Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials

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Supporting Information

General Methods

All reactions were performed in oven-dried glassware containing a teflon-coated stirring bar under a dry atmosphere of N_2. GC analyses were carried out using a HP6890 with HP-5 capillary column (Phenyl Methyl Siloxane 30 m x 320 x 0.25, 100/2.3-30-300/3) and a time program beginning with 2 min at 60 °C, followed by a 30 °C/min ramp to 300 °C, then 3 min at this temperature. Mass spectral data were acquired on a Varian GC-MS Saturn 2100 T. Column chromatography was performed using a Combi Flash Companion-Chromatography-System (Isco-Systems) and RediSep packed columns (12 g). NMR spectra were obtained on Bruker AMX 400 or Bruker AC 300 systems using $CDCl_3$ and DMSO-d_6 as solvents, with proton and carbon resonances at 400 MHz or 300 MHz and 101 MHz or 75 MHz, respectively. All NMR data are reported in ppm relative to the solvent signal for Chloroform-d_1 at 7.27 and 77.00 ppm and for DMSO-d_6 at 2.5 and 39.5 ppm for ^{1}H and ^{13}C NMR, respectively. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer or a Bruker alpha-p instrument with ATR sample assembly. Bands are given in cm^{-1} with intensities (vs very strong, s strong, m medium, w weak). The high resolution mass spectra (HRMS) were measured on a Waters GTC Premier or with a MAT95 of the company Finnigan. CHN-elemental analyses were performed with a Hanau Elemental Analyzer vario Micro cube. Molecular weight distributions were determined using a SEC system LC-20A from Shimadzu equipped with a SIL-20A autosampler, a PSS SDV analytical main-column (5 µm, 300 mm × 8.0 mm, 10000 Å), a PSS SDV analytical pre-column (5 µm, 50 mm × 8.0 mm), and a RID-10A refractive index detector in THF (flow rate 1 $mL \cdot min^{-1}$) at 50 °C. All determinations of molar mass were performed relative to PMMA standards (PSS, M_p 1100–981.000 Da). DSC experiments were carried out under nitrogen atmosphere with a DSC821e (Mettler Toledo) calorimeter using 40 µL aluminum crucibles and a sample mass of 6 – 8 mg. The glass transition temperature (T_g) was defined as the midpoint of the change in heat capacity occurring over the transition of the second heating cicle. The melting temperature (mp) of the polymers was reported as the minimum of the endothermic peak of the second heating scan. The baseline was measured with an empty 40 µL aluminum crucible. DTA/TGA measurements were performed with a Netzsch STA 409C instrument applying α-Al_2O_3 as a crucible material and reference sample. The samples were heated under synthetic air flow to 500 °C with a heating rate of 5 $K \times min^{-1}$, employing a sample mass of approximately 15 mg.

Chemicals

Commercial substrates were used as received unless otherwise stated. Solvents were purified and dried by standard procedures, and degassed by three freeze-pump-thaw cycles or in case of cyclohexane by argon sparge prior to use. The cardanol mixture NC700 [CAS No.: 8007-24-7] was received from Cardolite and used after purification via acidic and basic aqueous work-up. Eugenol was obtained from commercial sources and distilled prior to use. Ethylene was purchased from Air Liquide GmbH (purity 99,95%). The catalyst di-μ-bromobis(tri-*tert*butylphosphine)dipalladium(I) (**Pd-1**) was synthesised following a literature procedure.[1] The metathesis catalysts were donated by Umicore: **M73**, [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[5-(isobutoxycarbonylamido)-2-isopropoxy-benzylidene]ruthenium(II), CAS No.: 1025728-57-7; **M73iPr**, [1,3-Bis(2,6-diisopropylphenyl)-2-imidazolidinylidene]dichloro[5-(isobutoxycarbonylamido)-2-isopropoxybenzylidene]ruthenium(II), CAS No.: 1212009-05-6; **M93**, [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[(2-bromo-5-dimethylamino)phenylmethylene]ruthenium(II), CAS No.: 1415725-68-6; **M31**, [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(pyridyl)ruthenium(II), CAS No.: 1031262-76-6; **M51**, [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[[2-(1-methyl-2-oxopropoxy)phenyl]methylene] ruthenium(II), CAS No.: 1031262-71-1; **M42**, [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-[2-[[(2-methylphenyl)imino]methyl]-phenolyl]-[3-phenyl-1H-inden-1-ylidene](chloro)ruthenium(II), CAS No.: 934538-12-2. Diallyl carbonate (DAC) was synthesised from dimethyl carbonate and allyl alcohol as described recently.[2] Solvents used in the polymerisation reactions were of technical grade and were distilled in a rotary evaporator prior to use.

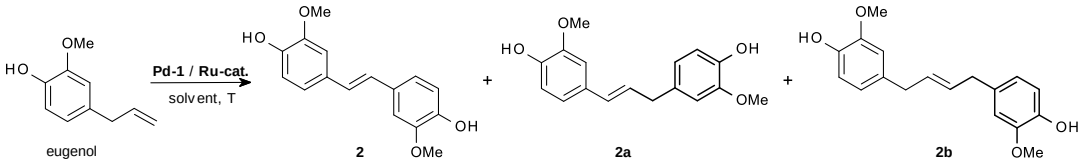
Experimental Procedures

1.1 Synthesis of di(hydroxyphenyl) derivatives from eugenol

1.1.1 Optimisation of the reaction conditions

Under a nitrogen atmosphere an oven-dried 20 mL vial with a teflon-coated stirring bar was charged with eugenol (156 µL, 1.00 mmol). A stock solution containing **Pd-1** (3.89 mg, 50.0 µmol) and the metathesis catalyst (10.0 µmol) in the given solvent (1 mL) was added via syringe. The resulting mixture was stirred at the given temperature for the given time. After cooling down to r.t., the precipitated product was filtered off, washed with toluene (5 mL) and pentane (2 mL), and dried under reduced pressure. To the combined organic phases *n*-decane (50.0 µL, 258 µmol) was added and a representative sample was filtered through a plug of celite and $MgSO_4$ and analysed by GC / GC-MS.

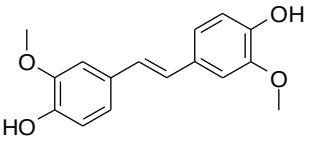
Table S1: Optimisation of the reaction conditions for the isomerising metathesis of eugenol



Entry	Ru-cat. / (mol%)	T (°C)	Solvent	2 (%)		isoeugenol[b]	2a (%)[b]	2b (%)[b]
1	**M51** (0.1)	50	THF	n.d.	n.d.[b]	90	4	5
2	"	"	DCM	n.d.	n.d.[b]	64	24	10
3	"	"	cyclohexane	62	3[b]	35	n.d.	n.d.
4	"	"	toluene	82	n.d.[b]	15	n.d.	n.d.
5	**G2** (0.1)	"	"	67	n.d.[b]	n.a.	n.a.	n.a.
6	**M31** (0.1)	"	"	31	n.d.[b]	60	8	n.d.
7	**M42** (0.1)	"	"	n.d.	n.d.[b]	99	n.d.	n.d.
8	**M73** (0.1)	"	"	79	n.d.[b]	19	n.d.	n.d.
9	**M93** (0.1)	"	"	80	n.d.[b]	19	n.d.	n.d.
10	**M51** (0.1)	r.t.	"	63	5[b]	33	n.d.	n.d
11	"	60	"	85	n.d.[b]	15	n.d.	n.d.
12	"	70	"	91	trace[b]	7	n.d.	n.d.
13	"	80	"	88	n.d.[b]	9	n.d.	n.d.
14[c]	**M51** (0.05)	70	"	84	trace[b]	13	n.d.	n.d.
15[c, d]	"	"	"	93	n.d.[b]	3	n.d.	n.d.

[a] Reaction conditions*:* eugenol (1 mmol), **Ru-cat.** (0.1 mol%), **Pd-1** (0.5 mol%), solvent (1 mL), 1 h, isolated yields; [b] GC yields after analysis of the components in the combined organic phases; [c] **Pd-1** (0.1 mol%); [d] 4 h; n.d. = not detected, n.a. = not analysed.

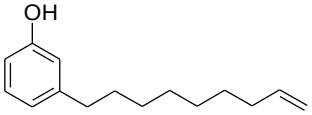
1.1.2 Preparative scale synthesis of (E)-4,4'-dihydroxy-3,3'-dimethoxystilbene [CAS No.: 7329-69-3] from eugenol



In a glove box, an oven-dried 50 mL vial with a teflon-coated stirring bar was charged with **Pd-1** (23.3 mg, 30.0 µmol) and **M51** (9.83 mg, 15.0 µmol). Eugenol (4.69 mL 30.0 mmol) was added via syringe under nitrogen atmosphere outside the glovebox. The resulting mixture was stirred at 70 °C for 4 h. After cooling down to r.t., the precipitated product was filtered off, washed with toluene (3x10 mL) and pentane (3x2 mL) and dried under reduced pressure to yield the desired product as a pale pink solid (3.31 g, 81%). Quantitative GC / GC-MS analysis of the combined organic phases revealed 10% unreacted isoeugenol, 3% of the cross-metathesis by-product between eugenol and isoeugenol (**2a**) and 4% of the eugenol self-metathesis by-product (**2b**).

mp 211 – 212 °C. Elemental analysis found: C, 70.6; H, 6.0. $C_{16}H_{16}O_4$ requires C, 70.6, H, 5.9%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 3373 (w), 3031 (w), 1598 (w), 1511 (s), 1462 (m), 1432 (m), 1385 (w), 1327 (w), 1279 (m), 1224 (vs), 1156 (s), 1117 (s), 1027 (vs), 948 (s), 847 (s), 817 (s), 730 (m), 650 (w). δH (400 MHz, DMSO-d_6): 9.05 (s, 2H), 7.14 (d, J = 2 Hz, 2H), 6.95 (s, 2H), 6.93 (dd, J = 8.0 Hz, J = 2.0 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 3.82 (s, 6H) ppm. δC (100 MHz, DMSO-d_6): 147.8, 146.1, 129.1, 125.7, 119.5, 115.6, 109.4, 55.5 ppm. MS (Ion trap, EI): *m/z* 272 (M^+, 100), 211 (12); HRMS-EI (TOF) found: 272.1035. $C_{16}H_{16}O_4$ requires 272.1048. The obtained analytic data matched those reported in the literature for (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene.[3]

1.2 Synthesis of 3-(non-8-enyl)phenol (1) via ethenolysis of cardanol [CAS No.: 1415155-47-3]



A 1 L autoclave was charged with dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine) ruthenium(II) (**HG1**) (120 mg, 0.20 mol%) and purged with ethylene 3 times. Under ethylene atmosphere, toluene (250 mL) and cardanol (29.8 g, 100 mmol) were added via syringe. The resulting mixture was stirred at 25 °C under 10 bar ethylene pressure for 12 h. After releasing the ethylene pressure, the solvent was removed under reduced pressure. Purification via fractional distillation (10^-

^{3} mbar, 160 – 170 °C oil bath temperature, 118 – 124 °C vapor temperature) yielded 3-(non-8-enyl)phenol as a light yellow oil (18.3 g, 84%).

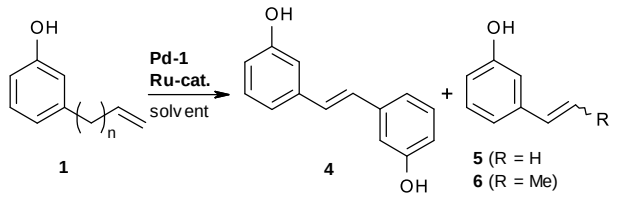
Elemental analysis found: C, 82.3, H, 10.2. $C_{15}H_{22}O$ requires C, 82.5, H, 10.2%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 3328 (m), 3076 (w), 2925 (s), 2854 (m), 1640 (w), 1610 (m), 1588 (s), 1487 (m), 1455 (s), 1350 (w), 1262 (m), 1234 (m), 1153 (m), 998 (w), 908 (s), 874 (w), 778 (s), 749 (m), 723 (w), 693 (vs). δH (400 MHz, $CDCl_3$): 7.16 (t, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 6.69 - 6.65 (m, 2H), 5.84 (ddt, *J* = 17.1 Hz, *J* = 10.3 Hz, *J* = 6.8 Hz, 1H), 5.05 - 4.94 (m, 2H), 4.77 (s br, 1 H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.09 - 2.03 (m, 2H), 1.63 - 1.57 (m, 2H), 1.39 - 1.28 (m, 8H) ppm. δC (101 MHz, $CDCl_3$): 155.3, 144.9, 139.2, 129.4, 121.0, 115.3, 114.1, 112.4, 35.8, 33.8, 31.2, 29.3, 29.2, 29.0, 28.9 ppm. MS (Ion trap, EI): *m/z* 218 (M^+, 10), 147 (19), 121 (16), 120 (15), 108 (100), 107 (26). HRMS-EI (TOF) found: 218.1683. $C_{15}H_{22}O$ requires 218.1670. The obtained analytic data matched those reported in the literature for 3-(non-8-enyl)phenol.[4]

1.3 Synthesis of di(hydroxyphenyl) derivatives from CNSL

1.3.1 Optimisation of the reaction conditions

In a glove box, a 35 mL oven-dried Ace pressure vessel with a teflon-coated stirring bar was charged with **Pd-1** (5.83 mg, 7.50 µmol) and the metathesis catalyst (10.0 µmol). Subsequently, 3-(non-8-enyl)phenol (109 mg, 0.50 mmol) and the solvent (2 mL) were added. The vessel was pressurised with ethylene outside the glovebox and the mixture was allowed to stir at the given temperature for the given time. After cooling down to r.t., the precipitated product was filtered off, washed with toluene (5 mL) and pentane (2 mL), and dried under reduced pressure. To the combined organic phases *n*-decane (50.0 µL, 258 µmol) was added and a representative sample was filtered through a plug of celite and $MgSO_4$ and analysed by GC / GC-MS.

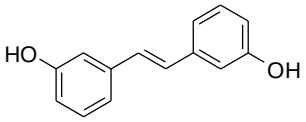
Table S2: Optimisation of the reaction conditions for the isomerising metathesis of 3-(non-8-enyl)phenol



Entry	Solvent	**Ru-cat.**	**4** (%)		**5** + **6** (%)[b]	R > CH_3 (%)[b]
1	THF	**M51**	n.d.	n.d.[b]	93	trace
2	DCM	"	n.d.	n.d.[b]	23	76
3	toluene	"	n.d.	n.d.[b]	8	90
4	cyclohexane	"	n.d.	n.d.[b]	n.d.	99
5	"	**M73iPr**	68	5[b]	18	trace
6	"	**M73**	n.d.	n.d.[b]	36	64
7	"	**M93**	n.d.	n.d.[b]	n.d.	99
8[c]	"	**M73iPr**	72	5[b]	14	trace
9[c, d]	"	"	69	trace[b]	15	trace
10[c, e]	"	"	79	5[b]	12	trace
11[f]	"	"	30	3[b]	trace	60

[a] Reaction conditions: **1** (0.5 mmol), **Pd-1** (1.5 mol%), **Ru-cat.** (2 mol%), C_2H_4 (6 bar), solvent (2 mL), 50 °C, 18 h, isolated yields; [b] GC yields after analysis of the components in the combined organic phases; [c] C_2H_4 (1 bar); [d] 70 °C; [e] C_2H_4-argon exchange after 6 h; [f] without C_2H_4; n.d. = not detected.

1.3.2 Preparative scale synthesis of (E)-3,3'-hydroxystilbene from 3-(non-8-enyl)phenol [CAS No.: 143207-60-7]



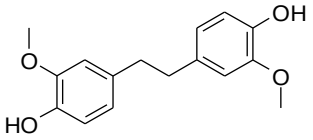
In a glove box, a 185 mL oven-dried Ace pressure vessel with a teflon-coated stirring bar was charged with **Pd-1** (117 mg, 0.15 mmol) and **M73iPr** (165 mg, 0.20 mmol). Subsequently, 3-(non-8-enyl)phenol (2.18 g, 10.0 mmol) and cyclohexane (40 mL) were added. The vessel was pressurised with 4 bar ethylene (ca. 3 equiv.) outside the glove box and the resulting mixture was stirred at 50 °C for 6 h. The excess ethylene was then removed by flushing the reaction vessel with argon and the reaction was allowed to stir at 50 °C for another 12 h. After cooling down to r.t., the precipitated product was filtered off, washed with toluene (3x5 mL) and pentane (3x2 mL) and dried under reduced pressure to yield the desired product as a gray solid (782 mg, 74%). Quantitative GC / GC-MS analysis of the combined organic phases revealed 21% of the C-2 phenol derivative **5**, 4% of the C-3 phenol derivative **6**.

mp 149 – 150 °C. Elemental analysis found: C, 70.05; H, 5.7. $C_{14}H_{12}O_2$ requires C, 79.2, H, 5.7%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 3231 (w), 1591 (s), 1450 (vs), 1375 (w), 1282 (s), 1219 (s), 1181 (m), 1157 (s), 1082 (w), 954 (vs), 858 (s), 778 (s), 746 (w), 684 (vs). δH (400 MHz, DMSO-d_6): 9.43 (s, 2H), 7.16 (t, J = 7.8 Hz, 2H), 7.06 (s, 2H), 7.02 (dt, J = 7.8 Hz, J = 1.5 Hz, 2H), 6.96 (t, J = 2.0 Hz, 2H), 6.68 (ddd, J = 8.0 Hz, J = 2.5 Hz, J = 0.8 Hz, 2H) ppm. δC (100 MHz, DMSO-d_6): 157.6, 138.3, 129.6, 128.4, 117.5, 114.8, 113.0 ppm. MS (Ion trap, EI): *m/z* 212 (M^+, 100), 211 (42), 195 (26), 194 (12), 193 (15), 181 (11), 165 (35), 153 (10). HRMS-EI (TOF) found: 212.0835. $C_{14}H_{12}O_2$ requires 212.0837. The obtained analytic data matched those reported in the literature for (*E*)-3,3'-hydroxystsilbene.[5]

1.4 General procedure for the synthesis of diphenylethanes

A 50 mL glass reactor was charged with hydroxystilbene (5.00 mmol), Pd/C (0.05 mmol) and EtOH (20 mL). The reactor was pressurised with 7 bar H_2 and heated at 50 °C for 5 h. After depressurising, the suspension was filtered through a plug of celite and eluted with EtOH (30 ml). The solvent was removed under reduced pressure to yield the pure desired product without further purification.

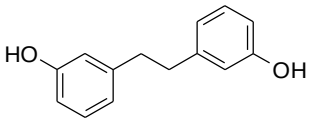
*1.4.1 Synthesis of 4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane (**3**) [CAS No.: 18256-53-6]*



Following the general procedure for the synthesis of diphenylethanes, 4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane was synthesised starting from (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene (1.37 g, 5.00 mmol) and isolated as a white solid (1.30 g, 95%).

mp 154 – 155 °C. Elemental analysis found: C, 70.1; H, 6.6. $C_{16}H_{18}O_4$ requires C, 70.1, H, 6.6%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 3399 (w), 2942 (w), 2850 (w), 1605 (w), 1509 (s), 1459 (w), 1432 (w), 1369 (w), 1264 (m), 1229 (vs), 1148 (s), 1114 (m), 1026 (vs), 930 (w), 855 (m), 819 (s), 795 (m), 714 (w), 650 (w). δH (400 MHz, DMSO-d_6): 8.64 (s, 2H), 6.75 (d, J = 2.0 Hz, 2H), 6.65 (d, J = 2.0 Hz, 2H), 6.58 (dd, J = 8.0 Hz, J = 1.8 Hz, 2H), 3.72 (s, 6H), 2.71 (s, 4H) ppm. δC (100 MHz, DMSO-d_6): 147.3, 144.5, 132.6, 120.4, 115.2, 112.6, 55.5, 37.1 ppm. MS (Ion trap, EI): *m/z* 274 (M^+, 19), 138 (13), 137 (100). HRMS-EI (TOF) found: 274.1198. $C_{16}H_{18}O_4$ requires 274.1205. The obtained analytic data matched those reported in the literature for (E)-4,4'-dihydroxy-3,3'-dimethoxystilbene.[6]

*1.4.2 Synthesis of 3,3'-dihydroxy-diphenylethane (**7**) [CAS No.: 70709-67-0]*



Following the general procedure for the synthesis of diphenylethanes, 3,3'-dihydroxy-diphenylethane was synthesised starting from (*E*)-3,3'-dihydroxystilbene (1.06 g, 5.00 mmol) and isolated as a white solid (1.01 g, 99%).

mp 139 – 140 °C. Elemental analysis found: C, 78.2; H, 6.7. $C_{14}H_{14}O_2$ requires C, 78.5, H, 6.6%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 3200 (w), 2926 (w), 2860 (w), 1586 (m), 1493 (w), 1450 (m), 1365 (w), 1274 (m), 1244 (m), 1220 (m), 1151 (m), 1077 (w), 936 (m), 867 (m), 784 (s), 734 (m), 693 (vs). δH (400 MHz, DMSO-d_6): 9.23 (s, 2H), 7.05 (t, J = 7.8 Hz, 2H), 6.65 - 6.61 (m, 4H), 6.57 (ddd, J = 8.0 Hz, J = 2.5 Hz, J = 0.8 Hz, 2H), 2.74 (s, 4H) ppm. δC (100 MHz, DMSO-d_6): 157.3, 143.0, 129.2, 119.0, 115.3, 112.8, 37.0 ppm. MS (Ion trap, EI): *m/z* 214 (M^+, 40), 107 (100), 77 (12); HRMS-EI (TOF) found: 214.0993. $C_{14}H_{14}O_2$ requires 214.0993. The obtained analytic data matched those reported in the literature for 3,3'-dihydroxy-diphenylethane.[7]

1.5 One-pot synthesis of diphenyethanes

*1.5.1 One-pot synthesis of 4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane (**3**) starting from eugenol*

In a glove box, a 250 mL autoclave equipped with a teflon beaker with a teflon-coated stirring bar was successively charged with **Pd-1** (23.3 mg, 0.03 mmol), **M51** (9.83 mg, 15.0 µmol) and eugenol (4.69 mL 30.0 mmol). The reaction mixture was stirred at 70 °C for 4 h outside the glovebox. After cooling down to r.t., Pd/C (160 mg, 0.15 mmol) and EtOH (120 mL) were added. The autoclave was pressurised with 10 bar H_2 and the reaction mixture was stirred at 50 °C for 5 h. After depressurising, the suspension was filtered through a plug of celite and eluted withEtOH (100 mL). The volatiles were removed under reduced pressure and the resulting solid was washed with a minimum of toluene (3x2 mL) and pentane (3x2 mL) to yield a white solid (3.28 g, 80%).

*1.5.2 One-pot synthesis of 3,3'-dihydroxy-diphenylethane (**7**) from 3-(non-8-enyl)phenol*

In a glove box, a 185 mL oven-dried Ace pressure vessel with a teflon-coated stirring bar was charged with **Pd-1** (117 mg, 0.15 mmol) and **M73iPr** (165 mg, 0.20 mmol). Subsequently, 3-(non-8-enyl)phenol (2.18 g, 10.0 mmol) and cyclohexane (40 mL) were added. The vessel was pressurised with 4 bar

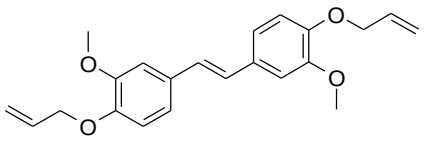
ethylene (ca. 3 equiv.) outside the glove box and the resulting mixture was stirred at 50 °C for 6 h. The excess ethylene was then removed by flushing the reaction vessel with argon and the reaction was allowed to stir at 50 °C for another 12 h. After cooling down to r.t., a solution of activated charcoal (1.20 mg, 0.10 mmol) in EtOH (40 mL) was added. The vessel was pressurised with 7 bar hydrogen and stirred at 50 °C for 5 h. After depressurising, the suspension was filtered through a plug of celite and eluted with EtOH (50 mL). The volatiles were removed under reduced pressure and the resulting solid was washed with a minimum of toluene (3x2 mL) and pentane (3x2 mL) to yield the desired product as a white solid (770 mg, 72%).

1.6 General procedure for the allylation of diols

Method A: A 10 mL Ace pressure vessel heated at 120 °C was charged with bisphenol (4.00 mmol) and DAC (3.41 g, 24.0 mmol). Up to additional 18 mmol DAC were used in case the bisphenol was not completely soluble. Subsequently TBAB (1.29 g, 4.00 mmol) was added and the solution was stirred at 120 °C for 20 h. After cooling to r.t., the compound was extracted with ethyl acetate (30 mL) and washed with water (2 × 20 mL). TBAB (1.21 g, 3.76 mmol, 94%) could be recovered from the aqueous phase by evaporation of the water. The organic layer was further washed with 1M aqueous HCl (20 mL) and brine (20 mL), then dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a *n*-hexane / ethyl acetate gradient.

Method B: A 100 mL oven-dried vial with a teflon-coated stirring bar was charged with the bisphenol (10.0 mmol), potassium carbonate (3.45 g, 25.0 mmol), allyl bromide (3.02 g, 25.0 mmol) and acetone (15 mL). The resulting mixture was stirred at 50 °C for 3 h. After cooling down to r.t., the compound was extracted with ethyl acetate (20 mL) and washed with water (15 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using a cyclohexane / ethyl acetate gradient.

