Trifluoromethylation of carbonyl groups in aromatic poly(ether ketone)s: formation of strongly polar yet surface-hydrophobic poly(arylenenecarbinol)s

Article

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Trifluoromethylation of carbonyl groups in aromatic poly(ether ketone)s: formation of strongly polar yet surface-hydrophobic poly(arylenenecarbinol)s

*Flavien Leroux, Roger A. Bennett, David F. Lewis and Howard M. Colquhoun**

Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK

SUPPORTING INFORMATION

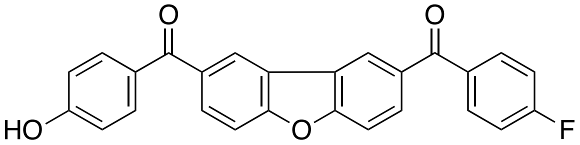
1. Materials, methods and instrumentation

Materials and Instrumentation.

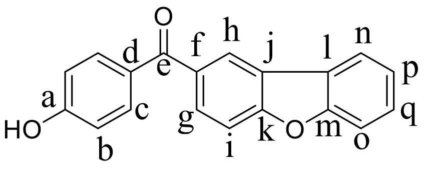
Starting materials anisole, tetrabutylammonium fluoride hydrate, trifluoromethanesulfonic acid and trifluoromethyltrimethylsilane were purchased from Fluorochem and were used as received. All other chemicals were purchased from Sigma-Aldrich and used as received with the exception of anhydrous potassium carbonate, which was heated at 100 °C under vacuum for 24 h prior to use. All solvents were used as supplied with the exception of tetrahydrofuran (THF), which was distilled under argon from sodium and benzophenone. Proton and ^{13}C NMR spectra were recorded on either a Bruker Nanobay 400 (9.39 T) or a Bruker DPX 400 (9.39 T) spectrometer operating at 400 MHz for ^{1}H NMR or 100 MHz for ^{13}C NMR, respectively. Samples for NMR analysis were prepared in $CDCl_3$, acetone-d_6 or DMSO-d_6. The data were processed using MestreNova. Proton chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ 0.00 ppm) for $CDCl_3$ and to the residual solvent peak (δ 2.05 ppm) for acetone-d_6 and (δ 2.50 ppm) for DMSO-d_6. ^{13}C NMR spectroscopy was carried out using either $CDCl_3$, acetone-d_6 or DMSO-d_6 and chemical shifts are reported relative to chloroform (δ 77.0 ppm), acetone-d_6 (δ 29.8 ppm) or DMSO-d_6 (δ 39.5 ppm). ^{1}H NMR coupling constants (J) are expressed in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer 100 Spectrum FT-IR using a diamond ATR sampling accessory. The infrared spectroscopic data were processed using Microsoft Excel 2016. Mass spectrometry was conducted using ThermoFisher Scientific Orbitrap XL LCMS. The sample was introduced by liquid chromatography and sample ionisation was achieved by electrospray ionisation (ESI). Gel permeation chromatography (GPC) was conducted using an Agilent Technologies 1260 Infinity system and the data were processed using Agilent GPC/SEC software; polystyrene was used as the calibrant. Samples for GPC analysis were dissolved in analytical grade THF (2 mg mL^{-1}) with butylated hydroxytoluene (BHT) stabiliser, and run using the same solvent as the mobile phase, eluting through two Agilent PLgel 5 µm MIXED-D 300 × 7.5 mm columns in series. Phase transitions (glass transitions, cold crystallizations and melting points) were identified by differential scanning calorimetry (DSC) using a TA Instruments DSC 2920. The following process was carried out on each DSC sample: heating from +25 °C to +300 °C at +5 °C min^{-1}, followed by cooling from +300 °C to +25 °C at -5 °C min^{-1} and then heating from +25 °C to +300 °C at +5 °C min^{-1}. The DSC sample size was 5-10 mg, and the data were processed using TA Universal Analysis Version 4.7A and Microsoft Excel 2016. Inherent viscosities (η_{inh}) were measured at 25 °C with 0.1% w/v polymer solutions in *N*-methyl-2-pyrrolidinone (NMP) or 96% sulfuric acid (H_2SO_4) using a Schott Instruments CT 52 viscometer. Polymer films for contact angle measurements were obtained by evaporation of polymer solutions in 2-methoxyethanol (polyol **15**, 20 mg mL^{-1}) or DMAc [polyketone **2** and poly(silylether) **11**] on glass microscope slides (BS 7011 supplied by VWR). Static contact angles were measured from photographs of 10 µL droplets of Milli-Q water dispensed onto a horizontal polymer surface using an auto-pipette. X-ray photoelectron spectroscopy (XPS) was carried out in a custom-modified UHV chamber equipped with an un-monochromated Al-Kα (1486.6 eV) X-ray source, hemispherical electron energy analyser (run at 20 eV pass energy) and sample transfer system. Polymer films for XPS were spin coated (40 s at 2400 rpm) from 20 µL of 1 % w/v polymer solution in a mixture of methanol (80%) and propan-2-ol (20%), onto as-received 6 MHz Au-coated quartz microbalance crystals (Inficon 750-1000-G10). QCM frequency changes (after air drying) gave deposition values of 6.7 µg and 5.2 µg of polymers **15** and **16**, respectively on the 1.2 cm^2 electrode, corresponding to film thicknesses of 36 and 29 nm. Samples were mounted on a tantalum plate and introduced into vacuum via a load lock. Binding energies were referenced to the Au $4f_{7/2}$ peak at 84.0 eV which was highly attenuated but still visible in the spectra. Photoemission peak quantification was performed in CasaXPS with Gaussian-Lorentzian mixed product curves on a Shirley background with widths constrained to those of the $C_{aromatic}$ species. Thermogravimetric data were obtained under nitrogen using a TA Instruments Q600SDT TGA analyser. Tensile stress-strain measurements were carried out at a strain rate of 1 mm/min using an AML X5-500 Single Column Universal Tester equipped with a 5 kN load cell and wedge grips.

2. Synthesis and characterization of monomers 8 and 9

Monomer 8:



(a) *2-(4'-Hydroxybenzoyl)dibenzofuran*: Dibenzofuran (16.8 g, 0.100 mol), 4-hydroxybenzoic acid (13.0 g, 0.094 mol) and a magnetic stirrer bar were added to a 250 mL conical flask which was then flushed with nitrogen. Trifluoromethanesulfonic (triflic) acid (100 cm^3) was added, the flask stoppered, and the reaction mixture stirred for 16 h. The dark brown solution was then added dropwise to water (1 L) and the suspension stirred vigorously until the pale yellow solid was broken up and well dispersed. The solid was filtered off, washed with water (2 x 500 mL) and then with hexane (500 mL), and air-dried on the filter. The crude solid was recrystallized from hot propan-2-ol, with hot filtration through Celite, to give 18.0 g of 2-(4-hydroxybenzoyl)-dibenzofuran as pale yellow crystals (62% yield). Mp = 233 °C.



^{1}H NMR (DMSO-d_6, 400 MHz): 6.95 (H$_b$, d, $^3J_{bc}$ = 9 Hz), 7.45 (H$_p$, t, ^3J = 8 Hz), 7.59 (H$_q$, t, ^3J = 8 Hz), 7.74 (H$_c$, t, $^3J_{cb}$ = 8 Hz), 7.77 (H$_o$, d, $^3J_{oq}$ = 8 Hz), 7.85 (H$_g$+H$_i$, m, ^3J = 9 Hz), 8.29 (H$_n$, d, $^3J_{np}$ = 8 Hz), 8.53 (H$_h$, s), 10.50 (OH, s) ppm.

^{13}C NMR (DMSO-d_6, 100 MHz): 111.5 (C$_i$), 111.8 (C$_o$), 115.2 (C$_b$), 121.8 (C$_n$), 122.9 (C$_h$), 123.2 (C$_j$+C$_l$), 123.5 (C$_P$), 128.3 (C$_q$+C$_d$), 129.2 (C$_g$), 132.6 (C$_c$), 133.4 (C$_f$), 156.1 (C$_m$), 157.3 (C$_k$), 161.9 (C$_a$), 193.8 (C$_e$) ppm.

FTIR (ATR/ν max) υ(O-H) = 3270 cm^{-1}, υ(C=O) = 1626 cm^{-1}, υ(C=C) = 1598 cm^{-1}, 1564 cm^{-1}, 1428 cm^{-1}, υ(C-O) aryl ether = 1284 cm^{-1}, 1269 cm^{-1}, υ (C-O) phenol = 1186 cm^{-1}, δ(C-H) = 849 cm^{-1}, δ(C-H) = 753 cm^{-1}.

ESI-MS m/z calculated for [$C_{19}H_{13}O_3$]$^+$: 289.0859, found m/z 289.0863.

