Supporting Information

Recyclable thermosets based on modified epoxy-amine network polymers

Lynn Anderson[a], Edward W. Sanders[a,b] and Matthew G. Unthank*[a]

a. Department of Applied Sciences, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK

b. Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK

* Corresponding author.

E-mail address: matthew.unthank@northumbria.ac.uk

1. Materials

All materials were purchased from commercial vendors listed in table 1 and used as received without further purification for synthesis unless specifically stated.

Table S1: Chemical List

Chemical	CAS	Supplier	Purity / Grade
1.1 Model Ligands			
Phenyl Glycidyl ether (PGE)	122-60-1	Acros Organics	99%
Cyclohexylamine (CHA)	108-91-8	Acros Organics	99%
Hexylamine (HA)	111-26-2	Acros Organics	99%
1.2. Monoboronic Acids/ Esters			
Phenyl boronic acid hydrate (PhBac)	98-80-6	Fluorochem	95%
(4,4,5,5-Tetramethy-1,3,2-dioxaborolan-2-yl)benzene (Phenylboronic acid pinacol ester)	24388-23-6	Fluorochem	98%
1.3. Diboronic Acids/ Esters			
1,4-phenylene diboronic acid	4612-26-4	Fluorochem	97%
1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1,4-phenylene diboronic acid dipinacol ester)	99770-93-1	Fluorochem	97%
1.4. Epoxy Resins			
1,4-butanediol glycidyl ether (BGE)	2425-79-8	Alfa Aesar	96%
DER 332 (Bisphenol A epoxy resin)	25068-38-6	Olin	>99%
1.5. Aliphatic Amines			
4,4'-diamino dicyclohexylmethane (4,4'-MDH)	1761-71-3	Alfa Aesar	98%
1,6-hexane diamine	124-09-4	Acros Organics	99.5%
1.6 Solvents/Reagents			
Tetrahydrofuran	109-99-9	Fischer	99.5% / Lab grade
Deuterated chloroform ($CDCl_3$)	865-49-6	Cambridge Isotope Laboratories	99.8% + 0.05% w/v TMS

Deuterated dimethyl sulfoxide (DMSO-6)	2206-27-1	Cambridge Isotope Laboratories	99.9% + 0.05% w/v TMS
Acetonitrile	75-05-8	Fischer	99.9% / HPLC grade
Butan-1-ol	71-36-3	Fischer	99%
n-Butyllithium, 2.5M solution in hexanes (n-BuLi)	109-72-8	Acros Organics	N/A
Triisopropyl borate	5419-55-6	Acros Organics	98%
Bromobenzene	108-86-1	Acros Organics	99%
2,3-Dimethyl-2,3-butanediol (pinacol)	76-09-5	Alfa Aesar	99%
Ethylene glycol (1,2-diol)	107-21-1	Acros Organics	99%

2. Analytical Methods and Equipment

2.1. Nuclear Magnetic Resonance (NMR)

NMR analyses were acquired at 25 °C using a JOEL ECS400 Delta spectrometer at frequencies of 399.78 MHz for ^{1}H-NMR, 100.53 MHz for ^{13}C-NMR and 128.28 MHz for ^{11}B-NMR. All chemical shifts are quoted as parts per million (ppm) relative to tetramethylsilane (TMS, δ = 0 ppm) as an internal standard in either deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d^6). Hydroxy (OH) group analyses were confirmed by doping samples with a drop of deuterated water (D_2O). ^{13}C-NMR assignment was confirmed by DEPT analysis. The spectral data is recorded as chemical shift (δ), relative integral, multiplicity (s=singlet, br=broad, d=doublet, t=triplet, q=quartet, quin=quintet, sext=sextet, dd=doublet of doublets, m=multiplet) and coupling constant (J = Hz).

2.2. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy was performed on a Bruker alpha Platinum-ATR and the outputs analysed in OPUS software. Absorption maxima are expressed in wavenumbers (cm^{-1}).

2.3. Mass Spectroscopy (MS)

Samples were acquired using a Thermo RSLC coupled to an ABSciex 6600 QTof. The equivalent of 1-5 µM (1-5 pmol/µl) was injected onto the system per run. The loading pump was used at high flow to run linear chromatography gradients. All samples were acquired in positive mode. The buffer system comprised of Buffer A 0.1% (v/v) Formic Acid and Buffer B 99.9% Acetonitrile, 0.1% (v/v) Formic Acid. Chromatographic separations were achieved using a Fortis C8 column, 100 mm x 2.1 mm, 3 µM particle size, 45 °C at a flow rate of 250 µl/min. Samples were loaded onto the column and desalted online for 1 minute, with eluent diverted to waste. A valve switch directed flow to the mass spectrometer. Samples were then eluted from the column using a linear gradient from 3-70% Buffer B over 12 min. Total run time was 17 min. The eluent was directed into an ABSciex 6600 QTof, operated in positive mode. Source conditions were; temperature 180°C, GS1 25, GS2 15, ISFV 4500v. Data was acquired in MS scan mode between 100-1000 m/z. Resolution of the instrument was 45,000 at m/z 829.54.

2.4. Gel Permeation Chromatography (GPC)

Polymer samples were dissolved in THF (2 mg/mL) and filtered through 0.2 µm nylon filters. Samples were analysed using an Agilent 1260 infinity II system equipped with a RI and viscometry detector, fitted with PLgel MiniMIX-E and PLgel MiniMIX-D columns in sequence, using a THF mobile phase and a flow rate of 0.6 mL/min or 0.4 mL/min. Analysis was performed against a calibration curve of polystyrene standards (EasiVial PS-M supplied by Agilent).

2.5. Thermogravimetric Analysis (TGA)

TGA analysis was conducted using a Perkin-Elmer Pyris 6 TGA thermal analyser and results analysed in Pyris software (version 11.1.1.0492). Polymer samples of between 16-20 mg weight were heated in ceramic crucibles from 30 °C to 650 °C at a constant rate of 20 °C per minute, under a flow of N_2 (40 mL/min). The residual mass was recorded as a percentage weight, of the original mass, that remained at 600 °C (within the range where mass remained constant after the degradation of organic material).

2.6. Differential Scanning Calorimetry (DSC)

Glass transition (T_g) analyses were conducted on all polymeric materials using a Perkin-Elmer Pyris DSC 8500 and analysed on Pyris software (version 11.1.1.0492). Samples had previously been thermally cured in an oven at 170 °C. Sample masses of 3-6 mg were weighed into standard aluminium DSC pans with perforated lids and were heated from -50 °C to 200 °C at a constant rate of 20 °C per minute (unless otherwise stated) and the T_g reported as the midpoint of the endothermic step in the heat flow signal output (T_g onset and endpoint was also recorded). Melting point analysis was conducted using a Perkin-Elmer Pyris DSC 8500 with an intercooler II and analysed on Pyris software (version 11.1.1.0492). Solid samples between 3-6 mg were weighed into standard aluminium DSC pans and heated from -50 °C to 300 °C at a constant rate of 20 °C per minute and the melting point taken from the peak of the endothermic event that corresponds to the melting transition on the heat flow signal output.

2.7. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA analyses were conducted for network polymers on a Perkin-Elmer DMA 8000 and analysed in Pyris software (version 11.1.1.0492). Temperature scans were performed on 30 mm x 5 mm x 0.3 mm samples and were analysed in tension geometry with a fixed length of 11.52 mm, a frequency of 1 Hz and a constant temperature ramp of 3 °C/min from -80 °C to 200 °C. Storage modulus (E'), loss modulus (E'') and tan delta (Tan δ) signals were recorded.

2.8. Laser Cutting

Samples were prepared for mechanical testing using a Glowforge^{TM} Basic equipped laser cutter with a 40W CO_2 laser tube.

2.9. Tensile Testing

Thin film polymer samples were laser cut to a modified ASTM standard 638-14-type V and experiments were conducted on either an Instron 5969 or Instron 3343 with a displacement ramp rate of 10 mm/min.

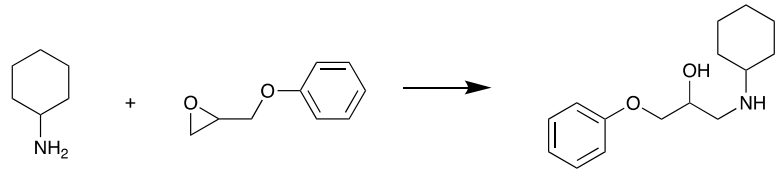
2.10. Hot Press (Mechanical) Recycling

Mechanical recycling was conducted using a 2 " x 3 " Mini Manual Hot Press Machine (TTLIFE) with LCD Controller at 700-1000 lbs pressure. Ground polymer samples were place between PTFE sheets before pressing at 170 °C for 30 minutes, before allowing to cool to 25 °C overnight. Samples were then removed from the press and prepared for testing.

3. Supplementary Data

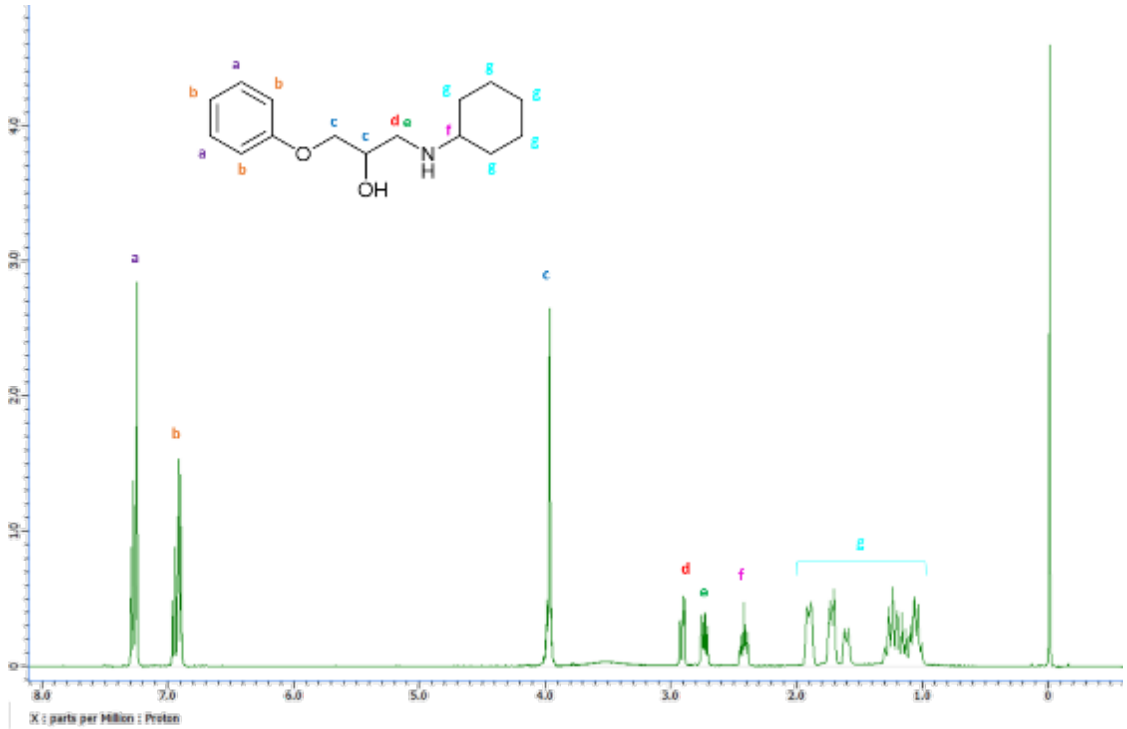
3.1. Experimental

Synthesis of β-amino diol **3**, via *N*-(cyclohexylamino)-3-phenoxypropan-2-ol

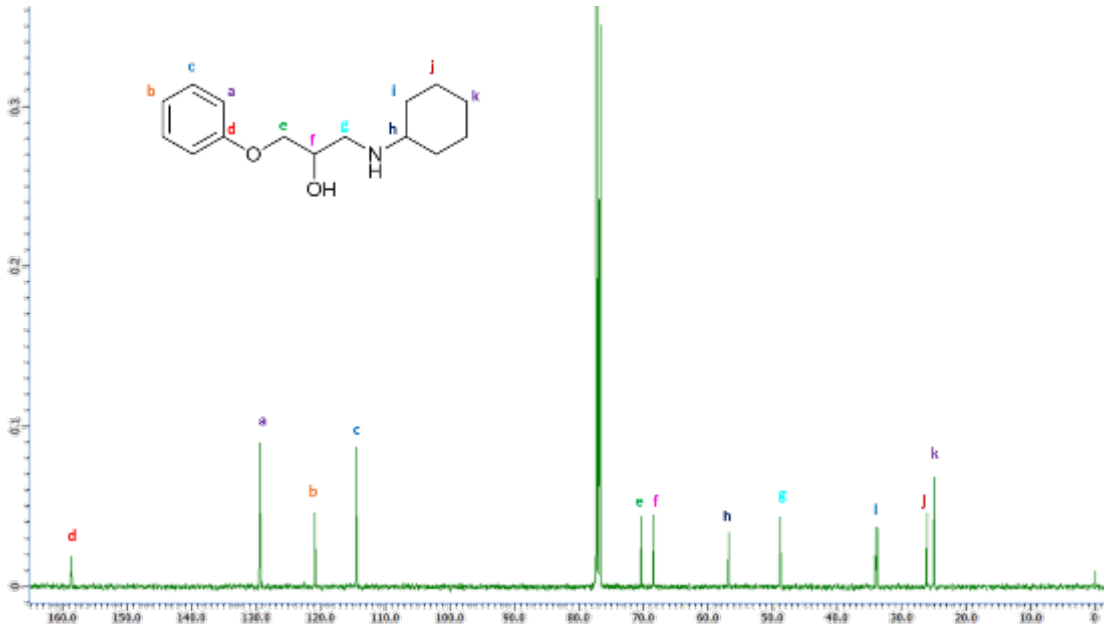


Cyclohexylamine (33.20 g, 0.335 moles, 5 equivs.) and phenylglycidyl ether (10.00 g, 0.067 moles, 1 equivs.) were combined in a round bottomed flask under an inert atmosphere of nitrogen gas with stirring. The reaction mixture was heated to 50 °C for a period of 4 hours before the excess cyclohexylamine was removed under reduced pressure using a rotary evaporator, resulting in the isolation of the crude product as a white solid (17.24 g). The crude product was recrystallized from toluene (25 mL) to produce a pure white solid (14.236 g, 85.9%, mp = 105 °C). δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.25-7.30 (m, 2H, CH-Ar), 6.93 (dd, J = 18.1, 7.6 Hz, 3H, CH-Ar), 3.95-4.01 (m, 3H, CH_2CH-OH), 2.90-2.93 (m, 1H, CH_2-NH), 2.74 (dd, J = 11.9, 7.3 Hz, 1H, CH_2-NH), 2.42 (tt, J = 10.3, 3.7 Hz, 1H, CH-N-cyclohexyl), 1.90 (d, J = 12.4 Hz, 2H, CH_2-cyclohexyl), 1.72 (q, J = 4.3 Hz, 2H, CH_2-cyclohexyl), 1.58-1.62 (m, 1H, CH_2-cyclohexyl), 1.00-1.31 (m, 5H, CH_2-cyclohexyl). δC (101 MHz; $CDCl_3$; Me_4Si) δ 158.7 (C-Ar), 129.5 (CH-Ar), 120.9 (CH-Ar), 114.5 (CH-Ar), 70.4 (CH_2-O), 68.4 (CH-OH), 56.7 (CH-NH), 48.8 (CH_2-NH), 34.0 (CH_2), 26.1 (CH_2), 25.0 (CH_2). ν^{max}/cm^{-1} 3275 (N-H stretch, 2° -amine), 3100 br. (O-H stretch, 2° alcohol), 3040 (C-H stretch, aromatic), 2928 and 2850 (C-H and C-H_2 stretch), 1597 and 1495 (C=C ring stretch, aromatic), 1458 (N-H bend, 2° amine), 1244 (C-N stretch) 1033 (C-O stretch). *m/z* 250.2164 (MH^+, 100% calc. for $C_{15}H_{24}NO_2$ = 250.1806).

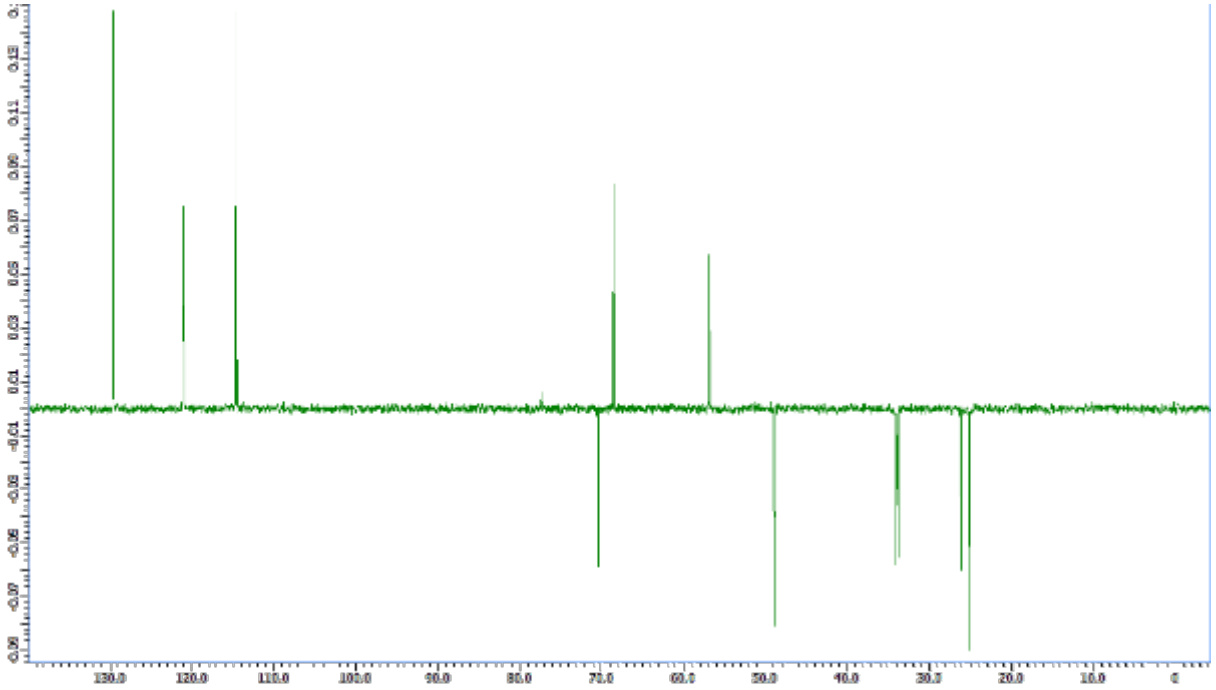
^{1}H-NMR



^{13}C NMR



^{13}C NMR- DEPT



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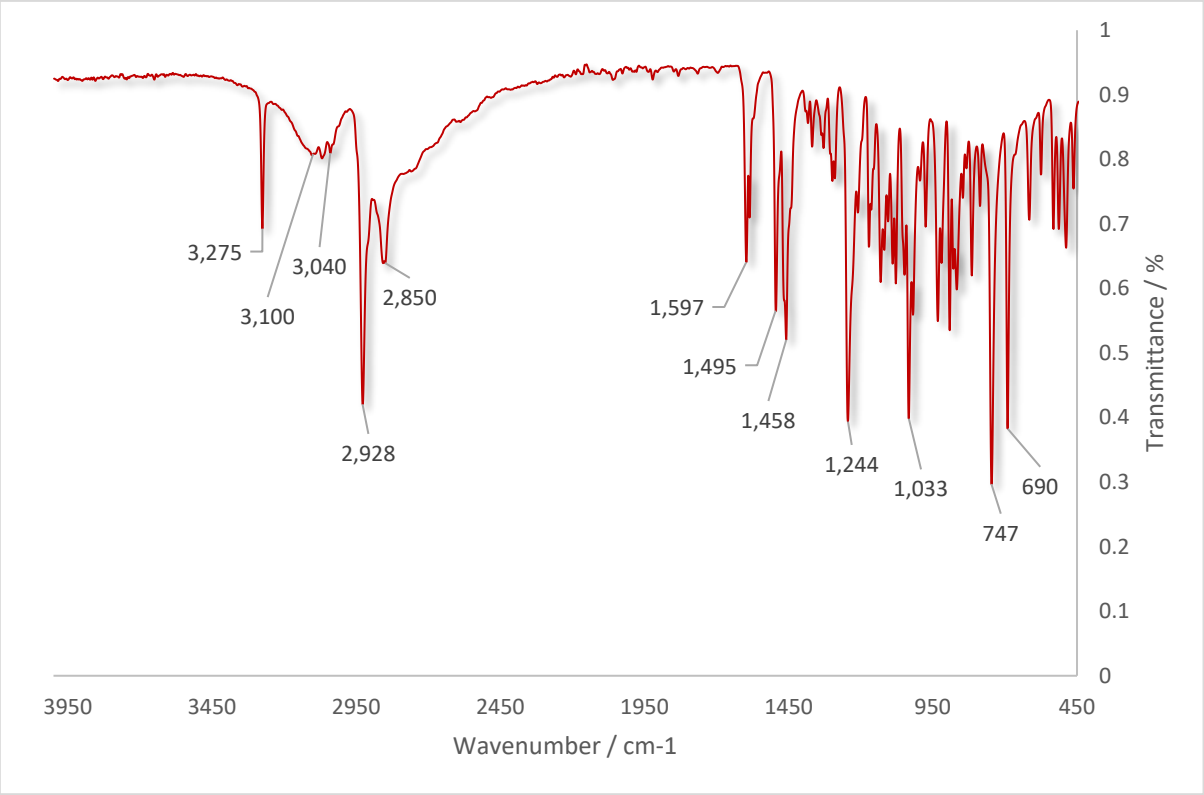
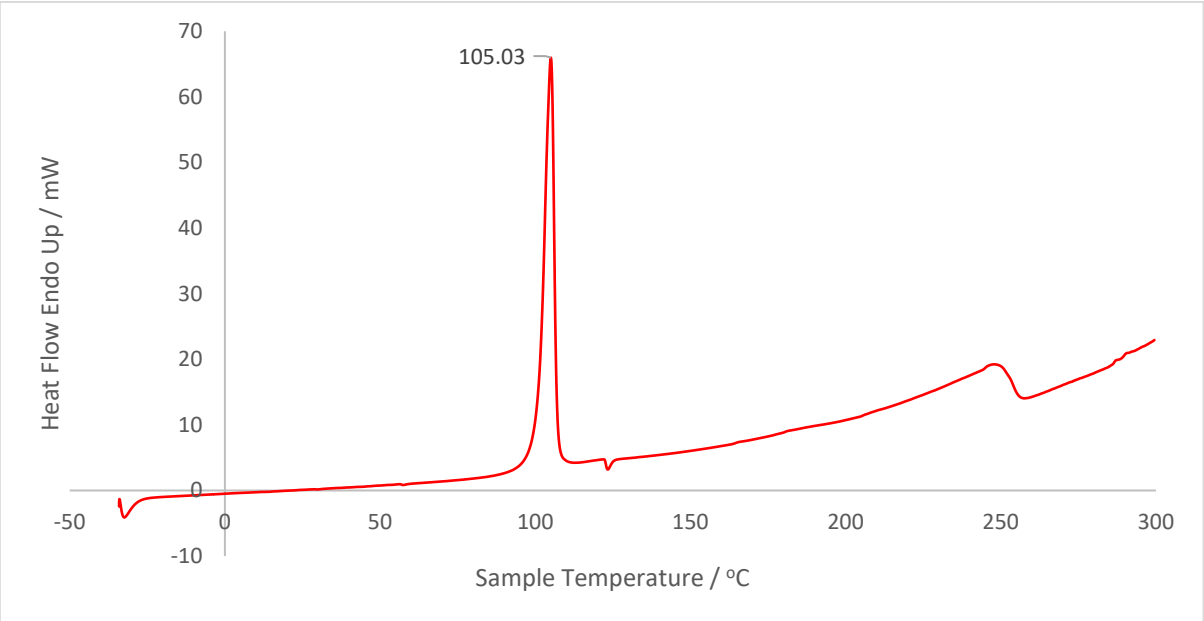
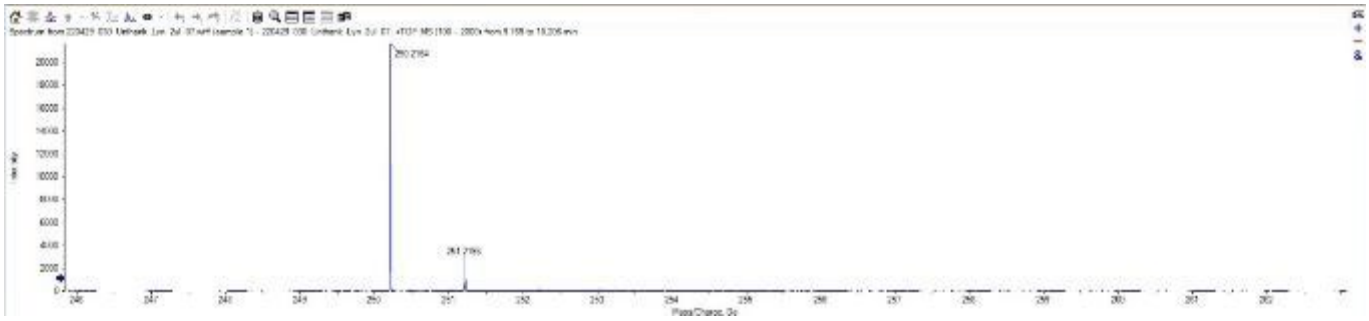


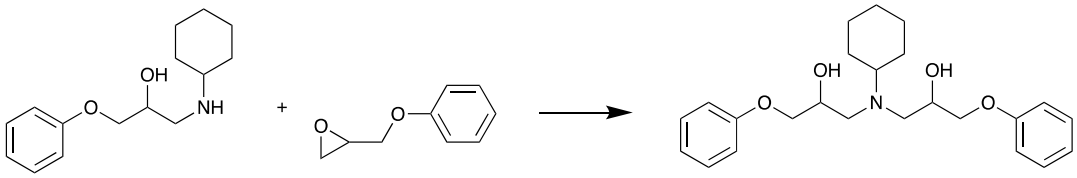
Melting Point Thermogram by DSC



High Resolution Mass Spectra

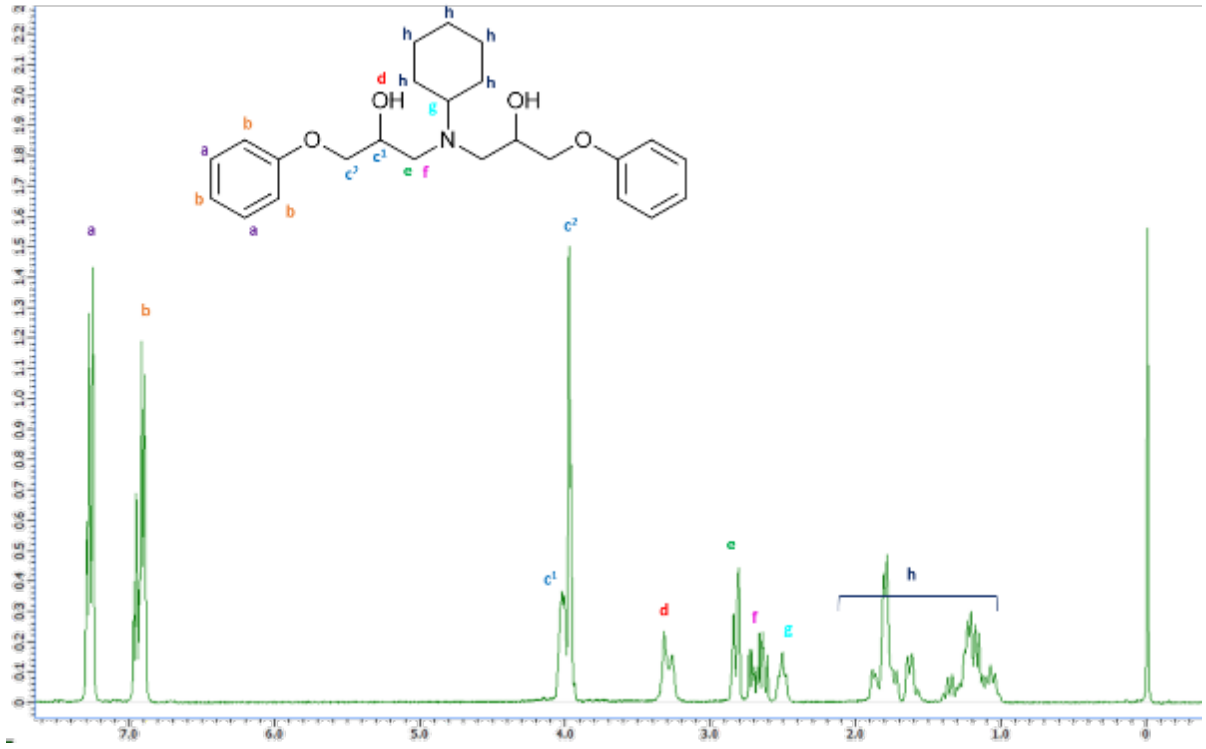


N,N-bis(2-hydroxy-3-phenoxy-propyl)-cyclohexanamine (β-amino diol (**3**)