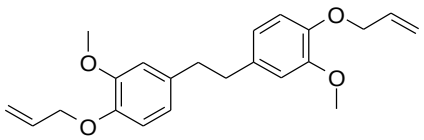
*1.6.1 Synthesis of (E)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (**A2**)*



Following method A, (*E*)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethene was synthesised starting from (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene (1.09 g, 4.00 mmol) and isolated as white solid (1.18 g, 84%). Following method B, it was isolated in 89% yield.

mp 141 – 142 °C. Elemental analysis found: C, 74.9; H, 6.8. $C_{22}H_{24}O_4$ requires C, 75.0, H, 6.9%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2838 (w), 1836 (w), 1646 (w), 1582 (m), 1468 (m), 1455 (m), 1421 (m), 1410 (m), 1383 (w), 1336 (w), 1290 (m), 1226 (s), 1180 (m), 1135 (s), 1033 (m), 989 (s), 959 (s), 915 (s), 852 (s), 801 (s), 727 (m), 634 (m), 614 (w), 574 (m), 551 (m), 463 (w), 441 (w). δH ($CDCl_3$, 300 MHz): 7.06 (d, *J* = 1.8 Hz, 2H), 7.00 (dd, *J* = 8.3, *J* = 1.9 Hz, 2H), 6.92 (s, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.09 (ddt, *J* = 17.2 Hz, *J* = 10.5 Hz, *J* = 5.4 Hz, 2H), 5.42 (dd, *J* = 17.3 Hz, *J* = 1.5 Hz, 2H), 5.30 (dd, *J* = 10.5 Hz, *J* = 1.3 Hz, 2H), 4.64 (ddd, *J* = 5.4 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, 4H), 3.94 (s, 6H) ppm. δC ($CDCl_3$, 75 MHz): 149.5, 147.6, 133.2, 130.9, 126.7, 119.4, 118.0, 113.41, 109.0, 69. 8, C, 55.8 ppm. MS (EI$^+$): *m/z* 352 (M$^+$, 100), 311 (50). HRMS (EI$^+$) found: 352.1671. $C_{22}H_{24}O_4$ requires 352.1669.

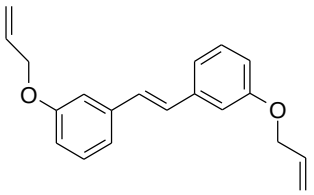
*1.6.2 Synthesis of 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (**A3**) [CAS No.: 40060-09-1]*



Following method A, 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane was synthesised starting from 4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane (1.10 g, 4.00 mmol) and isolated as white solid (1.25 g, 89%). Following method B, it was isolated in 89% yield.

mp 92 – 93 °C. Elemental analysis found: C, 74.4; H, 7.3. $C_{22}H_{26}O_4$ requires C, 74.55, H, 7.4%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2996 (w), 2932 (w), 2859 (w), 1589 (w), 1509 (m), 1466 (m), 1414 (m), 1362 (w), 1330 (w), 1260 (m), 1223 (s), 1162 (m), 1133 (s), 1010 (m), 993 (m), 935 (m), 844 (m), 803 (s), 755 (w), 653 (w), 628 (w), 590 (w), 545 (w), 457 (w), 417 (w). δH ($CDCl_3$, 300 MHz): 6.81 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 7.3 Hz, 2H), 6.66 (s, 2H), 6.09 (ddt, *J* = 17.1 Hz, *J*= 10.6 Hz, *J* = 5.4 Hz, 2H), 5.40 (dd, *J* = 17.3, 1.2 Hz, 2H), 5.28 (dd, *J* = 10.5, 0.9 Hz, 2H), 4.60 (d, *J* = 5.4 Hz, 4H), 3.84 (s, 6H), 2.85 (s, 4H) ppm. δC ($CDCl_3$, 75 MHz,): 149.2, 146.2, 134.8, 133.6, 120.3, 117.7, 113.6, 112.3, 70.2, 55.8, 37.6 ppm. MS (EI$^+$): *m/z* 354 (M$^+$,100), 177 (90). HRMS (EI$^+$) found: 354.1827. $C_{22}H_{26}O_4$ requires 354.1826.

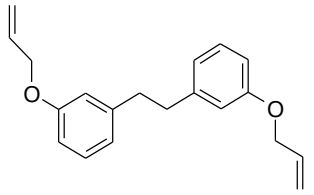
*1.6.3 Synthesis of (E)-1,2-bis(3-(allyloxy)phenyl)ethane (**A4**)*



Following method A, (*E*)-1,2-bis(3-(allyloxy)phenyl)ethene was synthesised starting from (*E*)-3,3'-hydroxystilbene (800 mg, 3.77 mmol) and isolated as yellow liquid (1.02 g, 93%). Following method B, it was isolated in 98% yield.

Elemental analysis found: C, 82.15; H, 7.05. $C_{20}H_{20}O_2$ requires C, 82.2, H, 6.9%. IR (ATR): $\tilde{\nu}_{max}/cm^{-1}$ 3079(w), 3025 (w), 2916(w), 2861 (w), 1577 (m), 1488 (m), 1444 (m), 1422 (w), 1264 (m), 1234 (m), 1156 (s), 1027 (m), 992 (m), 957 (m), 922 (s), 857 (m), 775 (s), 690 (vs), 568 (w), 537 (m). δH (400 MHz, DMSO-d_6): 7.28 (t, *J* = 7.8 Hz, 2H), 7.23 (s, 2H), 7.20 - 7.16 (m, 4H), 6.86 (ddd, *J* = 8.0 Hz, *J* = 2.3 Hz, *J* = 0.5 Hz, 2H), 6.12 - 6.02 (m, 2H), 5.42 (dq, *J* = 17.3 Hz, *J* = 1.5 Hz, 2H), 5.27 (dd, *J* = 10.5 Hz, *J* = 1.8 Hz, 2H), 4.61 (dt, *J* = 5.3 Hz, *J* = 1.5 Hz, 4H) ppm. δC (100 MHz, DMSO-d_6): 158.5, 138.5, 133.8, 129.7, 128.6, 119.3, 117.4, 114.2, 112.3, 68.2 ppm. MS (EI^+): *m/z* 292 (M^+,100), 251 (32), 210 (22), 181 (11), 165 (12), 145 (44), 132 (18), 127 (14), 115 (13), 107 (20). HRMS-EI (TOF) found: 292.1453. $C_{20}H_{20}O_2$ requires 292.1463.

*1.6.4 Synthesis of 1,2-bis(3-(allyloxy)phenyl)ethane (**A7**)*

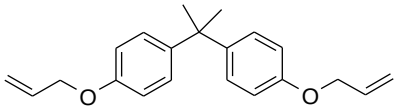


Following method A, 1,2-bis(3-(allyloxy)phenyl)ethane was synthesised starting from 3,3'-dihydroxy-diphenylethane (1.00 g, 4.67 mmol) and isolated as yellow liquid (1.29 g, 94%). Following method B, it was isolated in 90% yield.

Elemental analysis found: C, 81.5; H, 7.4. $C_{20}H_{22}O_2$ requires C, 81.6, H, 7.5%. IR (ATR): $\tilde{\nu}_{max}/cm^{-1}$ 3081 (w), 3031 (w), 2923 (w), 2859 (w), 1583 (s), 1487 (s), 1446 (m), 1422 (m), 1257 (s), 1155 (s), 1027 (s), 993 (s), 923 (s), 871 (m), 775 (s), 693 (vs), 567 (m), 527 (m). δH (400 MHz, DMSO-d_6): 7.17 (t, *J* = 7.8 Hz, 2H), 6.82 - 6.74 (m, 6H), 6.07 - 5.98 (m, 2H), 5. 38 (dq, *J* = 17.3 Hz, 1.8 Hz, 2H), 5.24

(dq, *J* = 10.5 Hz, *J* = 1.3 Hz, 2H), 4.52 (dt, *J* = 5.3 Hz, *J* = 1.5 Hz, 4H), 2.82 (s, 4H) ppm; δC (100 MHz, DMSO-d_6): 158.2, 143.1, 133.9, 129.2, 120.8, 117.3, 114.8, 112.0, 68.0, 37.0 ppm; CHN: calc.: C: 81.60, H: 7.53; found: C: 81.48, H: 7.36; MS (Ion trap, EI): *m/z* 294 (M^+, 42), 265 (18), 147 (100), 145 (21), 131 (10), 107 (12), 91 (17), 127 (14), 115 (13), 107 (20). HRMS-EI (TOF) found: 292.1614. $C_{20}H_{22}O_2$ requires 292.1619.

*1.6.5 Synthesis of 2,2-bis(4-allyloxyphenyl)propane (**ABPA**) [CAS No.: 3739-67-1]*



Following method B, 2,2-bis(4-allyloxyphenyl)propane was synthesised starting from bisphenol A (2.28 g, 10.0 mmol) and isolated as colourless oil (2.37 g, 77%).

Elemental analysis found: C, 81.6; H, 7.9. $C_{21}H_{24}O_2$ requires C, 81.8, H, 7.8%. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2966 (w), 2870 (w), 1607 (w), 1507 (s), 1456 (w), 1425 (w), 1362 (w), 1297 (w), 1225 (s), 1180 (s), 1022 (m), 996 (m), 923 (m), 826 (vs), 551 (m). δH (400 MHz, $CDCl_3$): 7.16 - 7.12 (m, 4H), 6.85 - 6.81 (m, 4H), 6.12 - 6.08 (m, 2H), 5.42 (dq, *J* = 17.3 Hz, *J* = 1.5 Hz, 2H), 5.29 (dq, *J* = 10.3 Hz, *J* = 1.0 Hz, 2H), 4.52 (dt, *J* = 5.5 Hz, *J* = 1.5 Hz, 4H), 1.65 (s, 6H) ppm. δC (100 MHz, $CDCl_3$): 156.4, 143.3, 133.5, 127.7, 117.6, 114.0, 68.8, 41.7, 31.1 ppm; MS (Ion trap, EI): *m/z* 308 (M^+, 29), 294 (20), 293 (100), 174 (9), 159 (8); HRMS-EI (TOF) found: 308.1779. $C_{21}H_{24}O_2$ requires 308.1776.

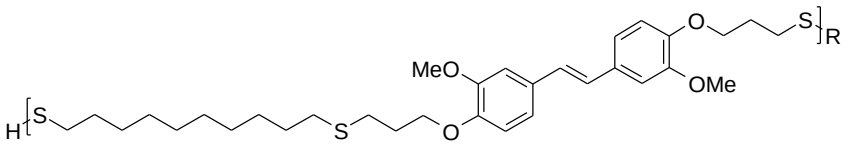
1.7 General procedure for the thiol-ene polymerisation

A 10 mL Ace pressure vessel was charged with diallyl (1 equiv.) and decane dithiol (146 mg, 707 µmol, 1 equiv.) under argon atmosphere. After stirring at 50 °C for 10 min, AIBN (2.8 mg, 17.0 µmol, 2.5 mol%) was added and the resulting mixture was heated at 75 °C for 5 h. The mixture was then dissolved in THF (2 mL) and the polymer was precipitated in cold methanol (30 mL), filtered and dried over phosphorous pentoxide at 10^{-3} mbar for 24 h.

Table S3: Summary of the analytical results for the thiol-ene polymerisation

Entry	Allylated monomer	Polymer	Yield [wt%]	*m.p.* [°C]	M_n [g/mol]	$Đ$	$T_{d\ 5\%}$ [°C]
1	**A2**	**TE2**	66	25 – 50	2700	1.7	301
2	**A4**	**TE4**	62	25 – 50	3100	7.1	316
3	**A3**	**TE3**	84	25 – 50	4300	3.0	336
4	**A7**	**TE7**	83	25 – 50	16600	5.3	311
5	**ABPA**	**TEBPA**	87	r.t.	5200	3.6	270

*1.7.1 Thiol-ene polymer of (E)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethene **TE2***



Following the general procedure for the thiol-ene polymerisation, **TE2** was obtained from (*E*)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (247 mg, 701 µmol) and isolated as yellow solid (260 mg, 66 wt% compared to used diene + dithiol). Additional THF (400 µL) was necessary as solvent as the monomer xx melts at 141 °C.

mp 25 – 50 °C. IR (ATR): $\tilde{\nu}_{max}/cm^{-1}$ 2923 (s), 2847 (m),1588 (m), 1508 (s), 1464 (s), 1421 (m), 1329 (w), 1261 (s), 1245 (s), 1213 (s), 1126 (s), 1026 (s), 950 (m), 923 (m), 839 (m), 799 (m), 723 (w), 632 (w), 544 (w), 453 (w). δH (300 MHz, $CDCl_3$): 7.05 (d, J = 1.3 Hz, 2H), 7.04 – 7.00 (m, 2H), 6.92 (s, 2H), 6.90 – 6.85 (m, 2H), 6.15 – 6.04 (m, 0.6 H), 5.45 – 5.29 (m, 1.2H), 4.64 (d, J = 5.4 Hz, 1.1H), 4.14 (t, J = 6.2 Hz, 3H), 3.92 (s, 6H), 2.72 (t, J = 7.0 Hz, 3H), 2.53 (t, J = 7.2 Hz, 4H), 2.17 – 2.08 (m, 3H), 1.63 – 1.54 (m, 5H), 1.42-1.27 (m, 15H) ppm. M_n = 2700 g/mol ($Đ$ = 1.7). $T_{d\ 5\%}$ = 301 °C.

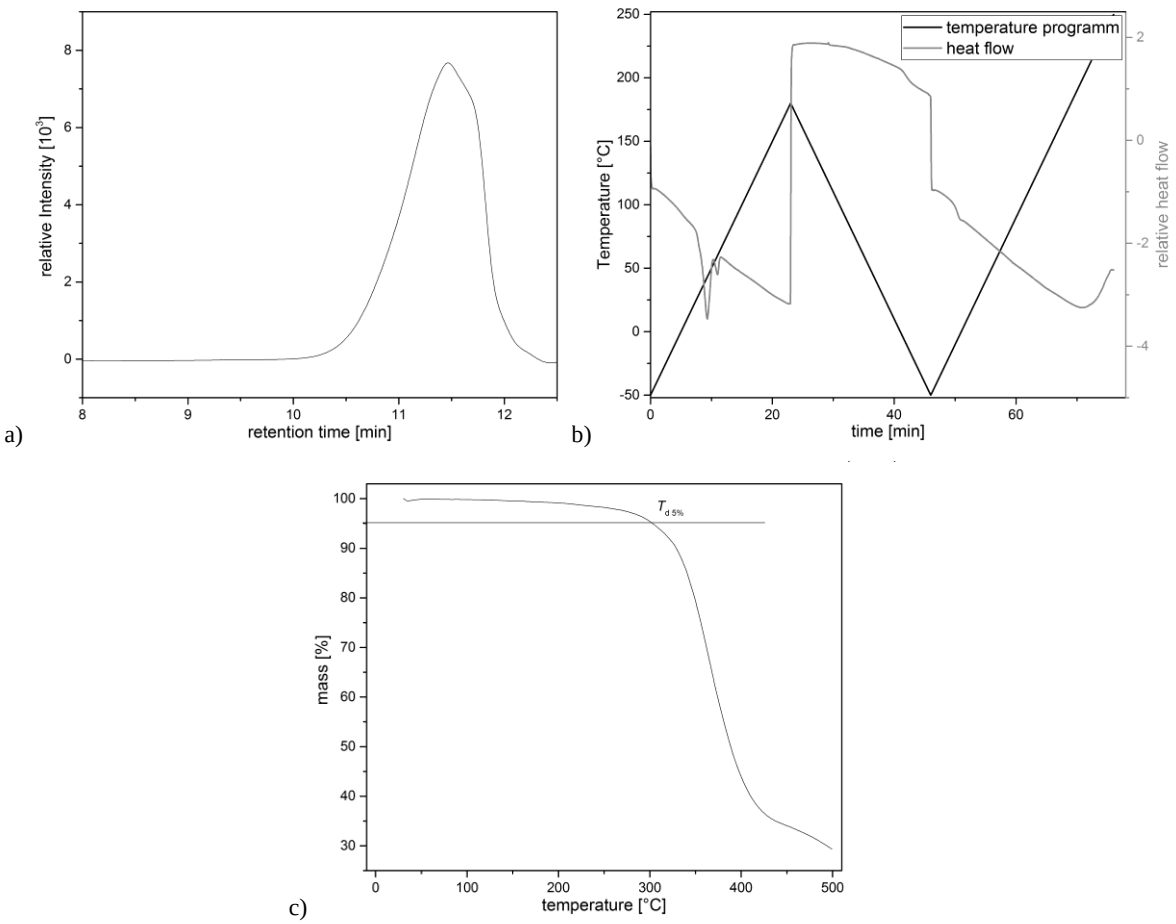
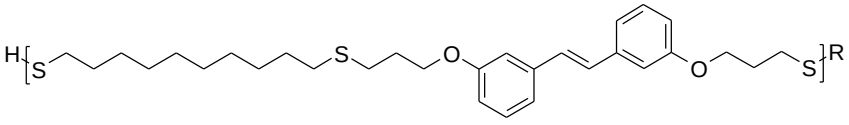


Figure 1.7-1: a) SEC trace, b) DSC analysis and c) TGA analysis of **TE2.**

*1.7.2 Thiol-ene polymer of (E)-1,2-bis(3-(allyloxy)phenyl)ethene (**TE4**)*



Following the general procedure for the thiol-ene polymerisation, **TE4** was obtained from (*E*)-1,2-bis(3-(allyloxy)phenyl)ethane (208 mg, 712 µmol) and isolated as white solid (220 mg, 62 wt% based on the diene and dithiol).

mp 25 – 50 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2918 (s), 2843 (s), 1603 (s), 1576 (s), 1484 (m), 1440 (s), 1389 (w), 1321 (w), 1273 (s), 1245 (s), 1158 (s), 1066 (m), 1030 (s), 950 (s), 859 (m), 771 (s), 716 (w), 687 (s), 616 (w), 536 (w), 465 (m). δH (300 MHz, $CDCl_3$): 7.27 (t, J = 7.8 Hz, 2H), 7.11 – 7.06 (m, 6H), 6.83 – 6.81 (m, 2H), 4.11 (t, J = 5.9 Hz, 4H), 2.73 (t, J = 7.1 Hz, 4H), 2.54 (t, J = 7.4 Hz, 4H), 2.13 –

2.04 (m, 4H), 1.64 – 1.55 (m, 4H), 1.42 – 1.28 (m, 12H) ppm. M_n = 3100 g/mol ($Đ$ = 7.1). $T_{d\,5\%}$ = 316 °C.

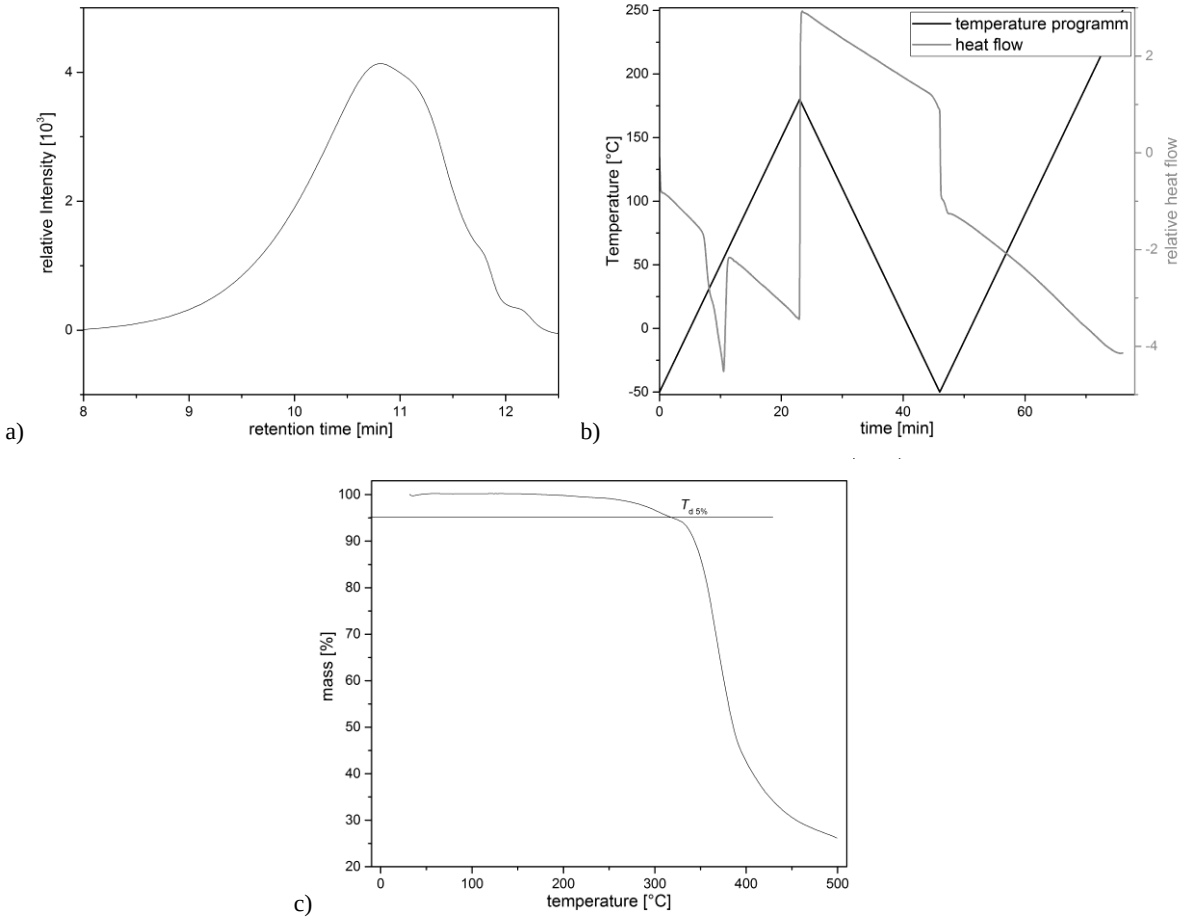
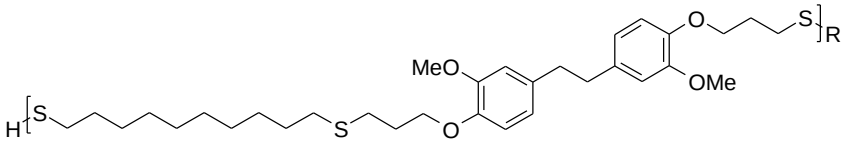


Figure 1.7-2: a) SEC trace, b) DSC analysis and c) TGA analysis of **TE4.**

*1.7.3 Thiol-ene polymer of 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (**TE3**)*



Following the general procedure for the thiol-ene polymerisation, **TE3** was obtained from 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (248 mg, 701 µmol) and isolated as solid (320 mg, 81 wt% based on the diene and dithiol).

mp 25 – 50 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2923 (s), 2847 (m), 1584 (w), 1513 (s), 1457 (s), 1416 (m), 1329 (w), 1261 (s), 1237 (s), 1225 (s), 1129 (s), 1026 (s), 923 (w), 851 (m), 795 (s), 767 (w), 752 (w), 728 (w), 636 (w), 592 (w), 540 (w), 457 (w). δH (300 MHz, $CDCl_3$): 6.82 (d, J = 8.0 Hz, 2H), 6.71 – 6.68

(m, 4H), 4.10 (t, J = 6.3 Hz, 4H), 3.82 (s, 6H), 2.84 (s, 4H), 2.71 (t, J = 6.9 Hz, 4H), 2.52 (t, J = 7.2 Hz, 4H), 2.15 – 2.08 (m, 4H), 1.63 – 1.54 (m, 4H), 1.41 – 1.28 (m, 12H) ppm. M_n = 4300 g/mol ($Đ$ = 3.0). $T_{d\ 5\%}$ = 336 °C.

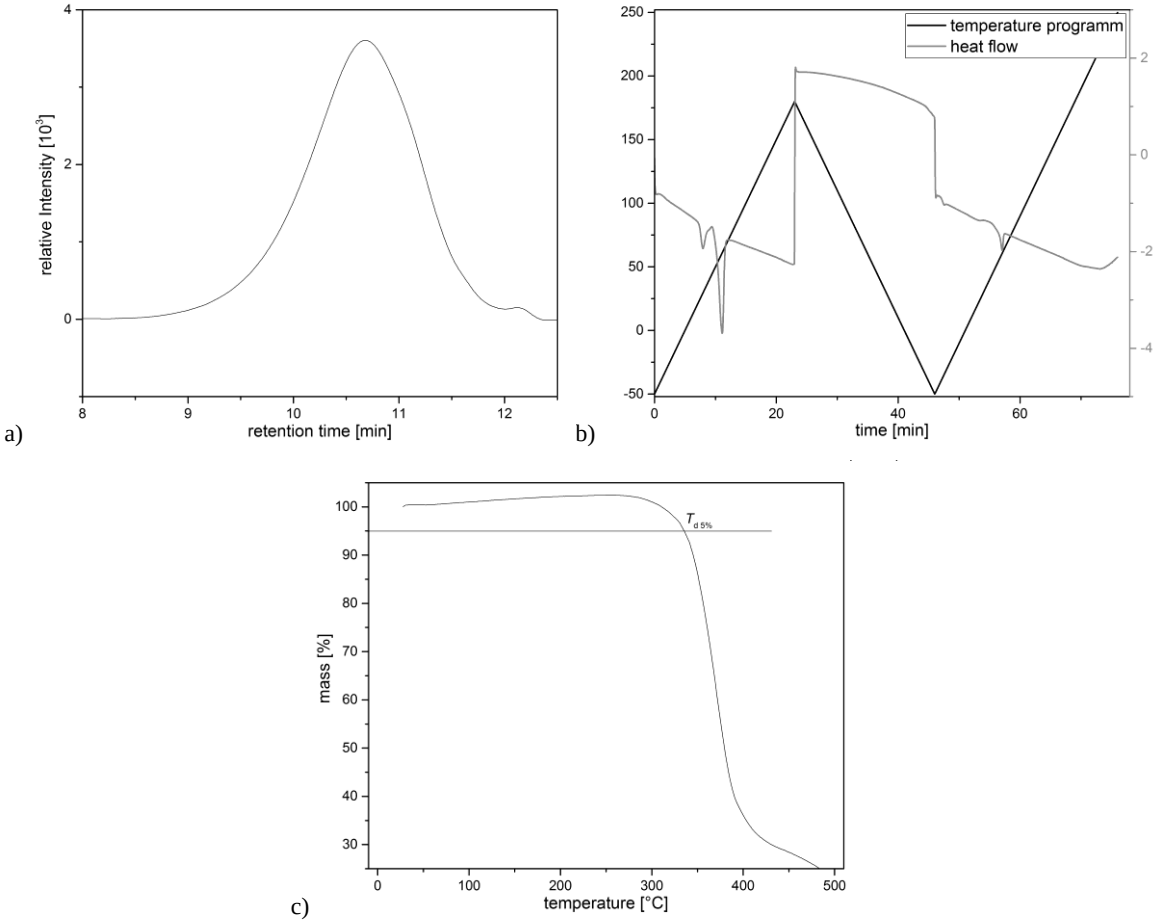
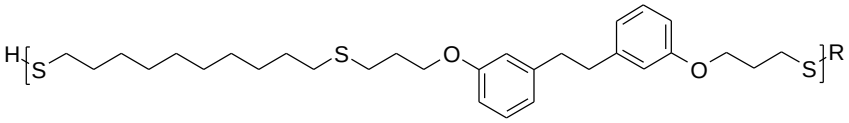


Figure 1.7-3: a) SEC trace, b) DSC analysis and c) TGA analysis of **TE3**.