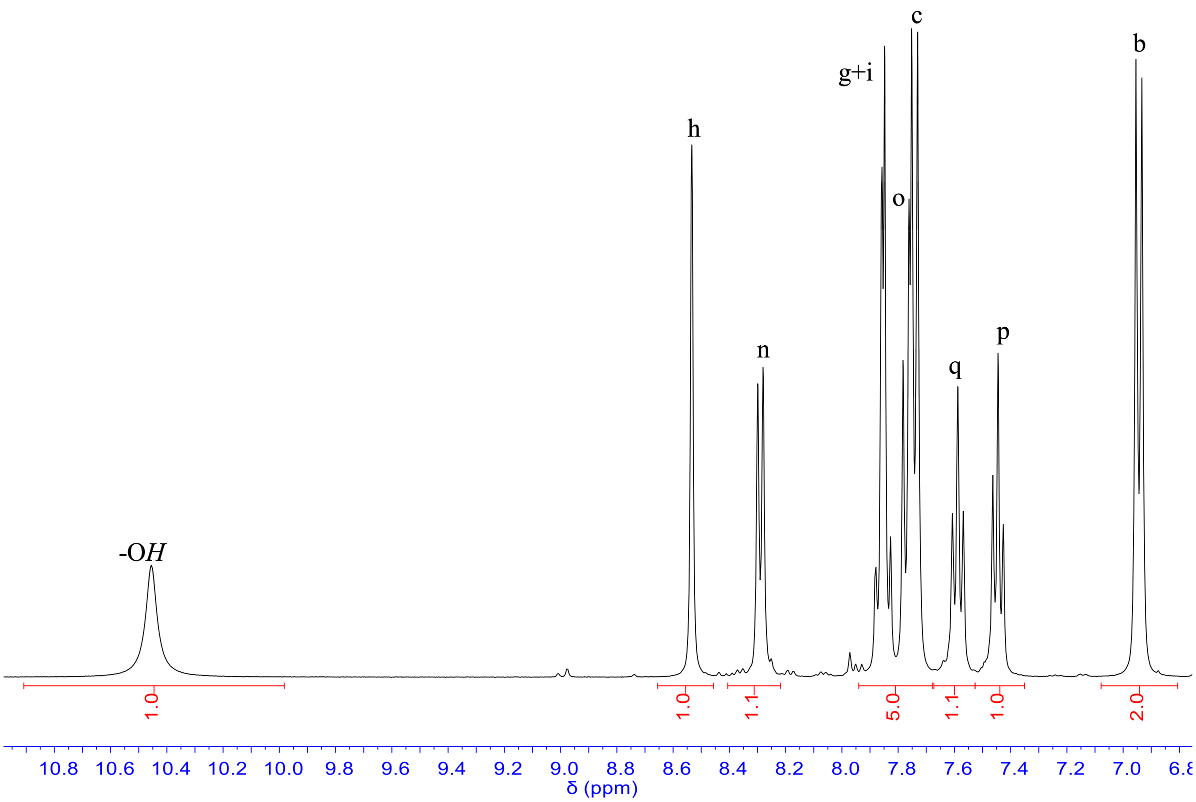


Figure S1. ^{1}H NMR spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran (400 MHz, DMSO-d_6).

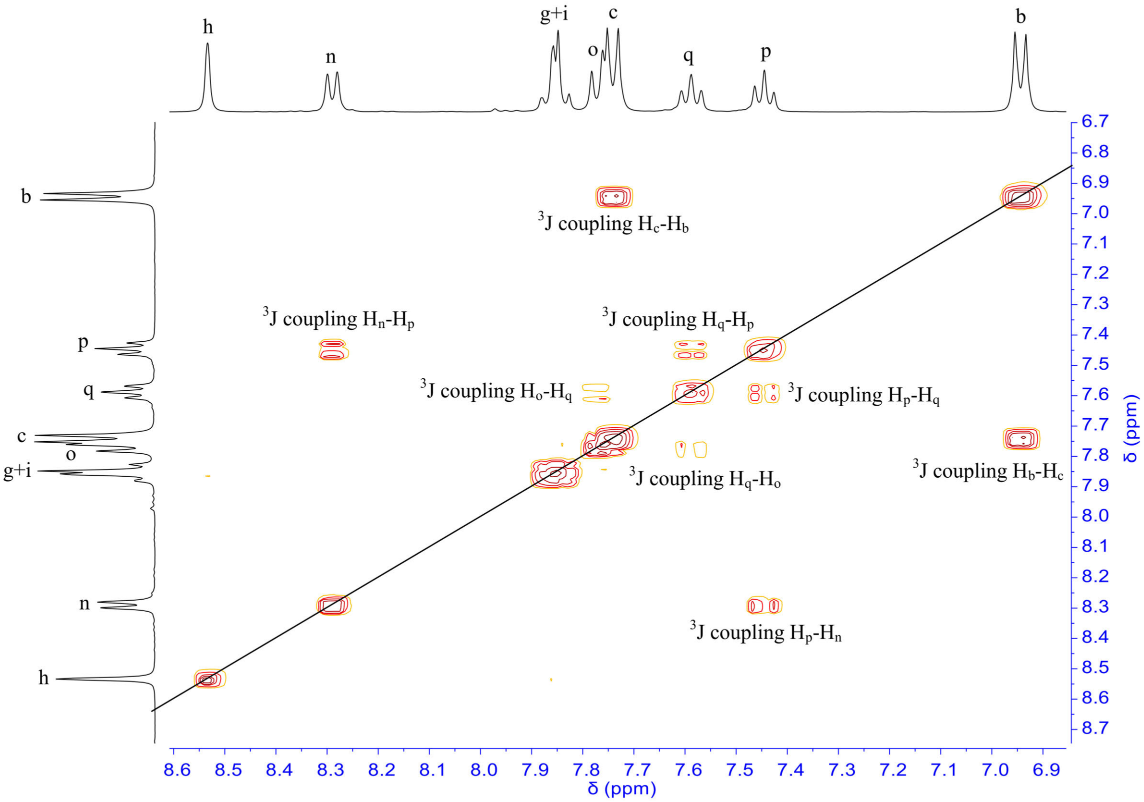


Figure S2. COSY (^{1}H-^{1}H) NMR spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran (400 MHz, DMSO-d_6).

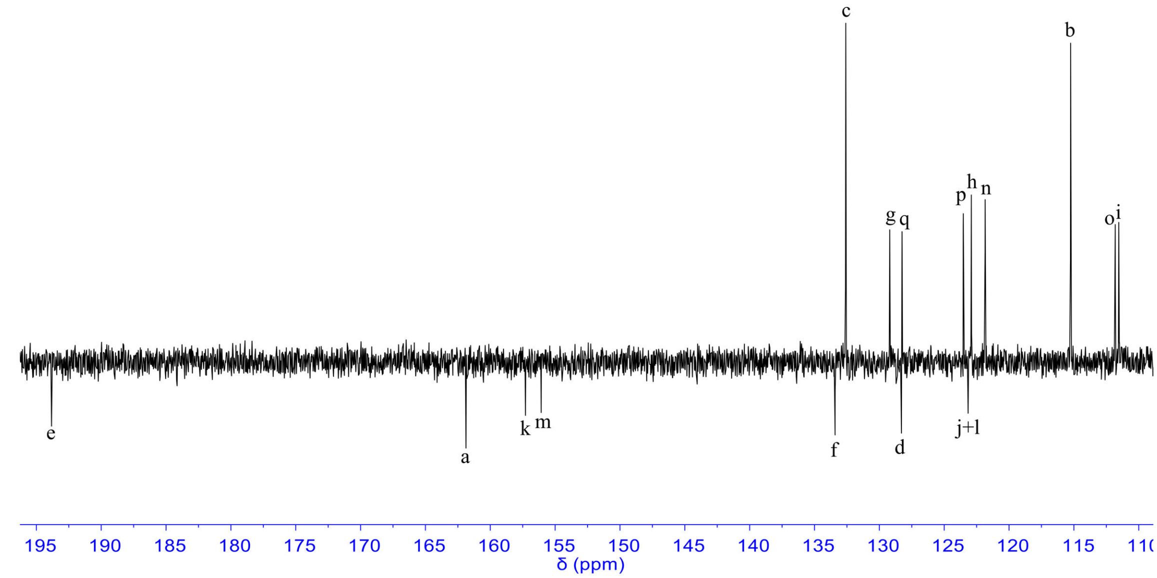


Figure S3. ^{13}C NMR (DEPT-135) spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran (100 MHz, DMSO-d_6).

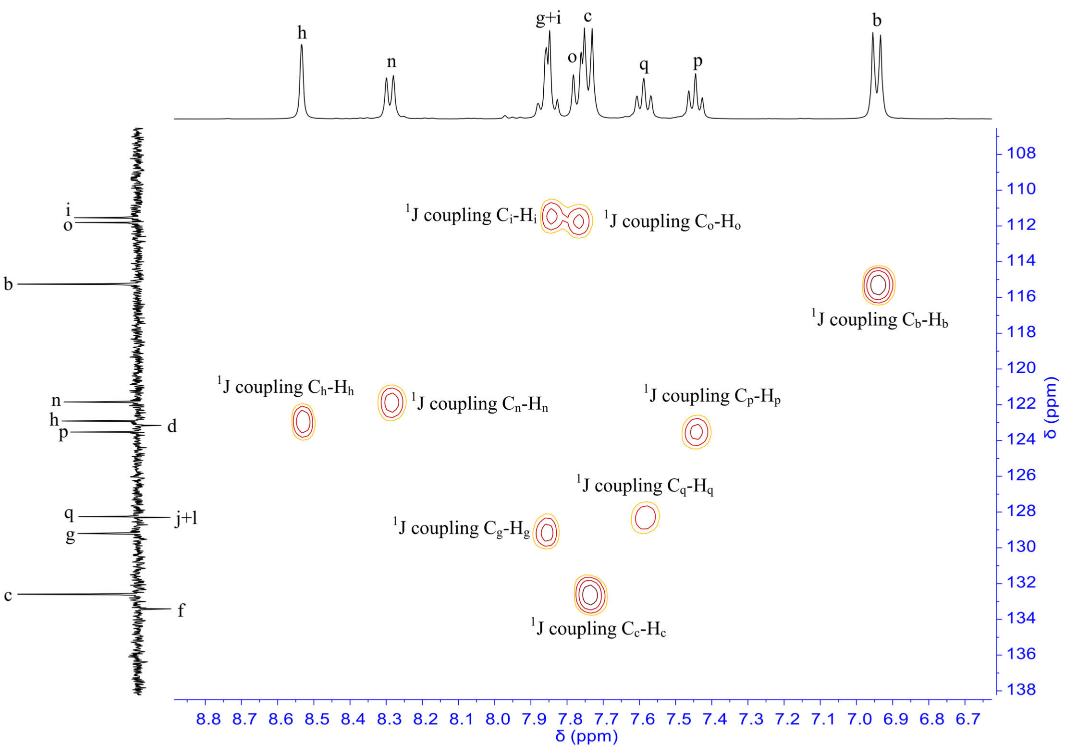
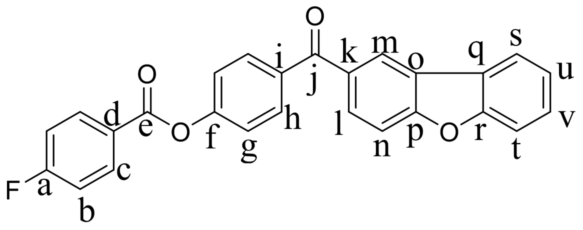


Figure S4. HSQC (^{1}H-^{13}C) NMR spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran (DMSO-d_6).

