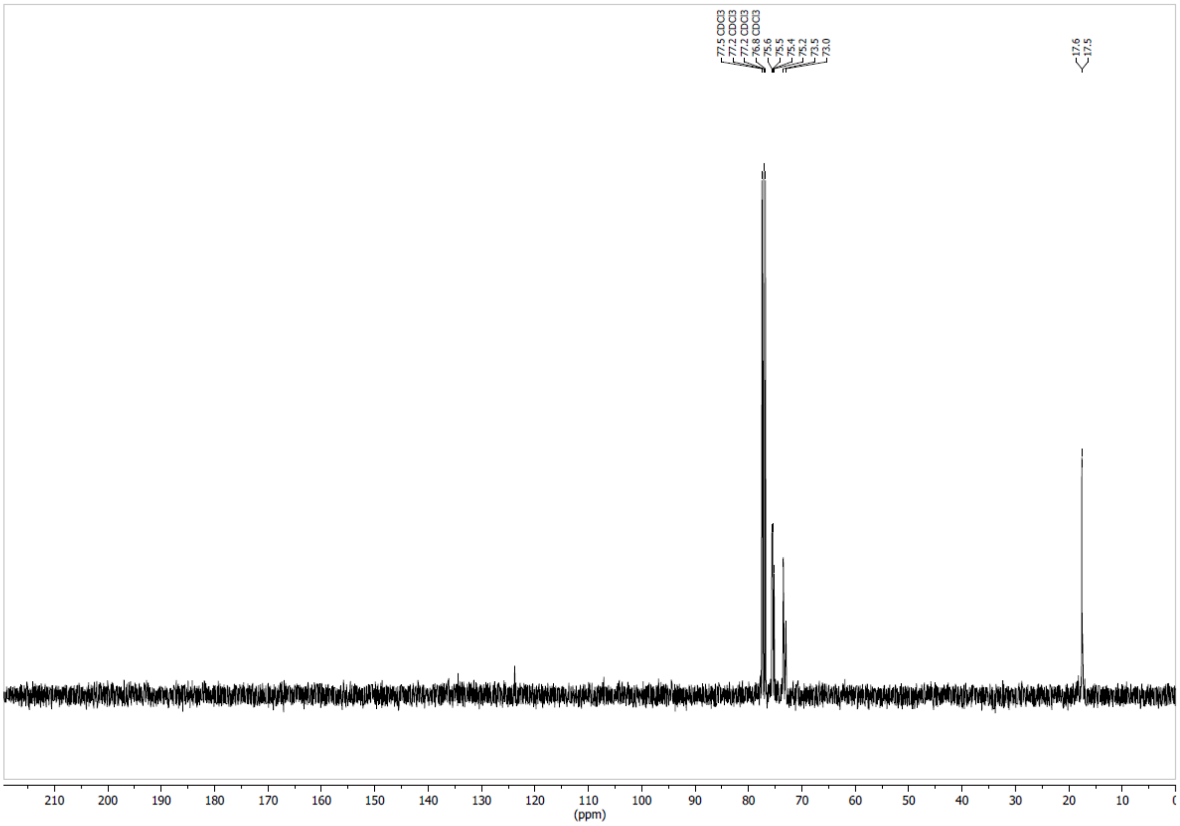


FT-IR Spectrum of PU-HS3 (Phthalic Acid)

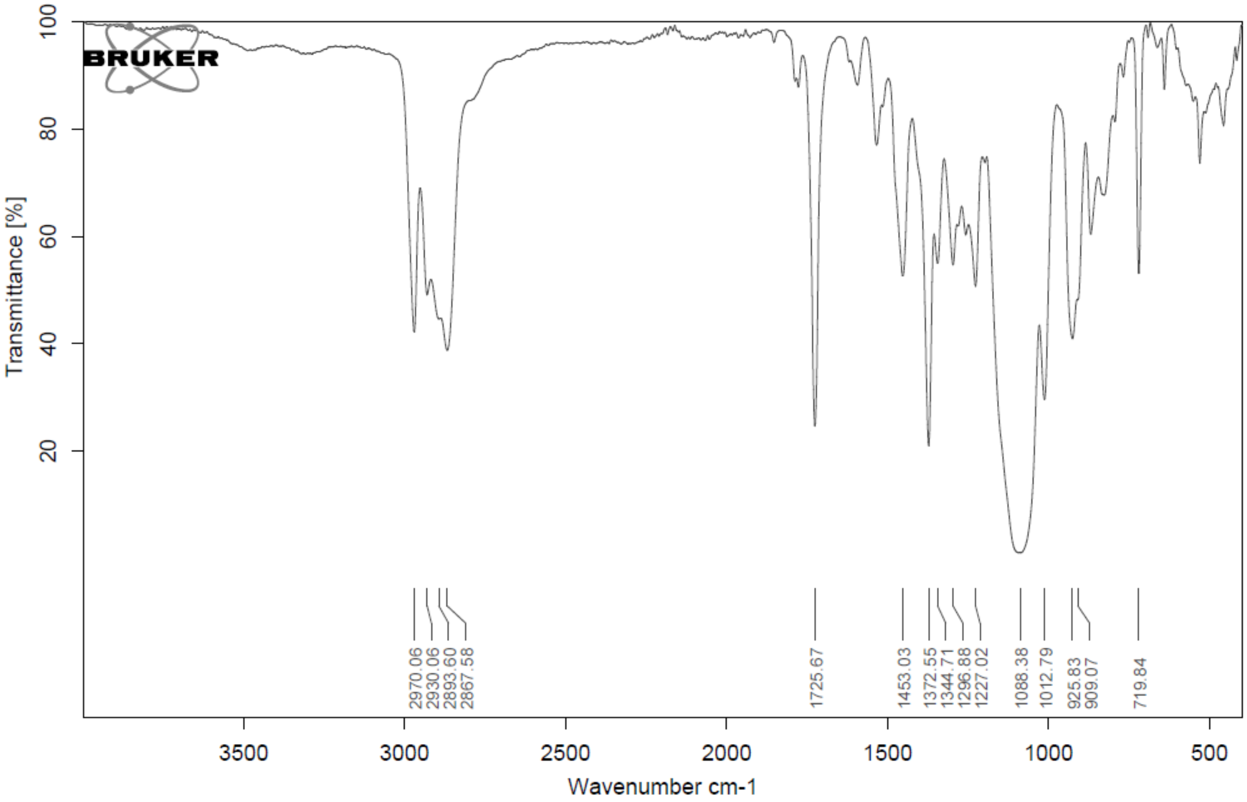


NMR Spectra of Polyol (Phthalic Acid)

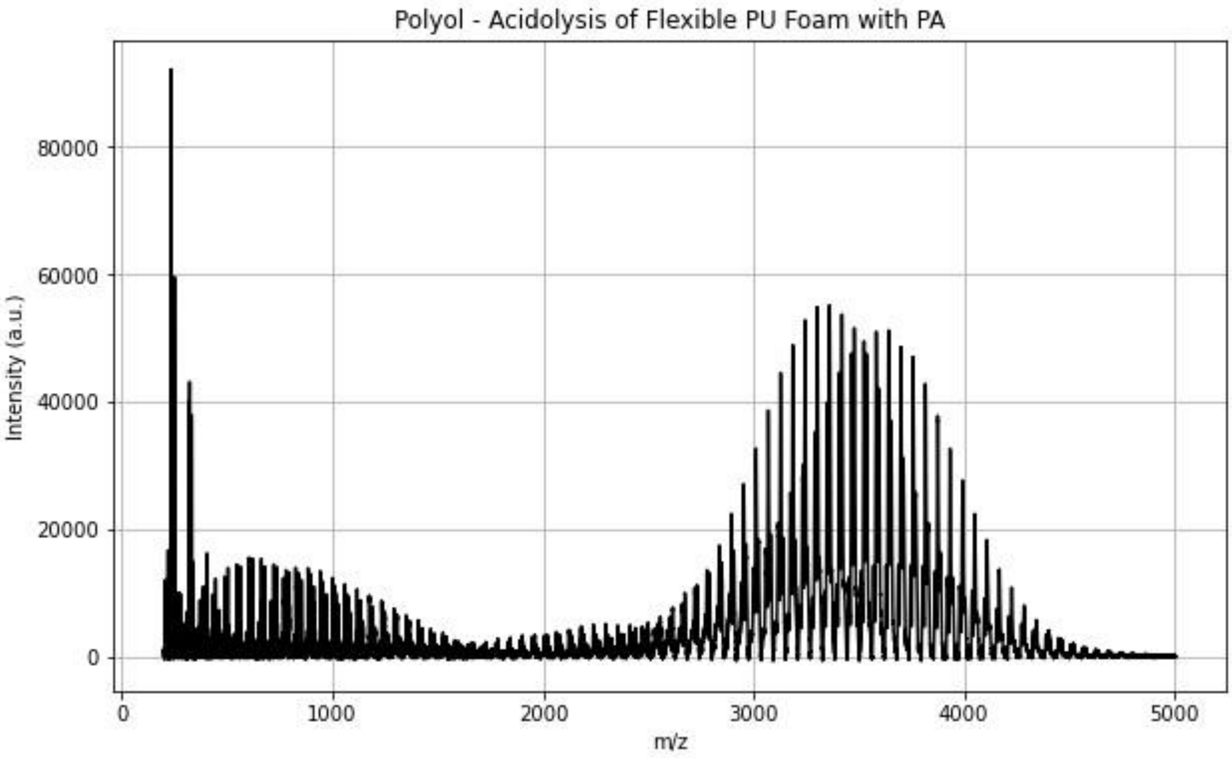




FT-IR Spectrum of Polyol (Phthalic Acid)



MALDI-TOF Spectrum of Polyol (Phthalic Acid)



SI-6. Acidolysis of Rigid Polyurethane Foam

SI-6.1. Rigid PU Foam Recipe and Calculation of Acid Equivalents for Acidolysis

The rigid foam was formulated from the following recipe:

Rigid PU Foam	wt%
(Sucrose + Propylene glycol + Ethylene glycol) + Propylene oxide	50
Glycerol + Propylene oxide	50
N,*N*-Dimethylcyclohexyl amine	1.2
Water	4.0
Polyalkyleneoxide methylsiloxane copolymer	1.5
Desmodur® 44V20L	140.7

The foam was shredded by hand into smaller pieces before being subjected to chemical depolymerisation via the acidolysis process using succinic acid. Calculations for amount of succinic acid (SA) used are shown below.

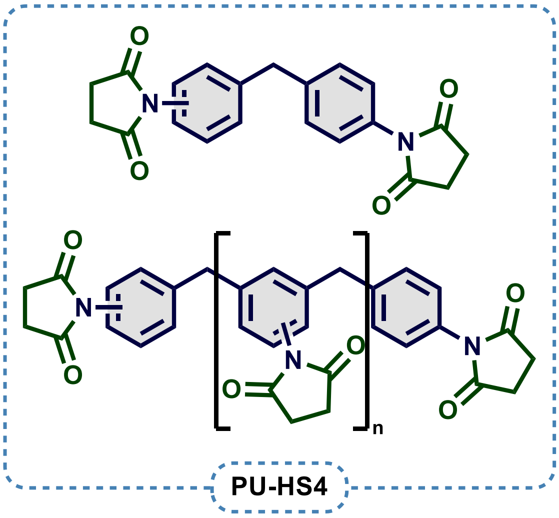
$$\mathrm{wt\%_{MDI}} = \frac{140.7}{50 + 50 + 1.2 + 4.0 + 1.5 + 140.7} = 56.9\%$$

$$\mathrm{m_{MDI}} = \mathrm{m_{PU}} \cdot \mathrm{wt\%_{MDI}}$$

$$\mathrm{n_{MDI/MDA}} = \frac{\mathrm{m_{MDI}}}{\mathrm{M_{MDI}}}$$

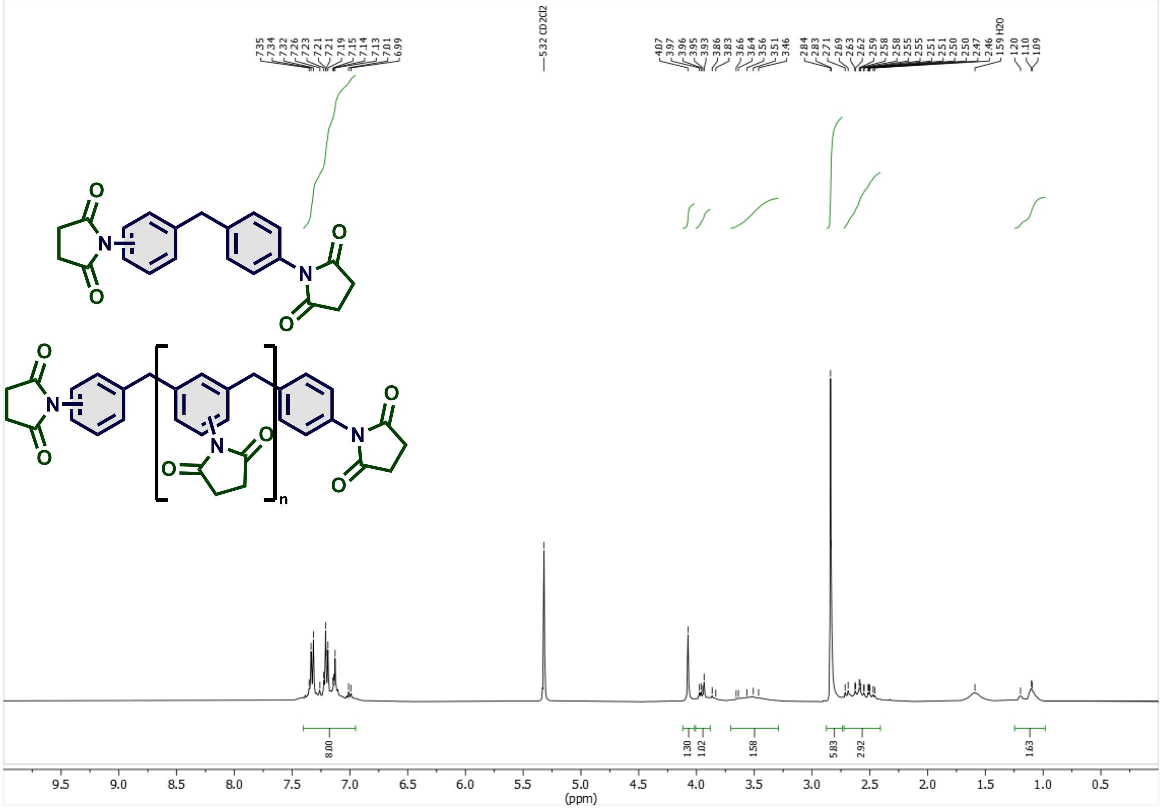
$$\mathrm{n_{SA}} = 2.1 \cdot \mathrm{n_{MDA}}$$

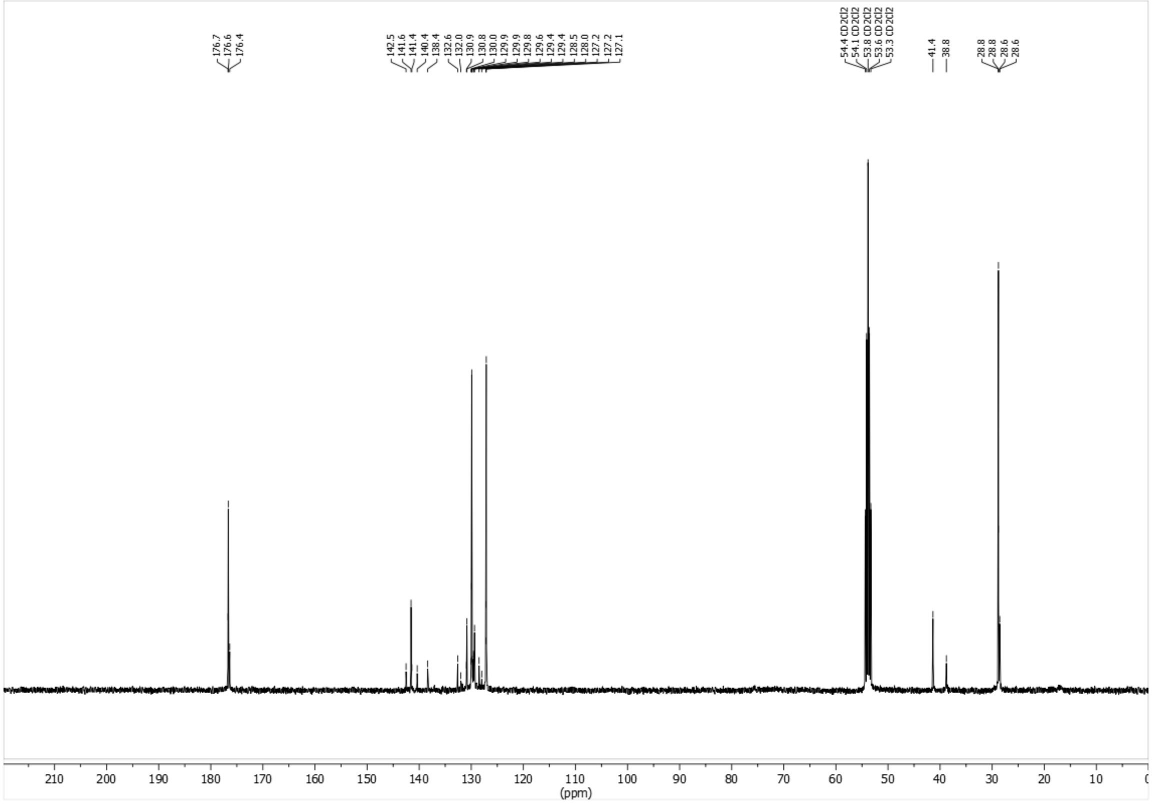
SI-6.2. Synthesis of PU-HS4 – Acidolysis Using Succinic Acid



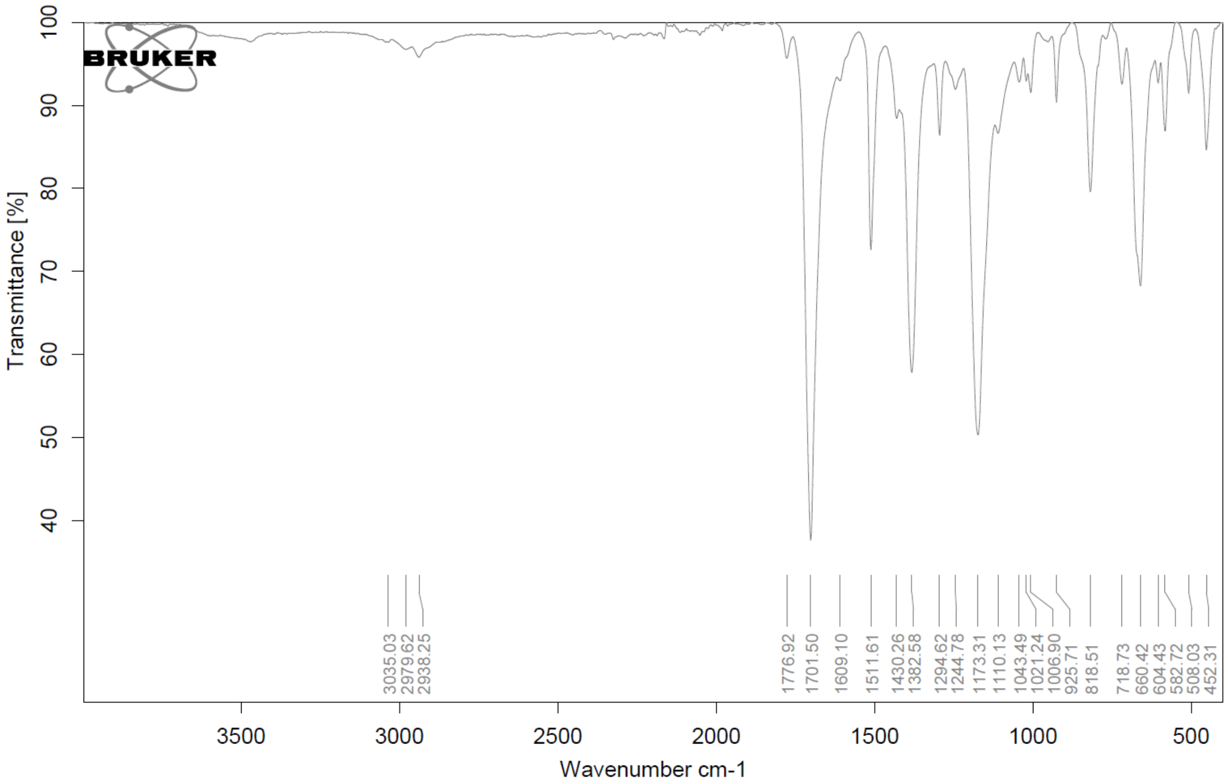
Succinic acid (6.48 g, 54.9 mmol, 2.4 equiv.) was added to a 100 mL three necked round-bottom flask equipped with a magnet. Over the course of an hour, rigid PU foam (10.1 g) was added in portions to the flask at 220 °C. Once the flask consisted of a homogeneous solution, the reaction was left 4 h under a continuous N_2 stream. After cooling to room temperature, a brown hard solid was obtained, which was mixed with Et_2O (150 mL) and left to stir overnight. The resulting solids were filtered, washed thoroughly with Et_2O, crushed to a fine powder in a mortar followed by another wash with Et_2O, and finally dried under reduced pressure, affording **PU-HS 4** (9.04 g) as a pale brown solid. The filtrate was transferred to a round-bottom flask and concentrated under reduced pressure, providing the polyol (2.99 g) as a brown liquid. **PU-HS4: IR (ATR)** ν (cm^{-1}): 3035 (sp^2 C–H, stretch), 2980–2938 (sp^3 C–H, stretch), 1702 (C=O, stretch). **HRMS (ESI+)**: m/z calcd. for $C_{21}H_{18}N_2O_4$ $[M+H]^+$: 363.1339, found 363.1333.

NMR Spectra of PU-HS4 (Succinic Acid)

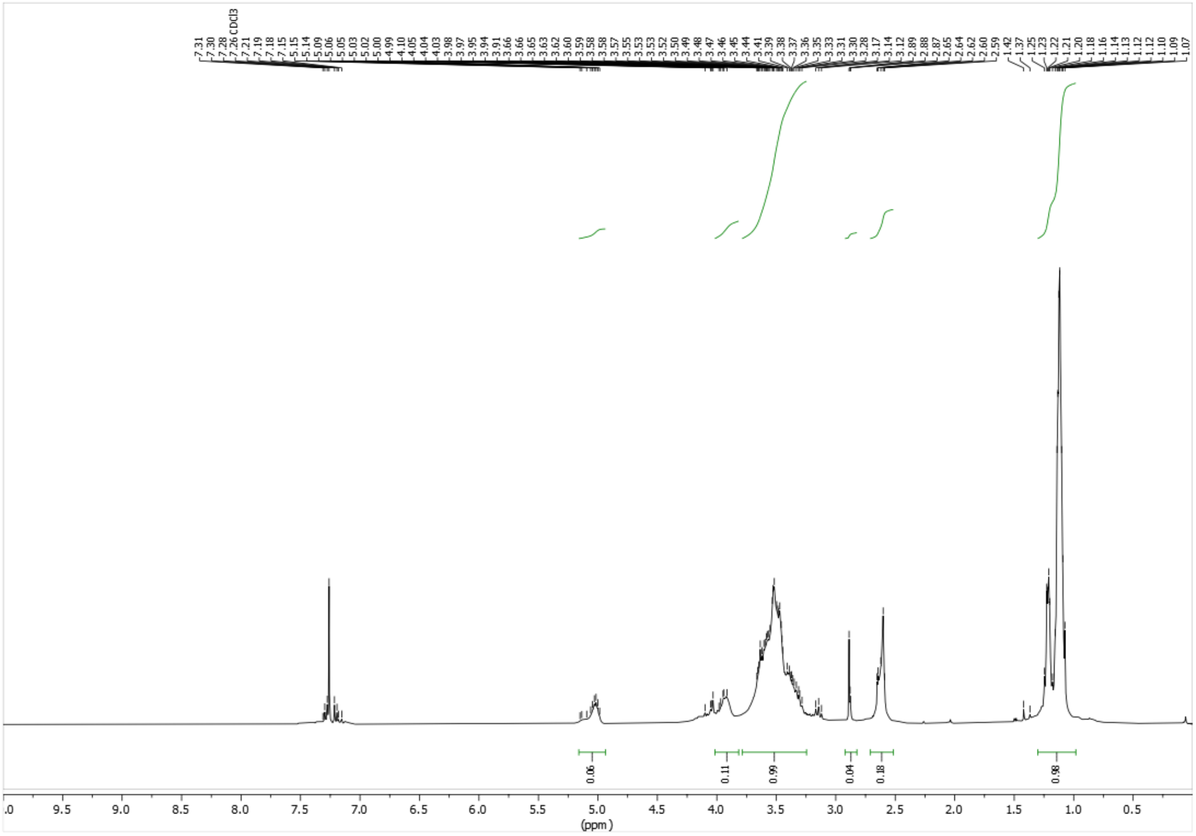


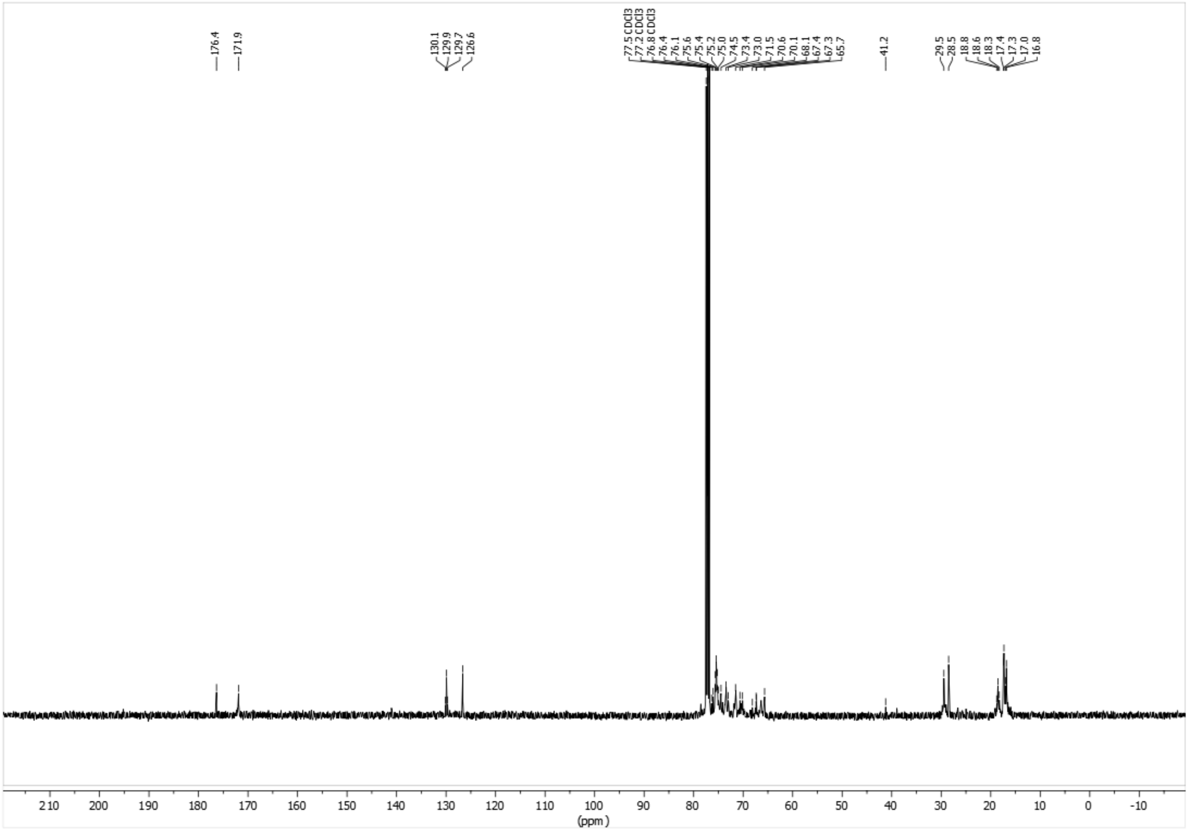


FT-IR Spectrum of PU-HS4 (Succinic Acid)