*1.7.4 Thiol-ene polymer of 1,2-bis(3-(allyloxy)phenyl)ethane (**TE7**)*



Following the general procedure for the thiol-ene polymerisation, **TE7** was obtained from 1,2-bis(3-(allyloxy)phenyl)ethane (206 mg, 701 µmol) and isolated as white solid (290 mg, 83wt% based on the diene and dithiol).

mp 25 – 50 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2923 (s), 2843 (m), 1608 (m), 1580 (s), 1488 (m), 1445 (s), 1385 (w), 1273 (s), 1249 (s), 1154 (s), 1090 (w), 1062 (m), 1034 (s), 954 (w), 875 (m), 775 (s), 716 (m), 687

(s), 612 (w), 448 (w). δH (300 MHz, $CDCl_3$): 7.22 – 6.17 (m, 2H), 6.80 – 6.74 (m, 6H), 4.04 (t, J = 6.1 Hz, 4H), 2.88 (s, 4H), 2.70 (t, J = 7.1 Hz, 4H), 2.53 (t, J = 7.3 Hz, 4H), 2.10 – 2.01 (m, 4H), 1.64 – 1.54 (m, 4H), 1.40 – 1.28 (m, 12H) ppm. M_n = 16600 g/mol ($Đ$ = 5.3). $T_{d\,5\%}$ = 311 °C.

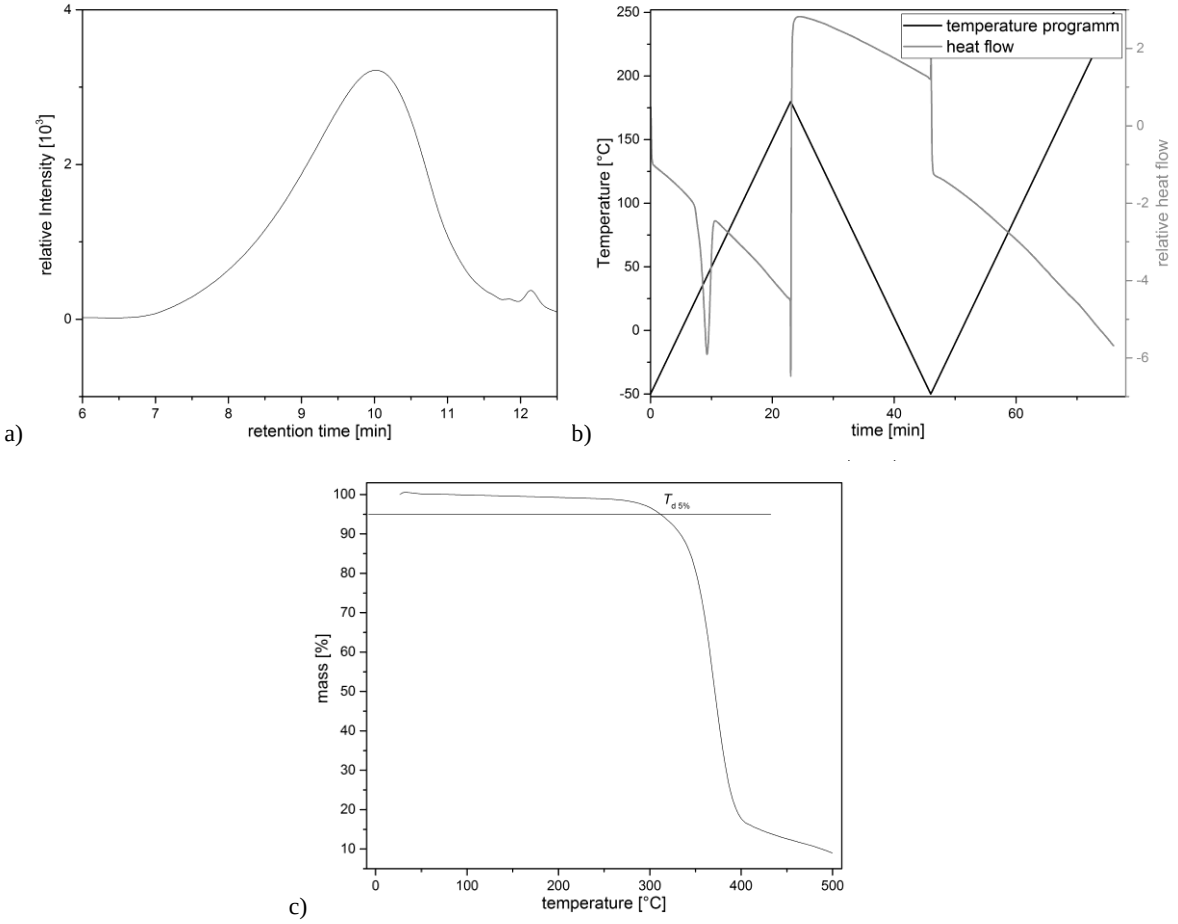
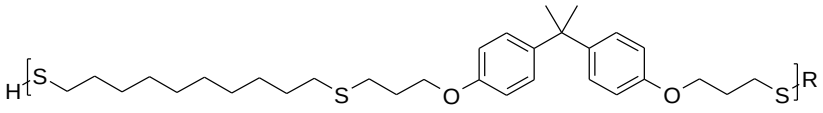


Figure 1.7-4: a) SEC trace, b) DSC analysis and c) TGA analysis of **TE7**.

*1.7.5 Thiol-ene polymer of 4,4'-(propane-2,2-diyl)bis((allyloxy)benzene) (**TEBPA**)*



Following the general procedure for the thiol-ene polymerisation, **TEBPA** was obtained from 4,4'-(propane-2,2-diyl)bis((allyloxy)benzene) (200 mg, 648 µmol) and isolated as white solid (290 mg, 87wt% based on the diene and dithiol).

mp r.t.. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2921 (s), 2850 (s), 1607 (m), 1581 (w), 1508 (s), 1466 (m), 1382 (w), 1296 (w), 1240 (s), 1180 (s), 1028 (s), 1011 (s), 927 (w), 826 (s), 807 (m), 724 (w), 572 (m), 554 (m). δH (300 MHz, $CDCl_3$): 7.12 (d, J = 8.7 Hz, 4H), 6.80 (d, J = 8.7 Hz, 4H), 4.03 (t, J = 6.0 Hz, 4H), 2.69 (t, J

= 7.2 Hz, 4H), 2.52 (t, J = 7.4 Hz, 4H), 2.08 – 2.00 (m, 4H), 1.63 – 1.54 (m, 10H), 1.36 – 1.28 (m, 12H). M_n = 5200 g/mol ($Đ$ = 3.6). $T_{d\,5\%}$ = 270 °C.

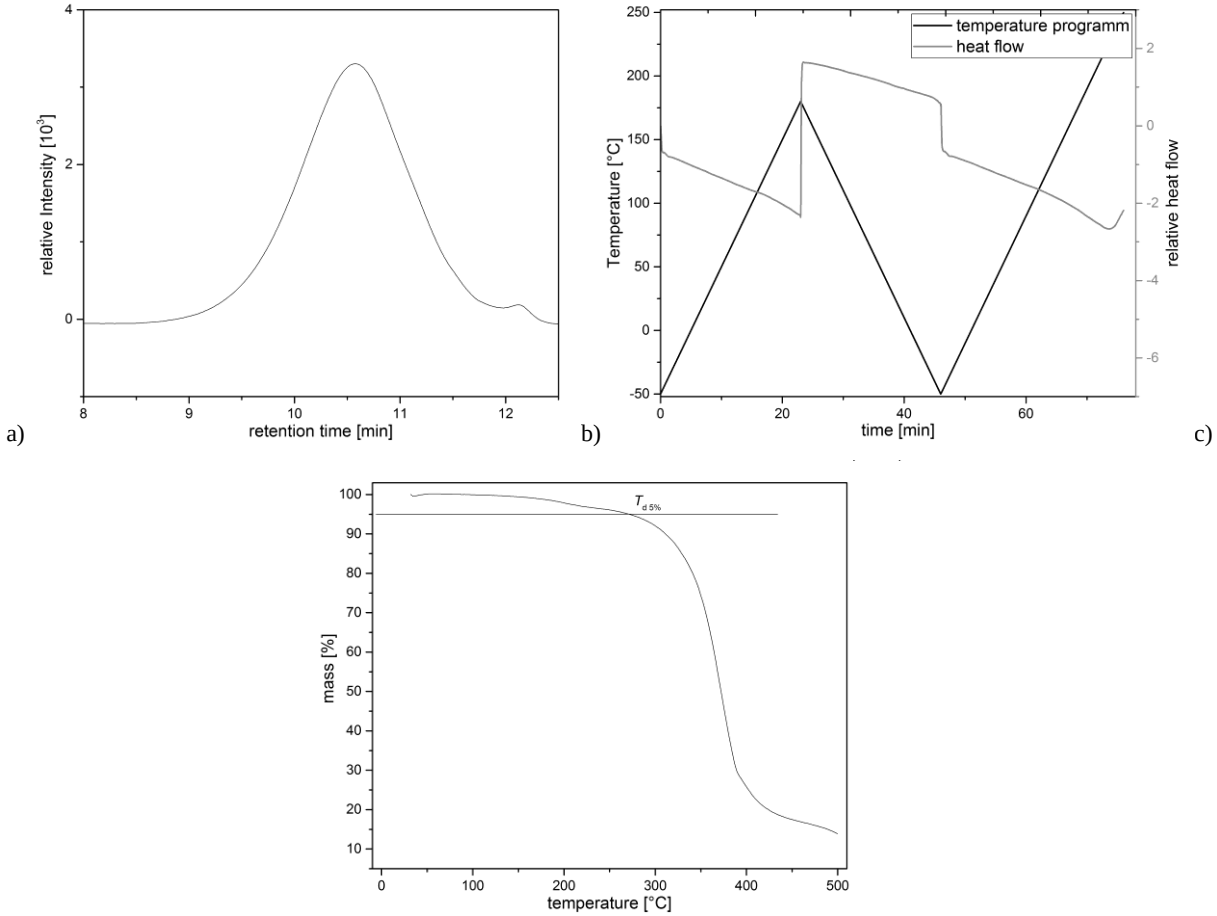


Figure 1.7-5: a) SEC trace; b) DSC analysis and c) TGA analysis of **TEBPA**.

1.8 General procedure for the synthesis of polycarbonates

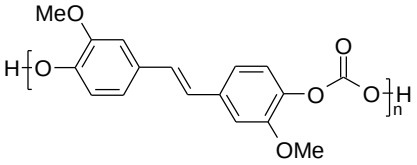
A 30 mL radley carousel tube was charged with bisphenol (1 equiv.), diphenyl carbonate (193 mg, 900 µmol, 1 equiv.) and lithium hydroxide (1.10 mg, 46.0 µmol, 5 mol%) under argon atmosphere. The resulting mixture was heated at 180 °C for 24 h. The reaction was quenched by cooling to r.t. and addition of THF (3 mL). The polymer was precipitated in cold methanol (30 mL), filtered and dried over phosphorous pentoxide at 10^{-3} mbar for 24 h.

Table S4: Summary of the analytical results for the polycarbonates

Entry	Monomer	Polymer	Yield [wt%]	mp [°C]	T_g [°C]	M_n [g/mol]	$Đ$	$T_{d\ 5\%}$ [°C]
1	**2**	**PC2**	81	146 – 148	127	2800	2.0	305
2	**4**	**PC4**	74	258 – 262	160	-[a]	-[a]	313
3	**3**	**PC3**	83	106 – 108	81	3500	1.5	319
4	**7**	**PC7**	68	143 – 146	25	2200	1.6	292
5	**BPA**	**PCBPA**	76	280 – 290	115	3000[b]	2.9[b]	332
6	**BPA2**	**PCBPA2**	54	224 – 228	79	2700	1.3	314

[a] not soluble in THF; [b] sample after 3.5 h, not soluble after whole reaction time; [c] 3 h reaction time.

*1.8.1 Polycarbonate of (E)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane **PC2***



Following the general procedure for the polycarbonates, **PC2** was obtained from (*E*)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (245 mg, 900 µmol) and isolated as white solid (181 mg, 74 wt% based on the diol).

mp.: 146 – 148 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 1778 (m), 1600 (m), 1507 (m), 1416 (m), 1301 (m), 1264 (m), 1222 (s), 1185 (s), 1148 (s), 1106 (s), 1033 (m), 954 (m), 875 (w), 845 (m), 808, (m), 766 (m), 730 (m), 687 (w), 633 (m), 548 (m), 463 (w). δH (300 MHz, DMSO-d_6): 7.46 – 6.77 (m, 8H), 3.95 – 3.84 (m, 6H) ppm. M_n = 2800 g/mol ($Đ$ = 2.0). T_g = 127 °C; $T_{d\ 5\%}$ = 305 °C.

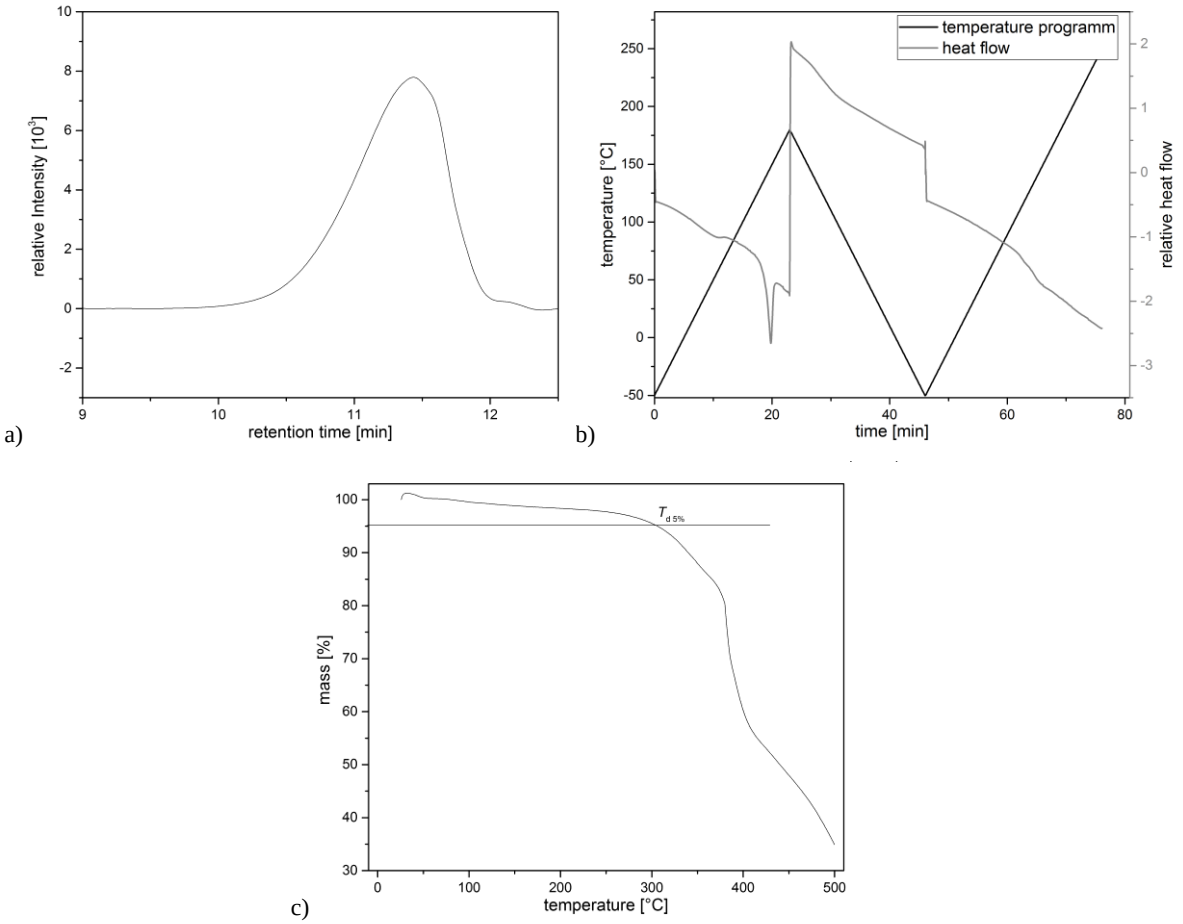
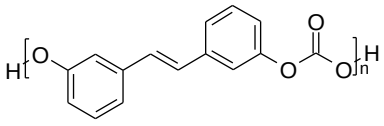


Figure 1.8-1: a) SEC trace, b) DSC analysis (heating program: -50 °C – 180 °C (10 K/min.); 180 °C – -50 °C (10 K/min.), -50 °C – 280 °C (10 K/min.)) and c) TGA analysis of **PC2** (heating rate: 5 K/min).

*1.8.2 Polycarbonate of (E)-1,2-bis(3-(allyloxy)phenyl)ethene and diphenyl carbonate (**PC4**)*



Following the general procedure for the polycarbonates, **PC4** was obtained from (*E*)-1,2-bis(3-(allyloxy)phenyl)ethane (191 mg, 901 µmol) and isolated as grey solid (154 mg, 81 wt% based on the diol). The product was not soluble for SEC or NMR analysis.

mp 258 – 262 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 3019 (w), 1763 (s, C=O), 1573 (m), 1487 (m), 1438 (m), 1244 (s), 1205 (s), 1137 (s), 997 (m), 962 (s), 929 (s), 880 (m), 783 (m), 759 (m), 730 (m), 686 (s), 590 (w), 546 (w), 516 (w), 458 (m). T_g: 160; $T_{d\,5\%}$ = 313 °C.

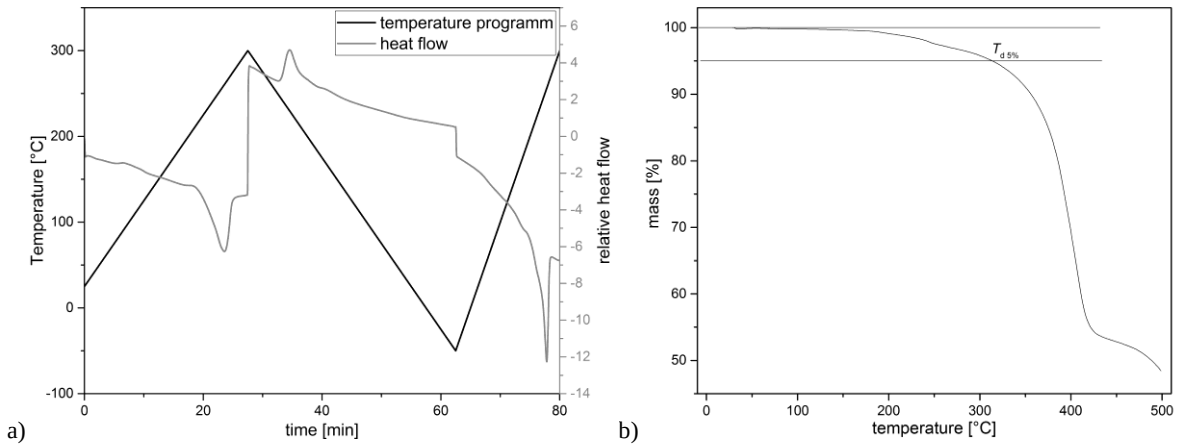
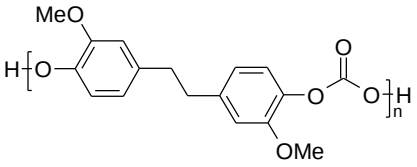


Figure 1.8-2: a) DSC analysis (heating program: -50 °C – 280 °C (10 K/min.); 280 °C – -50 °C (10 K/min.); -50 °C – 280 °C (20 K/min.)), b) TGA analysis of **PC4** (heating rate: 5 K/min).

*1.8.3 Polycarbonate of 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane and diphenyl carbonate (**PC3**)*



Following the general procedure for the polycarbonates, **PC3** was obtained from 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (247 mg, 901 µmol) and isolated as white solid (204 mg, 83 wt% based on the diol).

mp 106 – 108 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2940 (w), 1774 (m), 1598 (m), 1507 (m), 1458 (m), 1416 (m), 1282 (m), 1233 (s), 1185 (s), 1143 (s), 1112 (s), 1033 (m), 997 (m), 851 (w), 814 (m), 766 (m), 633 (w), 547 (w), 463 (w). δH (300 MHz, DMSO-d_6): 7.50 – 6.60 (m, 6H), 3.81 (s, 6H), 2.91 (s, 4H) ppm. M_n =3500 g/mol ($Đ$ = 1.5); T_g = 81 °C; $T_{d\,5\%}$ = 319 °C.

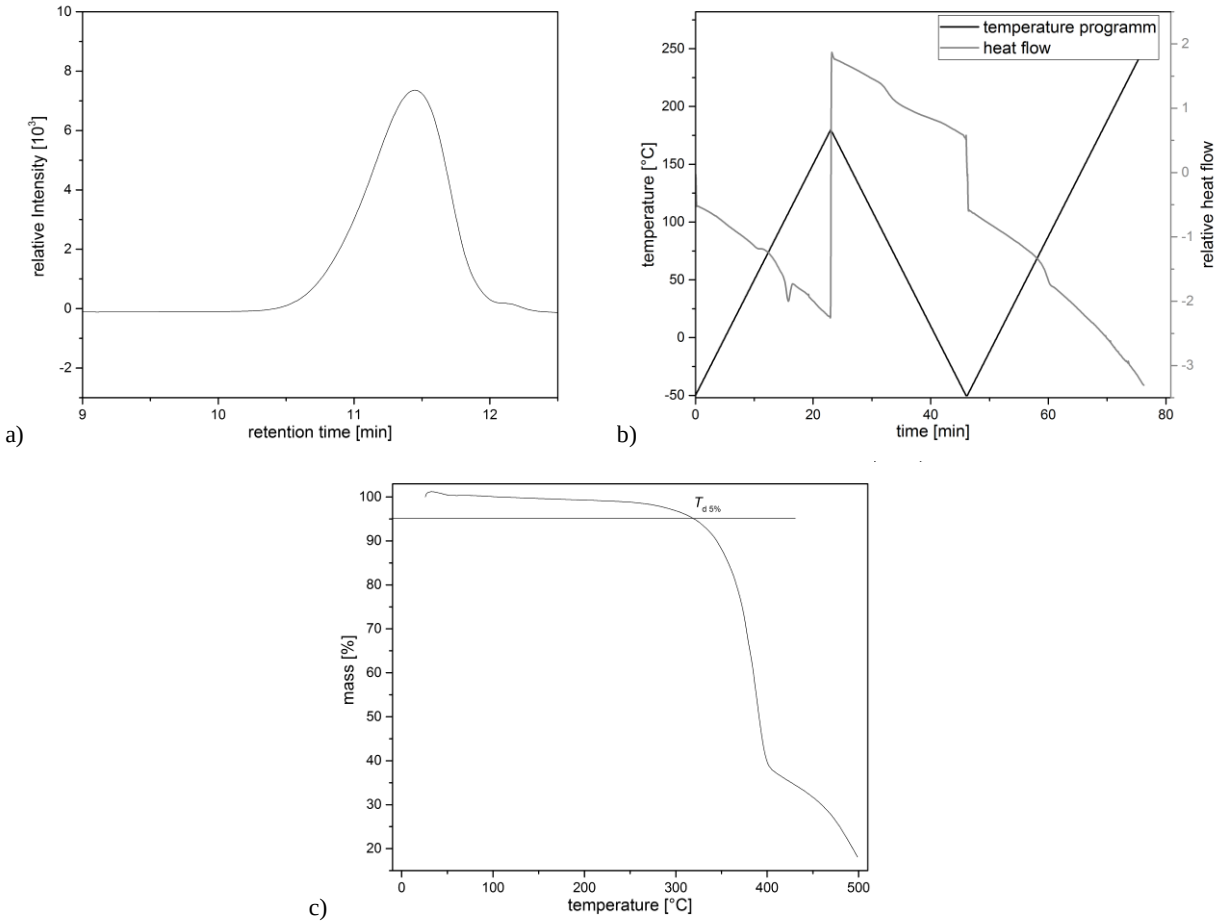
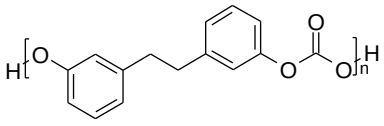


Figure 1.8-3: a) SEC trace, b) DSC analysis (heating program: -50 °C – 180 °C (10 K/min.); 180 °C – -50 °C (10 K/min.); -50 °C – 280 °C (10 K/min.)) and c) TGA analysis of **PC3** (heating rate: 5 K/min).

*1.8.4 Polycarbonate of 1,2-bis(3-(allyloxy)phenyl)ethane and diphenyl carbonate (**PC7**)*



Following the general procedure for the polycarbonates, **PC7** was obtained from 1,2-bis(3-(allyloxy)phenyl)ethane (193 mg, 901 µmol) and isolated as white solid (58 mg, 35 wt% based on the diol).

mp 143 – 146 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2933 (w), 1762 (s, C=O), 1617 (m), 1585 (m), 1483 (m), 1444 (m), 1208 (s, br), 1129 (s), 1078 (m), 1000 (m), 921 (m), 878 (m), 768 (m), 681 (s), 551 (w), 445 (w). δH (300 MHz, DMSO-d_6): 7.36 – 6.56 (m, 8H), 2.94 – 2.82 (m, 4H) ppm. M_n = 2200 g/mol ($Đ$ = 1.6). T_g = 25 °C; $T_{d\,5\%}$ = 292 °C.