(b) *2-(4'-Hydroxybenzoyl)dibenzofuran 4-fluorobenzoate ester*: 2-(4'-Hydroxybenzoyl)-dibenzofuran (12 g, 0.042 mol), 4-dimethylaminopyridine (0.508 g, 0.00416 mol) and triethylamine (11.6 mL, 0.0832 mol) were dissolved in THF (280 mL). 4-Fluorobenzoyl chloride (7 g, 0.04 mol) was added and the reaction mixture was stirred for 4 h. After 4 h, methanol (10 mL) was added and the mixture was stirred for 1 h to esterify residual acid chloride. The precipitate was filtered off and the volatiles removed under reduced pressure. The crude product was recrystallized from acetone, with hot filtration through Celite, to give the 4-fluorobenzoate ester of 2-(4'-hydroxybenzoyl)dibenzofuran as white crystals (12 g, 70% yield). Mp = 185 °C.



^{1}H NMR (CDCl$_3$, 400 MHz): 7.22 (H$_b$, t, $^3J_{bc}$= 8 Hz), 7.33-7.46 (H$_g$+H$_u$, m, $^3J_{gh}$= 8.4 Hz), 7.53 (H$_v$, t, ^3J= 8 Hz), 7.63 (H$_t$, d, $^3J_{tv}$ = 8 Hz), 7.67 (H$_n$, d, $^3J_{nl}$ = 9 Hz), 7.96 (H$_h$, d, $^3J_{hg}$ = 8 Hz), 8.00 (H$_s$+H$_l$, m), 8.26 (H$_c$, d, $^3J_{cb}$ = 8 Hz, $^4J_{c\text{-}F}$ = 3 Hz), 8.47 (H$_m$, s) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): 111.6 (C$_n$), 112.0 (C$_t$), 115.9-116.1 (C$_b$), 121.1 (C$_s$), 121.7 (C$_g$), 123.4 (C$_m$+C$_u$), 123.7 (C$_q$), 124.5 (C$_o$), 125.4 (C$_d$), 128.1 (C$_v$), 129.8 (C$_l$), 131.7 (C$_h$), 132.5 (C$_k$), 132.9-133.0 (C$_c$), 135.8 (C$_i$), 154.0 (C$_f$), 156.9 (C$_r$), 158.7 (C$_p$), 163.8 (C$_e$), 165.1-167.6 (C$_a$), 195.1 (C$_j$) ppm.

FTIR (ATR/ν max) υ(C-H) = 3118 cm^{-1}, 3060 cm^{-1}, υ(C=O) ester = 1731 cm^{-1}, υ(C=O) ketone = 1648 cm^{-1}, υ(C=C) = 1597 cm^{-1}, 1509 cm^{-1}, υ(C-O) aryl ether = 1264 cm^{-1}, 1242 cm^{-1}, υ(C-F) = 1198 cm^{-1}, υ(C-O) ester = 1075 cm^{-1}, δ(C-H) = 844 cm^{-1}, δ(C-H)= 756 cm^{-1}.

ESI-MS m/z calculated for [C$_{26}$H$_{16}$O$_4$F]$^+$: 411.1027, found m/z 411.1028.

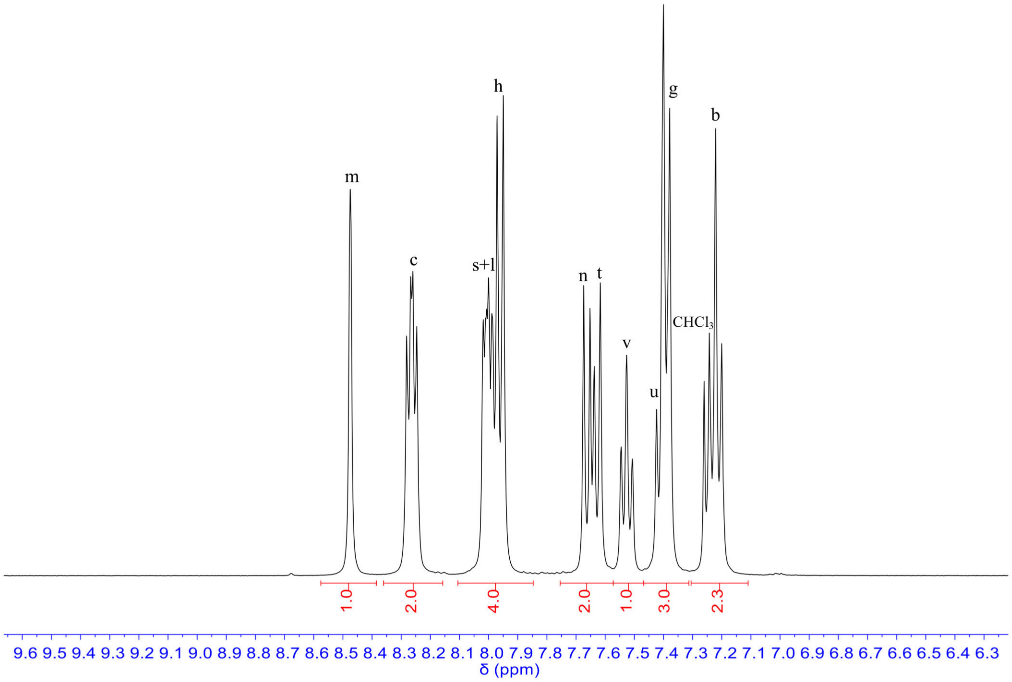


Figure S5. ^{1}H NMR spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran 4-fluorobenzoate ester (400 MHz, CDCl$_3$).

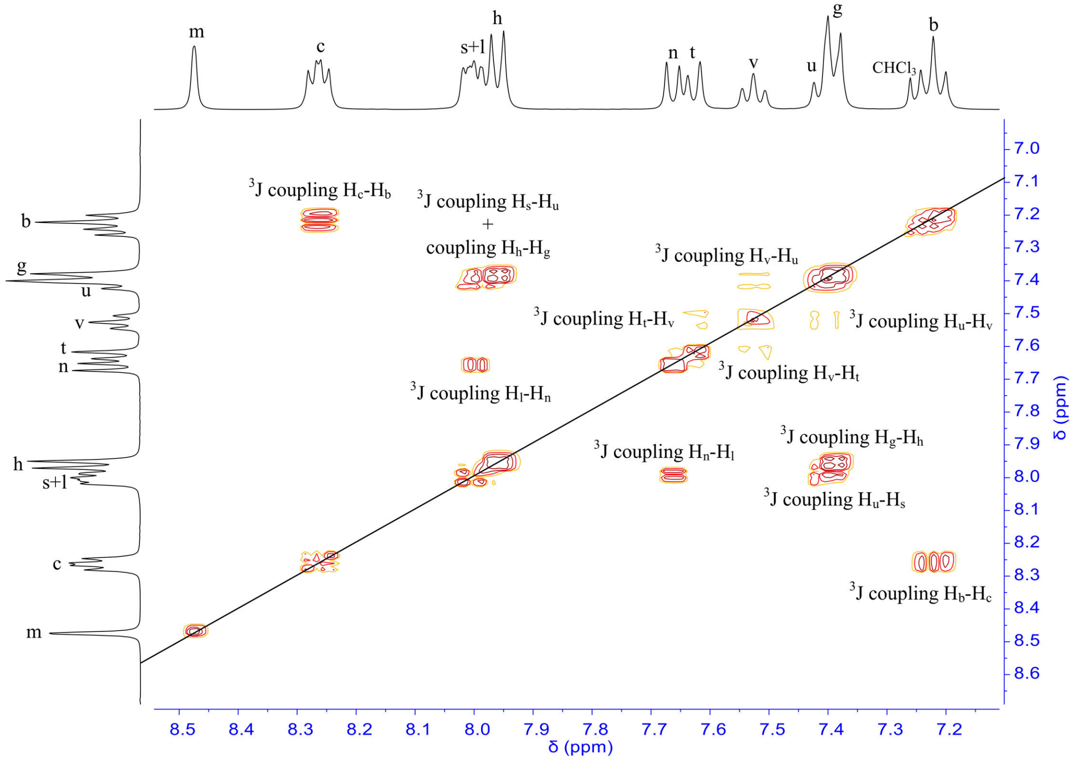


Figure S6. COSY (^{1}H-^{1}H) NMR spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran 4-fluorobenzoate ester (400 MHz, CDCl$_3$).