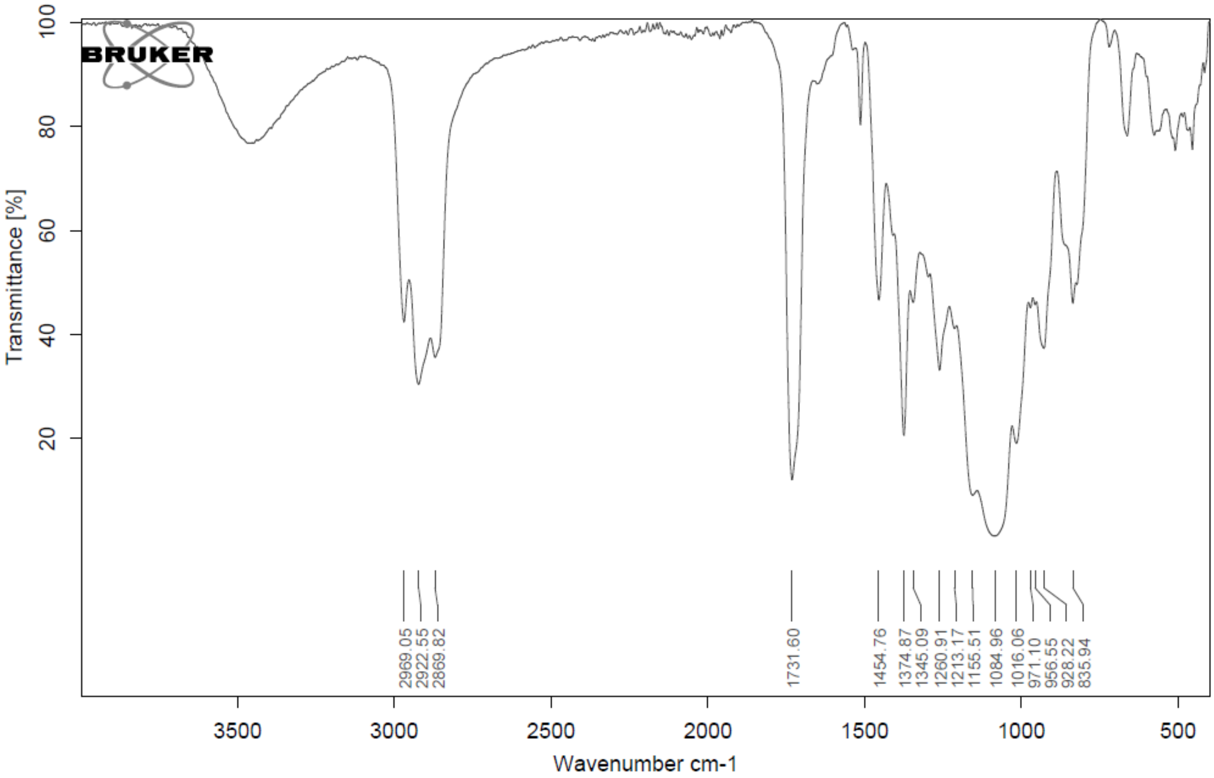


NMR Spectra of Polyol (Succinic Acid)

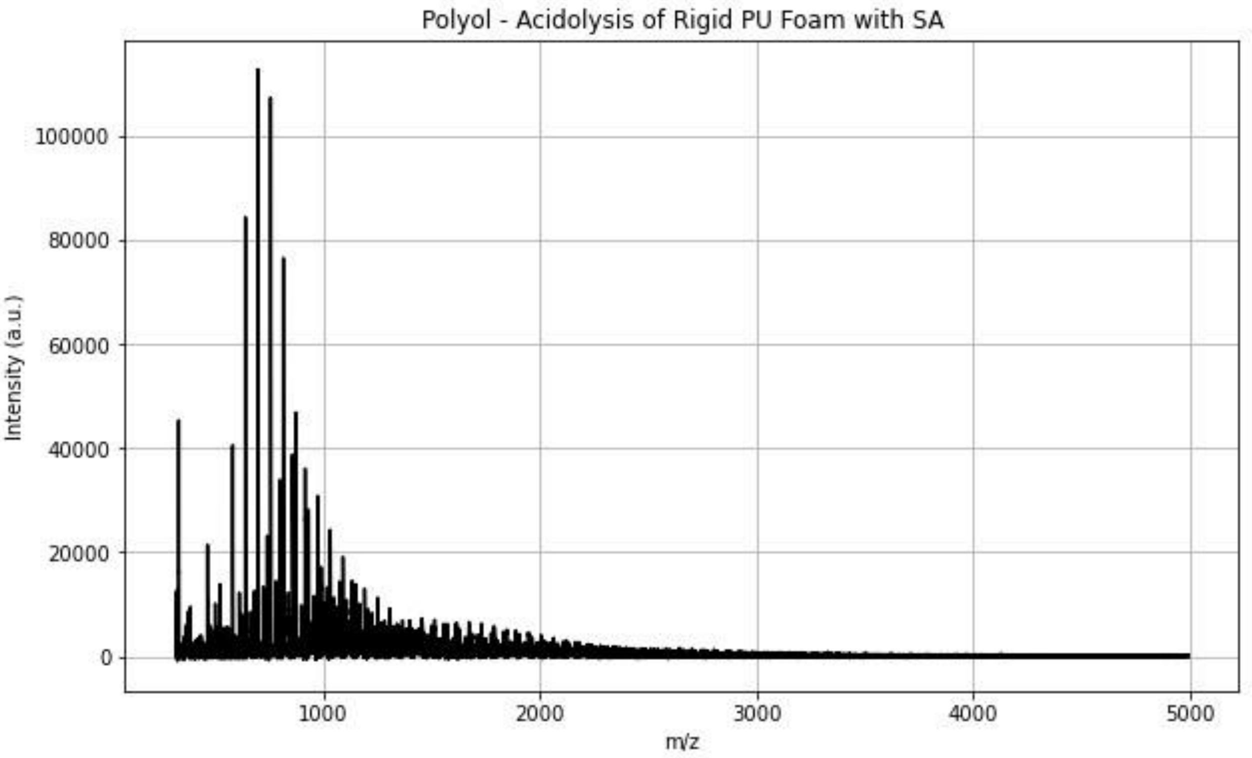




FT-IR Spectrum of Polyol



MALDI-TOF Spectrum of Polyol



SI-7. Combined Acidolysis and Hydrolysis for Valorisation of Aromatic Amines

SI-7.1. Valorisation of Flexible PU Foam using Succinic Acid

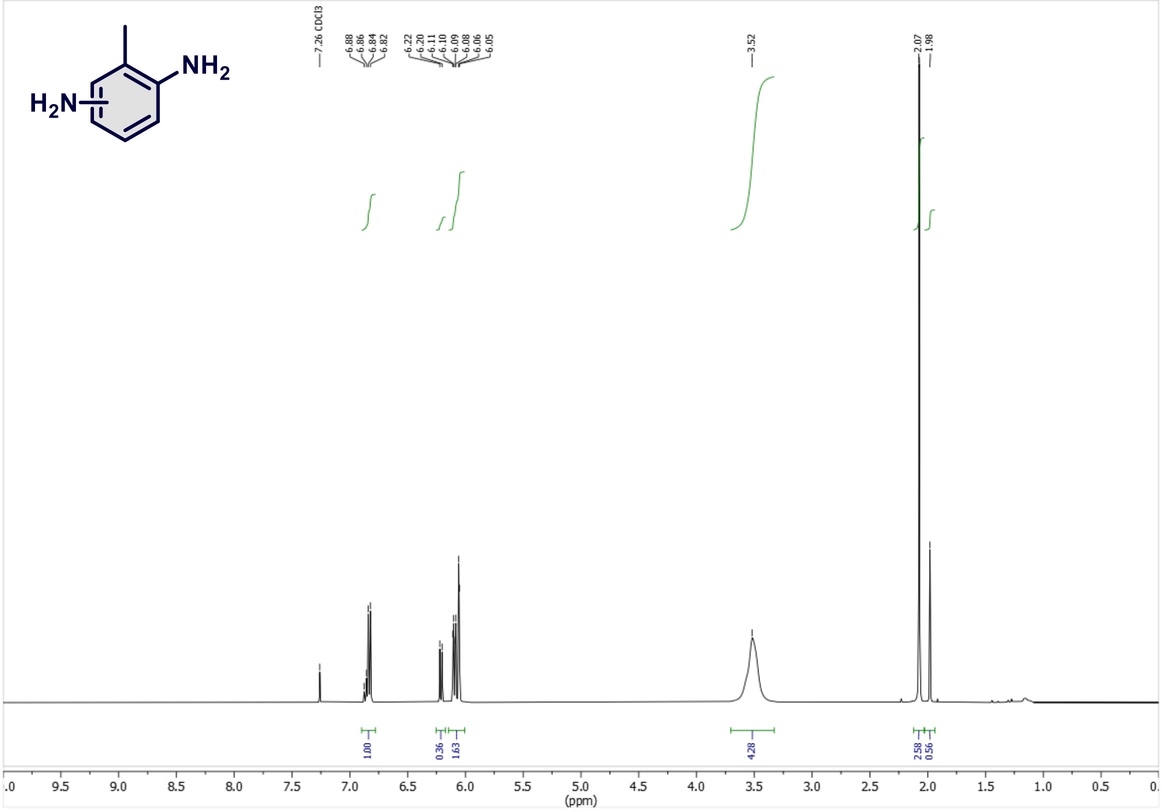
The hard segment was prepared as described in **SI-5.3**, where **PU-HS1** (5.43 g) and polyol (6.50 g) were obtained.

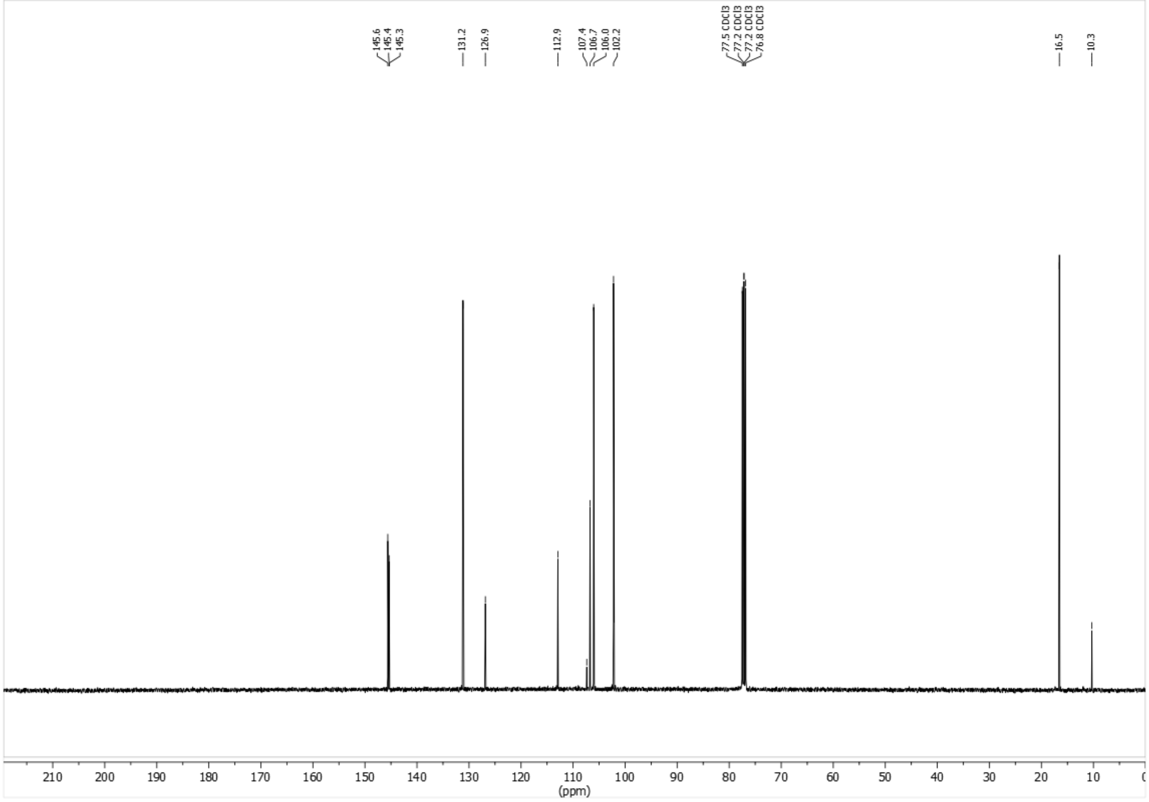
To a 250 mL round-bottom flask fitted with a magnet, **PU-HS1** (5.43 g) and a solution of 2M NaOH (100 mL, aq.) were added. The flask was equipped with a condenser and heated to reflux for 5 h. Following this, EtOAc (100 mL) was added, and the organic phase was separated from the aqueous phase. The aqueous phase was further extracted with EtOAc (5x50 mL), and the combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in EtOAc an filtered through a small silica-plug before solvent was removed under reduced pressure, affording TDA as a dark red solid (2.10 g, 17.2 mmol, 90%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ_H 6.88–6.82 (m, 1H+1H*), 6.22–6.20 (d, *J* = 7.4 Hz, 2H*), 6.11–6.05 (m, 2H), 3.52 (bs, 4H+4H*), 2.07 (s, 3H), 1.98 (s, 3H*).

^{13}C-NMR (101 MHz, $CDCl_3$) δ_C 145.6, 145.4, 145.3* (2C), 131.2, 126.9*, 112.9, 107.4*, 106.7* (2C), 106.0, 102.2, 16.5, 10.3*.

NMR Spectra of TDA fraction from Hydrolysis of PU-HS1



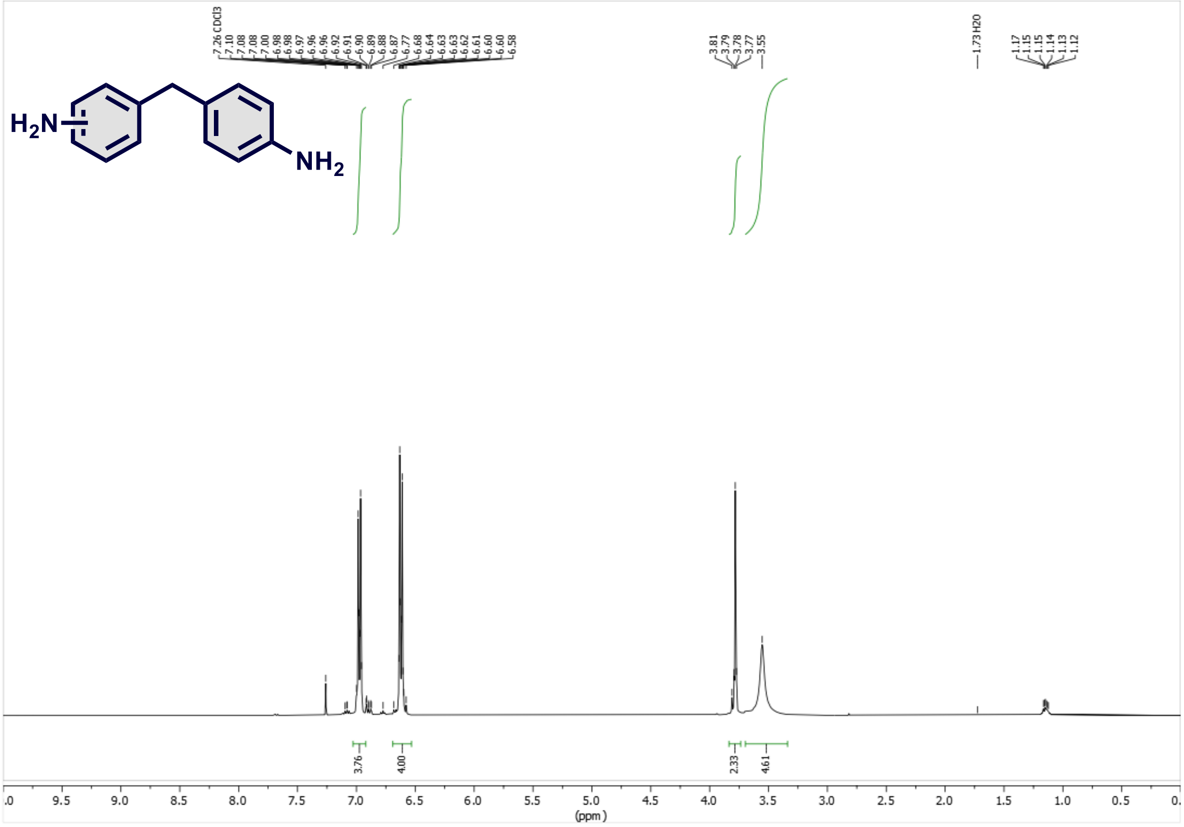


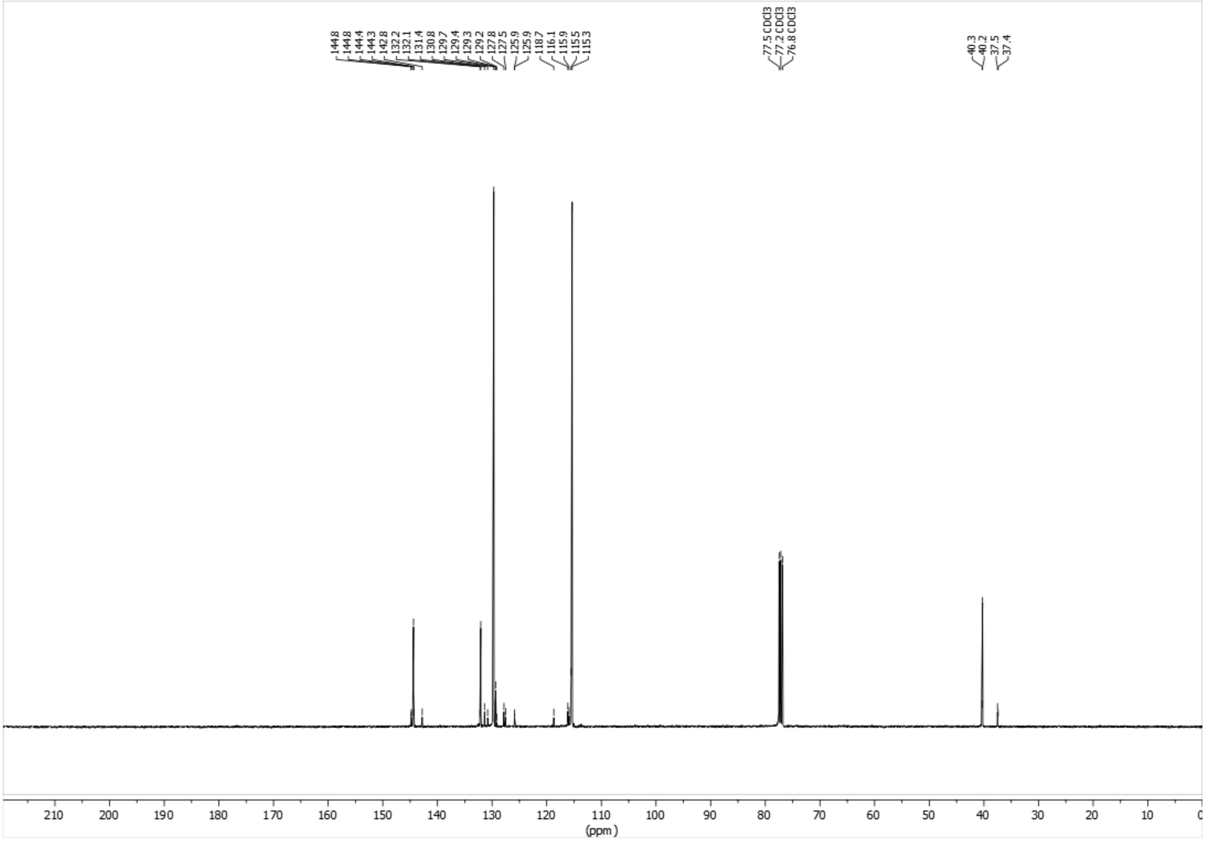
SI-7.2.1 Valorisation of Rigid PU Foam using Succinic Acid

The hard segment was prepared as described in **SI-6-2**, where **PU-HS4** (9.04 g) and polyol (2.99 g) were obtained.

To a 250 mL round-bottom flask fitted with a magnet, **PU-HS4** (9.04 g) and a solution of 2M NaOH (100 mL, aq.) were added. The flask was equipped with a condenser and heated to reflux for 5 h. Following this, EtOAc (100 mL) was added, and the organic phase was separated from the aqueous phase. The aqueous phase was further extracted with EtOAc (5x50 mL), and the combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was dissolved in EtOAc and filtered through a small silica-plug before solvent was removed under reduced pressure, affording 4,4’-MDA with traces of 2,4’-MDA as a red/orange solid (2.26 g, 50%).

NMR Spectra of MDA Fraction from Hydrolysis of PU-HS4



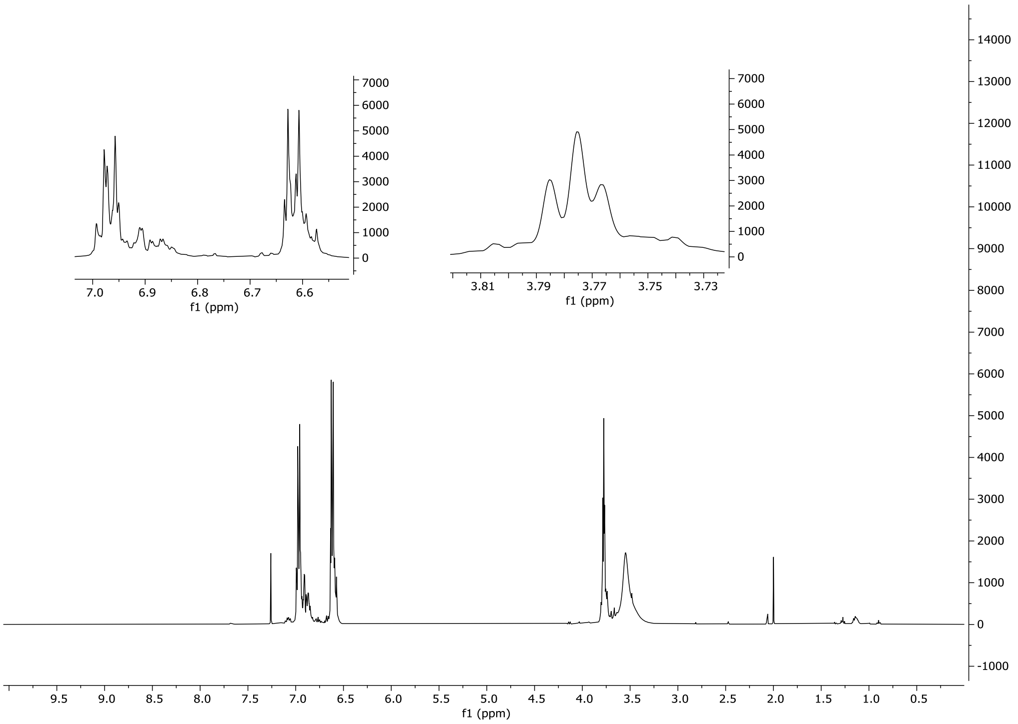


SI-7.2.2. Valorisation of Rigid PU Foam using Succinic Acid under Forcing Conditions

The hard segment was prepared as described in **SI-6-2**.

A Parr high pressure reactor with a Teflon inlay (30 mL) was charged with **PU-HS4** (454.3 mg) and 5 mL 4 M NaOH solution. The reaction mixture was heated to 160 °C and stirred for 20 h after which the reactor was cooled to room temperature. The black material was partially solubilized in HCl (2M) and CH_2Cl_2 to some extent while black solid flakes remained. The phases were separated, and the acidic aqueous phase was further washed with CH_2Cl_2 (x2) before being neutralized with NaOH (8M). The aqueous phase was extracted with CH_2Cl_2 (x3), the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo to give a mixture of anilines (145.6 mg, 59%).