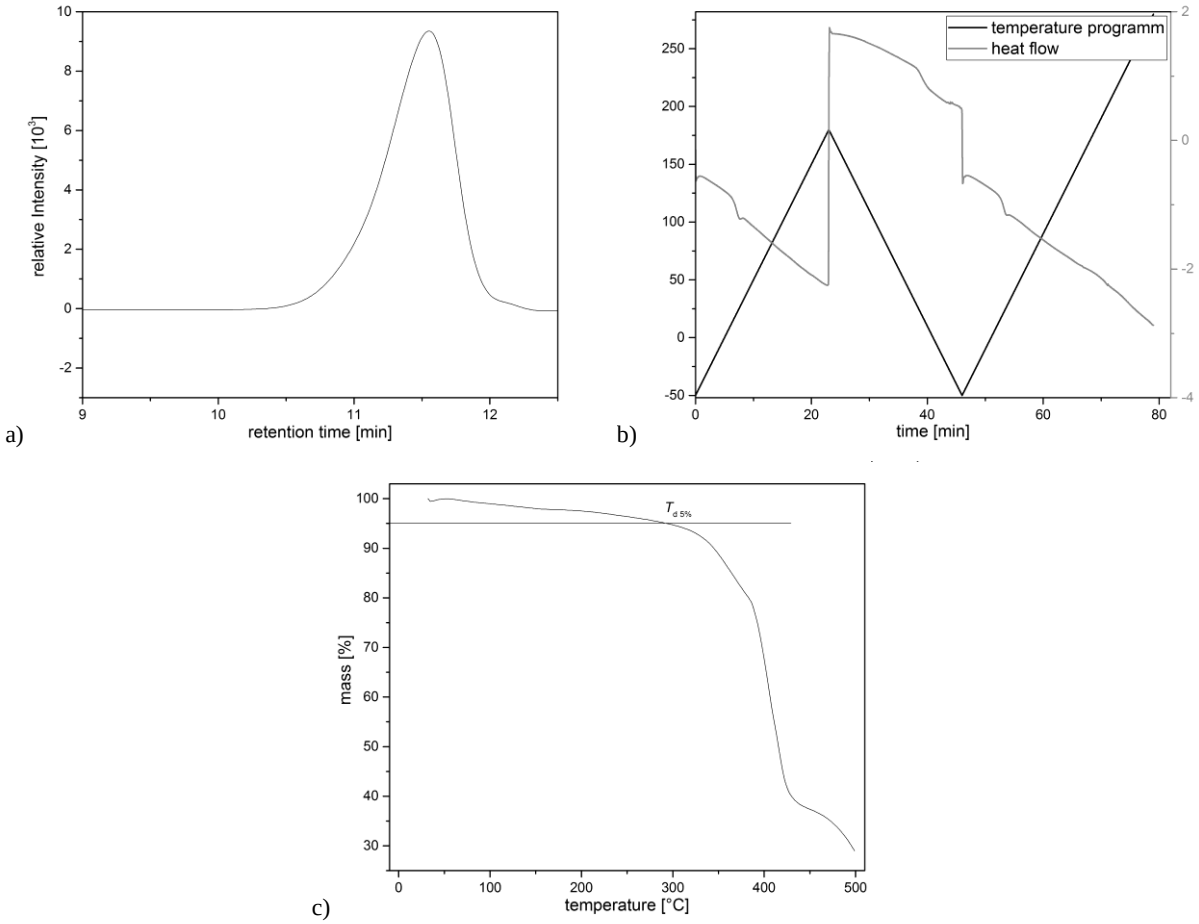
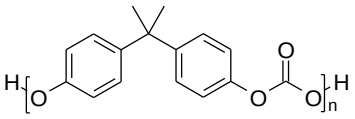


Figure 1.8-4: a) SEC trace, b) DSC analysis (heating program: -50 °C – 170 °C (10 K/min.), 170 °C – -50 °C (10 K/min.); -50 °C – 280 °C (10 K/min.)) and c) TGA analysis of **PC7**.

*1.8.5 Polycarbonate of 4,4'-(propane-2,2-diyl)bis((allyloxy)benzene) and diphenyl carboante (**PCBPA**)*



Following the general procedure for the polycarbonates, **PCBPA** was obtained from 4,4'-(propane-2,2-diyl)bis((allyloxy)benzene) (206 mg, 902 µmol) and isolated as white solid (154 mg, 76 wt%). The product was not soluble for SEC or NMR analysis.

mp 280 – 290 °C. IR (ATR): $\tilde{\nu}_{max}$/cm^{-1} 2967 (w), 1767 (s, C=O), 1594 (w), 1503 (m), 1406 (w), 1361 (w), 1229 (s), 1192 (s), 1157 (s), 1105 (m), 1078 (m), 1012 (s), 883 (w), 825 (m), 766 (m), 711 (w), 555 (m). M_n (after 3.5 hours) = 3000 g/mol ($Đ$ = 2.9); T_g = 115 °C $T_{d\,5\%}$ = 332 °C.

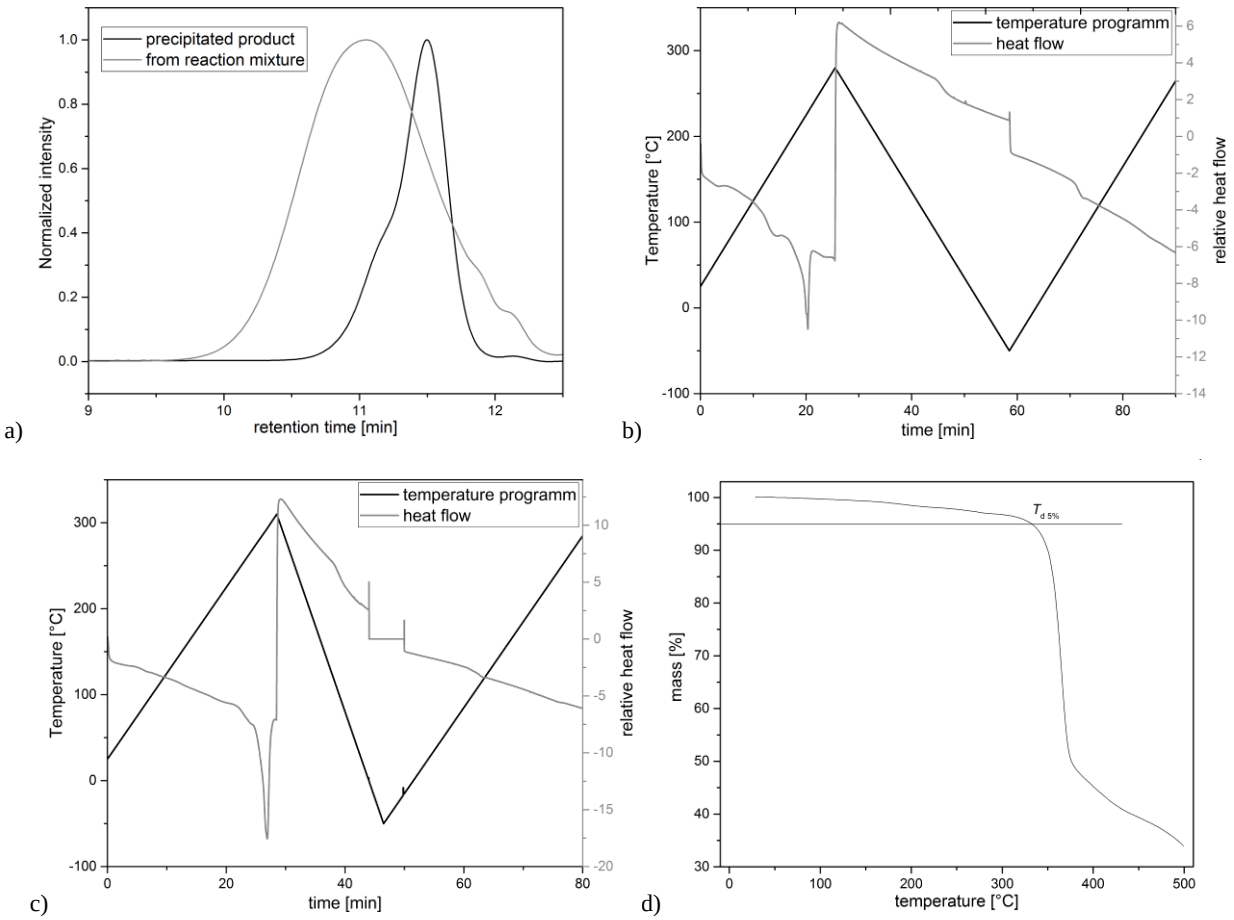


Figure 1.8-5: a) SEC trace of **PCBPA** after 3.5 h reaction time from the reaction mixture (M_n = 3000 g/mol, $Đ$ = 2.9) and of a precipitated product (M_n = 2700 g/mol, $Đ$ = 1.3); b) DSC analysis of low molecular weight BPA-based polycarbonate (**PCBPA2**) (heating program: -50 °C – 280 °C (10 K/min.); 280 °C – -50 °C (10 K/min.); -50 °C – 280 °C (10 K/min.)); and c) of **PCBPA** (heating program: -50 °C – 310 °C (10 K/min.); 310 °C – -50 °C (10 K/min.); -50 °C – 310 °C (10 K/min.)); d) TGA analysis of **PCBPA** (heating rate: 5 K/min).

1.9 Procedure for the yeast estrogen screen (YES) tests

1.9.1 General

The recombinant yeast strain was developed in the Biochemistry and Ecotoxicology Department of Bundesanstalt für Gewässerkunde (BAFG), Koblenz, based on the literature procedure described by Routledge et al.[8] and measures the the activation of the the human estrogen receptor (hER). The cells are stored as cryo-cultures in 350 µL aliquots at -80 °C. hER was fused to the chromosome of the yeast in a way which allows the binding to the estrogen responsive elements (ERE) and is expressed under the

control of the yeast copper metallothionein promoter (CUP1). The yeast contains expression plasmids with a PGK-ERE-lacZ structure. The reporter gene *lacZ* containing the ERE from *Xenopus* vitellogenin A2 encodes the enzyme *β*-galactosidase, which is released in the medium after a ligand (sample) binds to the ER. The estrogenic activity is measured photometrically by adding a chromogenic substrate, Chlorophenol red- β-D-galactosidase (CPRG), which is metabolized by the enzyme and leads to a change in the colour of the reaction.

1.9.2 Preparation of the different mediums

The synthetic medium (SD-Medium) was prepared by dissolving 67.0 g yeast nitrogen base without amino acids and 200 g glucose in 1 L of water and stored in 50 mL aliquots in the dark at < -18 °C no longer than 12 months.

The defined medium (DO-Medium) was prepared by dissolving in a total volume of 500 mL water in the following order: 2.00 g L-Serine, 1.00 g L-Threonine, 750 mg L-Valine, 500 mg L-Leucine, 250 mg L-Phenylalanine, 150 mg L-Isoleucine, 150 mg L-Tyrosine, 100 mg Adenine, 100 mg L-Arginine, 500 mg L-Aspartic acid, 500 mg L-Glutamic acid, 100 mg L-Histidine-HCl, 150 mg L-Lysine-HCl, 100 mg L-Methionine. DO-Medium was stored in 50 mL aliquots in the dark at < -18 °C no longer than 12 months.

The growth medium was prepared by adding 10 mL SD-Medium and 10 mL DO-Medium to mL water and stored in 50 mL aliquots in the dark at < -18 °C no longer than 6 months.

The exposure medium was prepared immediately before use by mixing 5 mL SD-Medium, 5 mL DO-Medium, 99.0 µL of a solution of 250 mg $CuSO_4 \cdot 5H_2O$ in 100 mL water, 67.0 µL of a solution of 1.00 g ampicillin sodium salt in 10 mL water and 67.0 µL of a solution of 1.00 g streptomycin sulfate salt in 10 mL water.

The lacZ buffer was prepared by dissolving 10.7 g $Na_2HPO_4 \cdot 5H_2O$, 0.75 g KCl, 0.25 g $MgSO4 \cdot 7H_2O$ in 950 mL water. The pH was adjusted to 7.0 by adding $NaH_2PO4 \cdot H_2O$ and the final volume was adjusted to 1 L with water. The solution was stored at r.t. no longer than 6 months. Right before use, per mL of lacZ buffer were added: 0.40 mg CPRG, 250 U Lyticase, 154 mg DL-Dithiothreitol.

1.9.3 Overnight culture

1 day before the test, 5 mL of growth medium were innoculated with a 350 µL of a cryo-culture and incubated for 22 h at 30 °C under constant agitation. After incubation, the optical density at 600 nm (OD 600) of a 1:10 dilution with groth medium was measured.

1.9.4 Plate setup

The assay was carried out in 96-well microtiter plates and sealed with polyurethane membrane foil. Water was used as negative control and a 0.3 % aqueous solution of ethanol was used as field blank. Each sample was tested in successive 1:3 dilution levels with 0.3 % aqueous solution of ethanol (all measured in 4 replicates) with a maximal concentration of 750 µg/L, which corresponds to the BPA concentration that activates the assay to a similar extend as 50 ng/L of the hormone reference 17*β*-estradiol. A concentration-response relationship of the reference 17*β*-estradiol was measured as well. For each sample, blank replicates were measured using the highest dilution. 80 µL were used for each well (samples, dilutions, negative control, field blank). The plate was inoculated with the yeast cells within 2 h after the setup.

1.9.5 Inoculation of the test plate

The OD of a 1:10 dilution with growth medium of the overnight culture and the growth medium alone as background correction were measured at 600 nm. The FAU (formazine attenuation unit) of the overnight culture was measured according to ISO 7027 (*Water quality — Determination of turbidity)*
The volume of the overnight culture (V_{onc}, in mL) was calculated using the following formula:
$V_{onc} = 4N / Df$,
where N is the number of plates used in parallel, and Df is the dilution factor calculated following:
Df = FAU / (requiredFAU*1,2),
where the required FAU is 25.

The required volume of the overnight culture was centrifugated at 2500 x *g* for 10 min. After disposing of the supernatant, the cells were diluted with exposure medium (4N mL).

All the wells containing blank replicates were filled with 40 µL of exposure medium and all the other wells with 40 µL of cell solution and the OD 600 was measured. The plate was incubated for 18 h at 30 °C. The following day the cells were resuspended by shaking and the OD 600 was measured again to

verify that no bacterial growth took place (an increase in the OD of the blank replicates indicates bacterial growth).

From each well, 30 µL were transferred to a new plate and 50 µL of the freshly prepared lacZ mixture were added to each well and the OD 580 was measured. The plate was further incubated for 1 h at 30 °C and the OD 580 was measured again (an increase in the OD 580 of the blank replicates indicates artificial cleavage of the CPRG by the sample).

1.9.6 Interpretation of the test

The estrogenic activity was graphically measured as a function of concentration and corrected absorbance by linear interpolation.

The corrected absorbance (A) for all wells (i) was calculated following the formula:

$A(i) = [A_{580}(i)-B_{580}(i)]/ [A_{600}(i)-B_{600}(i)]$,

where A_{580} is the absorbance of well i at 580 nm, A_{600} is the absorbance of well i at 600 nm, B_{580} is the mean absorbance at 580 nm of well i of the same concentration and B_{600} is the mean absorbance at 600 nm of well i of the same concentration.

Literature

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7. K. Hatas, K. Baba and M. Kozawa, *Chem. Pharm. Bull.*, 1979, **27**, 984
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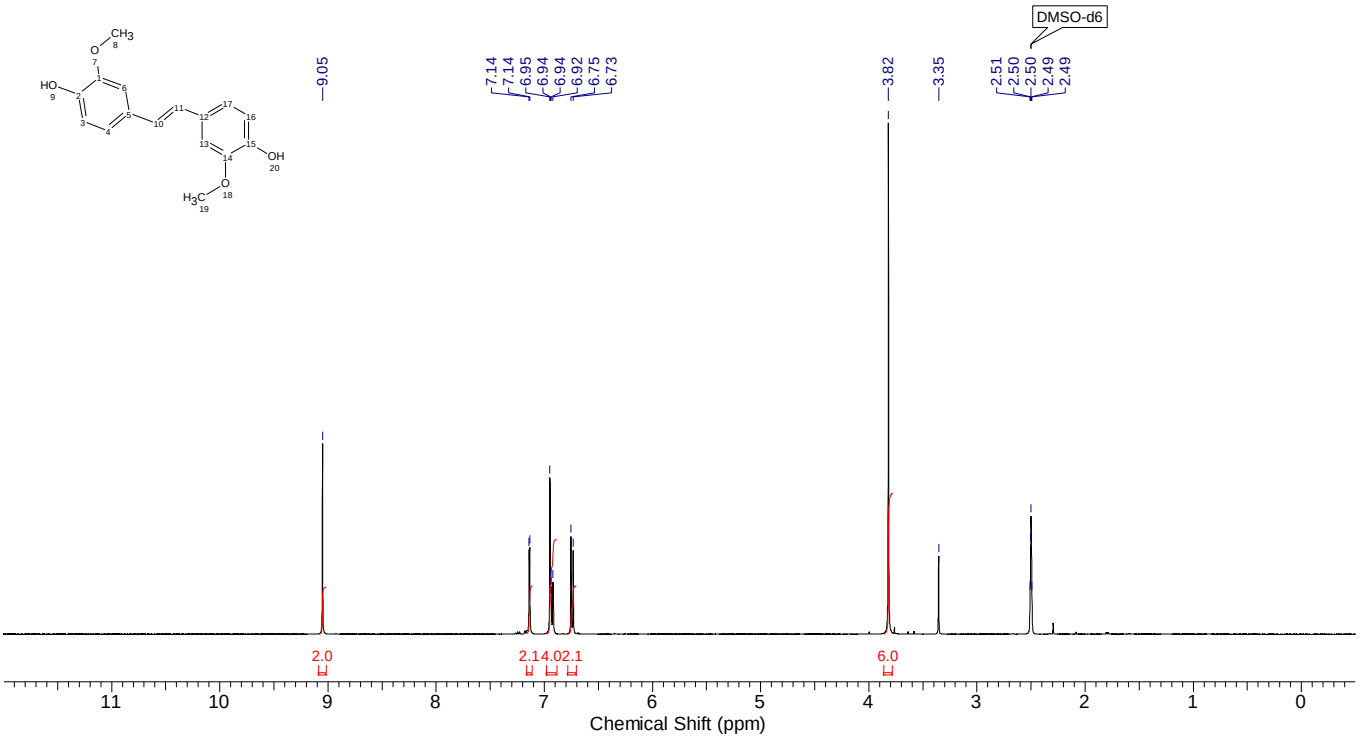
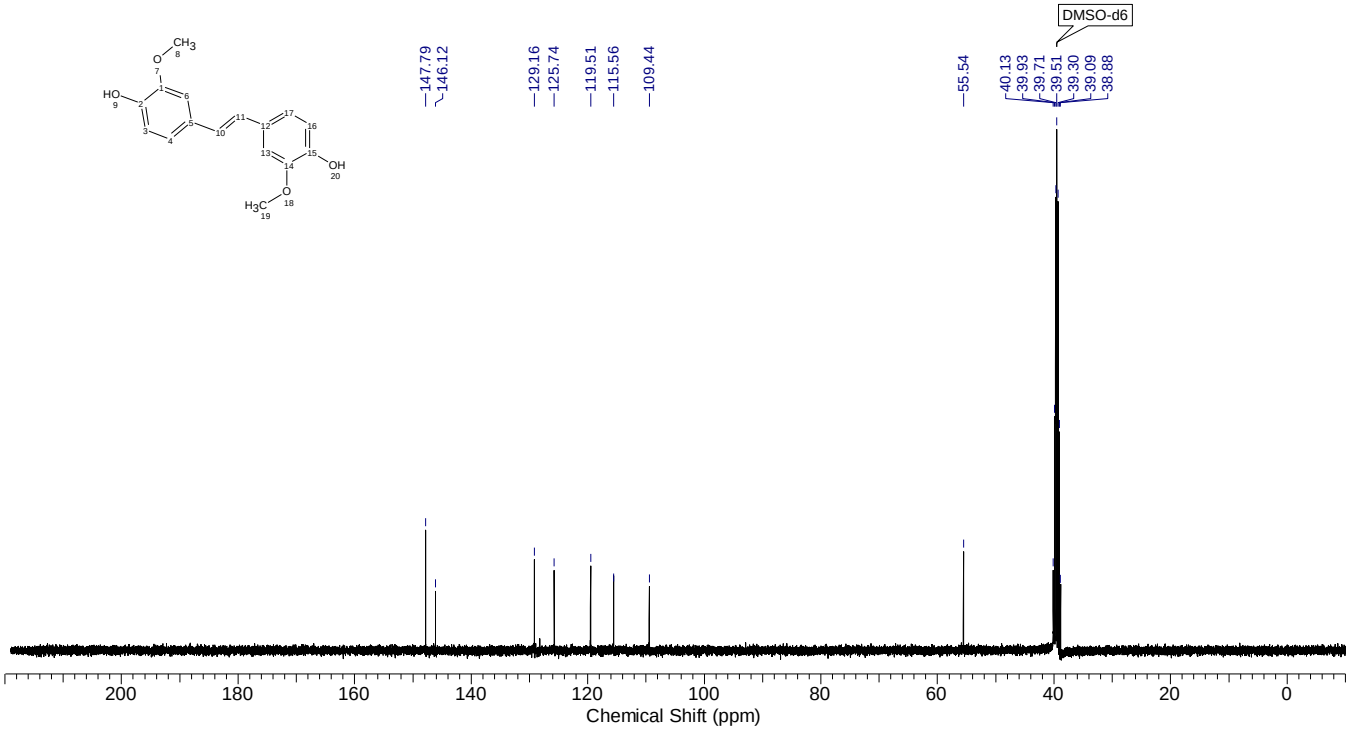
NMR Spectra

(*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene (2)

^{1}H-NMR (400 MHz, DMSO-d$_6$

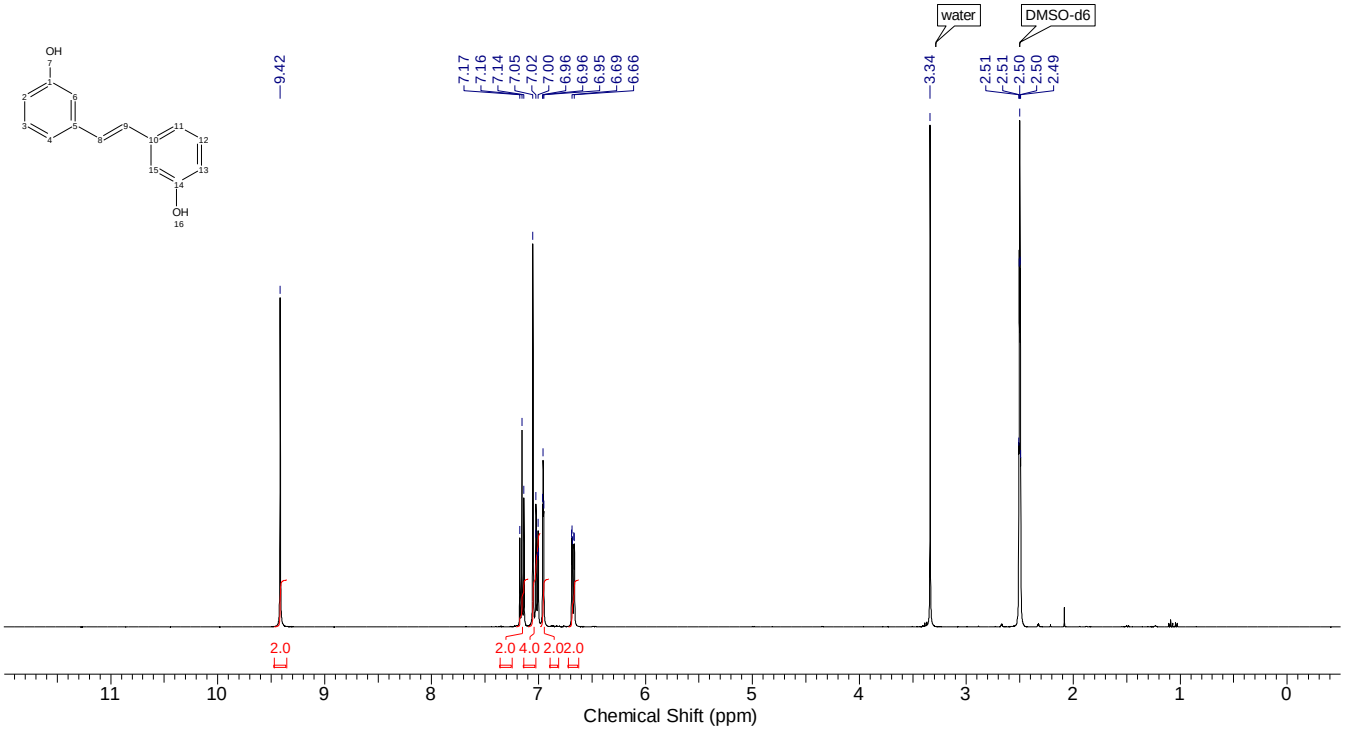


^{13}C-NMR (101 MHz, DMSO-d$_6$)