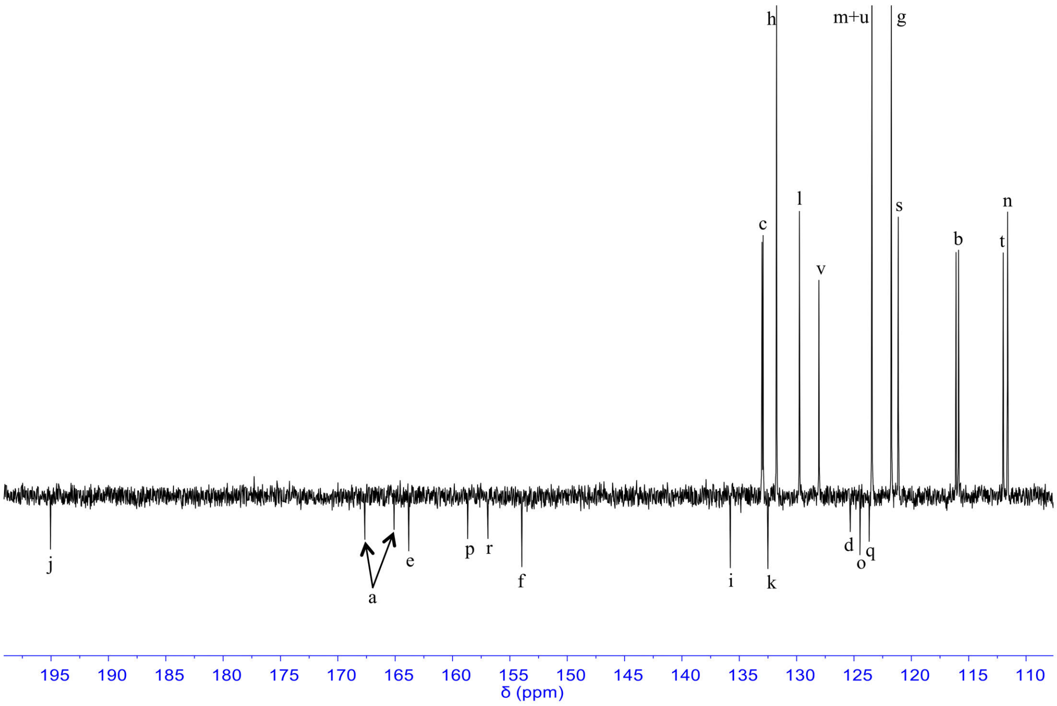


Figure S7. ^{13}C NMR (DEPT-135) spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran 4-fluorobenzoate ester (100 MHz, CDCl$_3$). Note the splitting of resonance "a" resulting from ^{13}C-^{19}F one-bond coupling.

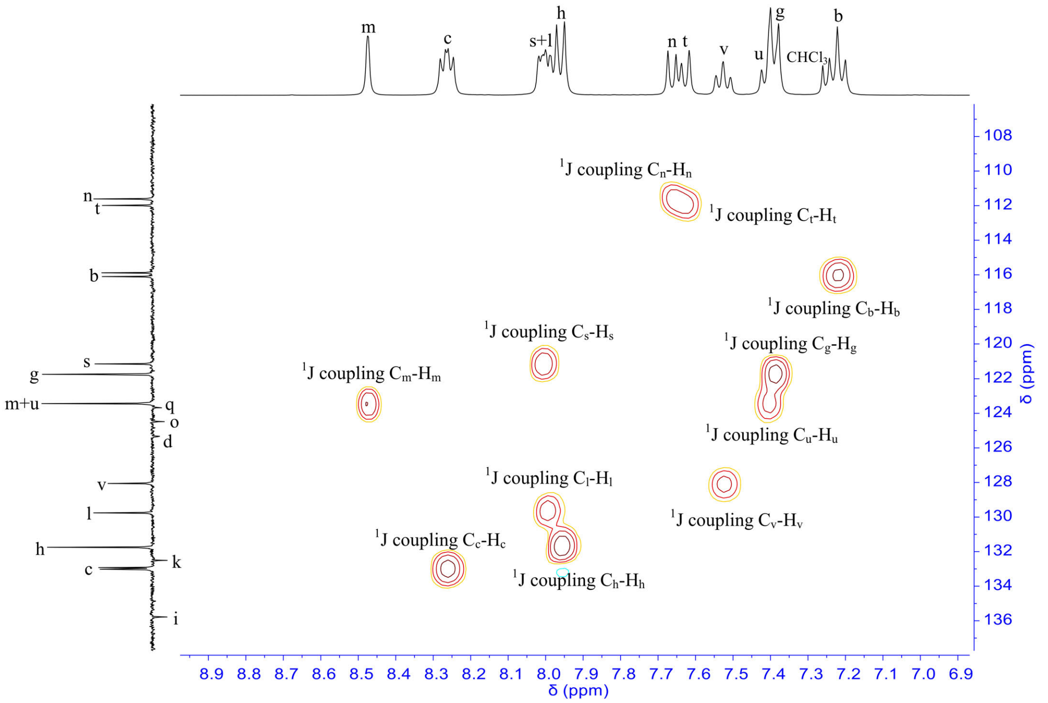
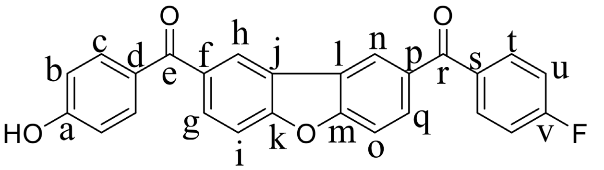


Figure S8. HSQC (^{1}H-^{13}C) NMR spectrum of 2-(4'-hydroxybenzoyl)dibenzofuran 4-fluorobenzoate ester (CDCl$_3$).

(c) *2-(4'-Fluorobenzoyl)-7-(4'-hydroxybenzoyl)dibenzofuran (**8**)*: The 4-fluorobenzoate ester of 2-(4-hydroxybenzoyl)dibenzofuran (3.50 g, 0.00854 mol) was added to 1,2-dichlorobenzene (19 mL) in a 3-necked, 100 mL round-bottomed flask, and the flask fitted with a reflux condenser and nitrogen inlet. Fresh, anhydrous aluminium chloride (5.8 g, 0.044 mol, five molar equivalents) was added to the flask and the reaction mixture was heated to 130 °C with stirring. After 6 h, HCl was no longer being evolved, and the mixture was cooled to room temperature and then poured very slowly into a mixture of acidified ice-water (100 ml water + 10 mL conc. HCl) and dichloromethane (160 mL). The mixture was stirred for 3 h and the solid product was filtered off, washed with water (200 mL) and dichloromethane (100 mL), and air-dried on the filter to give 2.45 g of crude product. This was recrystallized from hot methanol (ca. 250 mL) to give 2-(4'-fluorobenzoyl)-7-(4'-hydroxybenzoyl)dibenzofuran as pale brown crystals (1.85 g, 53% yield). Mp = 206 °C.



^{1}H NMR (DMSO-d_6, 400 MHz): 6.93 (H_b, d, $^3J_{bc}$ = 8 Hz), 7.42 (H_u, t, ^3J = 9 Hz), 7.73 (H_c, d, $^3J_{cb}$ = 8 Hz), 7.84-8.03 (H_g+H_i+H_o+H_q+H_t, m), 8.70 and 8.76 (H_n and H_h, s), 10.50 (OH, s) ppm.

^{13}C NMR (DMSO-d_6, 100 MHz): 111.8-112.1 (C_i+C_o), 115.2 (C_b), 115.5-115.7 (C_u), 123.1-123.4 (C_j+C_l), 123.8-124.4 (C_h+C_n), 128.2 (C_d), 129.8-130.0 (C_g+C_q), 132.6 (C_c), 132,7 (C_t), 132.8 (C_s), 133.9-134 (C_f+C_p), 157.9-158.4 (C_k+C_m), 161.9 (C_a), 163.4-165.9 (C_v), 193.7-193.9 (C_e+C_r) ppm.

FTIR (ATR/ν max) υ(O-H) = 3228 cm^{-1}, υ(C=O) ketone = 1645 cm^{-1}, 1625 cm^{-1}, υ(C=C) = 1591 cm^{-1}, 1571 cm^{-1}, υ(C-O) aryl ether = 1262 cm^{-1}, 1252 cm^{-1}, υ(C-F) = 1166 cm^{-1}, δ(C-H) = 844 cm^{-1}, δ(C-H) = 756 cm^{-1}.

ESI-MS m/z calculated for $[C_{26}H_{16}O_4F]^+$: 411.1027, found m/z 411.1027.

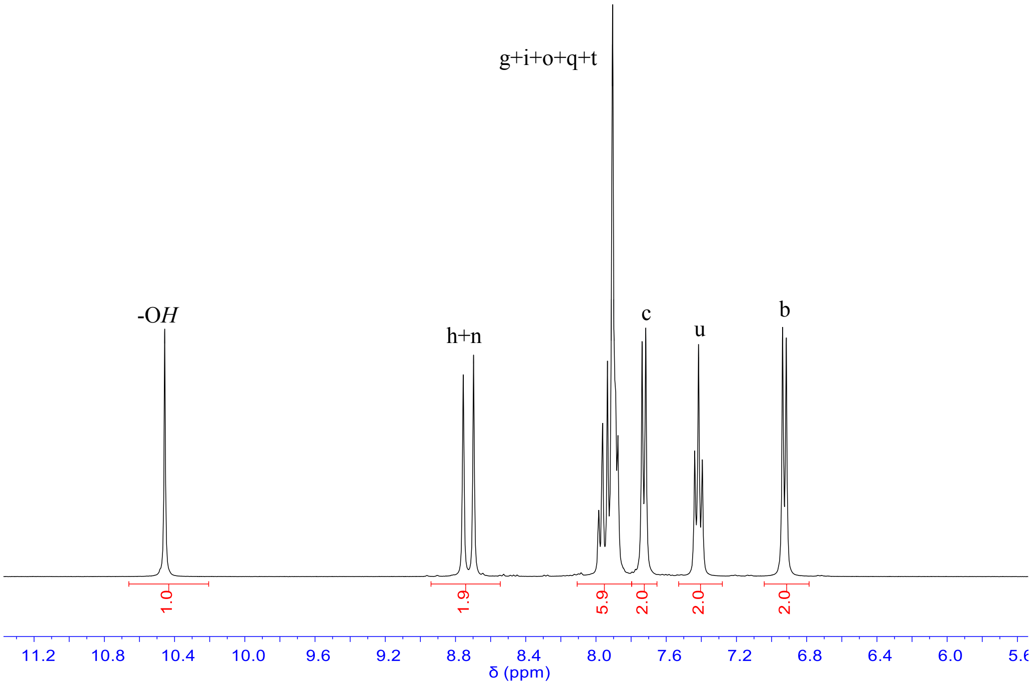


Figure S9. ^{1}H NMR spectrum of 2-(4'-fluorobenzoyl)-7-(4''-hydroxybenzoyl)dibenzofuran (**8**) (400 MHz, DMSO-d_6).

