# Depolymerizable poly(benzyl ether)-based materials for selective room temperature recycling

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# Supporting Information

## Contents



## General Experimental

All reactions were performed in flame-dried glassware under a positive pressure of argon unless otherwise noted. All reagents used were purchased commercially and were used as received unless otherwise noted. Air-and moisture-sensitive liquids were transferred by syringe or stainless steel cannula. 2,6-Dimethyl-7-phenyl-1,4-benzoquinone methide (**7**) was synthesized by following the reported procedure.[1] Tetrahydrofuran (THF),

acetonitrile (MeCN), dichloromethane (DCM), toluene (PhMe), and *N*,*N*-dimethylformamide (DMF) were purified by the method developed by Pangborn et al.[2] Methanol (MeOH) was dried over activated 3Å molecular sieves for 24 h and then distilled from fresh activated 3Å molecular sieves. Deionized water was purified using a Millipore-purification system (Barnstead EASYpure® II UV/UF). Flash-column chromatography was performed as described by Still et al.,[3] employing silica gel (60-Å pore size, 32–63 μm, standard grade, Dynamic Adsorbents). Thin layer chromatography was carried out on Dynamic Adsorbents silica gel TLC (20 × 20 cm w/h, F-254, 250 μm).

## Instrumentation

Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded using Bruker 300, 360 or 400 MHz NMR spectrometers at 25 °C. Proton chemical shifts are express in parts per million (ppm, δ scale) and are referenced to tetramethylsilane ($(CH_3)_4Si$, 0.00 ppm) or to residual protium in the solvent ($CDCl_3$, δ 7.24 ppm, $CD_3OD$, 3.31 and 4.78 ppm, THF-$d_8$, 1.73 and 3.58 ppm, or $CD_2Cl_2$, 5.32 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad peak), integration, and coupling constant (*J*) in hertz. Carbon nuclear magnetic resonance ($^{13}$C NMR) were recorded using Bruker 300 or 400 MHz NMR spectrometers at 25 °C. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, 77.23 ppm, $CD_3OD$, 49.15 ppm, THF-$d_8$, 25.4 and 67.6 ppm, or $CD_2Cl_2$, 54.0 ppm).

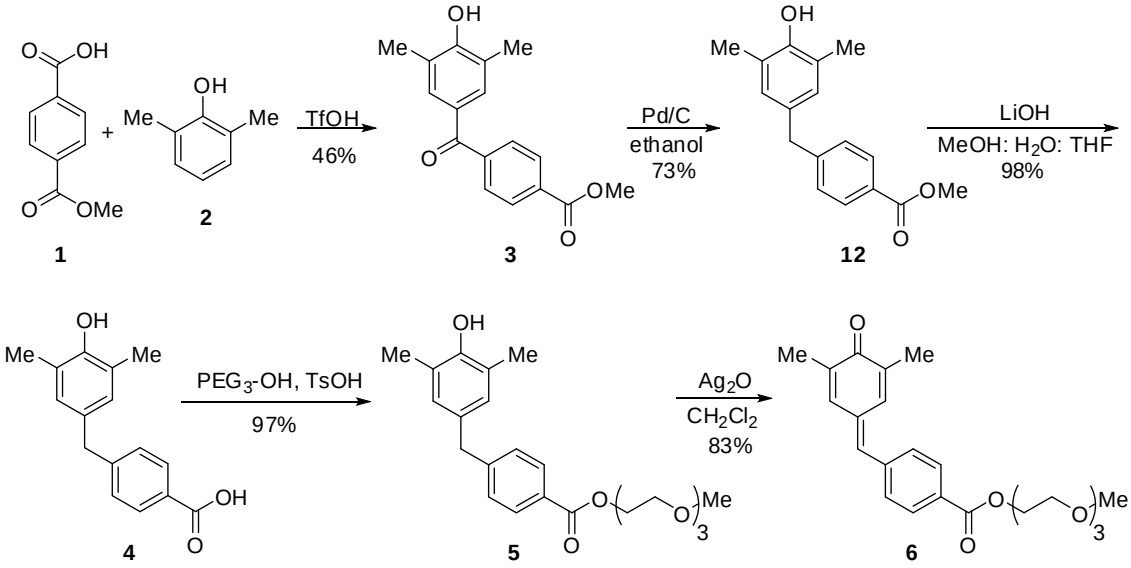
Gel permeation chromatography (GPC) analyses were performed using an Agilent Technologies 1200 GPC equipped with a refractive index detector, a Malvern Viscotek model 270 Dual Detector with right and low-angle light scattering, and either a Viscotek T-column (300 mm × 7.8 mm, CLM3012) and Agilent Resipore column (300 mm × 7.5 mm) in series or a single Agilent Resipore column (300 mm × 7.5 mm) using THF as the mobile phase (flow rate: 1 mL/min, 25 ℃). The GPC was calibrated using monodisperse polystyrene standards from Malvern.

Liquid chromatography coupled to a mass spectrometer (LCMS) data were obtained using an Agilent Technologies 1200 series analytical reversed-phase HPLC coupled to an Agilent Technologies 6120 quadrupole mass spectrometer. A portion of the HPLC stream was automatically injected into the mass spectrometer. The mass spectrometer (APCI) settings were as follows: gas temperature of 325 ℃, drying gas flow of 7 L/min, nebulizer pressure of 30 psig, and a voltage of 3000 V.

Contact angle measurements were performed using a Ramé-Hart automated goniometer equipped with a digital camera. Contact angles of water droplets (5 μL) on dried polymer films were analyzed using the software DROPimage Advanced.

Simultaneous differential scanning calorimetry and thermogravimetry analysis (SDT) was performed using a TA Instruments Q600 under $N_2$ atmosphere in open alumina pans. Samples were equilibrated to 40 ℃ then ramped to 500 ℃ at a rate of 5 ℃/min. The data was analyzed using the TA Instruments Universal Analysis V4.5 program.

## Synthesis of Monomers




**Scheme S1.** Synthesis of monomer **6**.

**Methyl 4-(4-hydroxy-3,5-dimethylbenzoyl)benzoate (3):**

Compound **1** (5.0 g, 28 mmol, 1 equiv) was dissolved in dry DCM (280 mL) and the resulting solution was cooled to 0 ℃. Oxalyl chloride (2.9 mL, 33.0 mmol, 1.2 equiv) was added dropwise to the 0 ℃ solution, followed by 1 mL of dry DMF. The reaction mixture was stirred for 1 h. The solution was concentrated under reduced pressure. To the resulting residue was added 2,6-dimethylphenol (3.36 g, 28 mmol, 1 equiv) and the mixture was cooled to 0 ℃. Trifluoromethanesulfonic acid (8.3 mL) was added in one portion and the solution was allowed to stir for 15 minutes. Subsequently the reaction was heated to 80 ℃ for 12 hours. The reaction mixture was cooled to 23 ℃ and then poured into ice water (150 mL). Ethyl acetate (300 mL) was added and the layers were separated. The organic layer was washed with brine (2 × 200 mL) then dried over sodium sulfate. The solids were removed using a fritted Büchner funnel and the resulting organic layer was concentrated under reduced pressure. The residue was purified by column

chromatography (elution with 30% EtOAc–hexanes) to afford **3** as an orange solid (3.2 g, 12.9 mmol, 46%). IR ($cm^{-1}$) 3250.0, 1718.9, 1631.3, 1582.9, 1266.2; $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 8.14 (d, 2 H, *J* = 9), 7.78 (d, 2 H, *J* = 9), 7.26 (s, 2 H), 5.25 (s, 1 H), 3.95 (s, 3 H), 2.29 (s, 6 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 195.4, 166.5, 157.1, 142.4, 132.6, 131.6, 129.5, 129.4, 129.0, 123.2, 52.5, 15.9; MS (TOF MS AP–, m/z): 283.1 ($M - H^+$); HRMS (TOF MS ES+) Calcd. for $C_{17}H_{17}O_4$ ($M + H^+$): 285.1127. Found: 285.1134.

**Methyl 4-(4-hydroxy-3,5-dimethylbenzyl)benzoate (12):**

Palladium (10% by weight on carbon powder) (0.68 g, 10% by weight of compound **3**) was added in one portion to a solution of compound **3** (6.8 g, 24 mmol, 1.0 equiv) in ethanol (239 mL) under an Ar atmosphere. The flask was evacuated and purged three times with $H_2$ gas. The reaction mixture was stirred vigorously for 4 h at 23 ℃ under an atmosphere of $H_2$ (balloon). The flask was evacuated, purged with argon, and the reaction mixture was filtered through a pad of celite. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (elution with 15% EtOAc–hexanes) to afford **12** as a light yellow solid (4.75 g, 17.5 mmol, 73%). IR ($cm^{-1}$) 3500.4, 1708.5, 1439.1, 1281.8; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.97 (d, 2 H, *J* = 8), 7.27 (d, 2 H, *J* = 8), 6.80 (s, 2 H), 4.78 (s, 1 H), 3.92 (s, 3 H), 3.91 (s, 2 H), 2.23 (s, 6 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 167.4, 150.9, 147.5, 131.7, 130.0, 129.2, 128.9, 127.9, 123.5, 52.1, 41.2, 16.0; MS (TOF MS AP–, m/z): 269.1 ($M - H^+$); HRMS (TOF MS ES–) Calcd. for $C_{17}H_{17}O_3$ ($M - H^+$): 269.1187. Found: 269.1151.

**4-(4-Hydroxy-3,5-dimethylbenzyl)benzoic acid (4):**

To a solution of **12** (4.75 g, 17.5 mmol, 1equiv) in methanol–THF (308 mL, 5: 1 respectively) at 0 ℃ was added a solution of lithium hydroxide monohydrate (3.7 g 88.0 mmol, 5.0 equiv) in water (44 mL) dropwise. The reaction was allowed to stir for 2 hours and was subsequently concentrated under reduced pressure. The residue was diluted with ethyl acetate (200 mL) and washed with 1 M aqueous sodium hydroxide (2 × 200 mL). The aqueous layers were combined and acidified to pH 1 by addition of concentrated aqueous hydrochloric acid. The aqueous layer was extracted with ethyl acetate (2 × 200 mL). The combined organic layers were dried over sodium sulfate, and the sodium sulfate was removed using a fritted Büchner funnel. The solvent was removed by rotary evaporation to afford compound **4** as a white solid (4.4g, 17.2 mmol, 98%), which was used without further purification. IR ($cm^{-1}$) 3420.5, 1691.3, 1422.6, 1280.2; $^{1}H$ NMR (400 MHz, $CD_3OD$): δ 7.93 (d, 2 H, *J* = 8), 7.28 (d, 2 H, *J* = 8), 6.77 (s, 2 H), 3.88 (s, 2 H), 2.18 (s, 6 H); $^{13}C$ NMR (100 MHz, $CD_3OD$): δ 168.6, 151.3, 147.3, 131.3, 129.5, 128.5, 128.4, 128.0, 124.4, 40.6, 15.2; MS (TOF MS AP–, m/z): 255.1 ($M - H^+$); HRMS (TOF MS ES–) Calcd. for $C_{16}H_{15}O_3$ ($M - H^+$): 255.1021. Found: 255.1034.

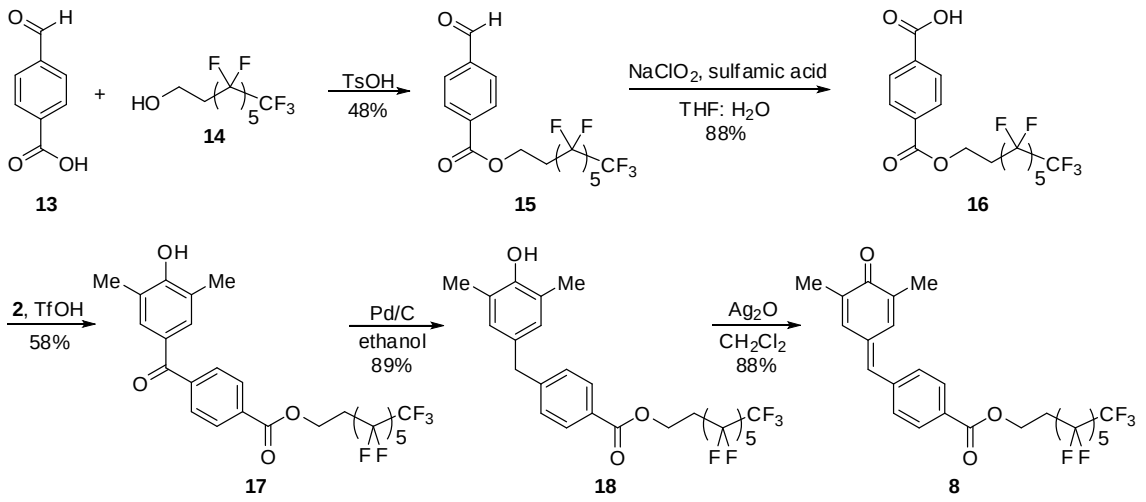
**2-(2-(2-Methoxyethoxy)ethoxy)ethyl-4-(4-hydroxy-3,5-dimethylbenzyl)benzoate (5):**

To a dry round bottom flask equipped with a Dean-Stark apparatus was added compound **4** (1.8 g, 6.7 mmol, 1 equiv) and triethylene glycol monomethyl ether (10.6 mL, 66.7 mmol, 10 equiv). *p*-Toluenesulfonic acid (0.29 g, 1.67 mmol, 0.25 equiv) was added and the solution was heated to 100 ℃ for 48 h. The solution was cooled to 23 ℃, diluted in ethyl acetate (200 mL) and washed with water (2 × 100 mL). The organic phase was

subsequently washed with brine (2 × 100 mL) then dried over soudium sulfate. The solids were removed using a fritted Büchner funnel and the resulting organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (elution with 20% EtOAc–hexanes) to afford **5** as a clear oil (2.7 g, 6.5 mmol, 97%). IR ($cm^{-1}$) 2871.2, 1715.7, 1270.3, 1097.9; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 2 H, *J* = 8), 7.26 (d, 2 H, *J* = 8), 6.79 (s, 2 H), 4.53 (s, 1 H), 4.48 (t, 2 H, *J* = 6), 3.91 (s, 2 H), 3.85-3.38 (overlap, ethylene glycol chain, 13 H), 2.22 (s, 6 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 166.4, 151.4, 147.6, 131.0, 129.7, 128.8, 127.6, 124.1, 71.8, 70.5, 69.1, 63.9, 58.8, 41.0, 16.3; MS (TOF MS AP–, m/z): 401.2 ($M - H^+$); HRMS (TOF MS ES–) Calcd. for $C_{23}H_{29}O_6$ ($M - H^+$): 401.1964. Found: 401.1946.

**2-(2-(2-methoxyethoxy)ethoxy)ethyl-4-((3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzoate (6):**

To a solution of **5** (1.8 g, 4.5 mmol, 1 equiv) in dry DCM (2.3 mL) was added silver (I) oxide (2.2 g, 9.5 mmol, 2.1 equiv). The reaction was allowed to stir 12 h after which the solution was filtered into a new vessel and concentrated under reduced pressure. Compound **6** (1.5 g, 3.7 mmol, 83%) was used without further purification. IR ($cm^{-1}$) 2875.5, 1716.4, 1615.7, 1271.6, 1099.6; $^{1}H$ NMR (360 MHz, $CDCl_3$): δ 8.16 (d, 2 H, *J* = 7.2), 7.54 (d, 2 H, *J* = 7.2), 7.48 (s, 1 H), 7.19 (s, 1 H), 7.10 (s, 1 H), 4.54 (t, 2 H, *J* = 3.6), 3.90-3.40 (overlap, ethylene glycol chain, 13 H), 2.11 (s, 3 H), 2.10 (s, 3 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 187.2, 166.2, 140.8, 138.4, 136.7, 133.7, 131.5, 130.7, 72.1, 70.8, 69.4, 64.3, 59.4, 16.9, 16.2; MS (TOF MS AP–, m/z): 400.2 ($M - H^+$); HRMS (TOF MS ES+) Calcd. for $C_{23}H_{29}O_6$ ($M + H^+$): 401.1964. Found: 401.1948.




**Scheme S2.** Synthesis of monomer **8**. Note: this monomer was prepared before the more efficient route was developed for monomer **6**.

### 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl-4-formylbenzoate (15):

To a dry round bottom flask equipped with a Dean-Stark apparatus was added compound **13** (2.9 g, 19.5 mmol, 1 equiv), **14** (8.5 mL, 39.0 mmol, 2 equiv) and dry PhMe (13 mL). *p*-Toluenesulfonic acid (0.28 g, 1.6 mmol, 0.1 equiv) was added and the solution was heated to 100 ℃ for 48 h. The solution was cooled to 23 ℃, diluted in ethyl acetate (200 mL) and washed with water (2 × 100 mL). The organic phase was subsequently washed with brine (2 × 100 mL) then dried over soudium sulfate. The solids were removed using a fritted Büchner funnel and the resulting organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (elution with 7.5% EtOAc–hexanes) to afford **15** as a white solid (4.6 g, 9.4 mmol, 48%). IR ($cm^{-1}$) 2972.1, 1714.3, 1692.8, 1076.2; $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 10.11 (s, 1 H), 8.20 (d, 2 H, $J$ = 6), 7.97 (d, 2 H, $J$ = 6), 4.68 (t, 2 H, $J$ = 6), 2.65 (m, 2 H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 191.4, 165.0, 139.4, 134.3, 130.2, 129.5, 129.4, 118.4, 117.0, 115.7, 113.2, 110.7, 108.2, 57.3, 30.7, 30.5, 30.3; MS (TOF MS AP–, m/z): 496.0 ($M - H^+$); HRMS (TOF MS EI+) Calcd. for $C_{16}H_9O_3F_{13}$ ($M + H^+$): 496.0344. Found: 496.0335.

**4-(((3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)oxy)carbonyl)benzoic acid (16):**

Compound **15** (5.5 g, 11.1 mmol, 1 equiv) was dissolved in THF (22 mL) and water (111 mL). To that solution was added sodium chlorite (5.0 g, 55 mmol, 5 equiv) and sulfamic acid (5.3 g, 55 mmol, 5 equiv). After 4 hours the solution was extracted with ethyl acetate, dried to silica and purified by column chromatography (elution with 10% EtOAc–hexanes) to afford **16** as a white solid (5.7 g, 9.8 mmol, 88%). IR ($cm^{-1}$) 2970.2, 1716.9, 1686.5, 1237.5, 1182.1; $^{1}H$ NMR (400 MHz, THF-$d_8$): δ 11.75 (br s, 1 H), 8.14 (s, 4 H), 4.69 (t, 2 H, J = 8), 2.82 (m, 2 H); $^{13}C$ NMR (75 MHz, THF-$d_8$): δ 164.4, 163.2, 133.6, 131.8, 129.0, 128.8, 128.5, 128.2, 128.0, 127.7, 127.4, 126.9, 117.2, 114.2, 109.8, 55.5, 28.3; MS (TOF MS AP–, m/z): 511.0 ($M - H^+$); HRMS (TOF MS ES–) Calcd. for $C_{16}H_8O_4F_{13}$ ($M - H^+$): 511.0215. Found: 511.0254.