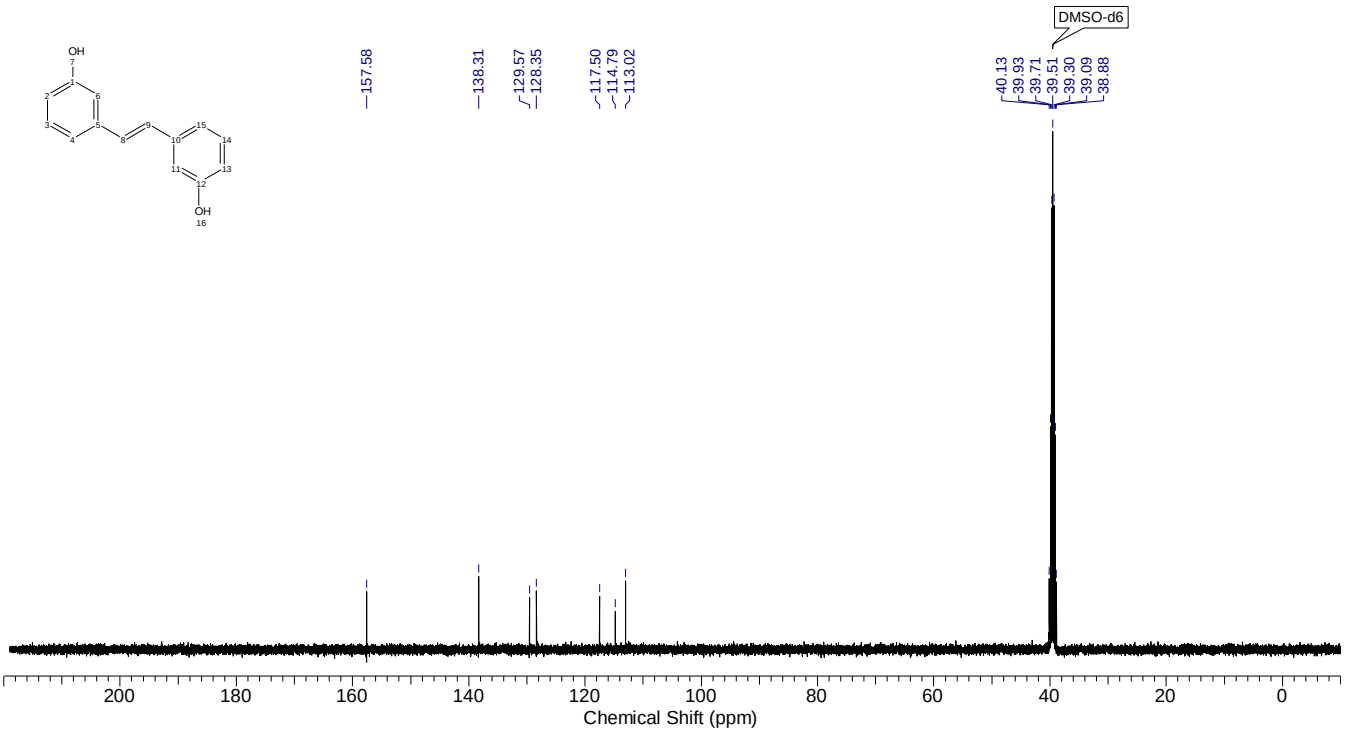


(*E*)-3,3'-hydroxystilbene (4)

^{1}H-NMR (400 MHz, DMSO-d$_6$)

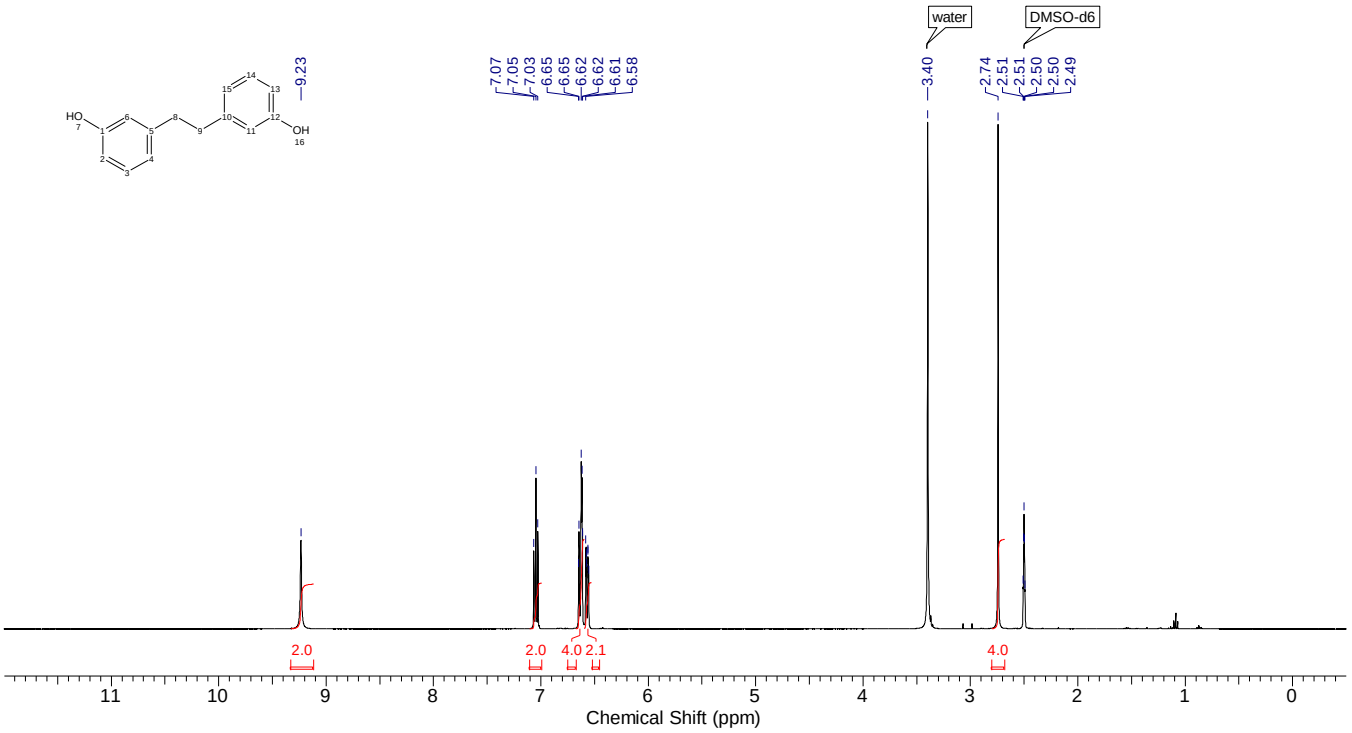


^{13}C-NMR (101 MHz, DMSO-d$_6$)

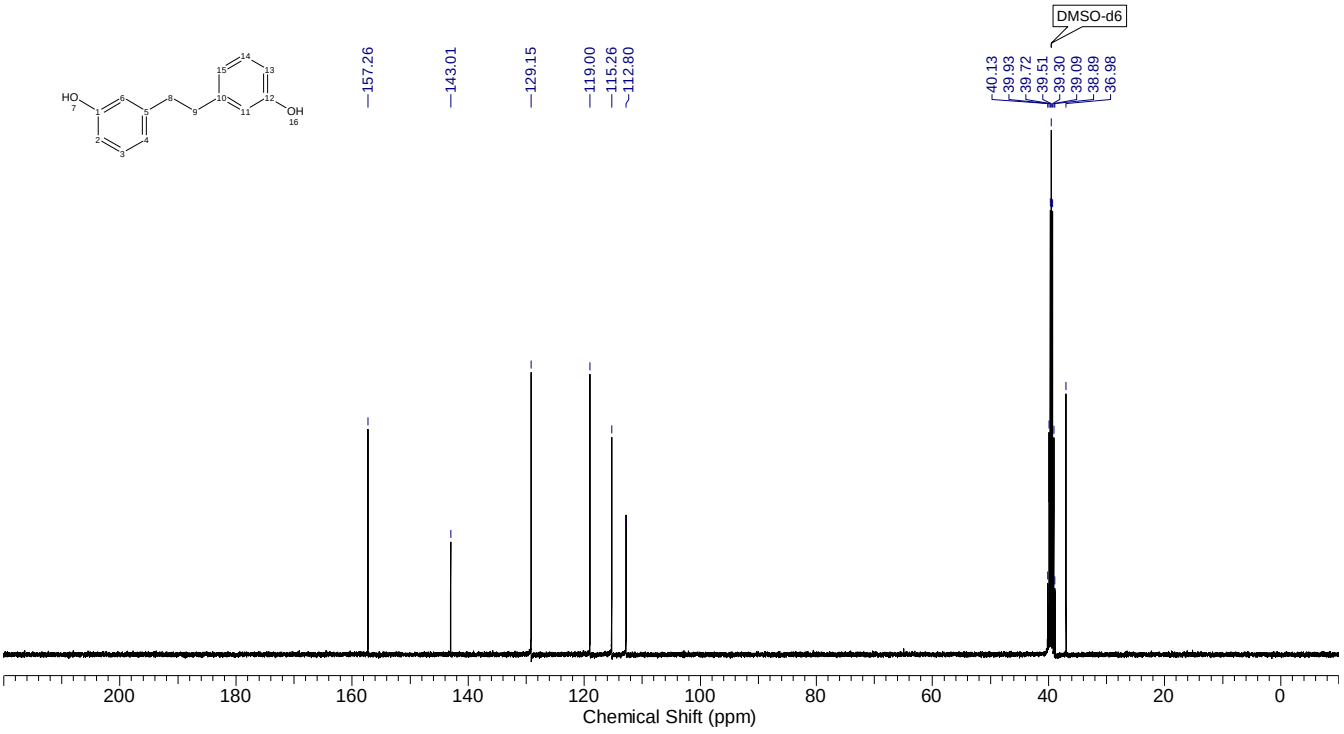


3,3'-dihydroxy-diphenylethane (7)

^{1}H-NMR (400 MHz, DMSO-d_6)

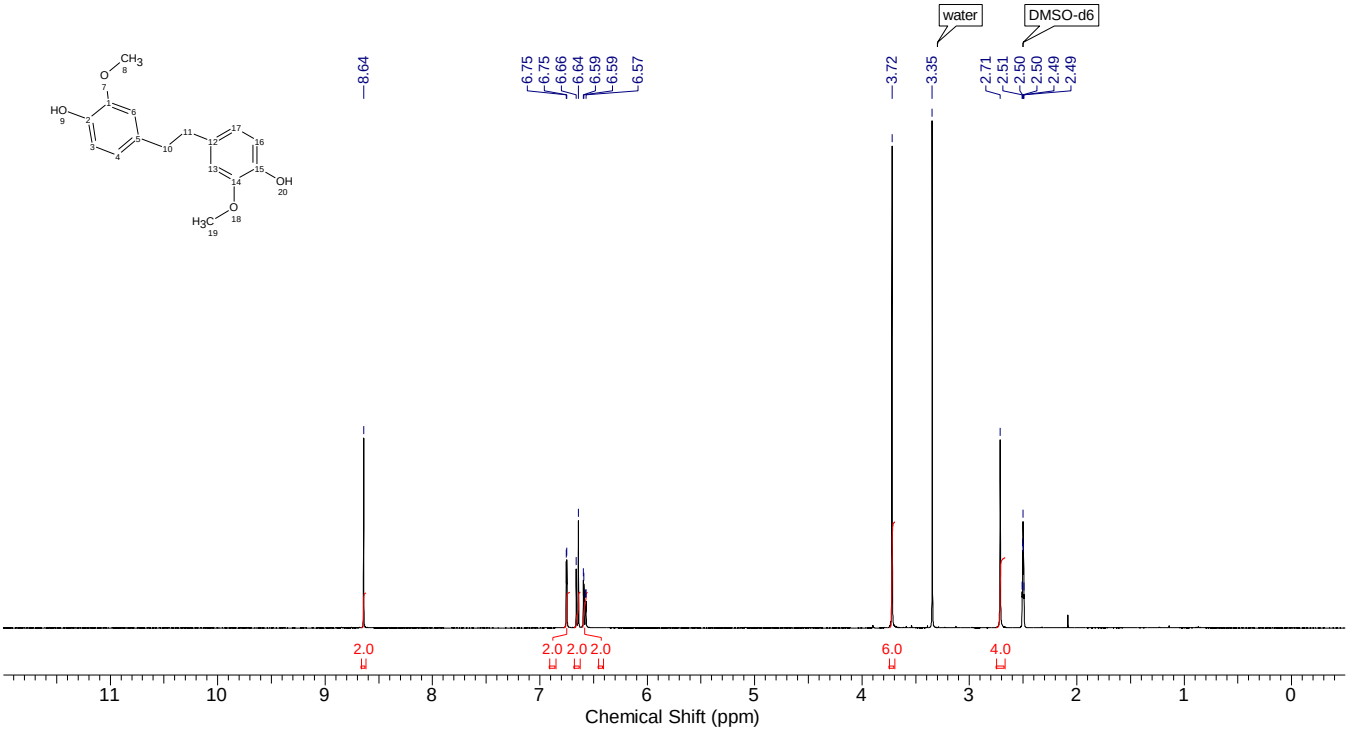


^{13}C-NMR (101 MHz, DMSO-d_6)

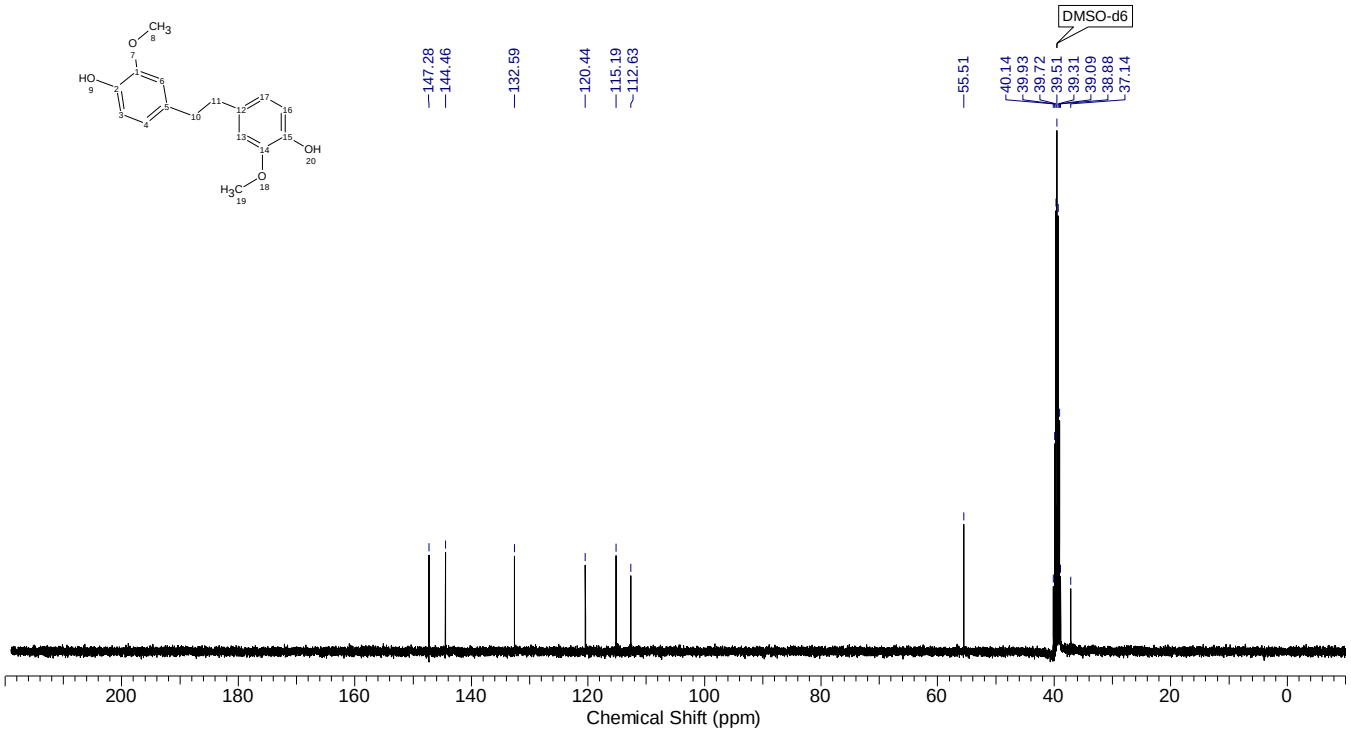


4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane (3)

^{1}H-NMR (400 MHz, DMSO-d$_6$)

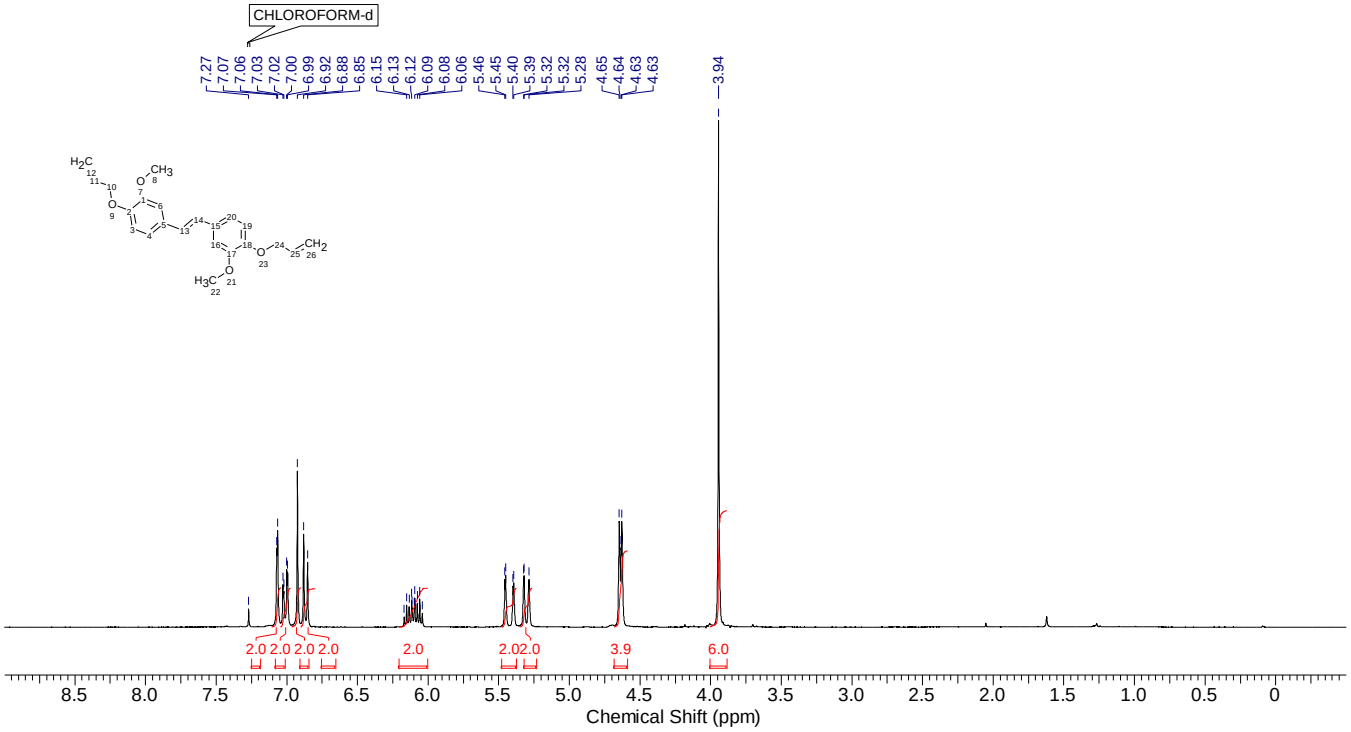


^{13}C-NMR (101 MHz, DMSO-d$_6$)

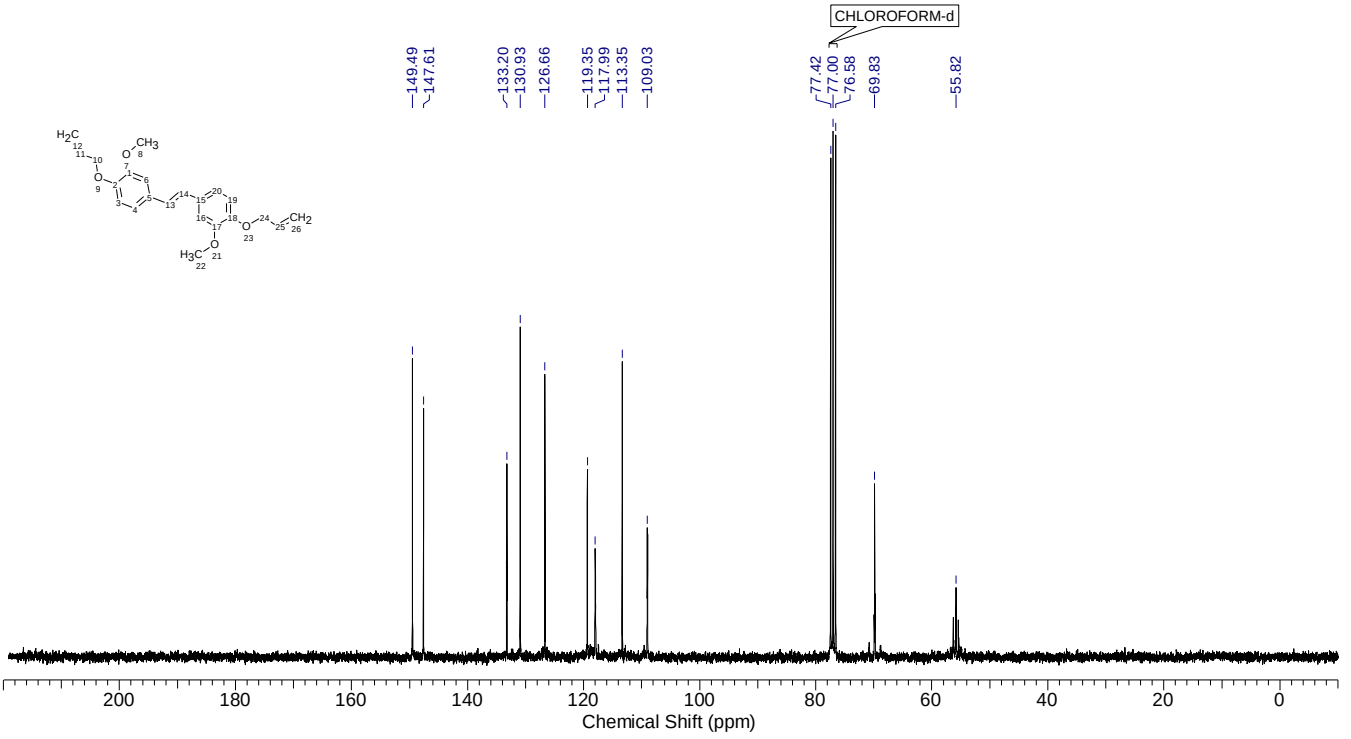


(*E*)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethene (A2)

^{1}H-NMR (300 MHz, $CDCl_3$)

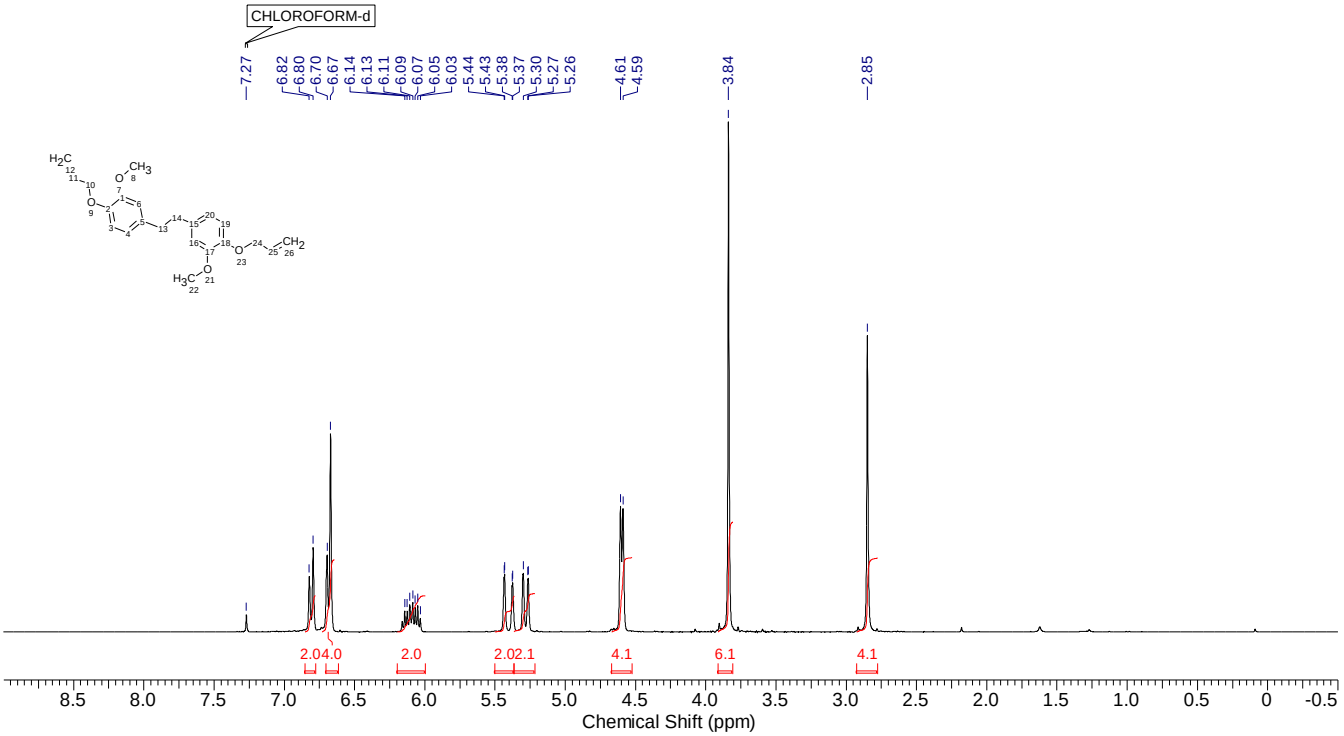


^{13}C-NMR (75 MHz, $CDCl_3$)