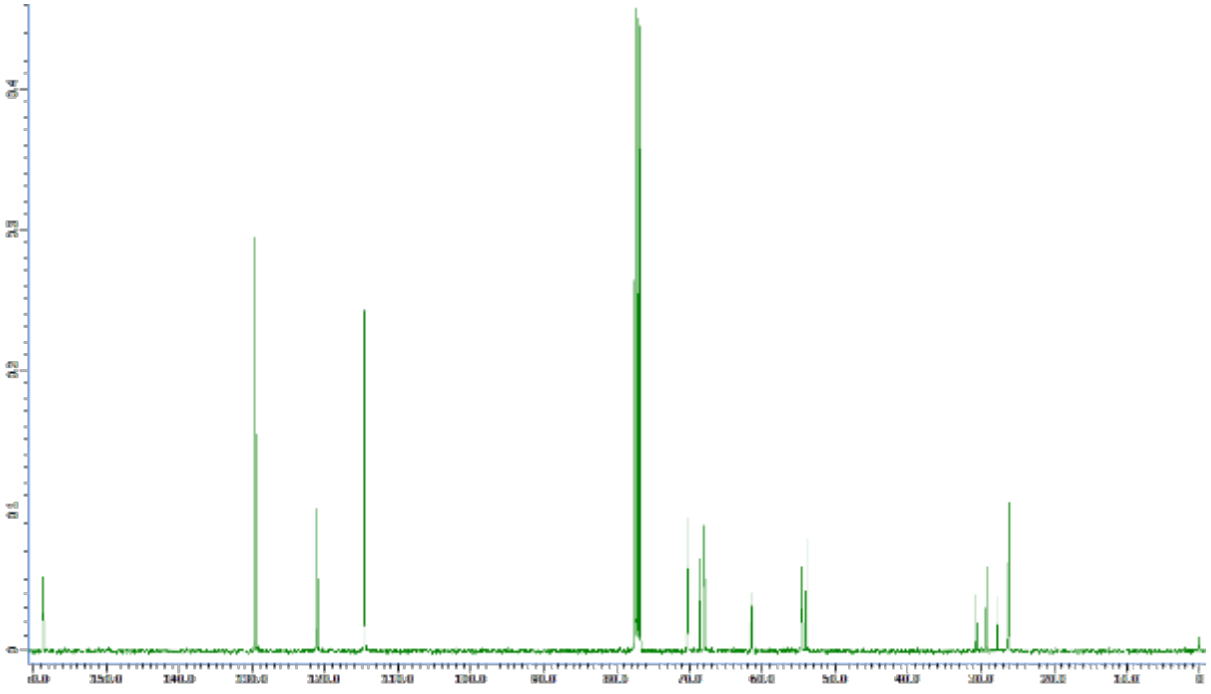


1-(cyclohexylamino)-3-phenoxypropan-2-ol (8.124 g, 0.032 mol) and phenylglycidyl ether (5.137 g, 0.033 moles, 1.05 equivs.) were combined in a round bottomed flask under an inert atmosphere of nitrogen gas with stirring. The reaction mixture was heated to 90 °C for 1 hour, followed by a further 4 hours at 100 °C before allowing to cool overnight producing the product as a pale yellow viscous liquid which was used without further purification (8.95 g, 0.022 mol, 67%). δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.27 (t, J = 7.6 Hz, 4H), 6.90-6.97 (m, 6H), 3.95-4.05 (m, 6H), 3.50 (br.s, 2H), 2.82 (dt, J = 22.90, 9.16 Hz, 2H), 2.66 (ddd, J = 28.5, 13.6, 8.6 Hz, 2H), 2.47-2.53 (m, 1H), 1.72-1.88 (m, 4H), 1.62 (d, J = 11.9 Hz, 1H), 1.04-1.39 (m, 5H). δC(101 MHz; $CDCl_3$; Me_4Si) δ 158.7 (C-Ar), 129.6 (CH-Ar), 121.1 (CH-Ar), 121.1 (CH- Ar), 114.6 (CH-Ar) , 70.2 (CH_2-O), 70.2 (CH_2-O), 68.6 (CH-OH), 68.0 (CH-OH), 61.6 (CH-N), 61.4 (CH-N), 54.6 (CH_2-N), 54.0 (CH_2-N), 30.6 (CH_2), 29.2 (CH_2), 27.8 (CH_2), 26.2 (CH_2), 26.2 (CH_2). ν^{max}/cm^{-1} 3589 (Free OH-stretch), 3311 (br. OH stretch), 3040 (CH stretch Aromatic), 2930-2836 (CH_2, CH stretch), 1600-1495 (C=C ring stretch Aromatic), 1242 (C-N stretch) 1086 (C-O stretch), 751-687 (CH bend mono substituted Aromatic). *m/z* 400.3061 (MH^+, 100% calc. for $C_{24}H_{34}NO_4$ = 400.2488)

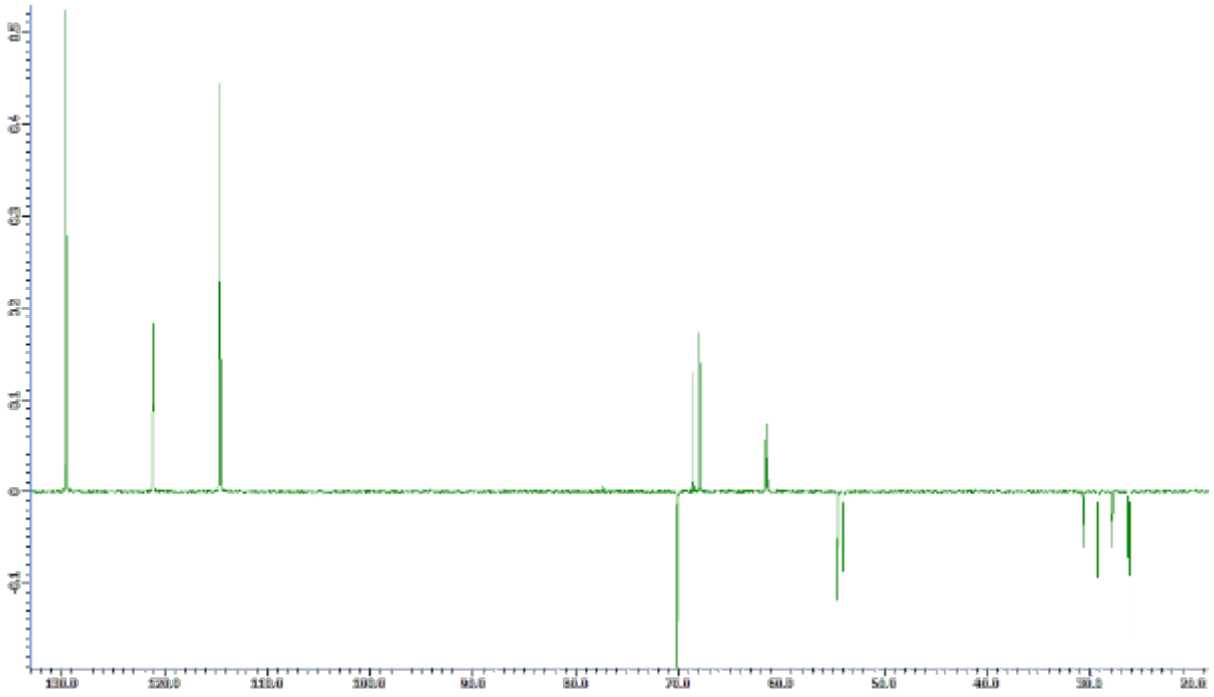
^{1}H NMR



^{13}C NMR



^{13}C NMR- DEPT



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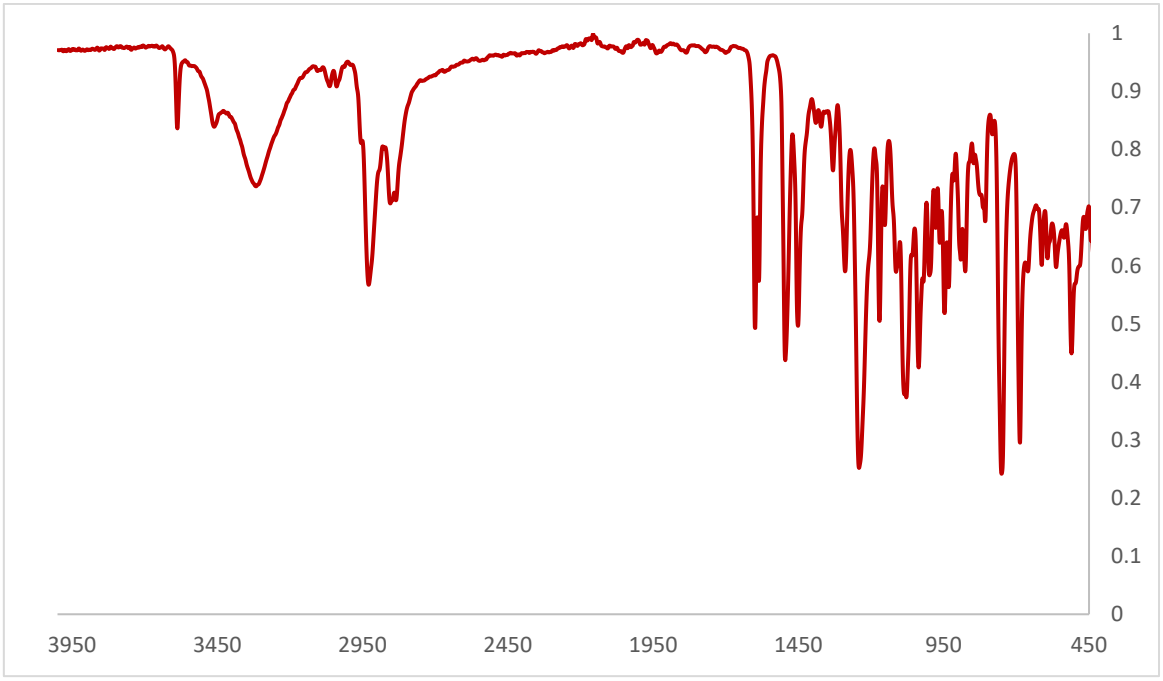
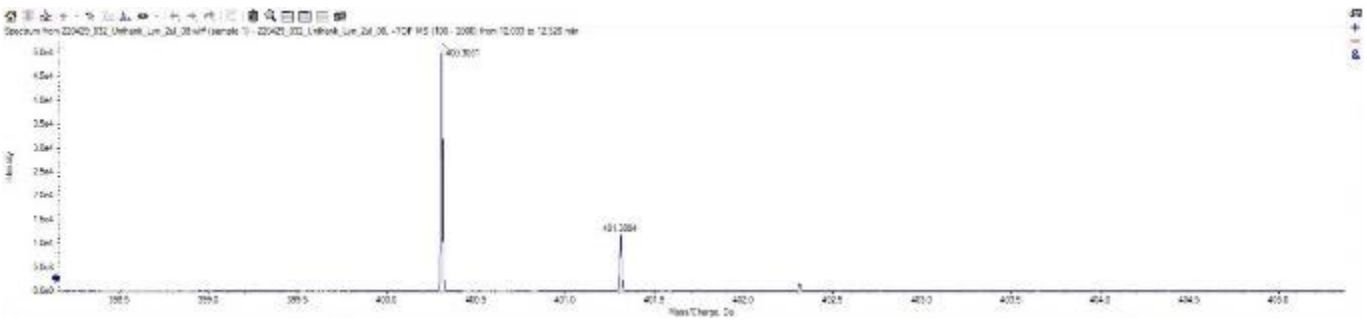


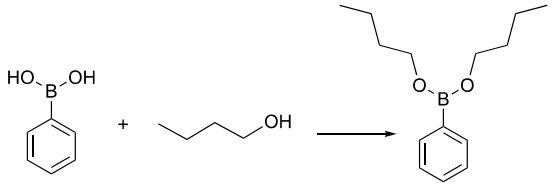
High Resolution Mass Spectra



Monoboronic esters 1a-1d

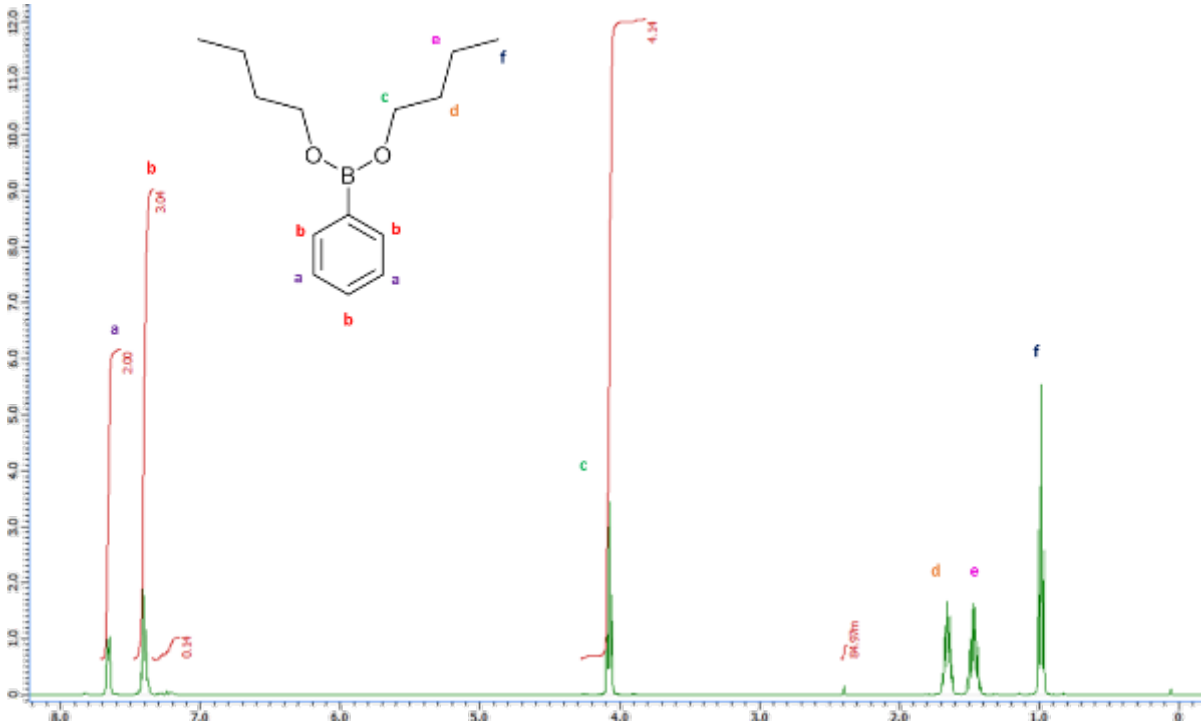
Monoboronic esters **1**a (1,2-ethane diol) and **1**d (n-butyl) were synthesised from phenylboronic acid according to the procedures below. **1**c (iso-propyl) was synthesised from bromobenzene and **1**b (pinacol) was purchased from Fluorochem and used as received (24388-23-6).

bis(butyl)phenylboronate (1d)

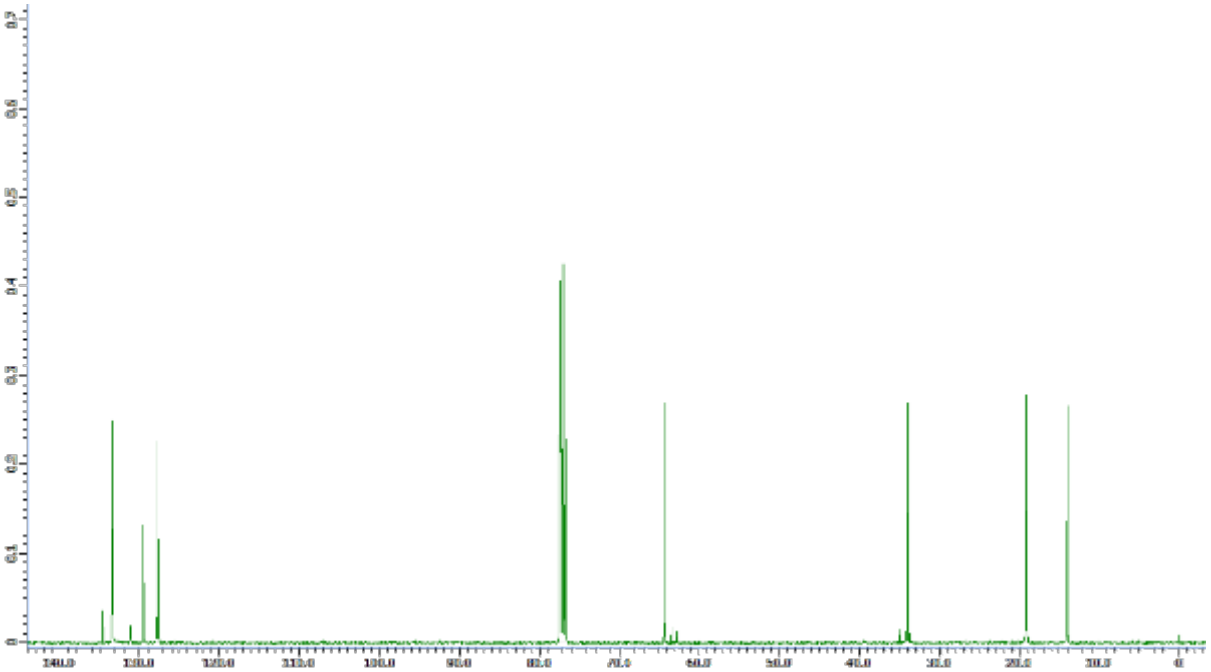


A mixture of phenylboronic acid (46.7 g, 0.334 mol) and butanol (98.93 g, 1.335 mol, 4 equivs) was stirred at 110 °C using Dean-Stark apparatus under nitrogen for 4 hours then left to stir at room temperature for 18 hours under nitrogen. The crude product was evaporated under reduced pressure affording a straw liquid (yield = 92%, Purity 98%). δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.66 (d, J = 7.3 Hz, 2H), 7.46-7.38 (m, 3H), 4.07 (t, J = 6.4 Hz, 4H), 1.69-1.62 (quin, 4H), 1.46 (sext, J = 14.9, 7.3 Hz, 4H), 0.98 (t, J = 7.6 Hz, 6H). δC (101 MHz; $CDCl_3$; Me_4Si) δ 133.4 (C-Ar), 129.5 (C-Ar), 127.7 (C-Ar), 64.4 (CH_2-O), 34.0 (CH_2), 19.0 (CH_2), 14.0 (CH_3). δB (128.28 MHz; $CDCl_3$ Me_4Si) 28 (s, br, Ph-$B(OR)_2$). ν^{max}/cm^{-1} 3054 (Ar-CH stretch) 2958-2873 (CH stretch), 1600 (C=C ring stretch), 1437 (CH_2 Bend – scissor), 1407 (CH_3 deformation), 1317 (B-O stretch), 1127 (C-O stretch), 1073 (B-C stretch), 1025-967 (C=C-H in plane bend), 758-699 (aromatic CH bend), 649 (B-O wag).

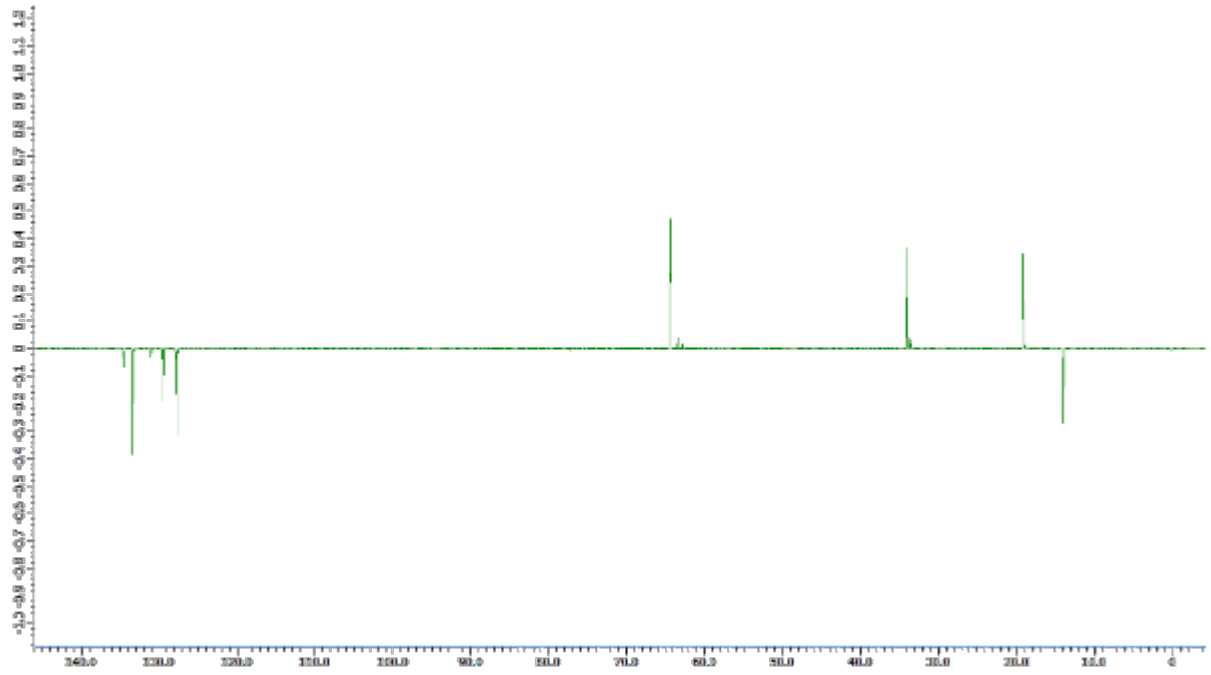
^{1}H NMR



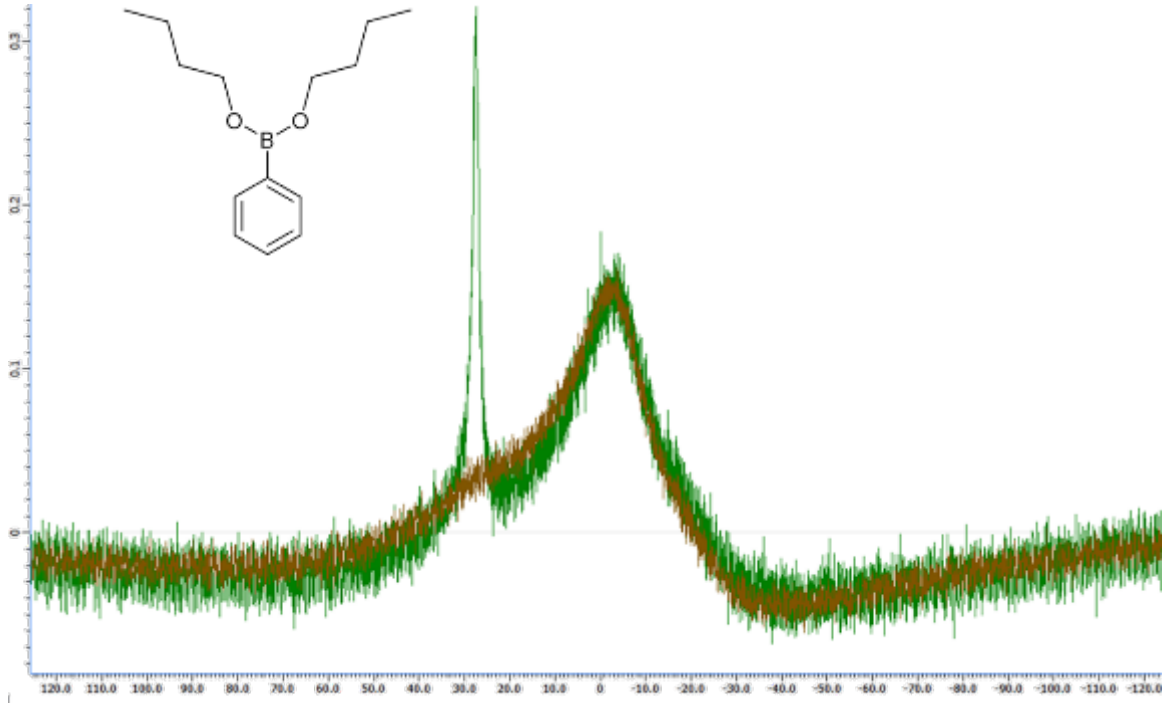
^{13}C NMR



^{13}C NMR- DEPT



^{11}B NMR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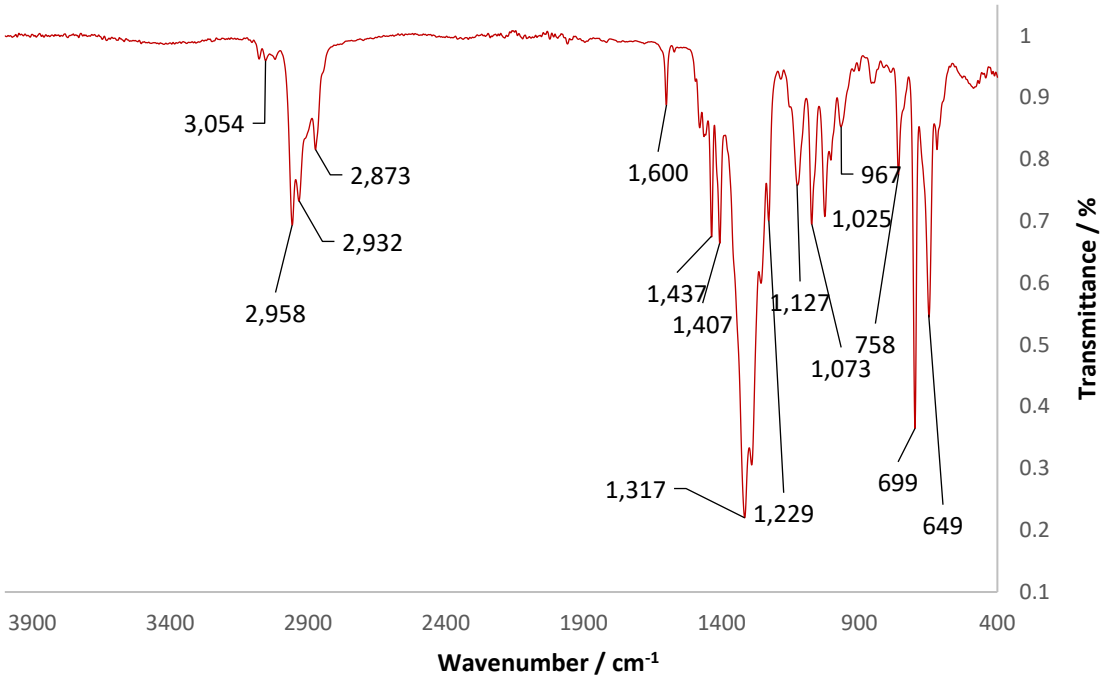
B
O

FTIR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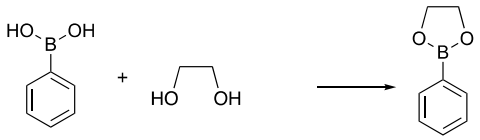
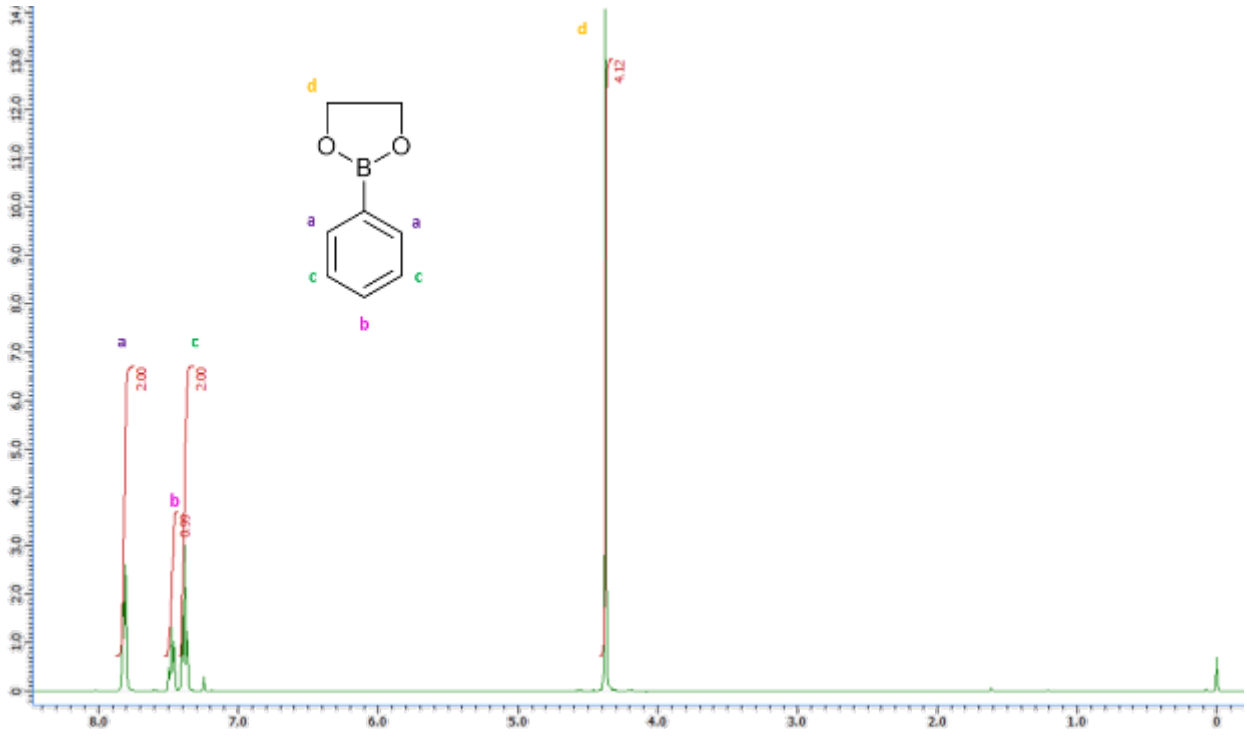
1,317
1,229
1,127
1,073
1,025
967
758
699
649
Transmittance / %
Wavenumber / cm-1
3900
3400
2900
2400
1900
1400
900
400
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

Phenylboronic acid 1,2-ethanediol ester (1a)

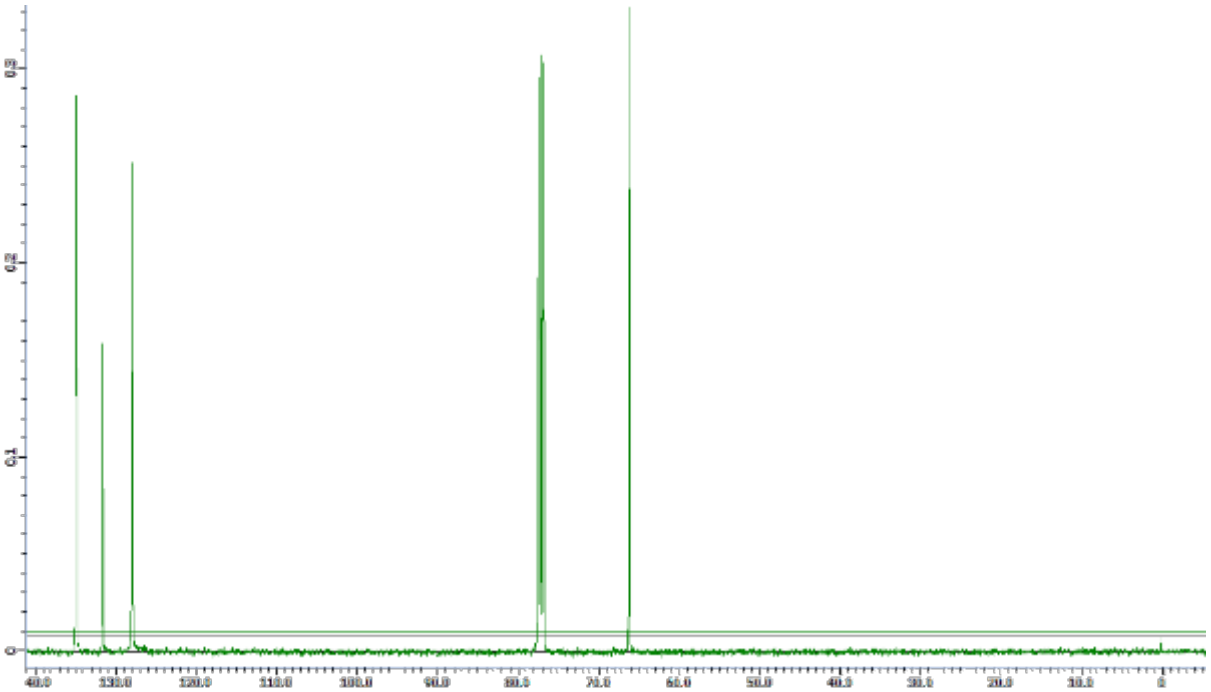


A mixture of phenylboronic acid (0.97 g, 0.007 mol), ethylene glycol (0.86 g, 0.014 mol, 2 equivs) and DCM (20 mL) were charged to a round bottom flask under nitrogen gas and stirred with excess $MgSO_4$ at room temperature for 18 hours. The mixture was filtered to remove the $MgSO_4$ and the filtrate concentrated under reduced pressure to give the crude product as a pale yellow liquid. The crude product was then purified by vacuum distillation affording the purified product as a pale yellow oil (87% yield). δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.82 (d, J = 6.9 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 4.37 (s, 4H). δC (101 MHz; $CDCl_3$; Me_4Si) δ 134.9 (C-Ar), 131.6 (C-Ar), 128.0 (C-Ar), 66.1 (CH_2O). δB (128.28 MHz; $CDCl_3$ Me_4Si) δ 31 (s, br, Ph-B$(OR)_2$). ν^{max}/cm^{-1}3053 (ar-CH stretch) 2979 (CH stretch), 2908 (CH_2 Stretch), 1602 (C=C ring stretch), 1499 (C=C ring stretch), 1480 (C=C ring stretch), 1440 (CH_2 Bend – scissor), 1395 (B-O stretch), 1371, (B-O stretch), 1332 (B-O stretch), 1213 (C-O stretch), 1091 (B-C stretch), 696-638 (aromatic CH bend), 639 (B-O Bend out of plane).