H-NMR Spectrum of aniline Fraction from Harsh Hydrolysis of PU-HS4

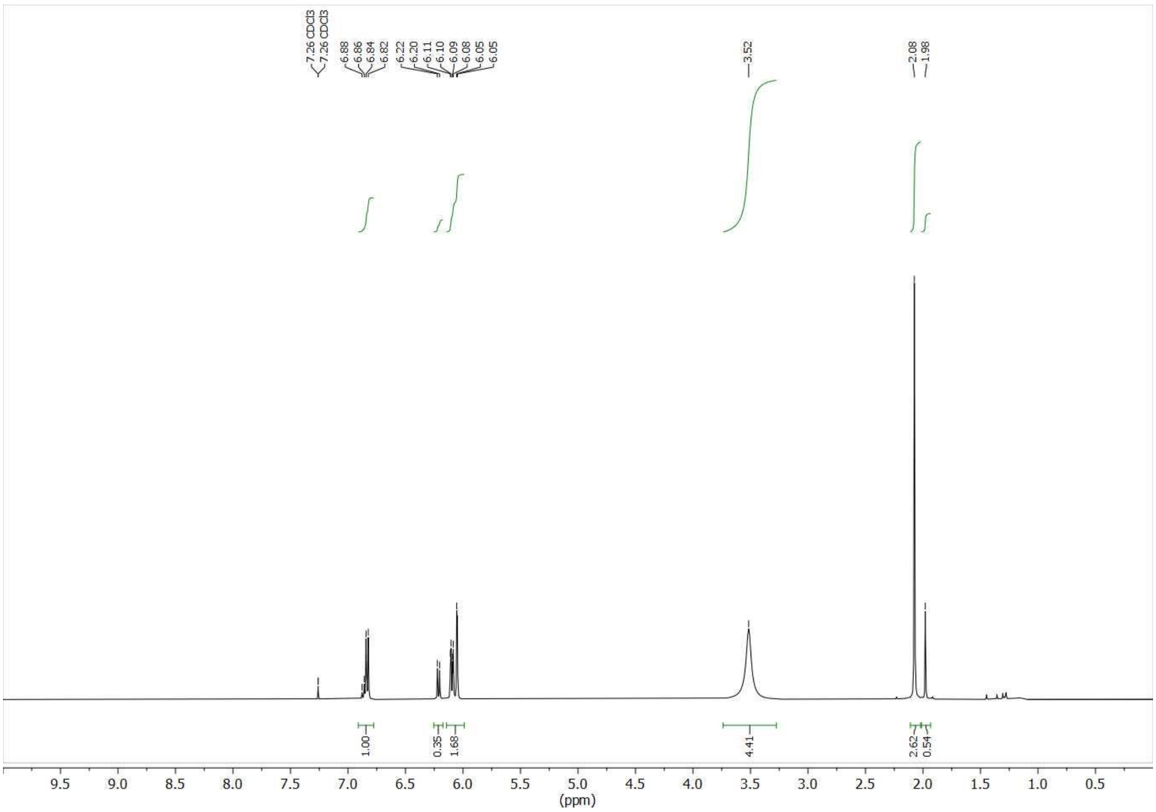


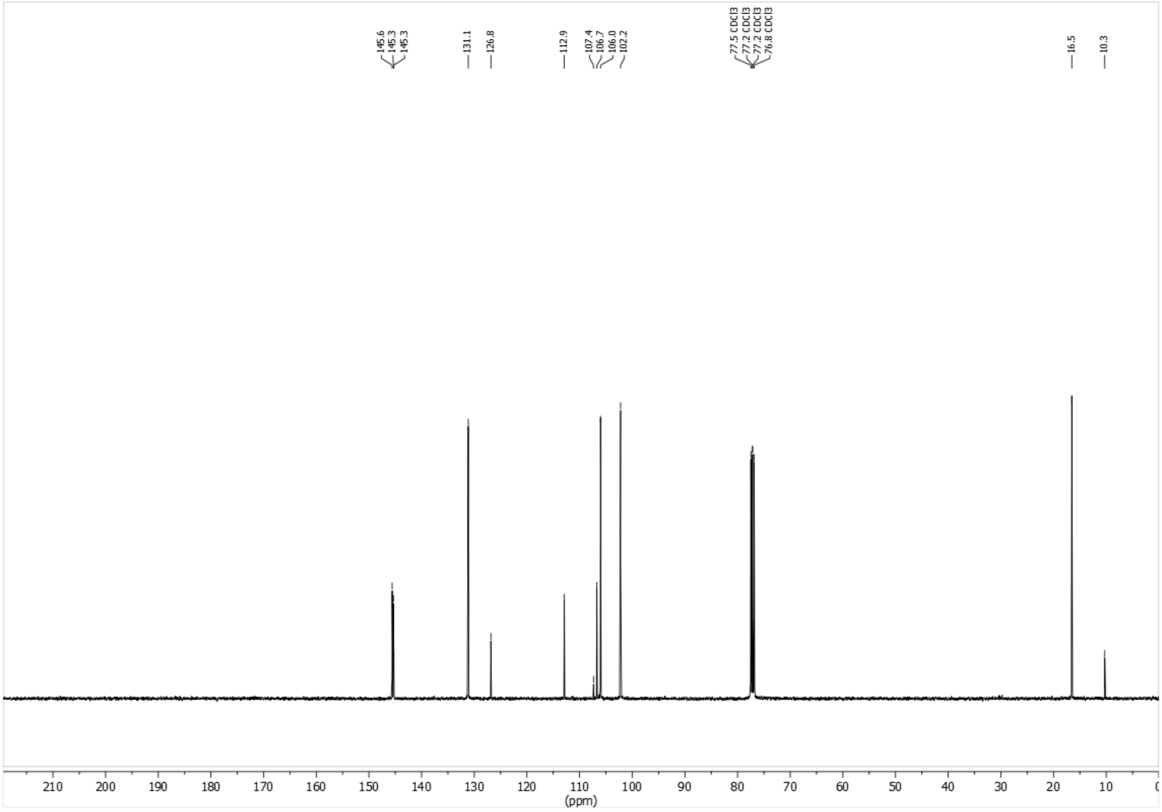
SI-7.3. Valorisation of Flexible PU Foam using Adipic Acid

The hard segment was prepared as describes according to **SI-5.4** with adipic acid, where **PU-HS2** (5.43 g) and polyol (8.59) were obtained.

In a 250 mL round-bottom flask fitted with a magnet, **PU-HS2** (5.40 g) and a solution of 2M NaOH (100 mL, aq.) were added. The flask was equipped with a condenser and heated to reflux for 5 h. Following this, EtOAc (100 mL) was added, and the organic phase was separated from the aqueous phase. The aqueous phase was extracted with EtOAc (5x50 mL), and the combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The remaining solid was dissolved in EtOAc and filtered through a silica-plug, which was washed with pentane and EtOAc. The solvent was removed under reduced pressure, resulting in TDA as a dark red solid (1.74 g, 4.71 mmol, 33%).

NMR Spectra of TDA Fraction from Hydrolysis of PU-HS2





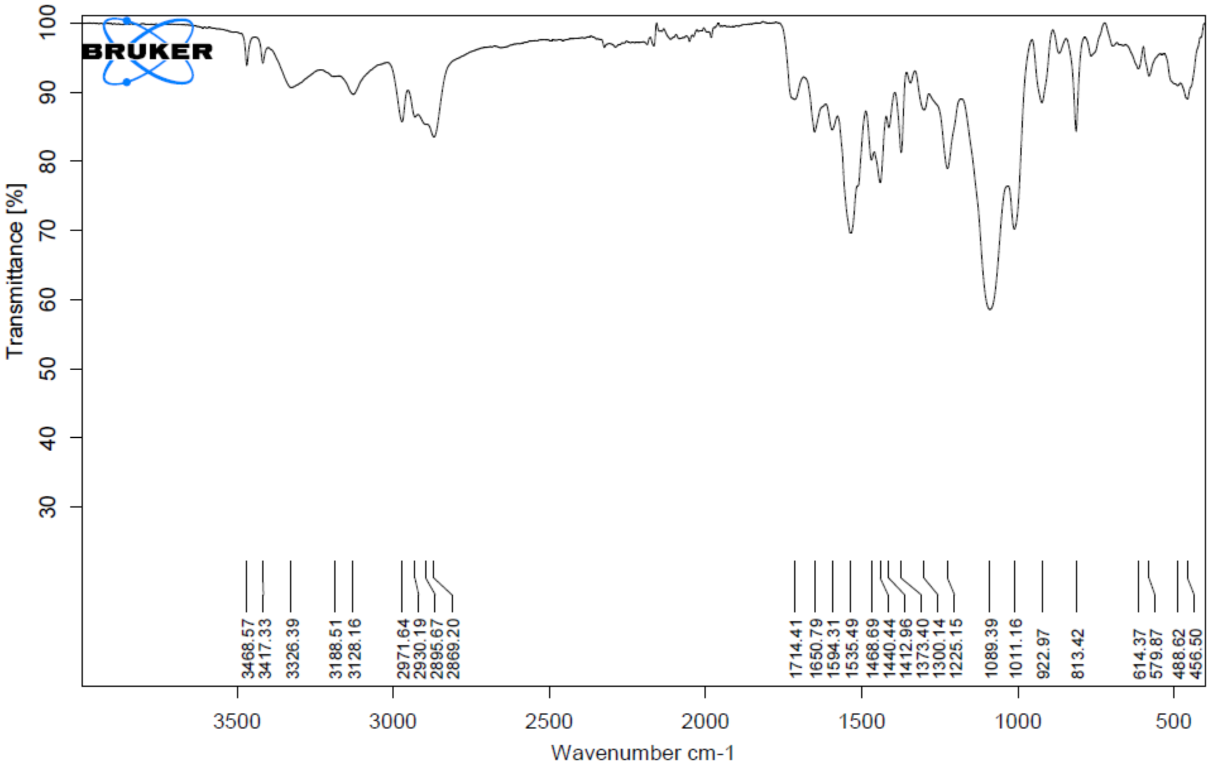
SI-7.4. Valorisation of Rebonded Flexible PU Foam using Succinic Acid

Rebonded Flexible PU Foam was acquired from www.tm-materialer.dk (brand: Polytex). Before acidolysis, the foam was shredded using a Frisch cutting mill fitted with a 1 mm filter.

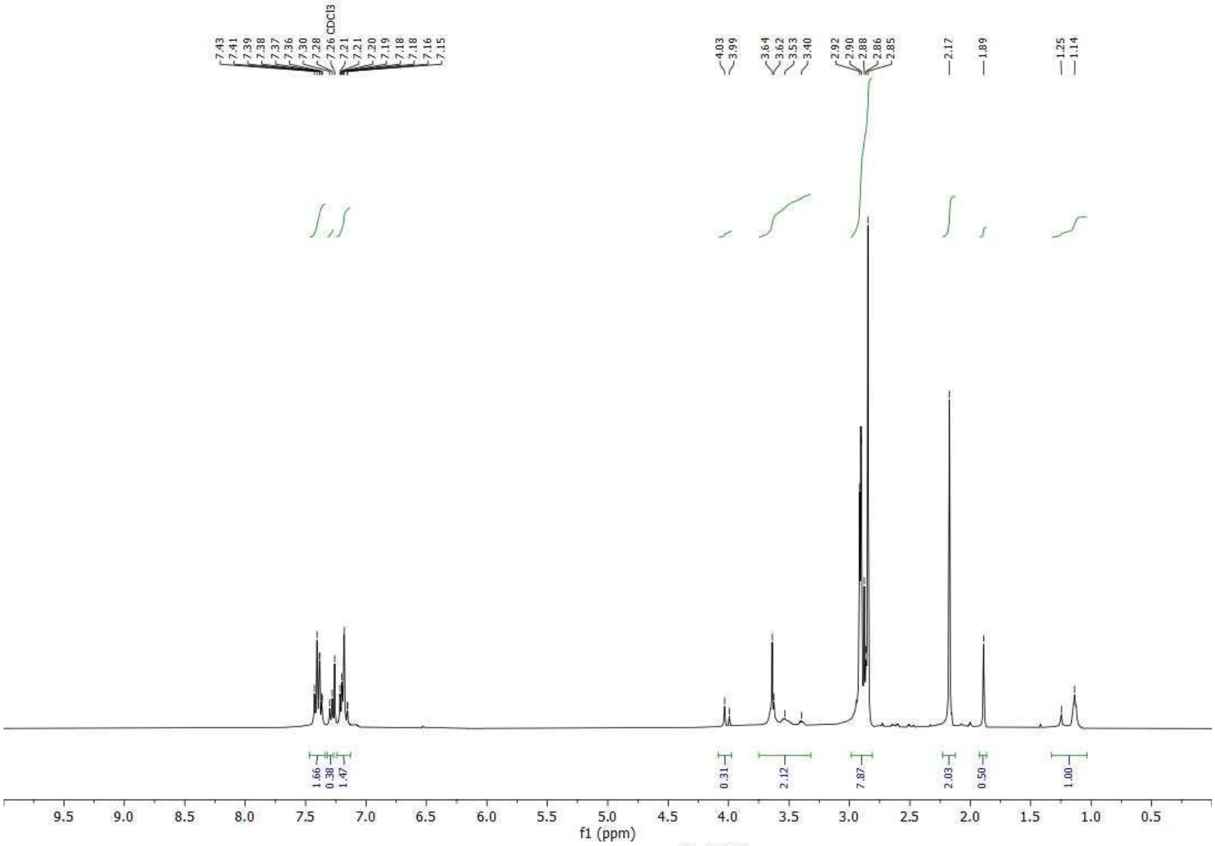
Rebonded Flexible PU foam (10.0 g) and succinic acid (3.60 g, 30.5 mmol, 2.1 equiv. (amount calculated based on previous literature)[3]) were added to a 250 mL three necked round-bottom flask equipped with a magnet. The flask was sealed with septa and heated to 220 °C for 4 h under a continuously N_2 stream. After cooling to room temperature, a green hard solid was obtained, which was added cyclohexane (150 mL) and left to stir overnight. The resulting solids were filtered, washed with several portions of cyclohexane, crushed to a fine powder in a mortar followed by another wash with cyclohexane, and finally dried under reduced pressure, resulting in **PU-HS5** (5.72 g) as an off-green solid. The filtrate was transferred to a round-bottom flask and the solvent was removed under reduced pressure, affording the polyol (5.62 g) as a clear yellow liquid.

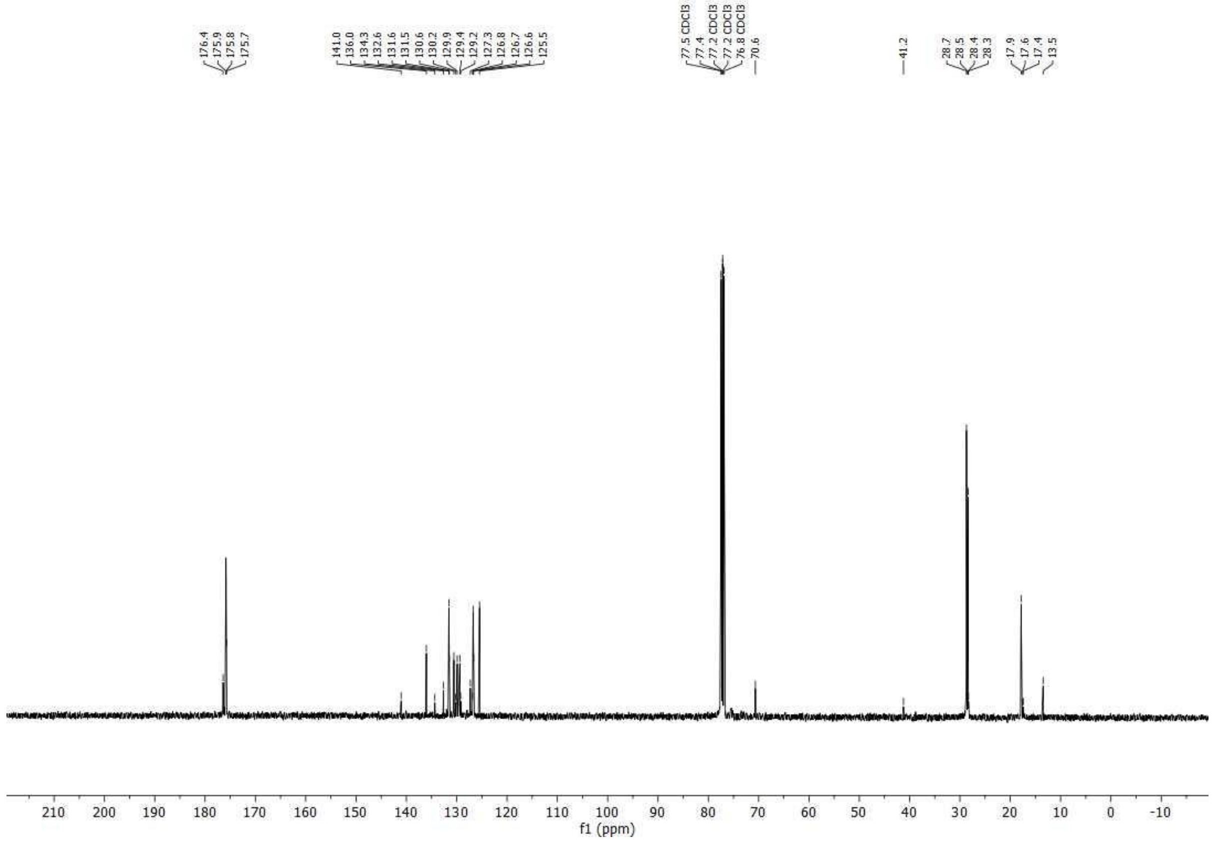
To a 250 mL round-bottom flask fitted with a magnet, **PU-HS5** (5.68 g) and a solution of 2M NaOH (100 mL, aq.) were added. The flask was equipped with a condenser and heated to reflux for 5 h. Following this, EtOAc (100 mL) was added and the organic phase was separated from the aqueous phase. The aqueous phase was further extracted with EtOAc (3x50 mL), and the combined organic phases were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording TDA/MDA mixture as a light brown solid (2.10 g).