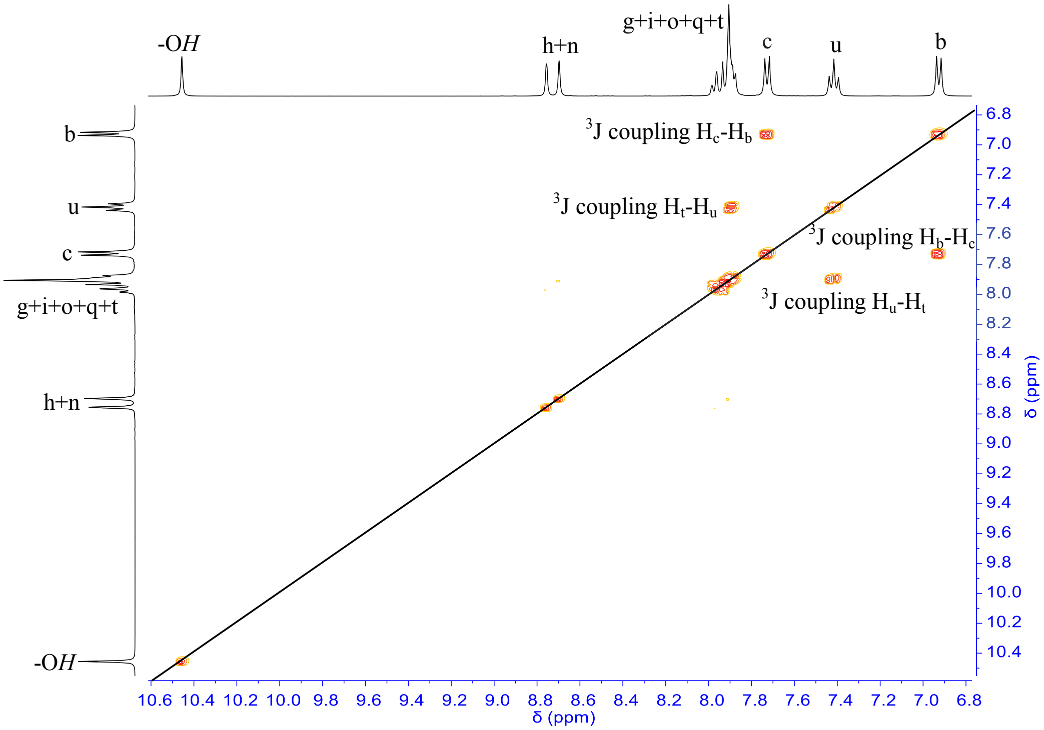


Figure S10. COSY (^{1}H-^{1}H) NMR spectrum of 2-(4'-fluorobenzoyl)-7-(4''-hydroxybenzoyl)-dibenzofuran (**8**) (400 MHz, DMSO-d_6).

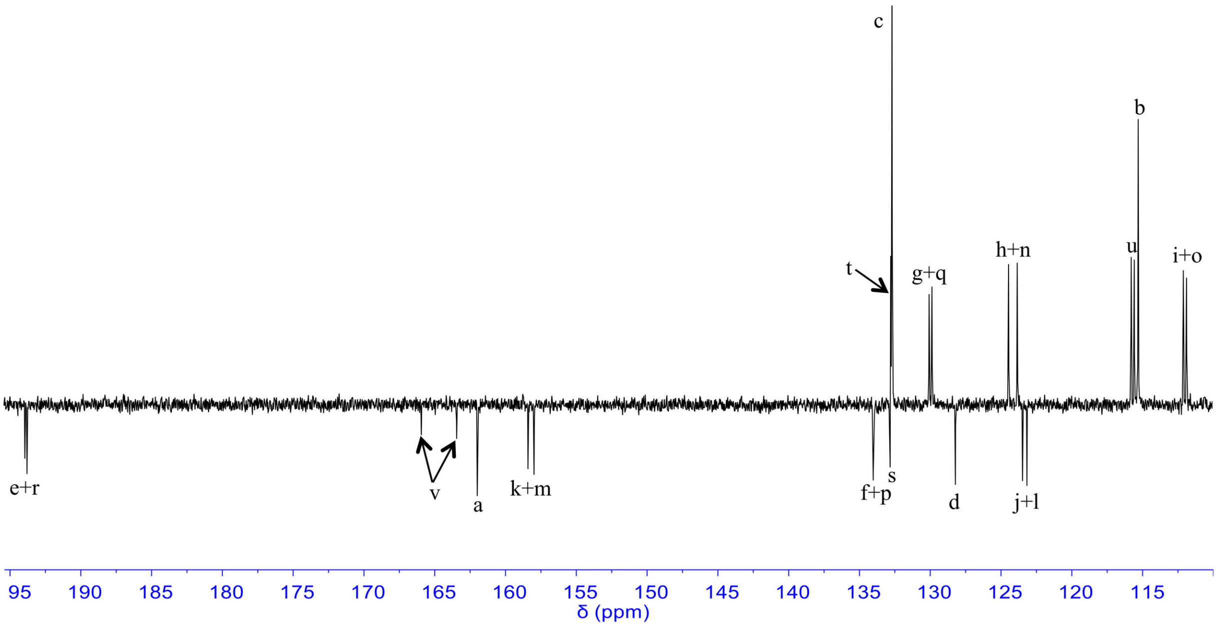


Figure S11. ^{13}C NMR (DEPT-135) spectrum of 2-(4'-fluorobenzoyl)-7-(4''-hydroxybenzoyl)-dibenzofuran (**8**) (100 MHz, DMSO-d_6). Note the splitting of resonance "v" resulting from ^{13}C-^{19}F one-bond coupling, and of resonance "u" from the corresponding two-bond coupling.

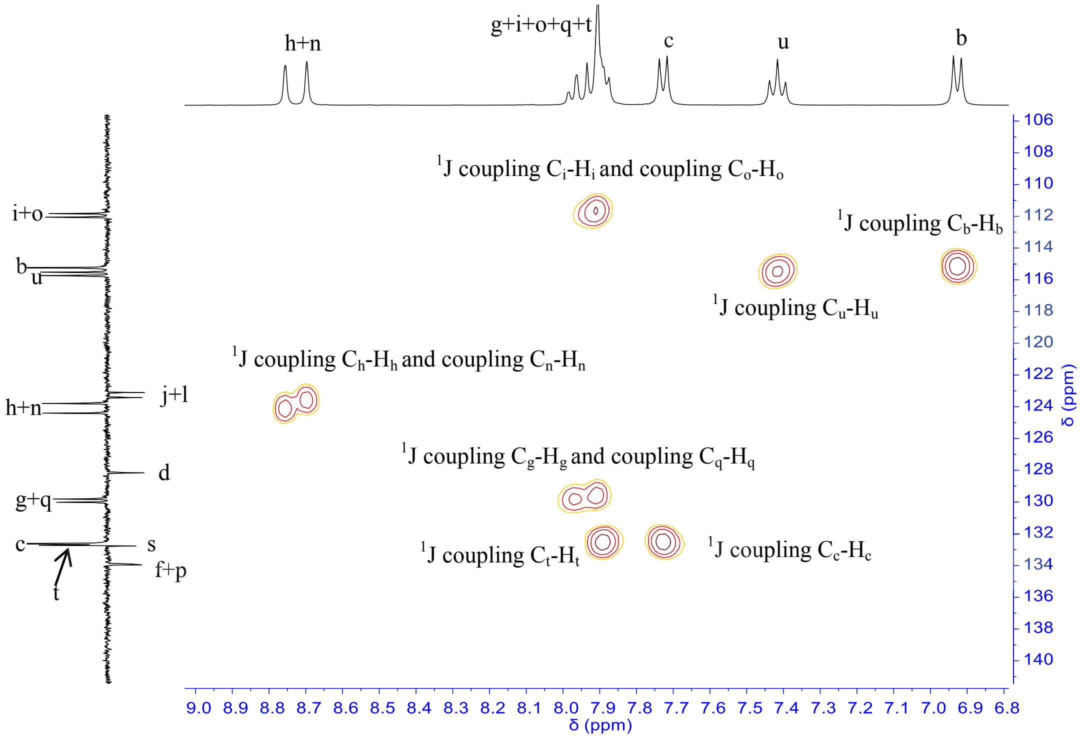
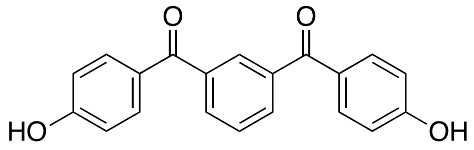
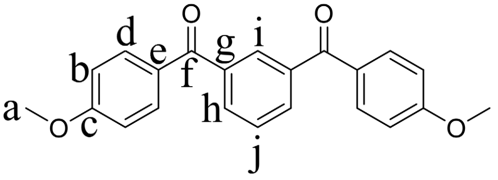


Figure S12. HSQC (^{1}H-^{13}C) NMR spectrum of 2-(4'-fluorobenzoyl -7-(4''-hydroxybenzoyl)-dibenzofuran (**8**) (DMSO-d_6).