**3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl-4-(4-hydroxy-3,5-dimethylbenzoyl)benzoate (17):**

Compound **16** (4.3 g, 8.4 mmol, 1 equiv) was dissolved in dry DCM (144 mL) and the resulting solution was cooled to 0 ℃. Oxalyl chloride (3.7 mL, 43.0 mmol, 5.0 equiv) was added dropwise to the 0 ℃ solution, followed by 0.5 mL of dry DMF. The reaction mixture was stirred for 1 h. The solution was concentrated under reduced pressure. To the resulting residue was added compound **2** (1.0 g, 8.4 mmol, 1 equiv) and the mixture was cooled to 0 ℃. Trifluoromethanesulfonic acid (5.6 mL) was added in one portion and the solution was allowed to stir for 15 minutes. Subsequently the reaction was heated to 80 ℃ for 12 hours. The reaction mixture was cooled to 23 ℃ and then poured into ice water (150 mL). Ethyl acetate (300 mL) was added and the layers were separated. The

organic layer was washed with brine (2 × 200 mL) then dried over sodium sulfate. The solids were removed using a fritted Büchner funnel and the resulting organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (elution with 15% EtOAc–hexanes) to afford **17** as a pale yellow solid (3.0 g, 4.9 mmol, 58%). IR ($cm^{-1}$) 3434.0, 1719.5, 1580.6, 1230.7, 1181.2, 1120.1; $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 8.17 (d, 2 H, *J* = 9), 7.82 (d, 2 H, *J* = 9), 7.53 (s, 2 H), 6.21 (s, 1 H), 4.71 (t, 2 H, *J* = 6), 2.68 (m, 2 H), 2.31 (s, 6 H); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 196.0, 166.0, 158.0, 153.7, 143.2, 132.3, 132.1, 130.1, 129.9, 129.7, 129.1, 123.9, 118.3, 115.0, 111.4, 108.4, 57.7, 31.2, 30.9, 16.4; MS (TOF MS AP–, m/z): 615.1 ($M - H^+$); HRMS (TOF MS ES–) Calcd. for $C_{24}H_{16}O_4F_{13}$ ($M - H^+$): 615.0841. Found: 615.0833.

**3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl-4-(4-hydroxy-3,5-dimethylbenzyl)benzoate (18):**

Palladium (10% by weight on carbon powder) (0.3 g, 10% by weight of compound **17**) was added in one portion to a solution of **17** (3.0 g, 4.9 mmol, 1.0 equiv) in ethanol (48.7 mL) under an Ar atmosphere. The flask was evacuated and purged three times with $H_2$ gas. The reaction mixture was stirred vigorously for 4 h at 23 °C under an atmosphere of $H_2$ (balloon). The flask was evacuated, purged with Ar, and the reaction mixture was filtered through a pad of celite. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash column chromatography (elution with 10% EtOAc–hexanes) to afford compound **18** as a white solid (2.6 g, 4.4 mmol, 89%). IR ($cm^{-1}$) 3444.5, 2968.8, 1712.6, 1201.5, 1139.9; $^{1}H$ NMR (300 MHz, $CDCl_3$): δ 8.00 (d, 2 H, *J* = 6), 7.31 (d, 2 H, *J* = 6), 6.83 (s, 2 H), 4.71 (s, 1 H), 4.66 (t, 2 H, *J* = 9), 3.94 (s, 2 H),

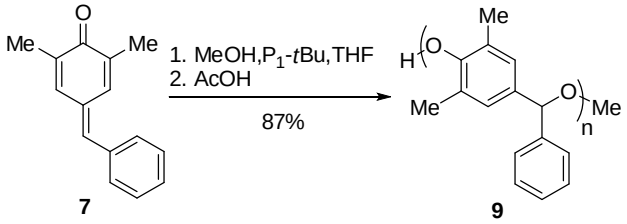
2.64 (m, 2 H), 2.25 (s, 6 H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 166.7, 151.2, 148.3, 132.0, 130.7, 130.4, 130.2, 129.8, 129.7, 129.4, 129.3, 129.1, 127.6, 123.7, 120.0, 118.0, 115.3, 111.4, 109.0, 57.1, 41.6, 31.3, 31.0, 30.7, 16.3; MS (TOF MS AP–, m/z): 601.1 ($M - H^+$); HRMS (TOF MS ES+) Calcd. for $C_{24}H_{20}O_3F_{13}$ ($M + H^+$): 603.1205. Found: 603.1197.

**3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 4-((3,5-dimethyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzoate (8):**

To a solution of **18** (2.5 g, 4.2 mmol, 1 equiv) in dry DCM (42 mL) was added silver (I) oxide (2.0 g, 8.7 mmol, 2.1 equiv). The reaction was allowed to stir 12 h after which the solution was filtered into a new vessel and concentrated under reduced pressure. Compound **8** (2.2 g, 3.7 mmol, 88%) was used without further purification. IR ($cm^{-1}$) 2922.4, 1717.2, 1608.8, 1187.8, 1119.3; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, 2 H, *J* = 4), 7.52 (d, 2 H, *J* = 4), 7.44 (s, 1 H), 7.14 (s, 1 H), 7.05 (s, 1 H), 4.66 (t, 2 H, *J* = 6), 2.63 (m, 2 H), 2.06 (s, 3 H), 2.05 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 187.2, 165.4, 140.4, 140.2, 138.4, 138.3, 136.5, 133.2, 130.7, 130.0, 129.8, 129.6, 120.0, 117.6, 116.0, 113.1, 111.0, 108.4, 57.0, 30.6, 16.8, 16.1; MS (TOF MS AP–, m/z): 600.1 ($M - H^+$); HRMS (TOF MS ES+) Calcd. for $C_{24}H_{18}O_3F_{13}$ ($M + H^+$): 601.1048. Found: 601.1042.

## Synthesis of Polymers

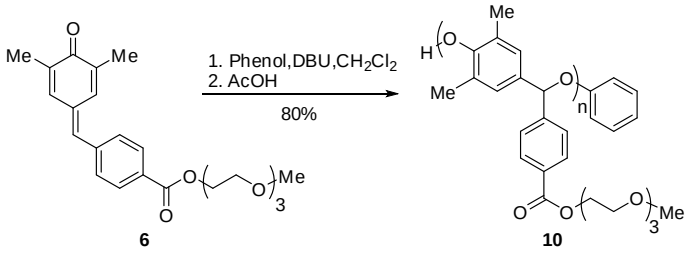
**Polymer 9:**




**Scheme S3.** Synthesis of polymer **9**.

(**9**, $M_n$ = 47.5 kDa). This polymer was prepared by following the reported procedure,[1] but with a minor modification. Compound **7** (1.58 g, 7.51 mmol, 1 equiv) was added to a flame-dried flask, which was backfilled with an Ar atmosphere. Anhydrous THF (7.5 mL, 1 M) was added to the flask. The solution was degassed via the freeze-pump-thaw method three times, backfilling with Ar on the final cycle. Dry MeOH (15.2 μL, 0.38 mmol, 0.05 equiv) was added in one portion at –20 °C, immediately followed by addition of $P_1$-*t*Bu phosphazene base (0.11 mL, 0.38 mmol, 0.05 equiv). After stirring for 2 h, the reaction mixture was quenched by addition of acetic acid (0.43 mL, 7.51 mmol, 1 equiv). The reaction mixture was stirred for 15 h at rt. The resulting polymer was precipitated in MeOH (50 mL) at 0 °C. The solvent was drained using a polymer washer.[4] The polymer was purified by dissolving in THF and precipitating by addition of MeOH (the process was repeated twice). Polymer **9** was isolated as a white powder (20 mg, 87%). $M_n$ = 47.5 kDa, $M_w$ = 66.4 kDa, PDI = 1.40. $^1$H NMR (360 MHz, $CD_2Cl_2$): δ 7.34 (br m, 5 H), 6.91 (br m, 2 H), 5.66 (br s, 1 H), 1.88 (br s, 6 H); $^{13}$C NMR (100 MHz, $CD_2Cl_2$): δ 155.1, 142.0, 136.7, 131.1, 128.1, 127.2, 85.7, 17.0.

**Polymer 10:**

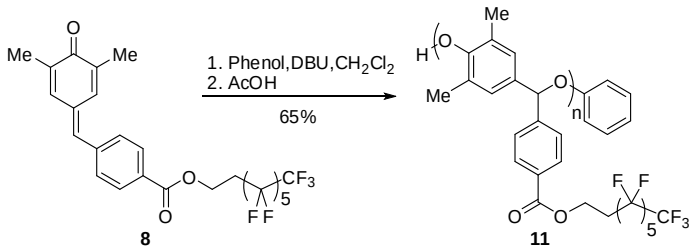



**Scheme S4.** Synthesis of polymer **10**.

(**10**, $M_n$ = 38.0 kDa). A solution of **6** (1.5 g, 3.8 mmol, 1 equiv) in dry DCM (3.8 mL) was cooled to –28 ℃. To that was added a 0.1 M solution of 1,8-Diazabicyclo[5.4.0]undec-7-ene and phenol (37.5 μL, 0.001 equiv) in dry DCM in one portion. The reaction was allowed to stir for 14 h. Subsequently *i*-butyric acid was added and the reaction stirred for an addition 12 h. The solution was then warmed to room temperature and the resulting polymer was precipitated by addition to water (40 mL) at 23 ℃. $N_2$ was bubbled through this solution for 15 min and the solvent was drained. The resulting polymer was dried under vacuum (1.1 mmHg) for 12 h. Subsequently the polymer was redissolved in a 3:1 solution of acetonitrile to water respectively (15 mL). The solution was then sealed in dialysis tubing and allowed to stir in a solution of 3:1 acetonitrile and water (1 L) for 12 h. The solution containing polymer **10** was diluted with ethyl acetate (100 mL), washed with brine (2 × 50 mL) and dried over sodium sulfate. The solids were removed using a fritted Büchner funnel and the resulting organic layer was concentrated under reduced pressure to afford polymer **10** (1.2 g, 80%) as a light yellow solid. $M_n$ = 38.0 kDa, $M_w$ = 56.4 kDa, PDI = 1.49; $^1$H NMR (300 MHz, $CDCl_3$): δ 8.01 (br t, 2 H, *J* = 6), 7.45 (br d, 2 H, *J* = 6), 6.84 (br d, 2 H, *J* = 18), 5.63 (br s, 1 H), 4.47 (br s, 2 H), 3.83-3.34 (overlap, ethylene glycol chain, 13 H), 1.83 (s, 6 H); $^{13}$C

NMR (75 MHz, $CDCl_3$): δ 166.7, 155.4, 147.4, 136.6, 131.7, 129.6, 127.7, 85.8, 72.3, 71.7, 71.0, 70.3, 69.6, 64.5, 59.4, 17.6.

**Polymer 11:**




**Scheme S5.** Synthesis of polymer **11**.

(**11**, $M_n$ = 5.7 kDa). A solution of **8** (1.2 g, 2.0 mmol, 1 equiv) in dry DCM (2.0 mL) was cooled to -28 ℃. To that was added a 0.1 M solution of 1,8-Diazabicyclo[5.4.0]undec-7-ene and phenol (20.0 μL, 0.001 equiv) in dry DCM in one portion. The reaction was allowed to stir for 14 h. Subsequently *i*-butyric acid was added and the reaction stirred for an addition 12 h. The solution was then warmed to room temperature and the resulting polymer was precipitated by addition to MeOH (40 mL) at 23 ℃. $N_2$ was bubbled through this solution for 15 min and the solvent was drained. The resulting polymer was dried under vacuum (1.1 mmHg). Subsequently the polymer was redissolved in THF (2 mL) and precipitated in methanol. The redissolution in THF followed by precipitation in methanol occurred two more times to afford polymer **11** (0.78 g, 65%) as a white solid. $M_n$ = 5.7 kDa, $M_w$ = 7.1 kDa, PDI = 1.24; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.00 (br s, 2 H, *J* = 6), 7.47 (br d, 2 H, *J* = 4), 6.85 (br d, 2 H, *J* = 16), 5.66 (br s, 1 H), 4.63 (br s, 2 H), 3.77 (br s, 0.33 H), 2.61 (br s, 2 H), 1.85 (s, 3 H), 1.84 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.9, 155.1, 147.3, 136.1, 131.3, 129.8, 129.5, 128.7, 127.2, 119.3, 117.5, 115.8, 113.8, 110.3, 108.4, 85.4, 68.0, 57.0, 30.5, 17.1.

## General Procedure for Base-Mediated Depolymerization of the Functionalized Poly(benzyl ethers)

A portion of polymer (5 mg for polymer **9**, 4.3 mg for polymer **10**, 4.0 mg for polymer **11**) was dissolved in 925 µL of solvent (DCM for polymer **9** and **10**, and α,α,α-trifluorotoluene for polymer **11**). To that solution was added 75 µL of DBU, affording a 0.5 M solution. The resulting depolymerization was monitored by GPC analysis.

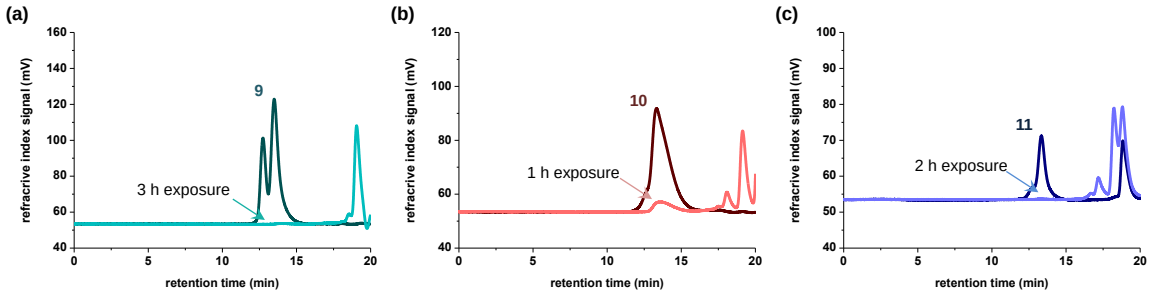



**Figure S1.** Change in GPC traces of (a) polymer **9**, (b) **10**, and (c) **11** before and after exposure to 0.5 M DBU for 3 h, 1 h, and 2 h, respectively.

## Procedure for Molding and Solid-State Depolymerization of Polymer 10

A mold in the shape of a U was cut into a silicon pad on top of a glass slide. To this mold was added polymer **10** and both the material and the mold were heated to 90 ℃ for 10 min. Subsequently the polymer was pressed into the mold using a PTFE rod. Another portion of material was added and the system was heated to 90 ℃ for 10 min and then pressed. The material was allowed to cool to room temperature and the U was removed from the mold. Two U-shaped materials were fabricated using this method. One of the them (weighing 80 mg) was placed in a solution of DBU (0.5 M) in 50 mL of 3:1 $H_2O$–*i*-PrOH and the other U (weighing 88 mg) was placed in 50 mL of 3:1 $H_2O$–*i*-PrOH without DBU. In addition to the molded U, a poly(ethylene) "P" and a poly(propylene) "S" were placed in the solution.

## Procedure for Measuring Contact Angles of Polymer 11

The polymer (20 mg) was dissolved in 200 µL of THF and deposited onto a vertical strip of paper (1 cm × 5 cm surface area). The remaining solution was allowed to drip off. The paper strip was dried under reduced pressure for 12 h and then adhered to a glass slide using double-sided tape. The surface contact angle of each film was measured three times using a goniometer.

**Table S1.** Contact angle data from polymer **11** and **9** for control.

| Polymer | Trial 1 | Trial 2 | Trial 3 | Average | Standard deviation |
|---|---|---|---|---|---|
| **11** | 129.8 ° | 129.6 ° | 132.8 ° | 130.7 ° | 1.8 ° |
| **9** | 97.7 ° | 98.2 ° | 98.7 ° | 98.2 ° | 0.5 ° |

## Procedure for Polymer Recovery from a Mixture of Poly(styrene) and Polymer 11

Equal portions of poly(styrene) (50 mg) and polymer **11** (50 mg) were dissolved in 975 μL of THF. To the solution was added 75 μL of DBU, resulting in a 0.5 M solution. After 2 h, the remaining polymer was precipitated in MeOH (40 mL) at 23 °C. $N_2$ was bubbled through this solution for 15 min and the solvent was drained. The resulting polymer was dried under vacuum (1.1 mmHg). Subsequently the polymer was redissolved in THF (1 mL) and precipitated in MeOH. The remaining polymer was collected. The recovered polymer was proven to be pure poly(styrene) (analyzed by NMR and GPC) and weighed 30 mg corresponding to a 60% recovery.

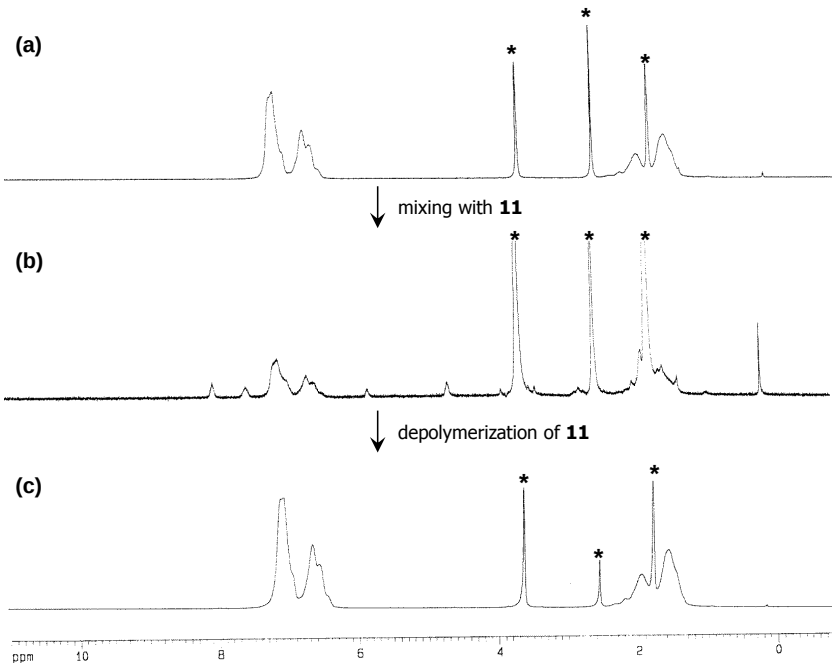
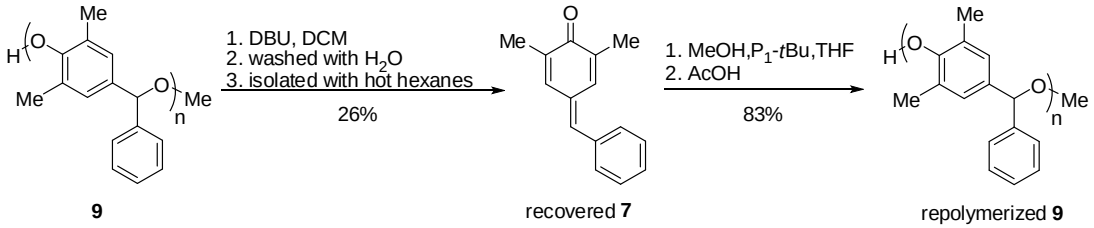



**Figure S2.** $^1$H NMR spectra of (a) poly(styrene), (b) a mixture of poly(styrene) and polymer **11**, and (c) recovered poly(styrene) after the mixture was treated with 0.5 M DBU for 2 h. Peaks at asterisks are from THF-$d_8$.

## Recycling Quinone Methide Monomer 7 After Depolymerization




**Scheme S6.** Recycling procedures for polymer **9**.

To recover the quinone methide monomer **7**, polymer **9** (1.34 g) was dissolved in 50 mL of dry DCM and treated with DBU (0.94 mL, approx. 225 equiv) at rt. After stirring for 3 h at rt, the yellowish solution was washed with water (2 × 100 mL), dried over sodium sulfate, the solids were removed by filtration, and the resulting solution was concentrated. The resulting yellowish solid was dissolved in hot hexanes and filtered to remove an insoluble material. The filtrate was concentrated and dried under vacuum. The recovered monomer was used for the next polymerization without further purification (26%).