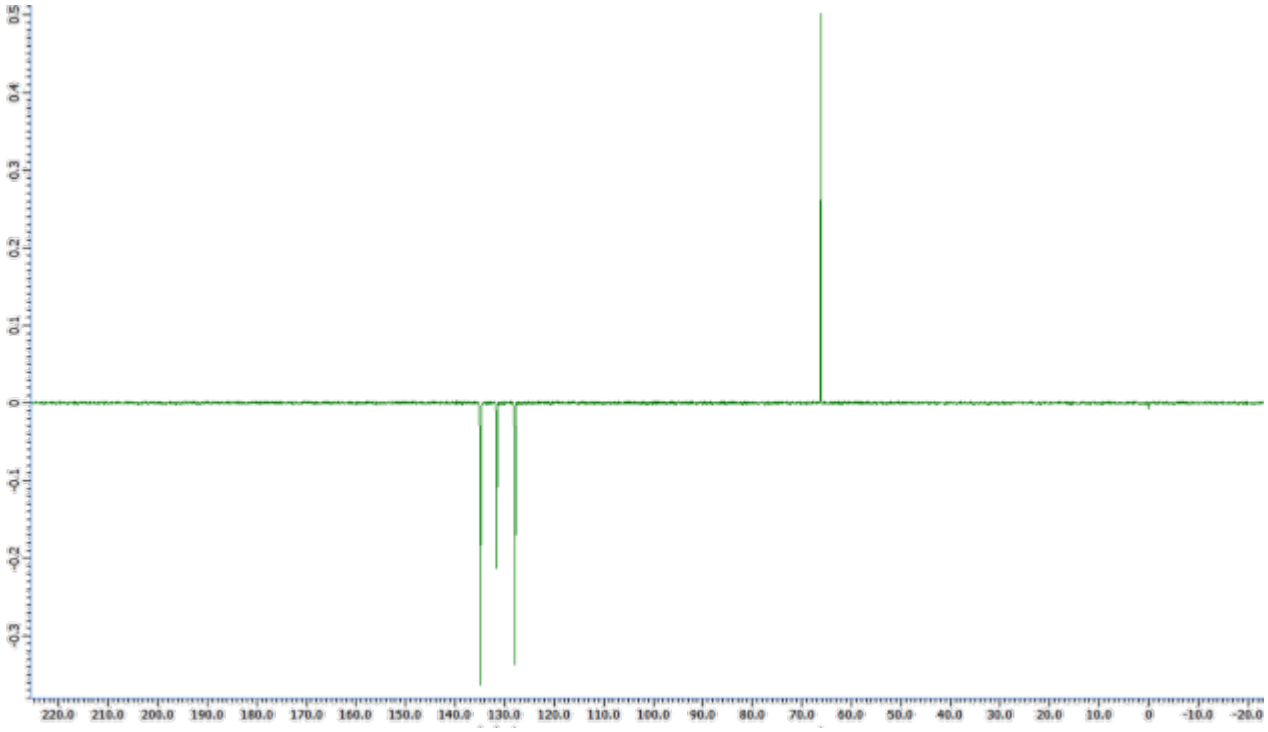
^{1}H-NMR



^{13}C NMR



^{13}C NMR-DEPT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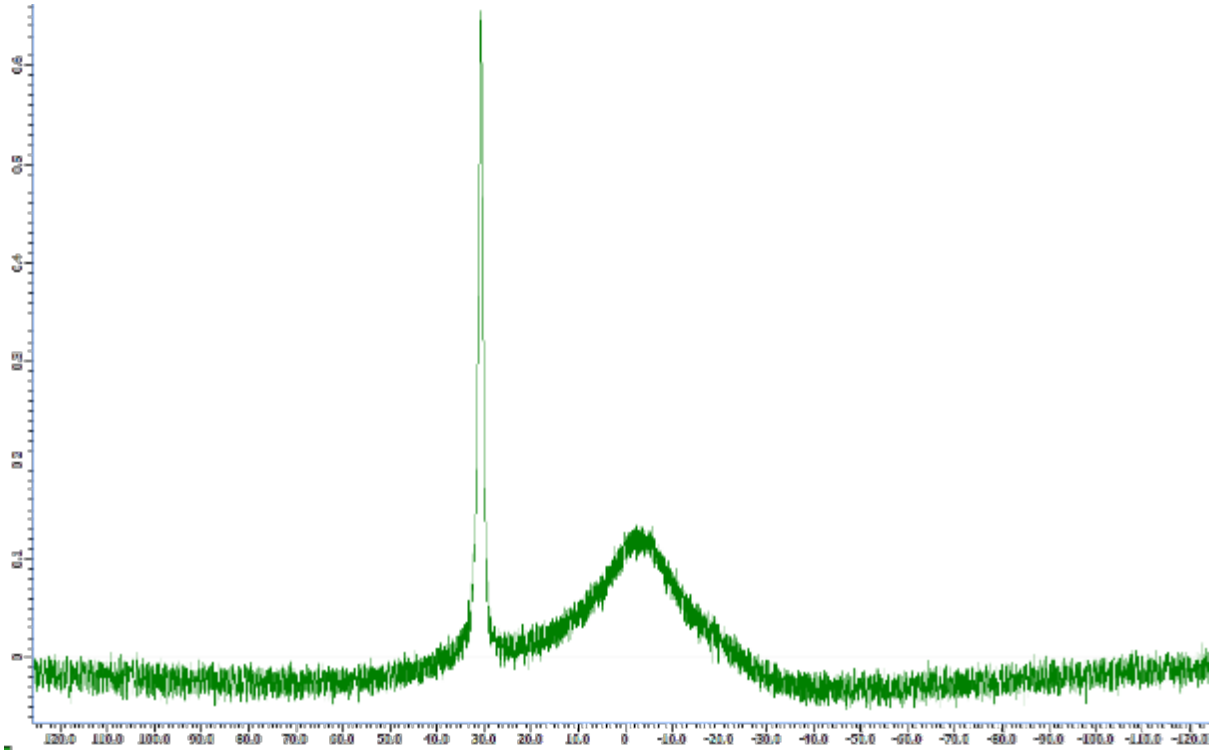
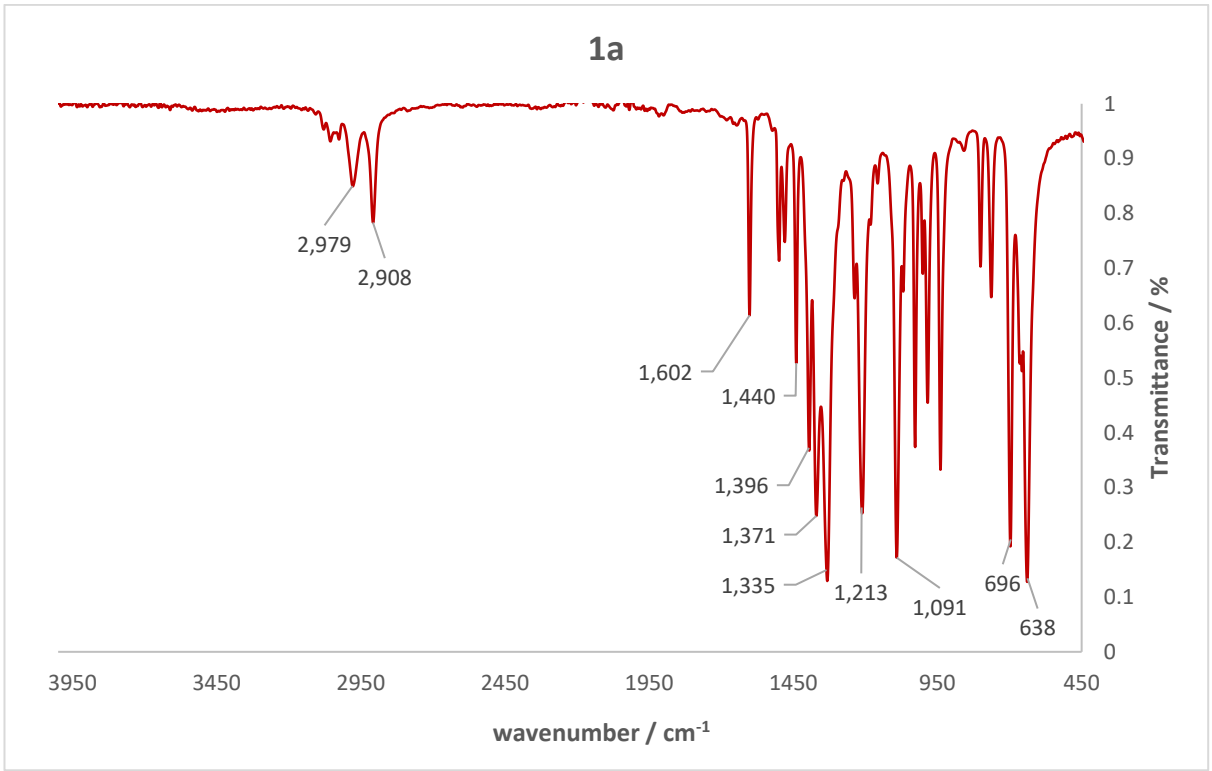
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

^{11}B NMR



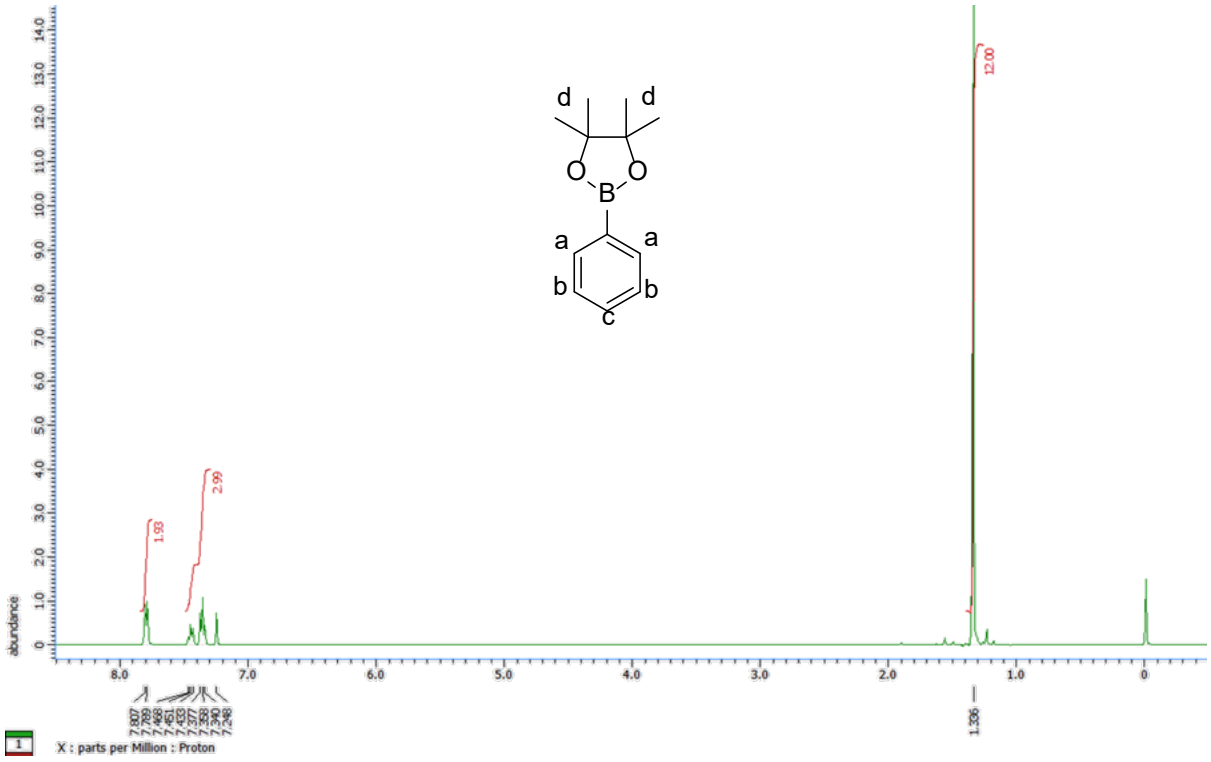
FTIR


1a
2,979
2,908
1,602
1,440
1,396
1,371
1,335
1,213
1,091
696
638
Transmittance / %
wavenumber / cm-1
3950
3450
2950
2450
1950
1450
950
450
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

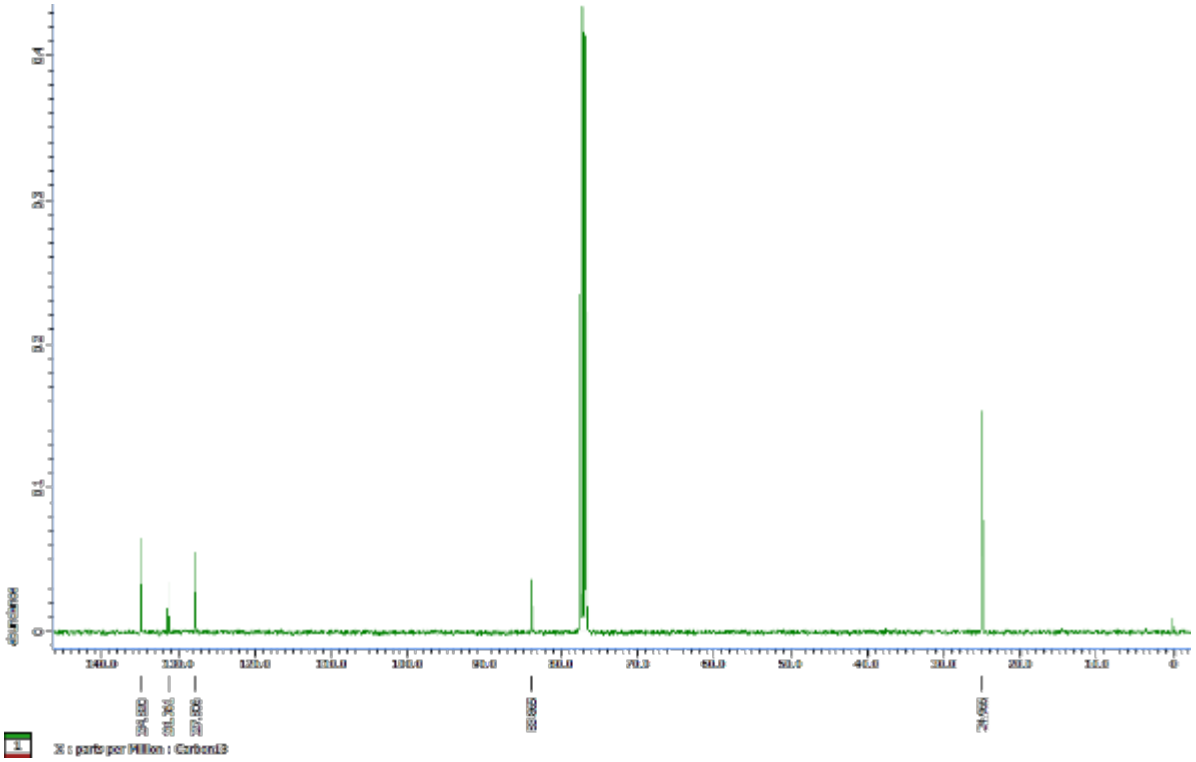
Phenylboronic acid pinacol ester (1b)

Phenylboronic acid pinacol ester was purchased from Fluorochem and used as received. δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.80 (m, 2H), 7.45 (m, 1H), 7.34-7.38 (m, 2H), 1.34 (s, 12H). δC (101 MHz; $CDCl_3$; Me_4Si) δ 134.8 (C-Ar), 131.4 (C-Ar), 127.8 (C-Ar), 83.9 ($(CH_3)_2C$-), 24.9 (CH_3). δB (128.28 MHz; $CDCl_3$ Me_4Si) δ 28 (s, br, Ph-$B(OR)_2$). vmax/cm—1 2979-2944 (CH stretch), 1600 (C=C ring stretch), 1437 (CH2 Bend – scissor), 1356 (B-O stretch), 1138 (C-O stretch), 1091 (B-C stretch).

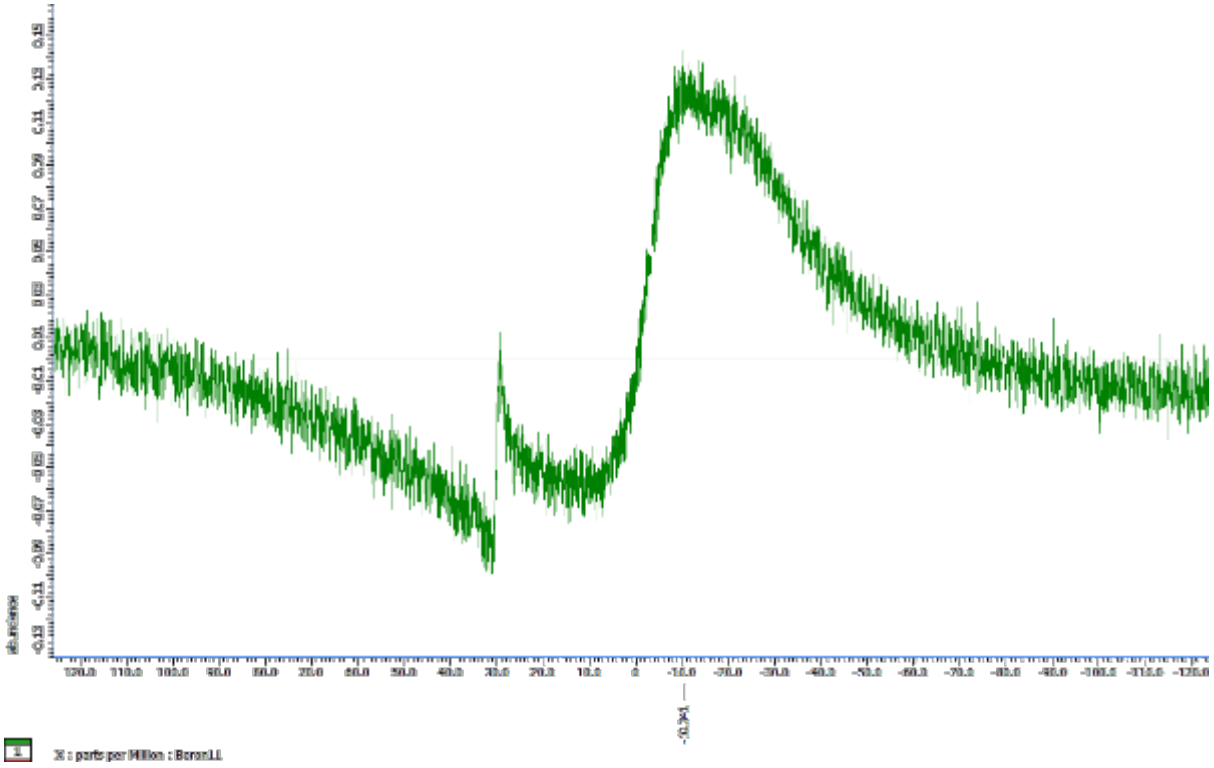
^{1}H NMR

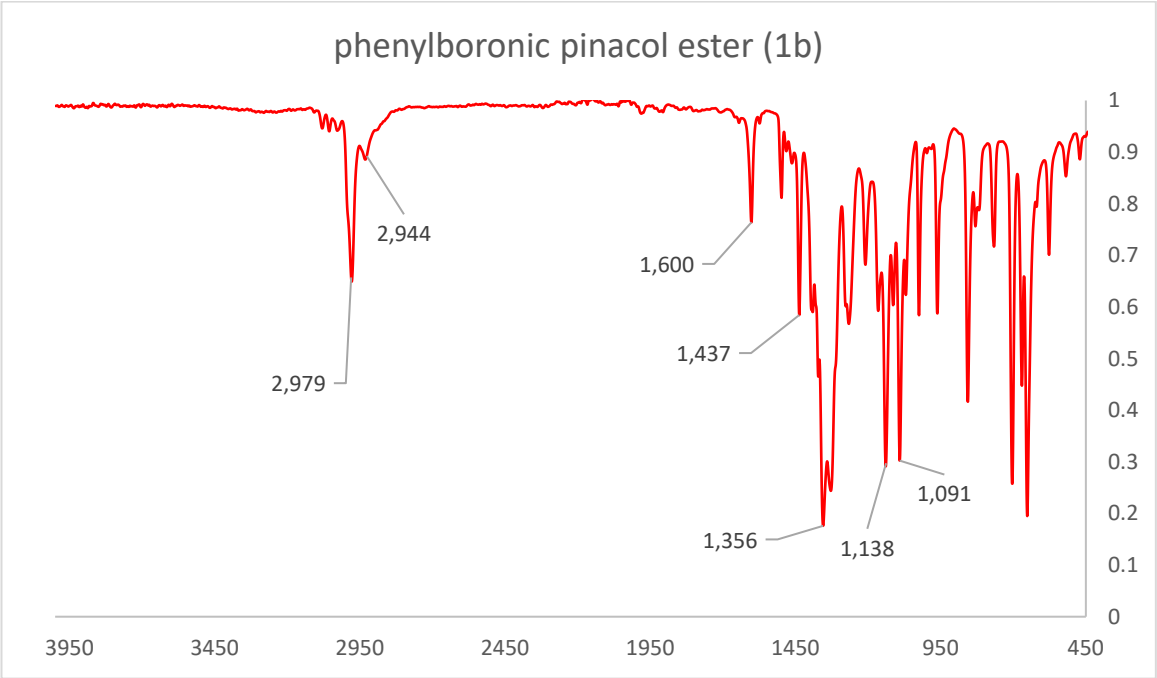


^{13}C-NMR

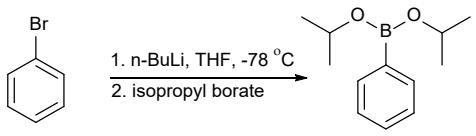


^{11}B-NMR



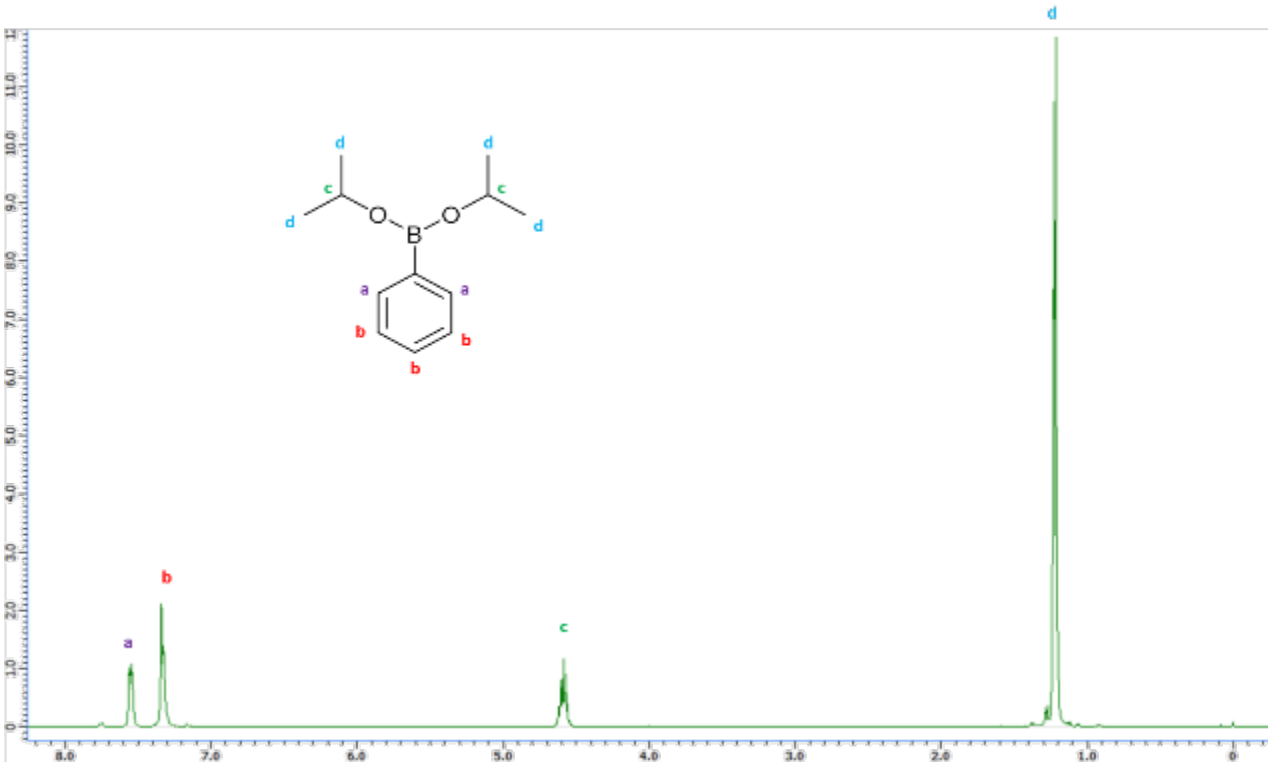


bis(propan-2-yl)phenylboronate (1c)

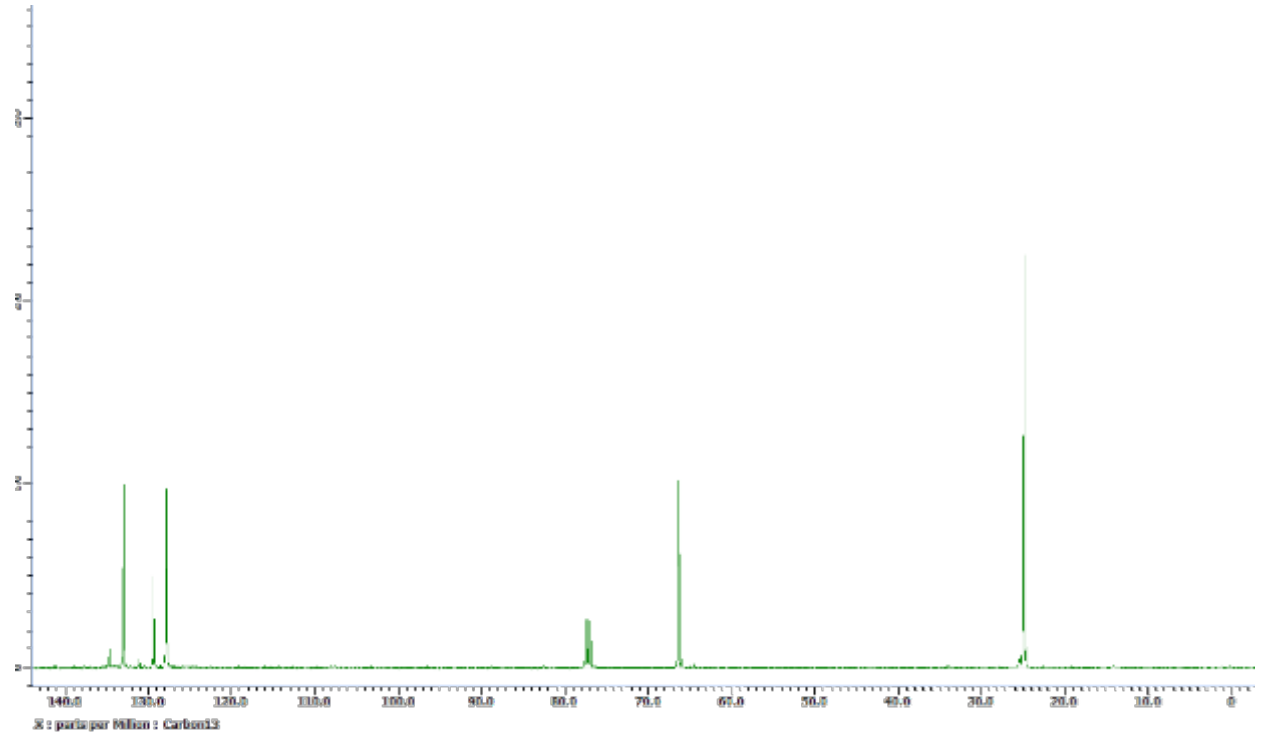


The isopropyl monoboronic ester **(1c)** was synthesised in accordance with the method developed by Wesela-Bauman et al.[1] Bromobenzene (6.3 mL, 0.060 mol) was added dropwise to a sealed vessel under an inert nitrogen atmosphere, at -78 °C, containing a mixture of anhydrous THF (30 mL) and n-BuLi (25.2 mL, 0.063 mol). The mixture was left to stir at -78 °C for 30 minutes. Triisopropyl borate (14.5 mL 0.063 mol) was added dropwise to the reaction vessel at -78 °C and stirred for a further 30 minutes. The reaction vessel was warmed to room temperature and quenched with 2M HCl in diethyl ether (37.5 mL, 0.075 mol). The solvents were removed from the mixture under reduced pressure and the resulting pale-yellow residue was subjected to fractional distillation producing a colourless liquid (78% yield, 9.67 g). (Bpt = 65-75 °C, 6 mmHg). δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.56-7.54 (m, 2H), 7.34-7.33 (m, 3H), 4.62-4.60 (q, J = 6.0 Hz, 2H), 1.23-1.21 (d, J= 6.0 Hz, 12H). δC (101 MHz; $CDCl_3$; Me_4Si) δ 133.0 (C-Ar), 129.4 (C-Ar), 127.9 (C-Ar), 66.3 (CH_3CHO), 24.9 (CH_3). δB (128.28 MHz; $CDCl_3$ Me_4Si) δ 28 (s, br, Ph-$B(OR)_2$). ν^{max}/cm^{-1} 3054 (Ar-CH stretch), 2971-2927 (CH stretch), 1599-1434 (C=C ring stretch), 1375 (B-O stretch), 1308 (B-O stretch), 1117 (C-O stretch) 948 (B-C stretch) 699-651 (aromatic CH bend), 651 (B-O bend - wag).