Monomer 9:



(a) *1,3-Bis(4-methoxybenzoyl)benzene*: A mixture of isophthaloyl chloride (12.5 g, 60 mmol) and anisole (14.0 g 130 mmol) in 35 mL of dichloromethane was added dropwise with stirring at 0 °C to 18 g (0.014 mol) of aluminium chloride in 25 mL of dichloromethane, under dry nitrogen. The reaction mixture was warmed to room temperature and held for 4 h before pouring into a 500 mL of ice-water, and the organic layer was then separated. The aqueous layer was extracted with dichloromethane (3 times), and the combined organic solution was evaporated to dryness under reduced pressure. Recrystallization of the residue from ethanol afforded 1,3-bis(4-methoxybenzoyl)benzene (13.0 g, 63% yield). Mp = 147 °C.



^{1}H NMR ($CDCl_3$, 400 MHz): 3.89 (H_a, s), 6.97 (H_b, d, $^3J_{bd}$ = 8 Hz), 7.61 (H_j, t, $^3J_{jh}$ = 8 Hz), 7.84 (H_d, d, $^3J_{db}$ = 9 Hz), 7.96 (H_h, d, $^3J_{hi}$ = 8 Hz), 8.08 (H_i, s) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): 55.6 (C_a), 113.8 (C_b), 128.4 (C_j), 129.6 (C_e), 130.6 (C_i), 132.6 (C_d), 132.7 (C_h), 138.4 (C_g), 163.5 (C_c), 194.7 (C_f) ppm.

FTIR (ATR/ν max) υ(C-H) = 2979 cm^{-1}, 2936 cm^{-1}, 2844 cm^{-1}, υ(C=O) ketone = 1650 cm^{-1}, υ(C=C) = 1590 cm^{-1}, 1508 cm^{-1}, υ(C-O) alkyl-aryl ether = 1250 cm^{-1}.

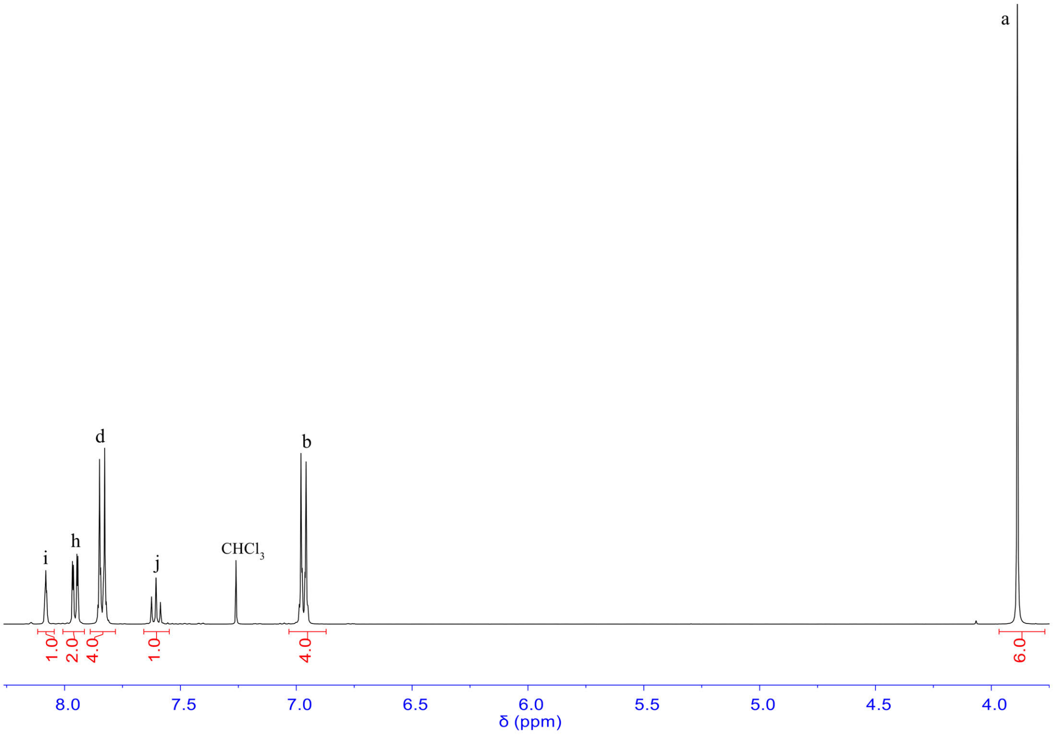


Figure S13. ^{1}H NMR spectrum of 1,3-bis(4'-methoxybenzoyl)benzene (400 MHz, $CDCl_3$).

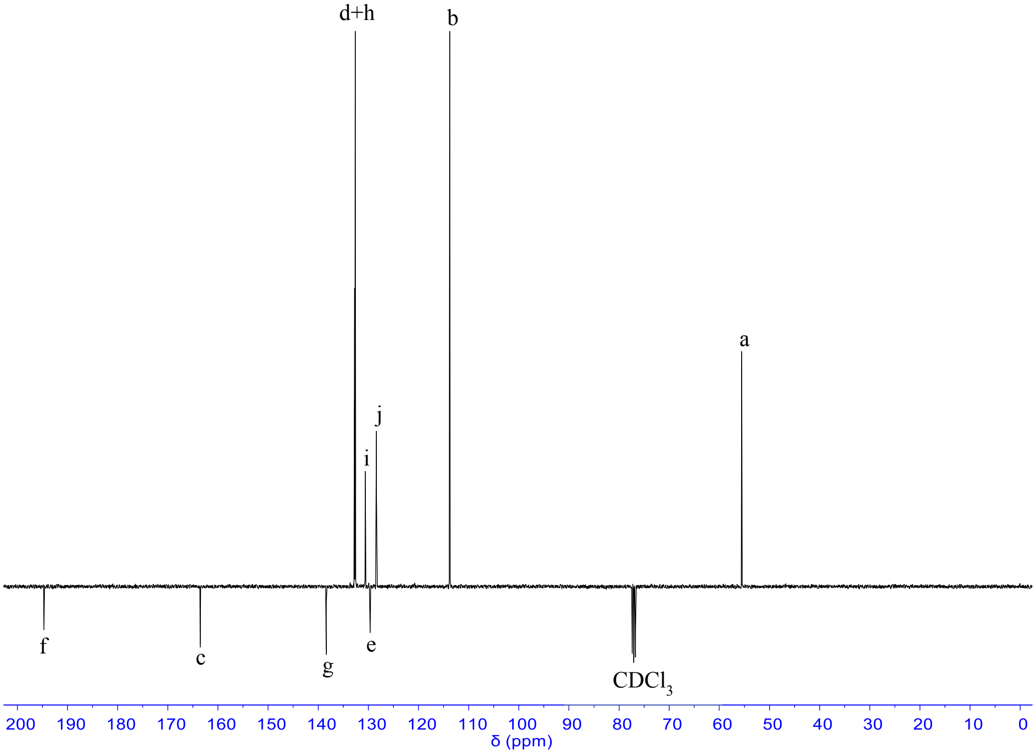
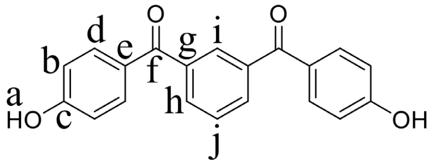


Figure S14. ^{13}C NMR (DEPT-135) spectrum of 1,3-bis(4'-methoxybenzoyl)benzene (100 MHz, $CDCl_3$).

(b) *1,3-Bis(4'-hydroxybenzoyl)benzene (**9**)*:

1,3-Bis(4'-methoxybenzoyl)benzene (11.5 g, 33 mmol) was dissolved in a mixture of 100 mL of acetic acid and 70 mL of 48% hydrobromic acid, and the mixture was heated at 120 °C for 24 h, cooled, and poured into ice water. The resulting precipitate was collected by filtration and washed copiously with water before drying *in vacuo* at 80 °C overnight to give crude 1,3-bis(4-hydroxybenzoyl)benzene (11.5 g). Recrystallization from a mixture of acetic acid and water (6:1 v/v) afforded pure 1,3-bis(4'-hydroxybenzoyl)benzene as a pale orange powder (8.6 g, 82% yield). Mp = 216 °C.



^{1}H NMR (DMSO-d_6, 400 MHz): 6.92 (H_b, d, $^3J_{bd}$ = 9 Hz), 7.72 (H_d+H_j, m, $^3J_{db}$ = 9 Hz), 7.87 (H_i, s), 7.93 (H_h, d, $^3J_{hj}$ = 8 Hz), 10.50 (H_a, s) ppm.

^{13}C NMR (DMSO-d_6, 100 MHz): 115.3 (C_b), 127.5 (C_e), 128.8 (C_j), 129.7 (C_i), 132.2 (C_h), 132.6 (C_d), 138.0 (C_g), 162.2 (C_c), 193.5 (C_f) ppm.

ESI-MS m/z calculated for $[C_{20}H_{15}O_4]^+$: 319.0965, found m/z 319.0968.