Repolymerization was conducted by following the same procedure for polymer **9**. The recovered monomer **7** (0.1 g, 0.48 mmol, 1 equiv), MeOH as an initiator (0.96 μL, 0.02 mmol, 0.05 equiv), $P_1$-*t*Bu base (7.27 μL, 0.02 mmol, 0.05 equiv), and acetic acid as an end cap (0.03 mL, 0.48 mmol, 1 equiv) were used to afford repolymerized **9** (83%). $M_n$ = 36.8 kDa, $M_w$ = 49.6 kDa, PDI = 1.35; $^1$H NMR (400 MHz, $CD_2Cl_2$): δ 7.31 (br m, 5 H), 6.90 (br m, 2 H), 5.65 (br s, 1 H), 1.87 (br s, 6 H).

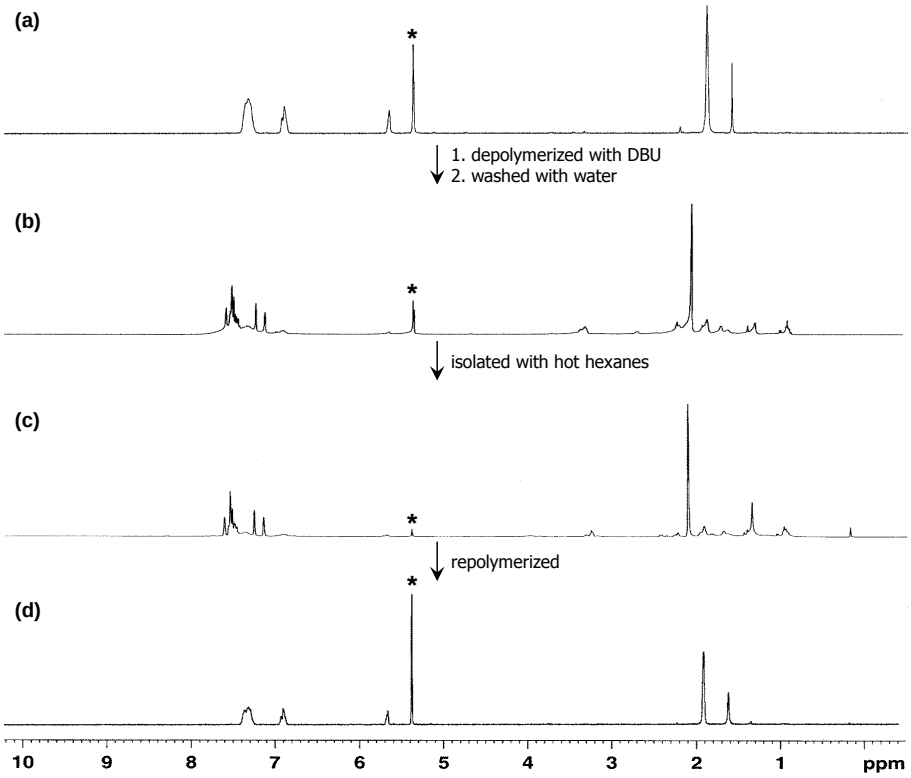



**Figure S3.** $^{1}$H NMR spectra of (a) pristine polymer **9**, (b) after depolymerization with DBU and following washing with water, (c) after isolation with hot hexanes, and (d) after repolymerization. Peaks at asterisks are from $CD_2Cl_2$.

## References


1. Olah, M. G.; Robbins, J. S.; Baker, M. S.; Phillips, S. T. *Macromolecules* **2013**, *46*, 5924–5928.
2. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
3. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
4. Seo, W.; Phillips, S. T. *J. Am. Chem. Soc.* **2010**, *132*, 9234–9235.