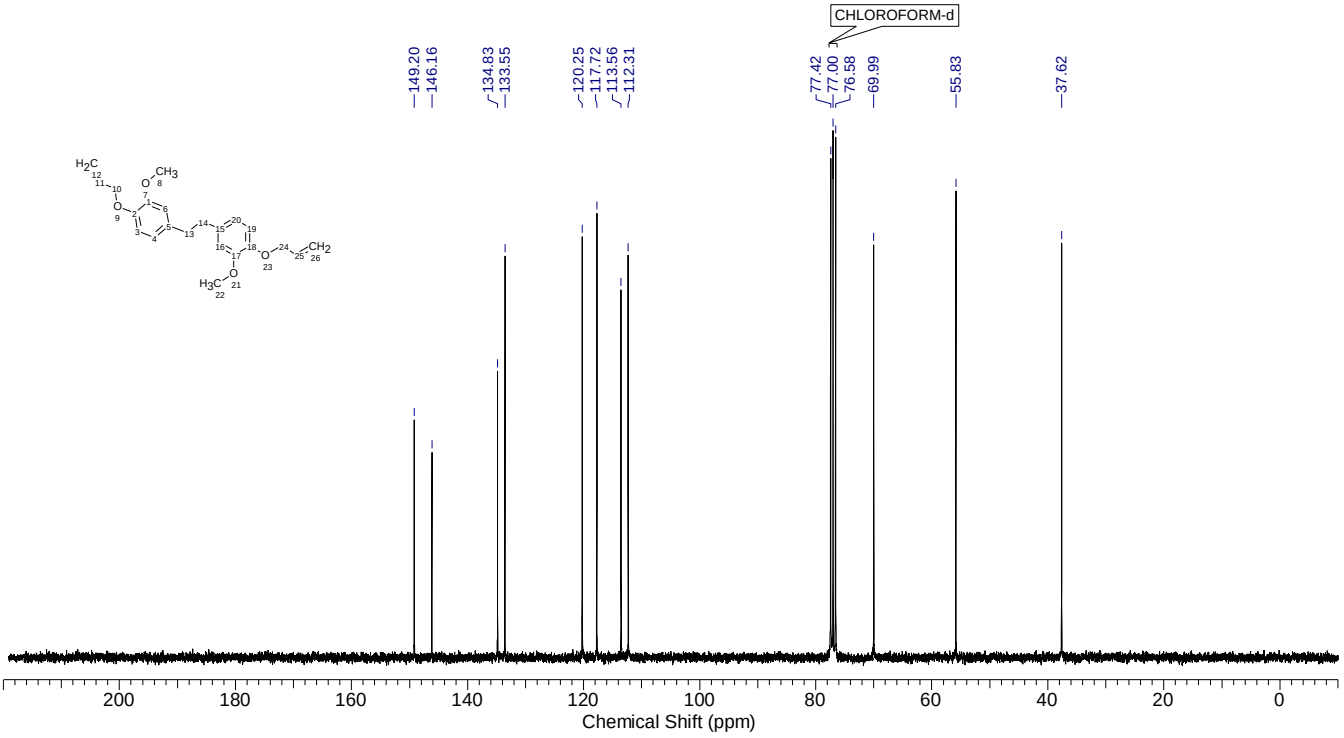


1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (A3)

^{1}H-NMR (300 MHz, $CDCl_3$)

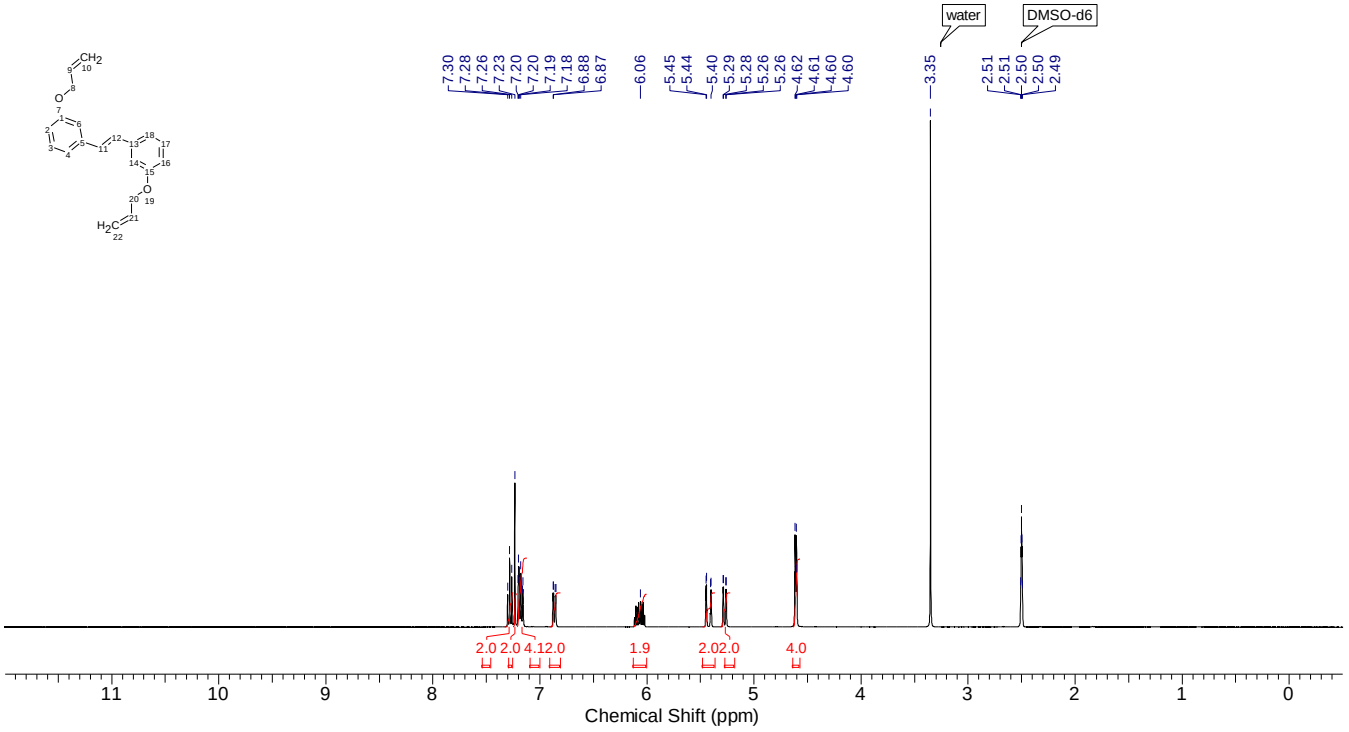


^{13}C-NMR (75 MHz, $CDCl_3$)

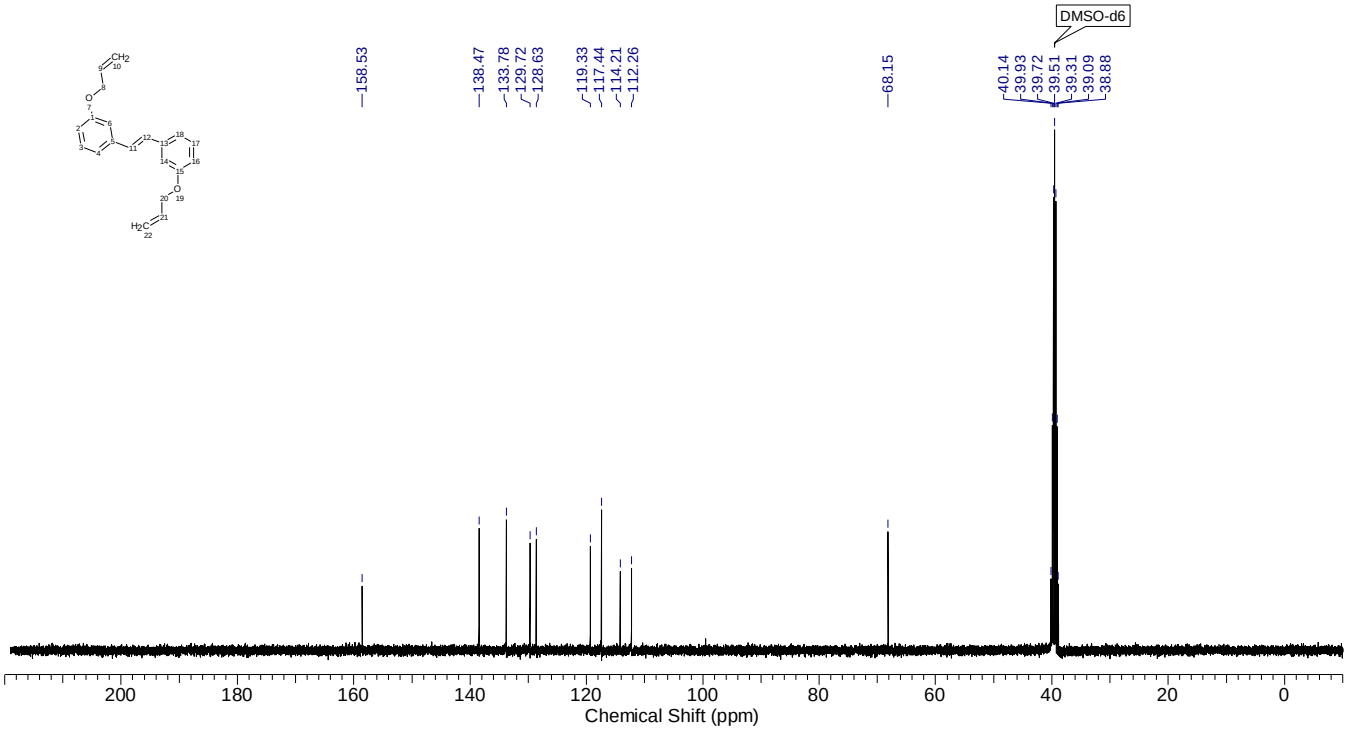


(*E*)-1,2-bis(3-(allyloxy)phenyl)ethene (A4)

^{1}H-NMR (400 MHz, DMSO-d$_6$)

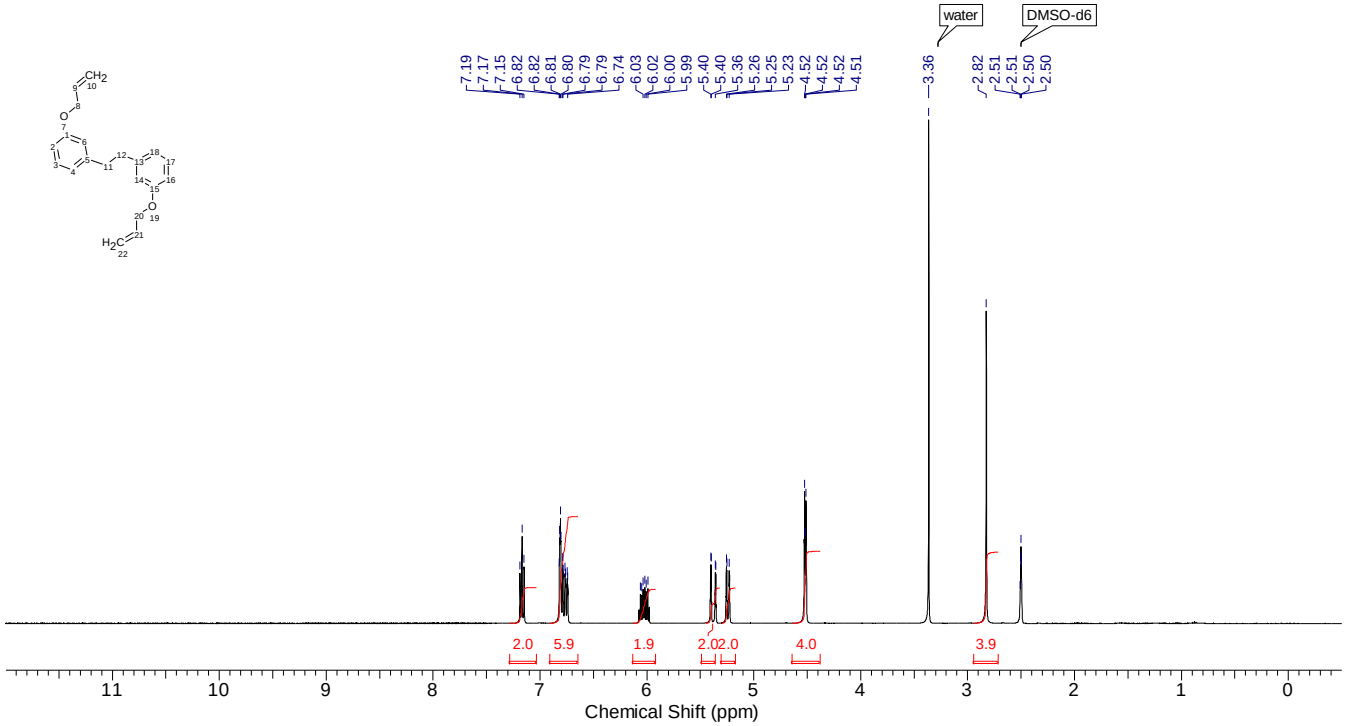


^{13}C-NMR (101 MHz, DMSO-d$_6$)

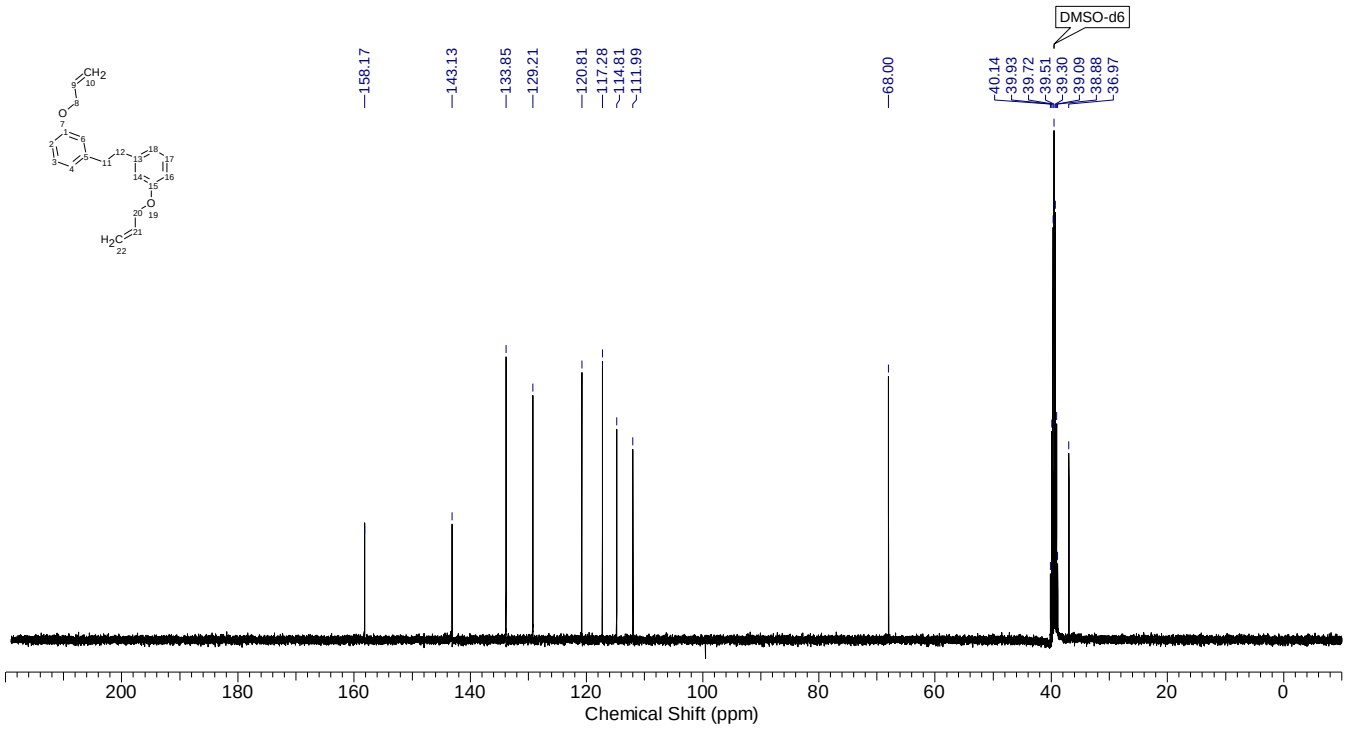


1,2-bis(3-(allyloxy)phenyl)ethane (A7)

^{1}H-NMR (400 MHz, DMSO-d$_6$)

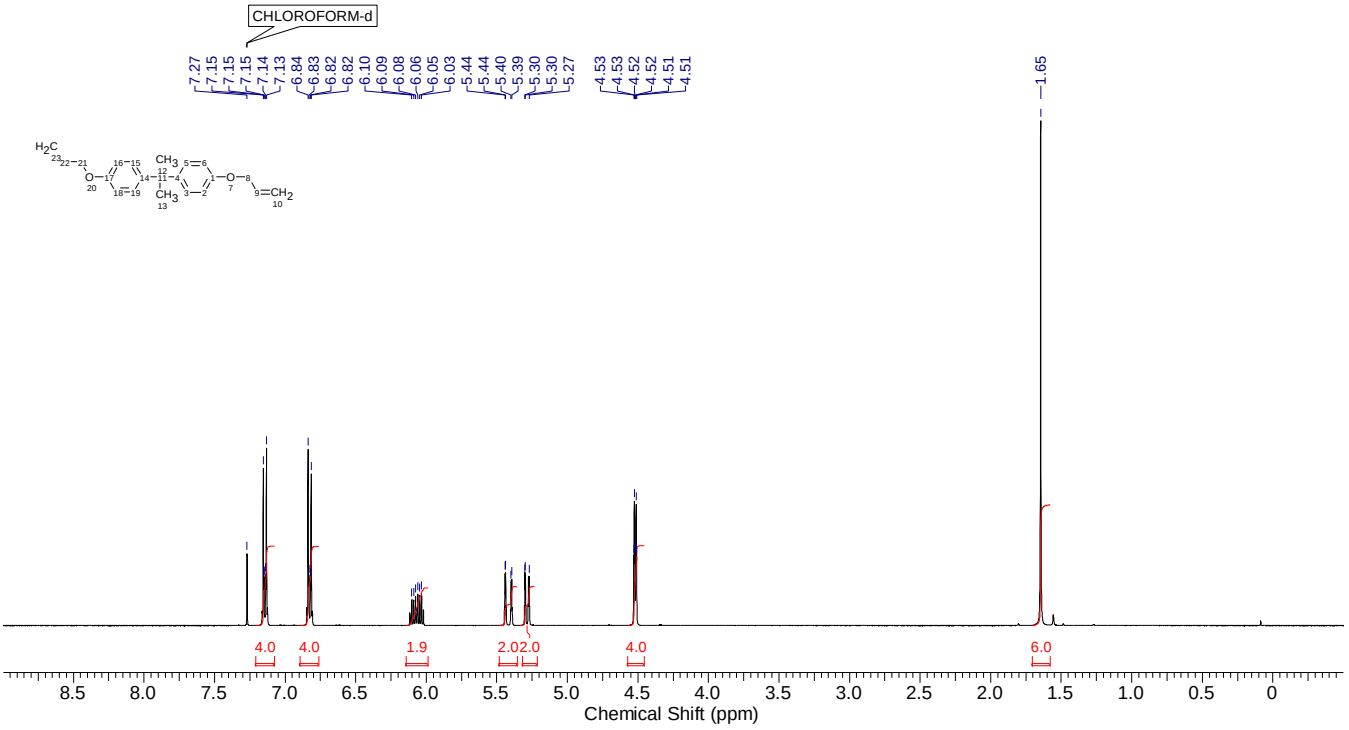


^{13}C-NMR (101 MHz, DMSO-d$_6$)

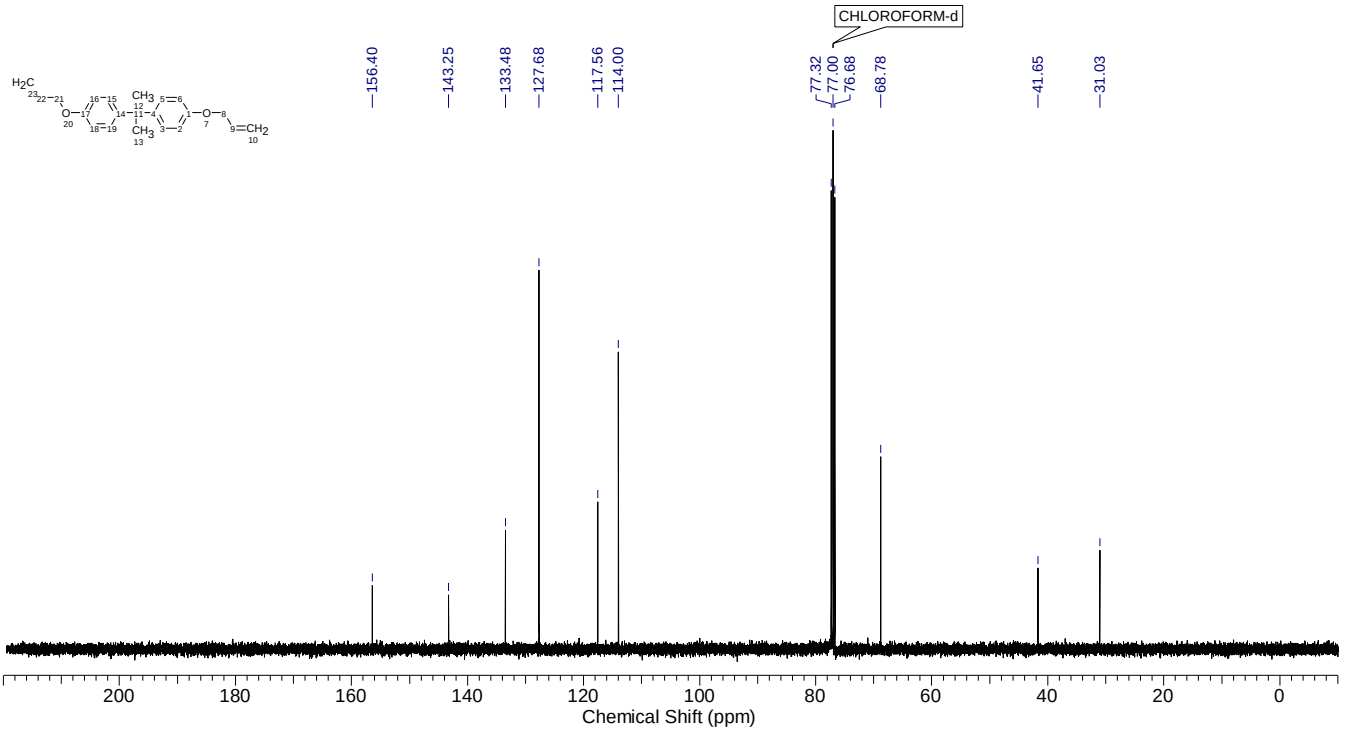


2,2-bis(4-allyloxyphenyl)propane (ABPA)

^{1}H-NMR (400 MHz, $CDCl_3$)

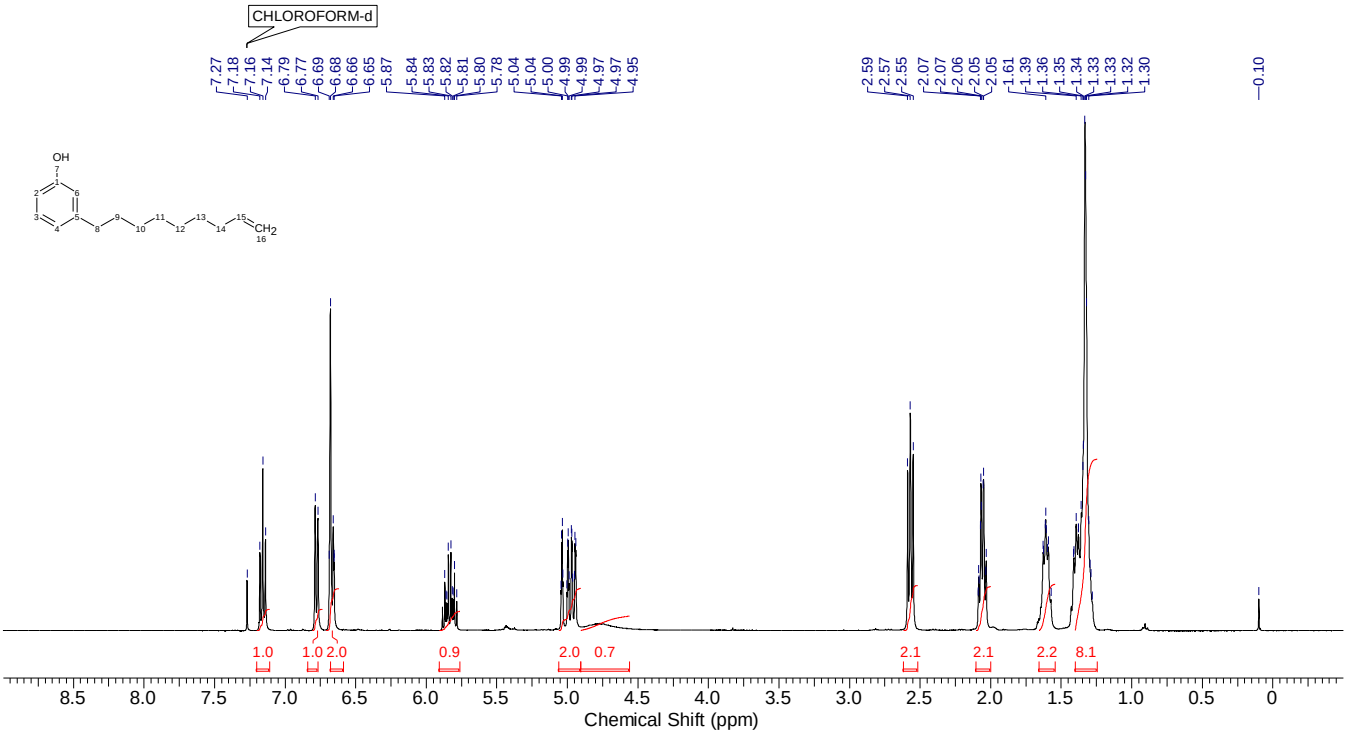


^{13}C-NMR (101 MHz, $CDCl_3$)