FTIR (ATR/v max) υ(O-H) = 3270 cm^{-1}, υ(C=O) ketone = 1638 cm^{-1}, υ(C=C) = 1601 cm^{-1}, 1569 cm^{-1}, υ(C-O) phenol = 1158 cm^{-1}.

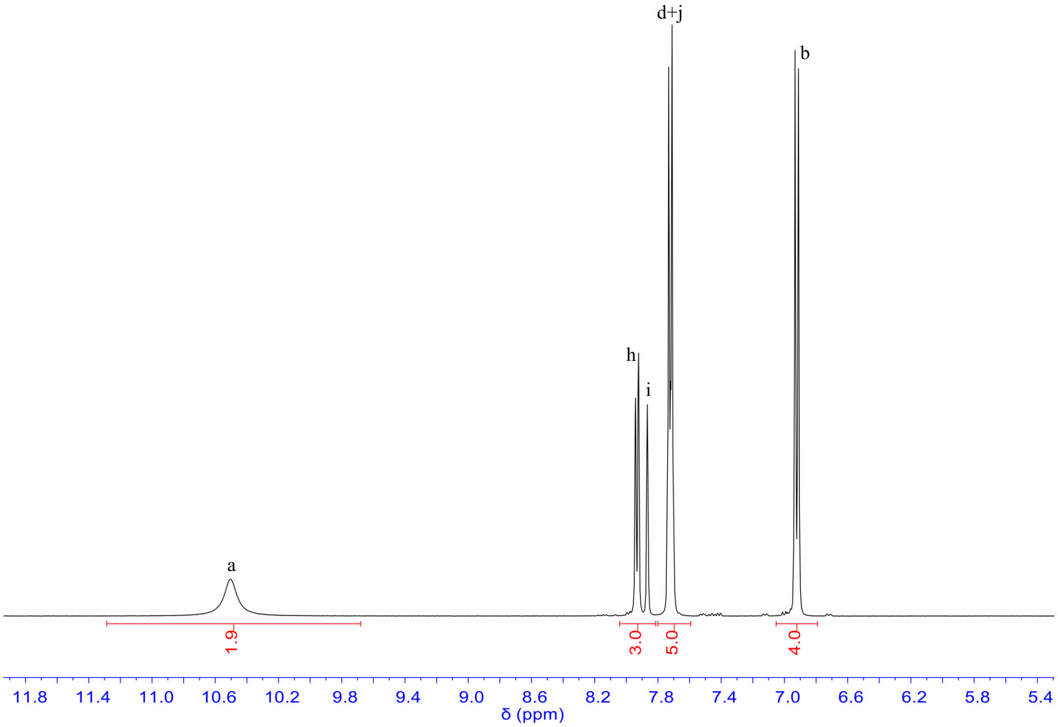


Figure S15. ^{1}H NMR spectrum of 1,3-bis(4'-hydroxybenzoyl)benzene (**9**) (400 MHz, DMSO-d_6).

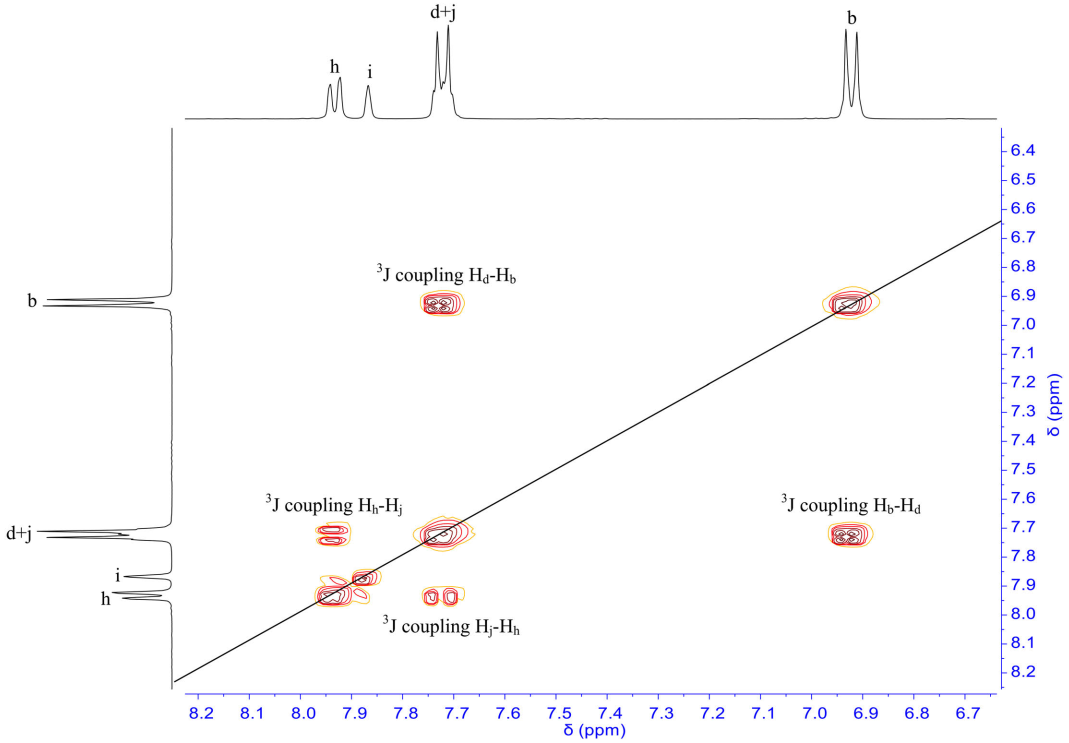


Figure S16. COSY (^{1}H-^{1}H) NMR spectrum of 1,3-bis(4'-hydroxybenzoyl)benzene (**9**) (400 MHz, DMSO-d_6).

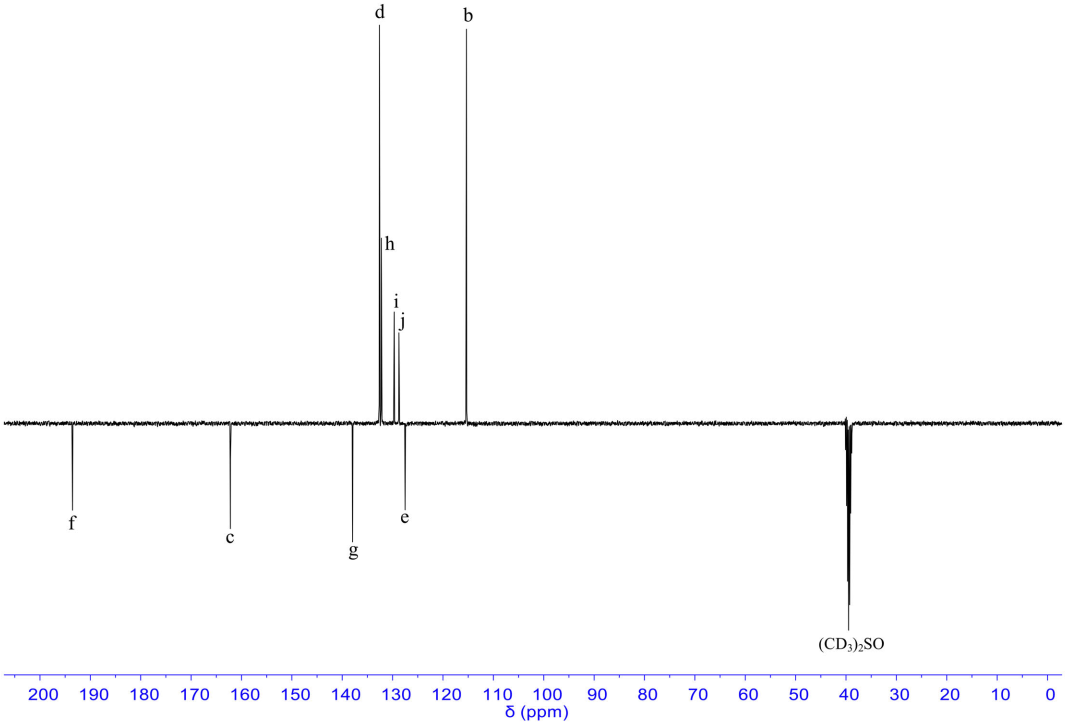


Figure S17. ^{13}C NMR (DEPT-135) spectrum of 1,3-bis(4'-hydroxybenzoyl)benzene **9** (100 MHz, DMSO-d_6).