# NMR Spectra

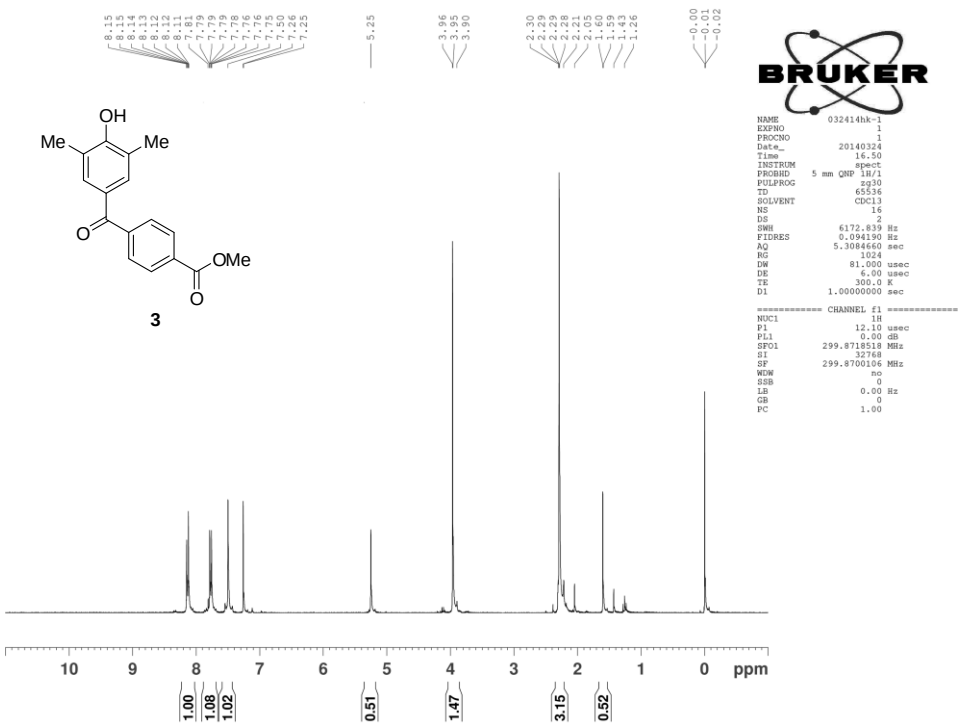



**Figure S4.** $^{1}$H NMR spectrum of **3**.

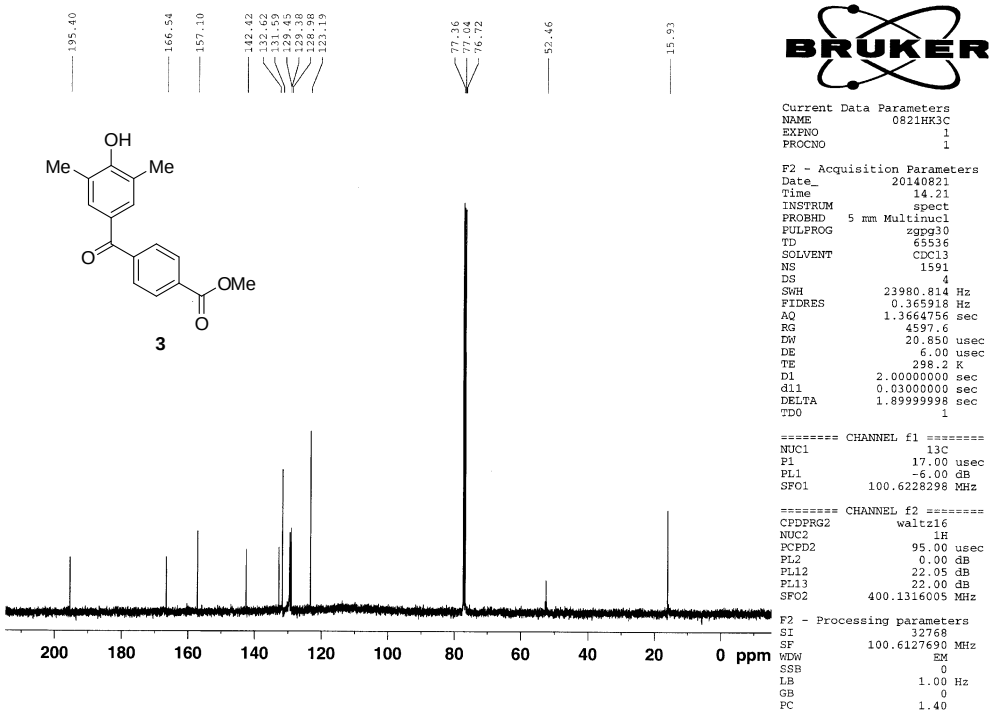



**Figure S5.** $^{13}$C NMR spectrum of **3**.

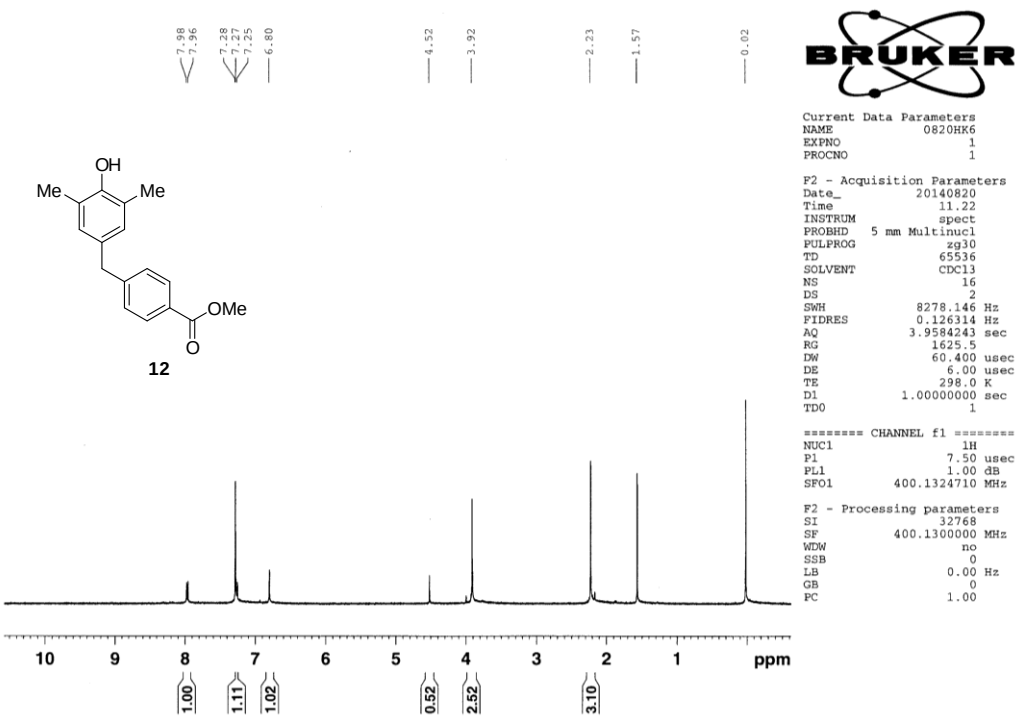



**Figure S6.** $^{1}$H NMR spectrum of **12**.

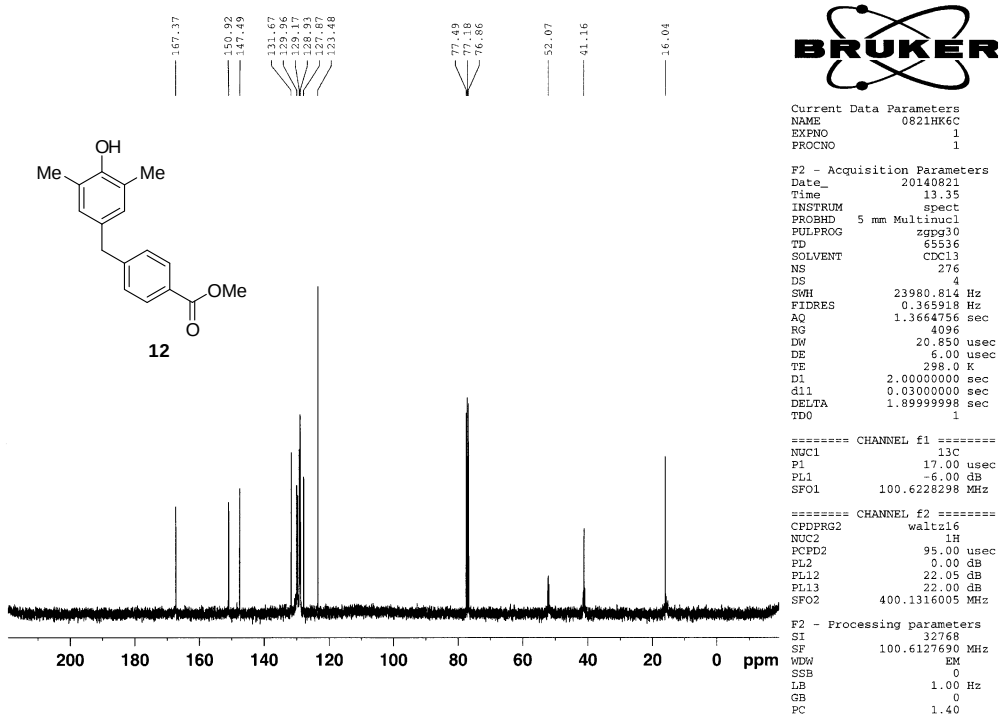



**Figure S7.** $^{13}$C NMR spectrum of **12**.

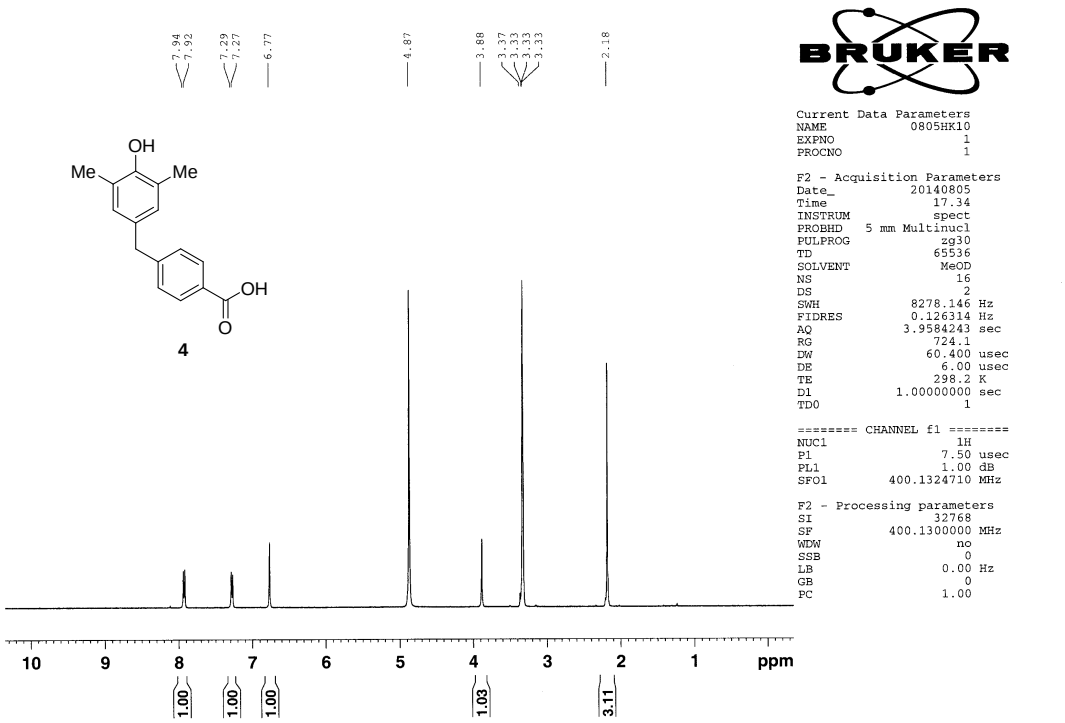



**Figure S8.** $^{1}$H NMR spectrum of **4**.

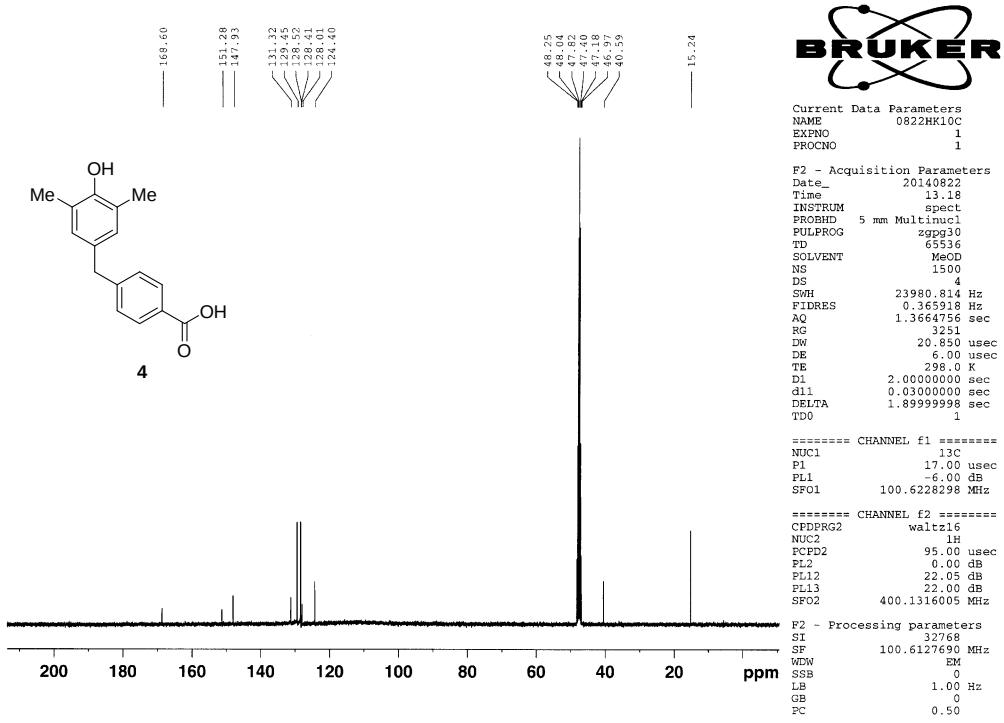



**Figure S9.** $^{13}$C NMR spectrum of **4**.

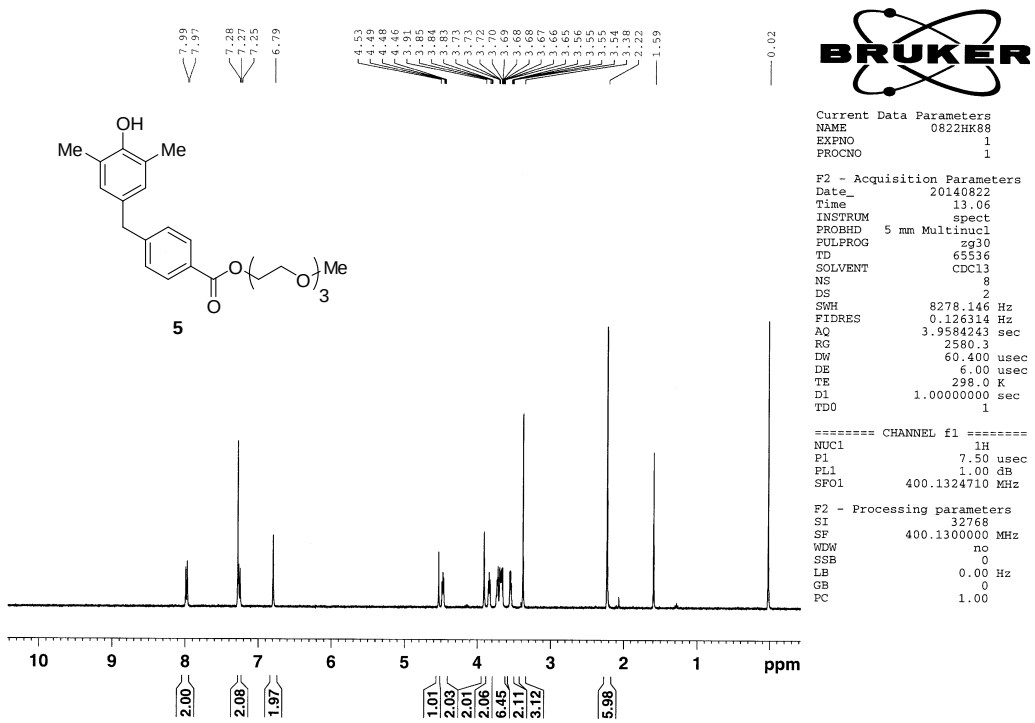



**Figure S10.** $^{1}$H NMR spectrum of **5**.

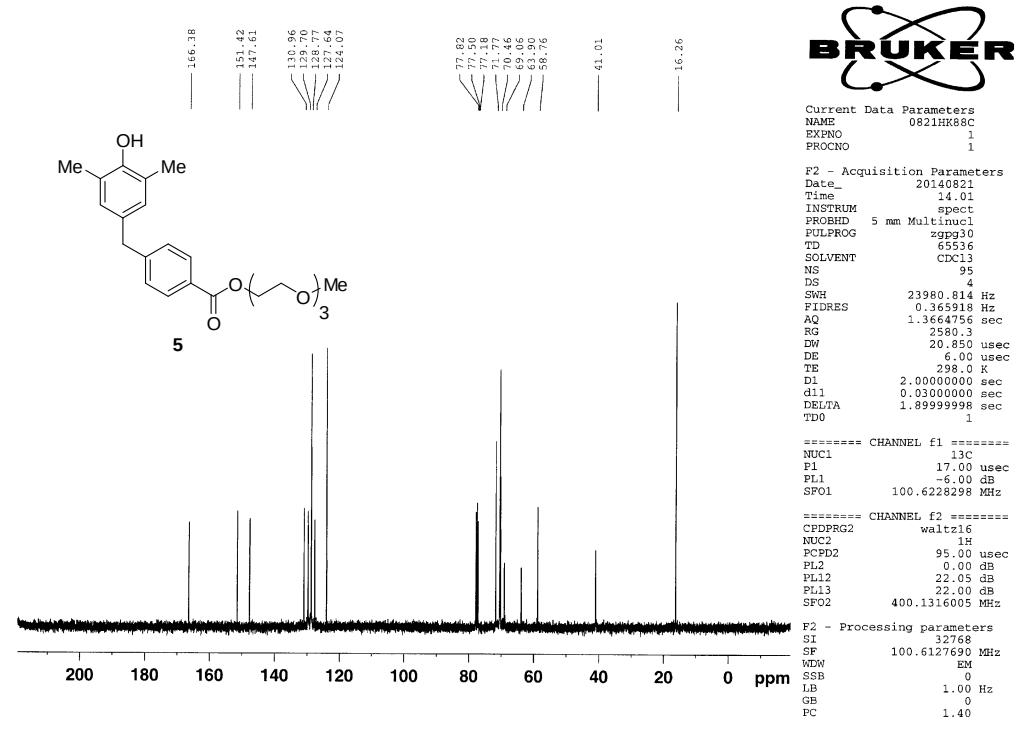



**Figure S11.** $^{13}$C NMR spectrum of **5**.

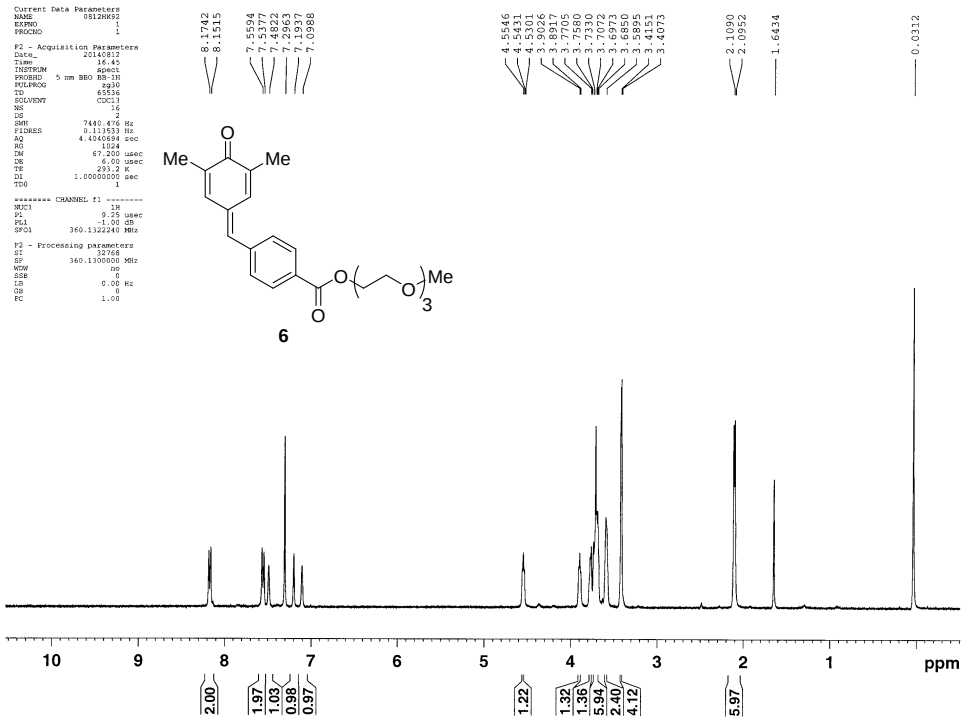



**Figure S12.** $^{1}$H NMR spectrum of **6**.

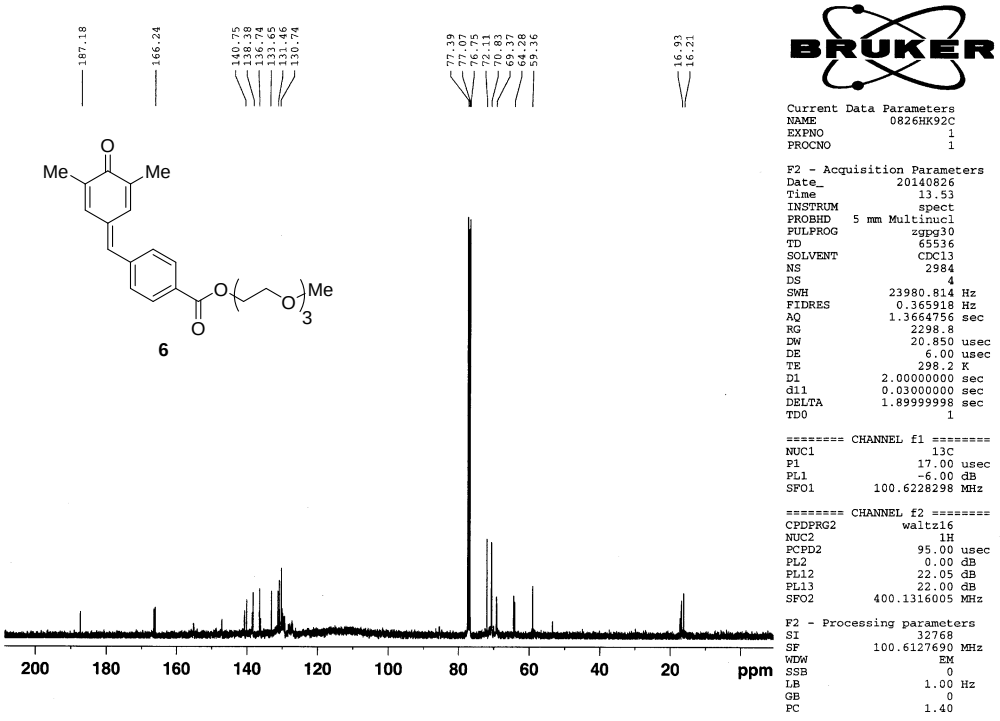



**Figure S13.** $^{13}$C NMR spectrum of **6**.

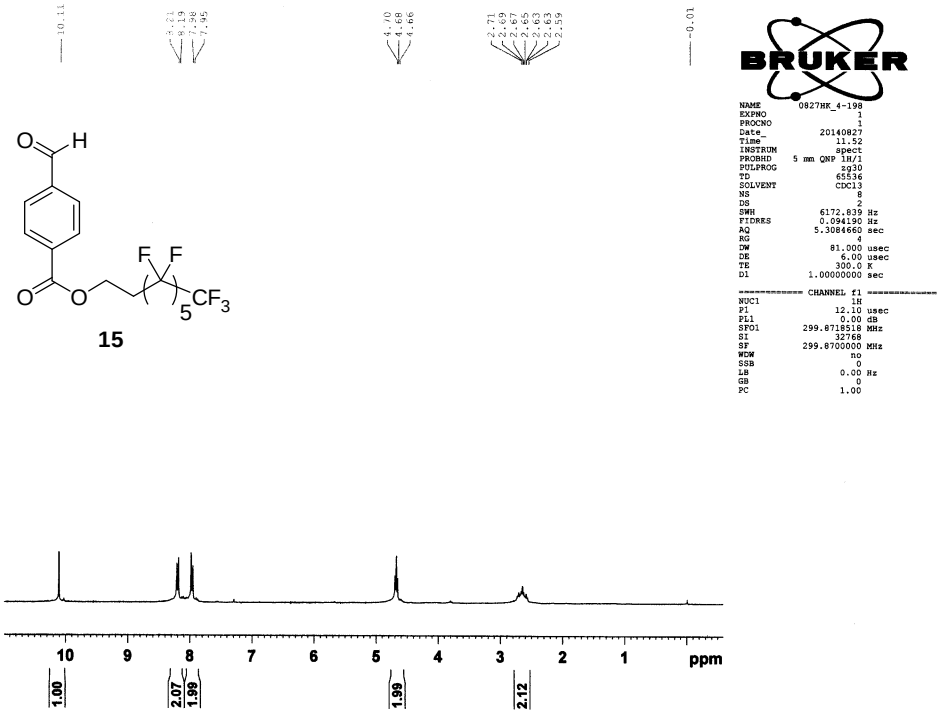



**Figure S14.** $^{1}$H NMR spectrum of **15**.

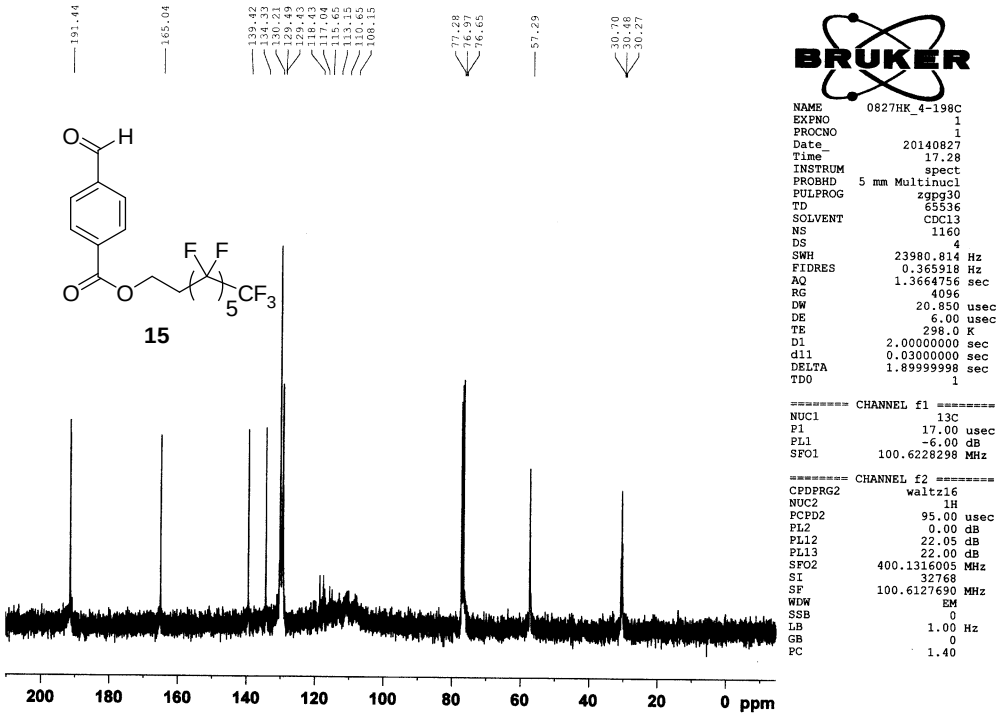