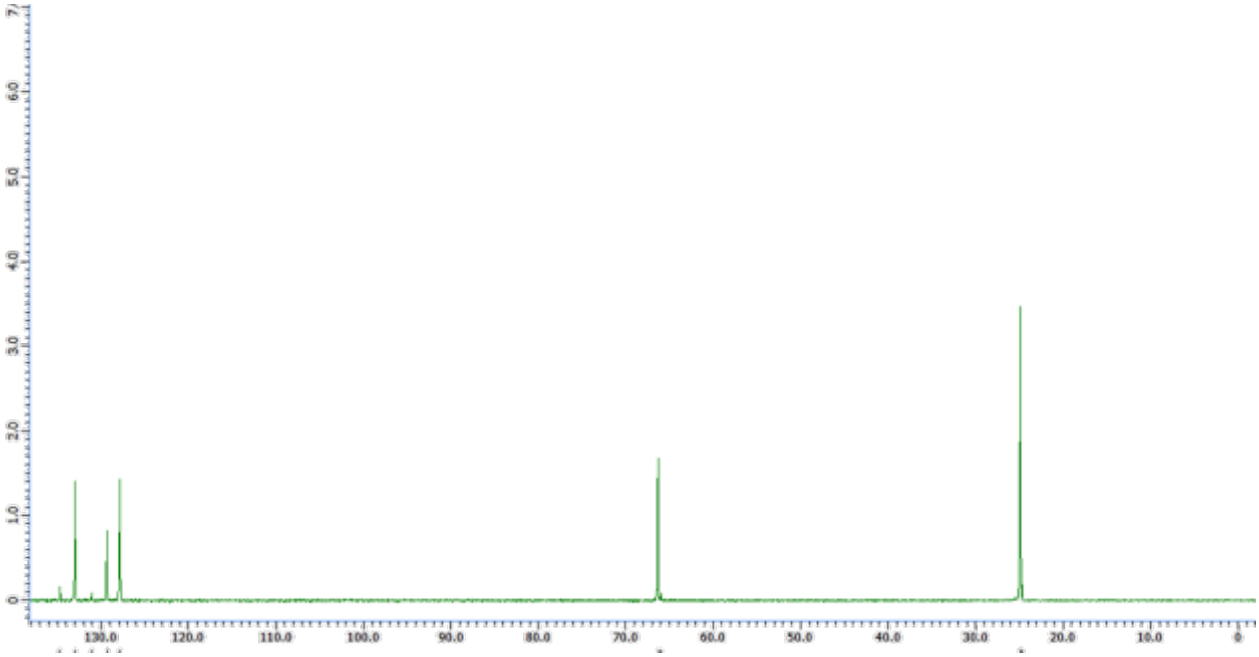
^{1}H NMR



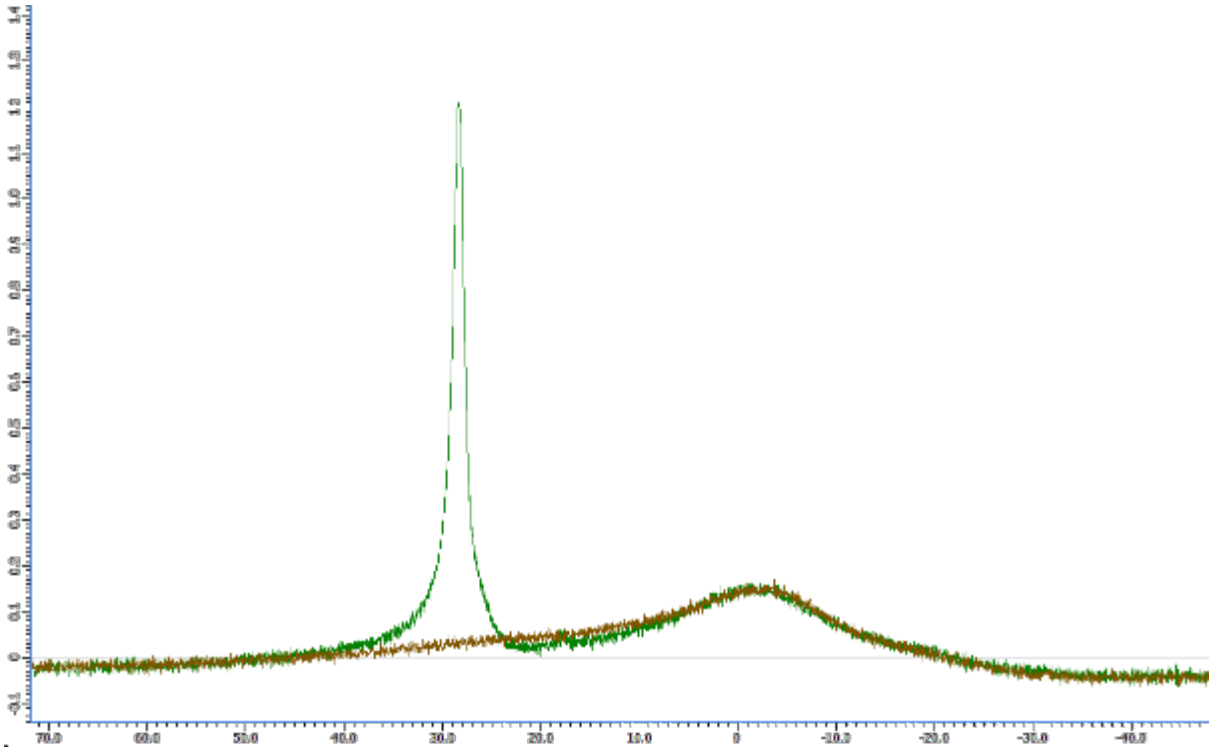
^{13}C NMR



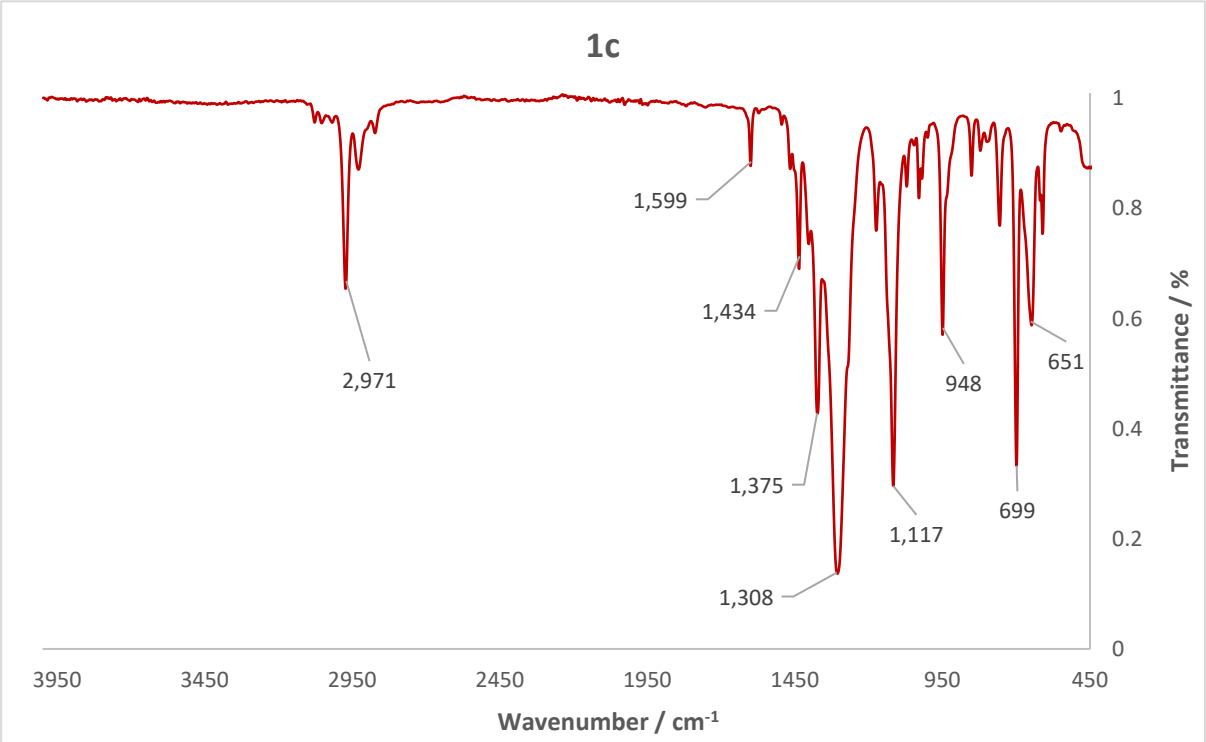
^{13}C NMR - DEPT



^{11}B NMR

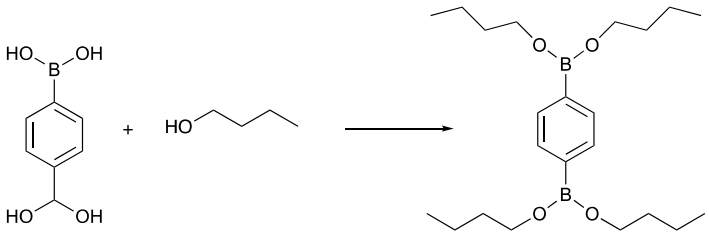


FTIR



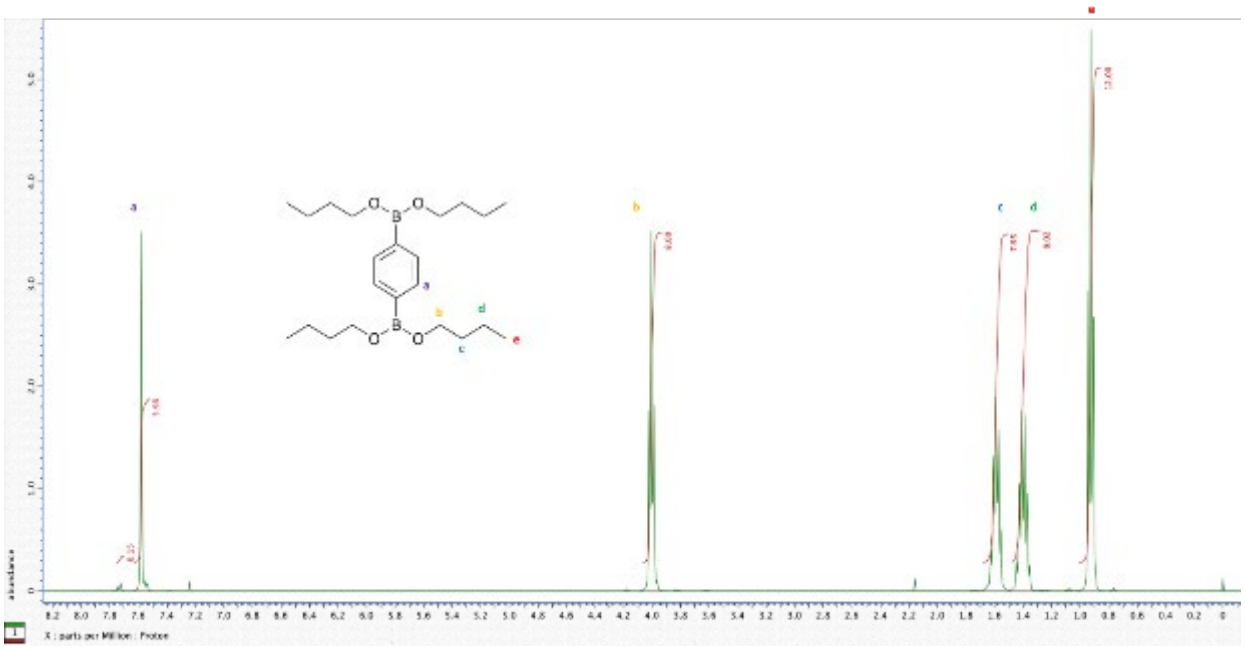
Diboronic esters

1,4-Phenylenediboronic acid tetrabutyl ester (2d)

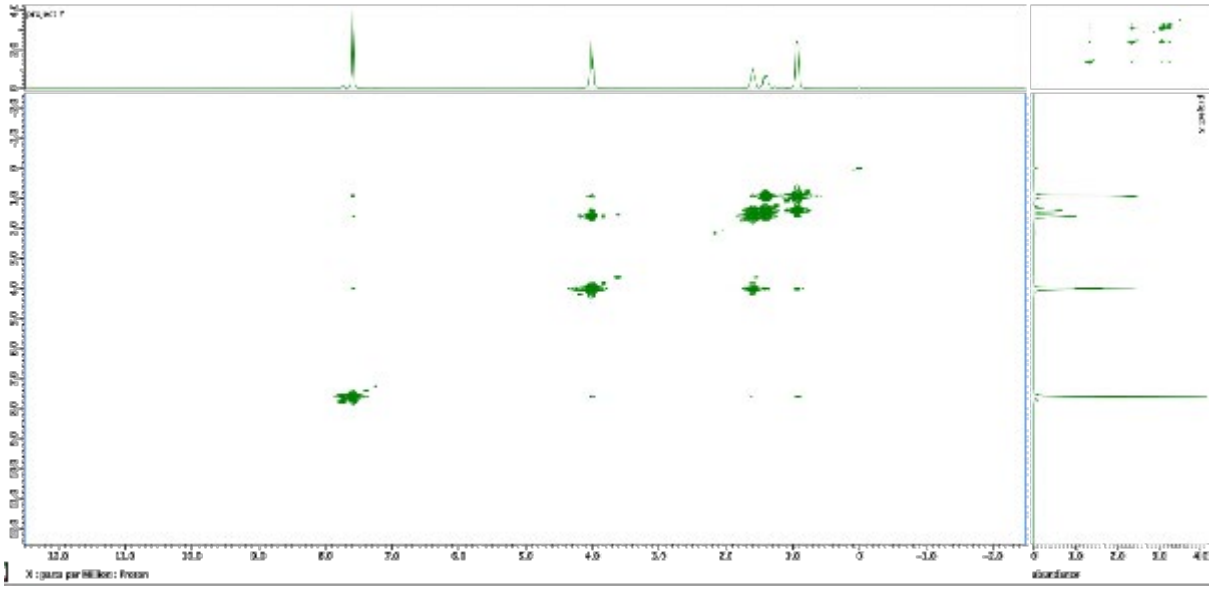


1,4-phenylenediboronic acid (3.00 g, 0.018 mol) and excess n-butanol (170 g, 2.29 mol, 127 equivs) were combined in a round bottom flask and stirred at room temperature for 24 hours under nitrogen. The reaction mixture was then evaporated slowly under reduced pressure affording the product as a colourless liquid, which was used without further purification (yield = 76%, Purity 98%). δH (400 MHz; $CDCl_3$; Me_4Si) 7.58 (s, 4H), 4.00 (t, J = 6.4 Hz, 8H), 1.55-1.62 (p, J = 7.3 Hz, 8H), 1.40 (sx, J = 7.3Hz, 8H), 0.92 (t, J = 7.3 Hz, 12H). δC (101 MHz; $CDCl_3$; Me_4Si) 14.1 (CH_3), 19.1 (CH_2), 34.0 (CH_2), 64.3 (CH_2-O), 132.5 (C-Ar), 134.8 (br. C-Ar). δB (128.28 MHz; $CDCl_3$ Me_4Si) δ 30 (s, br, Ph-B$(OR)_2$). ν^{max}/cm^{-1} 3064 (Ar-CH stretch), 2955-2874 (CH stretch), 1508-1464 (C=C ring stretch), 1410-1308 (B-O stretch), 1117 (C-O stretch), 1067-1023 (B-C stretch), 825 (para-aromatic CH bend), 659 (B-O bend - wag).

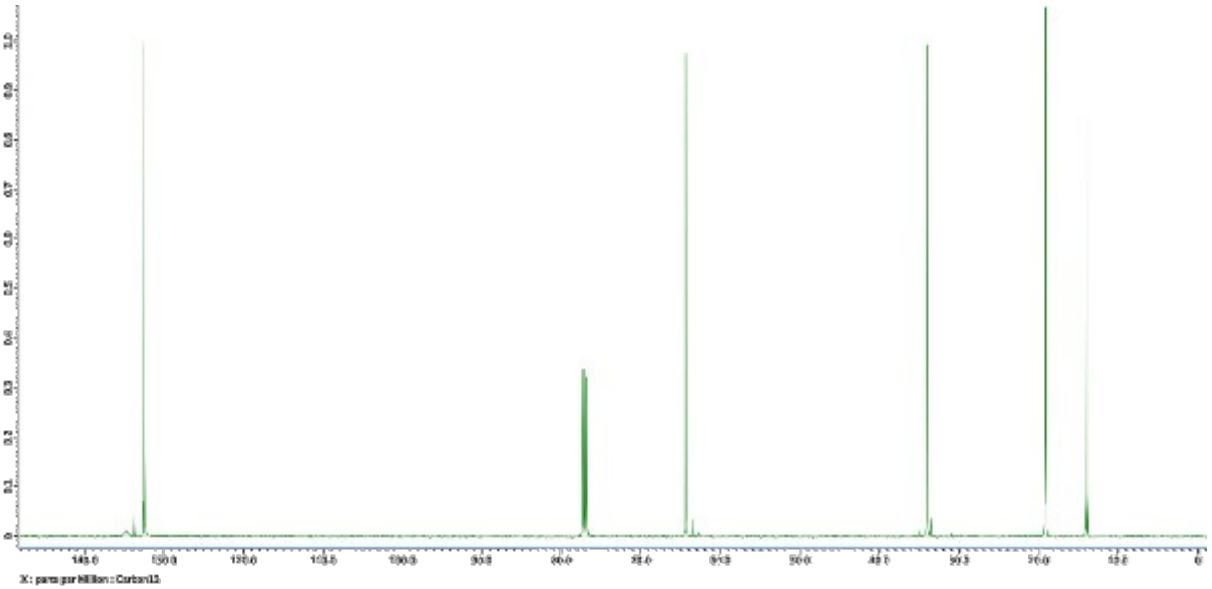
^{1}H-NMR



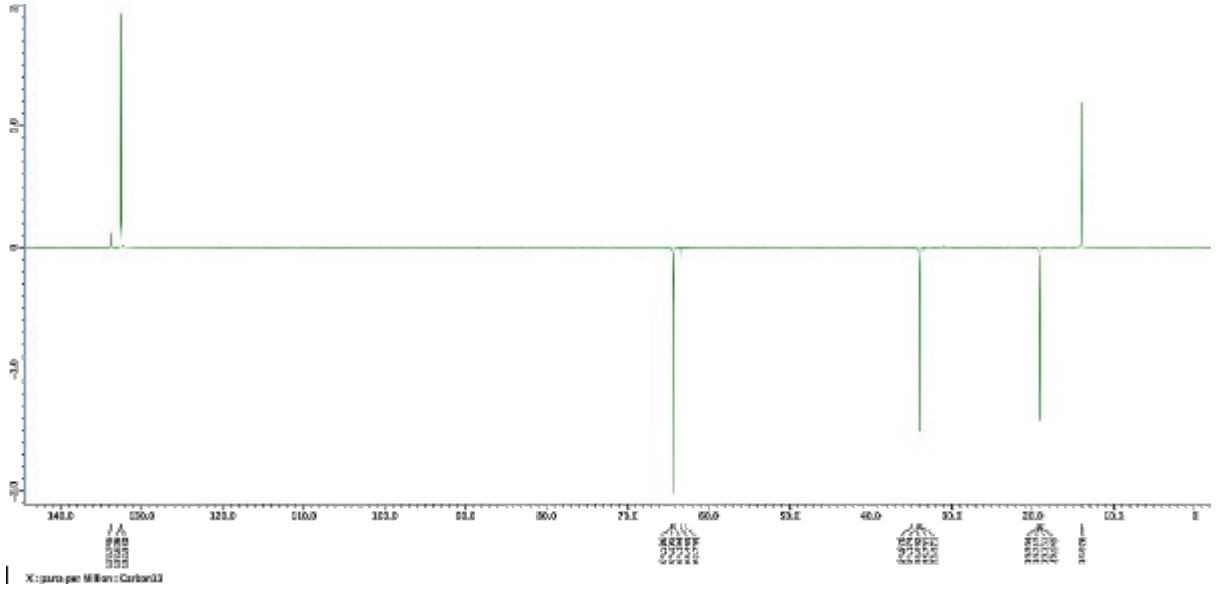
^{1}H-NMR-COSY



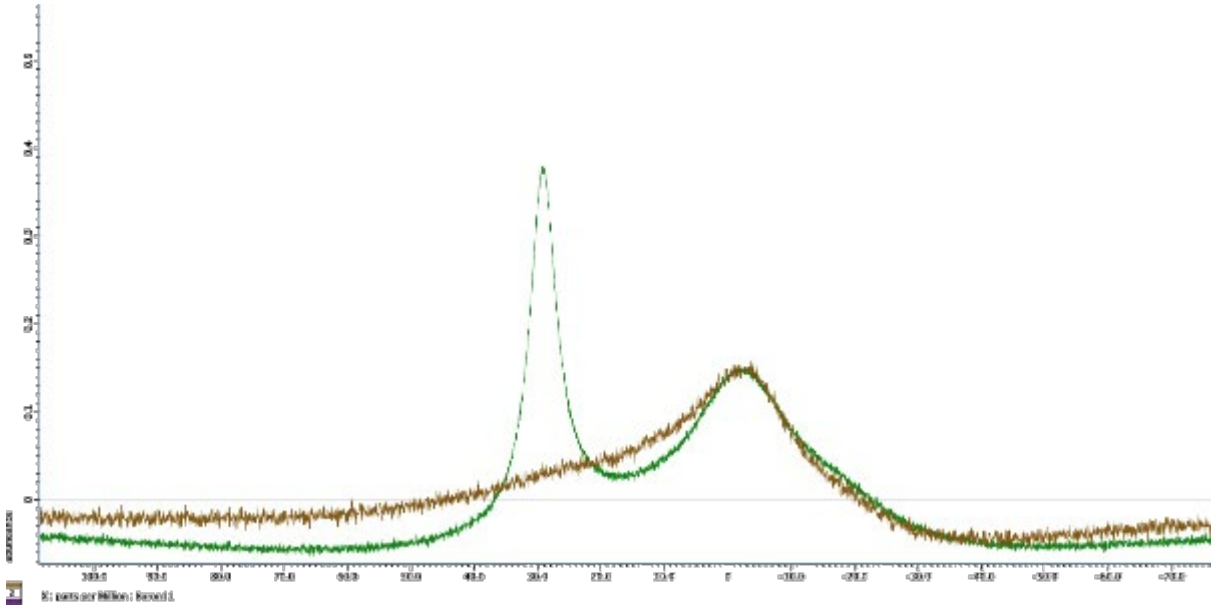
^{13}C NMR



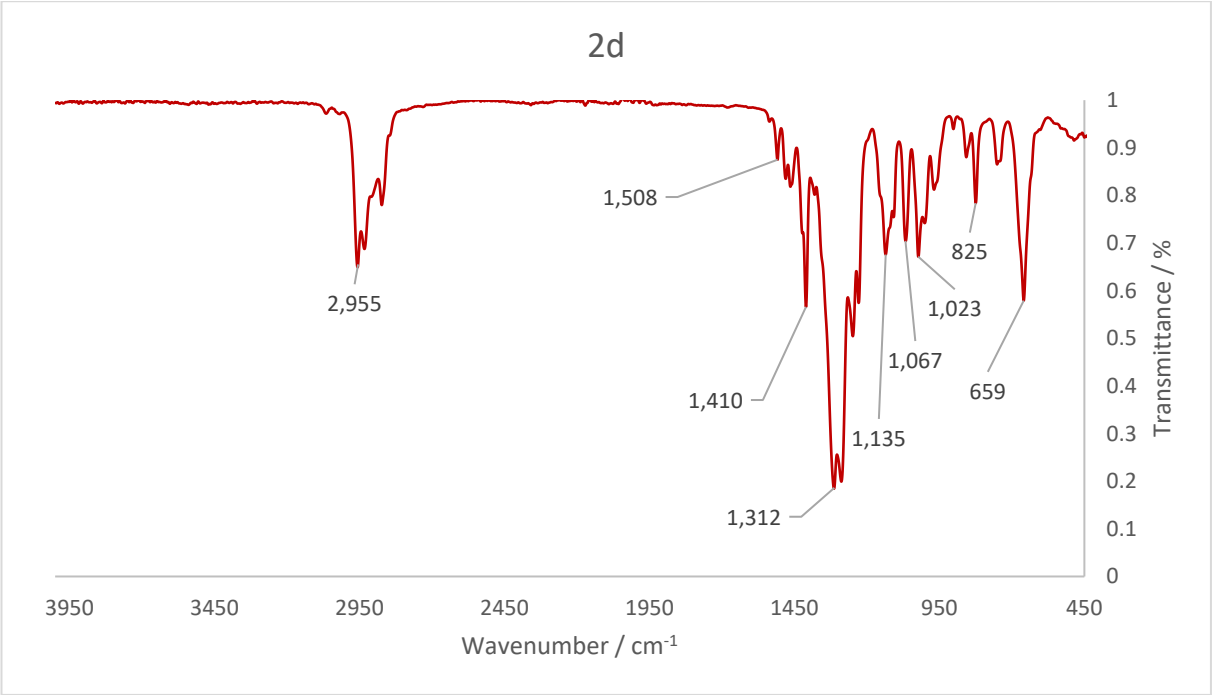
^{13}C NMR- DEPT



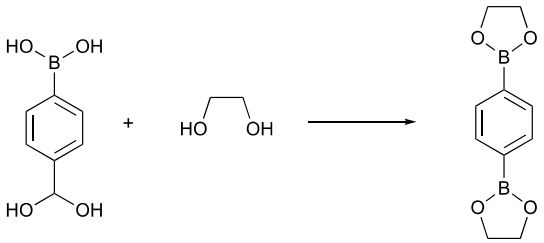
^{11}B NMR



FTIR

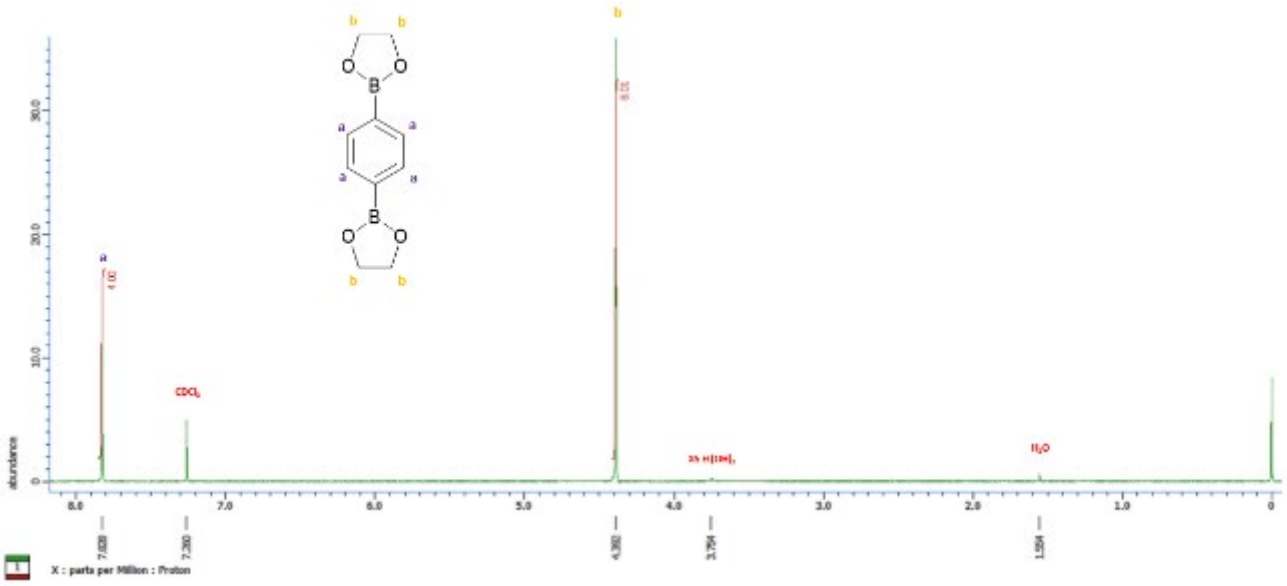


1,4-Phenylenediboronic bis(1,2-diol) ester (2a)