FT-IR Spectrum of Rebonded Flexible PU Foam

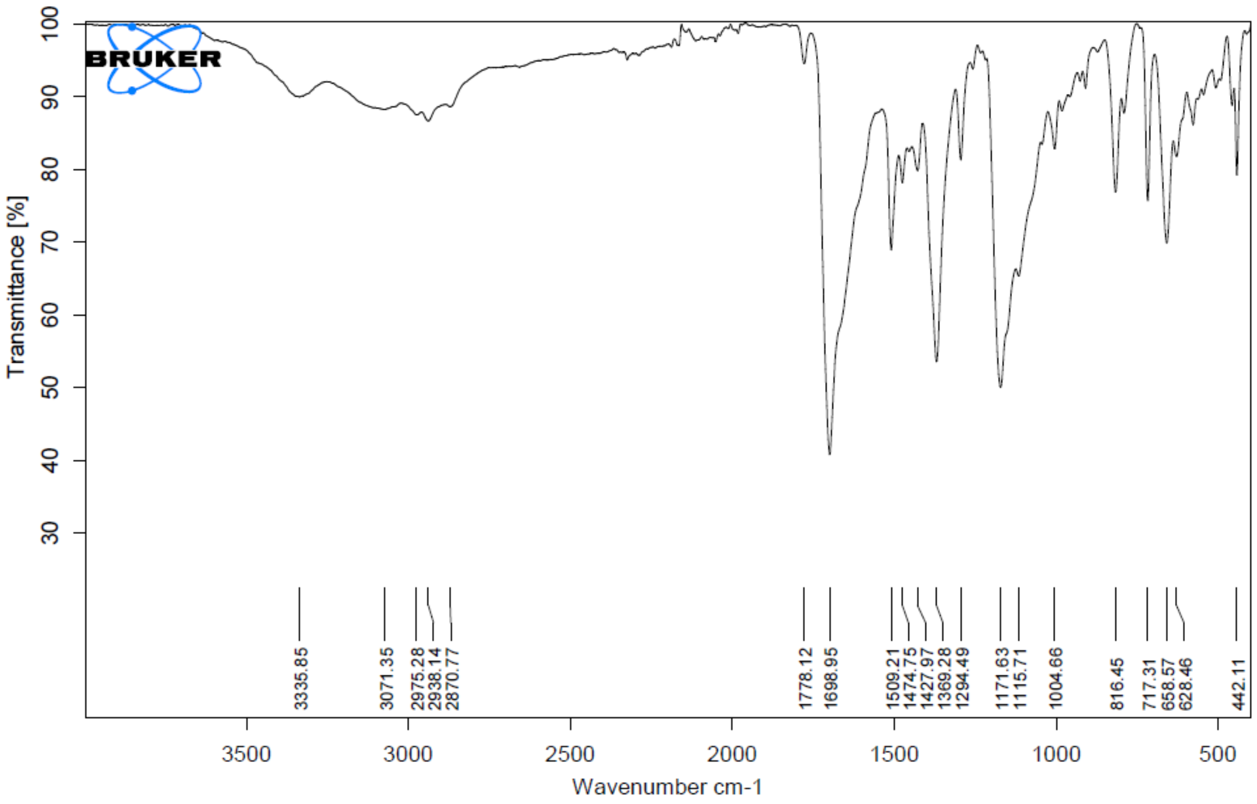


NMR Spectra of PU-HS5

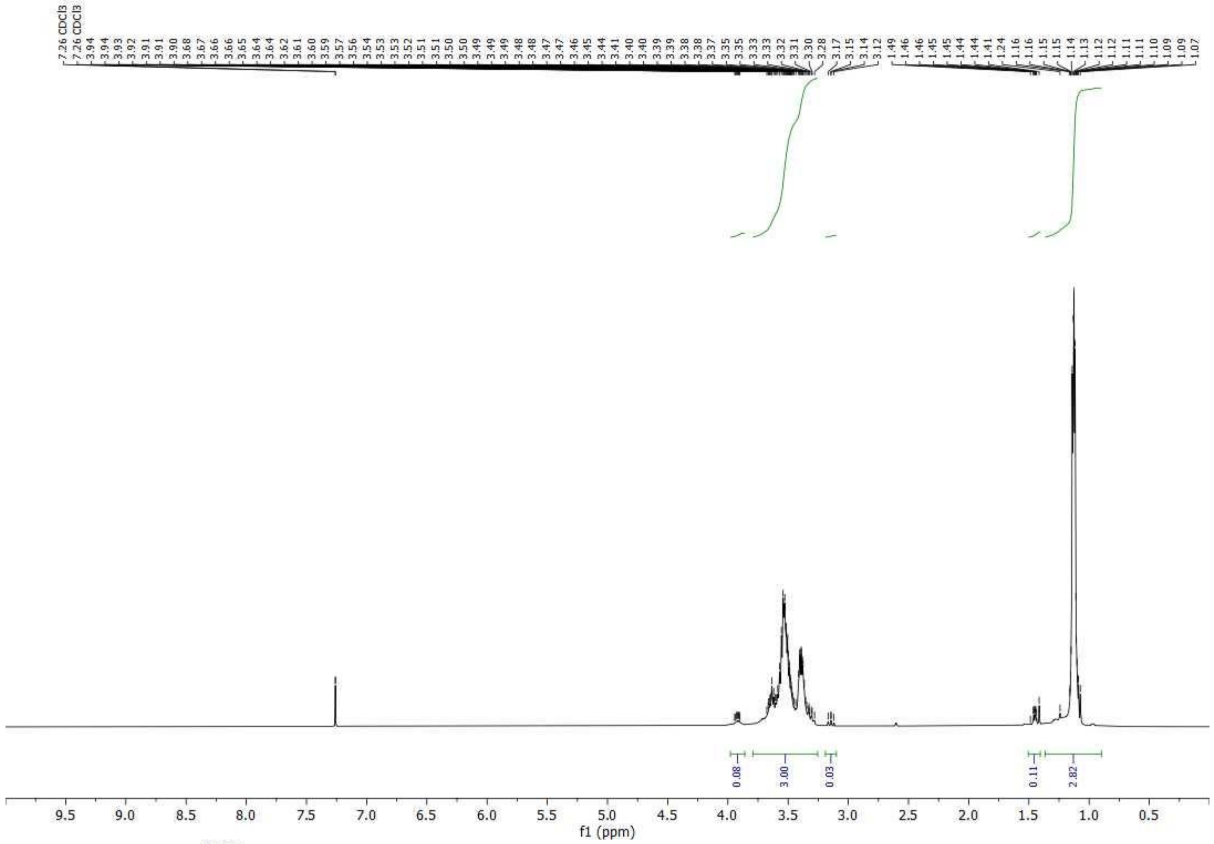


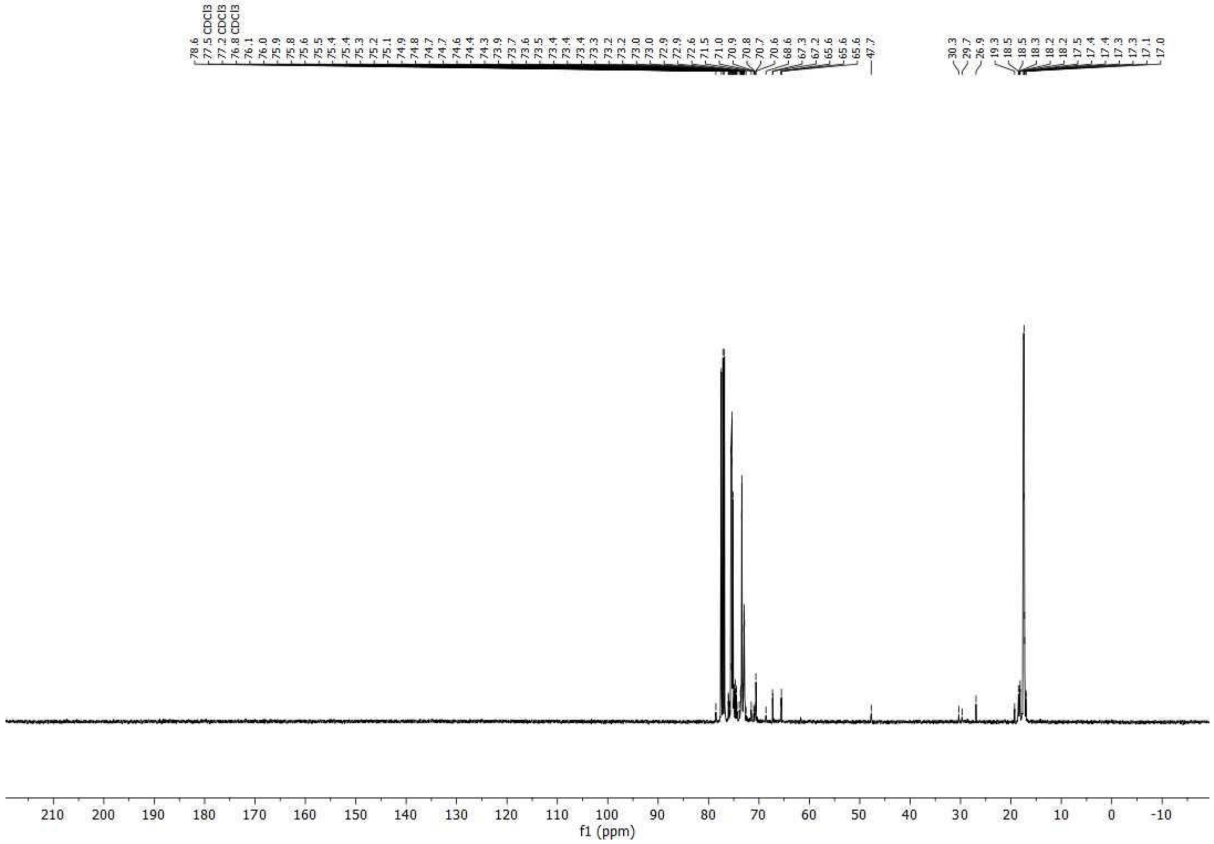


FT-IR Spectrum of PU-HS5

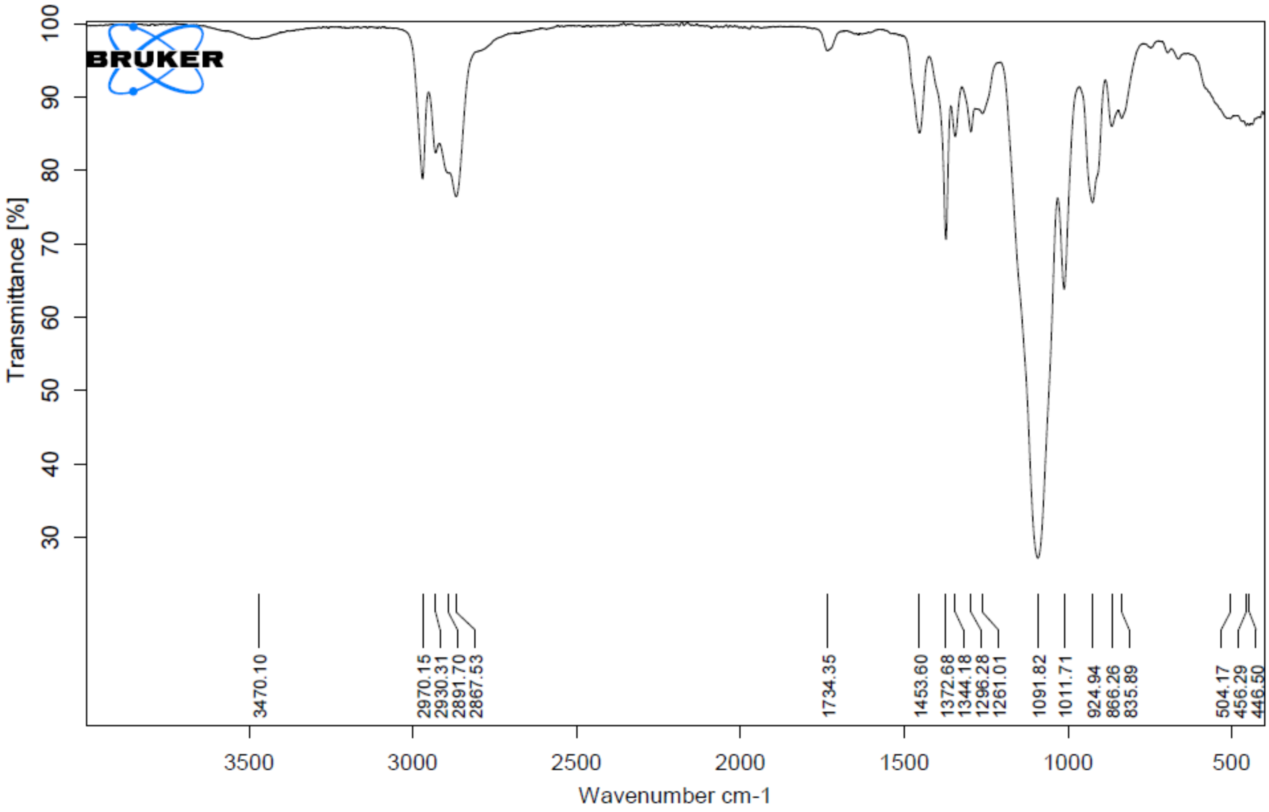


NMR Spectra of Polyol

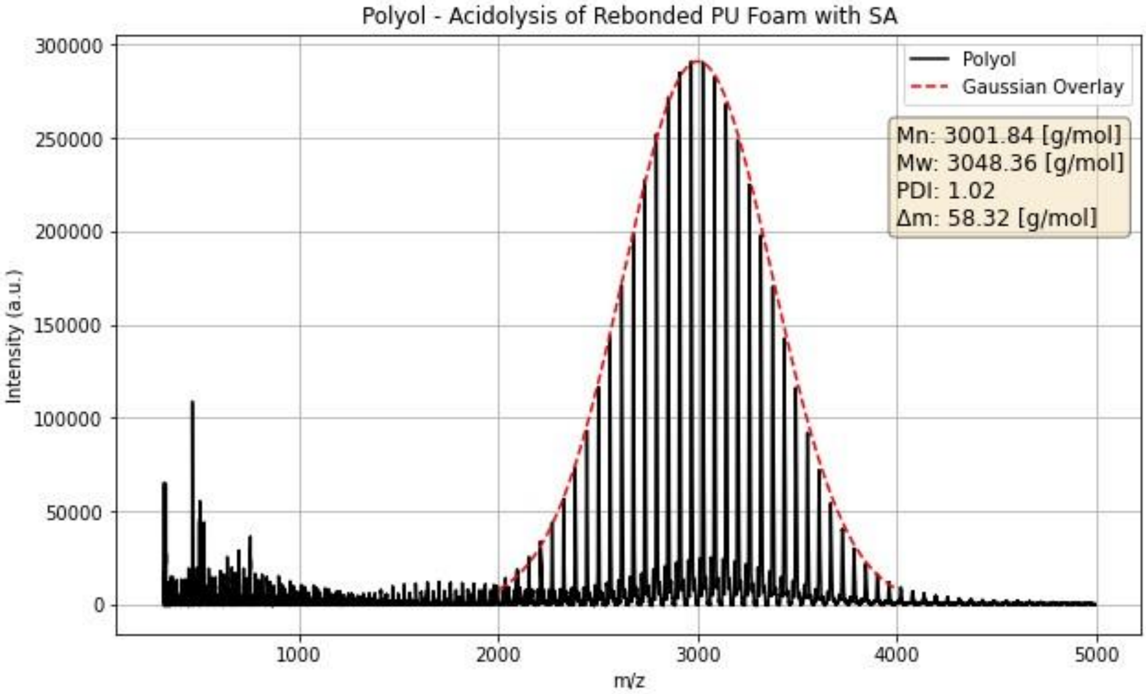




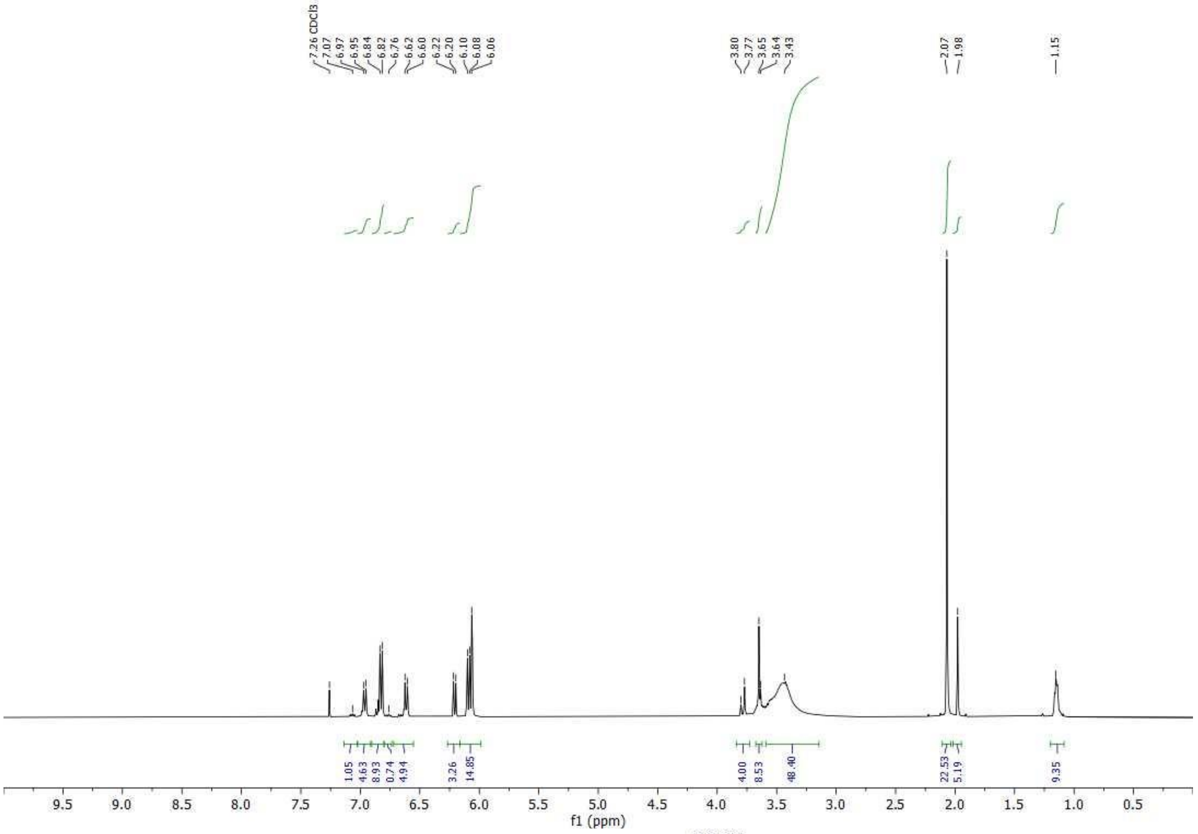
FT-IR Spectrum of Polyol

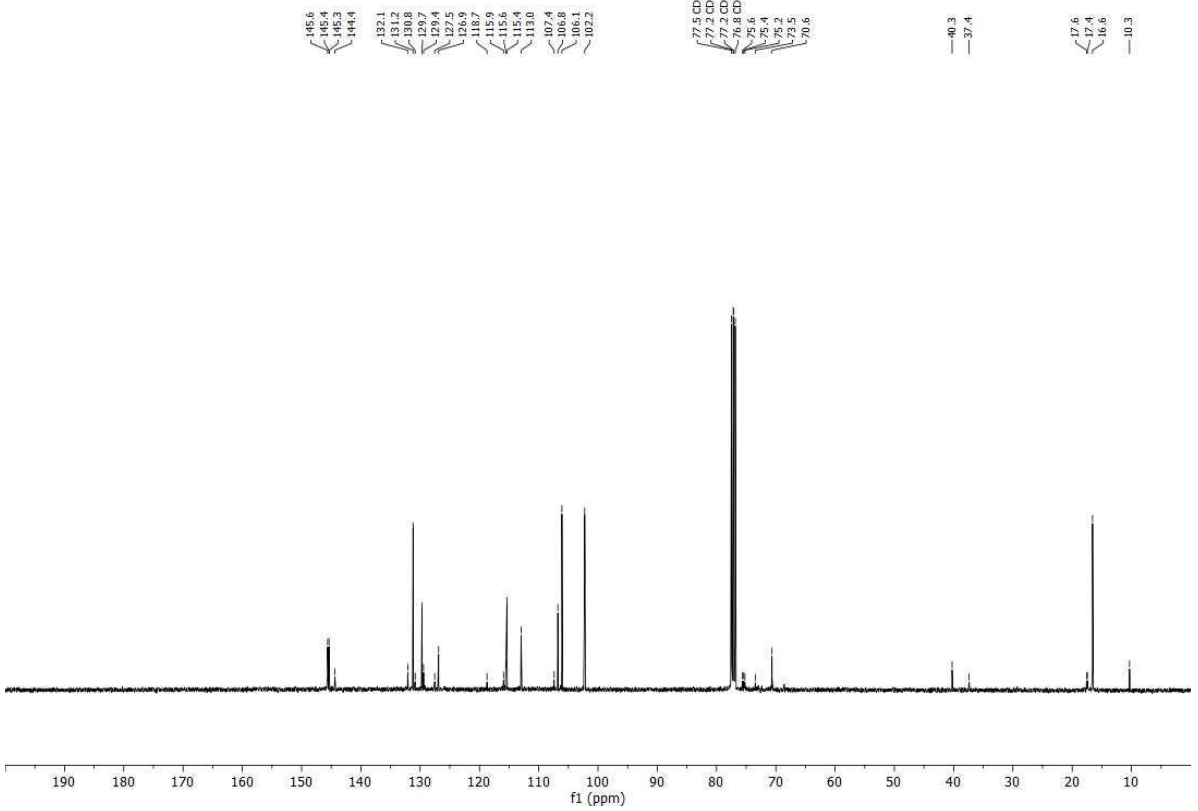


MALDI-TOF Spectrum of Polyol



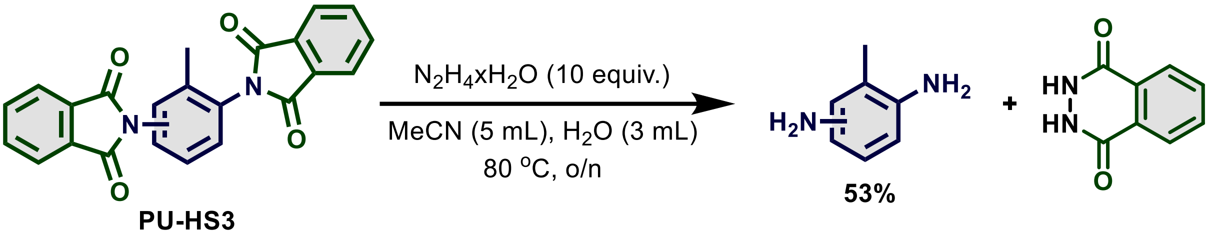
NMR Spectra of Aniline Fraction from Hydrolysis of PU-HS5





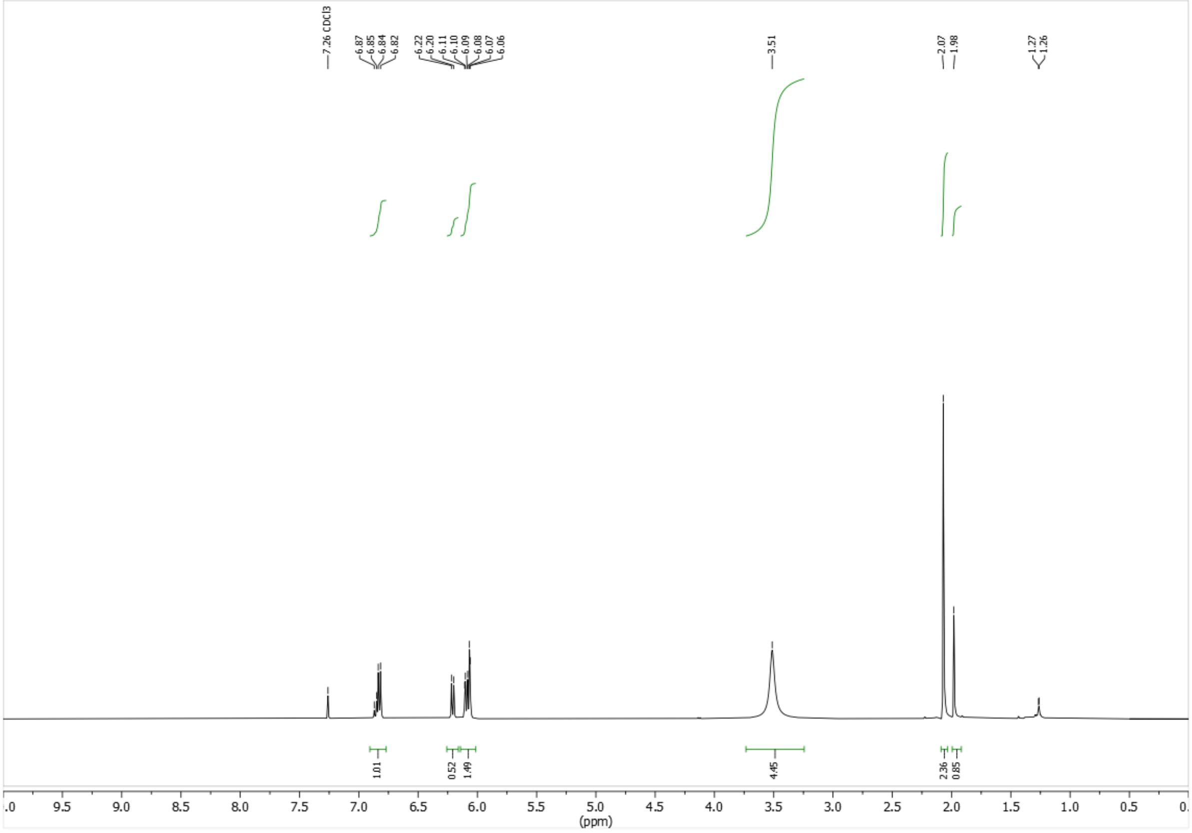
SI-8. Nucleophilic Substitution for Dianiline Recovery from PU-HS3

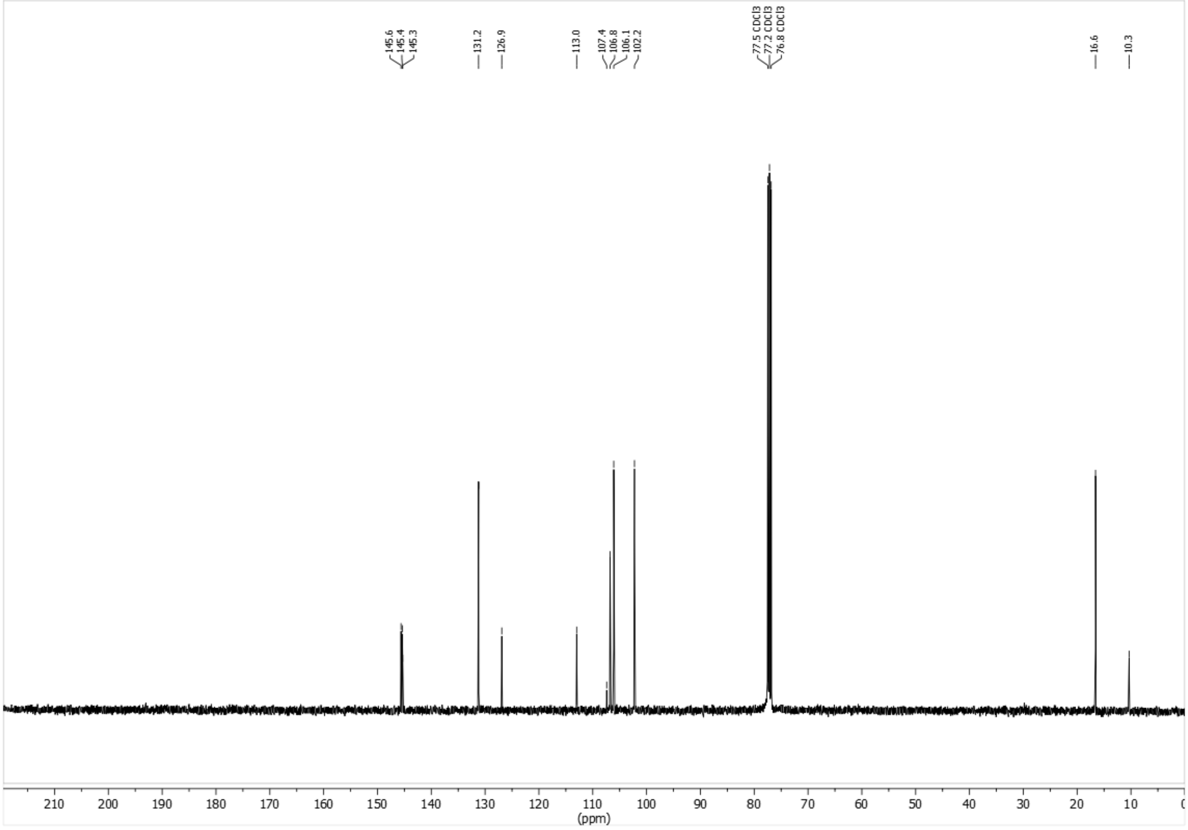
SI-8.1. Using Hydrazine Hydrate



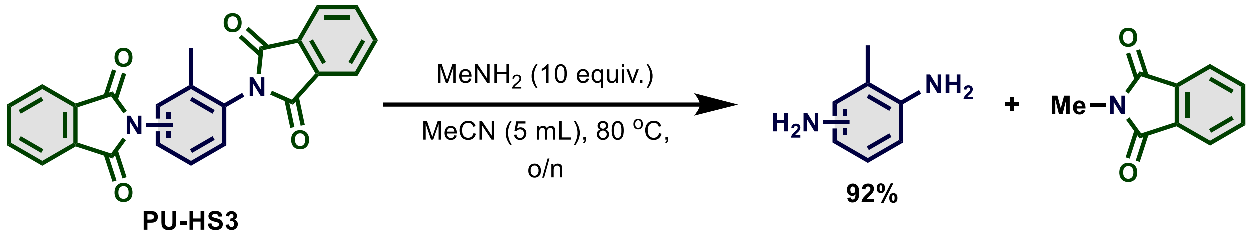
PU-HS3 (50.0 mg, 0.13 mmol, 1.0 equiv.) was dissolved in MeCN (5 mL) in a 25 mL round-bottom flask fitted with a magnet. Hydrazine hydrate (81.5 µL, 1.31 mmol, 10.0 equiv.) was diluted in H_2O (3 mL) and added to the round-bottom flask, which was left to stir at rt for 1.5 h. The crude was concentrated onto celite and isolated by flash column chromatography to afford TDA as a yellow solid (8.4 mg, 0.07 mmol, 53%).

NMR Spectra of TDA from PU-HS3 using Hydrazine Hydrate



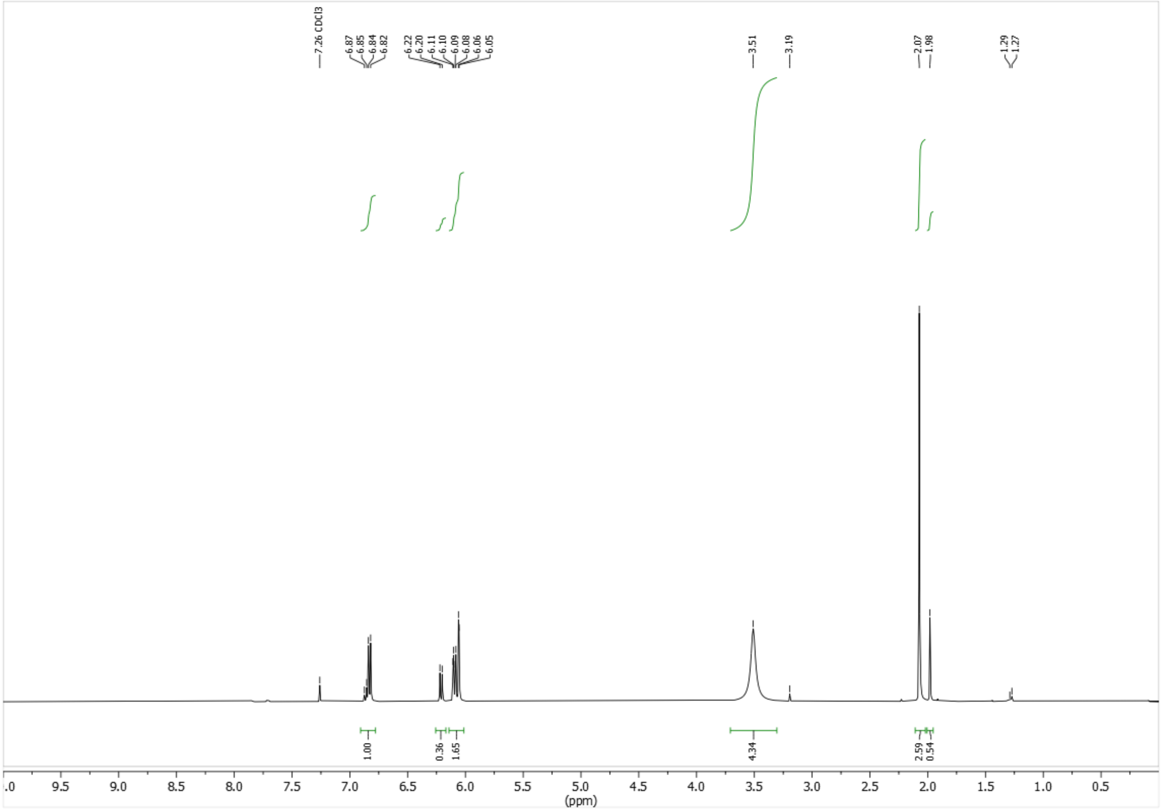


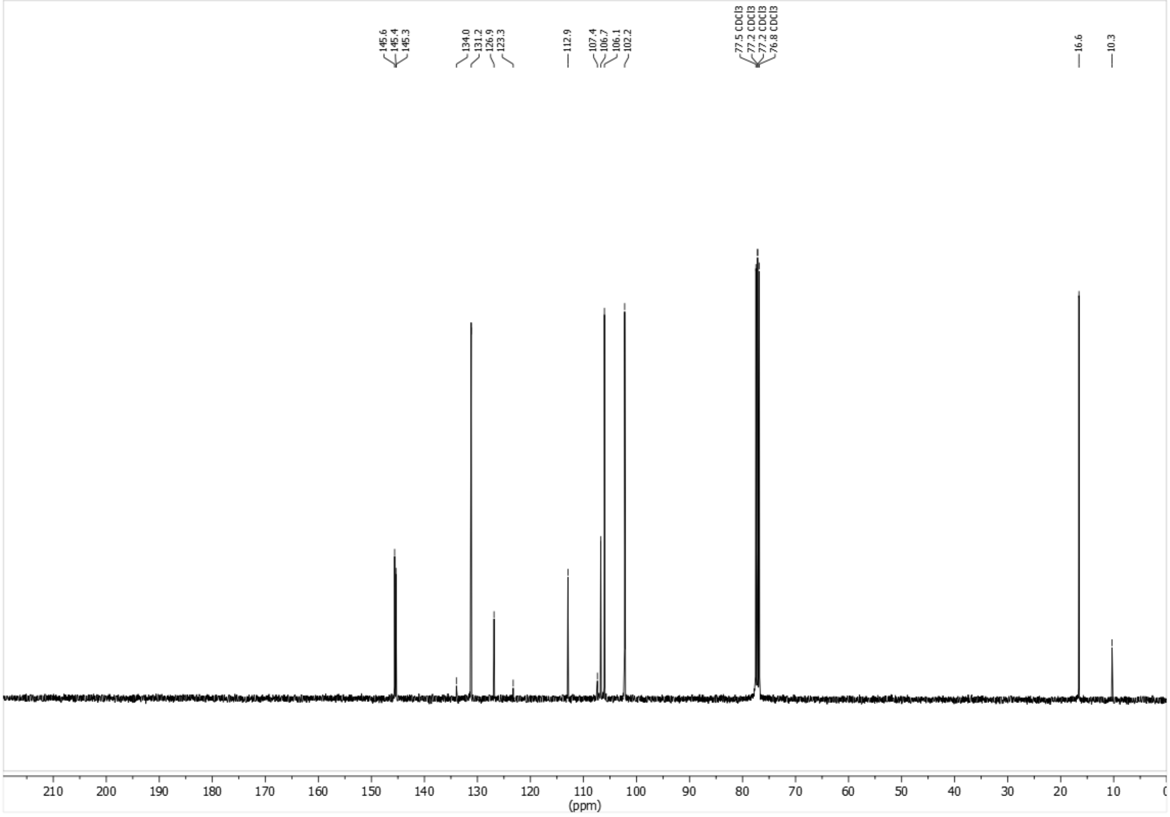
SI-8.2. Using Methylamine



PU-HS3 (51.0 mg, 0.13 mmol, 1.0 equiv.) was dissolved in MeCN (5 mL) in an 8 mL vial fitted with a magnet. A solution of $MeNH_2$, 40% in water, (115.4 µL, 1.33 mmol, 10.0 equiv.) was added to the vial and the reaction was left to stir at 80 °C overnight. The product was concentrated onto celite and isolated by flash column chromatography, resulting in TDA as a yellow solid (15.0 mg, 0.12 mmol, 92%).