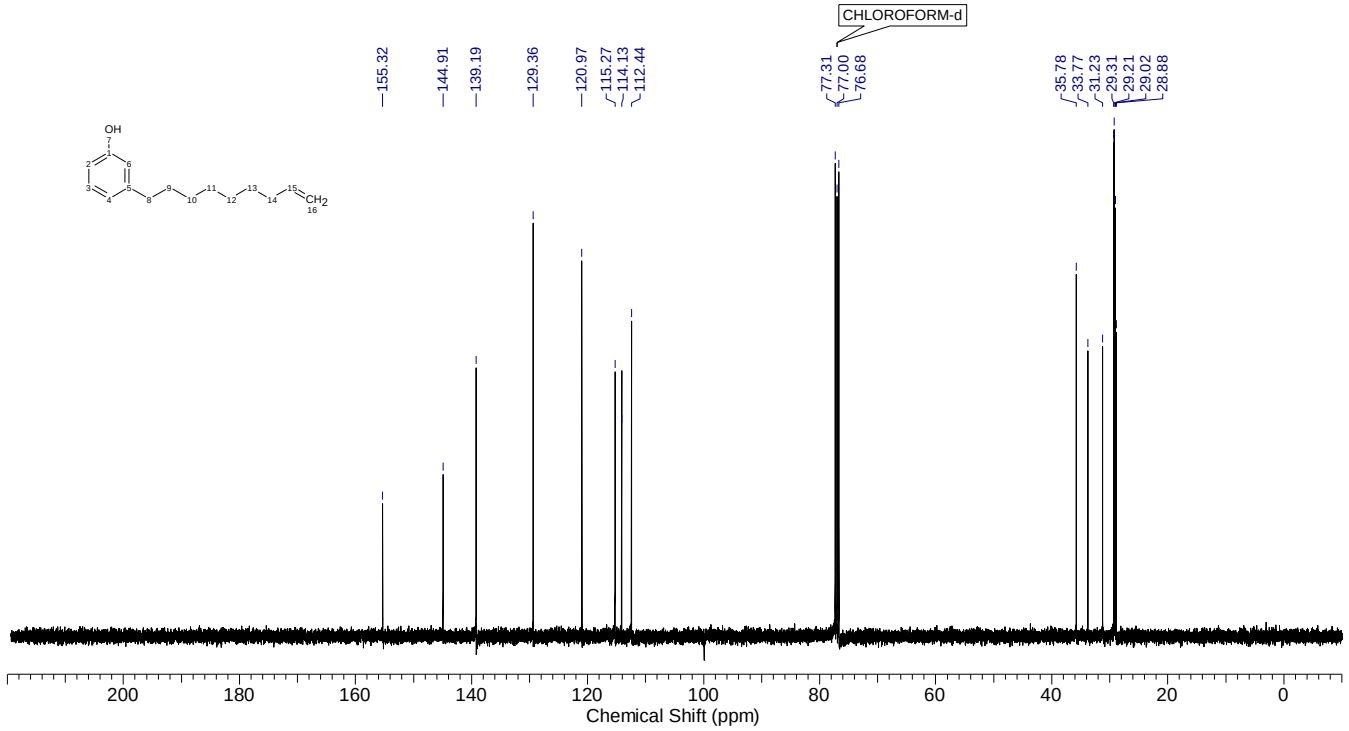


3-(non-8-enyl)phenol (1)

^{1}H-NMR (400 MHz, $CDCl_3$)

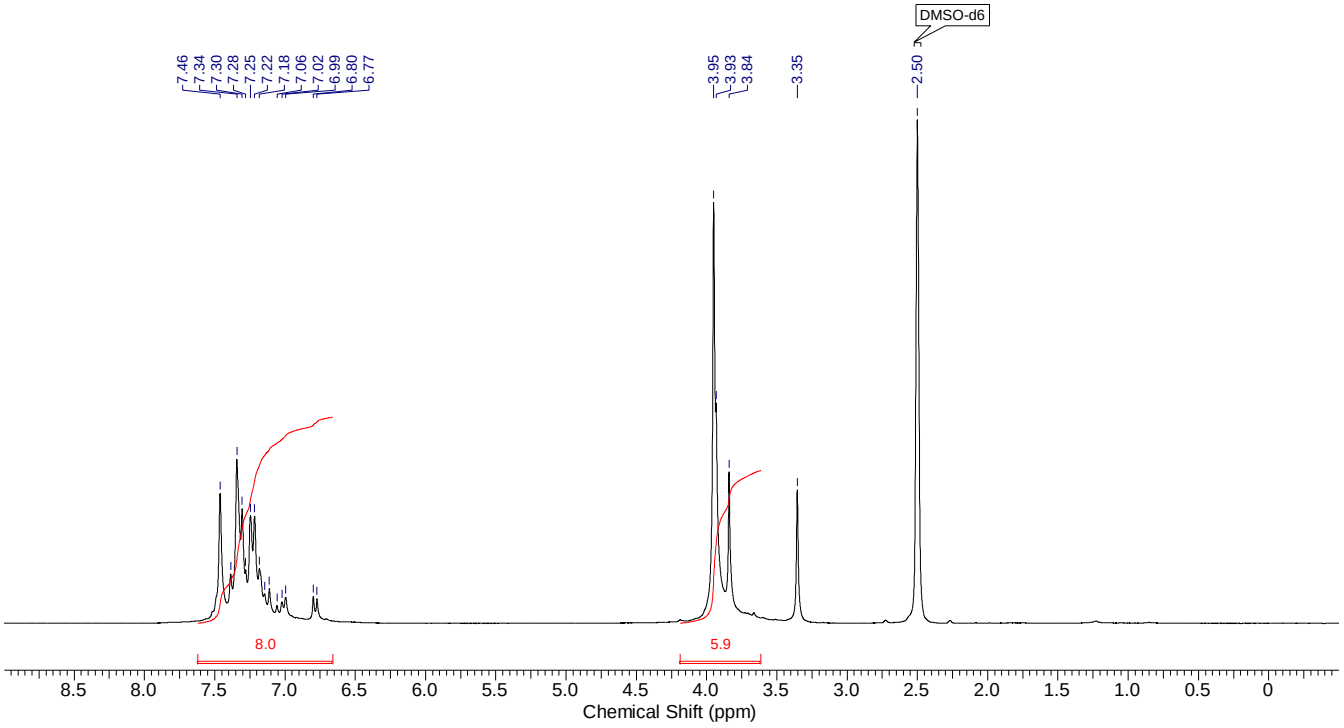


^{13}C-NMR (101 MHz, $CDCl_3$)



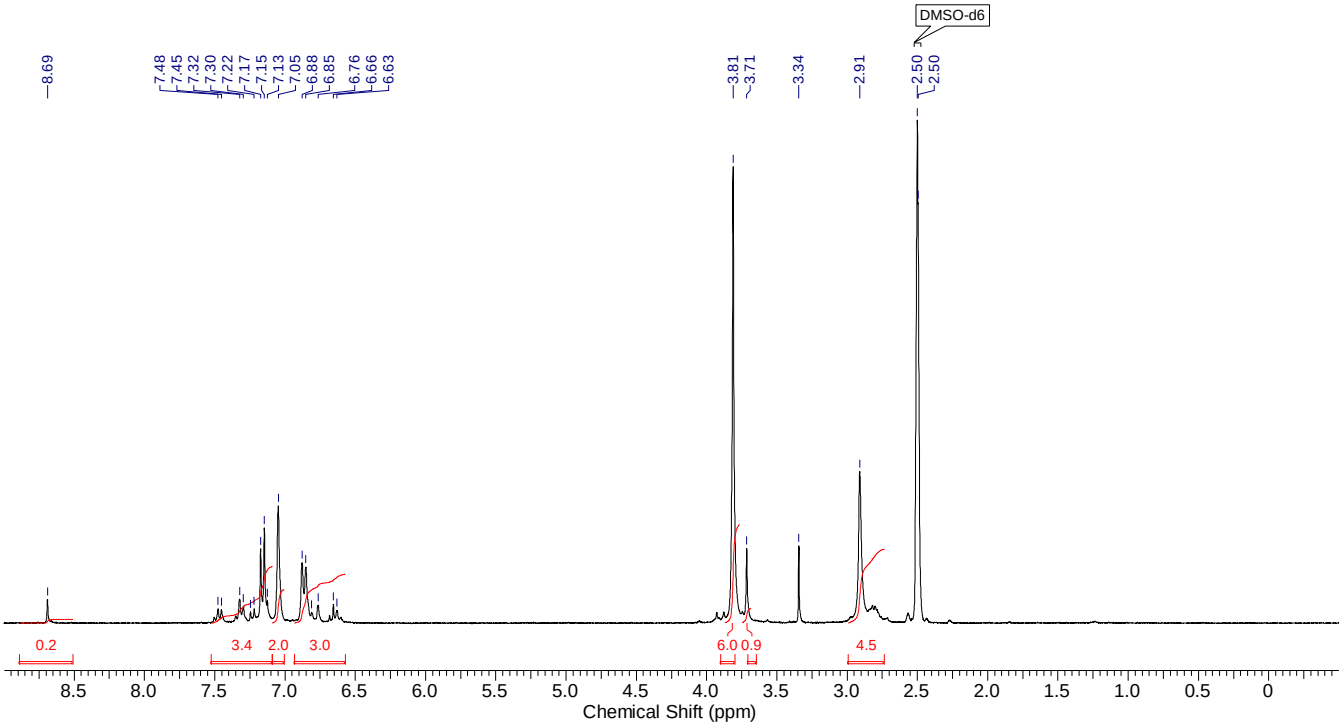
Polycarbonate of (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene (PC2)

^{1}H-NMR (300 MHz, $CDCl_3$)



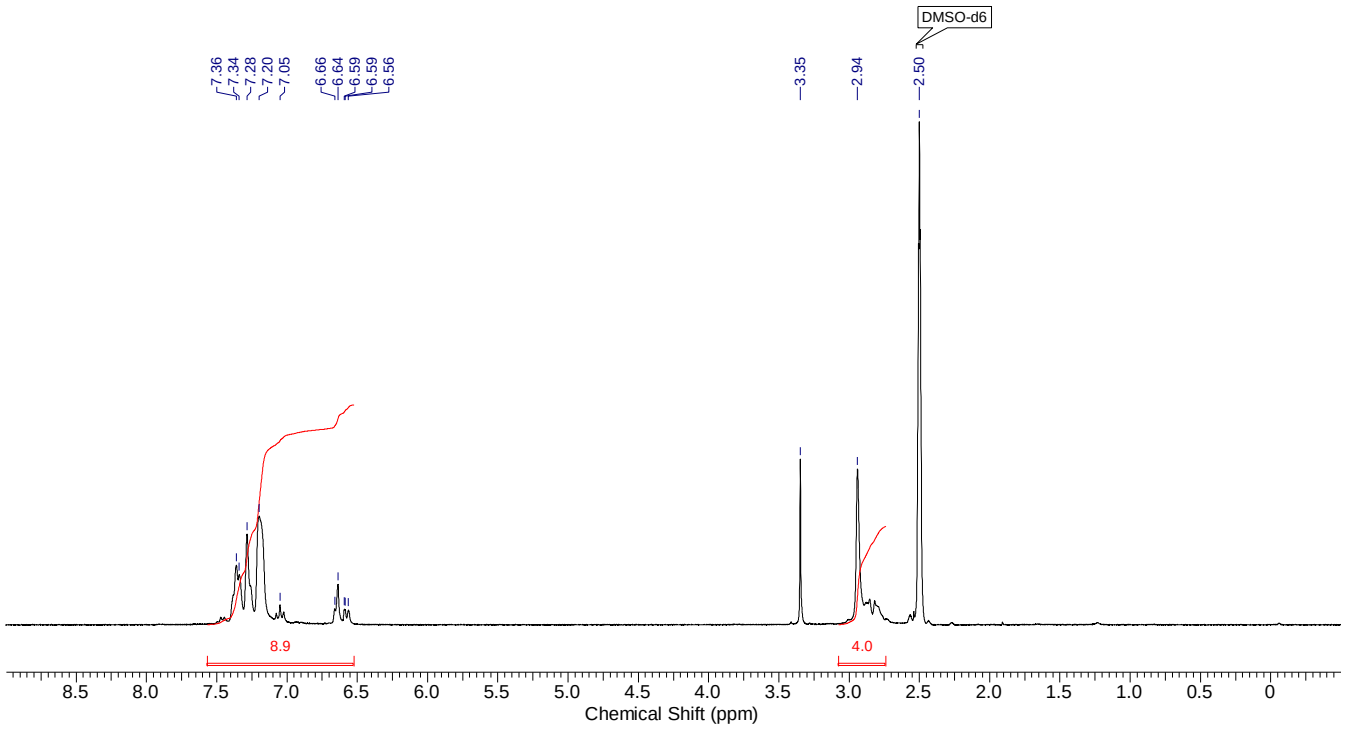
Polycarbonate of 4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane (PC3)

^{1}H-NMR (300 MHz, $CDCl_3$)



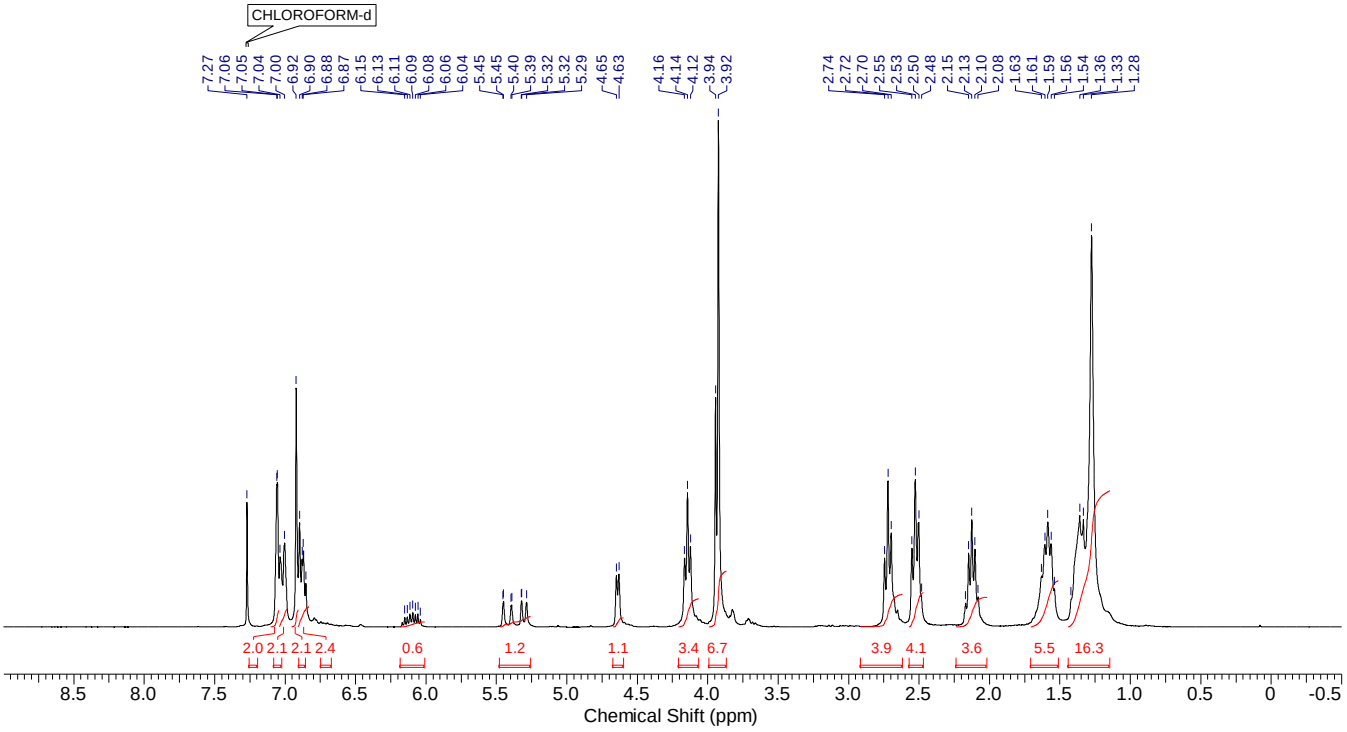
Polycarbonate of 3,3'-dihydroxy-diphenylethane (PC7)

^{1}H-NMR (300 MHz, $CDCl_3$)



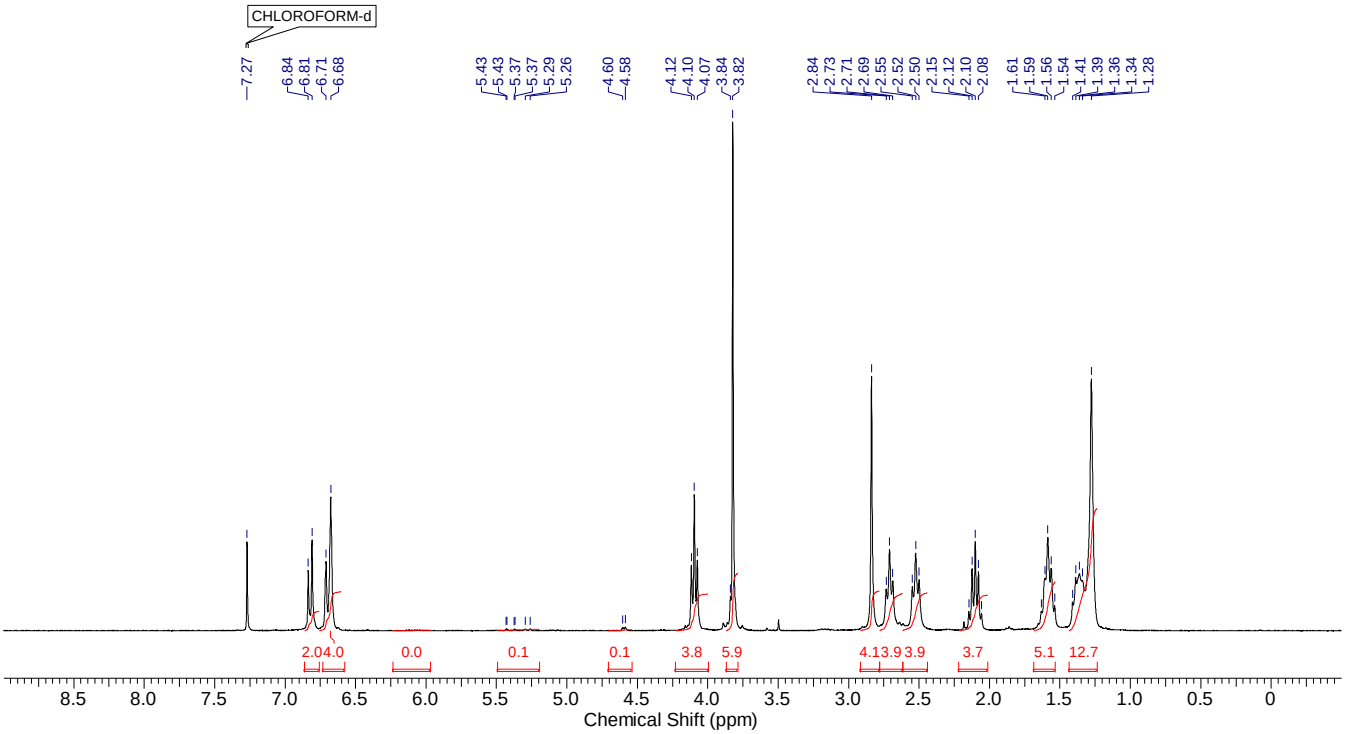
Thiol-ene polymer of (E)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethene (TE2)

^{1}H-NMR (300 MHz, $CDCl_3$)



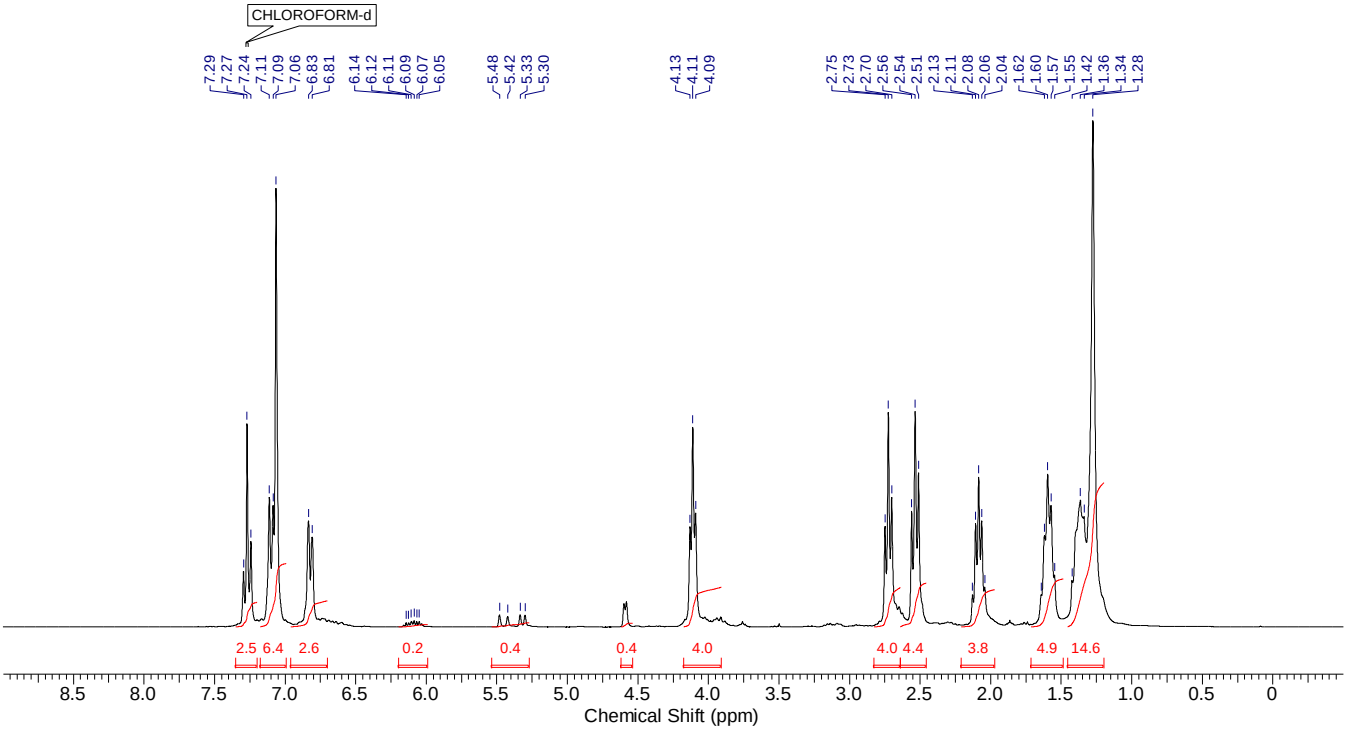
Thiol-ene polymer of 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (TE3)

^{1}H-NMR (300 MHz, $CDCl_3$)



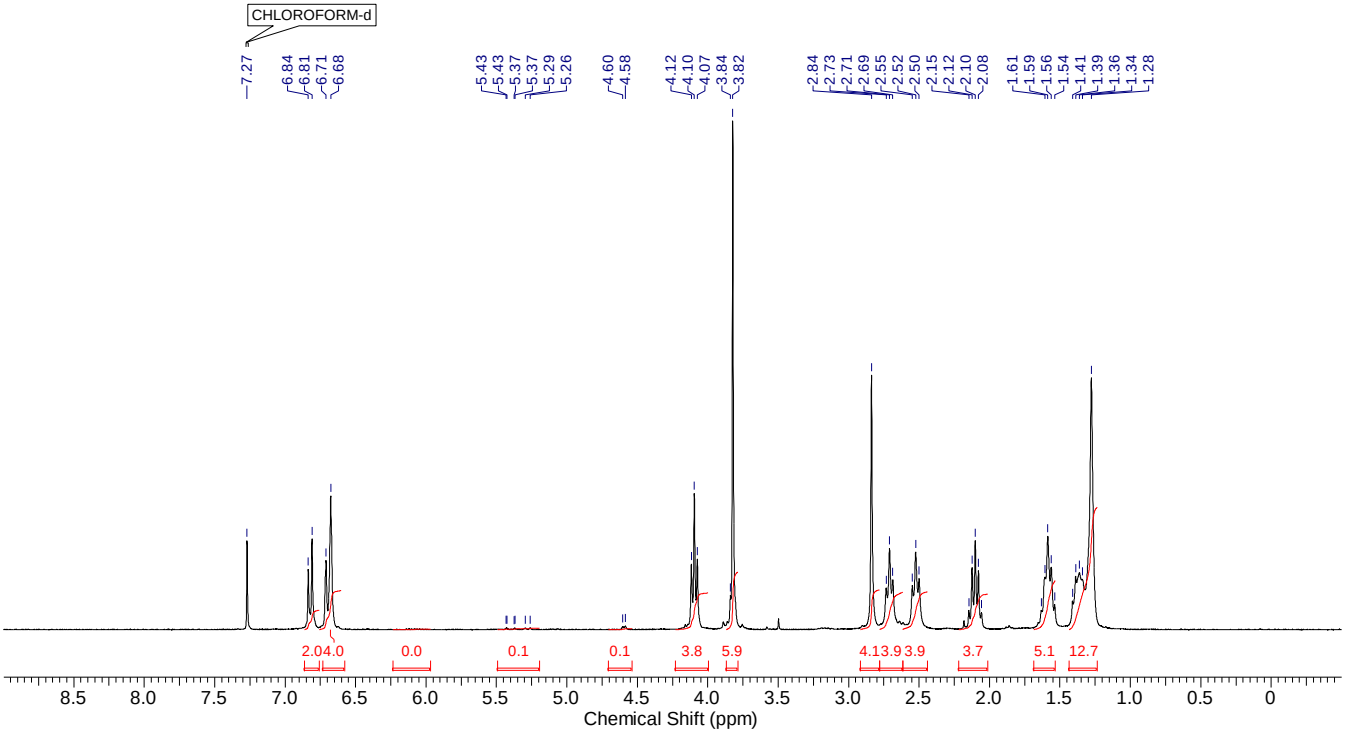
Thiol-ene polymer of (*E*)-1,2-bis(3-(allyloxy)phenyl)ethene (TE4)