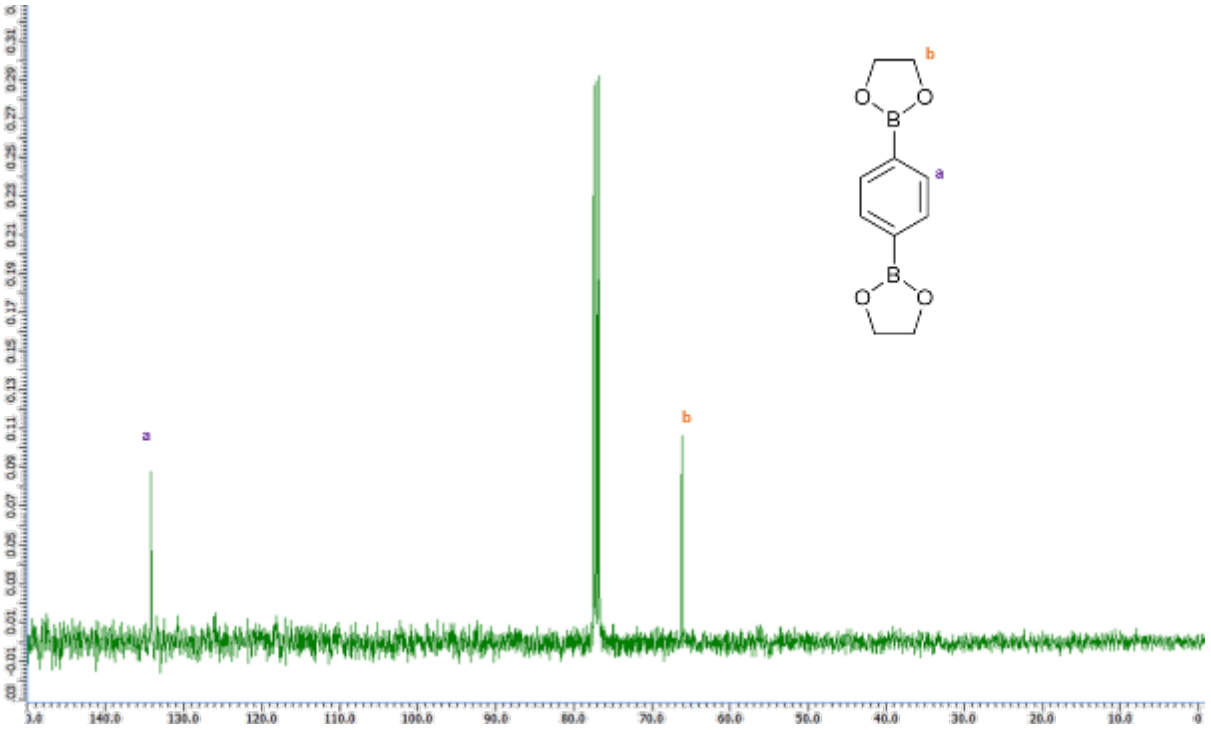


1,4-phenylenediboronic acid (10.0 g, 0.060 mol) was suspended in toluene (250 mL) and ethylene glycol (11.2 g, 0.180 mol, 3 equivs.) then was refluxed for 3 hours under nitrogen and water removed by azeotropic distillation using Dean-Stark apparatus. Solvent was then removed under reduced pressure affording the crude product as a white solid. The crude product was recrystalised from toluene and washed in cold toluene before drying in a vacuum oven at 100 °C for 30 minutes. The product was isolated as a white solid (yield = 10.95 g, 84%, Mpt = 238 °C). δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.82 (s, 4H, CH-Ar) 4.39 (s, 8H, CH_2). δC (101 MHz; $CDCl_3$; Me_4Si) δ 134.2 (C-Ar), 66.2 (CH_2-O). δB (128.28 MHz; $CDCl_3$ Me_4Si) δ 29 (s, br, Ph-B$(OR)_2$). ν^{max}/cm^{-1} 3033 (Ar-CH stretch), 2982-2908 (CH stretch), 1519-1478 (C=C ring stretch), 1406-1327 (B-O stretch), 1212-1104 (C-O stretch), 986 (B-C stretch), 842 (para-aromatic CH bend), 645 (B-O bend - wag).

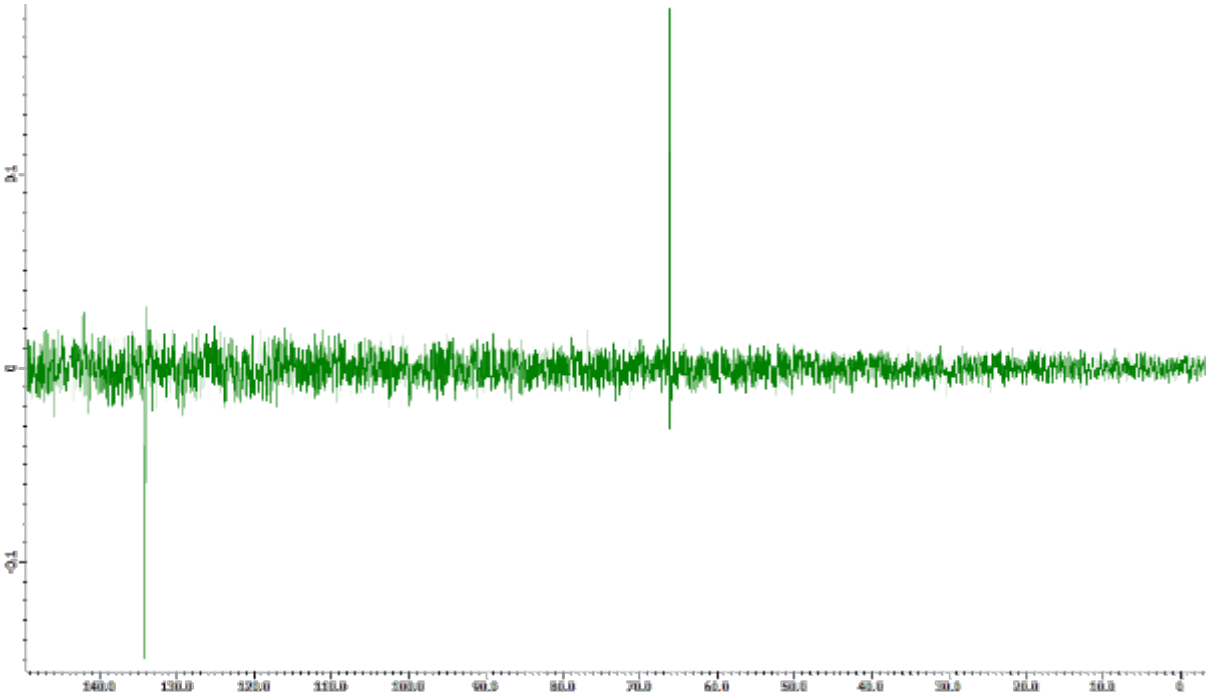
^{1}H-NMR


b
b
O
B
O
a
a
a
a
B
O
O
b
b
b
4.00
6.01
a
CDCl3
H2O
abundance
30.0
20.0
10.0
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.639
7.280
4.380
3.754
1.554
X : parts per Million : Proton

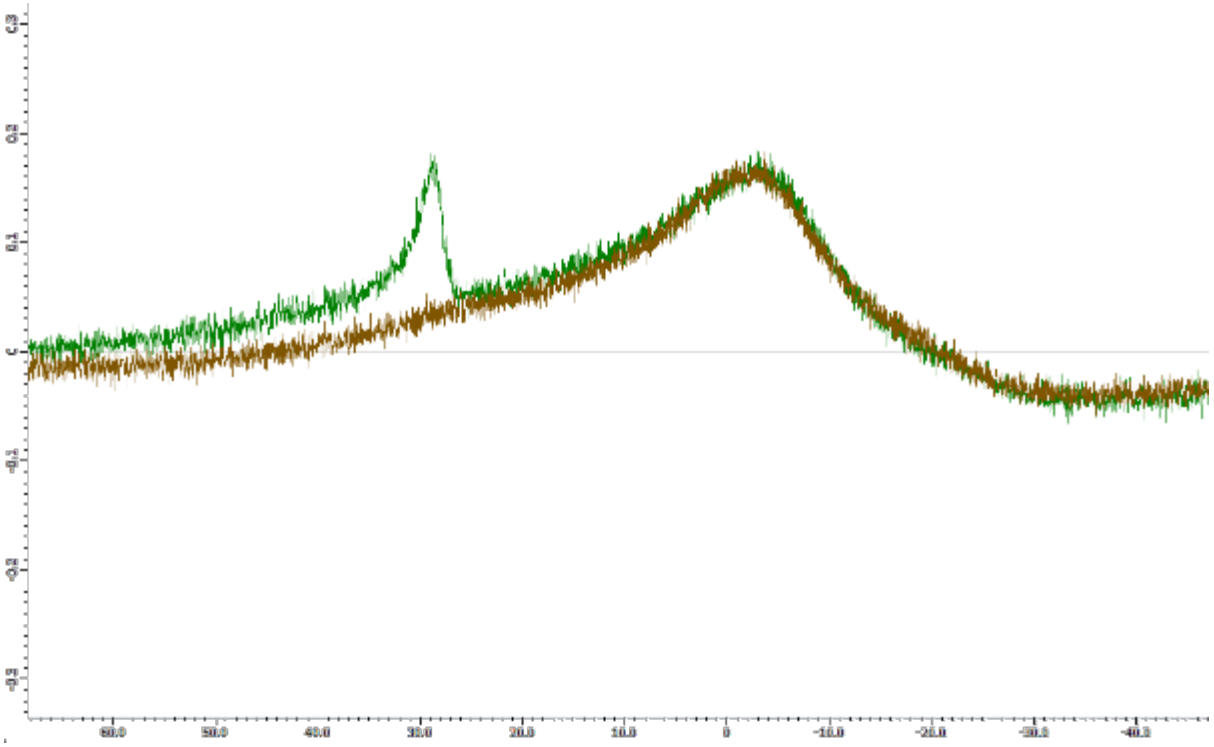
^{13}C NMR



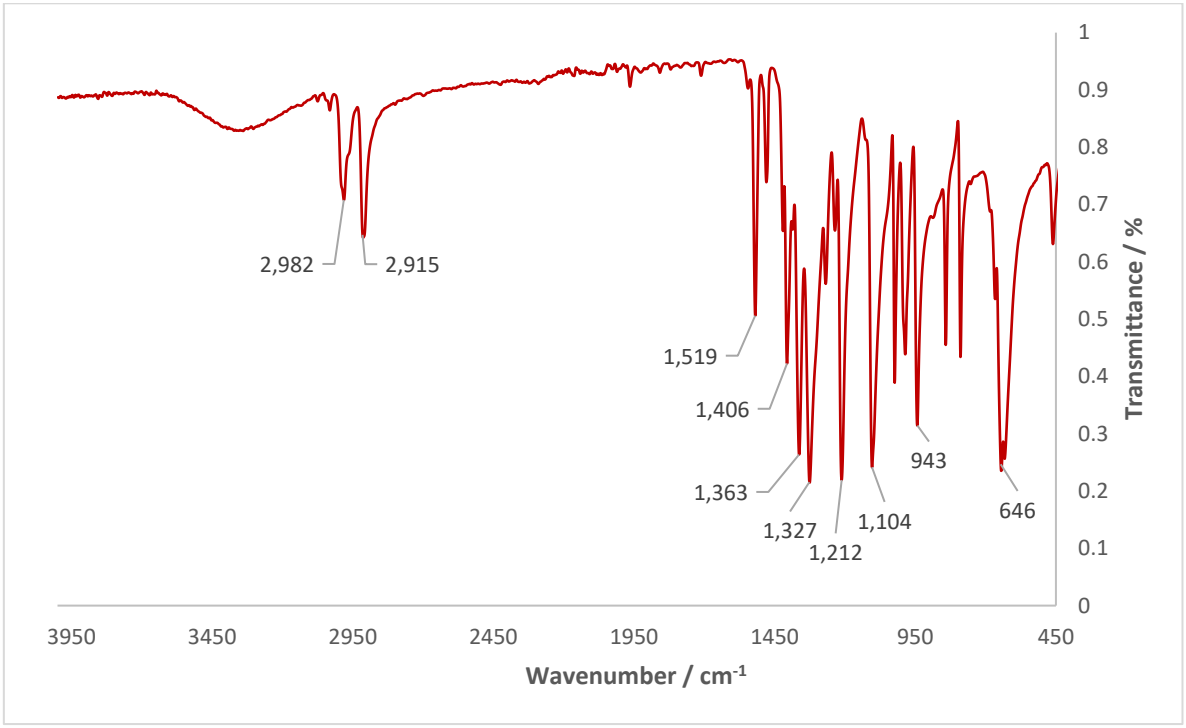
^{13}C NMR-DEPT



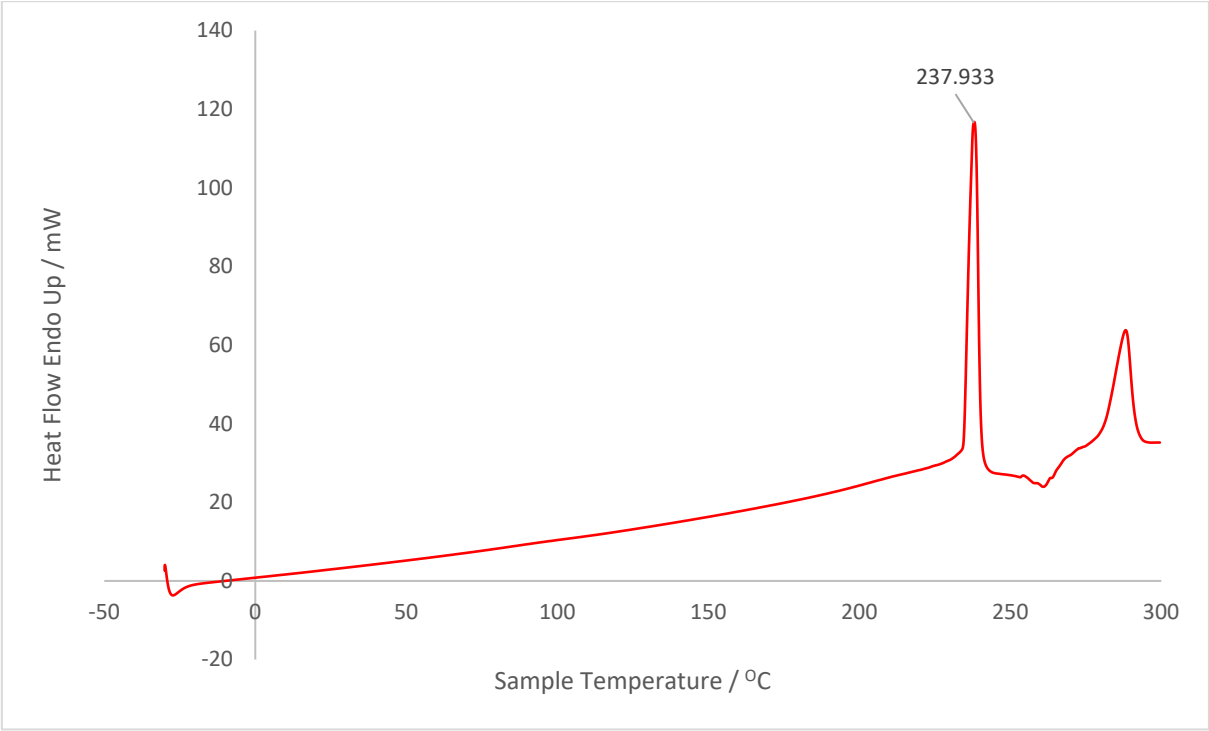
^{11}B NMR



FTIR


2,982
2,915
1,519
1,406
1,363
1,327
1,212
1,104
943
646
Transmittance / %
Wavenumber / cm-1
3950
3450
2950
2450
1950
1450
950
450
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

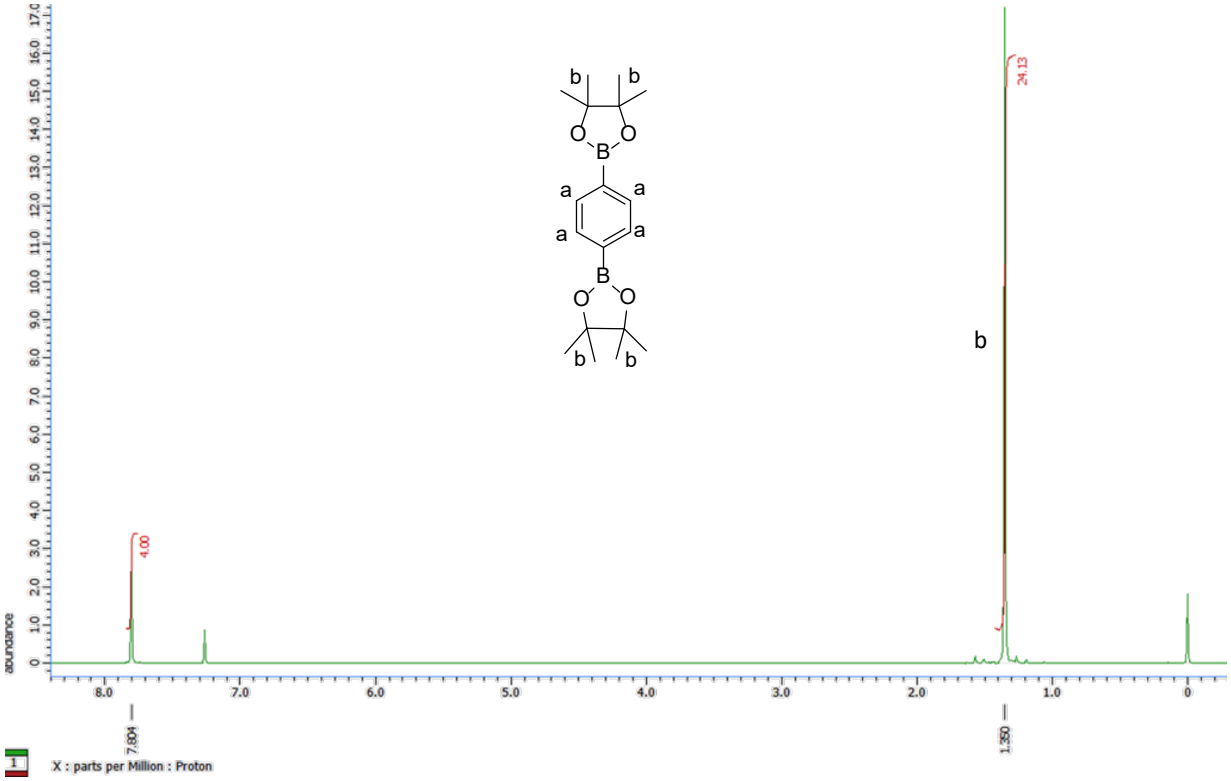
Melting Point Thermogram by DSC



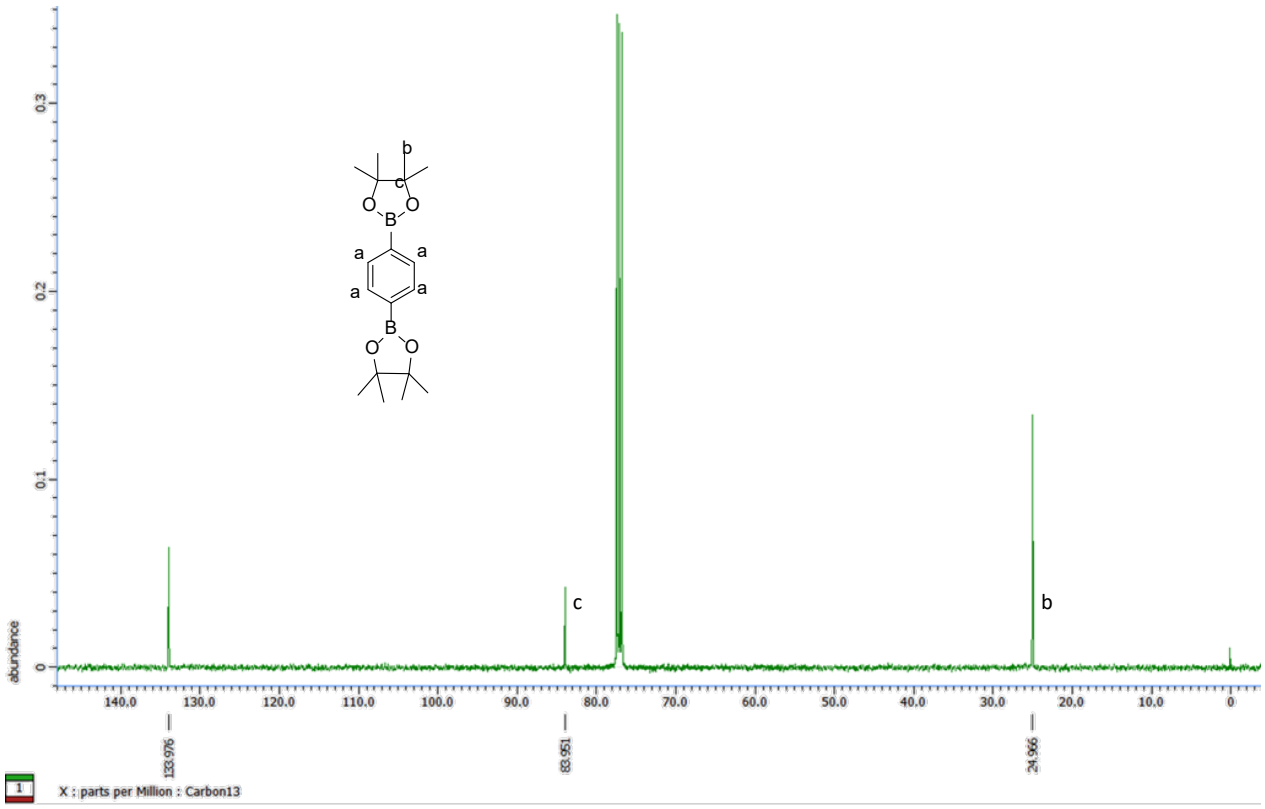
1,4-phenylene diboronic acid dipinacol ester (2b)

1,4-phenylene diboronic acid dipinacol ester was purchased from Fluorochem and used as received. δH (400 MHz; $CDCl_3$; Me_4Si) δ 7.80 (s, 4H, CH-Ar) 1.35 (s, 12H, 4 x CH_3). δC (101 MHz; $CDCl_3$; Me_4Si) δ 134.0 (C-Ar), 84.0 (C-O), 25.0 (CH_3). δB (128.28 MHz; $CDCl_3$ Me_4Si) δ 29 (s, br, Ph-B$(OR)_2$). ν^{max}/cm^{-1} 2983-2930 (CH stretch), 1519 (C=C ring stretch), 1340 (B-O stretch), 1139-1096 (C-O stretch).