**Figure S15.** $^{13}$C NMR spectrum of **15**.

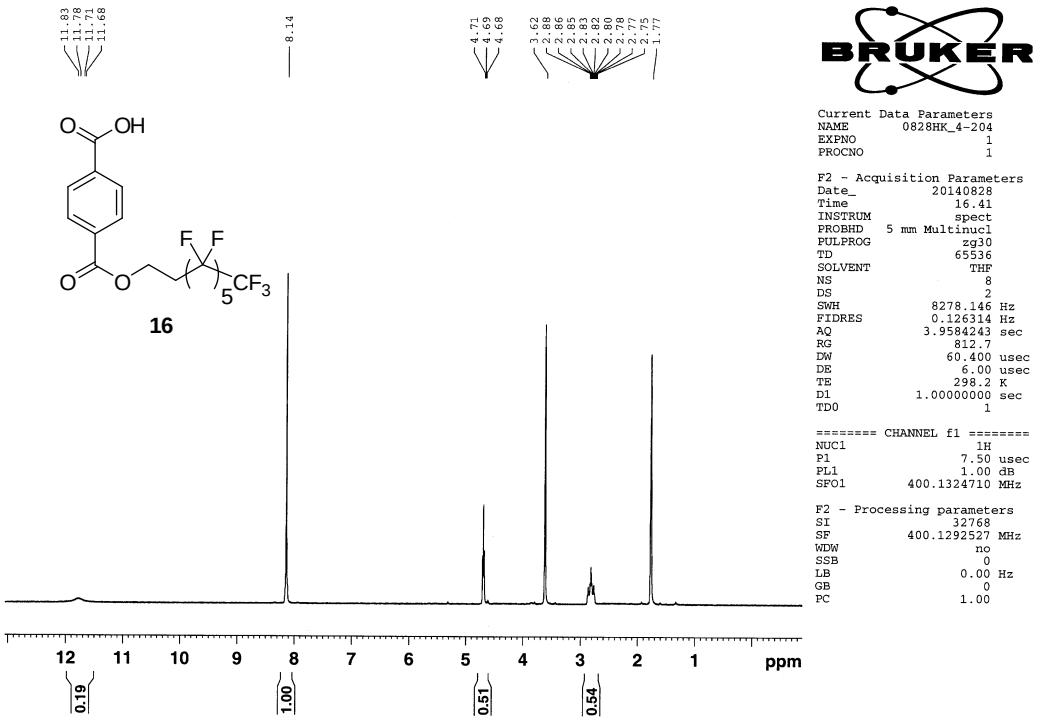



**Figure S16.** $^{1}$H NMR spectrum of **16**.

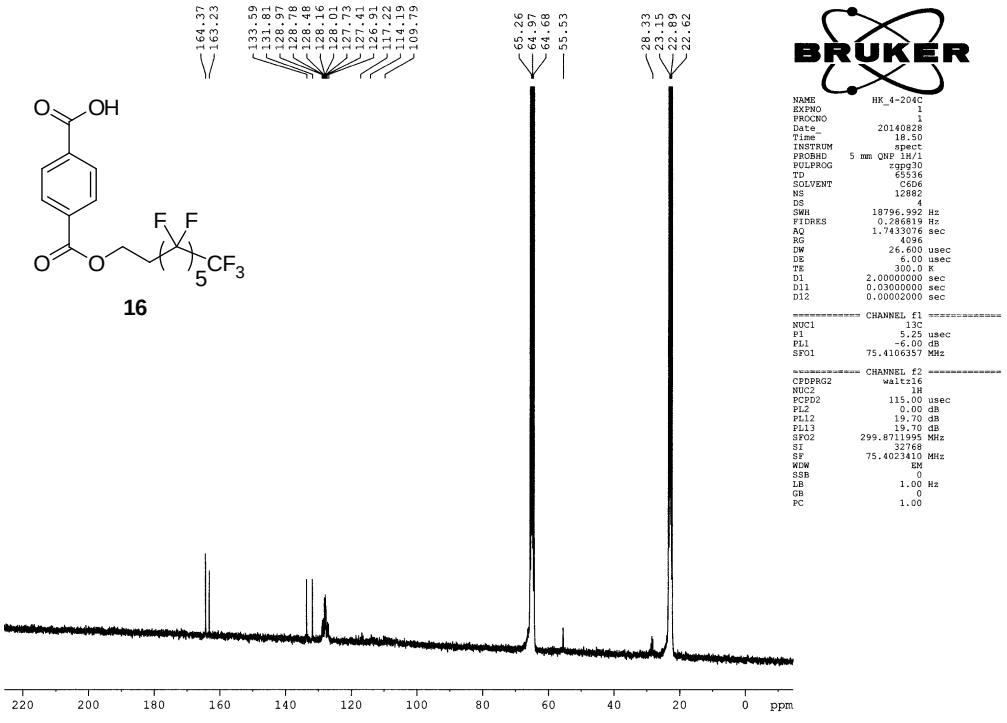



**Figure S17.** $^{13}$C NMR spectrum of **16**.

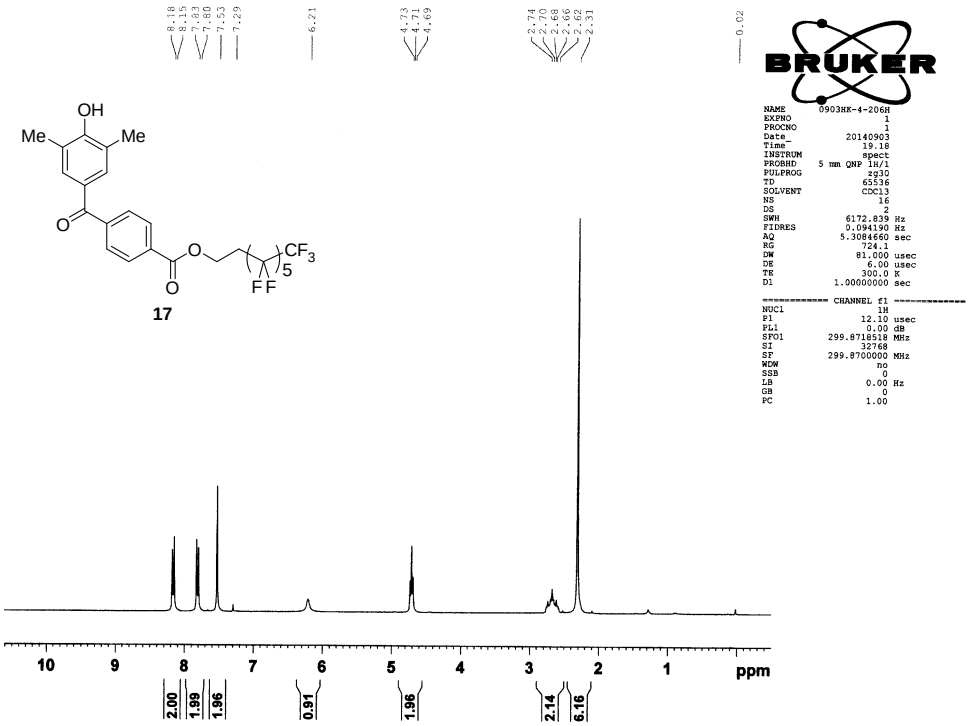



**Figure S18.** $^{1}$H NMR spectrum of **17**.

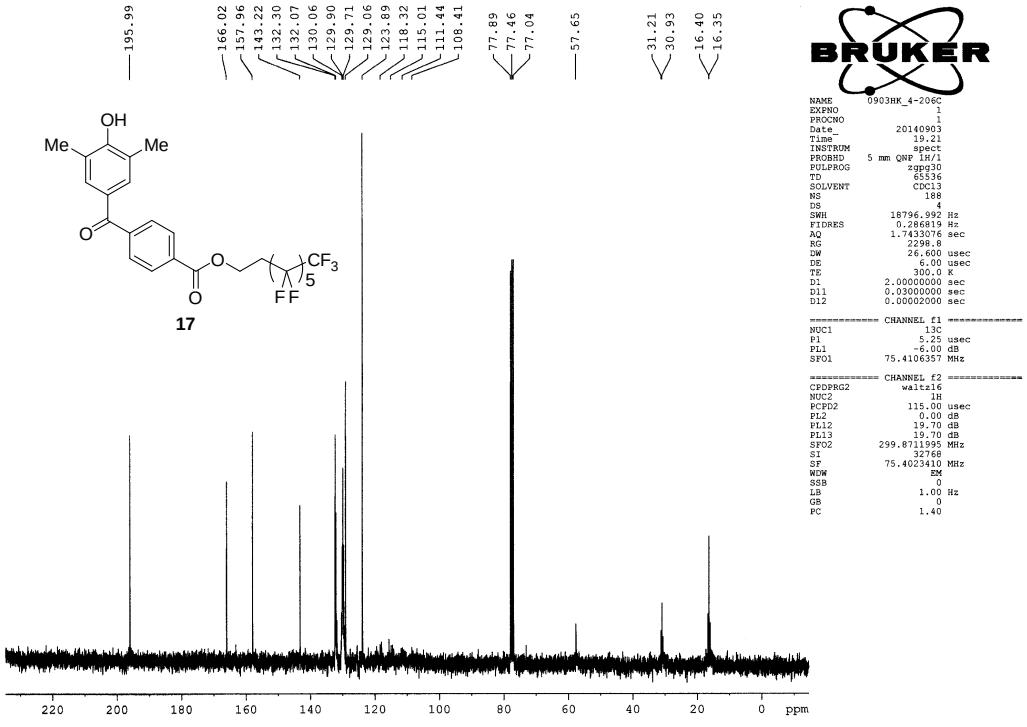



**Figure S19.** $^{13}$C NMR spectrum of **17**.

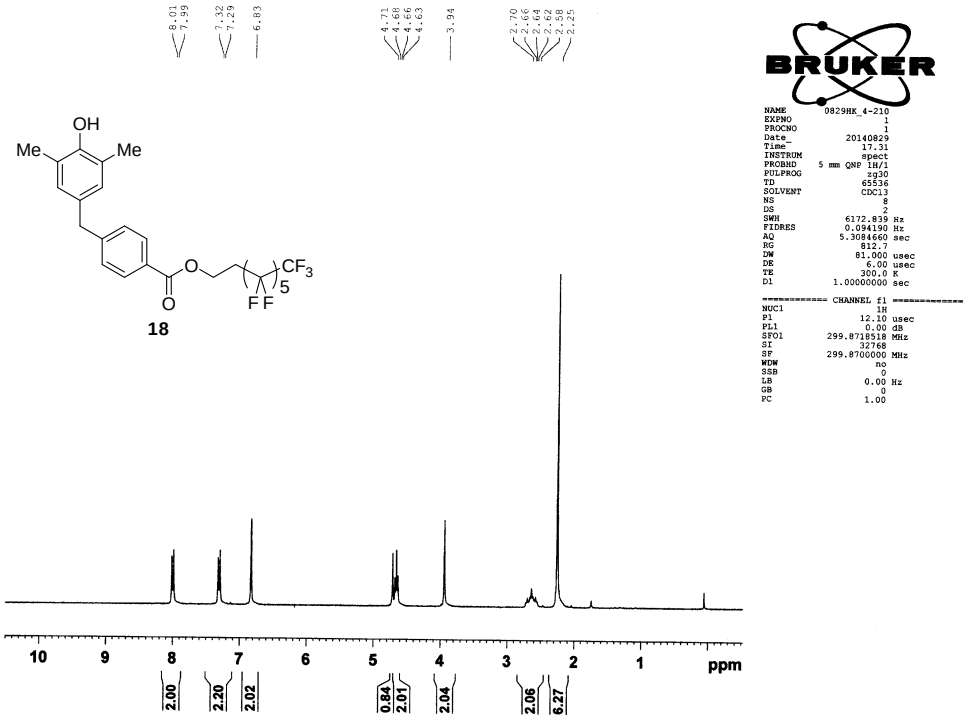



**Figure S20.** $^{1}$H NMR spectrum of **18**.

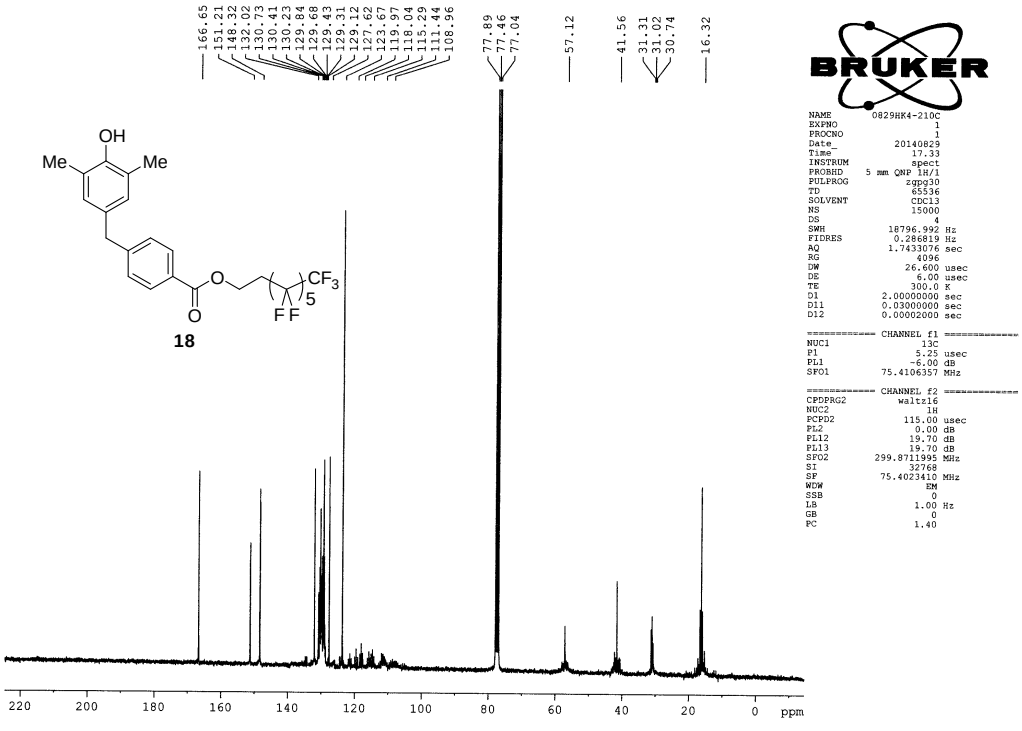



**Figure S21.** $^{13}$C NMR spectrum of **18**.

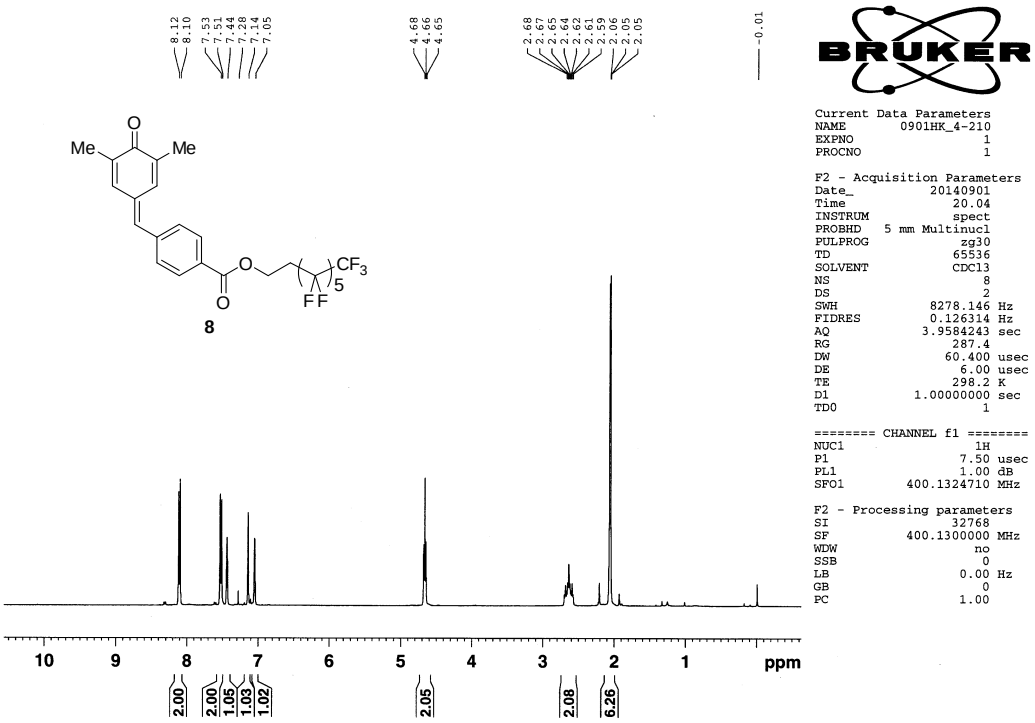



**Figure S22.** $^{1}$H NMR spectrum of **8**.

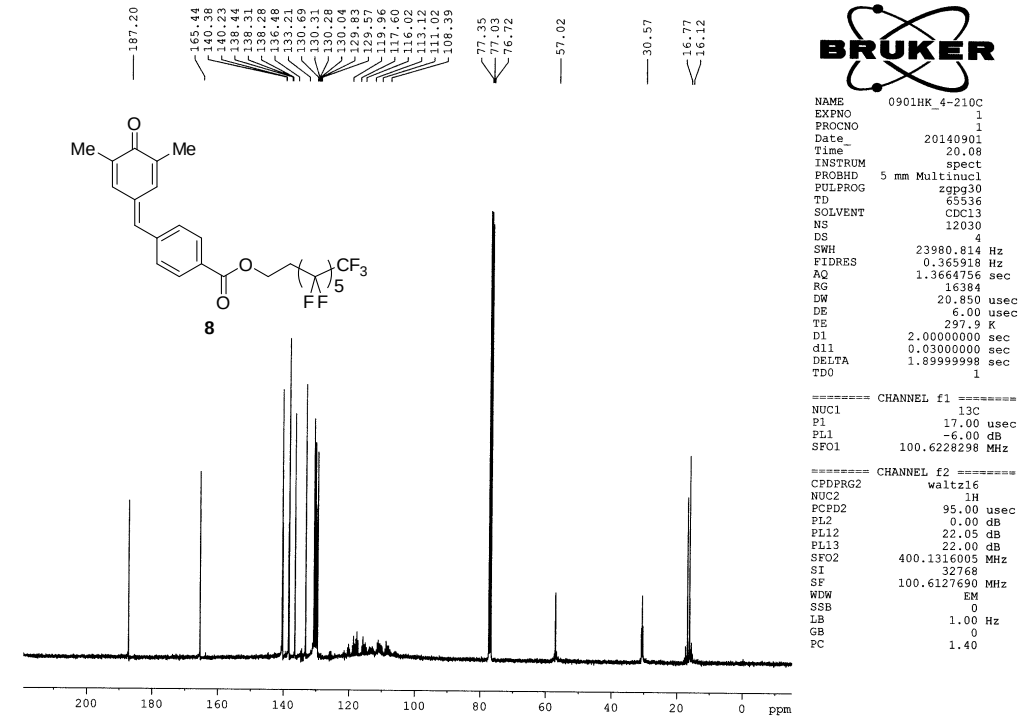



**Figure S23.** $^{13}$C NMR spectrum of **8**.

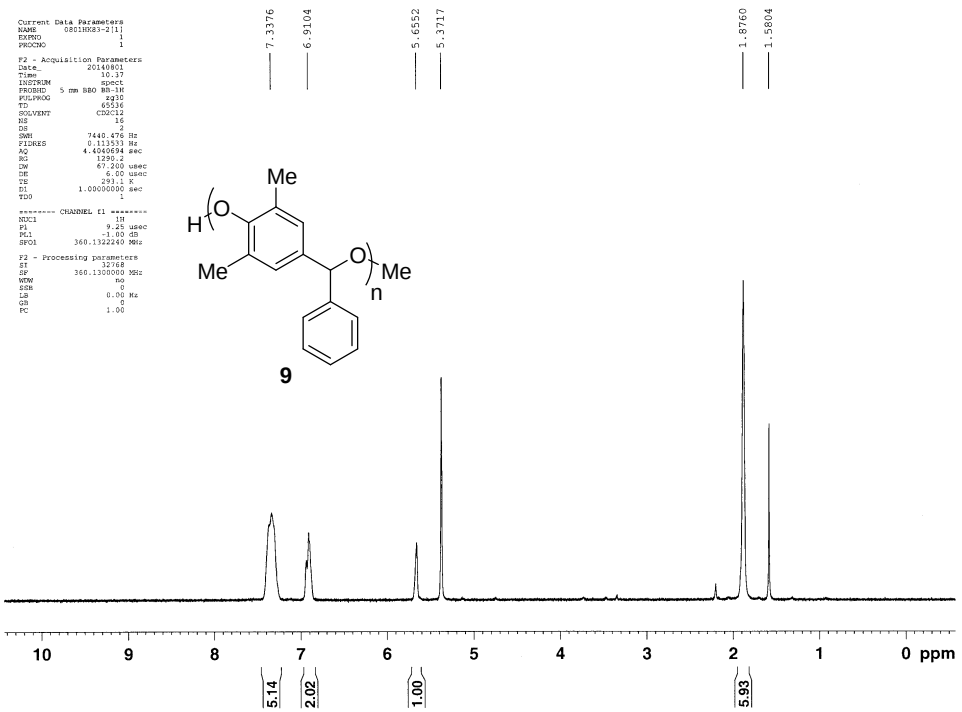



**Figure S24.** $^{1}$H NMR spectrum of **9** ($M_n$ = 47.5 kDa).

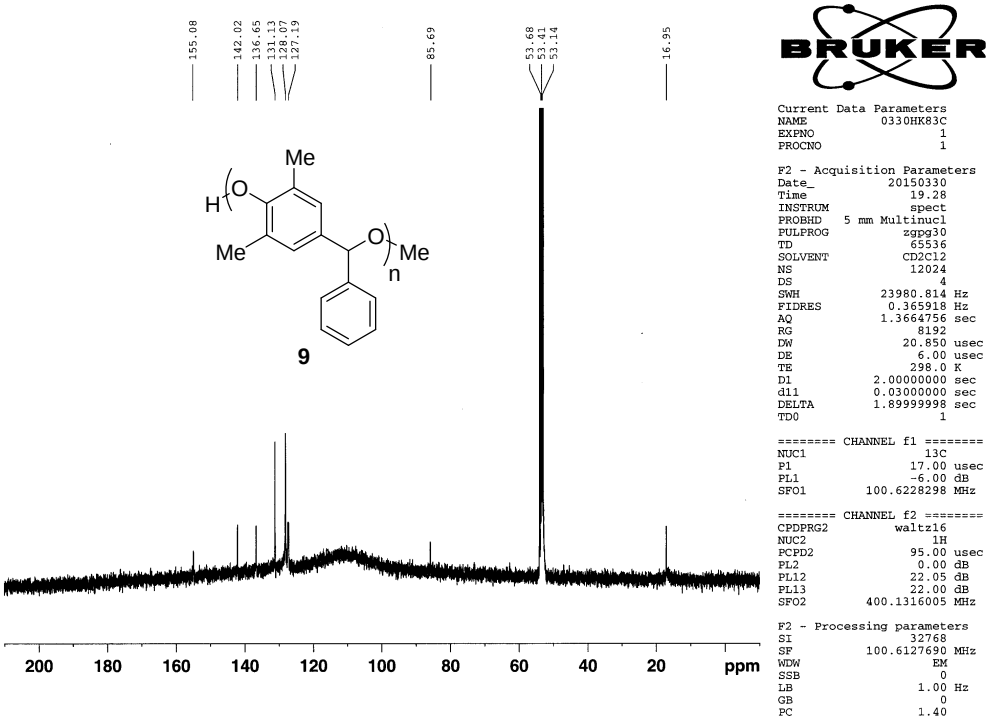