NMR Spectra of TDA from PU-HS3 using Methylamine

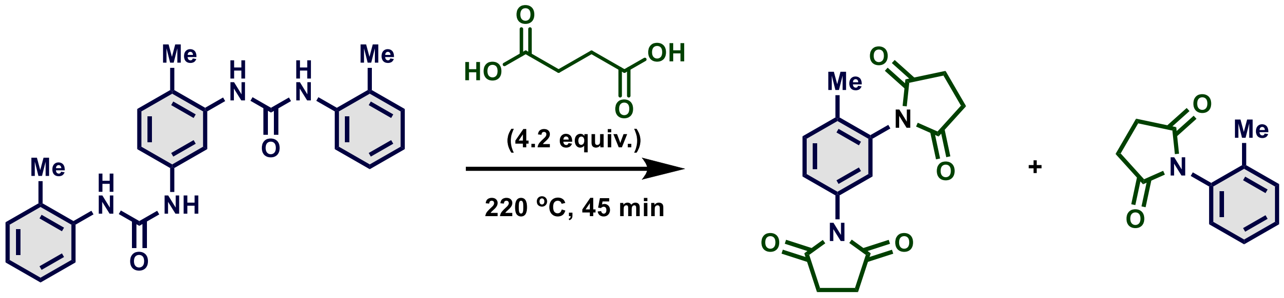




SI-9. Acidolysis on Model Substrates

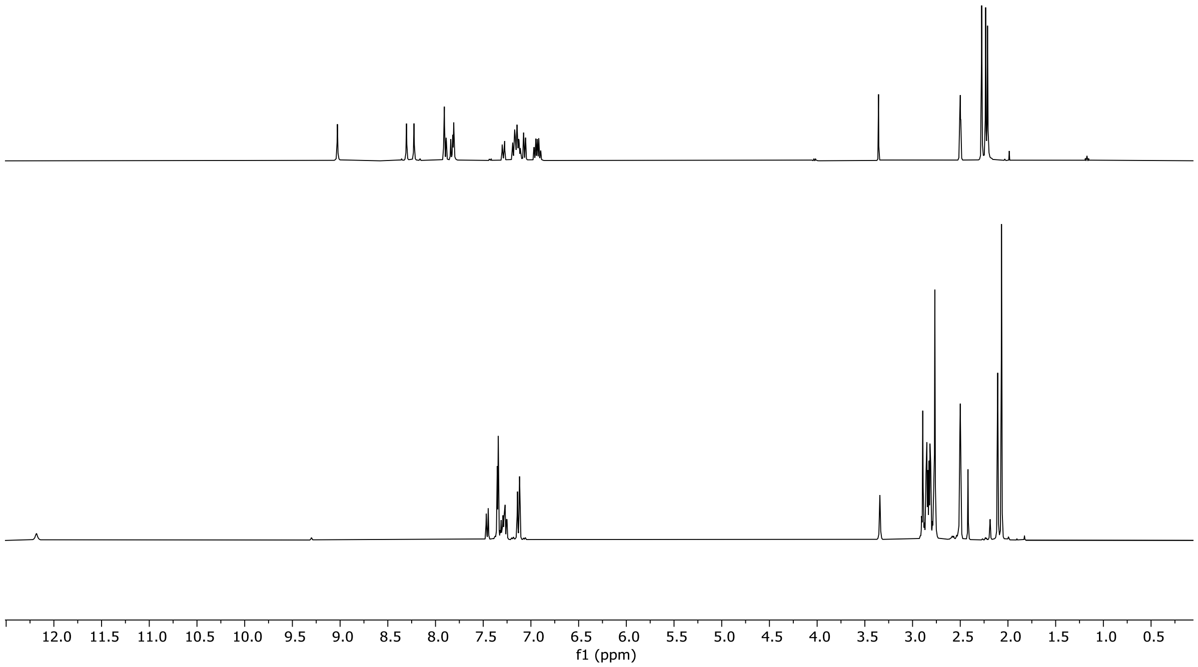
SI-9.1. Acidolysis on Urea Model Substrate

For substrate synthesis and characterisation see Johansen *et. al.*[3]

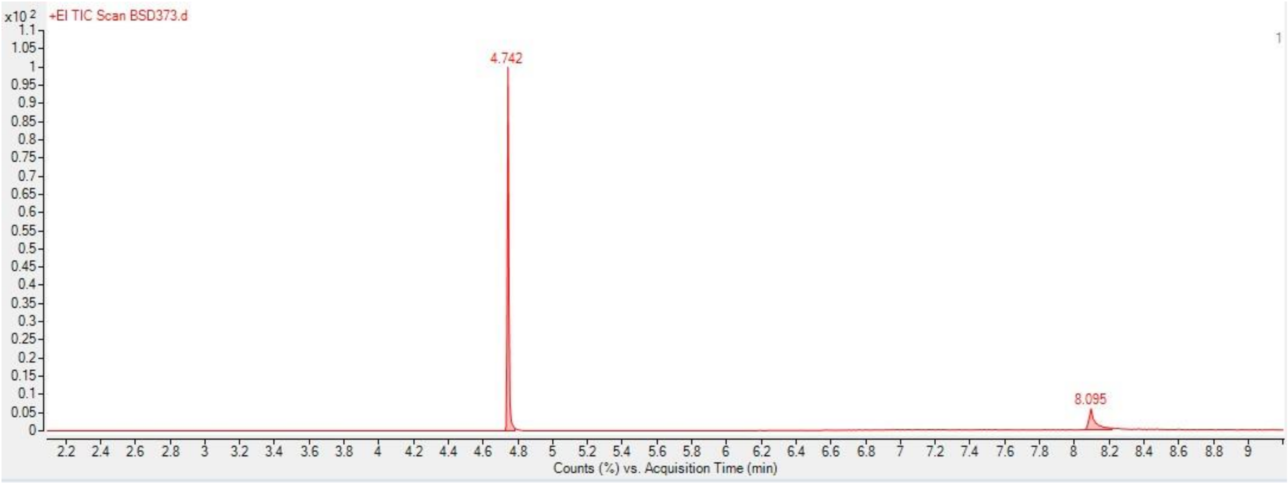


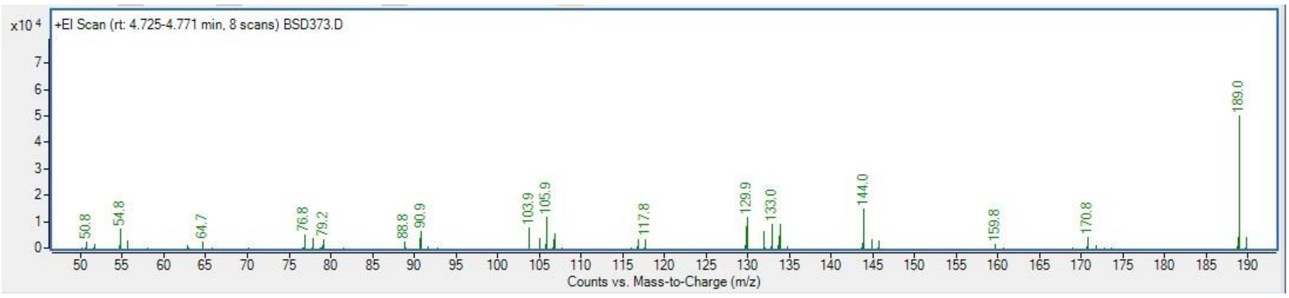
A 10 mL pressure tube was loaded with urea model substrate (194 mg, 0.5 mmol) and Succinic acid (248 mg, 2.1 mmol) before being sealed. The reaction mixture was heated to 220 °C in an aluminium block under stirring for 45 min. The pale brown solution partially solidified upon cooling. Analysis of the reaction mixture by H-NMR and GC-MS revealed full conversion of the urea substrate and formation of the two expected imides.

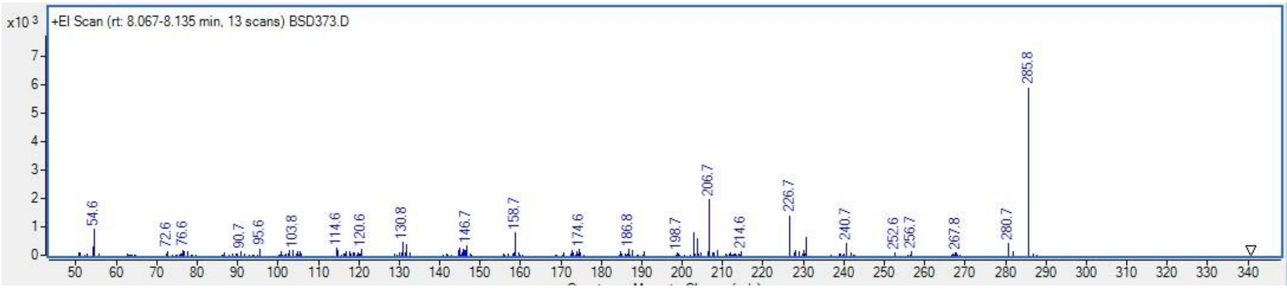
H-NMR (DMSO-d6) Overlay of Substrate (Top) and Reaction Mixture (Bottom)



GC-MS Chromatogram and Mass Spectra




x10 4
+EI Scan (rt: 4.725-4.771 min, 8 scans) BSD373.D
7
6
5
4
3
2
1
0
50.8
54.8
64.7
76.8
79.2
88.8
90.9
103.9
105.9
117.8
129.9
133.0
144.0
159.8
170.8
189.0
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
Counts vs. Mass-to-Charge (m/z)


x10 3
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7
6
5
4
3
2
1
0
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72.6
76.6
90.7
95.6
103.8
114.6
120.6
130.8
146.7
158.7
174.6
186.8
198.7
206.7
214.6
226.7
240.7
252.6
256.7
267.8
280.7
285.8
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60
70
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90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
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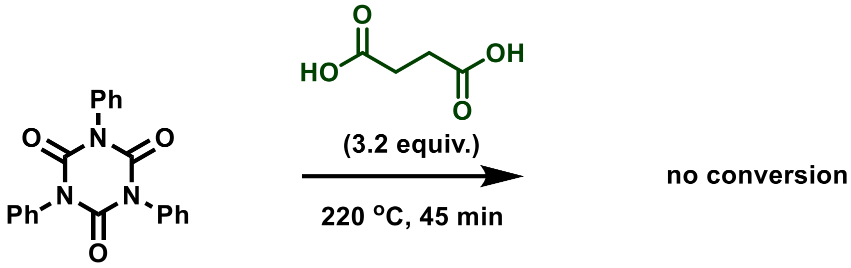
330
340

SI-9.2. Acidolysis of Isocyanurate Model Substrate

For substrate synthesis and characterisation see Johansen *et. al.*[3]



A 10 mL pressure tube was loaded with isocyanurate model substrate (178 mg, 0.5 mmol) and Succinic acid (186 mg, 1.58 mmol) and sealed. The reaction mixture was heated to 220 °C in an aluminium block under stirring for 45 min. The mixture remained solid and significant condensation of white solids were observed at the top of the tube. Analysis of the reaction mixture by H-NMR revealed no conversion of the isocyanurate substrate. Prolonged reaction time (16 h) and addition of virgin polyol as solvent did not affect the outcome of the reaction.

SI-10. References

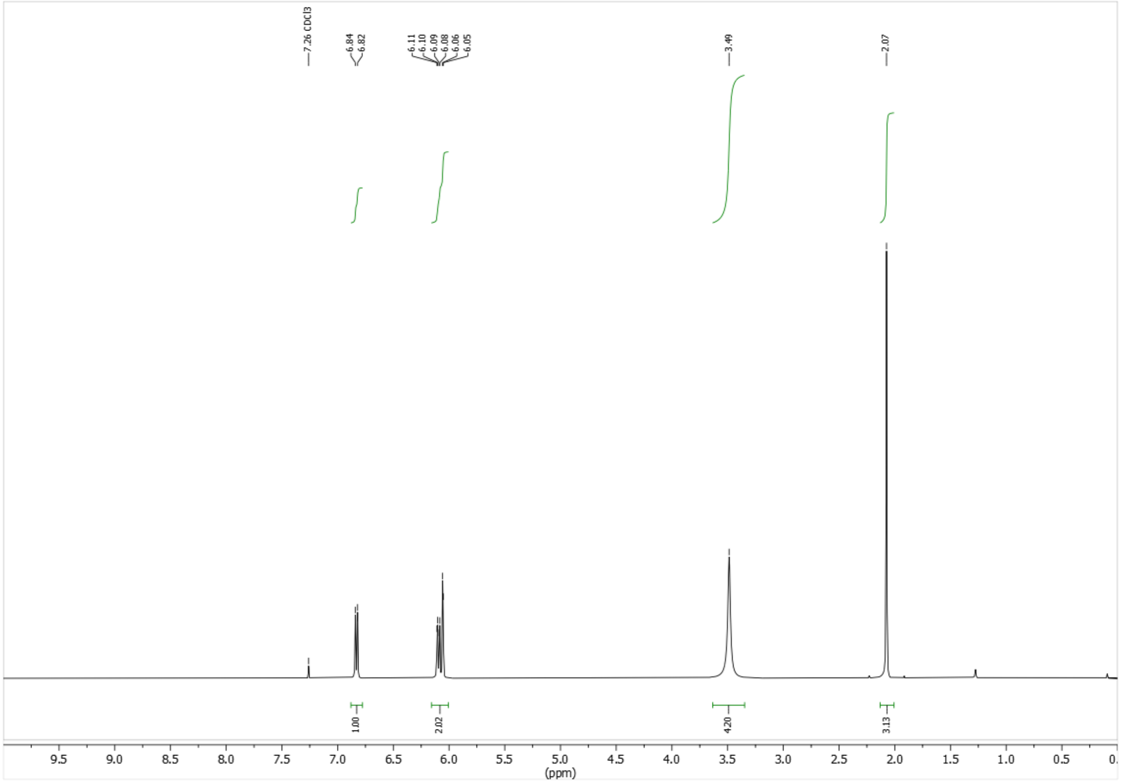
1 L. Gausas, B. S. Donslund, S. K. Kristensen and T. Skrydstrup, *ChemSusChem*, 2022, **15**, e202101705.

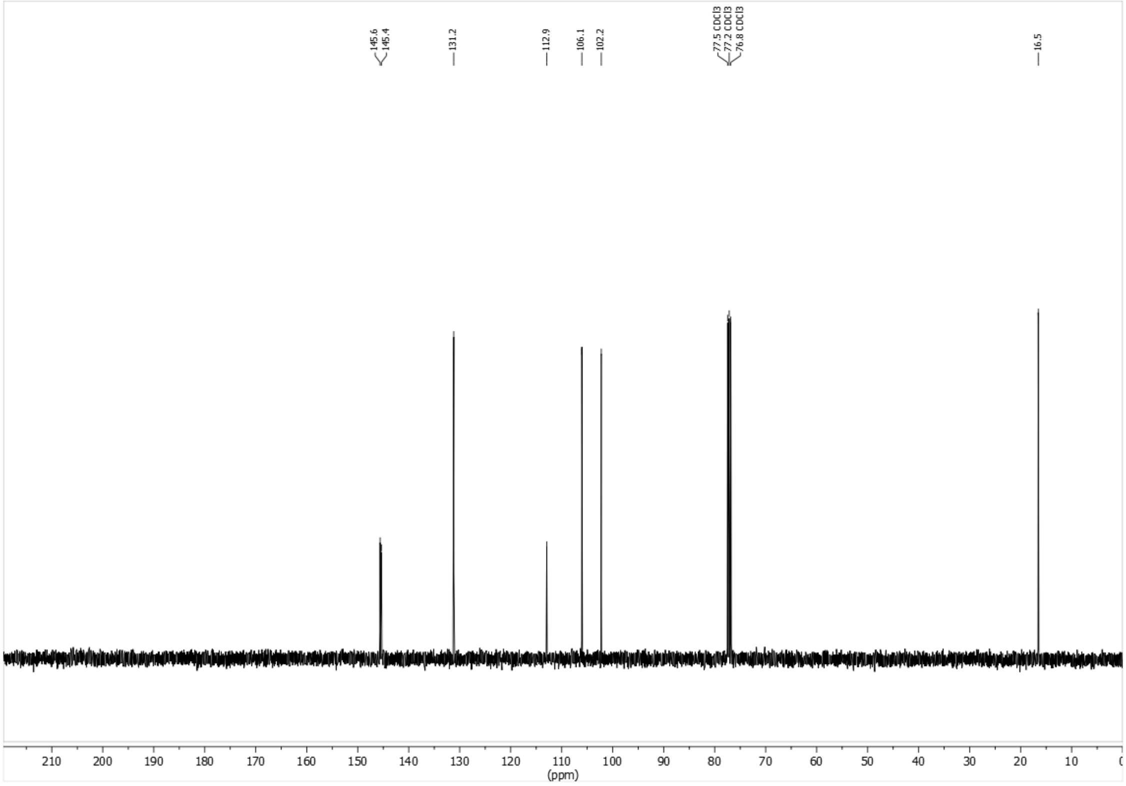
2 E. Fogler, J. A. Garg, P. Hu, G. Leitus, L. J. W. Shimon and D. Milstein, *Chem. Eur. J.*, 2014, **20**, 15727–15731.

3 M. B. Johansen, B. S. Donslund, S. K. Kristensen, A. T. Lindhardt and T. Skrydstrup, *ACS Sustainable Chem. Eng.*, **2022**, *10*, 11191–11202.

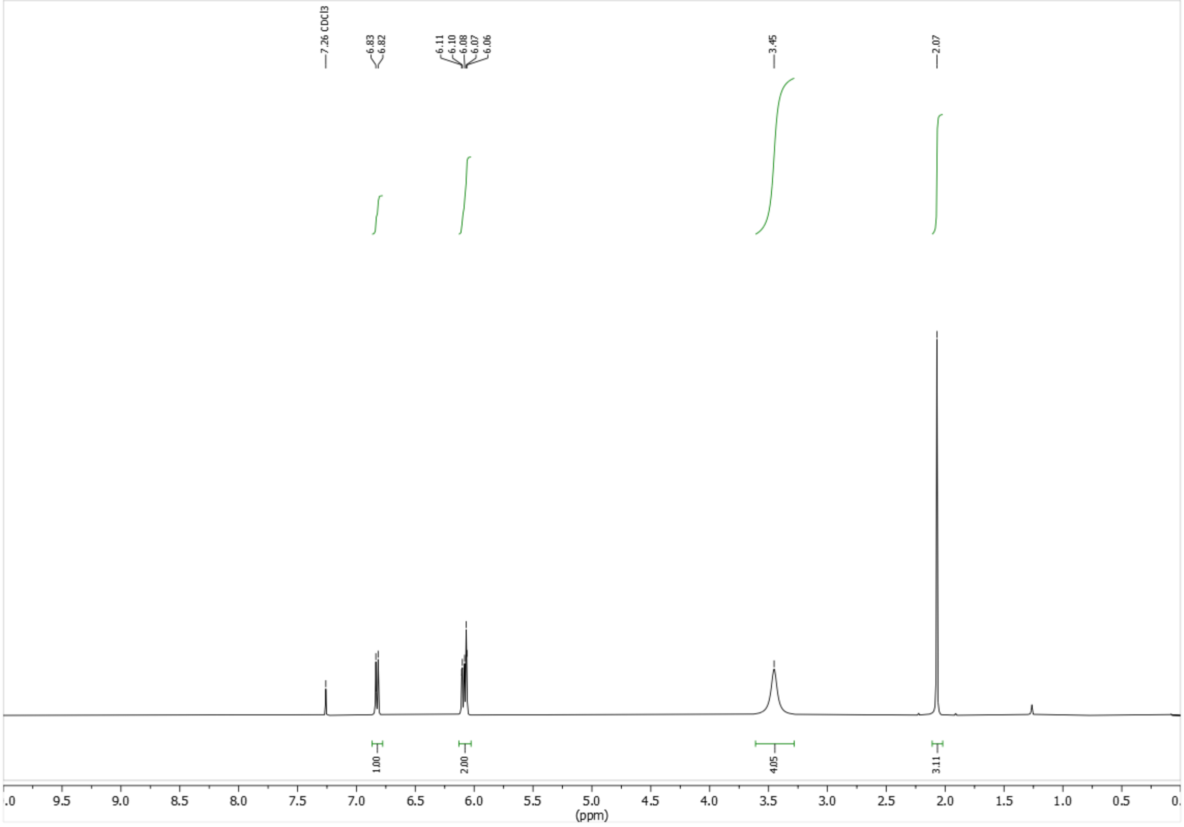
SI-11. NMR Spectra

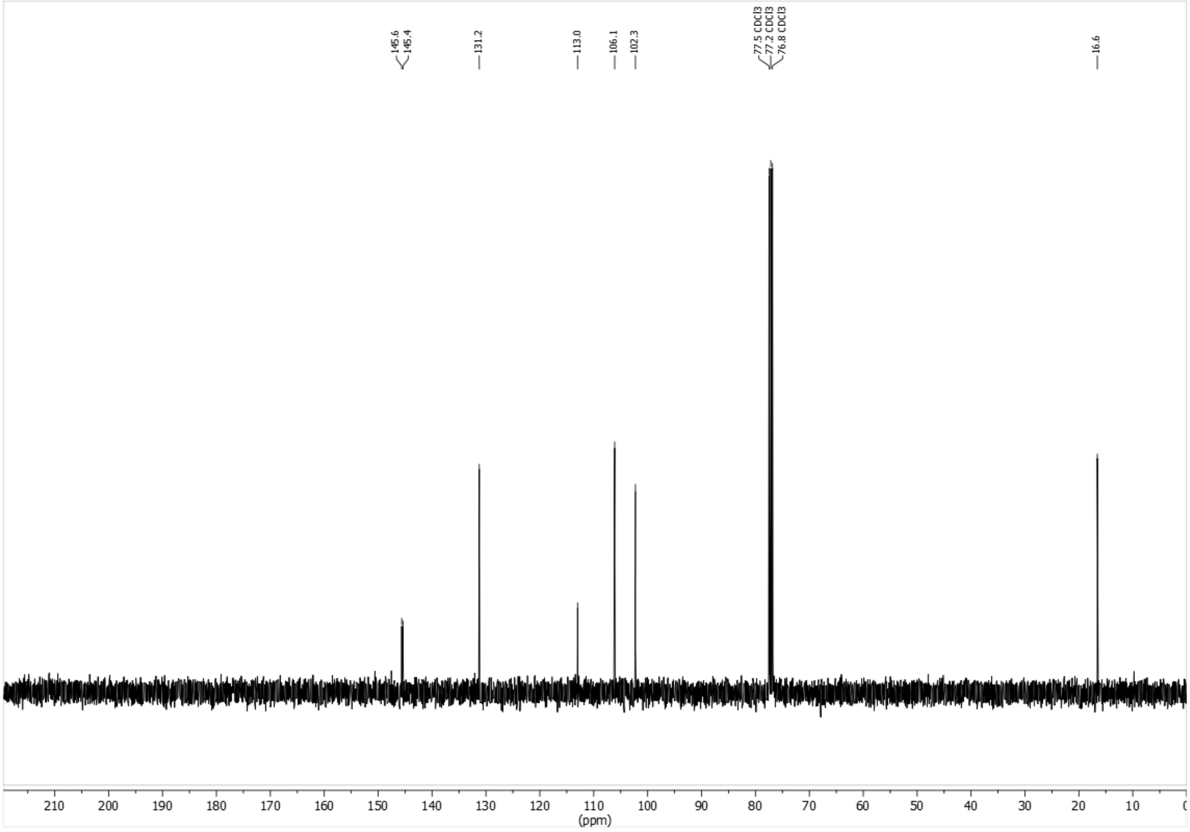
2,4-TDA from Acidic Hydrolysis of Model 1