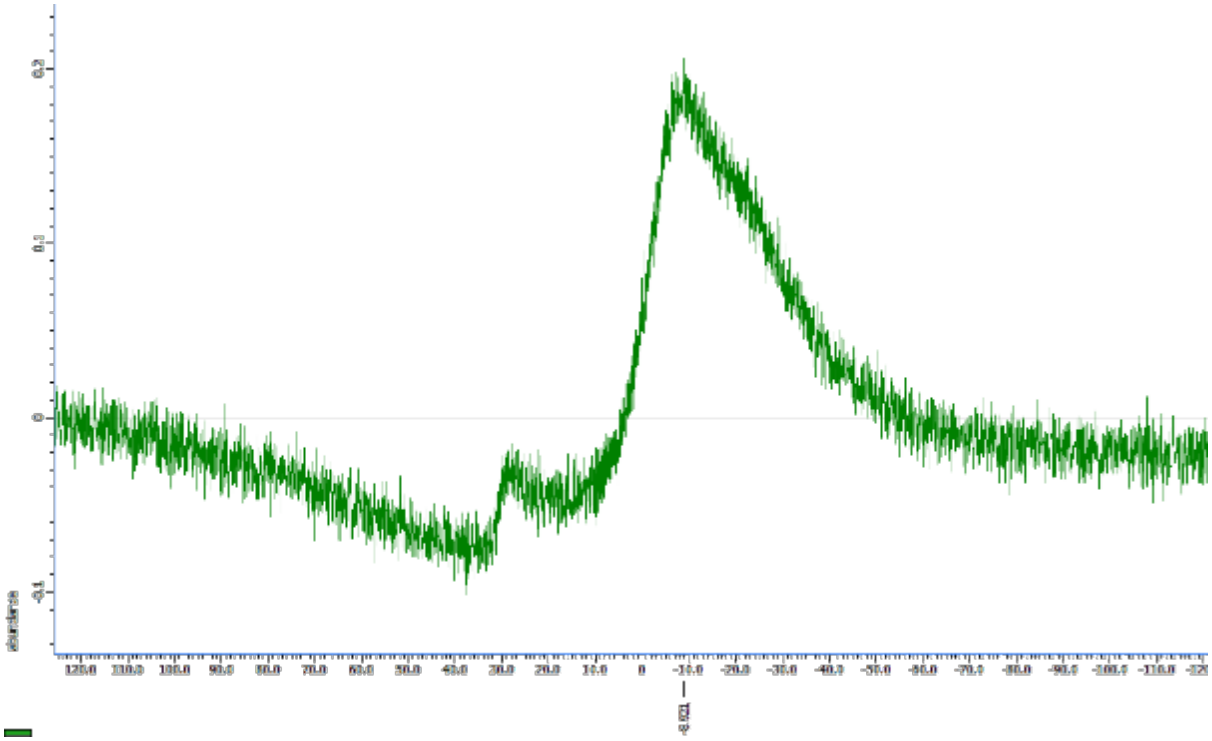
^{1}H NMR - Diboronic pinacol ester (2b)

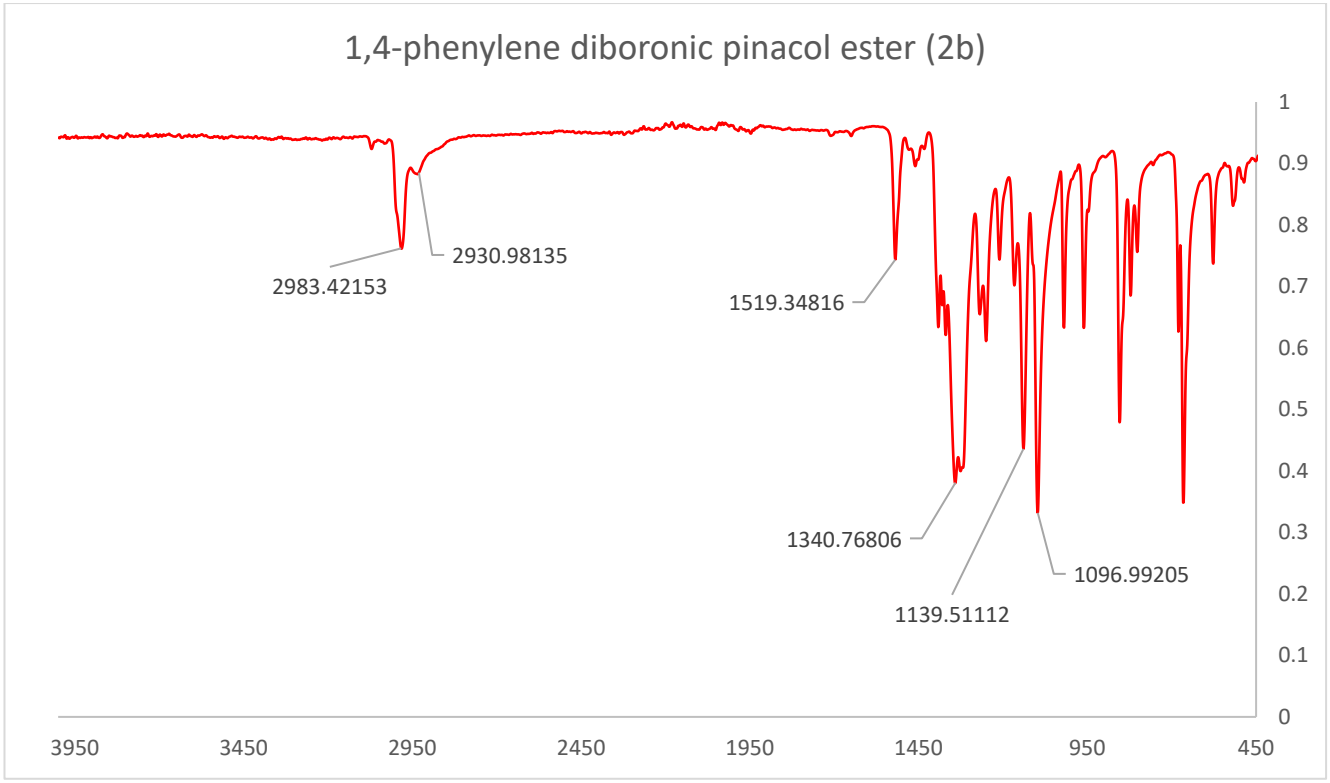


^{13}C NMR - Diboronic pinacol ester (2b)

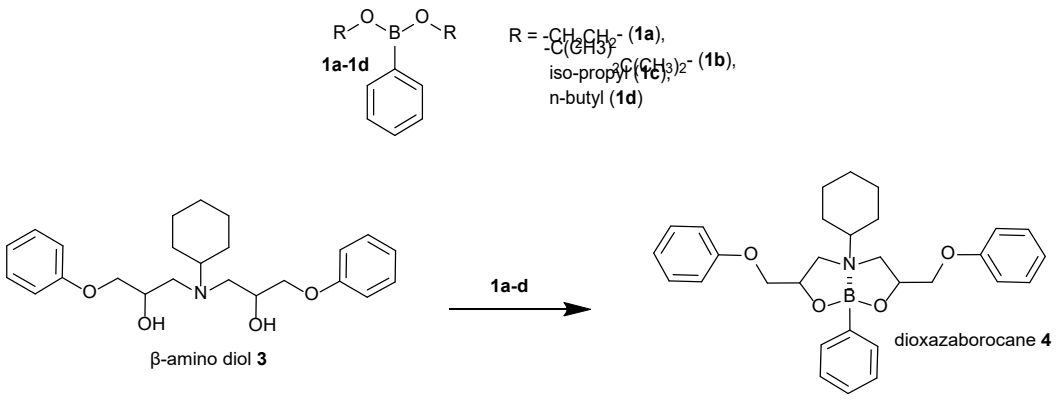


^{11}B NMR - diboronic pinacol ester (2b)



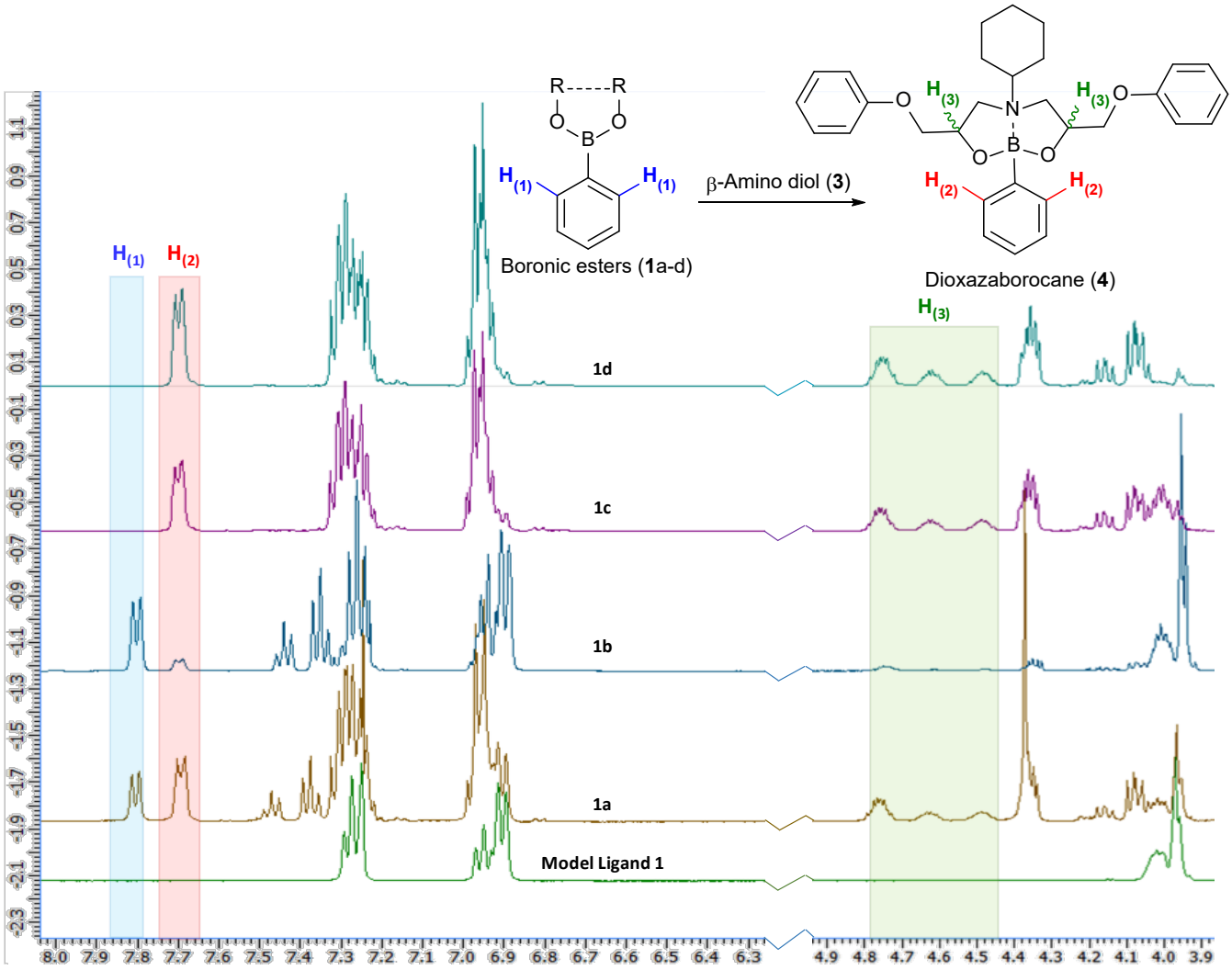


Model Reaction: β-amino diol 3 with monoboronic ester (1a-1d)



Method

The method for the reaction of β-amino diol **1** with monoboronic ester (**1**a-**1**d) was as follows. A stock solution of β-amino diol **3** in deuterated chloroform was prepared (0.4 M). The β-amino diol **3** stock solution (5 mL, 0.4 M, 0.002 mol) and an equal molar equivalent (0.002 mol) of the selected monoboronic ester (**1**a-**1**d) were mixed and analysed by ^{1}H-NMR at a predetermined time period. The ratio of unreacted boronic ester (**1**a-**1**d) to model dioxazaborocane product **4** was determined by integration of aromatic signals of boronic ester ($\mathbf{H}_{(1)}$, **1**a-**1**d) at 7.81 ppm to the more electron rich aromatic signals of dioxazaborocane **4** at 7.7 ppm ($\mathbf{H}_{(1)}$, see below).



Monoboronic Ester	$H_{(1)}$	$H_{(2)}$	Yield of dioxazaborocane product **4** (%)
1a	0.74	2.00	73.0
1b	13.99	2.00	12.5
1c	0.00	2.00	100.0
1d	0.00	2.00	100.0

Polymer synthesis

The preparation for all polymers and crosslinked (thermoset) polymeric materials was conducted by a simple one pot synthesis. Linear polymers were formulated to have a number average functionality of 5 amino-diol groups and a series of 0-100 mol% crosslinked thermoset (per moles of amino diol) polymers were prepared with either butyl diboronic ester **2**d (dioxazaborocane crosslinked D-series) or diamine crosslinker, selected from either 1,6-hexandiamine or 4,4'-diaminodicyclohexylmethane (4,4'-MDH) (amine control materials = A series).

Dioxazaborocane crosslinked D-series polymers (D0-D100) were prepared according to the procedure below.

1,4-butanediol glycidyl ether (BGE, 4.00 g, 0.020 moles), phenyl glycidyl ether (PGE, 1.49 g, 0.010 moles) and n-hexylamine (HA, 2.50 g, 0.025 moles) were combined in a round bottom flask under nitrogen with stirring. To the reaction mixture the appropriate mass of 1,4-phenylenediboronic acid tetrabutyl ester (**2**d) was added according to Table S2. The reaction mixture was stirred at 55 °C for 1 hour and 45 minutes under nitrogen whilst viscosity slowly increased, before drawing down onto a non-stick PTFE sheet using a 400 µm draw-down bar to control film thickness. The resulting films were allowed to cure at room temperature for 16 hours under nitrogen, followed by a post cure schedule ramp at 80 (1 hour), 120 (1 hour) then 170 °C (1 hour, total 3 hours thermal cure). After cooling to room temperature, the resulting polymeric films were removed from the PTFE sheet to give dioxazaborocane crosslinked epoxy-amine polymers (D0-D100) or viscous liquid films (D0-D40).

Table S2: Dioxazaborocane polymers (D0-D100 series) where the desired crosslinking percentage comes from calculation of the percentage from the total equivalent amine moles in the formulation.

Crosslinker stoichiometry (mol%)	Dibutyl boronic ester content (g, mol)
100	4.82, 0.012
80	3.86, 0.010
60	2.89, 0.007
40	1.92, 0.005
20	0.96, 0.002
0	0.0, 0.0

Epoxy-amine control materials, A series (A20-A100) were prepared according to the procedure below.

1,4-butanediol glycidyl ether (4.00 g, 0.020 moles), phenyl glycidyl ether (1.49 g, 0.010 moles) were combined in a round bottom flask under nitrogen with stirring. To the reaction mixture, the appropriate mass of n-hexylamine (HA) and 1,6-hexanediamine was added according to Table 3 (below). The reaction mixture was stirred at 55°C for 1 hour and 45 minutes under nitrogen whilst viscosity slowly increased, before drawing down onto a non-stick PTFE sheet using a 400 µm draw-down bar to control film thickness. The resulting film was allowed to cure at room temperature for 16 hours under nitrogen, followed by a post cure schedule ramp at 80 (1 hour), 120 (1 hour) then 170 °C (1 hour, total 3 hours thermal cure). After cooling to room temperature, the resulting polymeric films were removed from the PTFE sheet to give solid sheets of epoxy-amine polymer (A60-A100) or viscous liquid films (A0-A40).

Table S3: Epoxy-amine polymers (A0-100 series) where the desired crosslinking percentage comes from the calculation of the percentage from the total equivalent epoxy moles in the formulation and the remaining non-crosslinking amine content arises from the difference of the total epoxy moles less the crosslinking equivalent moles.

	Amine Crosslinker	**Non-crosslinking amine**
Crosslinking / mol%	1,6-hexane diamine content (g, mol)	n-Hexylamine Content (g, mol)
100	1.44, 0.012	0.00, 0.000
80	1.15, 0.010	0.50, 0.005
60	0.86, 0.007	1.00, 0.010
40	0.57, 0.005	1.50, 0.015
20	0.29, 0.002	2.00, 0.021
0	-	2.50, 0.025

All A^2 series polymers ($A^2$20-$A^2$100) were prepared according to the procedure below.

1,4-butanediol glycidyl ether (BGE, 4.00 g, 0.020 moles), phenyl glycidyl ether (PGE, 1.49 g, 0.010 moles) were combined in a round bottoms flask under nitrogen with stirring. To the reaction mixture, the appropriate mass of

n-hexylamine (HA) and 4,4'-MDH was added according to Table 4 (below). The reaction mixture was stirred at 55 °C for 1 hour and 45 minutes under nitrogen whilst viscosity slowly increase, before drawing down onto a non-stick PTFE sheet using a 400 µm draw-down bar to control film thickness. The resulting film was allowed to cure at room temperature for 16 hours under nitrogen, followed by a post cure schedule ramp at 80 (1 hour), 120 (1 hour) then 170 °C (1 hour, total 3 hours thermal cure). After cooling to room temperature, the resulting polymeric films were removed from the PTFE sheet to give sheets of epoxy-amine polymer (A60-A100) or viscous liquid films (A0-A40).

Table S4: Epoxy- amine polymer ($A^2$0-100 series) crosslinking content where the desired crosslinking percentage comes from the calculation of the percentage from the total equivalent epoxy moles in the formulation and the remaining non-crosslinking amine content arises from the difference of the total epoxy moles less the crosslinking equivalent moles.

	Amine Crosslinker	**Non-crosslinking amine**
Crosslinking / mol%	4,4'-MDH Content (g, mol)	n-Hexylamine Content (g, mol)
100	2.60, 0.012	0.00, 0.000
80	2.08, 0.010	0.50, 0.005
60	1.56, 0.007	1.00, 0.010
40	0.57, 0.005	1.50, 0.015
20	0.29, 0.002	2.00, 0.021
0	-	2.50, 0.025

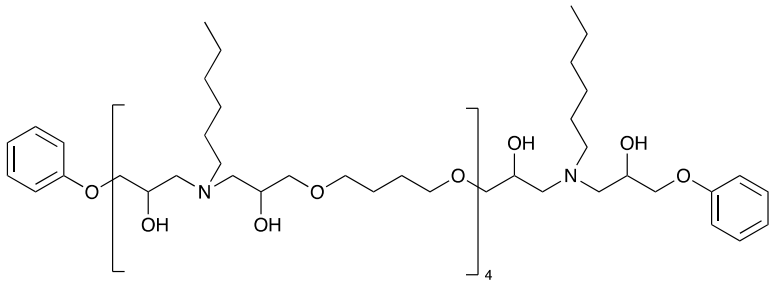
All A^3 series polymers ($A^3$20-$A^3$100) were prepared according to the procedure below.

Bisphenol A epoxy resin (DGBE, 4.00 g, 0.012 moles), phenyl glycidyl ether (PGE, 0.88 g, 0.006 moles) were combined in a round bottom flask under nitrogen with stirring. To the reaction mixture the appropriate mass of cyclohexylamine (CHA) and 4,4'-MDH was added according to Table 5 (below). The reaction mixture was stirred at 55 °C for 45 minutes under nitrogen whilst viscosity slowly increase, before drawing down onto a non-stick PTFE sheet using a 400 µm draw-down bar to control film thickness. The resulting film was allowed to cure at room temperature for 16 hours under nitrogen, followed by a post cure schedule ramp at 80 (1 hour), 120 (1 hour) then 170 °C (1 hour, total 3 hours thermal cure). After cooling to room temperature, the resulting polymeric films were removed from the PTFE sheet to give sheets of epoxy-amine polymer ($A^3$60-$A^3$100).

Table S5: Epoxy-amine polymer ($A^3$20-100 series) crosslinking content where the desired crosslinking percentage comes from the calculation of the percentage from the total equivalent epoxy moles in the formulation and the remaining non-crosslinking amine content arises from the difference of the total epoxy moles less the crosslinking equivalent moles.

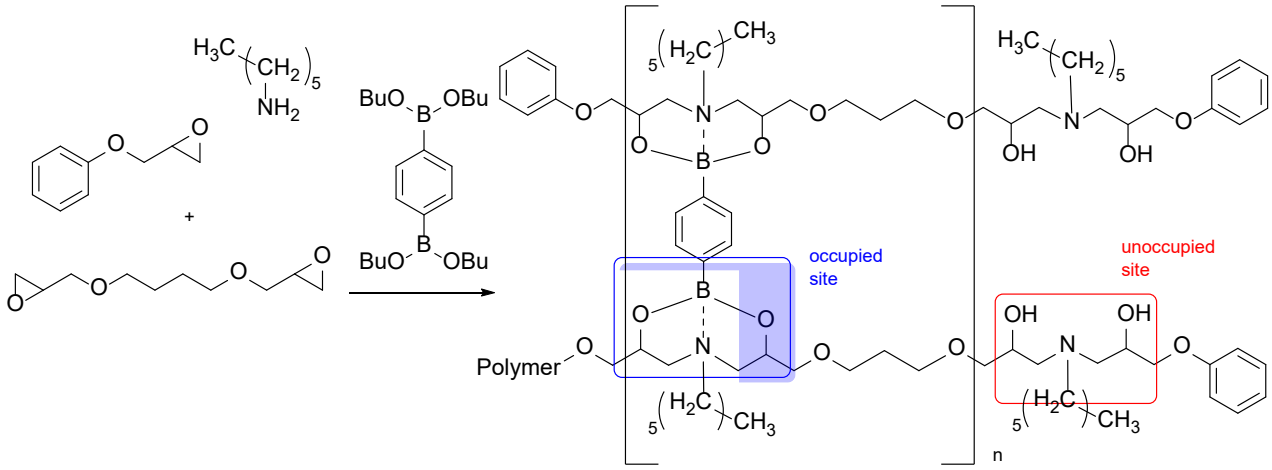
	Amine Crosslinker	**Non-crosslinking amine**
Crosslinking / mol%	4,4'-MDH Content (g, mol)	Cyclohexylamine Content (g, mol)
100	1.55, 0.007	0.00, 0.000
80	1.23, 0.006	0.29, 0.003
60	0.93, 0.004	0.58, 0.006

Representative structure of linear (non-crosslinked) epoxy-amine polymer (D0)

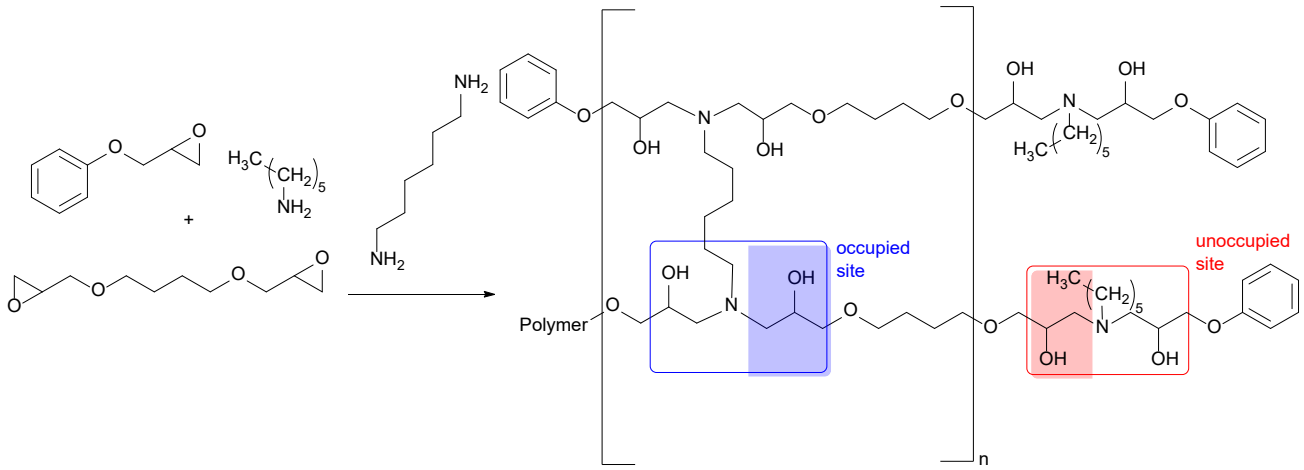


Target number average molecular weight (Mn) = **1615.32 gmol^{-1}**

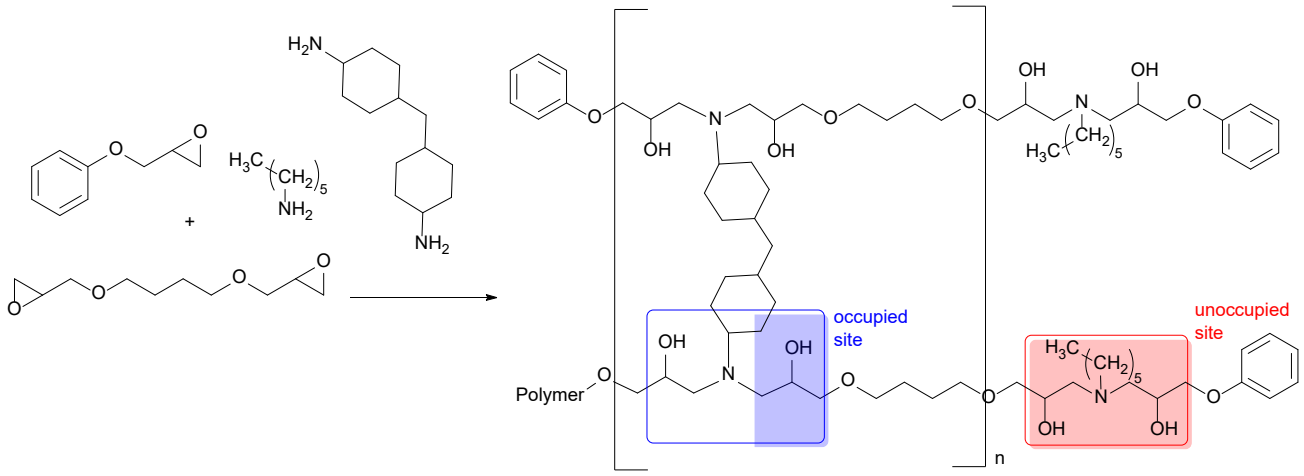
Representative structure of epoxy-amine-dioxazaborocane polymers (D20-D100), where degree of occupied vs unoccupied crosslinking sites depends on the mole% of 1,4-phenylenediboronic acid tetrabutyl ester (**2**d) according to Table 2.



Representative structure of A-series epoxy-amine (control, A20-A100) network polymers, where degree of occupied vs unoccupied crosslinking sites depends on the mole% of 1,6-hexanediamine according to Table 3.



Representative structure of A^2-series epoxy-amine (control, $A^2$20-$A^2$100) network polymers, where degree of occupied vs unoccupied crosslinking sites depends on the mole% of 4,4'-MDH according to Table 4.



Representative structure of A^3-series epoxy-amine (control, $A^3$20-$A^3$100) network polymers, where degree of occupied vs unoccupied crosslinking sites depends on the mole% of 4,4'-MDH according to Table 5.

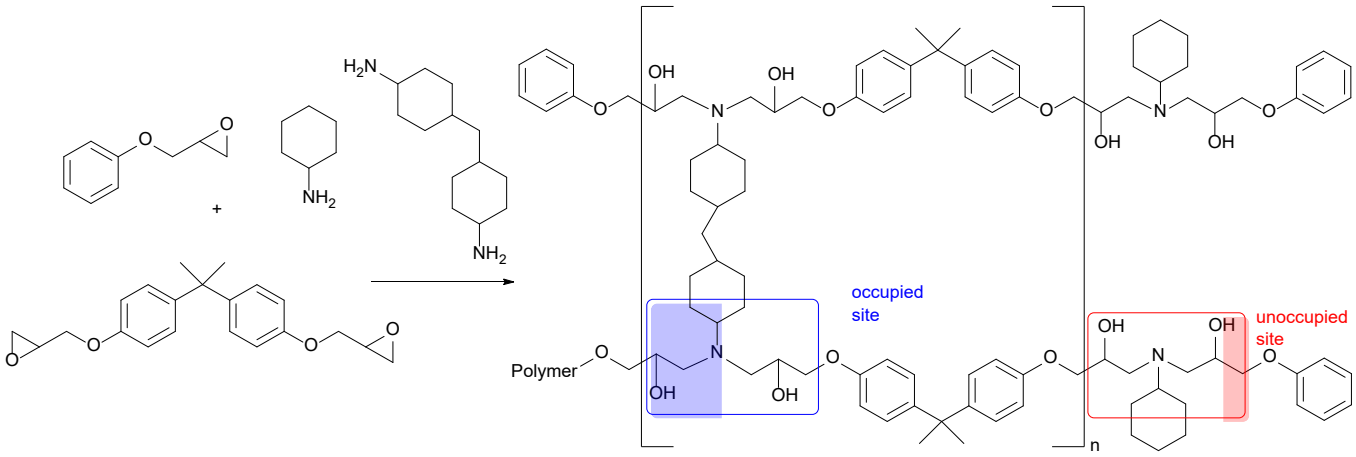
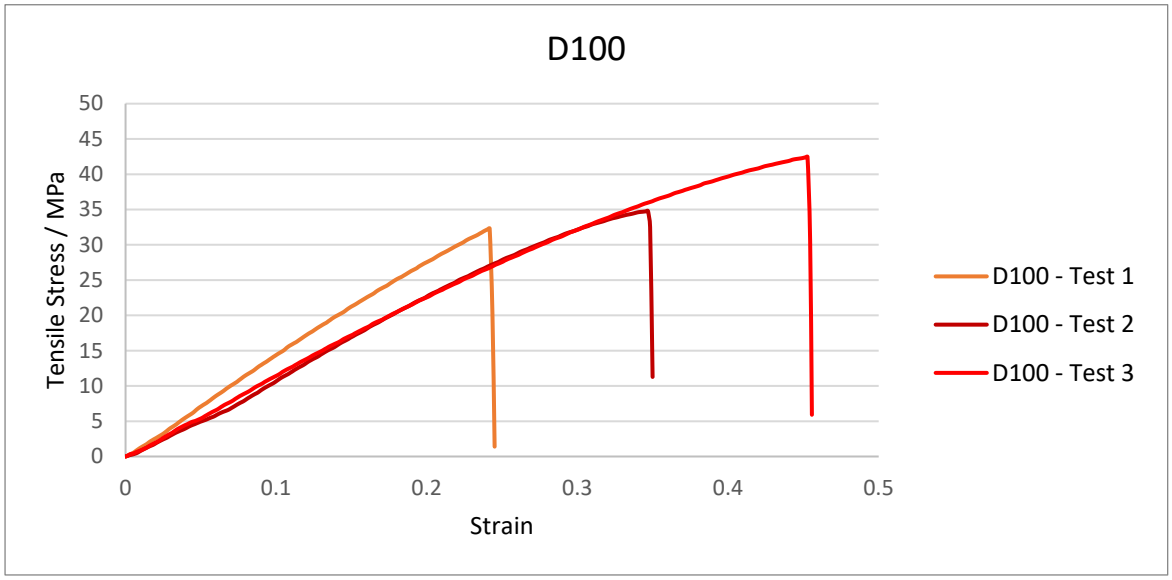


Table 6: Tensile properties of virgin dioxazaborocane (D60-D100), recycled dioxazaborocane (D^R60-D^R100) , and high T_g epoxy- amine control ($A^3$60- $A^3$100) materials

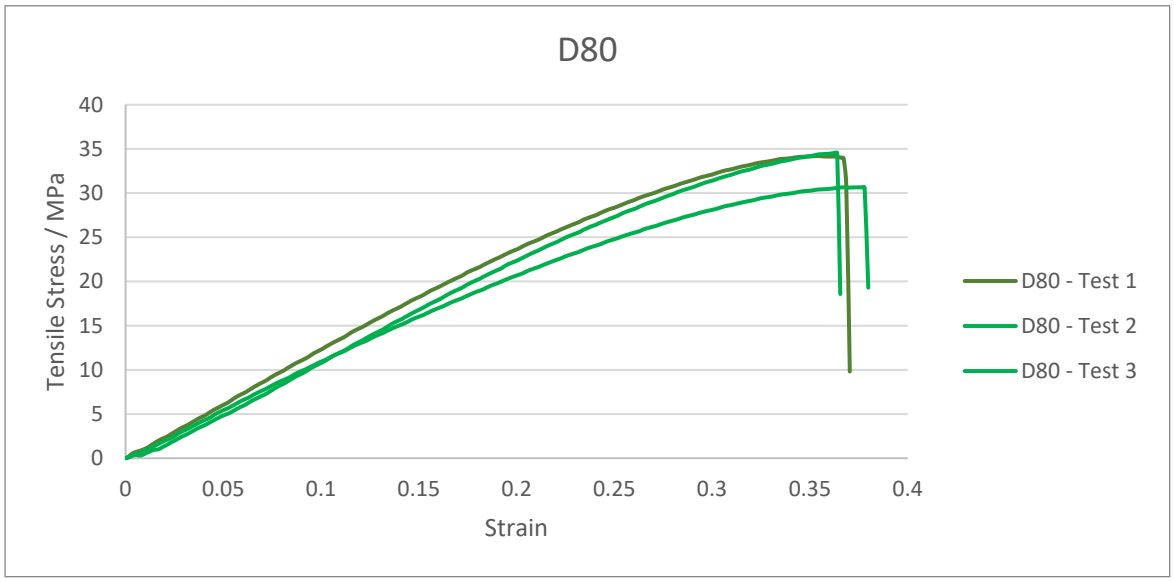
Polymer	Ultimate tensile strength / MPa	std dev (+/-)	Youngs Modulus / MPa	std dev (+/-)	Strain at Break	std dev (+/-)	Stress at break / MPa	std dev (+/-)
D60	4.713	0.168	0.415	0.018	8.533	0.409	4.620	0.081
D80	33.132	1.758	119.130	6.177	0.373	0.005	33.056	1.731
D100	36.480	2.992	127.857	11.281	0.343	0.086	37.071	3.825
D-R-60	1.789	0.153	0.180	0.008	8.280	0.647	1.470	0.342
D-R-80	30.106	2.517	96.212	7.736	0.522	0.056	26.883	4.107
D-R-100	37.965	2.461	136.457	25.031	0.402	0.065	34.279	4.550
A-3-60	44.813	4.467	343.670	23.469	0.129	0.009	44.094	3.892
A-3-80	68.125	2.652	321.490	10.771	0.227	0.025	68.125	2.652
A-3-100	68.879	3.062	308.978	14.420	0.273	0.019	68.864	3.045