**Figure S25.** $^{13}$C NMR spectrum of **9** ($M_n$ = 47.5 kDa).

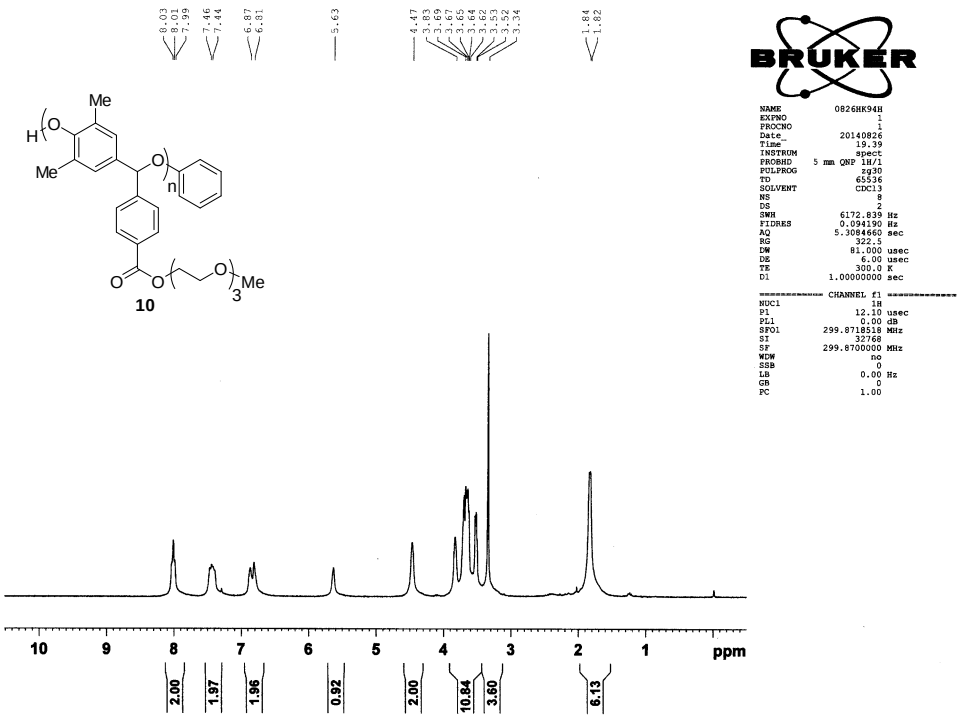



**Figure S26.** $^{1}$H NMR spectrum of **10** ($M_n$ = 38.0 kDa).

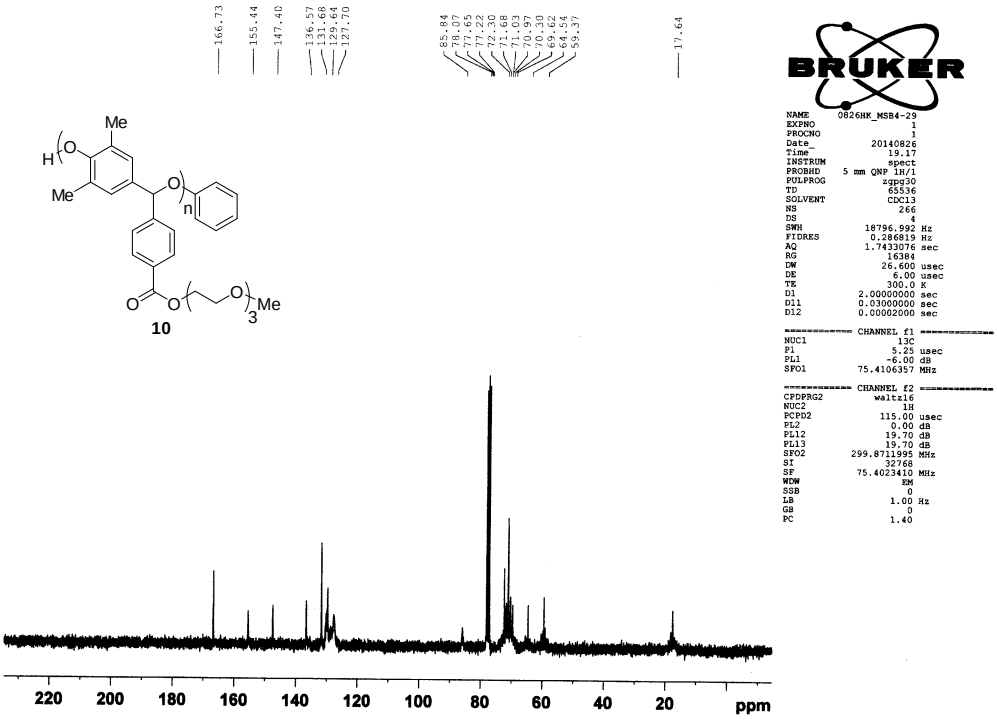



**Figure S27.** $^{13}$C NMR spectrum of **10** ($M_n$ = 38.0 kDa).

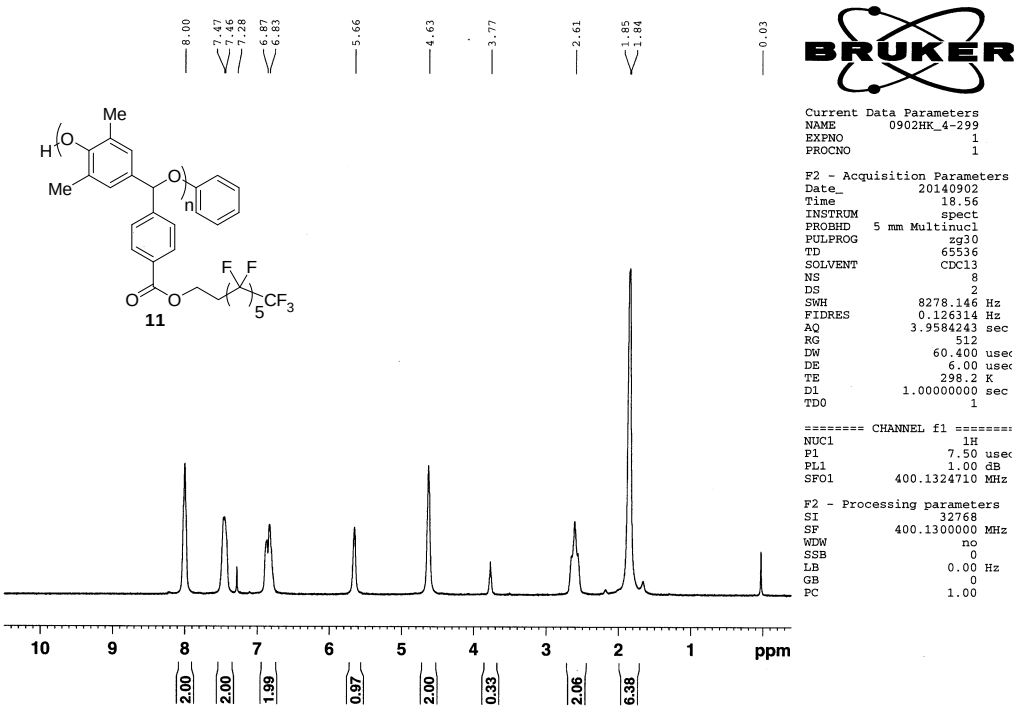



**Figure S28.** $^{1}$H NMR spectrum of **11** ($M_n$ = 5.7 kDa).

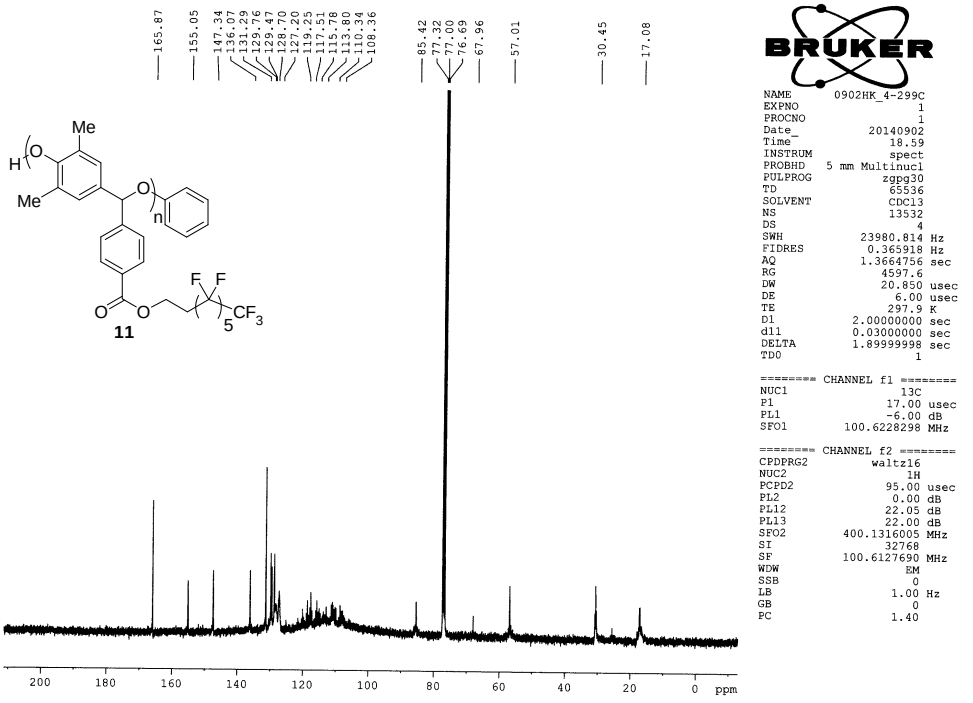



**Figure S29.** $^{13}$C NMR spectrum of **11** ($M_n$ = 5.7 kDa).

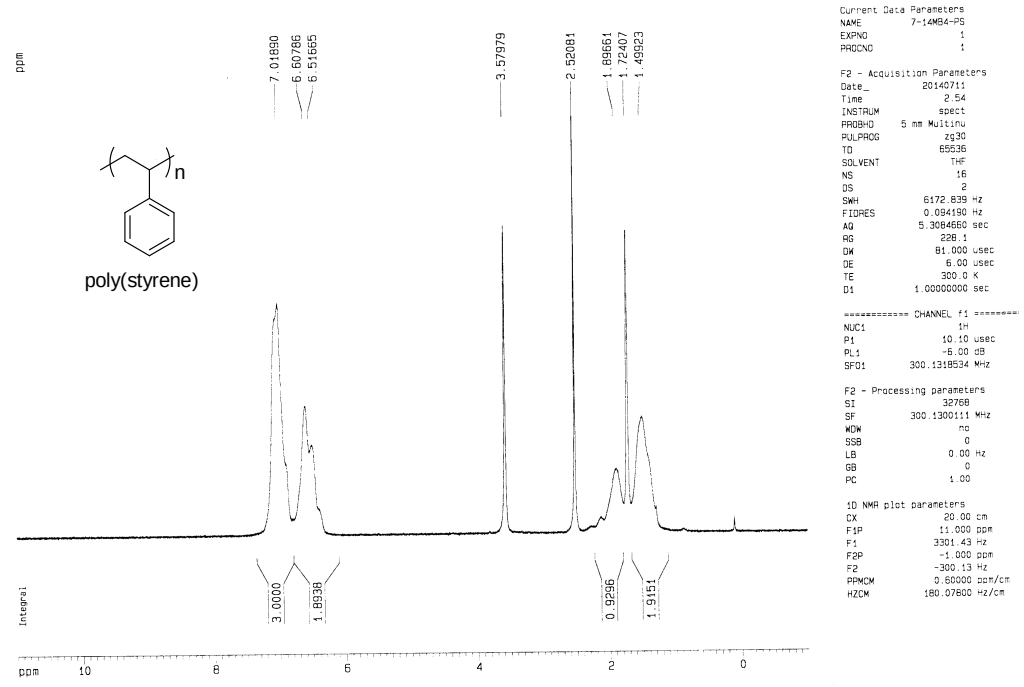



**Figure S30.** $^{1}$H NMR spectrum of poly(styrene).

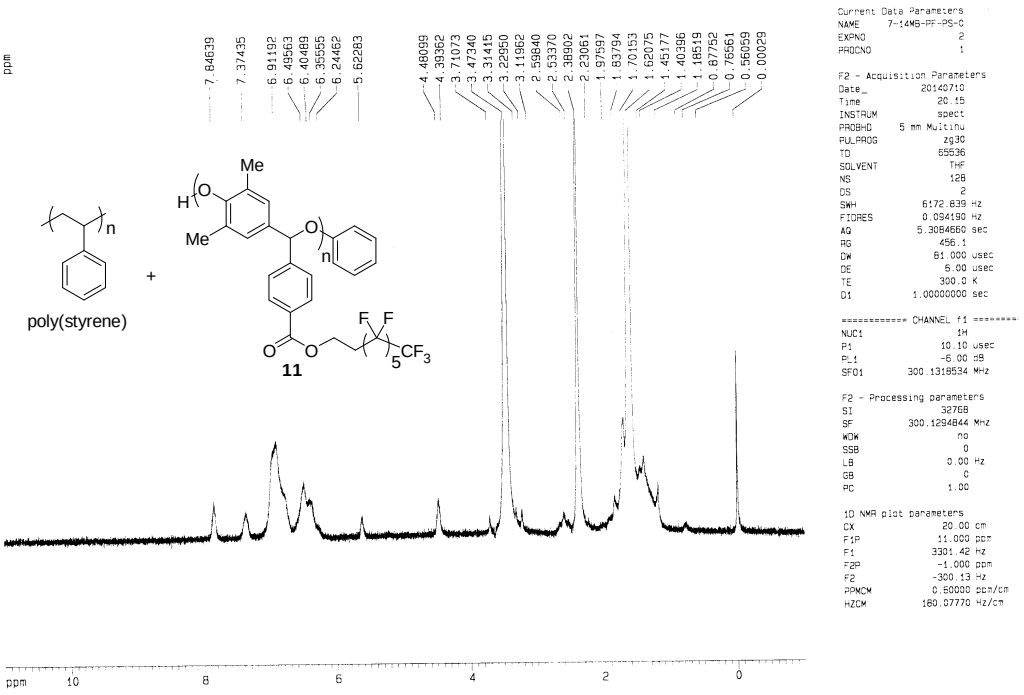



**Figure S31.** $^{1}$H NMR spectrum of a mixture of poly(styrene) and polymer **11**.

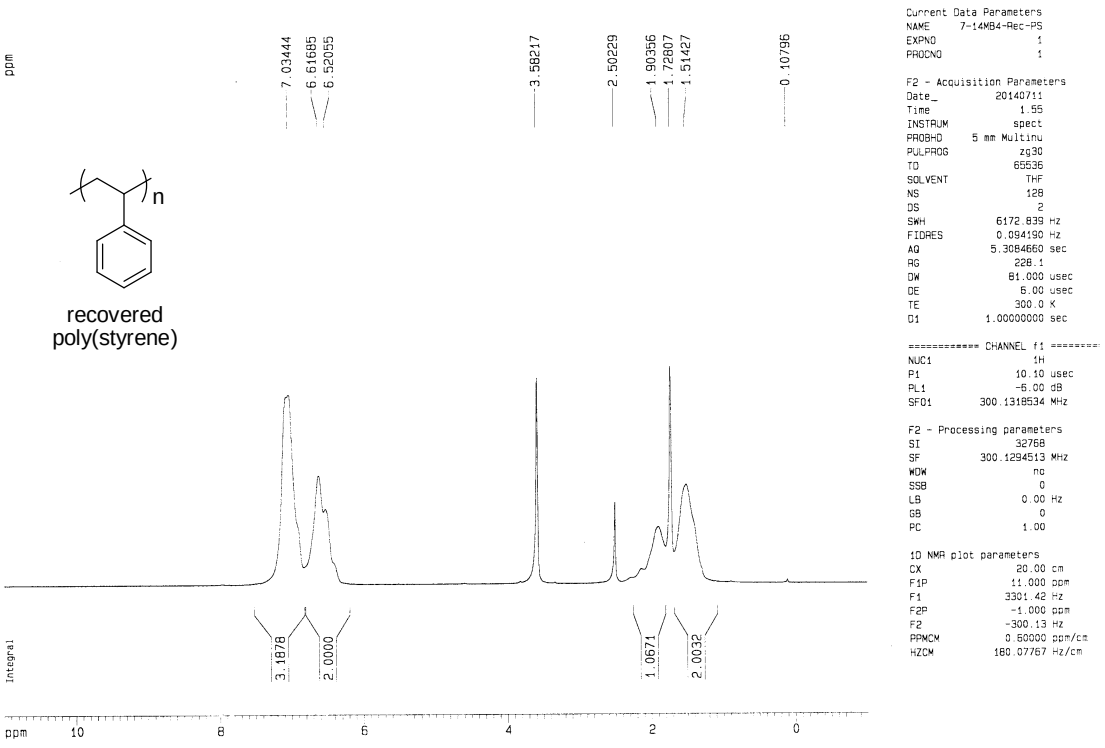



**Figure S32.** $^{1}$H NMR spectrum of recovered poly(styrene).

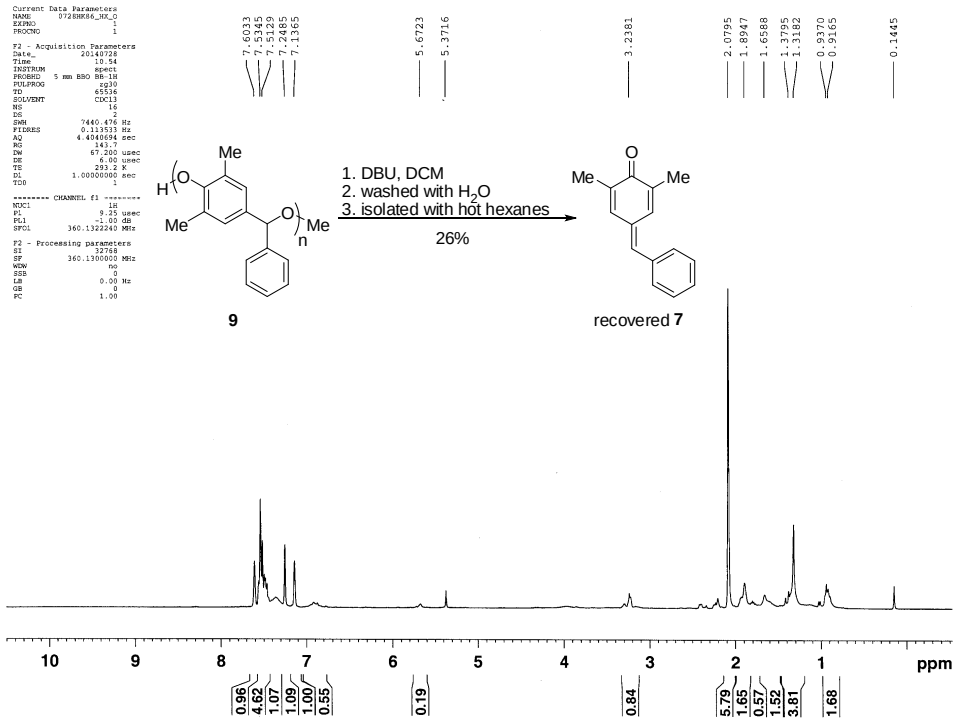



**Figure S33.** $^{1}$H NMR spectrum of recovered **7** after depolymerization of polymer **9**.

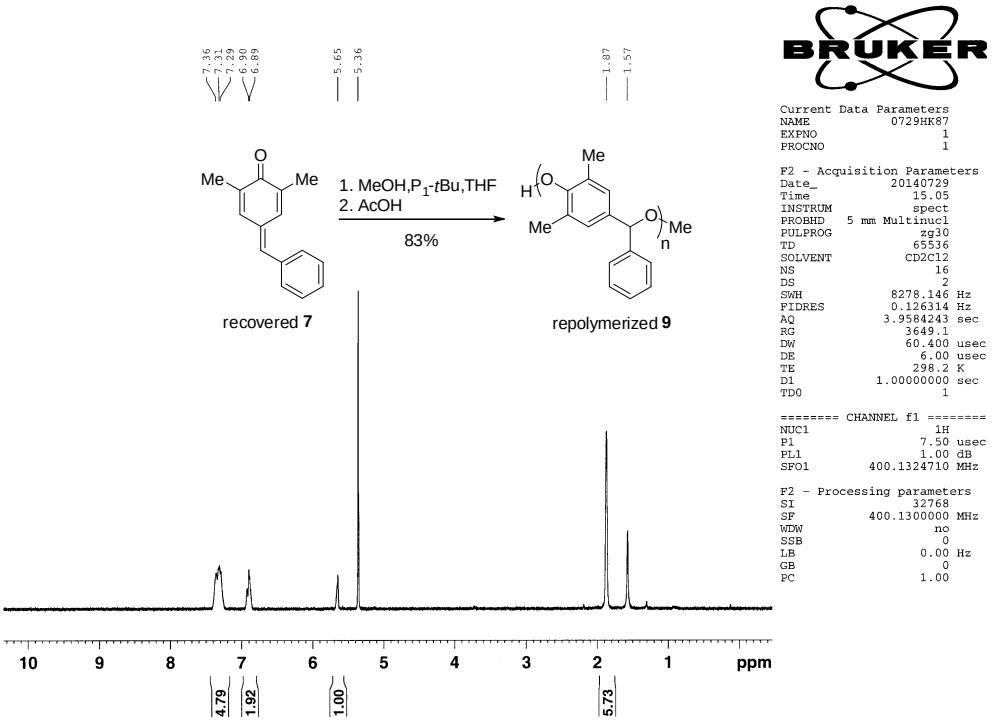
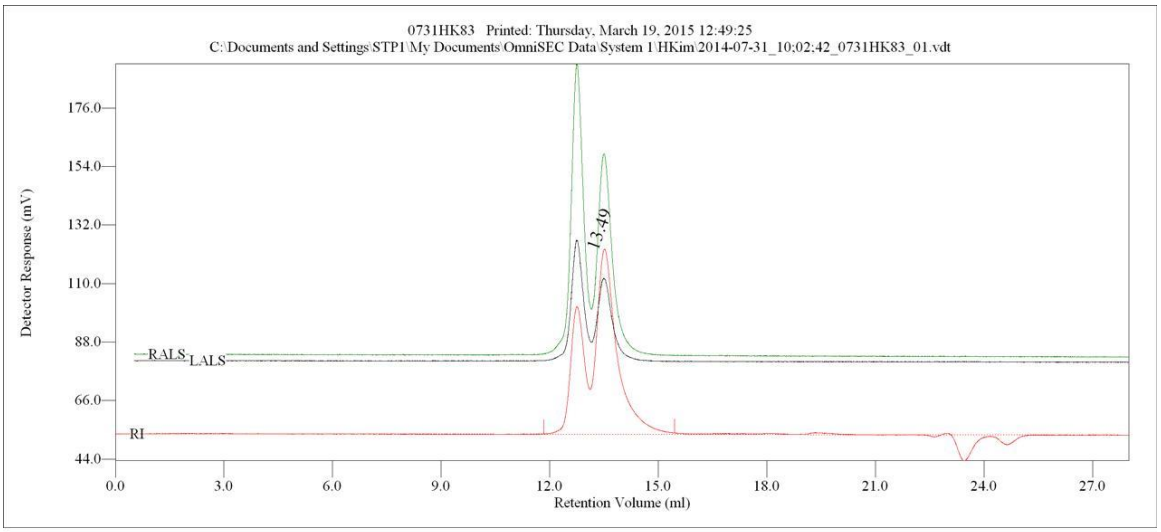