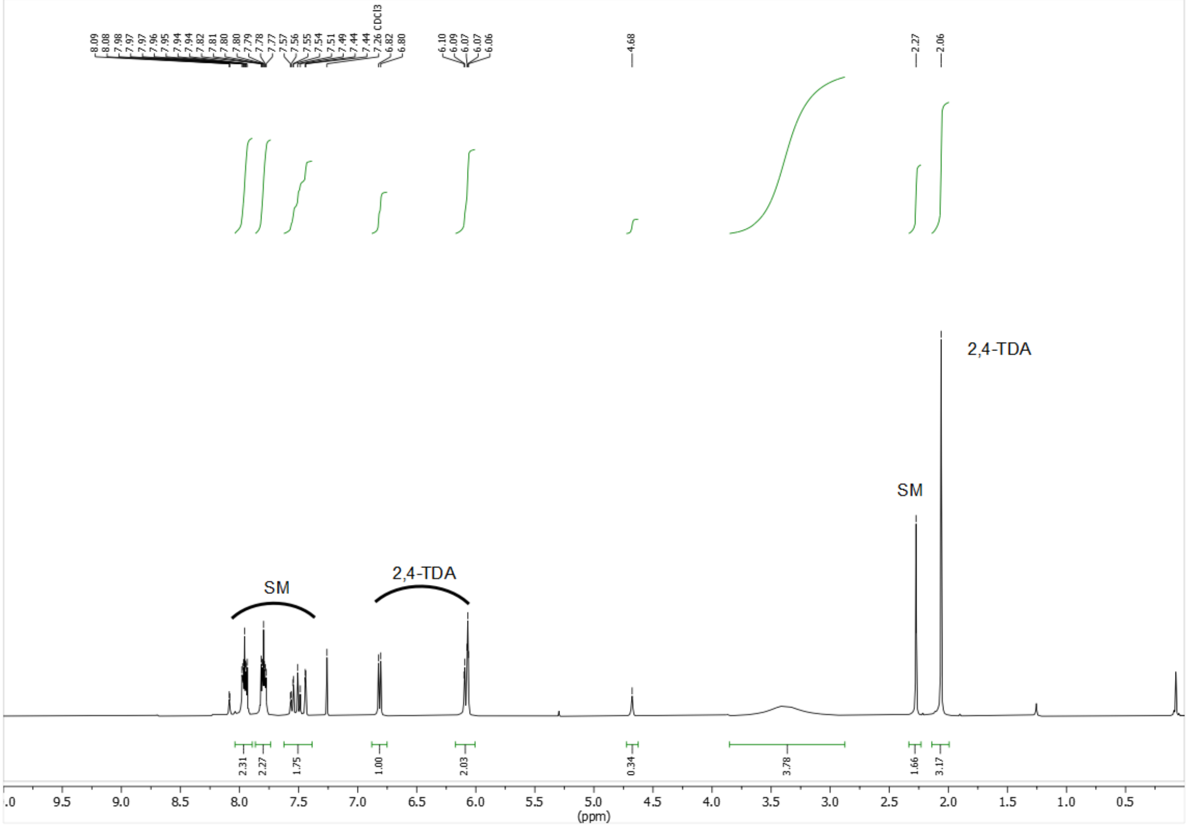


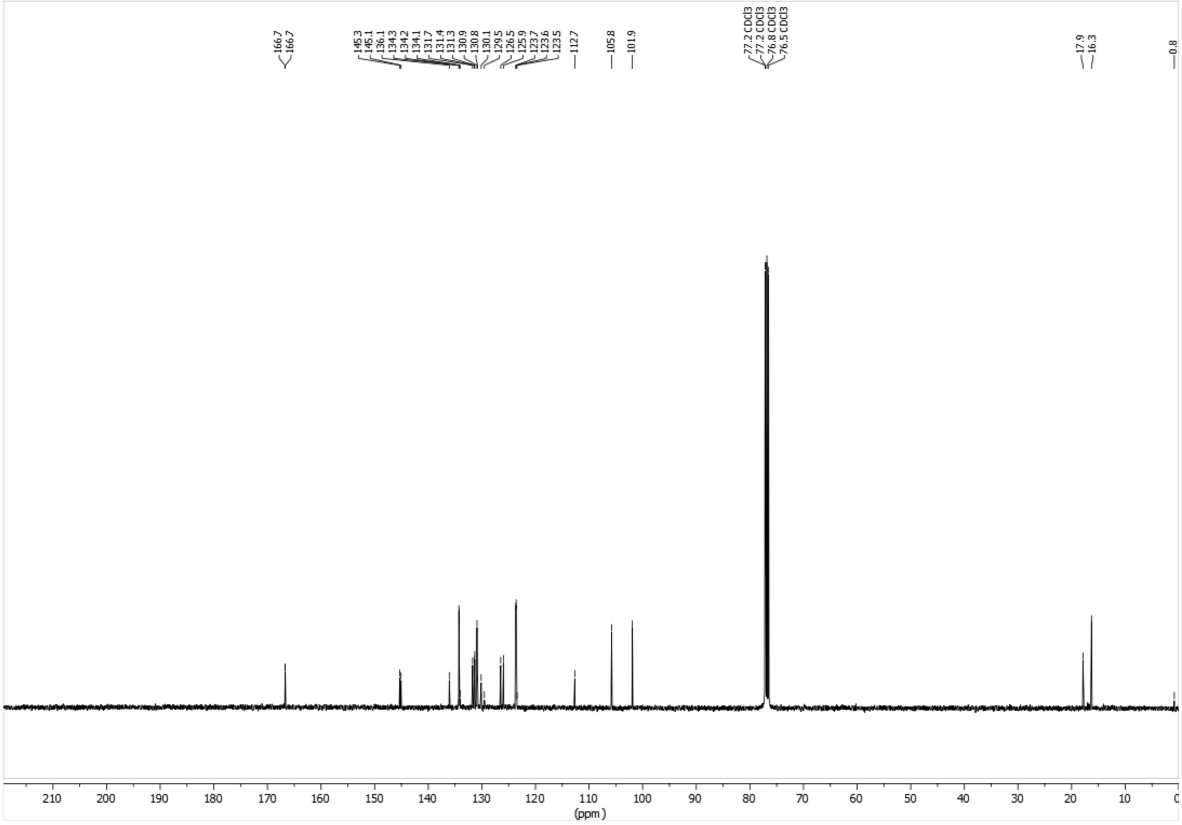
2,4-TDA from Acidic Hydrolysis of Model 2



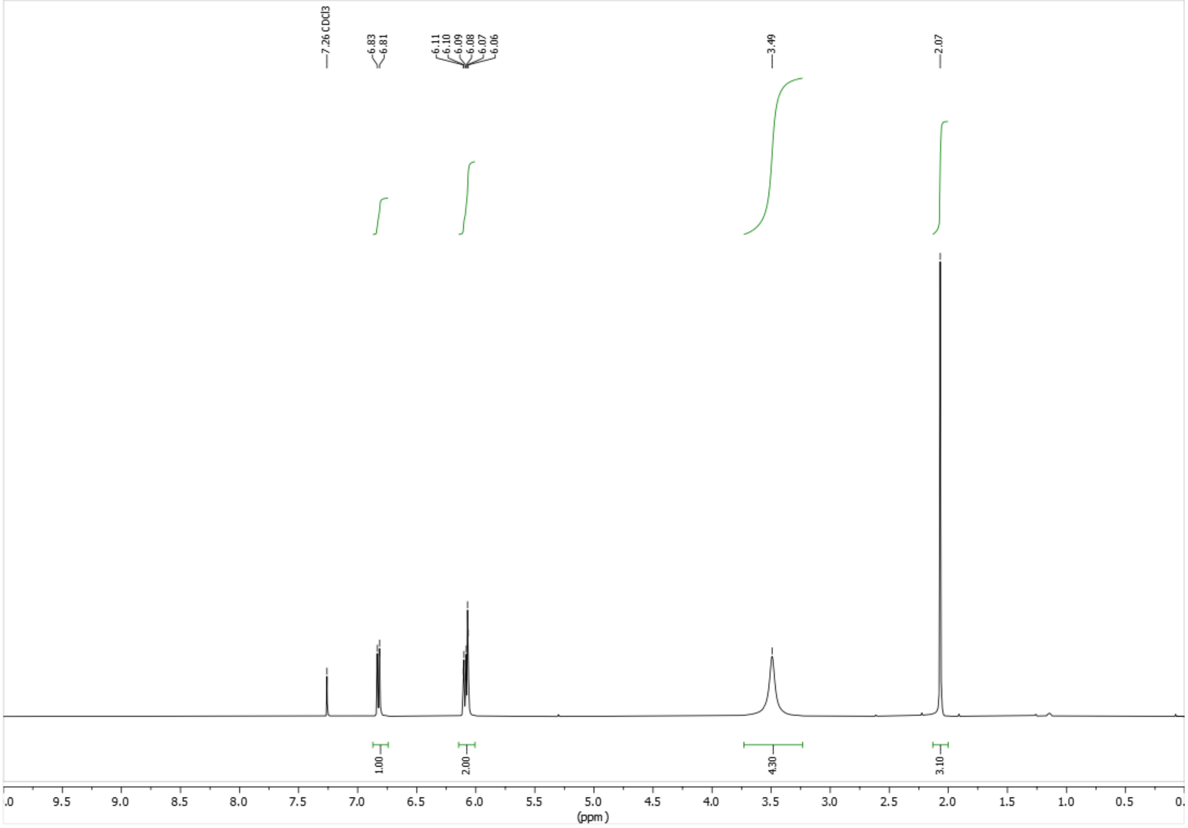


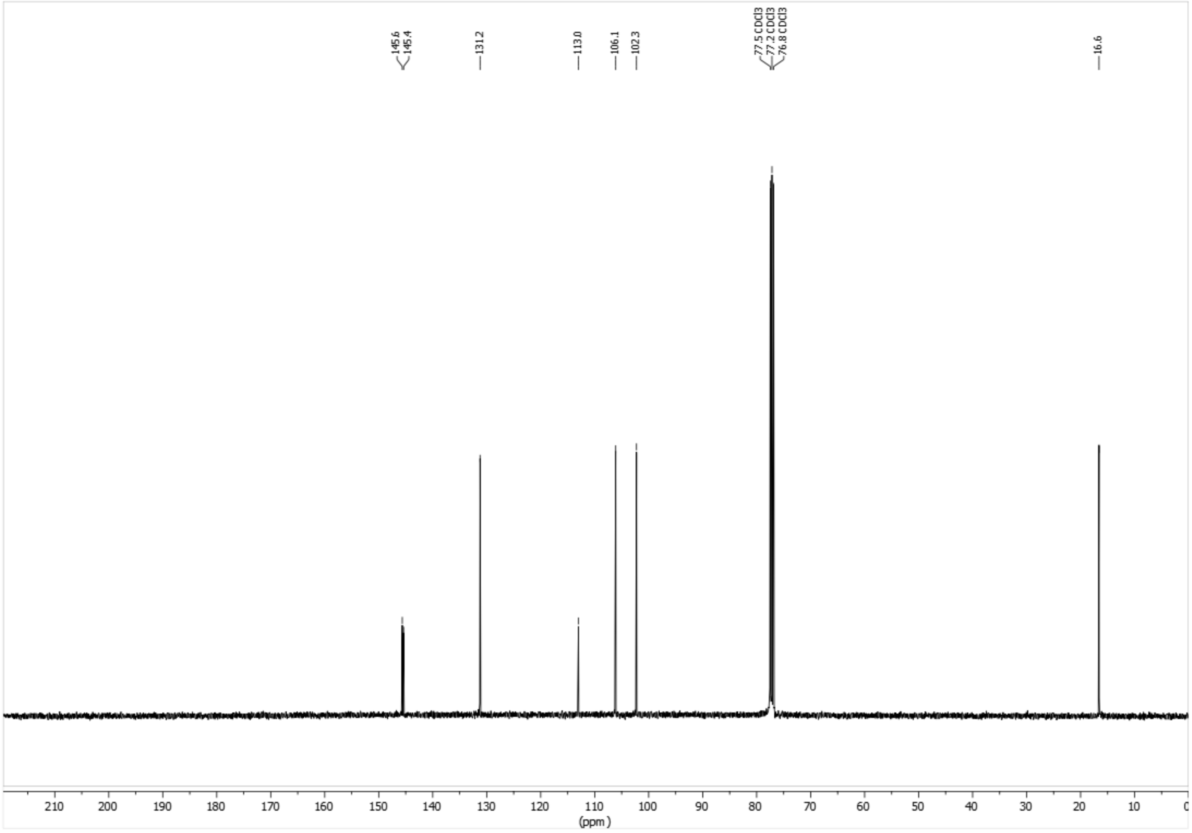
2,4-TDA Fraction from Acidic Hydrolysis of Model 3



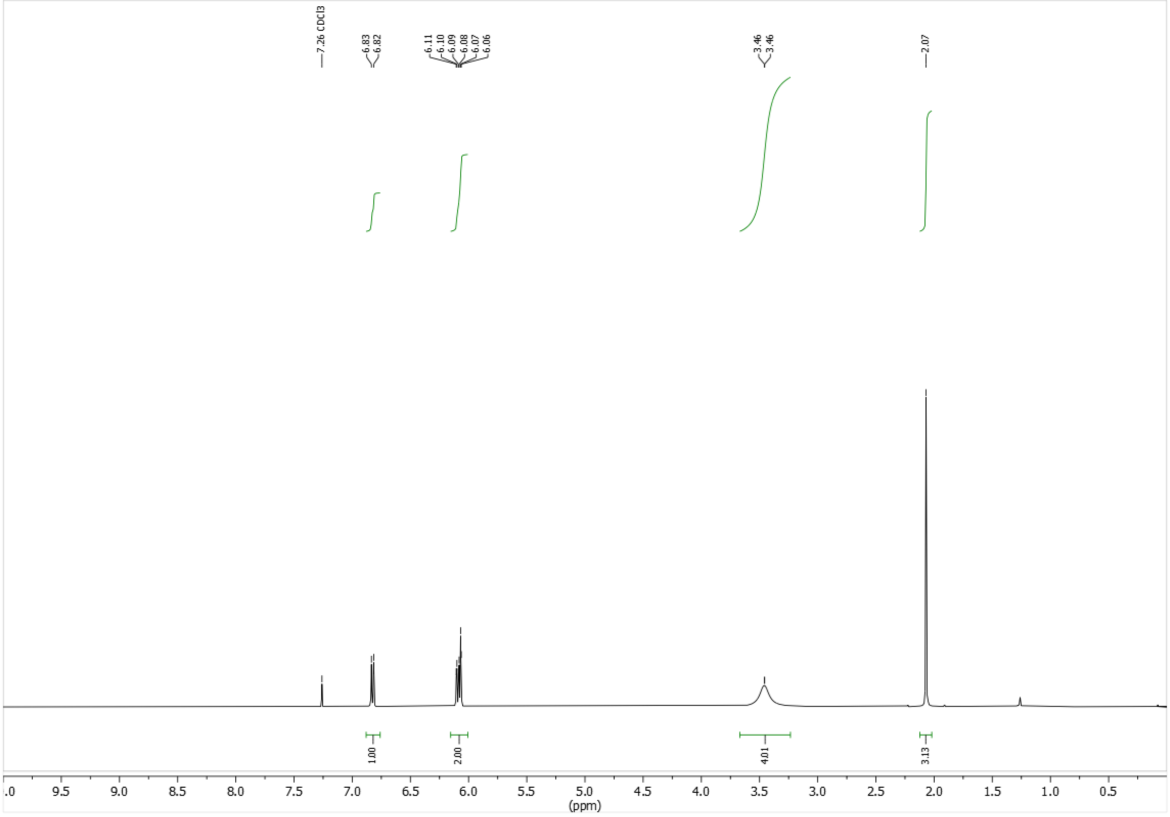


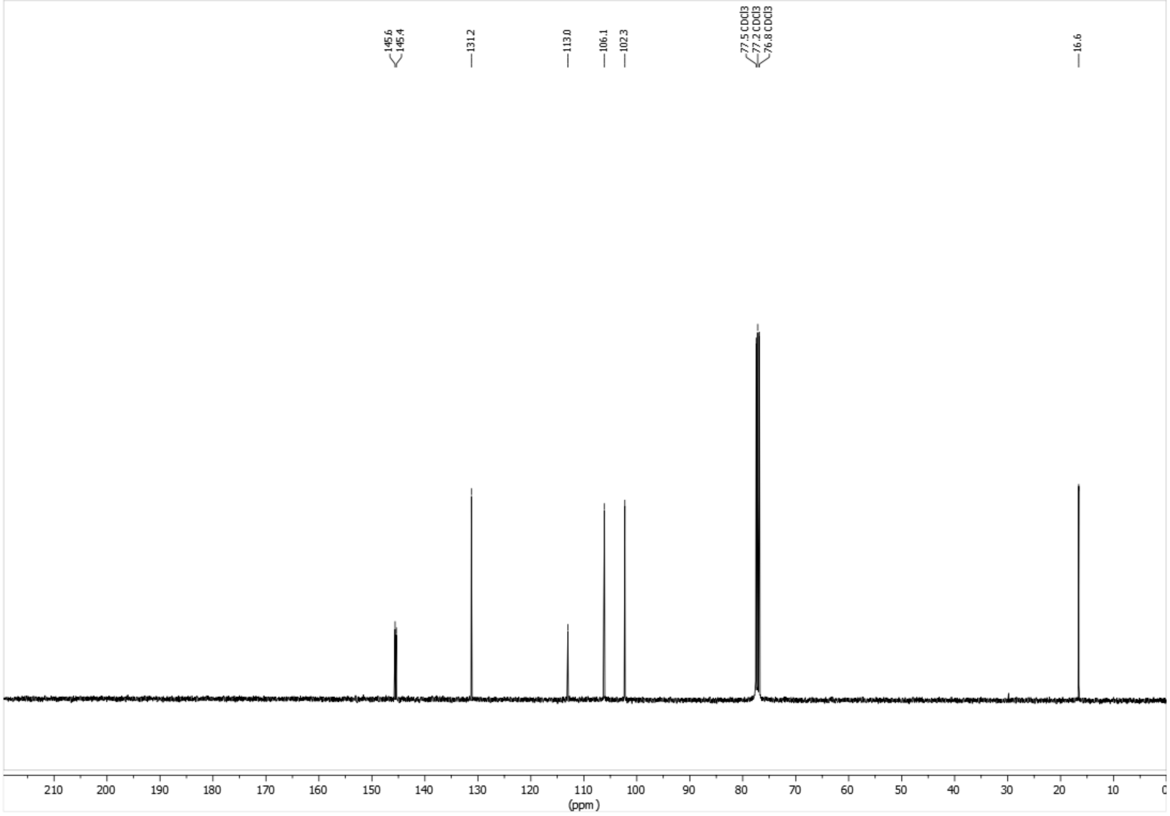
2,4-TDA from Alkaline Hydrolysis of Model 1



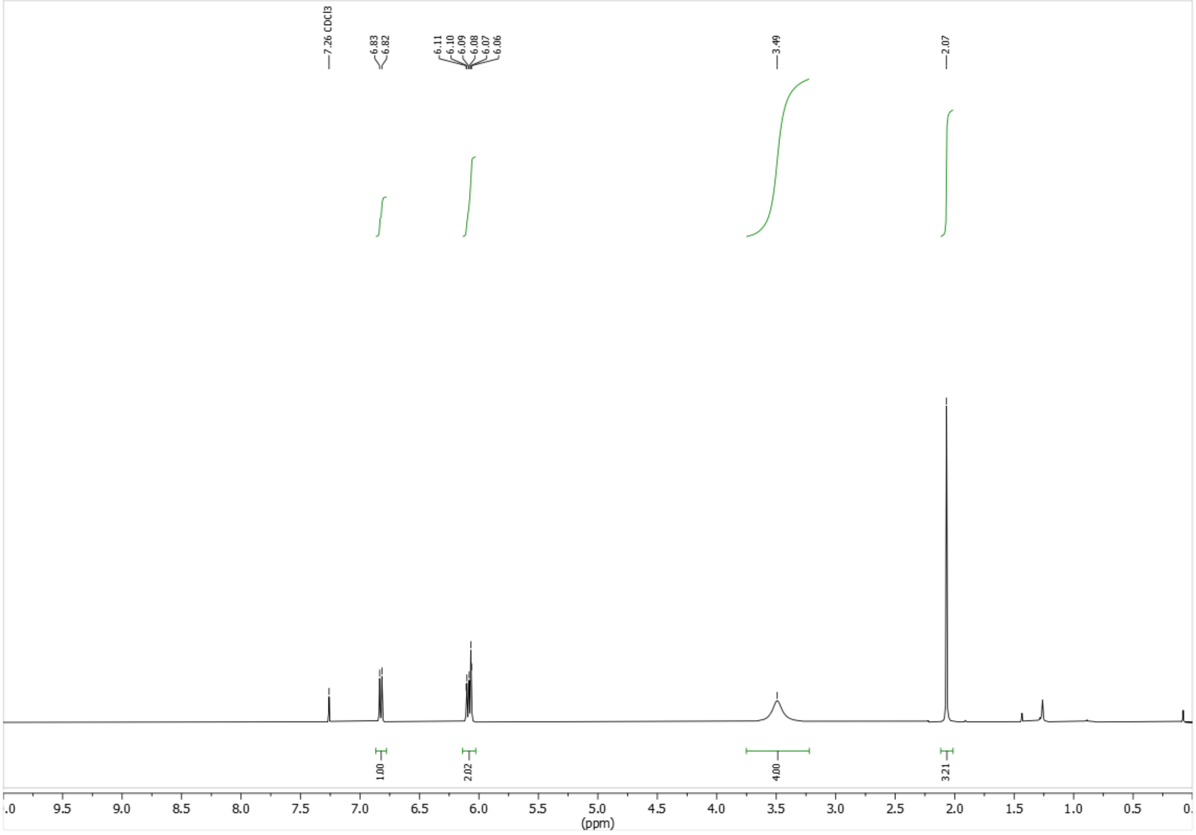


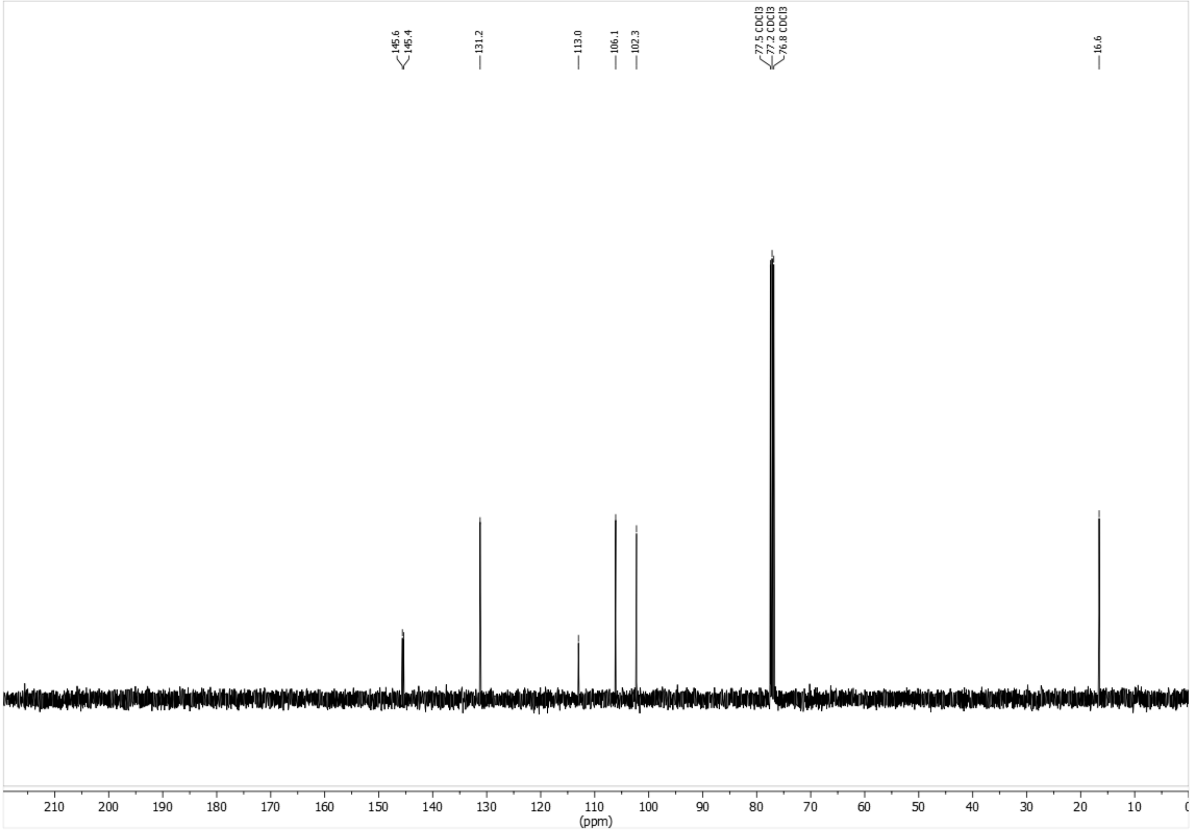
2,4-TDA from Alkaline Hydrolysis of Model 2