Experimental methods

D100 stress-strain graph

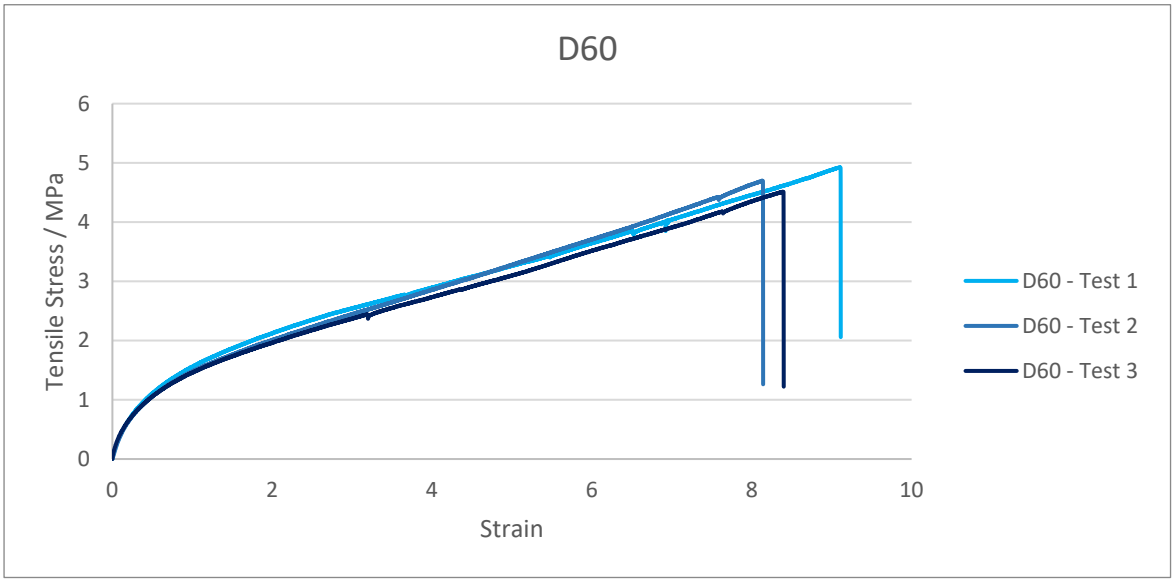


D80 stress-strain graph

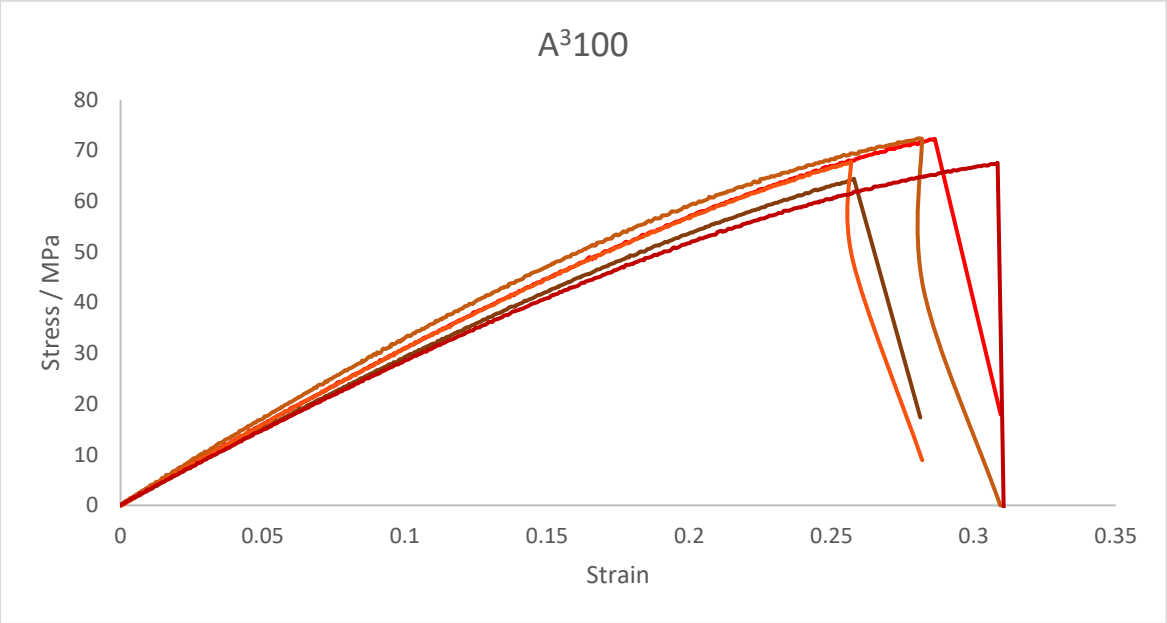


Experimental methods

D60 stress-strain graph

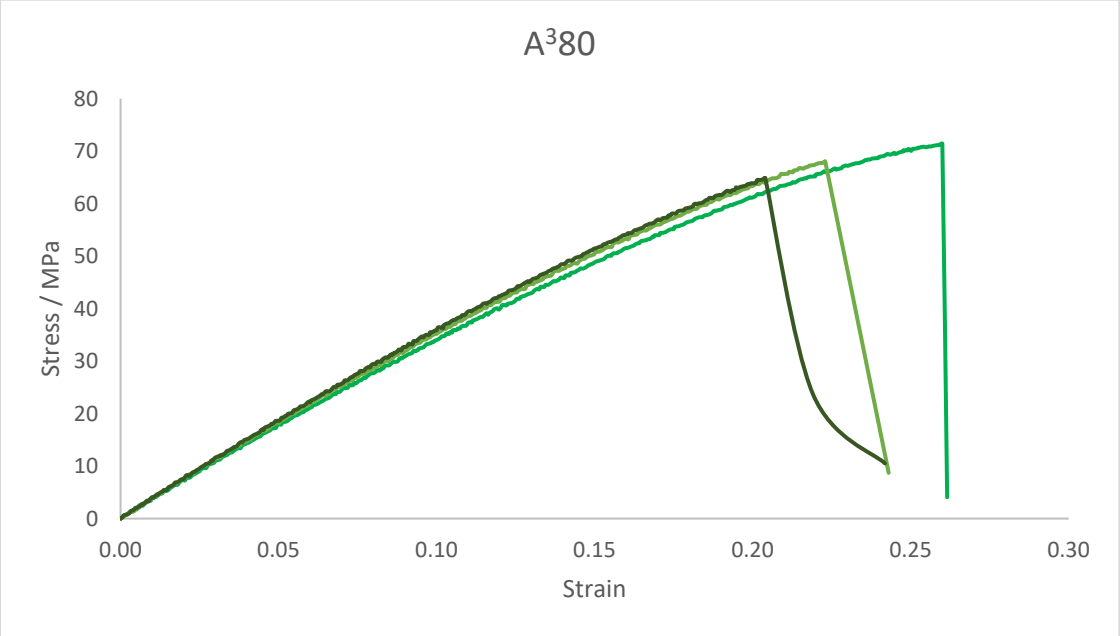


A^3100 stress-strain graph

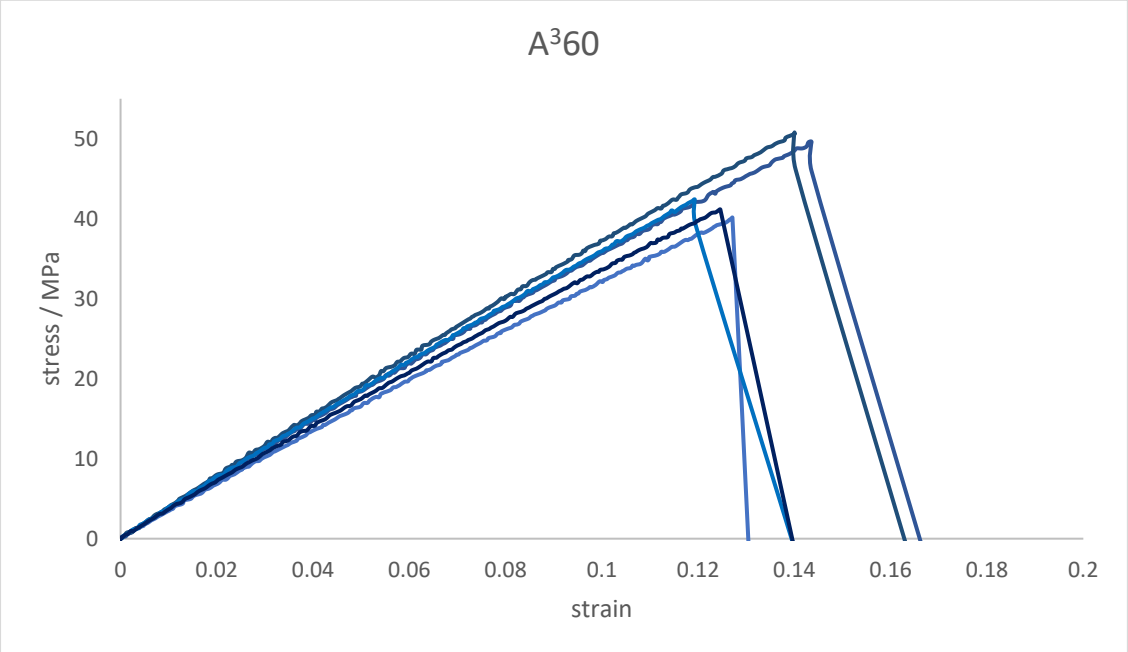


Experimental methods

A^{3}80 stress-strain graph

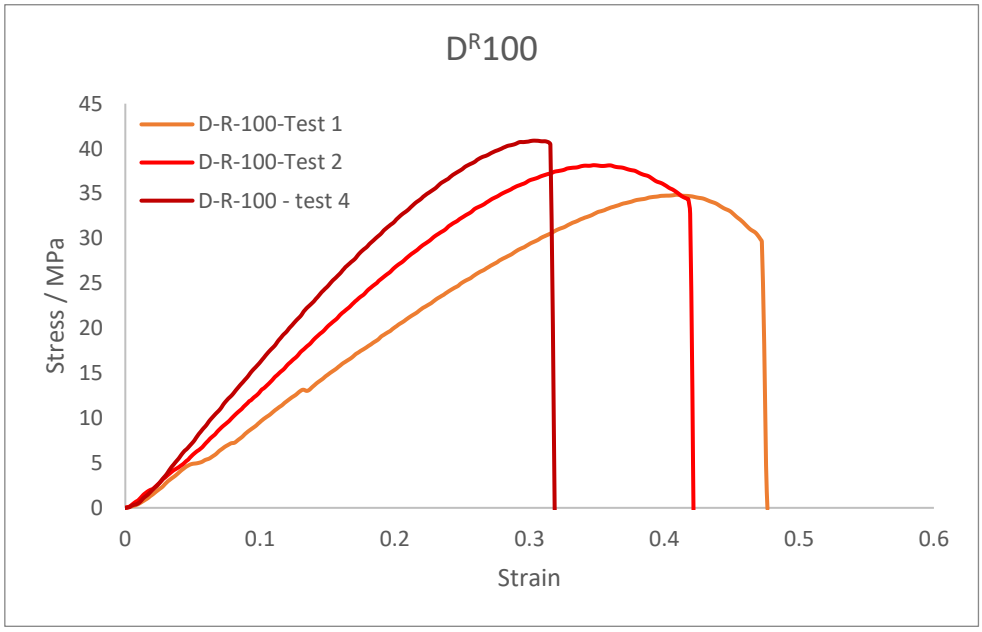


A^{3}60 stress-strain graph

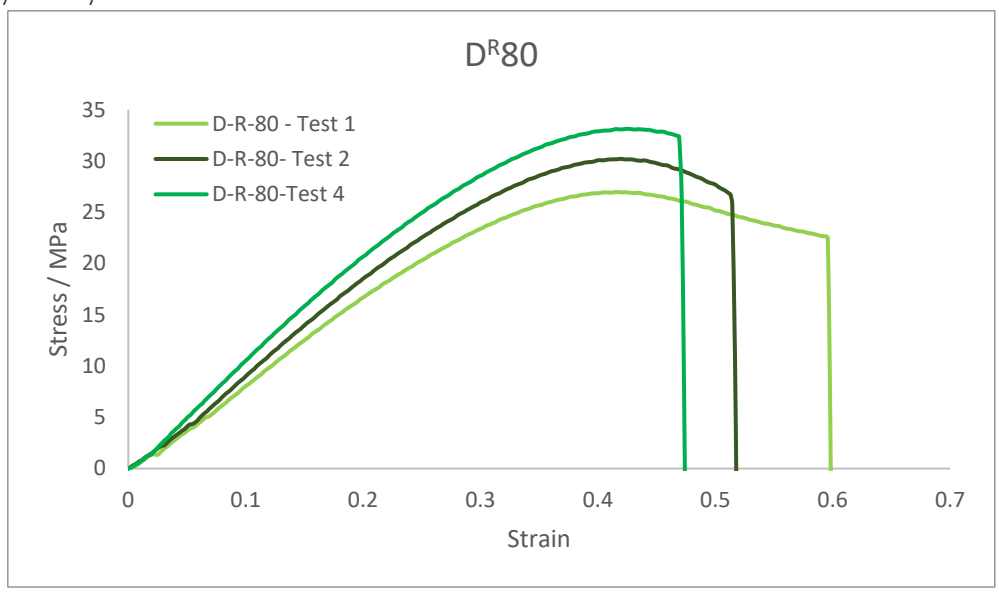


Experimental methods

100% Recycled Dynamic - D^R100

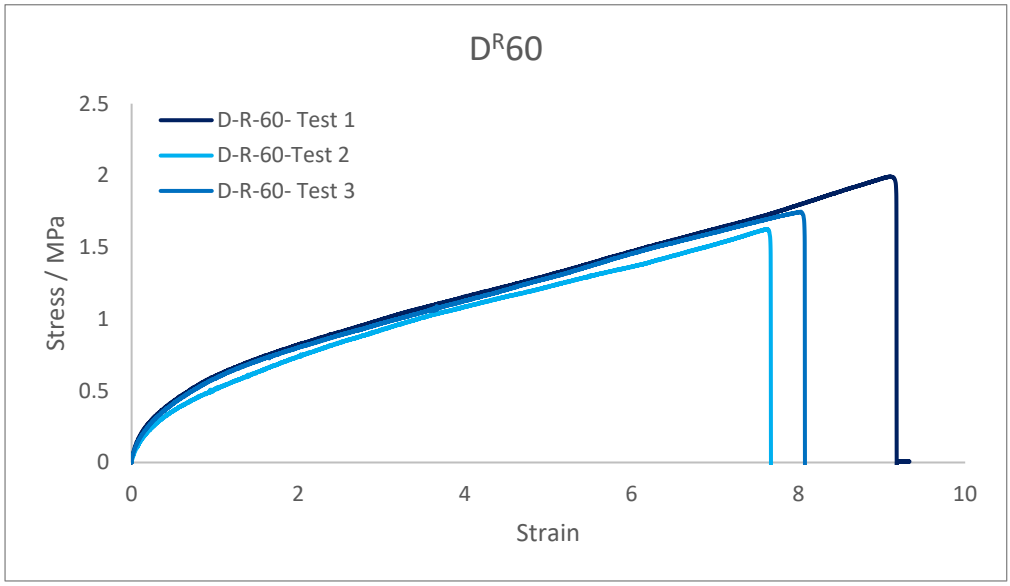


80% Recycled Dynamic - D^R80

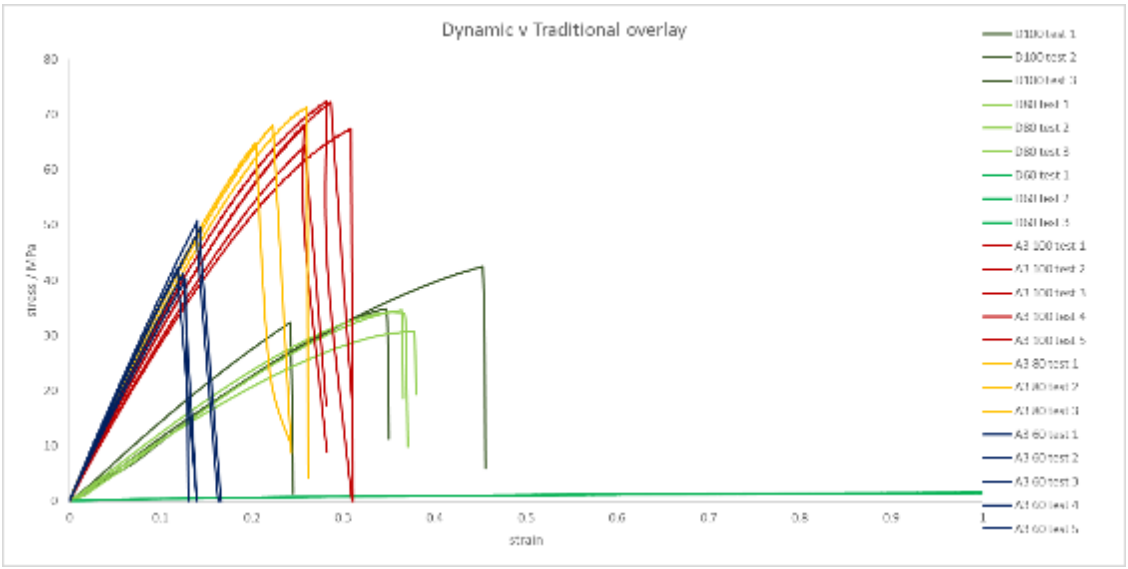


Experimental methods

60% Recycled Dynamic - D^R60

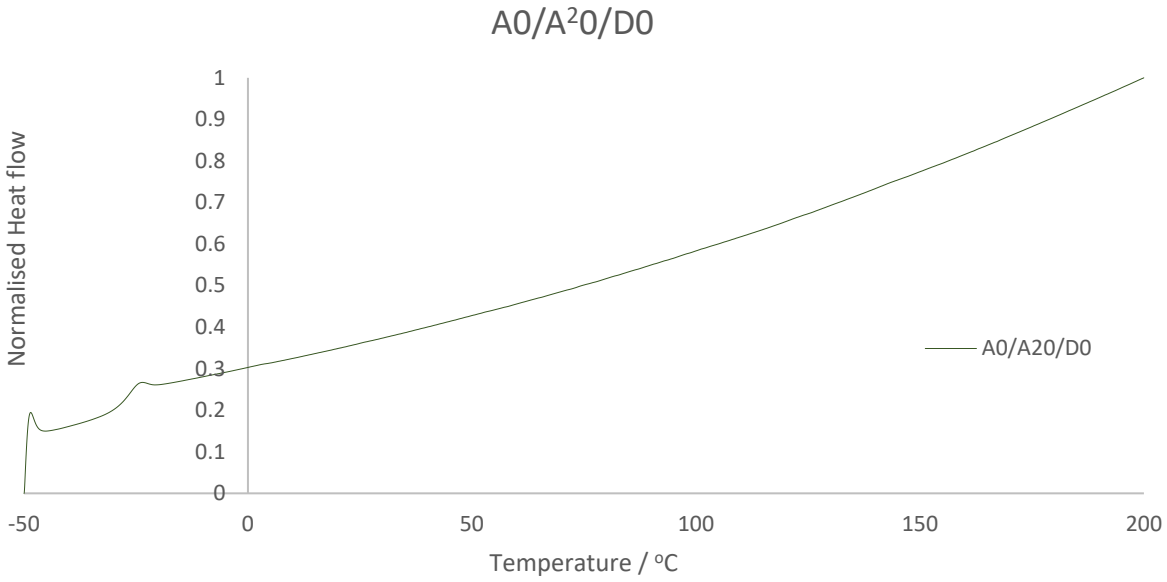


Epoxy-amine-dioxazaborocane (D series) vs epoxy-amine (A^3 series) – stress over strain graphs*

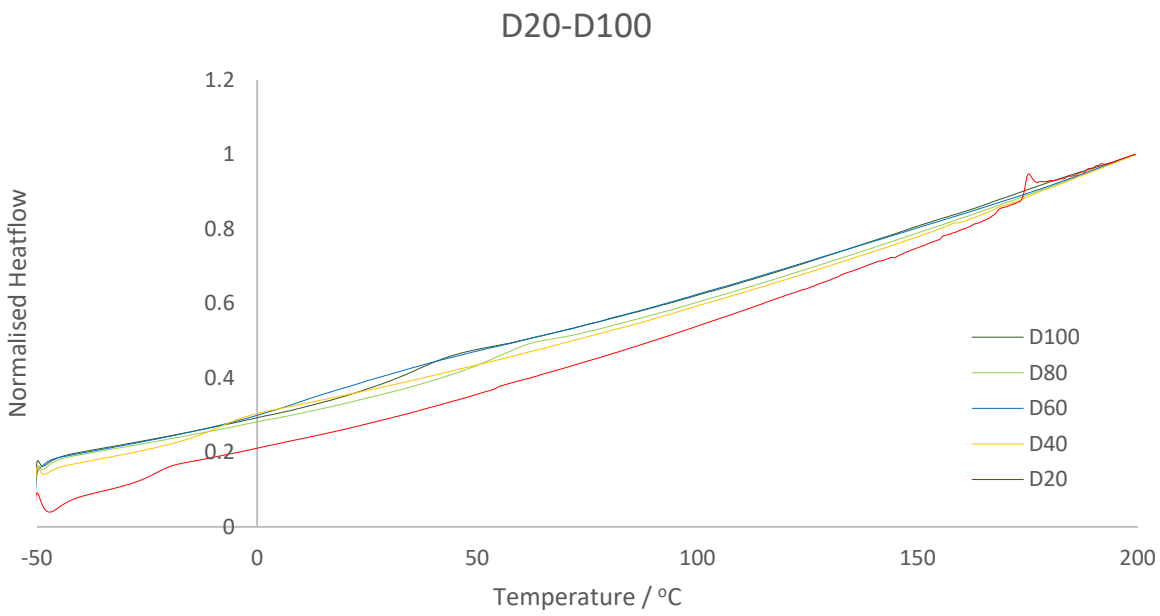


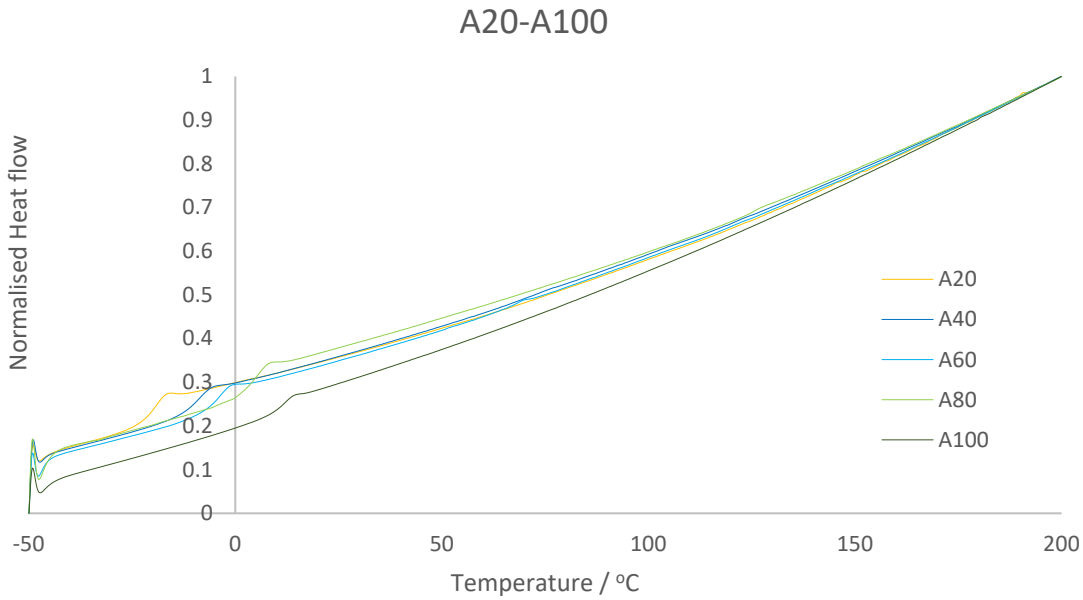
* Note: D60 in rubbery state due to Tg below test temperature resulting in very high strain values and beyond the scale of the x-axis.