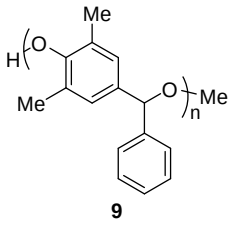

**Figure S34.** $^{1}$H NMR spectrum of repolymerized **9** from recovered **7** ($M_n$ = 36.8 kDa).

# GPC Chromatograms




Multi-Detectors - Homopolymers : Results

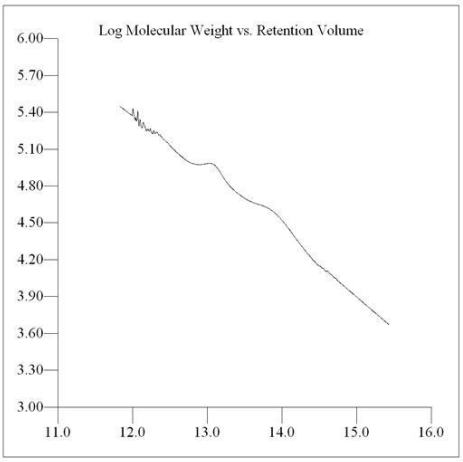
| | |
|---|---|
| Peak RV - (ml) | 13.493 |
| Mn - (Daltons) | 47,514 |
| Mw - (Daltons) | 66,361 |
| Mz - (Daltons) | 82,730 |
| Mp - (Daltons) | 50,526 |
| Mw / Mn | 1.397 |
| Percent Above Mw: 0 | 0.000 |
| Percent Below Mw: 0 | 0.000 |
| IV - (dl/g) | 0.0000 |
| Rh - (nm) | 0.000 |
| Rg - (nm) | No Calc |
| Wt Fr (Peak) | 1.000 |
| Mark-Houwink a | 0.000 |
| Mark-Houwink logK | 0.000 |
| Branches | 0.000 |
| Branch Freq. | 0.000 |
| RI Area - (mvml) | 67.15 |
| UV Area - (mvml) | 0.00 |
| RALS Area - (mvml) | 80.42 |
| LALS Area - (mvml) | 33.29 |
| IVDP Area - (mvml) | 0.00 |




**9**

| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 5.000 | 0.000 |
| Sample Recovery (%) | 0.000 | 69.879 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |

| Annotation | |
|---|---|
| Method File | OLDCALIBRATION-0000.vcm |
| Limits File | 0731HK83_01-080314CALIBRATION-0000-0001.lim |
| Date Acquired | Jul 31, 2014 - 10:02:42 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |



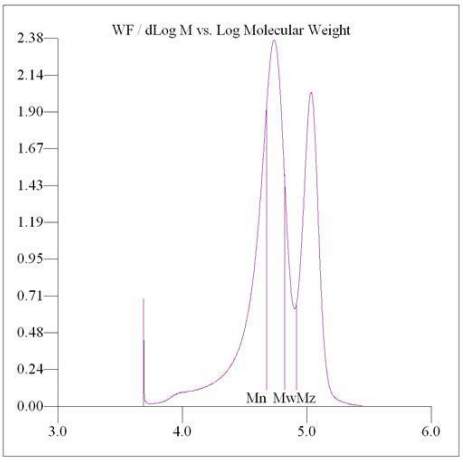
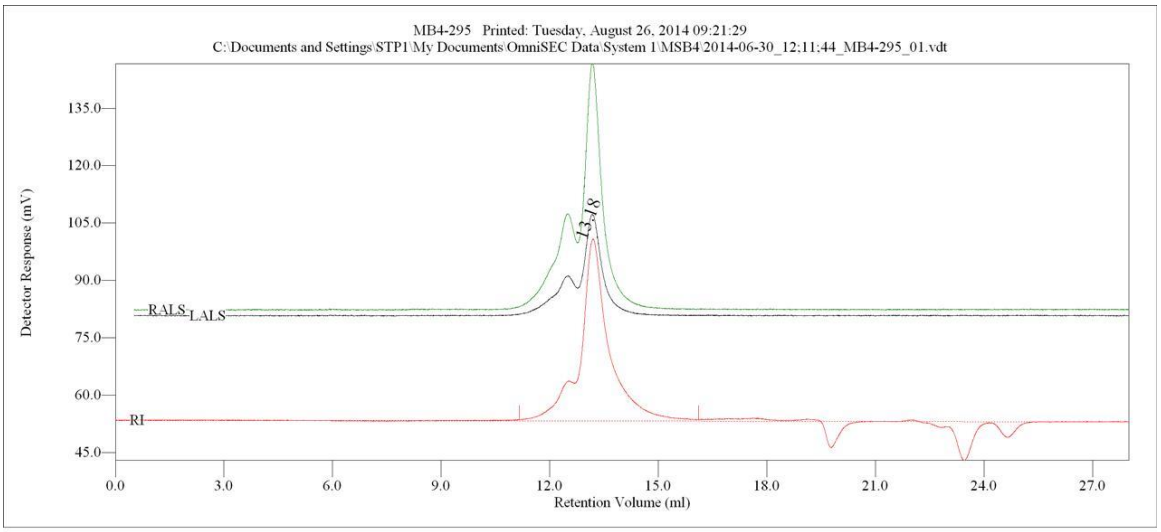



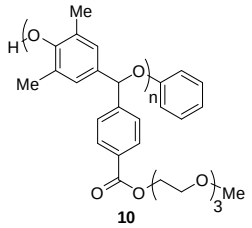

**Figure S35.** GPC chromatogram of polymer **9** ($M_n$ = 47.5 kDa).



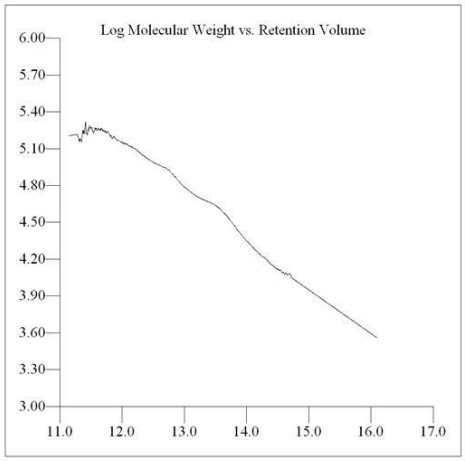

Molecular weight data for peak 1 is non-monotonic. Please read Help - FAQ entry.

Multi-Detectors - Homopolymers : Results

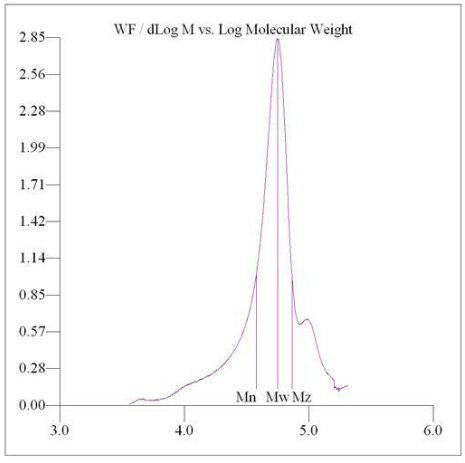
| | |
|---|---|
| Peak RV - (ml) | 13.177 |
| Mn - (Daltons) | 37,953 |
| Mw - (Daltons) | 56,406 |
| Mz - (Daltons) | 73,555 |
| Mp - (Daltons) | 52,492 |
| Mw / Mn | 1.486 |
| Percent Above Mw: 0 | 0.000 |
| Percent Below Mw: 0 | 0.000 |
| IV - (dl/g) | 0.0000 |
| Rh - (nm) | 0.000 |
| Rg - (nm) | No Calc |
| Wt Fr (Peak) | 1.000 |
| Mark-Houwink a | 0.000 |
| Mark-Houwink logK | 0.000 |
| Branches | 0.000 |
| Branch Freq. | 0.000 |
| RI Area - (mvml) | 44.04 |
| UV Area - (mvml) | 0.00 |
| RALS Area - (mvml) | 54.78 |
| LALS Area - (mvml) | 22.63 |
| IVDP Area - (mvml) | 0.00 |




**10**

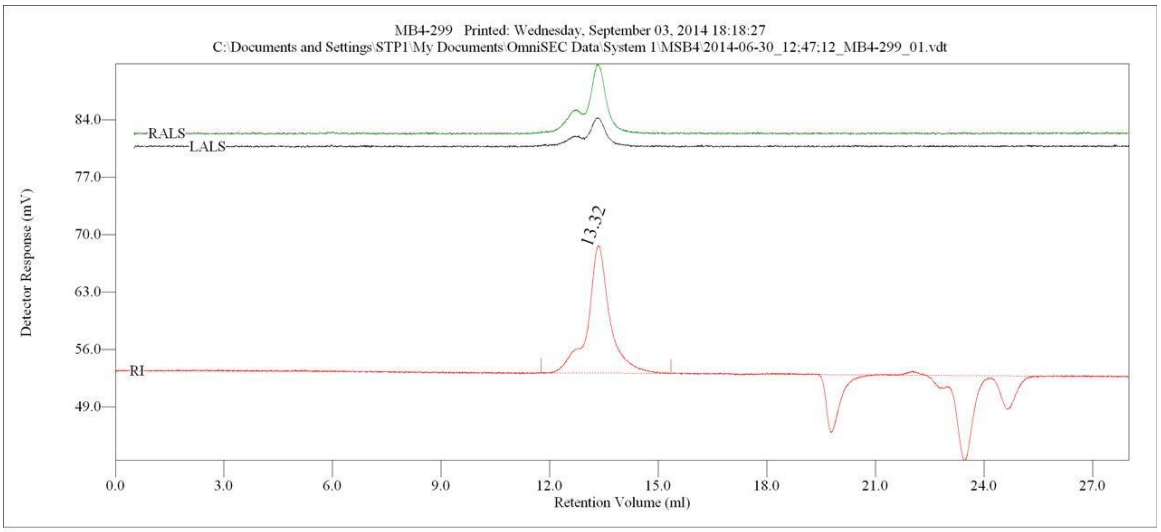



| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 4.000 | 0.000 |
| Sample Recovery (%) | 0.000 | 57.281 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |




| Annotation | |
|---|---|
| Method File | calibration101113-0000.vcm |
| Limits File | ;11;44_MB4-295_01-calibration101113-0000-0001.lim |
| Date Acquired | Jun 30, 2014 - 12:11:44 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |

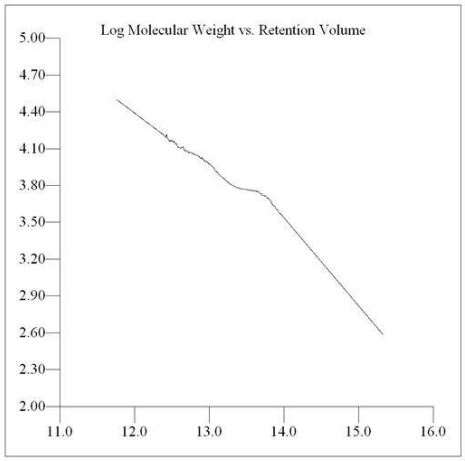
**Figure S36.** GPC chromatogram of polymer **10** ($M_n$ = 38.0 kDa).




Multi-Detectors - Homopolymers : Results

| | |
|---|---|
| Peak RV - (ml) | 13.323 |
| Mn - (Daltons) | 5,741 |
| Mw - (Daltons) | 7,101 |
| Mz - (Daltons) | 8,398 |
| Mp - (Daltons) | 6,289 |
| Mw / Mn | 1.237 |
| Percent Above Mw: 0 | 0.000 |
| Percent Below Mw: 0 | 0.000 |
| IV - (dl/g) | 0.0000 |
| Rh - (nm) | 0.000 |
| Rg - (nm) | No Calc |
| Wt Fr (Peak) | 1.000 |
| Mark-Houwink a | 0.000 |
| Mark-Houwink logK | 0.000 |
| Branches | 0.000 |
| Branch Freq. | 0.000 |
| RI Area - (mvml) | 11.01 |
| UV Area - (mvml) | 0.00 |
| RALS Area - (mvml) | 5.78 |
| LALS Area - (mvml) | 2.35 |
| IVDP Area - (mvml) | 0.00 |

**11**




| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 3.300 | 0.000 |
| Sample Recovery (%) | 0.000 | 17.356 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |

| Annotation | |
|---|---|
| Method File | calibration101113-0000.vcm |
| Limits File | ;47;12_MB4-299_01-calibration101113-0000-0000.lim |
| Date Acquired | Jun 30, 2014 - 12:47:12 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |

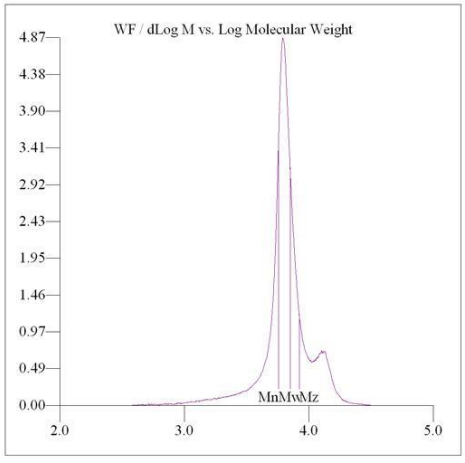
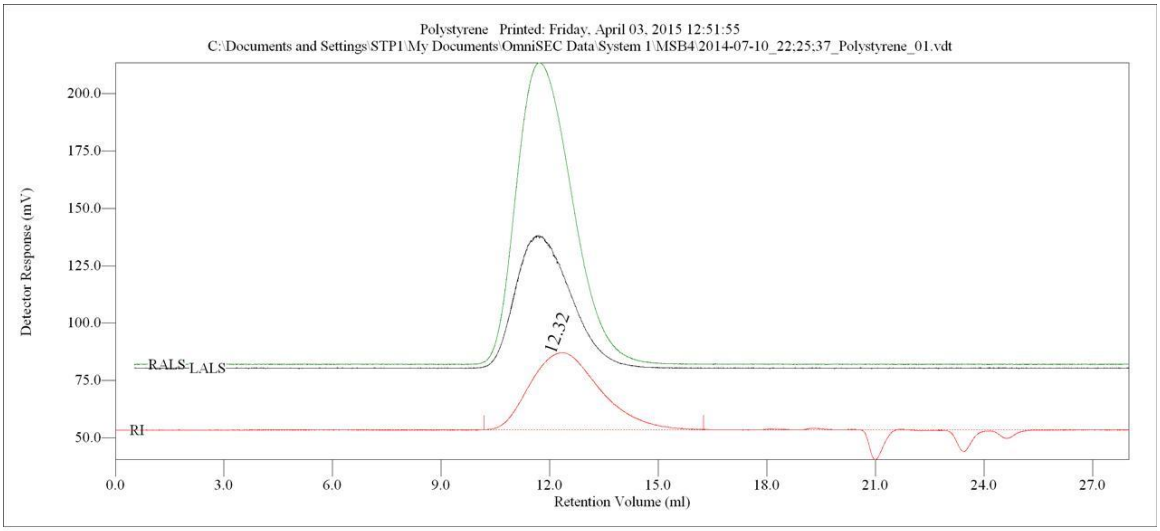
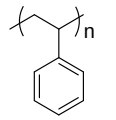



**Figure S37.** GPC chromatogram of polymer **11** ($M_n$ = 5.7 kDa).

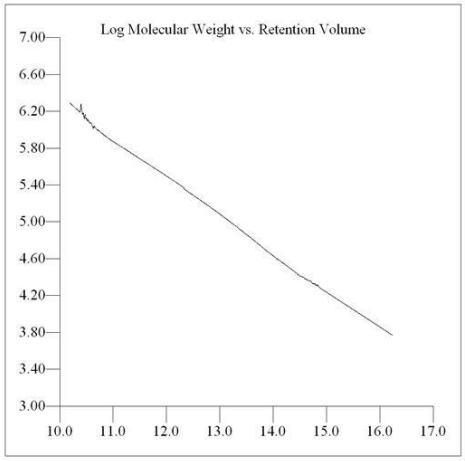



Multi-Detectors - Homopolymers : Results

| | |
|---|---|
| Peak RV - (ml) | 12.320 |
| Mn - (Daltons) | 118,236 |
| Mw - (Daltons) | 257,368 |
| Mz - (Daltons) | 410,829 |
| Mp - (Daltons) | 236,339 |
| Mw / Mn | 2.177 |
| Percent Above Mw: 0 | 0.000 |
| Percent Below Mw: 0 | 0.000 |
| IV - (dl/g) | 0.0000 |
| Rh - (nm) | 0.000 |
| Rg - (nm) | 17.495 |
| Wt Fr (Peak) | 1.000 |
| Mark-Houwink a | 0.000 |
| Mark-Houwink logK | 0.000 |
| Branches | 0.000 |
| Branch Freq. | 0.000 |
| RI Area - (mvml) | 74.87 |
| UV Area - (mvml) | 0.00 |
| RALS Area - (mvml) | 233.59 |
| LALS Area - (mvml) | 102.14 |
| IVDP Area - (mvml) | 0.00 |




poly(styrene)




| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 4.000 | 0.000 |
| Sample Recovery (%) | 0.000 | 97.384 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |

| Annotation | |
|---|---|
| Method File | calibration101113-0000.vcm |
| Limits File | 5;37_Polystyrene_01-calibration101113-0000-0002.lim |
| Date Acquired | Jul 10, 2014 - 22:25:37 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |

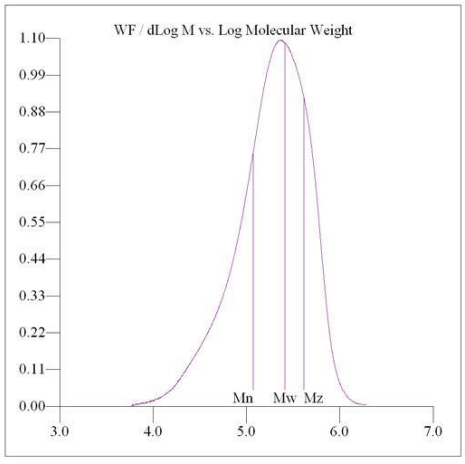
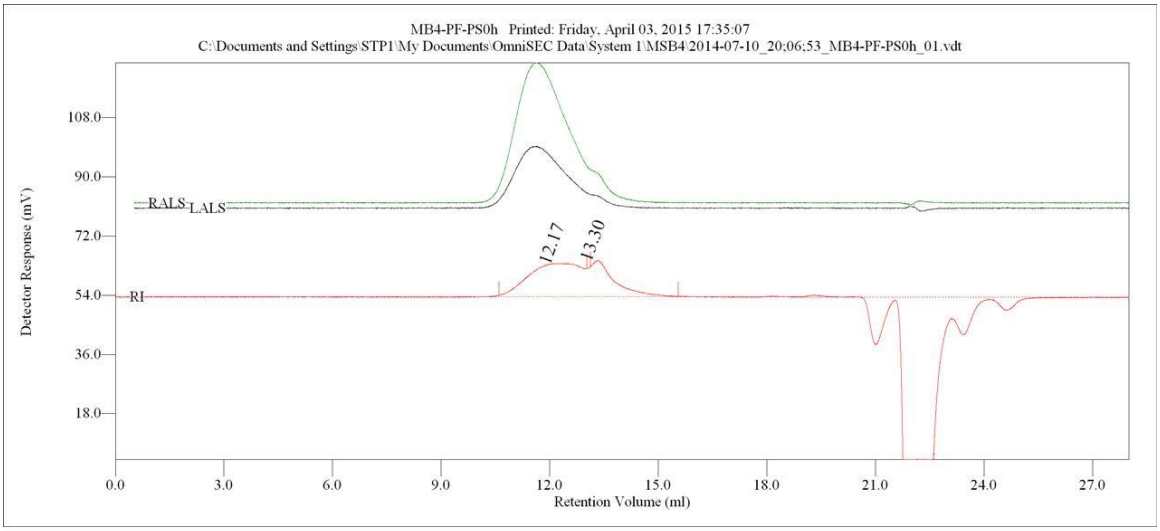