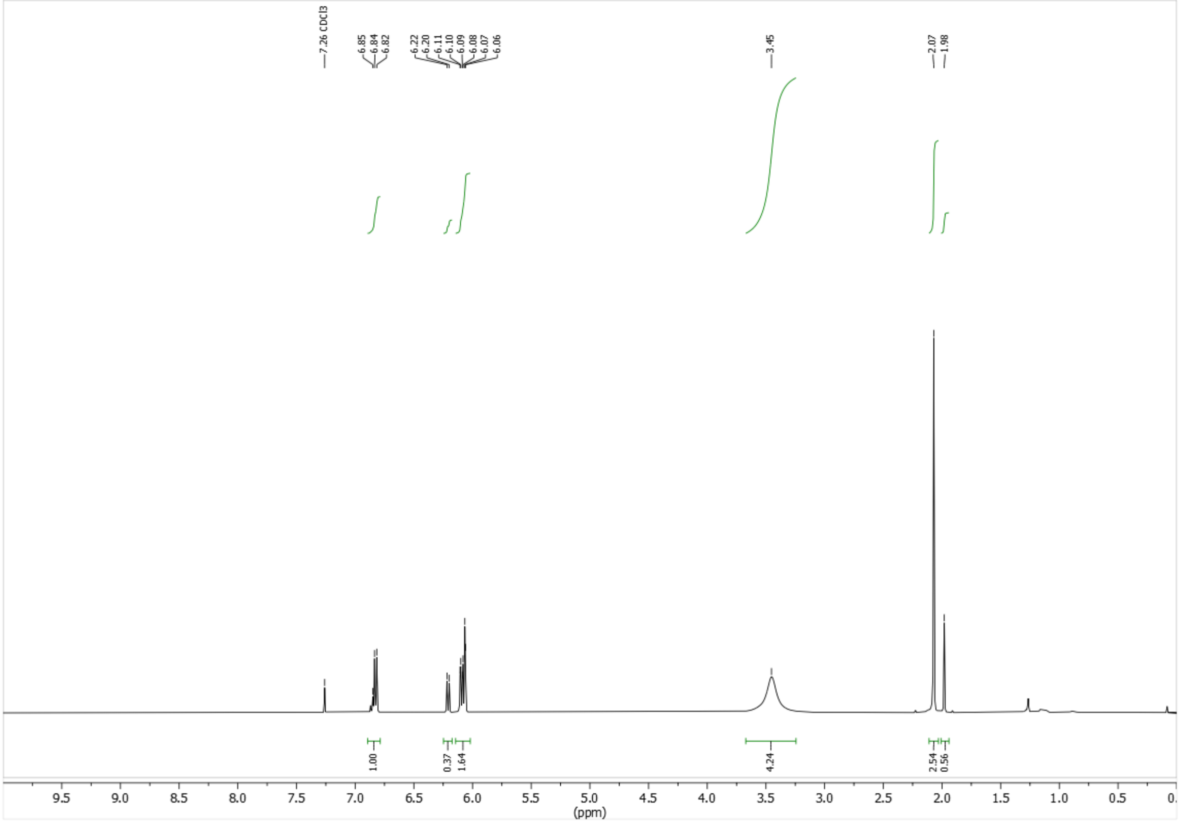


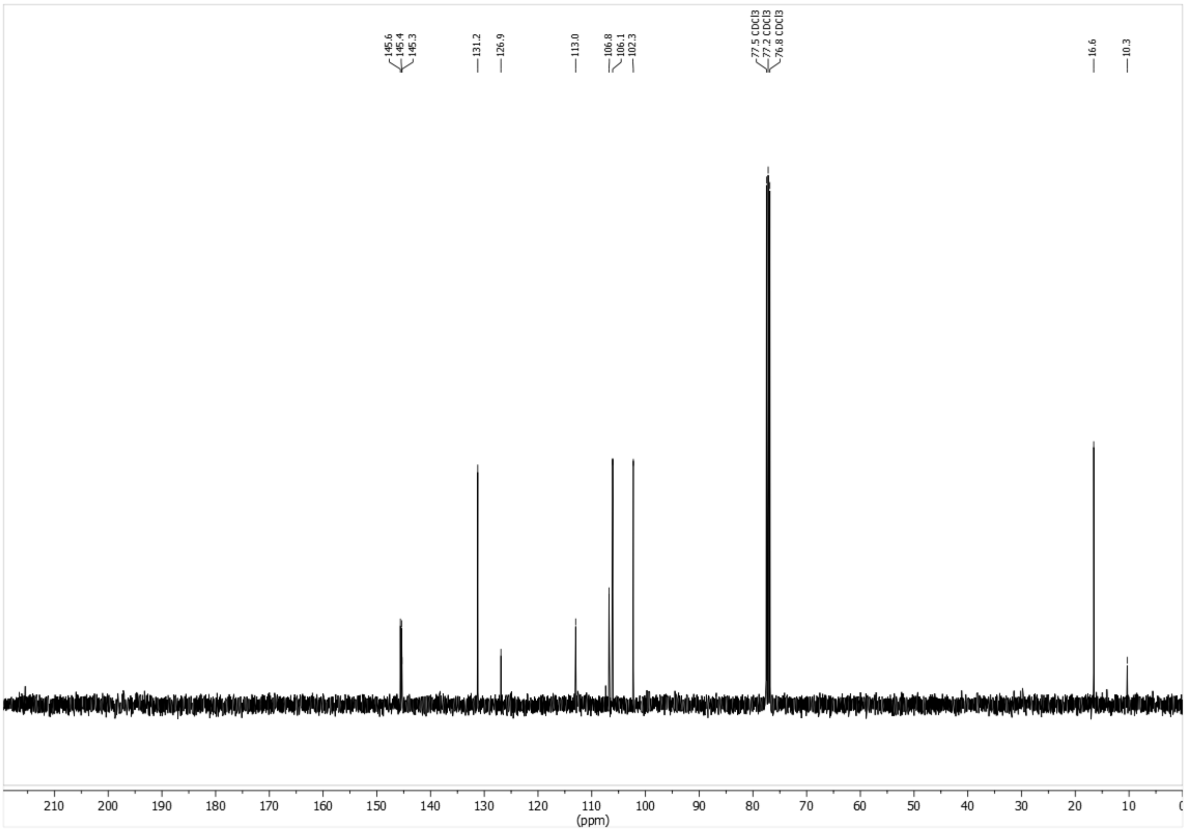
2,4-TDA from Alkaline Hydrolysis of Model 3