DSC data to support Table 1 in main document

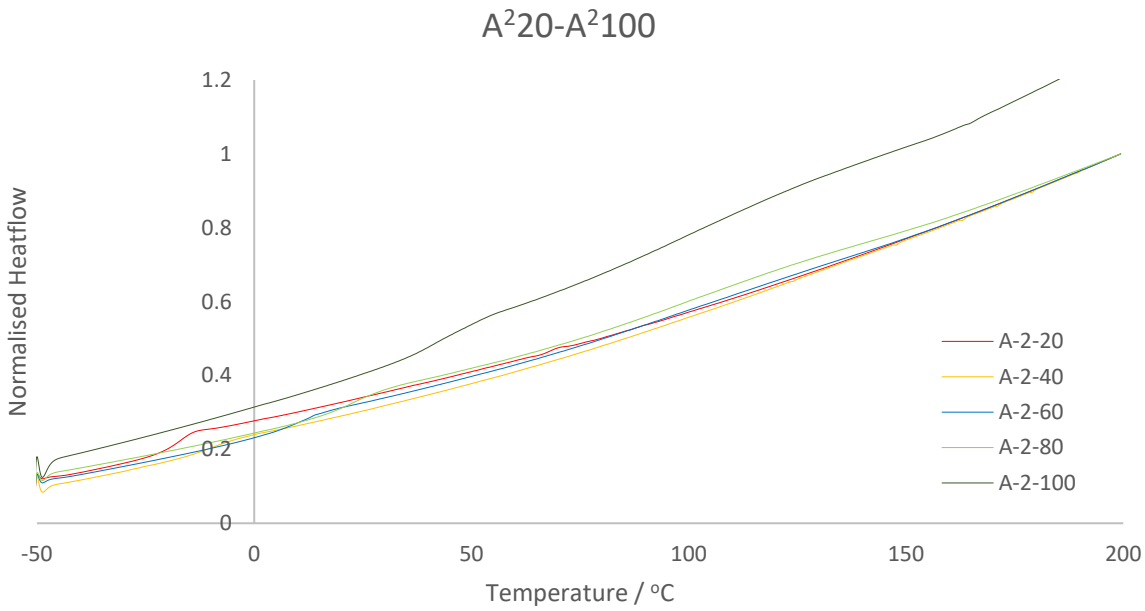


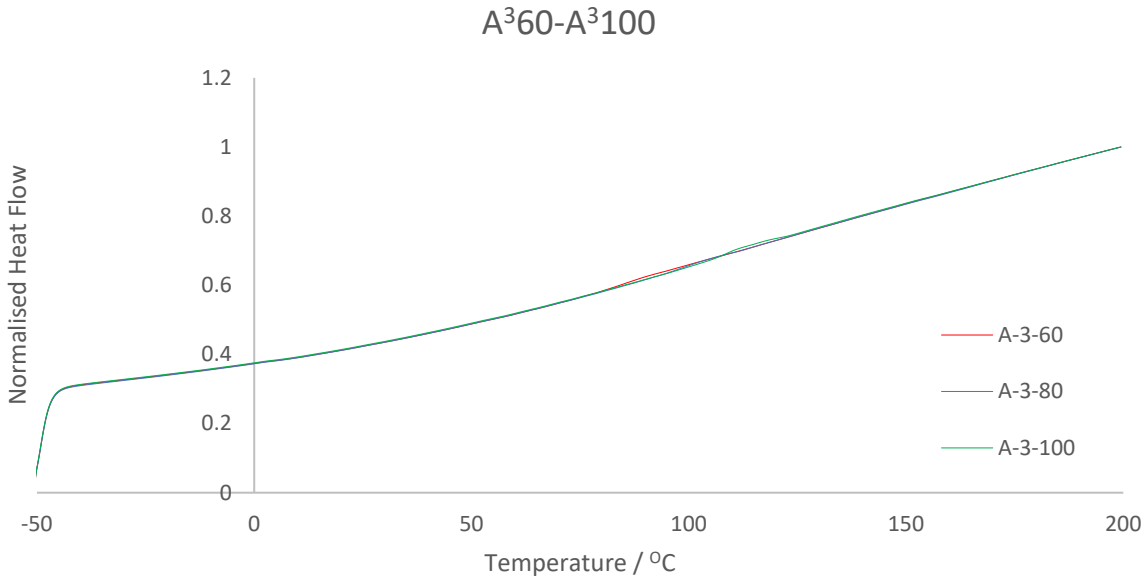
Experimental methods



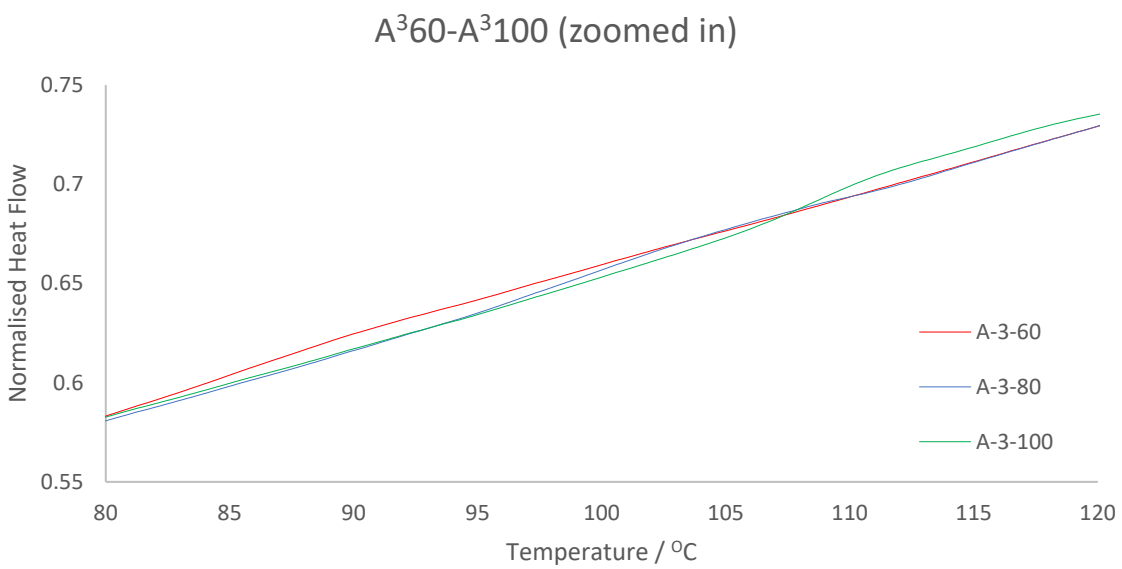


Experimental methods





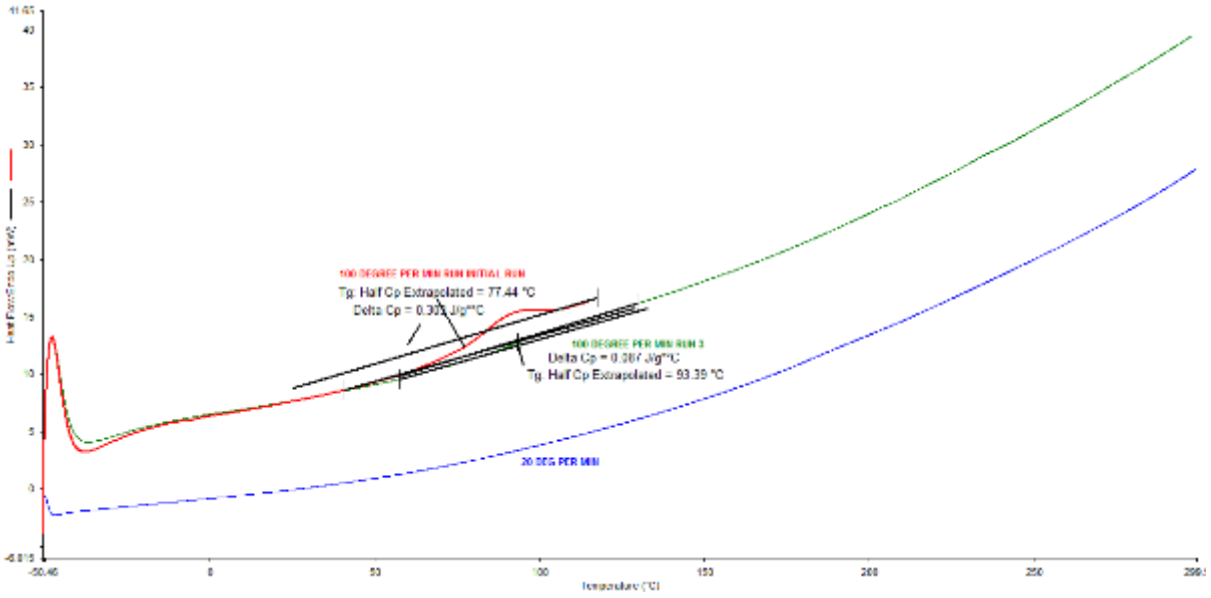
Experimental methods



<u>DSC data to support multiple mechanical recycling study</u>

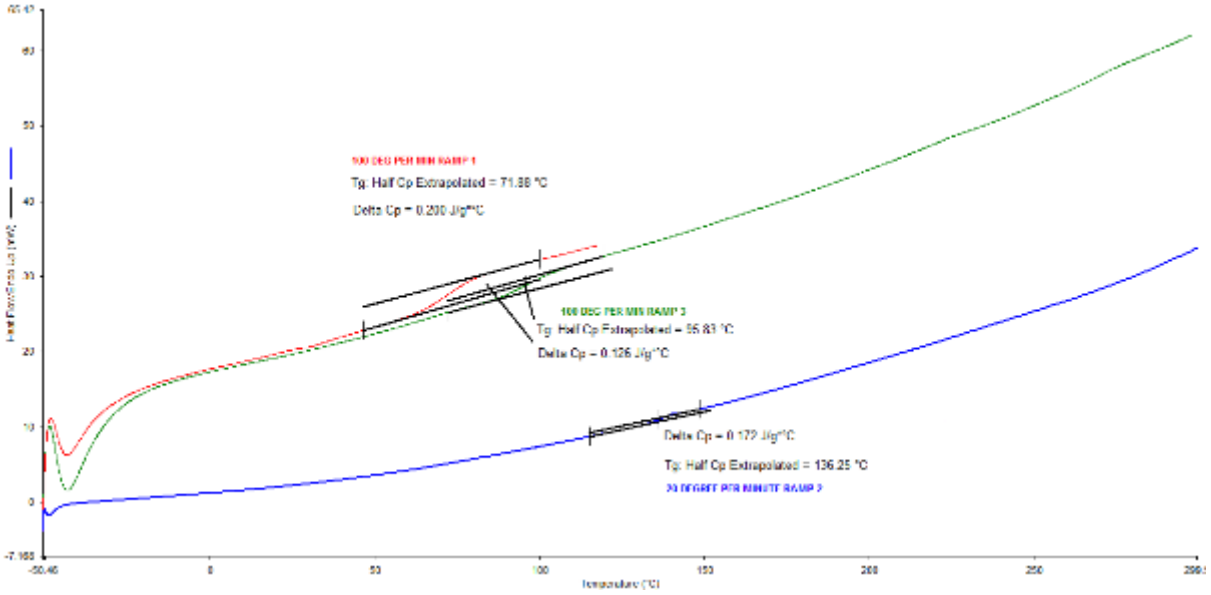
Glass transition (T_g) analyses for multiple mechanical recycling study were conducted using a 100 °C/min heating rate to enhance the T_g signal using a Perkin-Elmer Pyris DSC 8500 and analysed on Pyris software (version 11.1.1.0492). Sample masses of 3-6 mg were weighed into standard aluminium DSC pans with perforated lids and were heated from -50 °C to 120 °C at a constant rate of 100 °C per minute and the T_g reported as the midpoint of the endothermic step in the heat flow signal output.

D80 Virgin

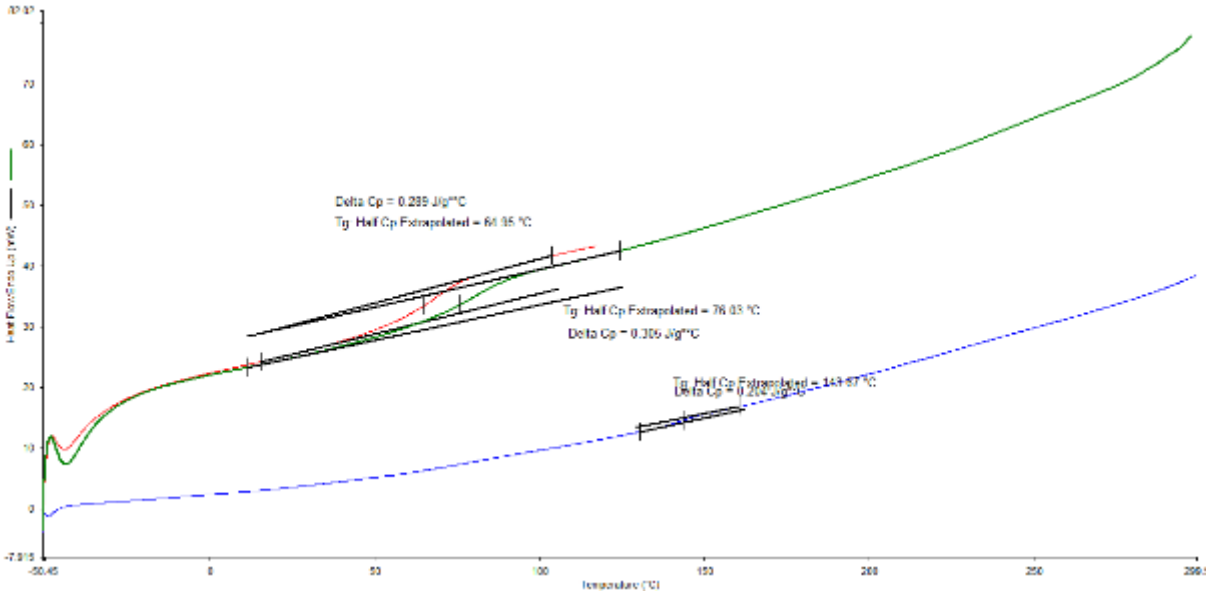


Experimental methods

$D^{R1}80$ (1st recycled material)

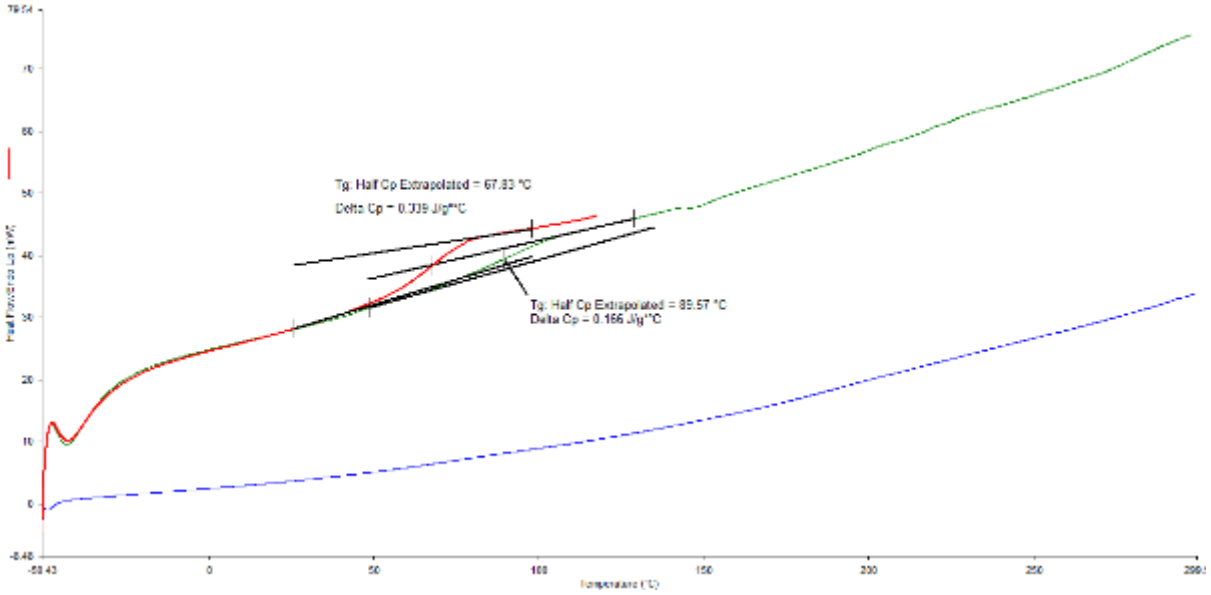


$D^{R2}80$ (2nd recycled material)

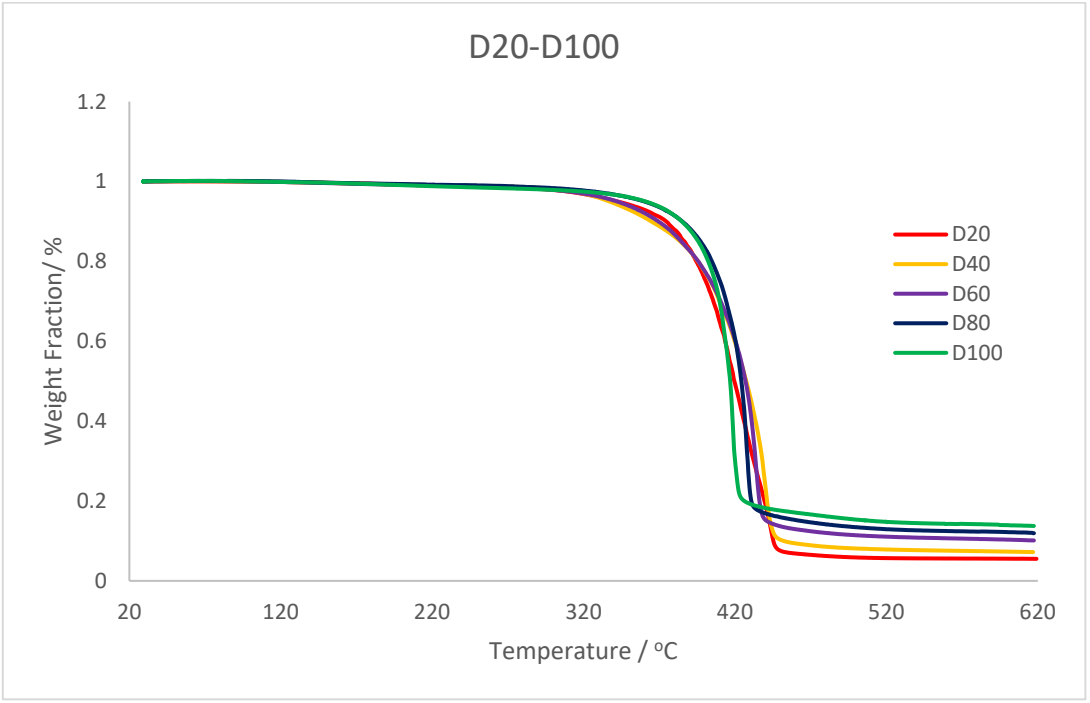


Experimental methods

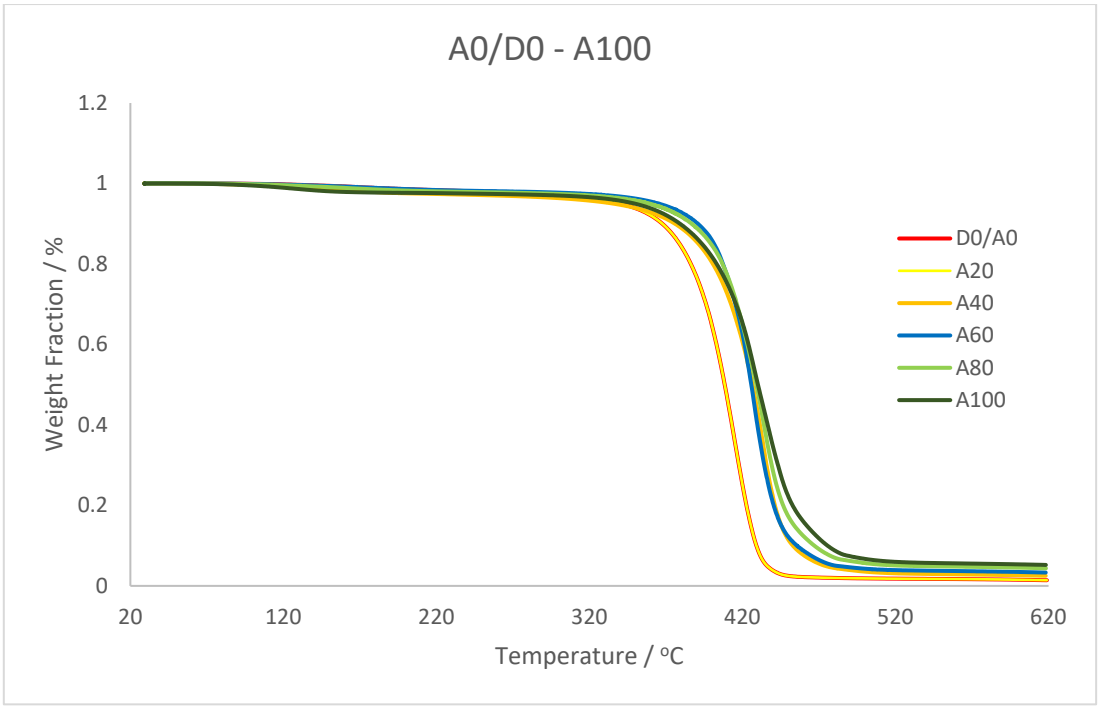
$D^{R3}80$ (3^{rd} recycled material)

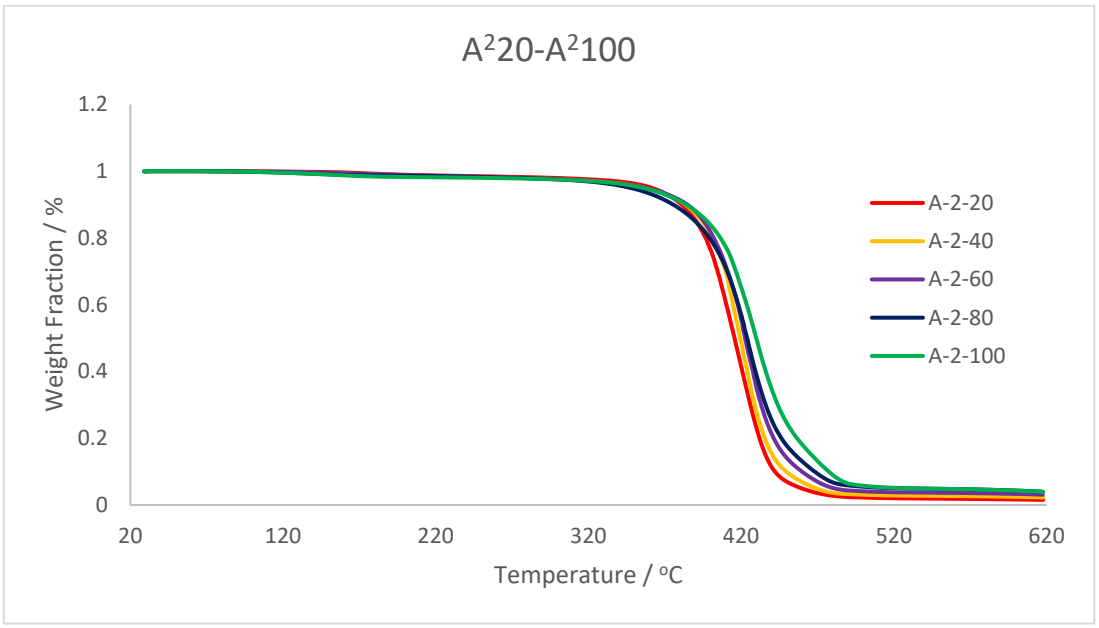


TGA data to support Table 1 in main document

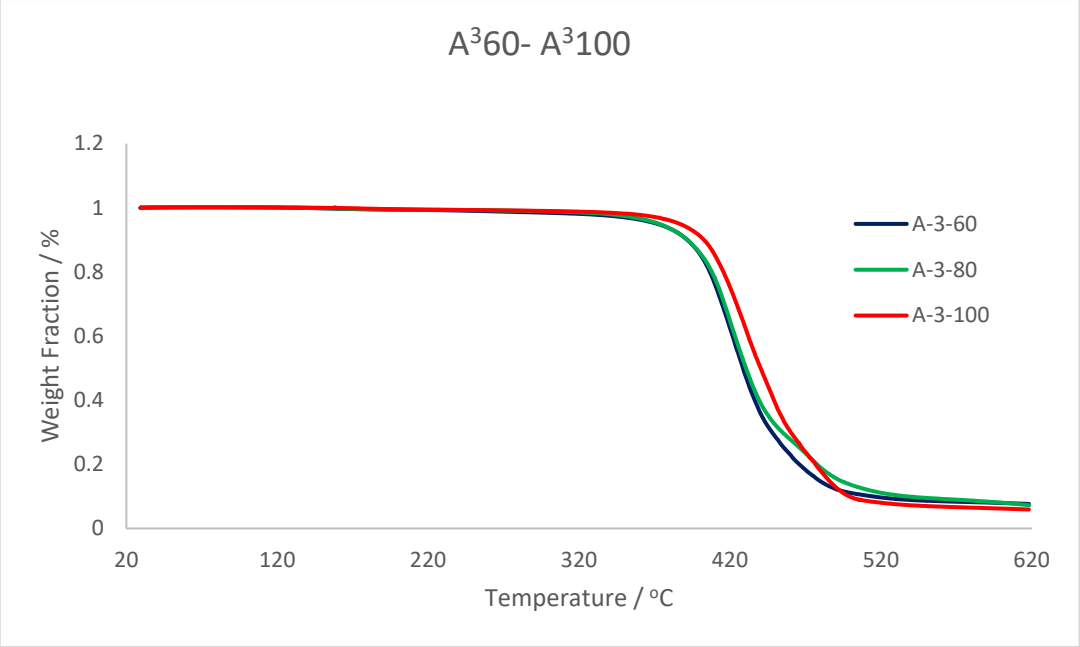


Experimental methods

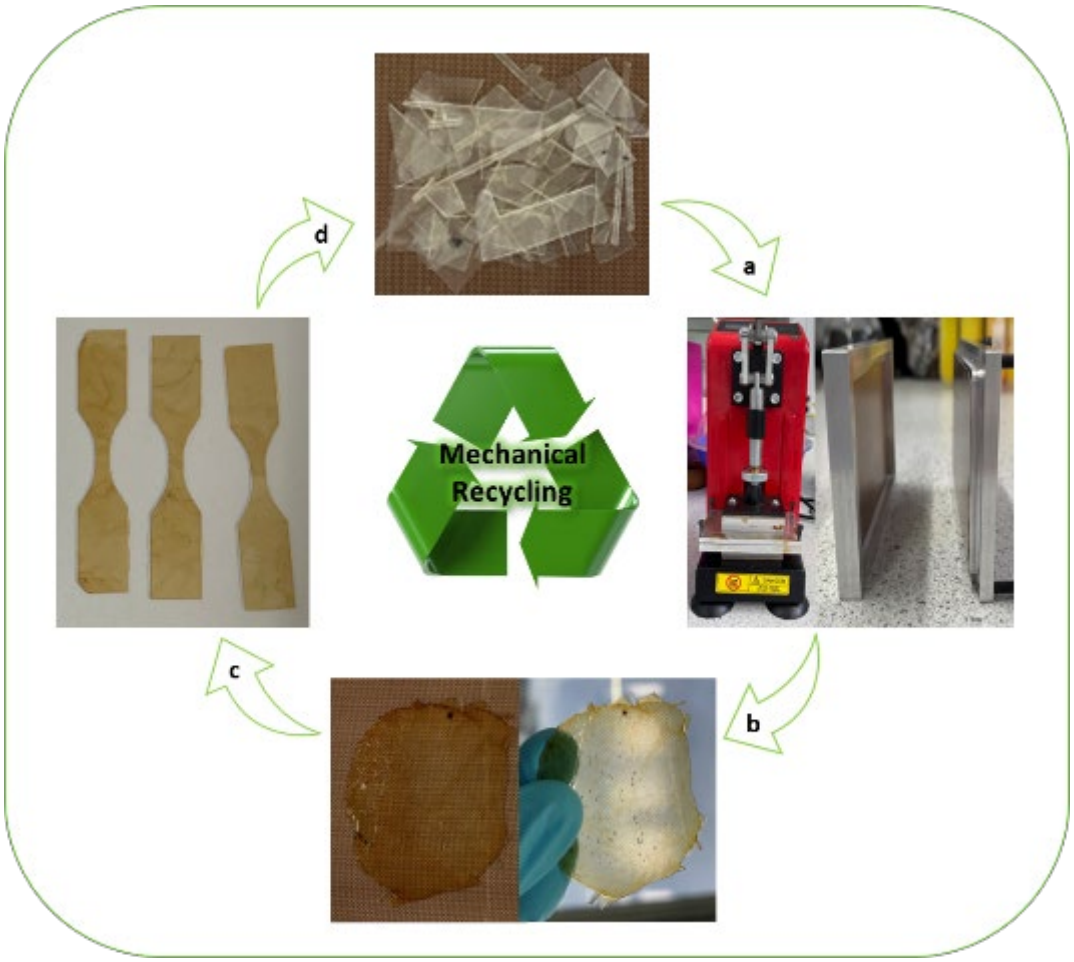




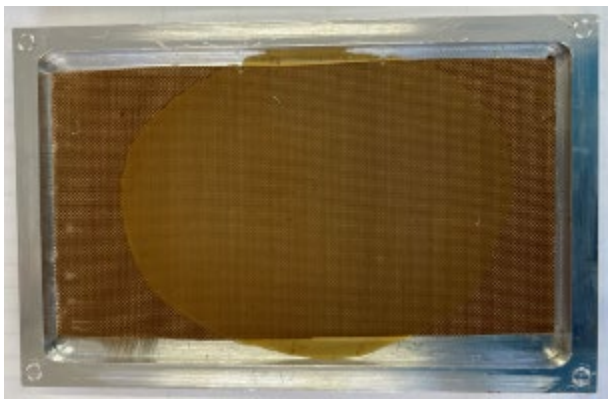
Experimental methods



Hot press recycling: Schematic to show the process by which D series materials can undergo mechanical recycling via a simple ‘hot-press process’ at 170 °C for 30 minutes



Mechanical recycling of D80 polymer where steps a-d are as follows: a) broken virgin D80 material is added to the mould and pressed at 170 °C for 30 mins then annealed overnight, b) recycled polymer is removed from the mould as a new polymer sheet, c) recycled sheet can be cut to dimensions for mechanical testing and d) broken recycled polymer can be reprocessed again.



Close up of the aluminium vessel, lined in PTFE, in which D series materials undergo mechanical recycling

Experimental methods

Gel Permeation Chromatography – supporting data

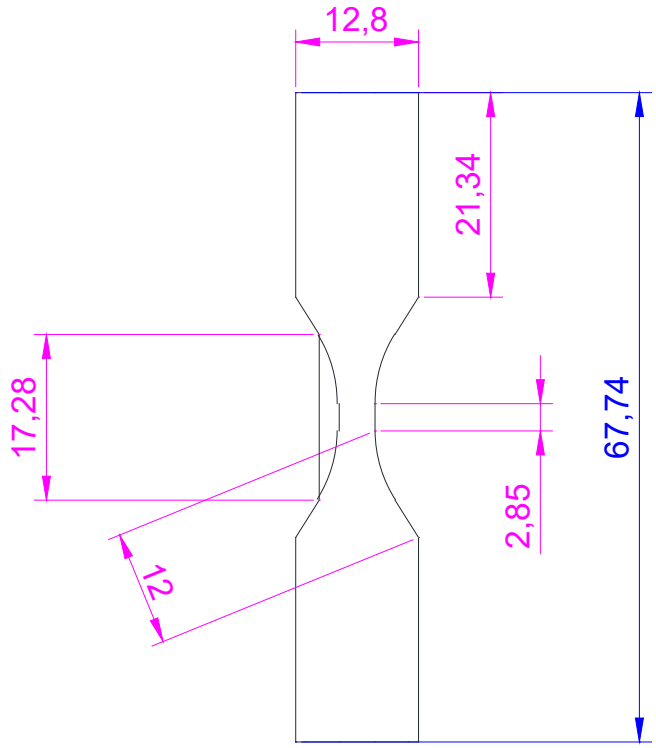
Method

GPC samples for analysis of chemically recycled (disassembled) network polymers were prepared as follows. A sample of D100 (0.1 g) was immersed in THF (10 mL) and treated with either n-butyl phenylboronic acid (bis(butyl)phenylboronate, 0.2257 g, 0.000964 mol, 5 equiv. based on calculated moles of dioxazaborocane groups in D100) or pinacol (0.1139 – 0.2278g, 0.000964 – 0.001928 mol, 5 – 10 equiv. based on calculated moles of dioxazaborocane groups in D100). The solutions were held for 5 days at room temperature to promote dissolution. The samples were then diluted to a concentration of 2 mg/mL (based on original D100 mass), filtered through a 0.2 µm nylon filter and analysed by GPC.

Molecular weight results

GPC Results			
Material and recycling chemical	**Mn (g/mol)**	**Mw (g/mol)**	**Polydispersity**
D0 control	1556	1816	1.17
D0 control with PBA	1845	2103	1.14
D100 post THF/PBA immersion	1312	1751	1.33
D100 post THF/pinacol immersion	1387	1812	1.31

Tensile Sample Dimensions



Dogbone dimensions used in tensile measurements. All cross-sectional areas for stress results were measured physically with a vernier before the test, at the middle of the gage length. Strain comes from the displacement / length of the narrowest section (gage length).

Experimental methods

[1] G. Wesela-Bauman, M. Urban, S. Luliński, J. Serwatowski and K. Woźniak, *Org. Biomol. Chem.*, 2015, **13**, 3268.