**Figure S38.** GPC chromatogram of poly(styrene) ($M_n$ = 118.2 kDa).



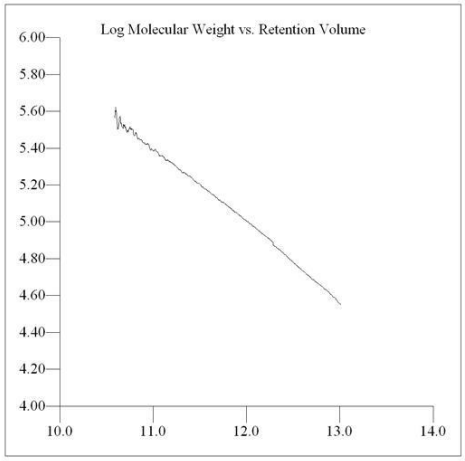

Multi-Detectors - Homopolymers : Results

| | | |
|---|---|---|
| Peak RV - (ml) | 12.170 | 13.303 |
| Mn - (Daltons) | 79,614 | 14,111 |
| Mw - (Daltons) | 106,374 | 17,001 |
| Mz - (Daltons) | 141,017 | 18,770 |
| Mp - (Daltons) | 86,159 | 20,440 |
| Mw / Mn | 1.336 | 1.205 |
| Percent Above Mw: 0 | 0.000 | 0.000 |
| Percent Below Mw: 0 | 0.000 | 0.000 |
| IV - (dl/g) | 0.0000 | 0.0000 |
| Rh - (nm) | 0.000 | 0.000 |
| Rg - (nm) | 19.642 | No Calc |
| Wt Fr (Peak) | 0.680 | 0.320 |
| Mark-Houwink a | 0.000 | 0.000 |
| Mark-Houwink logK | 0.000 | 0.000 |
| Branches | 0.000 | 0.000 |
| Branch Freq. | 0.000 | 0.000 |
| RI Area - (mvml) | 17.34 | 8.17 |
| UV Area - (mvml) | 0.00 | 0.00 |
| RALS Area - (mvml) | 66.18 | 5.38 |
| LALS Area - (mvml) | 28.98 | 2.13 |
| IVDP Area - (mvml) | 0.00 | 0.00 |

poly(styrene) + **11**

| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 4.000 | 0.000 |
| Sample Recovery (%) | 0.000 | 33.186 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |

| Annotation | |
|---|---|
| Method File | calibration101113-0000.vcm |
| Limits File | 3_MB4-PF-PS0h_01-calibration101113-0000-0007.lim |
| Date Acquired | Jul 10, 2014 - 20:06:53 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |



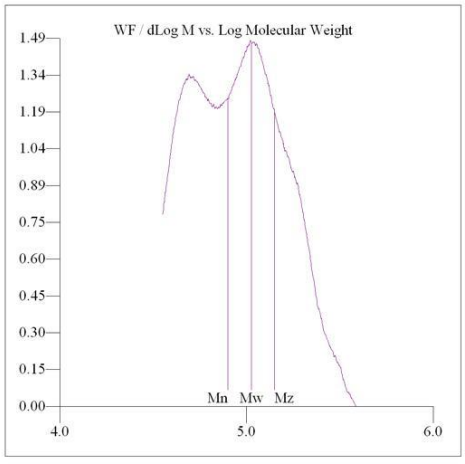
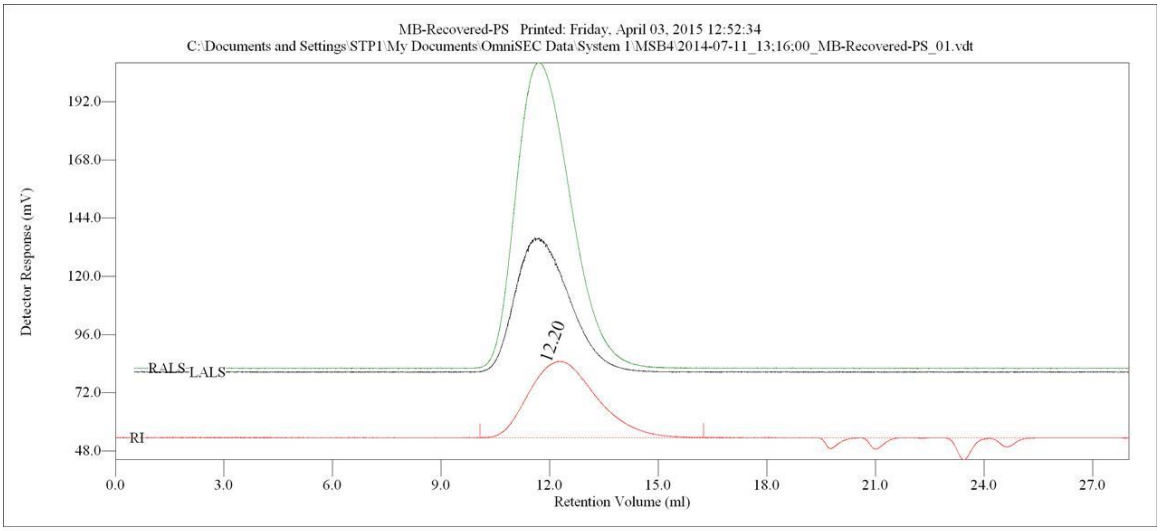
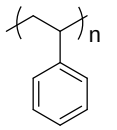




**Figure S39.** GPC chromatogram of a mixture of poly(styrene) and polymer **11**.




Multi-Detectors - Homopolymers : Results

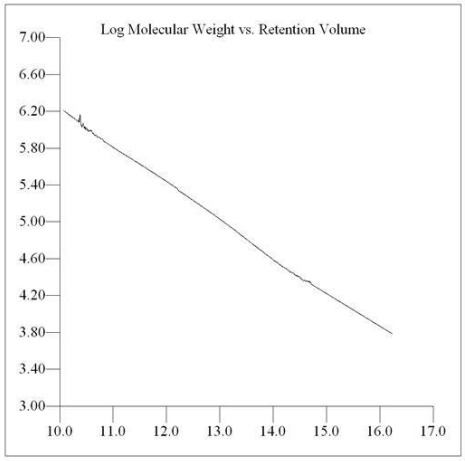
| | |
|---|---|
| Peak RV - (ml) | 12.197 |
| Mn - (Daltons) | 117,286 |
| Mw - (Daltons) | 234,683 |
| Mz - (Daltons) | 361,856 |
| Mp - (Daltons) | 230,588 |
| Mw / Mn | 2.001 |
| Percent Above Mw: 0 | 0.000 |
| Percent Below Mw: 0 | 0.000 |
| IV - (dl/g) | 0.0000 |
| Rh - (nm) | 0.000 |
| Rg - (nm) | 16.267 |
| Wt Fr (Peak) | 1.000 |
| Mark-Houwink a | 0.000 |
| Mark-Houwink logK | 0.000 |
| Branches | 0.000 |
| Branch Freq. | 0.000 |
| RI Area - (mvml) | 68.01 |
| UV Area - (mvml) | 0.00 |
| RALS Area - (mvml) | 219.07 |
| LALS Area - (mvml) | 95.49 |
| IVDP Area - (mvml) | 0.00 |




recovered poly(styrene)

| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 4.100 | 0.000 |
| Sample Recovery (%) | 0.000 | 86.300 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |

| Annotation | |
|---|---|
| Method File | calibration101113-0000.vcm |
| Limits File | IB-Recovered-PS_01-calibration101113-0000-0001.lim |
| Date Acquired | Jul 11, 2014 - 13:16:00 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |



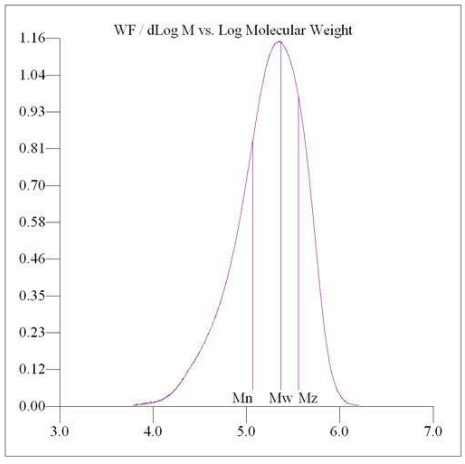
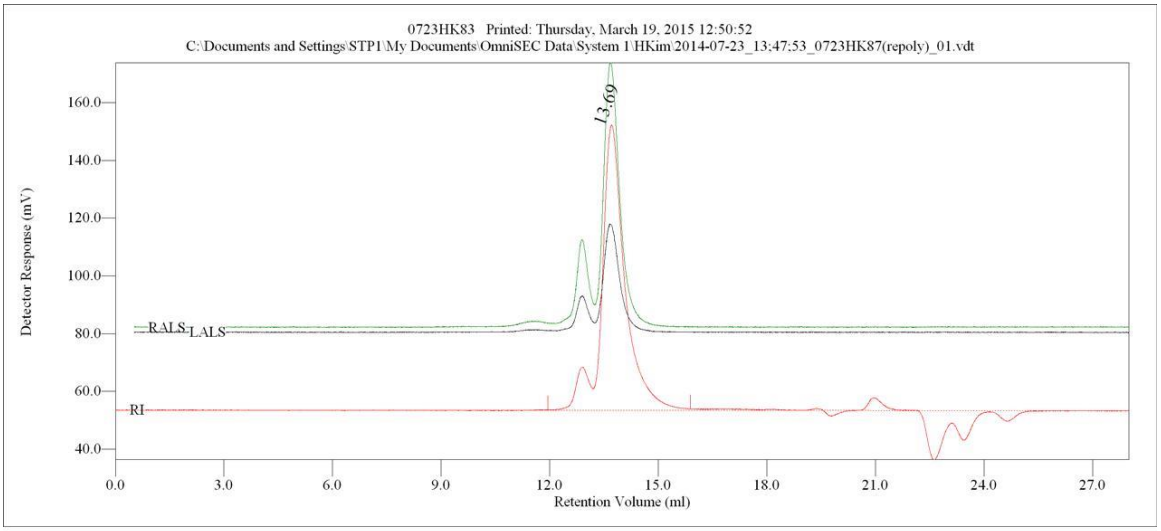
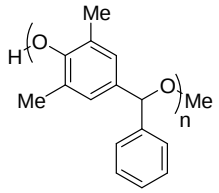




**Figure S40.** GPC chromatogram of recovered poly(styrene) ($M_n$ = 117.3 kDa).

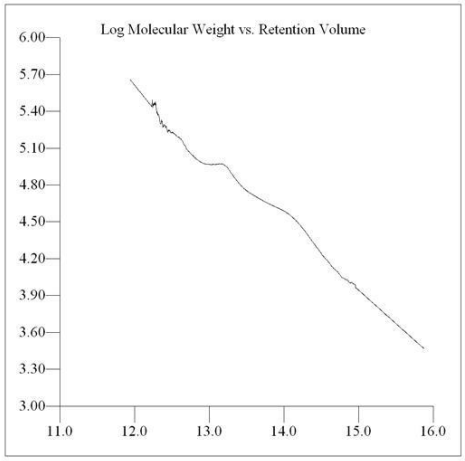



Multi-Detectors - Homopolymers : Results

| | |
|---|---|
| Peak RV - (ml) | 13.687 |
| Mn - (Daltons) | 36,796 |
| Mw - (Daltons) | 49,570 |
| Mz - (Daltons) | 62,031 |
| Mp - (Daltons) | 48,206 |
| Mw / Mn | 1.347 |
| Percent Above Mw: 0 | 0.000 |
| Percent Below Mw: 0 | 0.000 |
| IV - (dl/g) | 0.0000 |
| Rh - (nm) | 0.000 |
| Rg - (nm) | No Calc |
| Wt Fr (Peak) | 1.000 |
| Mark-Houwink a | 0.000 |
| Mark-Houwink logK | 0.000 |
| Branches | 0.000 |
| Branch Freq. | 0.000 |
| RI Area - (mvml) | 74.31 |
| UV Area - (mvml) | 0.00 |
| RALS Area - (mvml) | 60.19 |
| LALS Area - (mvml) | 24.78 |
| IVDP Area - (mvml) | 0.00 |




repolymerized **9**




| Sample Parameters | Input | Calculated |
|---|---|---|
| Sample Conc - (mg/ml) | 5.000 | 0.000 |
| Sample Recovery (%) | 0.000 | 77.322 |
| dn/dc - (ml/g) | 0.1850 | 0.0000 |
| dA/dc - (ml/g) | 1.0000 | 0.0000 |

| Annotation | |
|---|---|
| Method File | OLDCALIBRATION-0000.vcm |
| Limits File | 87(repoly)_01-080314CALIBRATION-0000-0001.lim |
| Date Acquired | Jul 23, 2014 - 13:47:53 |
| Solvent | DMF |
| Acquisition Operator | admin : Administrator |
| Calculation Operator | admin : Administrator |
| Column Set | Varian |
| System | System 1 |
| Flow Rate - (ml/min) | 1.000 |
| Inj Volume - (ul) | 50.0 |
| Volume Increment - (ml) | 0.00333 |
| Detector Temp. - (deg C) | 22.0 |
| Column Temp. - (deg C) | 25.0 |
| OmniSEC Build Number | 359 |

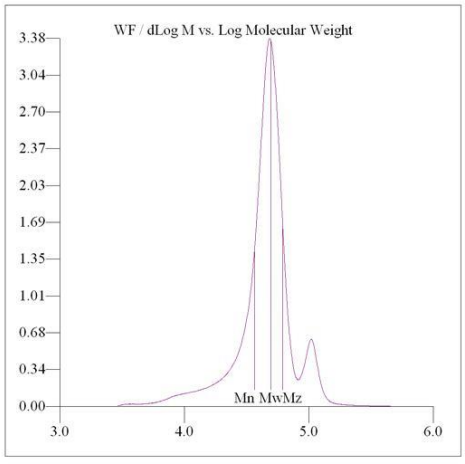



**Figure S41.** GPC chromatogram of repolymerized **9** ($M_n$ = 36.8 kDa).

## SDT Thermograms

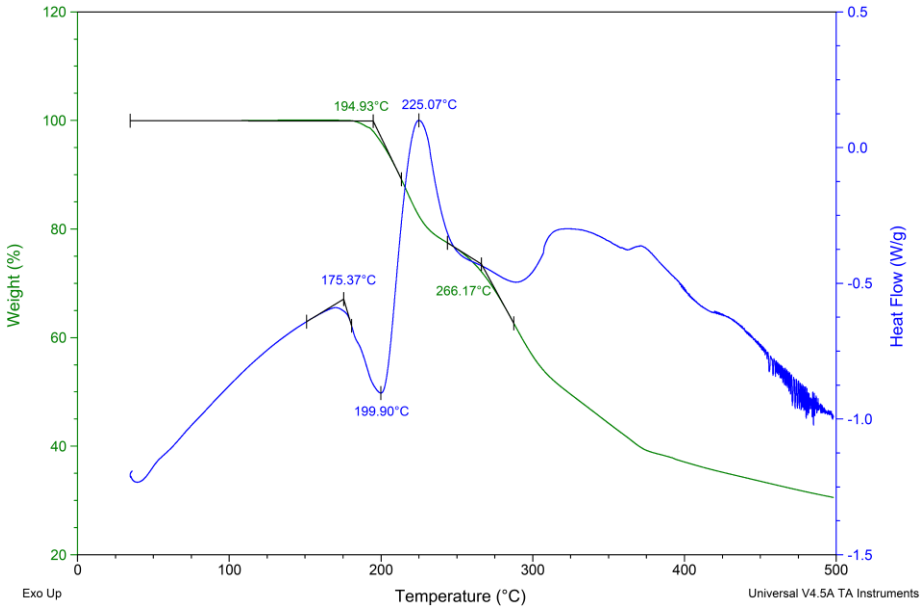



**Figure S42.** SDT thermogram of polymer **9** ($M_n$ = 47.5 kDa).

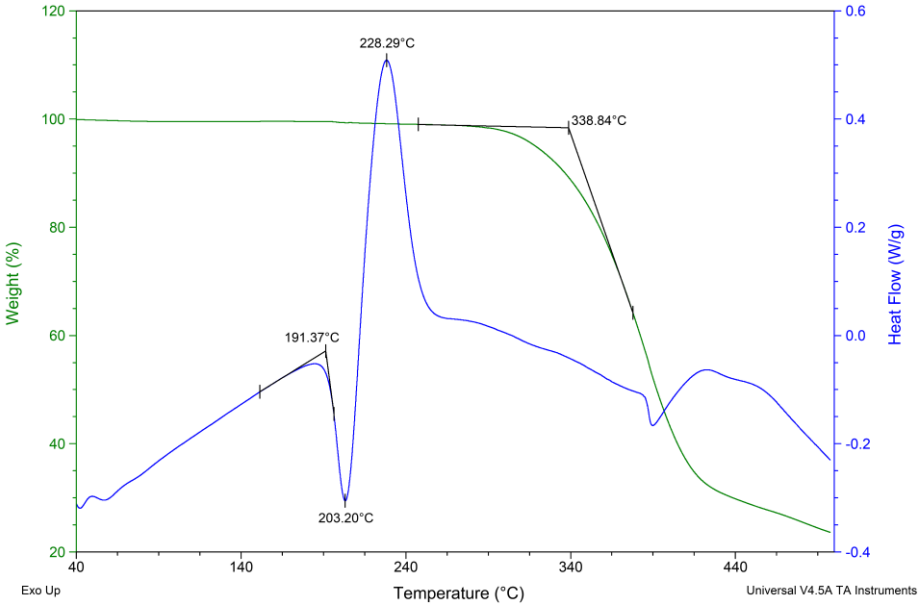



**Figure S43.** SDT thermogram of polymer **10** ($M_n$ = 38.0 kDa).

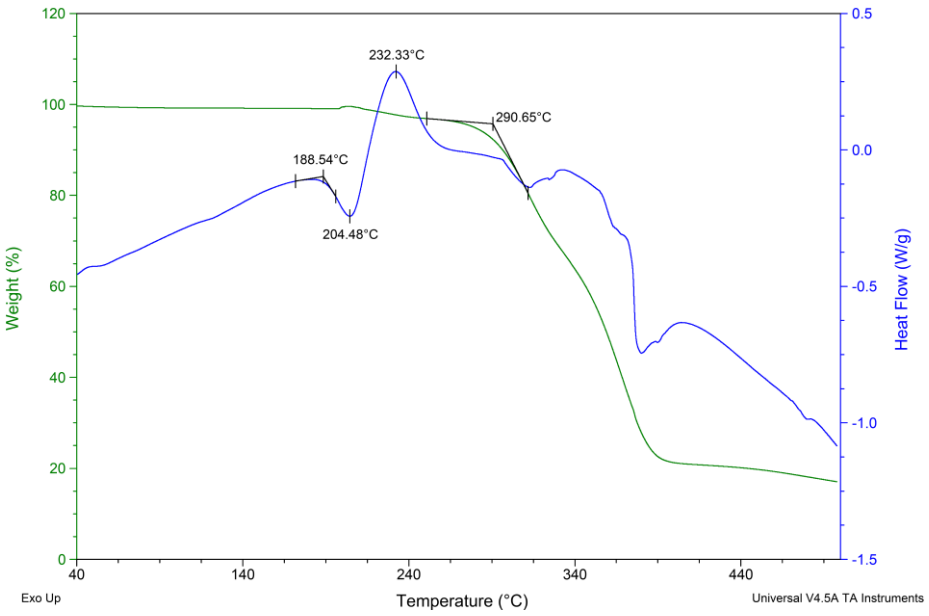



**Figure S44.** SDT thermogram of polymer **11** ($M_n$ = 5.7 kDa).