^{1}H-NMR (300 MHz, $CDCl_3$)



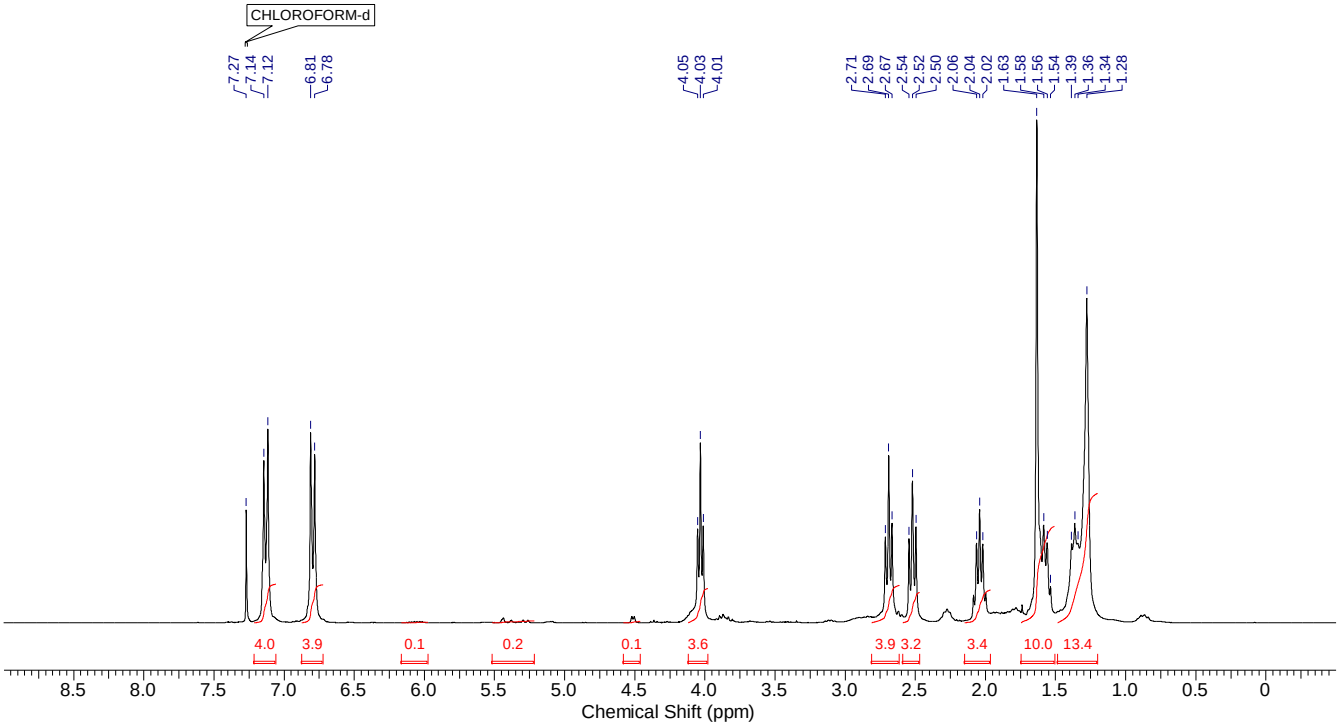
Thiol-ene polymer of 1,2-bis(3-(allyloxy)phenyl)ethane (TE7)

^{1}H-NMR (300 MHz, $CDCl_3$)



Thiol-ene polymer of 2,2-bis(4-allyloxyphenyl)propane (TEBPA)

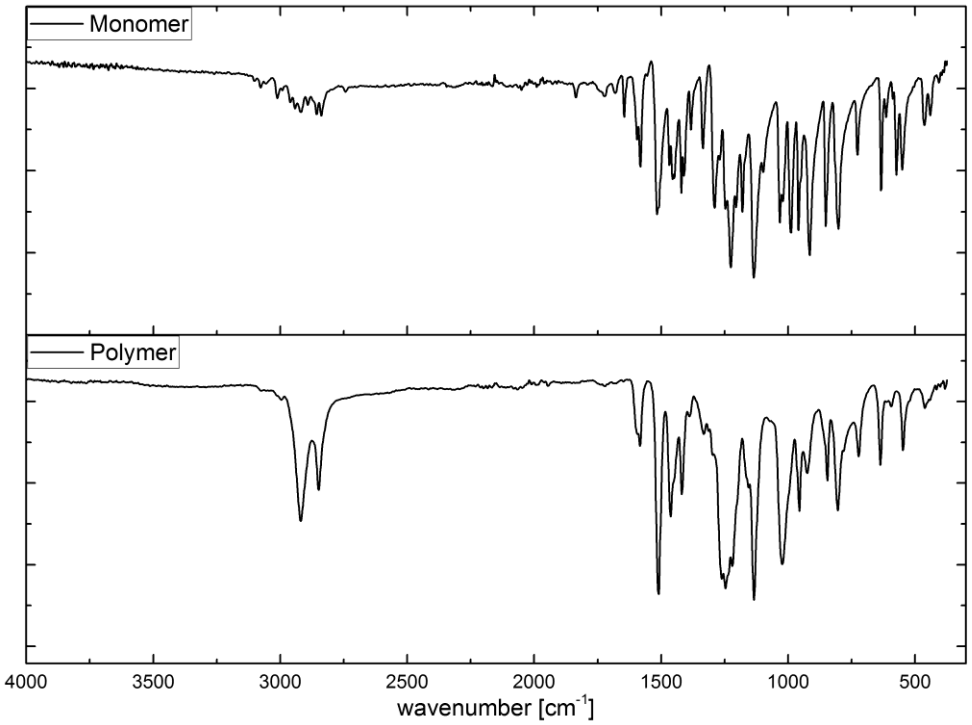
^{1}H-NMR (300 MHz, $CDCl_3$)



IR Spectra

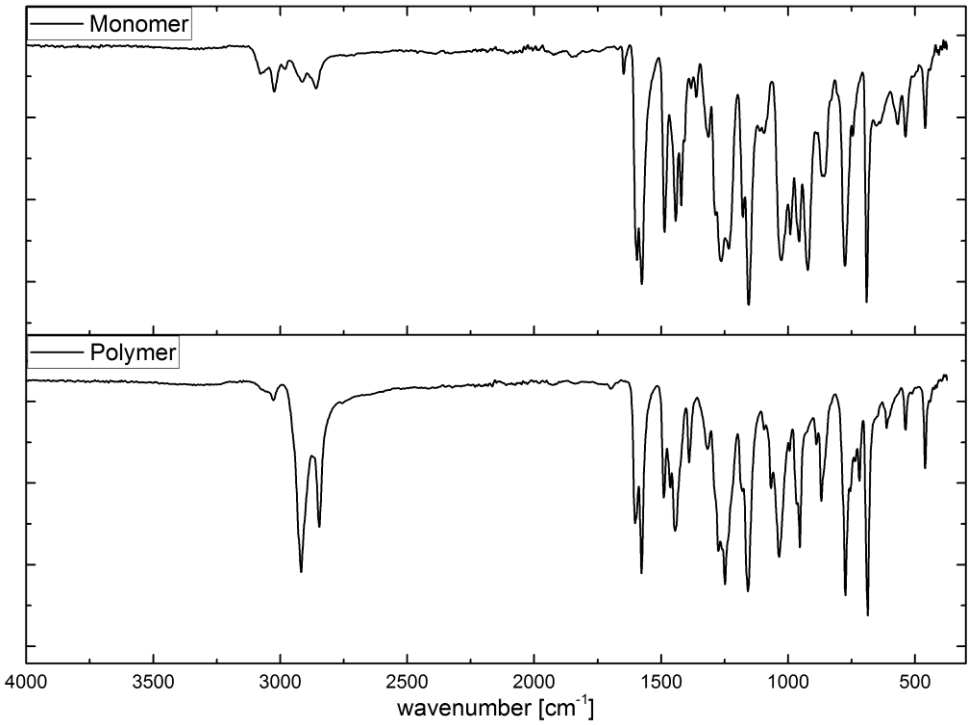
Thiol-ene polymer of (*E*)-1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (TE2)

IR (ATR)



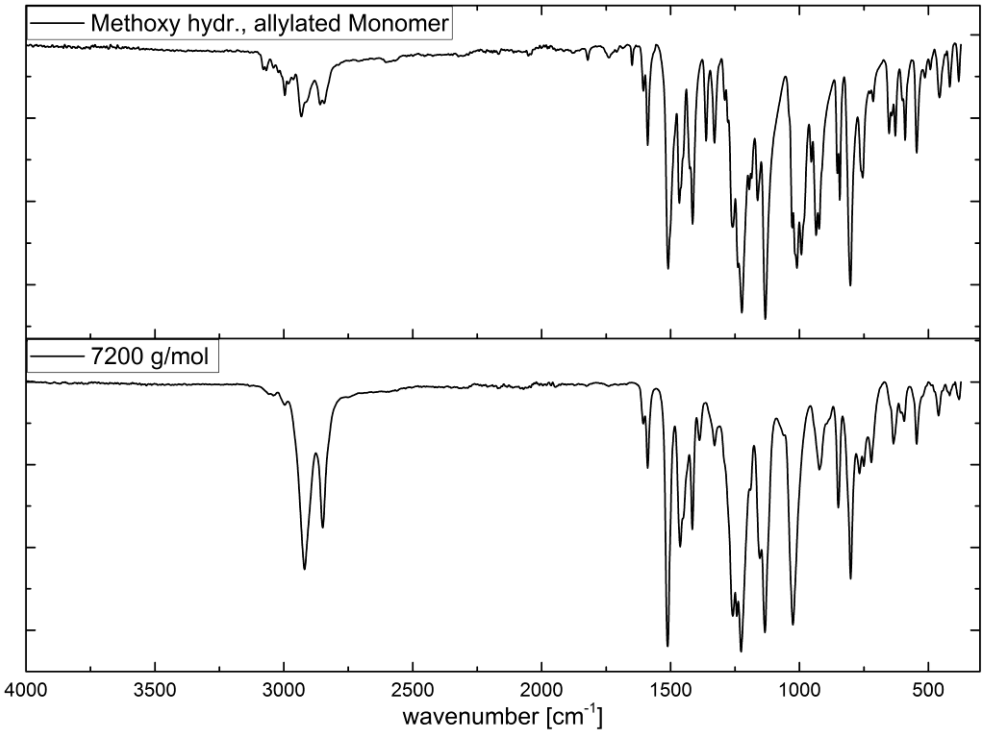
Thiol-ene polymer of (*E*)-1,2-bis(3-(allyloxy)-phenyl)ethene (TE4)

IR (ATR)



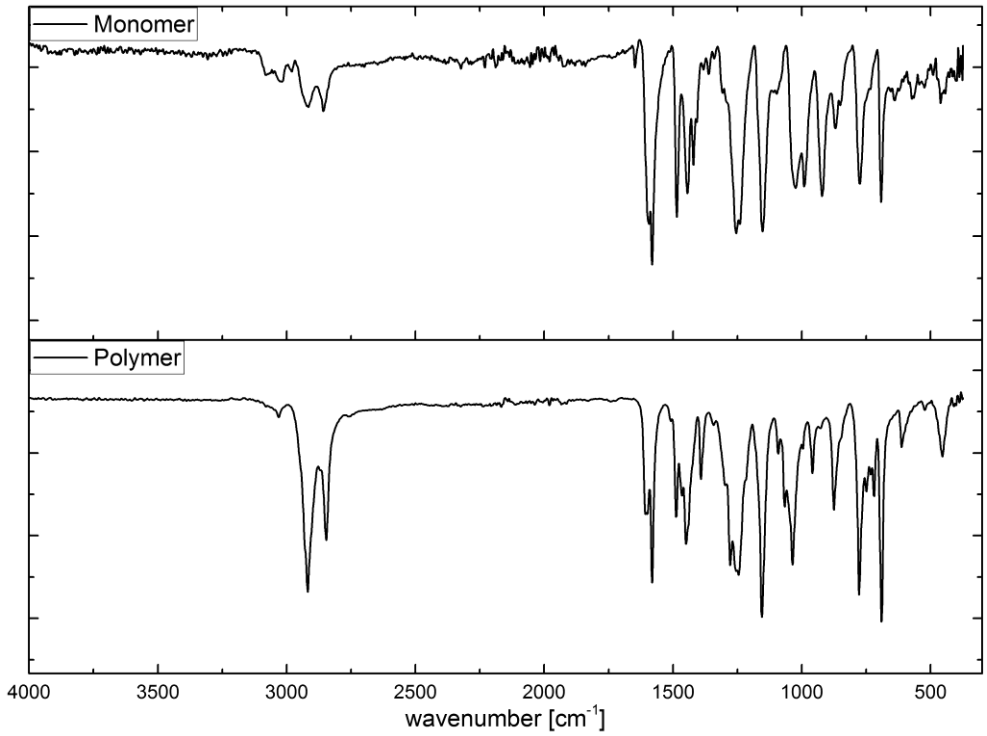
Thiol-ene polymer of 1,2-bis(4-(allyloxy)-3-methoxyphenyl)ethane (TE3)

IR (ATR)



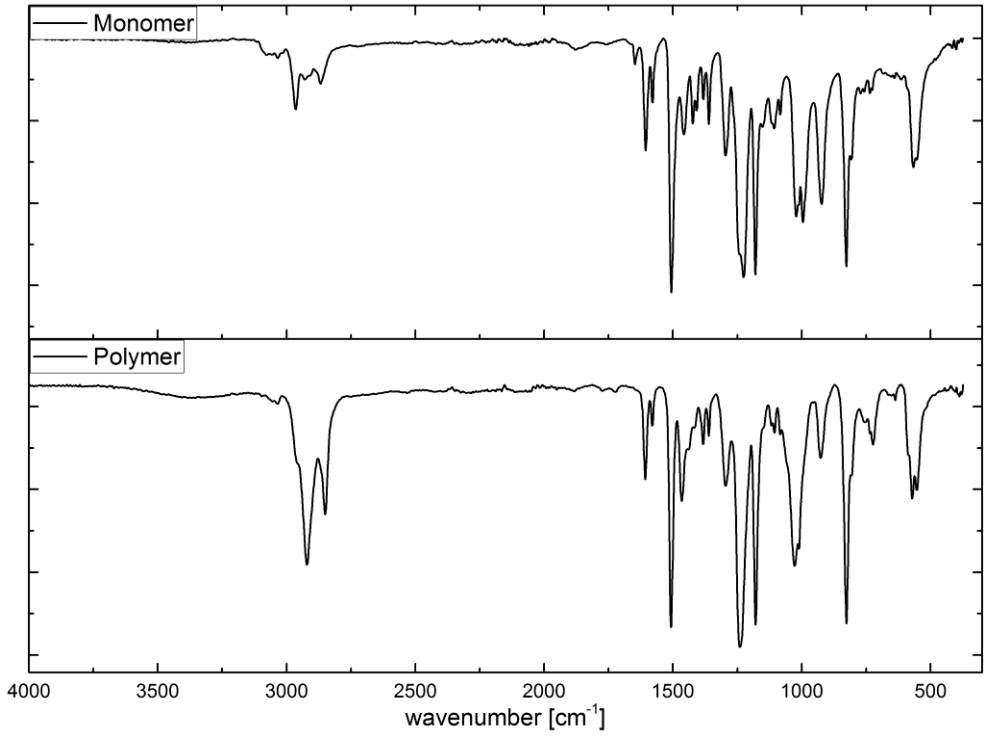
Thiol-ene polymer of 1,2-bis(3-(allyloxy)-phenyl)ethane (TE7)

IR (ATR)



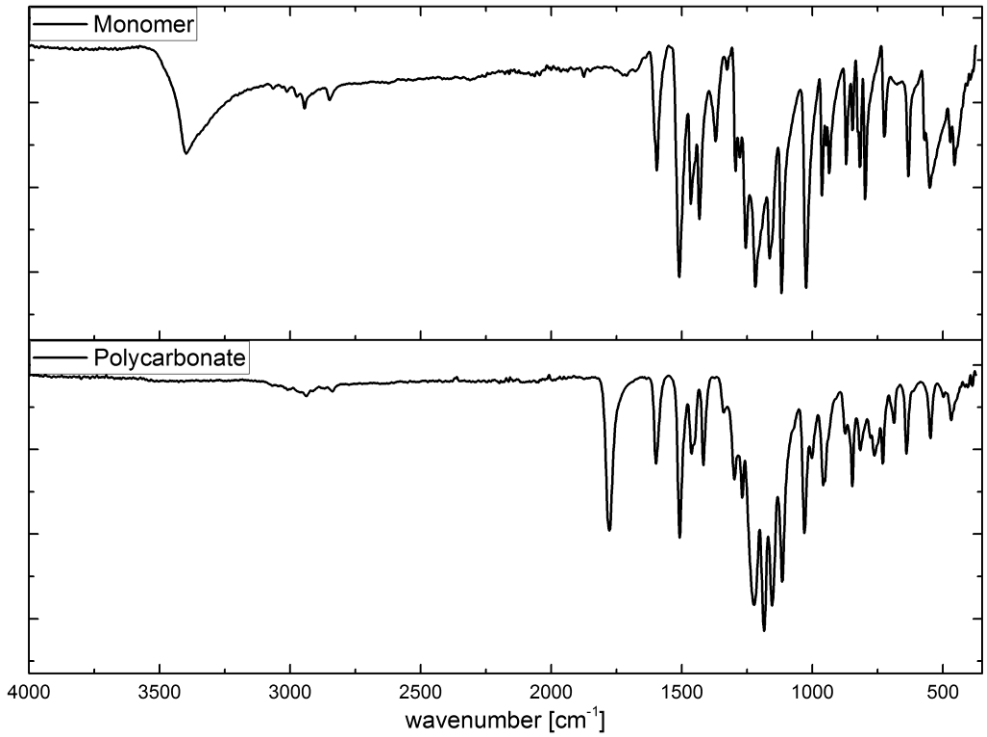
Thiol-ene polymer of 4,4'-(propane-2,2-diyl)bis((allyloxy)benzene) (TEBPA)

IR (ATR)



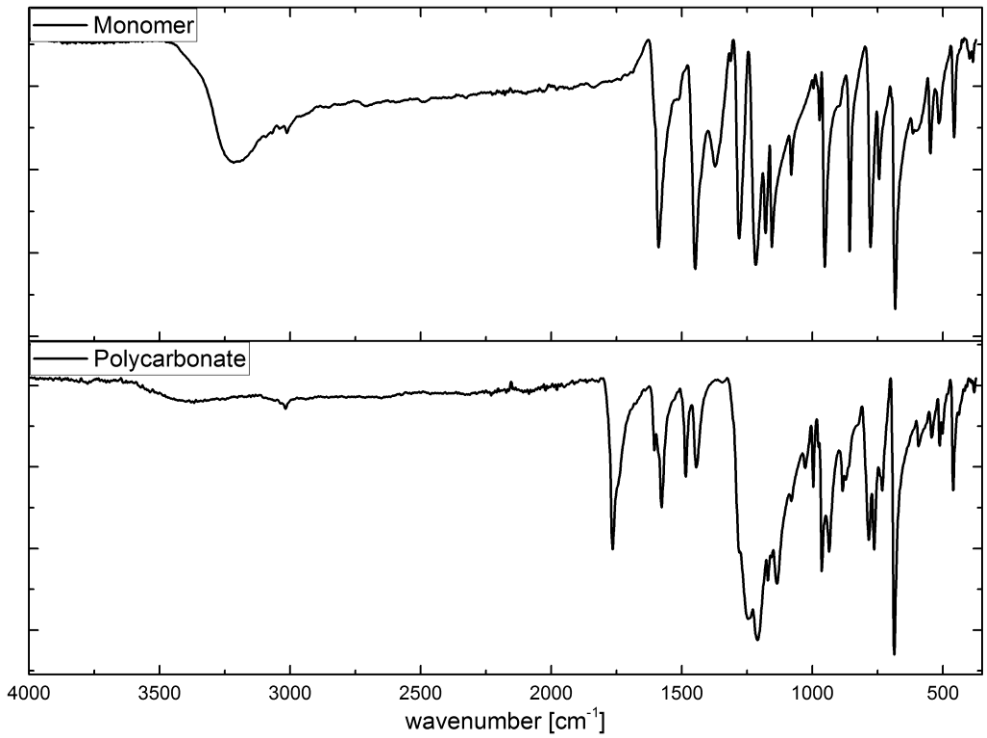
Polycarbonate of (*E*)-4,4'-dihydroxy-3,3'-dimethoxystilbene (PC2)

IR (ATR)



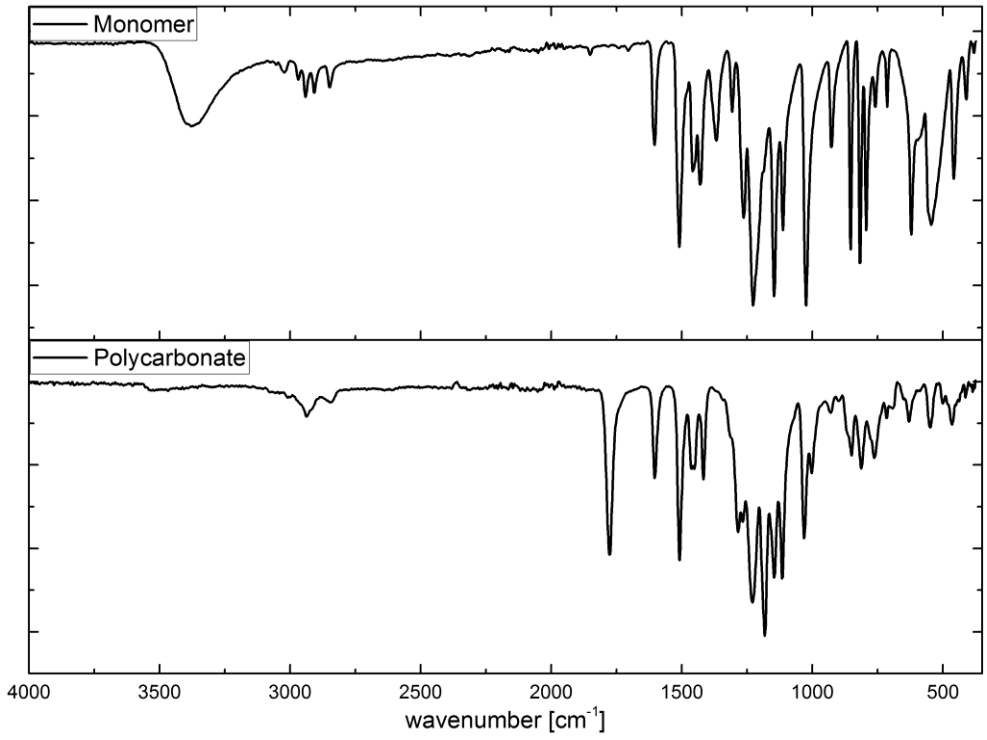
Polycarbonate of (*E*)-3,3'-hydroxystilbene (PC4)

IR (ATR)



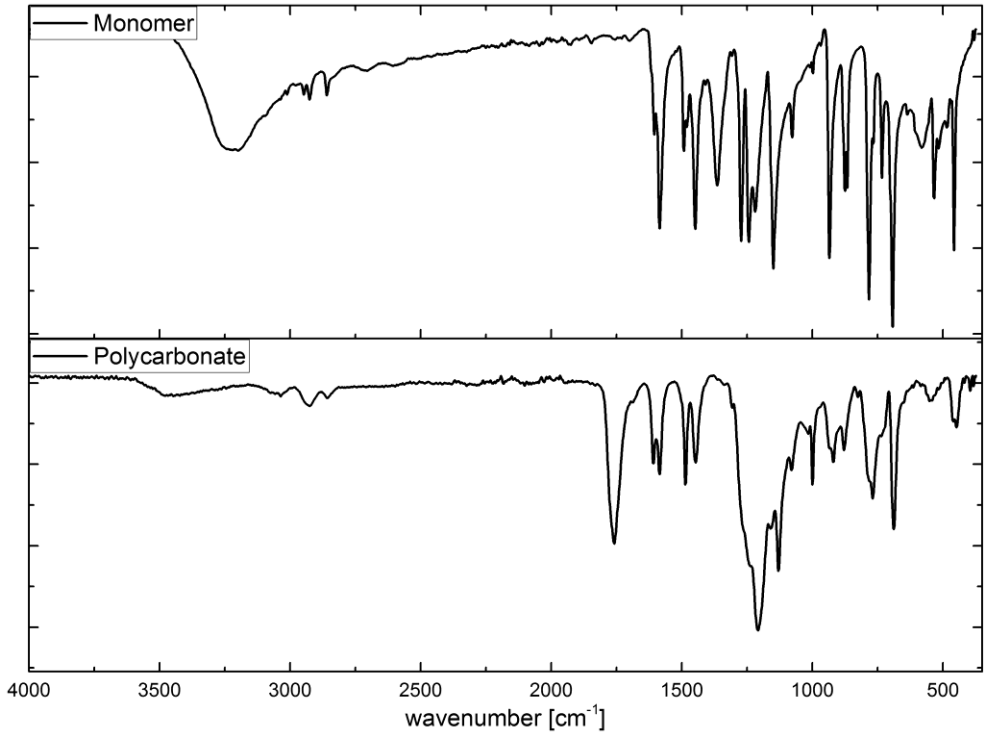
Polycarbonate of 4,4'-dihydroxy-3,3'-dimethoxy-diphenylethane (PC3)

IR (ATR)



Polycarbonate of 3,3'-dihydroxy-diphenylethane (PC7)

IR (ATR)



Polycarbonate of bisphenol A (PCBPA)

IR (ATR)