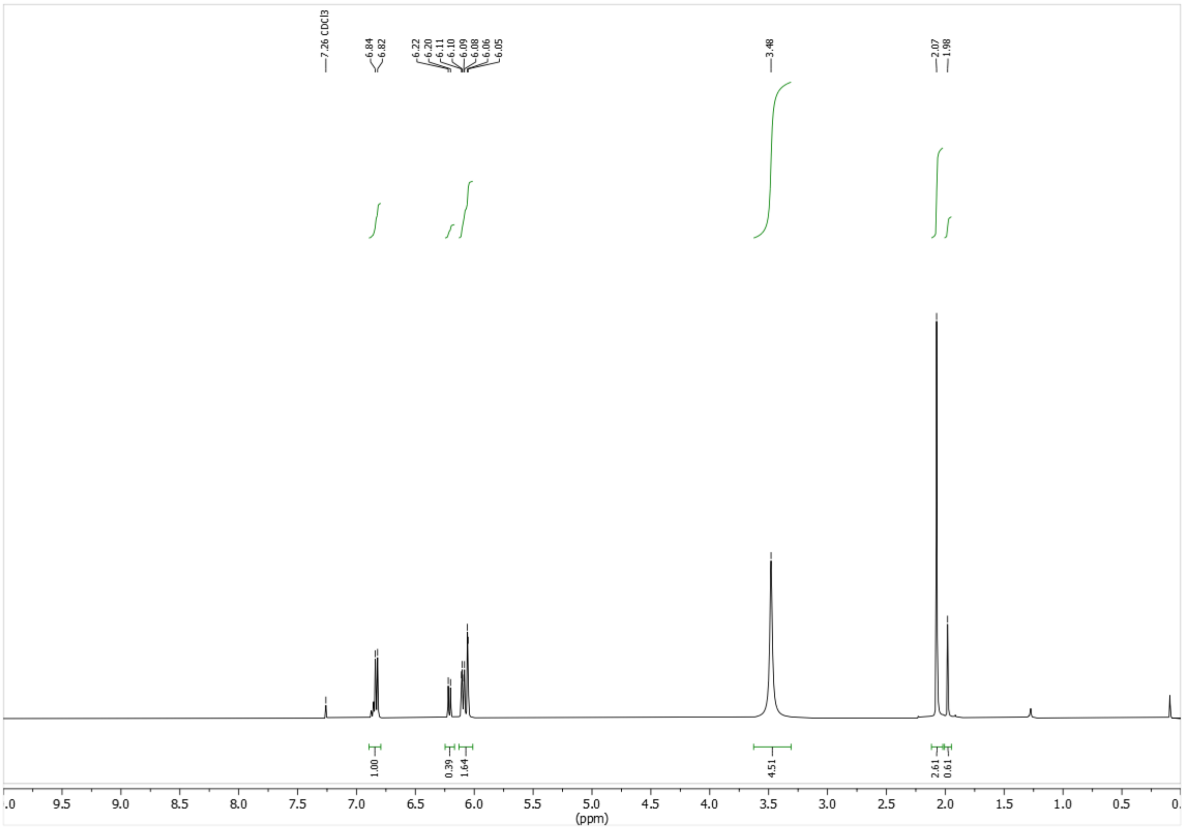


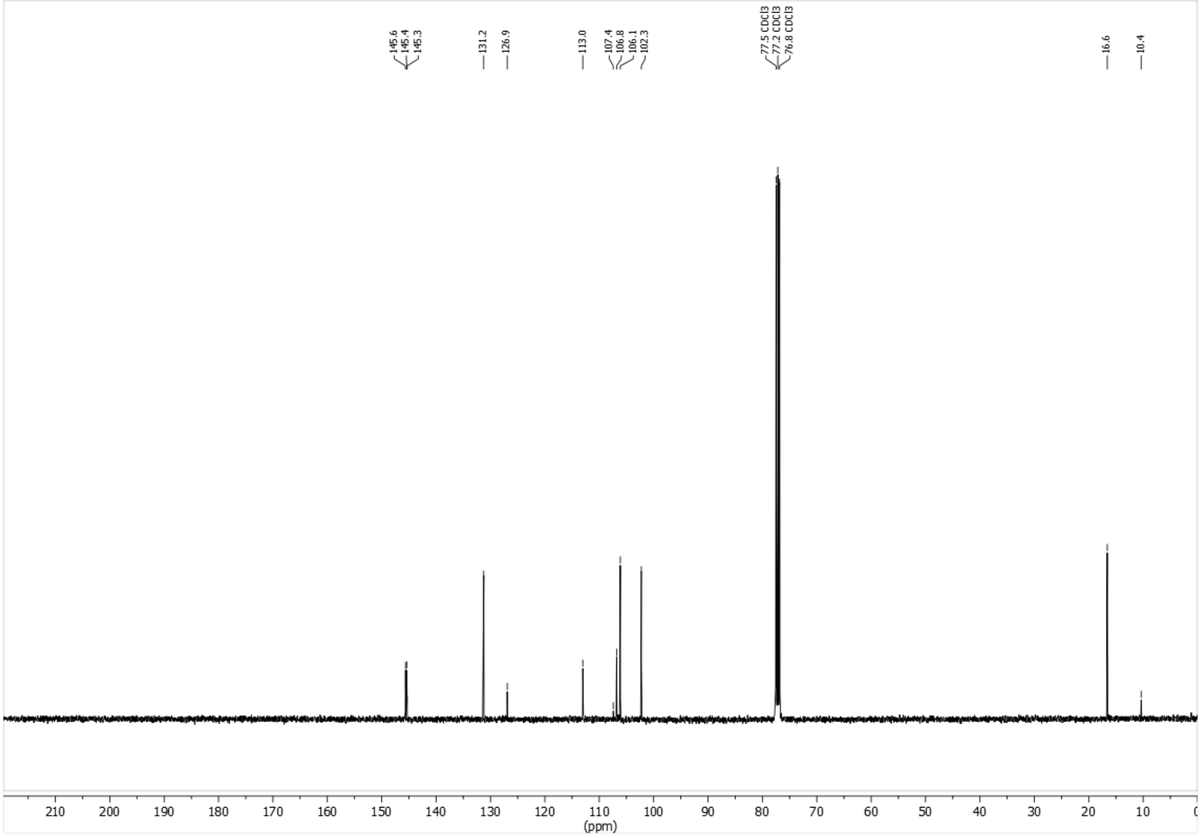
TDA from Acidic Hydrolysis of PU-HS1



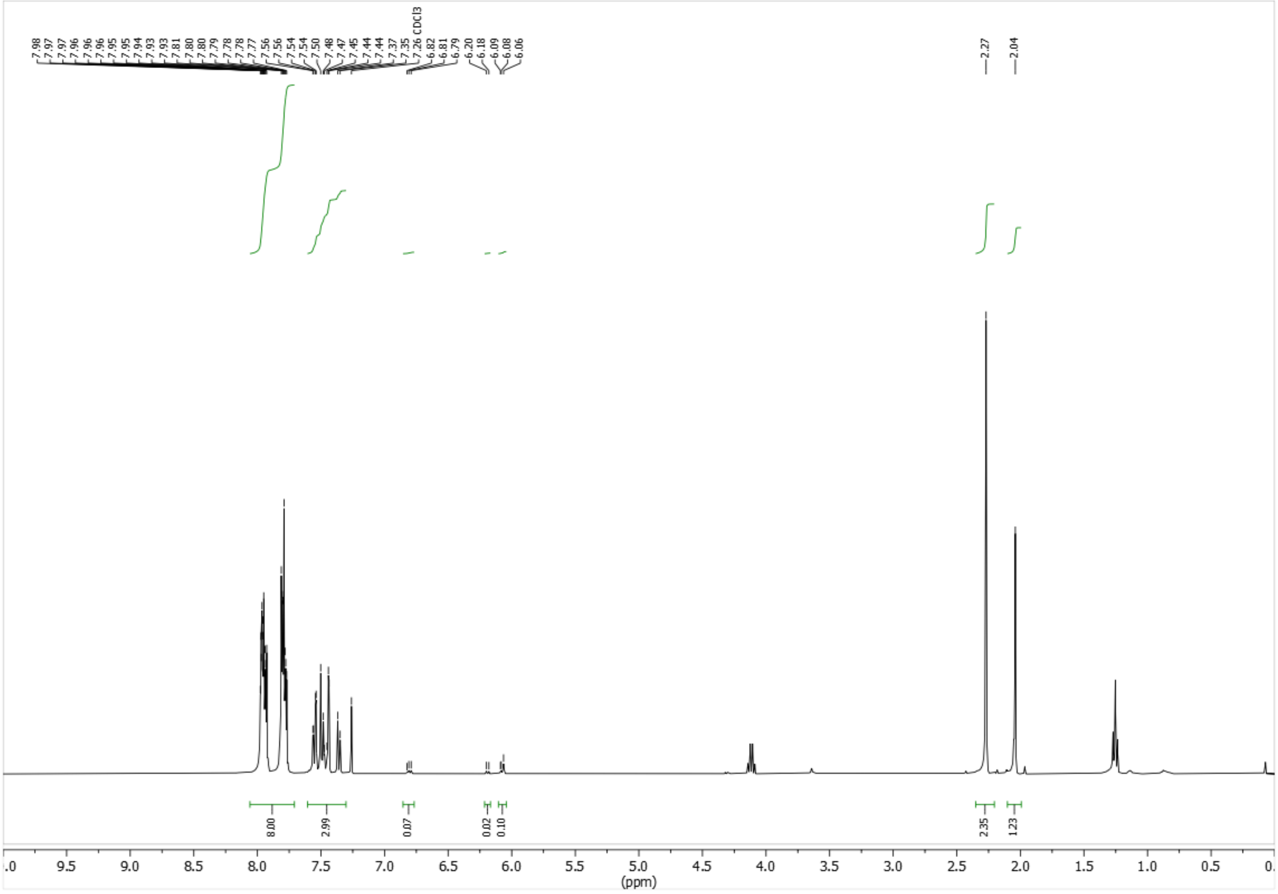


TDA from Acidic Hydrolysis of PU-HS2

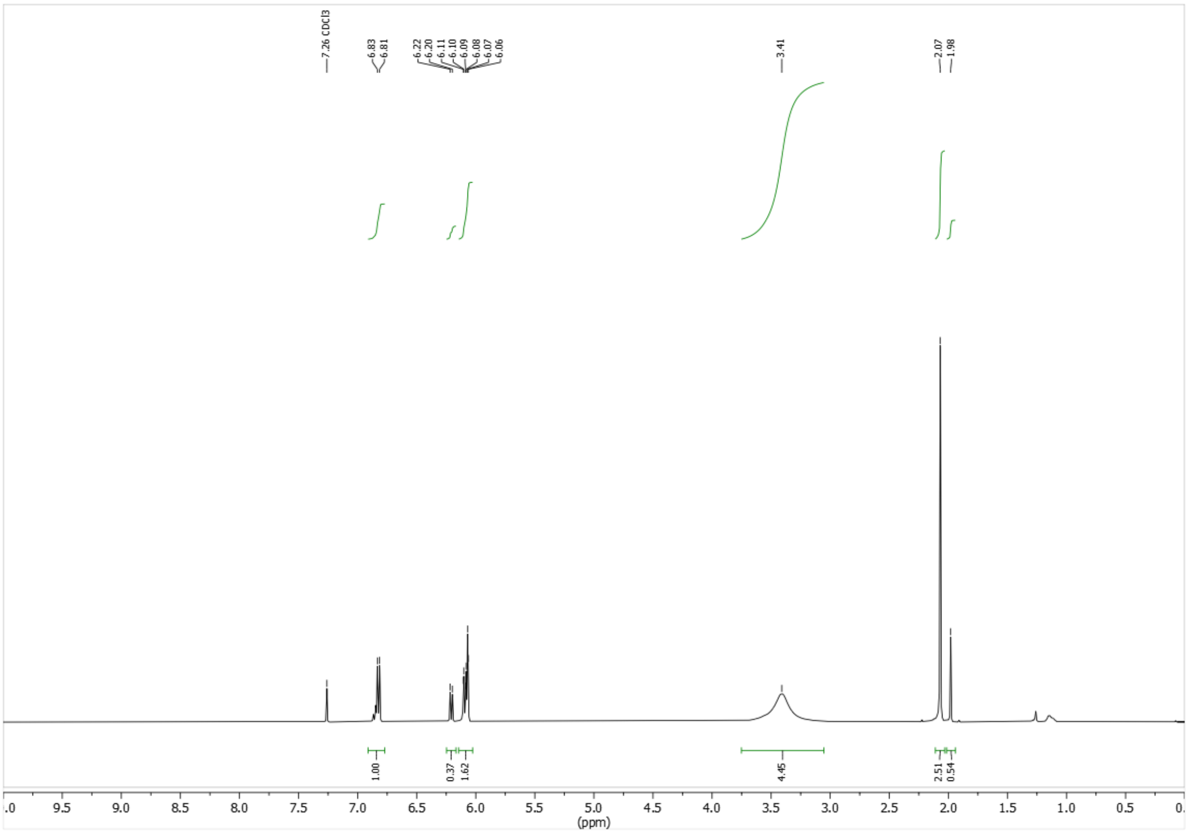


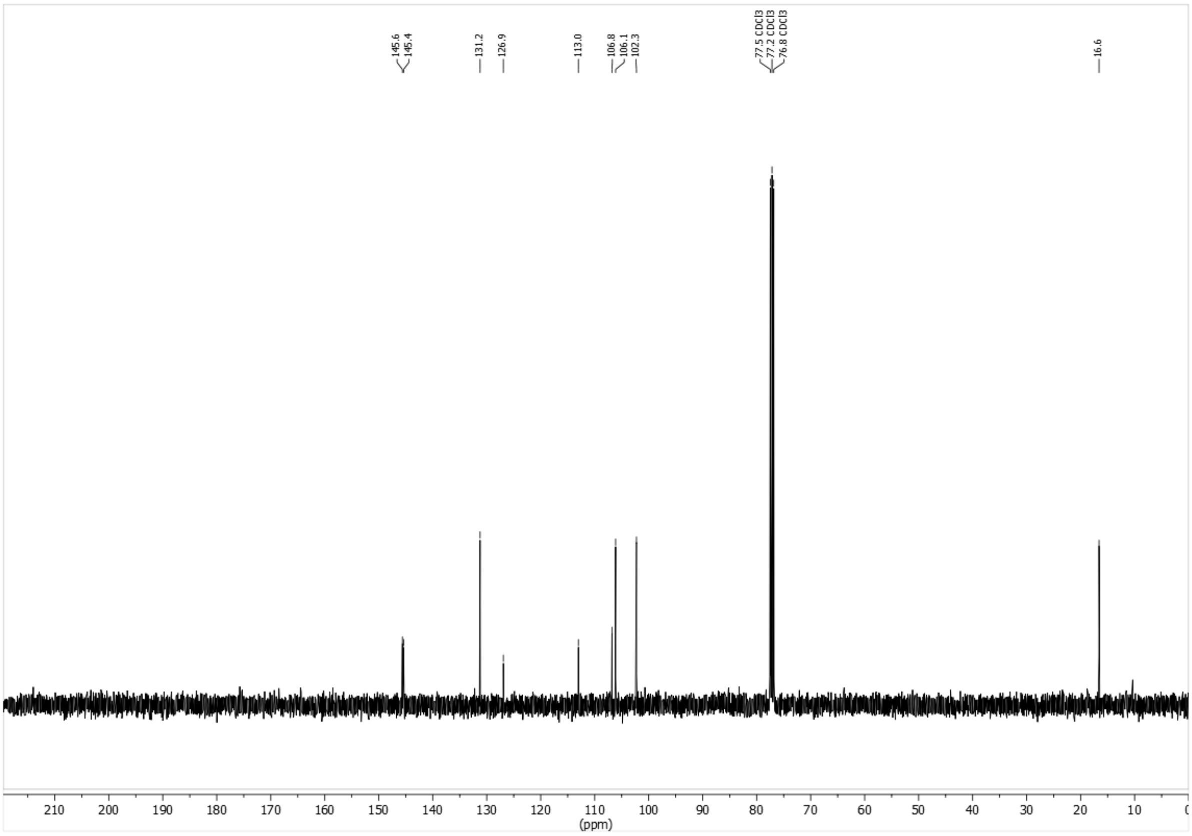


Organic Phase from Acidic Hydrolysis of PU-HS3

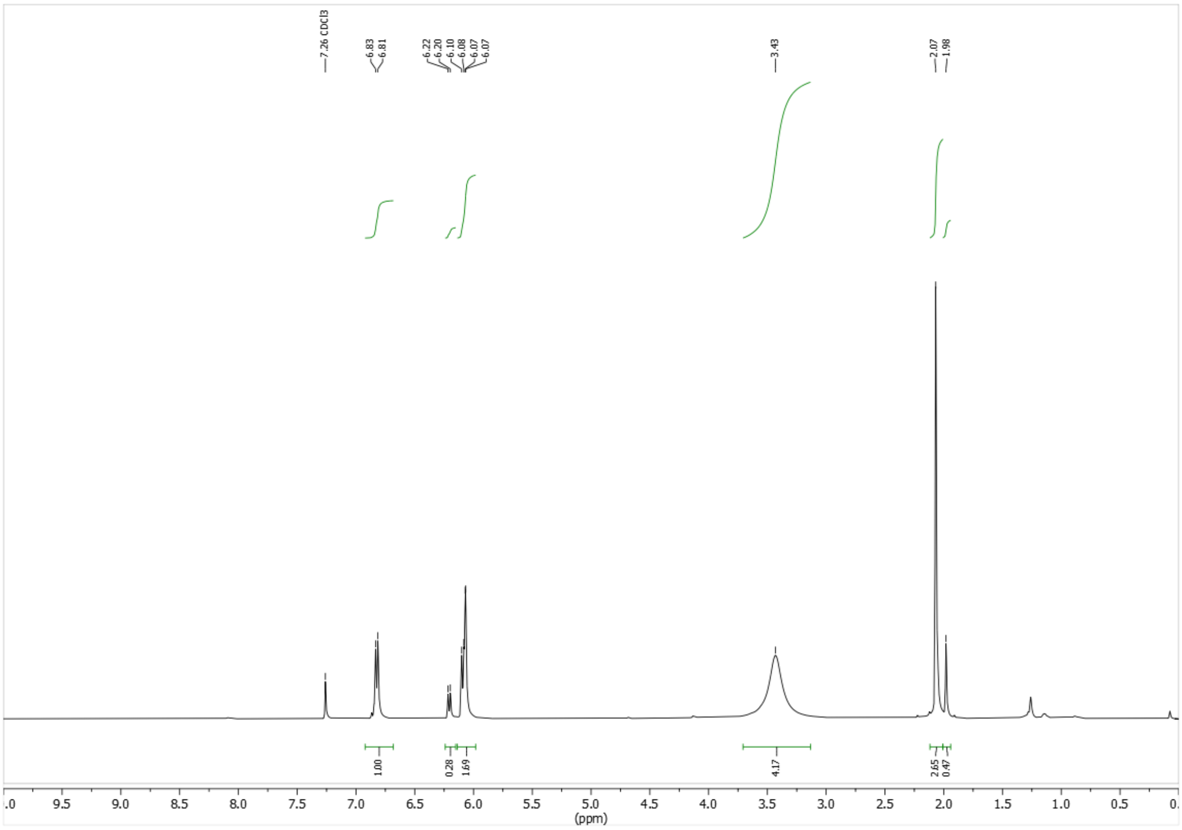


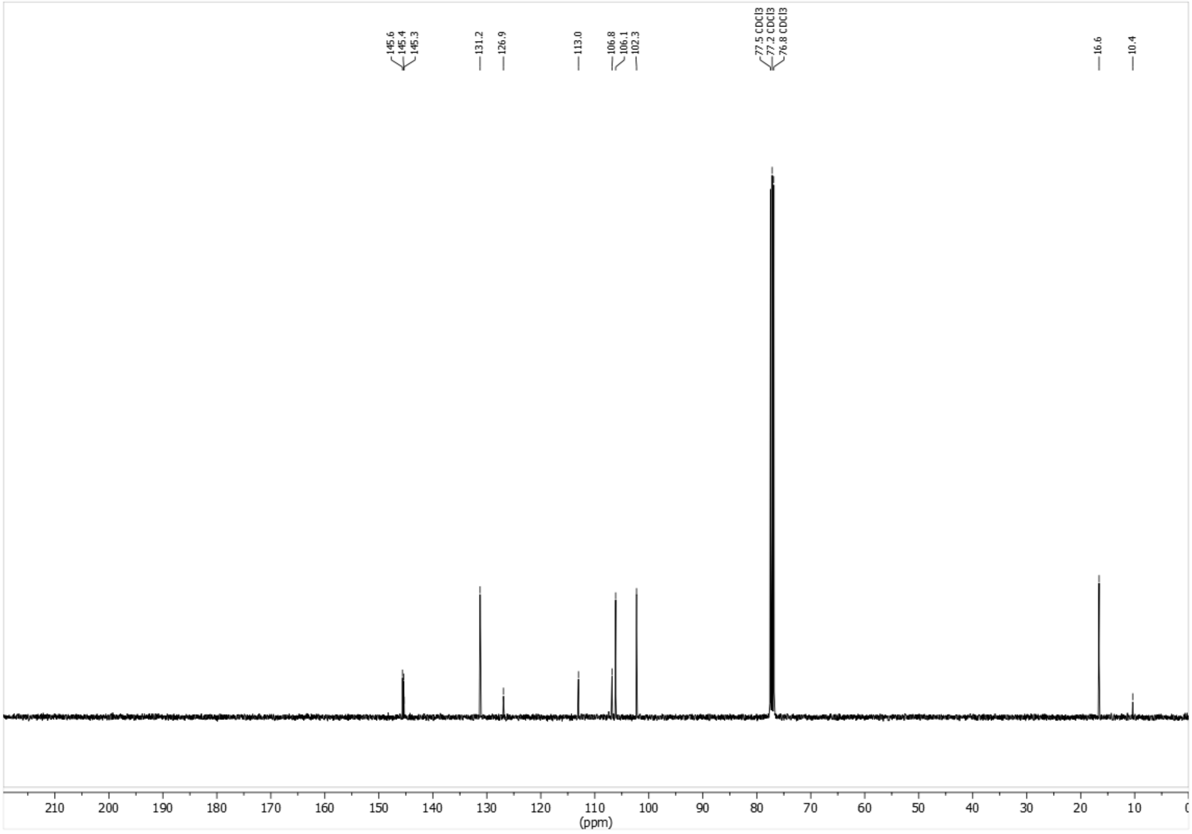
TDA from Alkaline Hydrolysis of PU-HS1



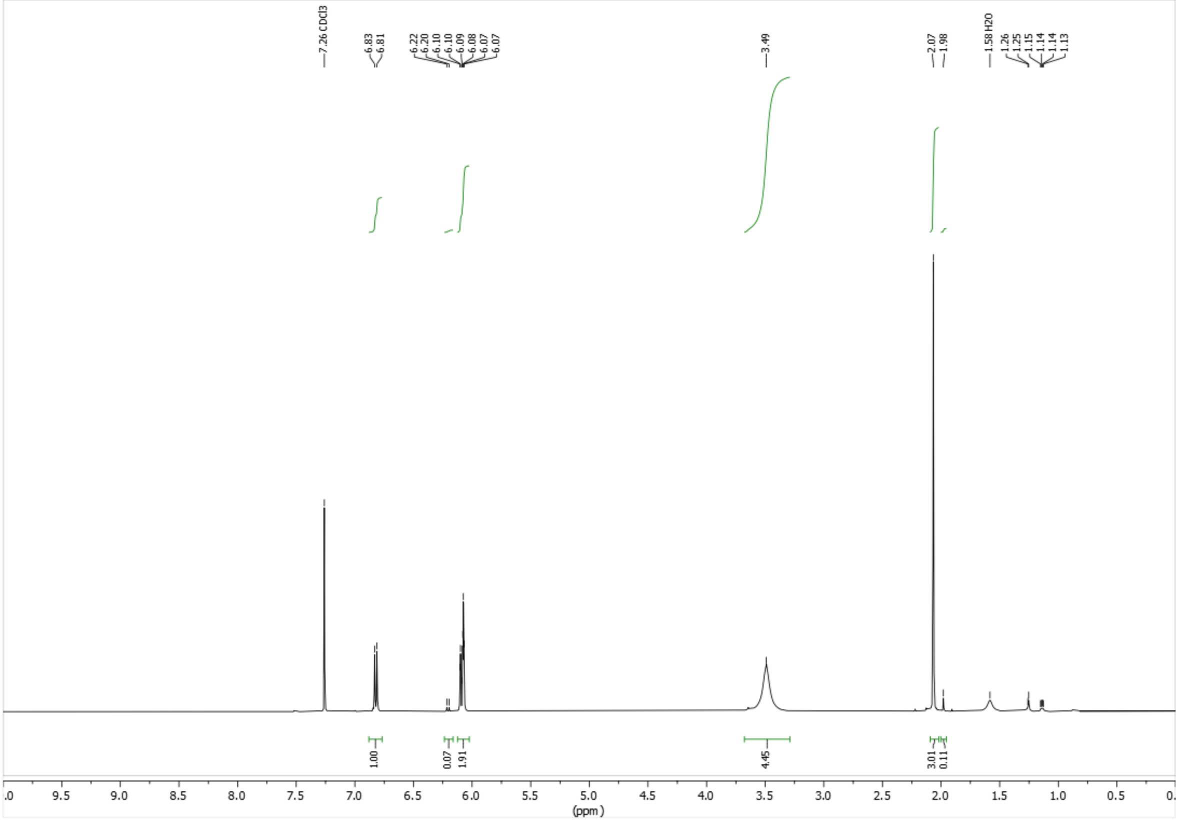


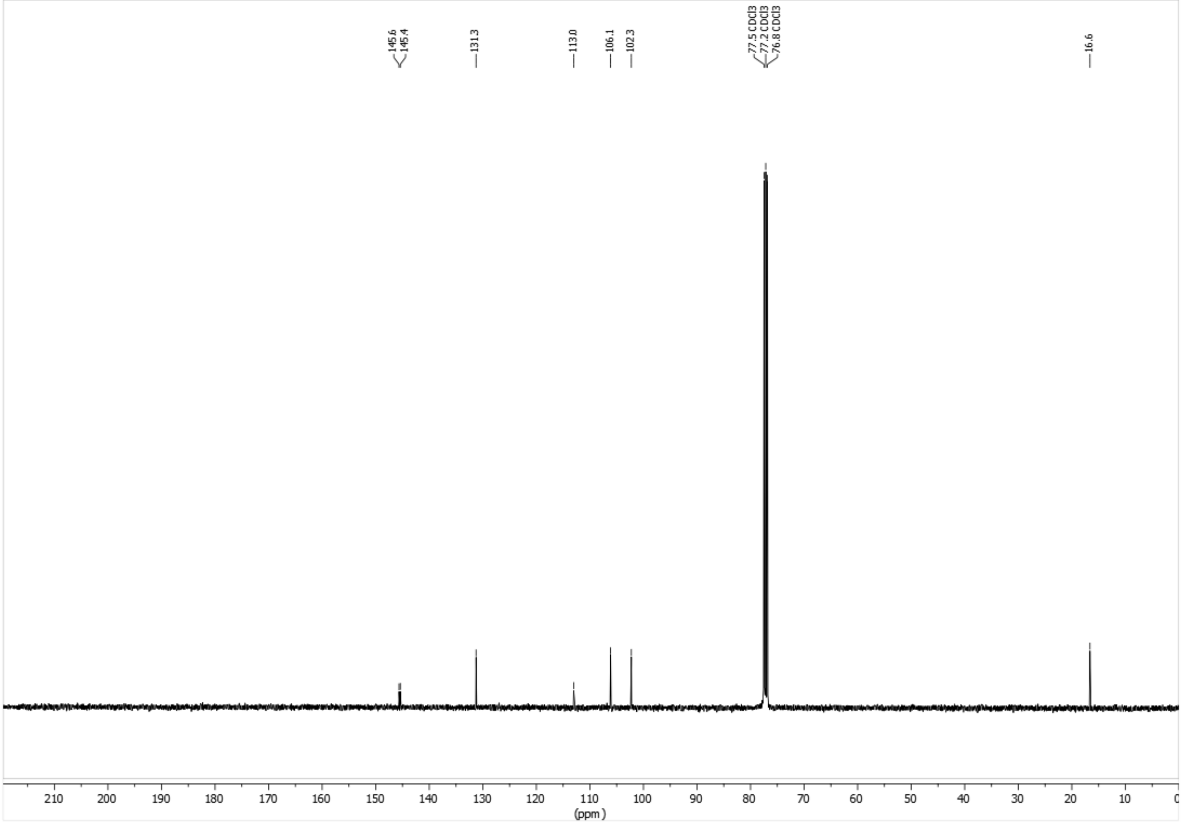
TDA from Alkaline Hydrolysis of PU-HS2



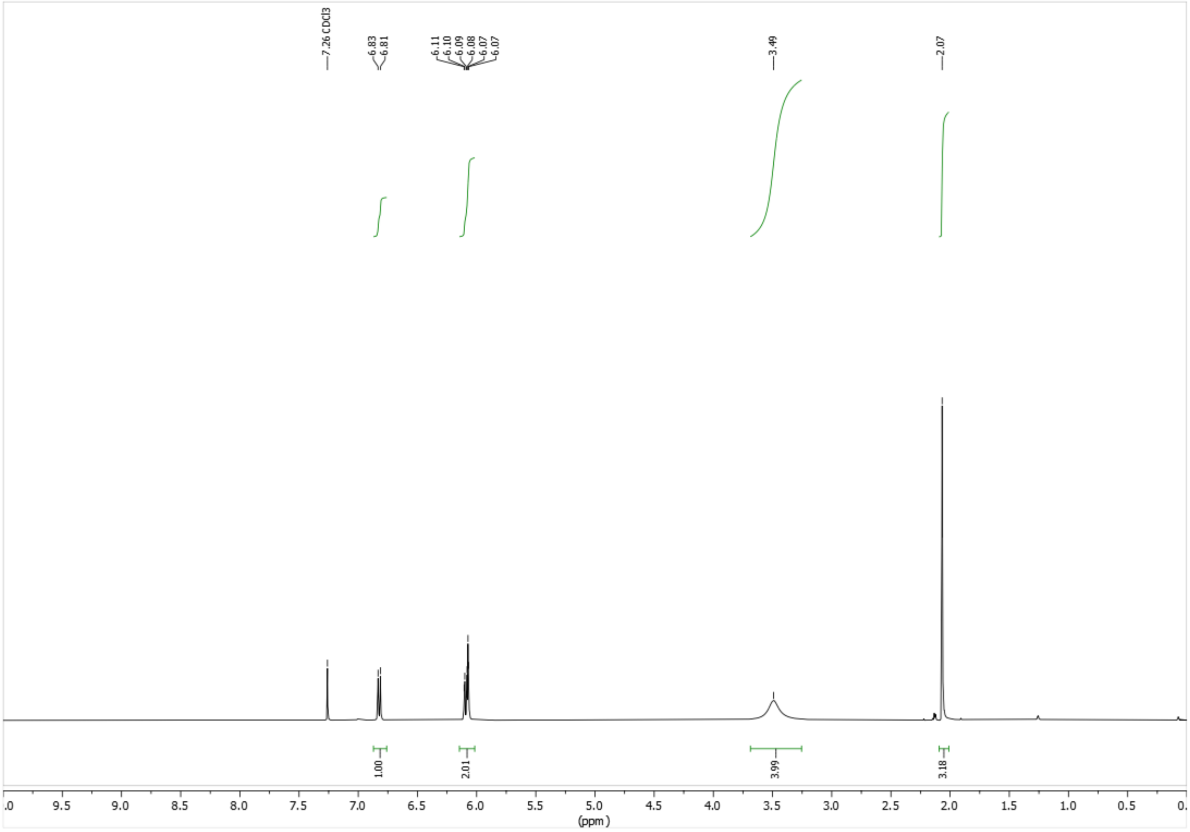


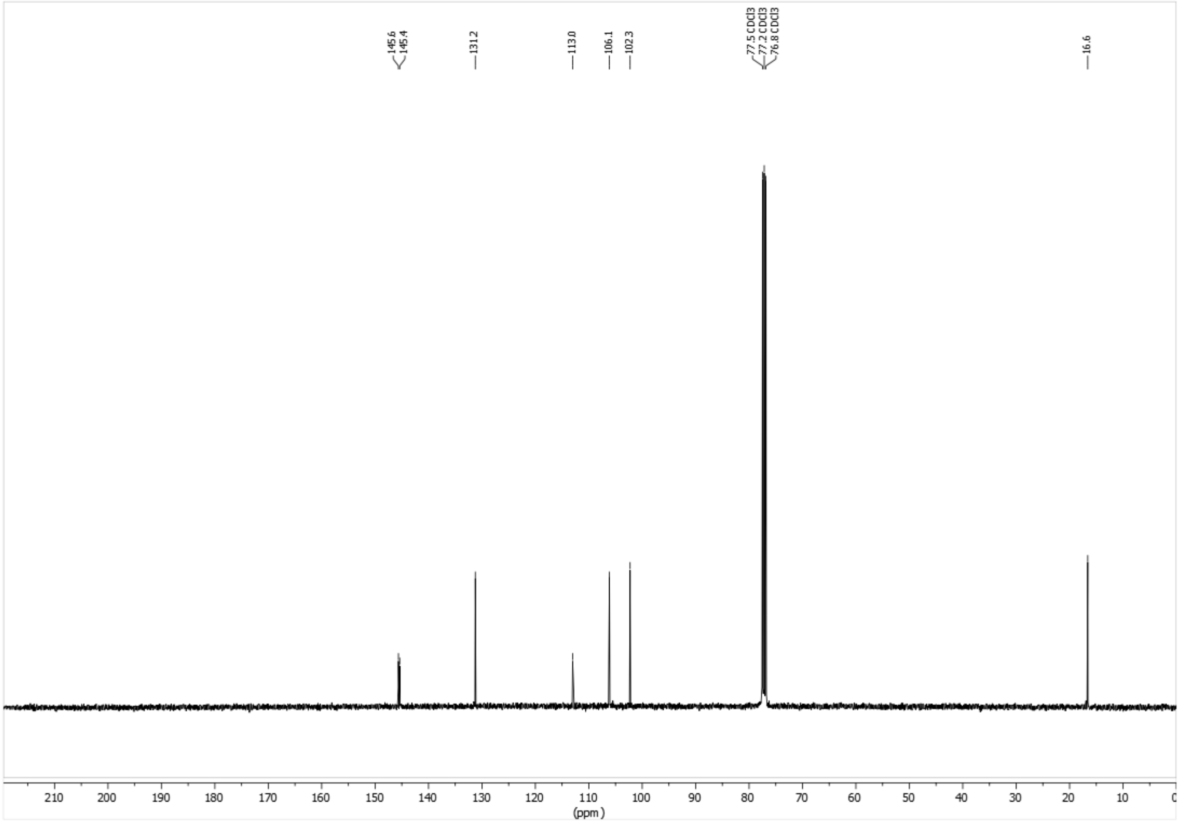
TDA from Alkaline Hydrolysis of PU-HS3



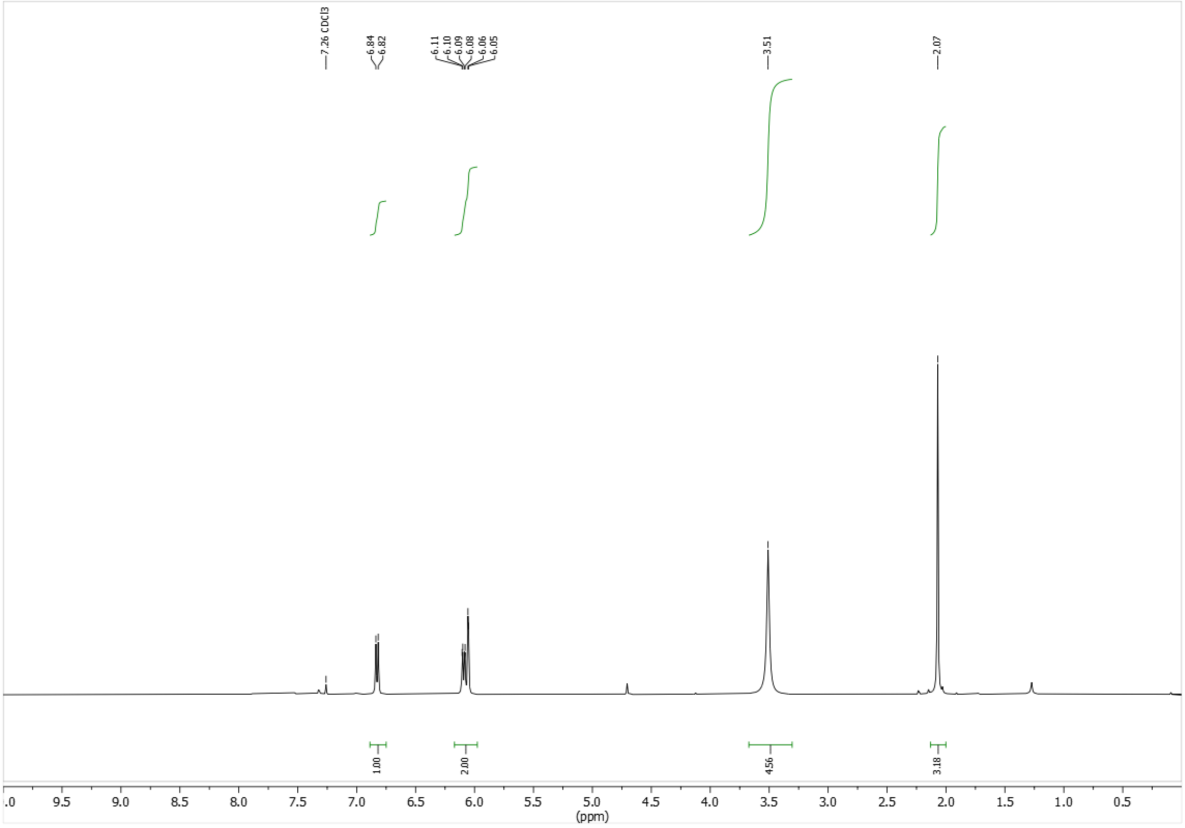


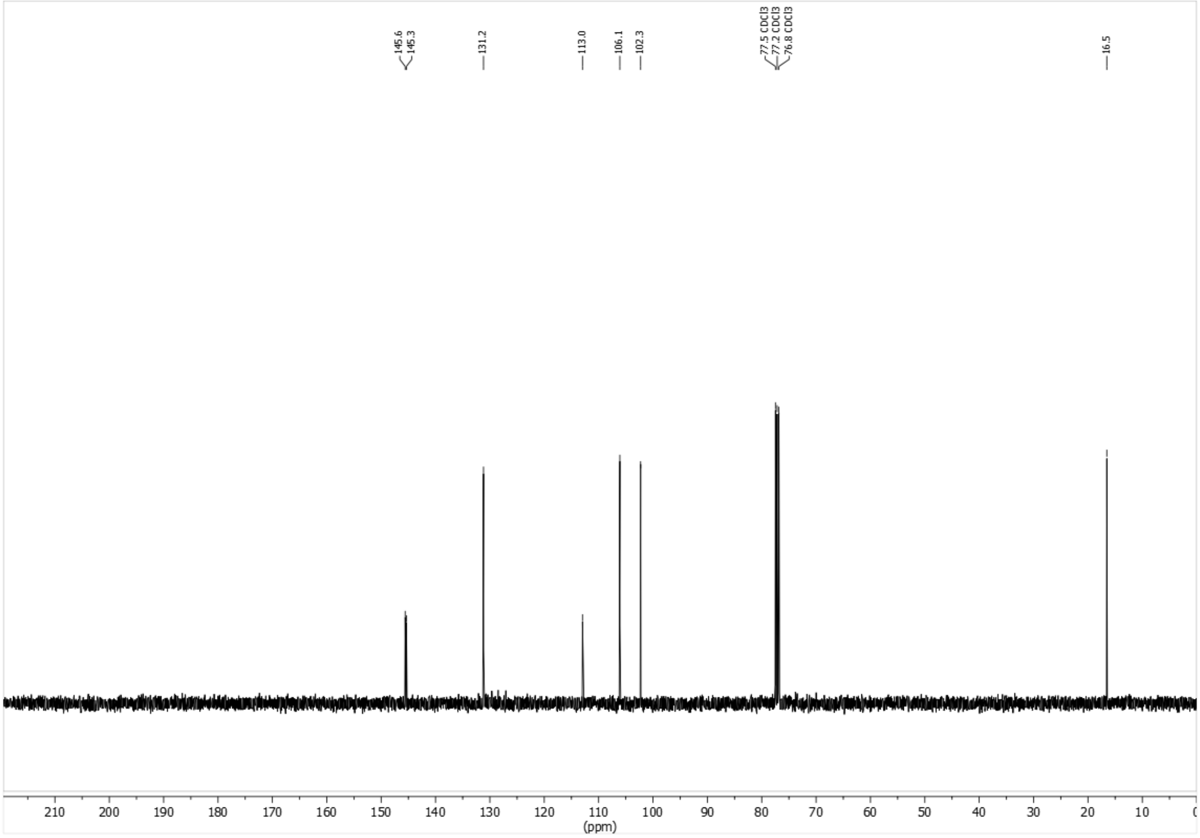
2,4-TDA from Ruthenium Catalysed Hydrogenation of Model 1





2,4-TDA from Ruthenium Catalysed Hydrogenation of Model 3





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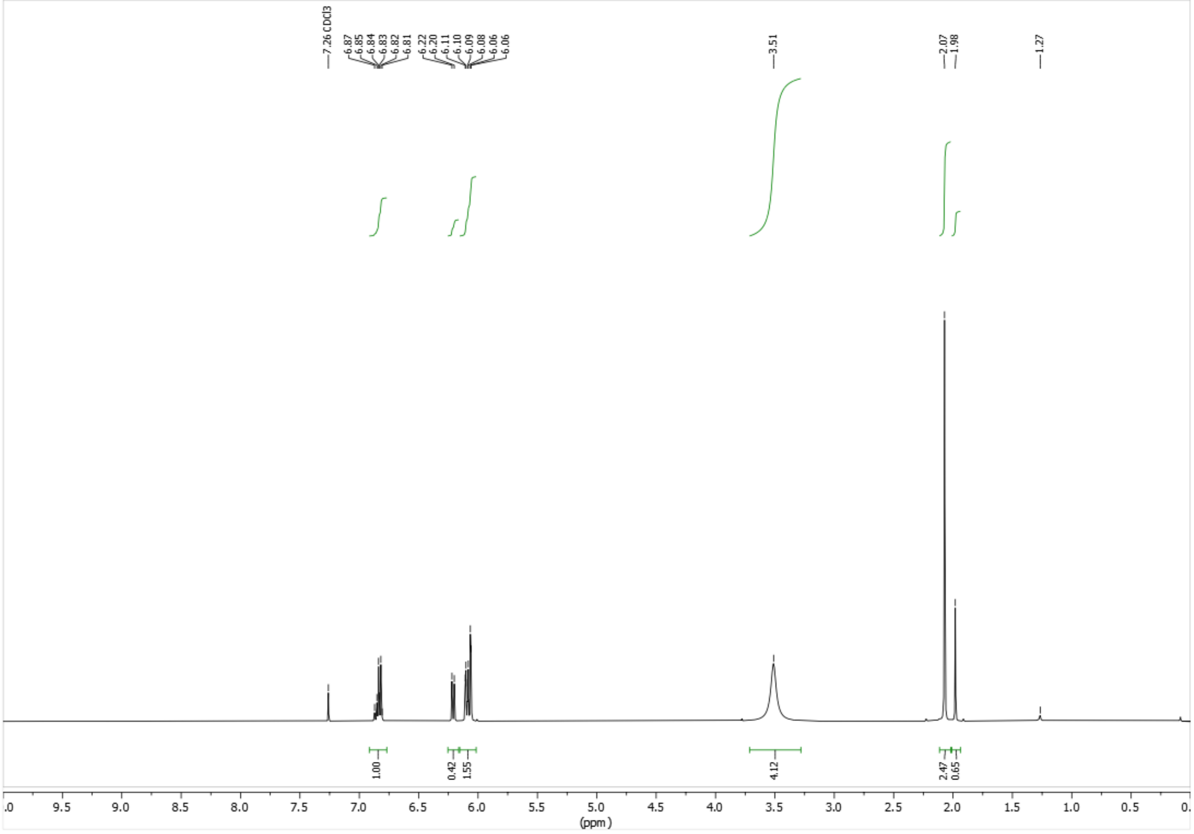

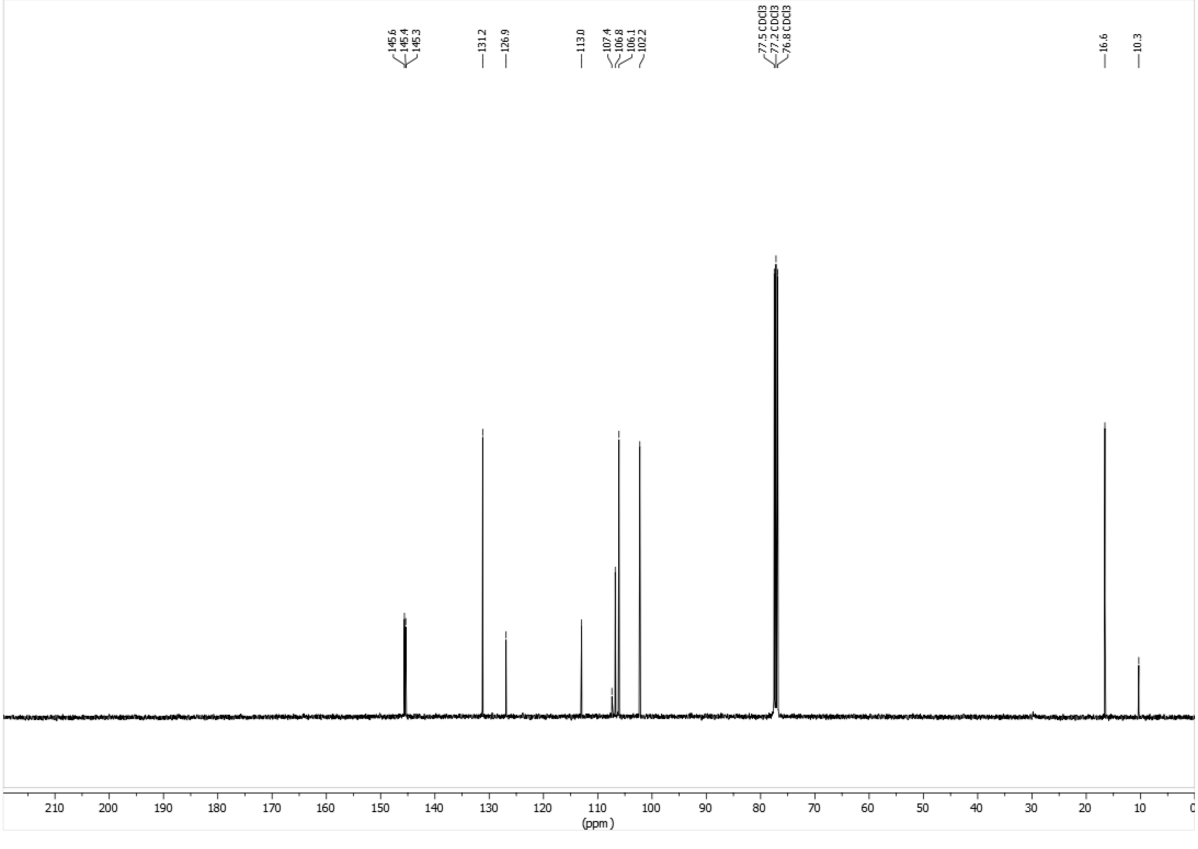

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