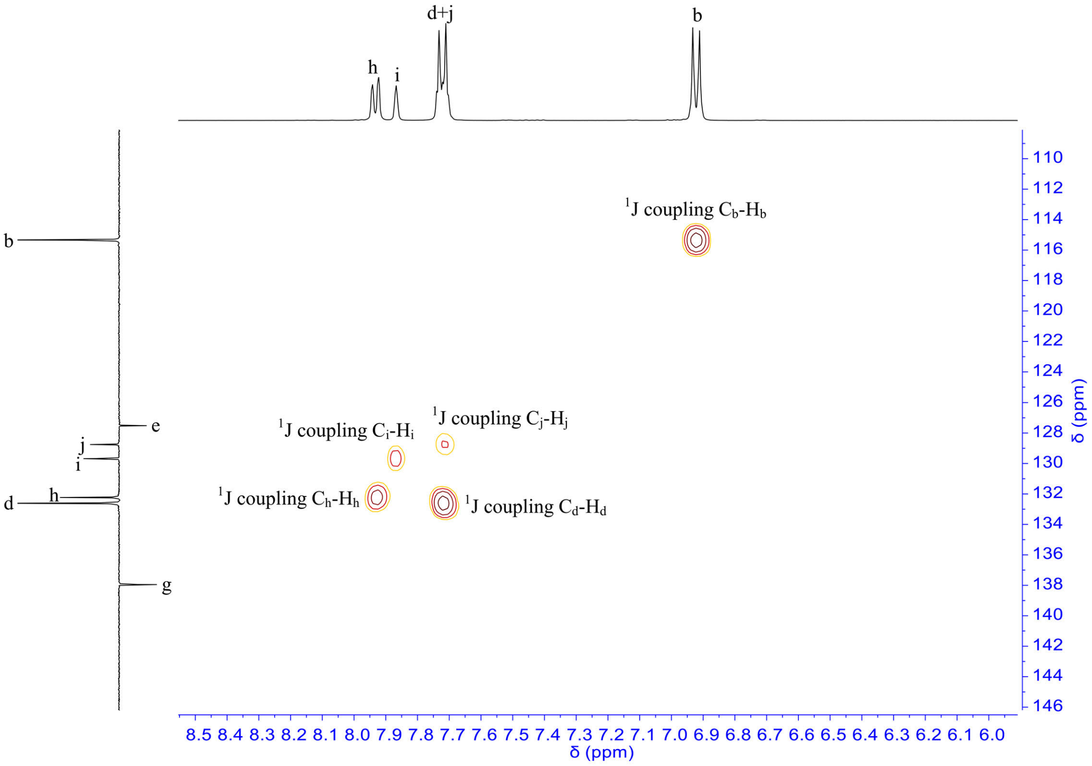
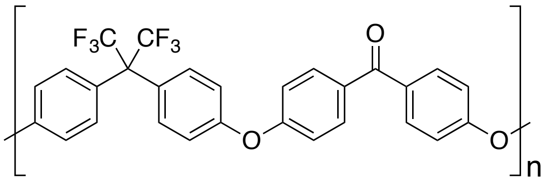


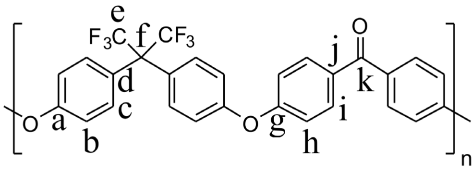
Figure S18. HSQC (^{1}H-^{13}C) NMR spectrum of 1,3-bis(4'-hydroxybenzoyl)benzene (**9**) (DMSO-d_6).

3. Synthesis and characterization of poly(ether ketone)s 1 – 4



Poly(ether ketone) 1*:*

Potassium carbonate (0.863 g, 6.25 mmol), NMP (10 mL) and toluene (8 mL) were introduced into a 50 mL round-bottom flask fitted with a stirrer, a Dean-Stark trap, a condenser and, a nitrogen inlet and outlet. The temperature was raised to 180 °C and water was removed by azeotropic distillation with toluene over two hours. A solution of 4,4-(hexafluoroisopropylidene)diphenol (2.017g, 6.00 mmol) and 4,4’-difluorobenzophenone (1.309 g, 6.00 mmol) in hot NMP (3 mL) was then added rapidly with stirring under nitrogen, and azeotropic distillation was continued. After 7 hours, the mixture was cooled to room temperature and poured into methanol (100 mL). The precipitated polymer was filtered off, washed with water (2 × 60 mL) and dried at 100 °C *in vacuo*. The polymer was re-precipitated twice into methanol (100 mL) from solution in the minimum amount of dichloromethane. After drying at 100 °C *in vacuo*, poly(ether ketone) **1** was obtained as a white solid (2.48 g, 80% yield).



^{1}H NMR (CDCl$_3$, 400 MHz): 7.08 (H$_b$, d, $^3J_{bc}$ = 8 Hz), 7.12 (H$_h$, d, $^3J_{hi}$ = 8 Hz), 7.43 (H$_c$, d, $^3J_{cb}$ = 8 Hz), 7.84 (H$_i$, d, $^3J_{ih}$ = 8 Hz) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): 118.3 (C$_h$), 118.9 (C$_b$), 128.8 (C$_d$), 132.0 (C$_c$), 132.3 (C$_i$), 133.0 (C$_j$), 156.6 (C$_a$), 160.1 (C$_g$), 194.1 (C$_k$) ppm.

FTIR (ATR/v max) υ(C=O) ketone = 1655 cm^{-1}, υ(C=C) = 1594 cm^{-1}, 1499 cm^{-1}, υ(C-O) aryl ether = 1239 cm^{-1}, υ(C-F) = 1171 cm^{-1}.

T_g (mid-point) = 155 °C. M_n = 13.0; M_w = 23.6 kDa; $Đ$ = 1.97; η_{inh} = 0.39 dL g^{-1} (NMP).

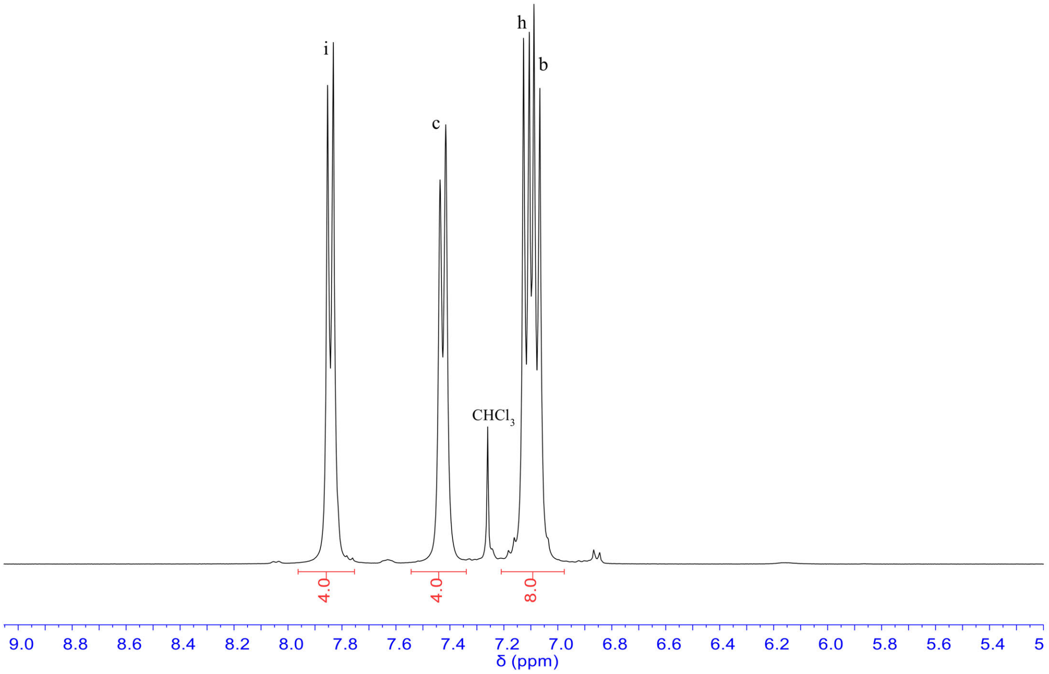


Figure S19. ^{1}H NMR spectrum of poly(ether ketone) **1** (400 MHz, CDCl$_3$).

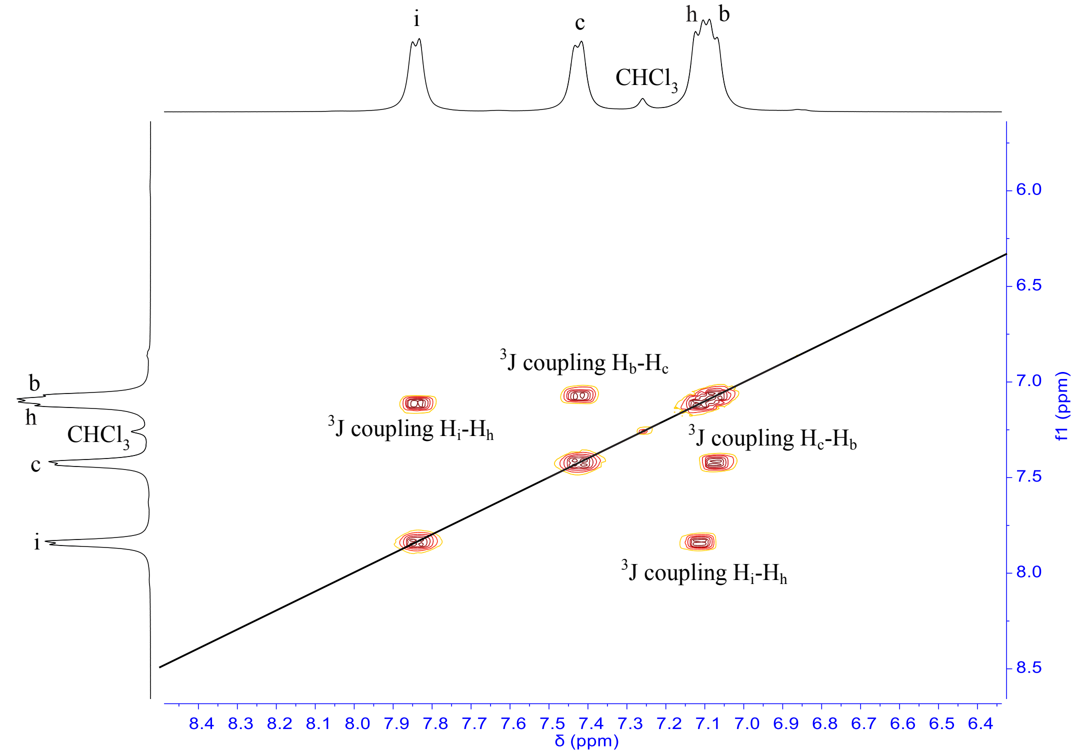


Figure S20. COSY (^{1}H-^{1}H) NMR spectrum of poly(ether ketone) **1** (400 MHz, CDCl$_3$).

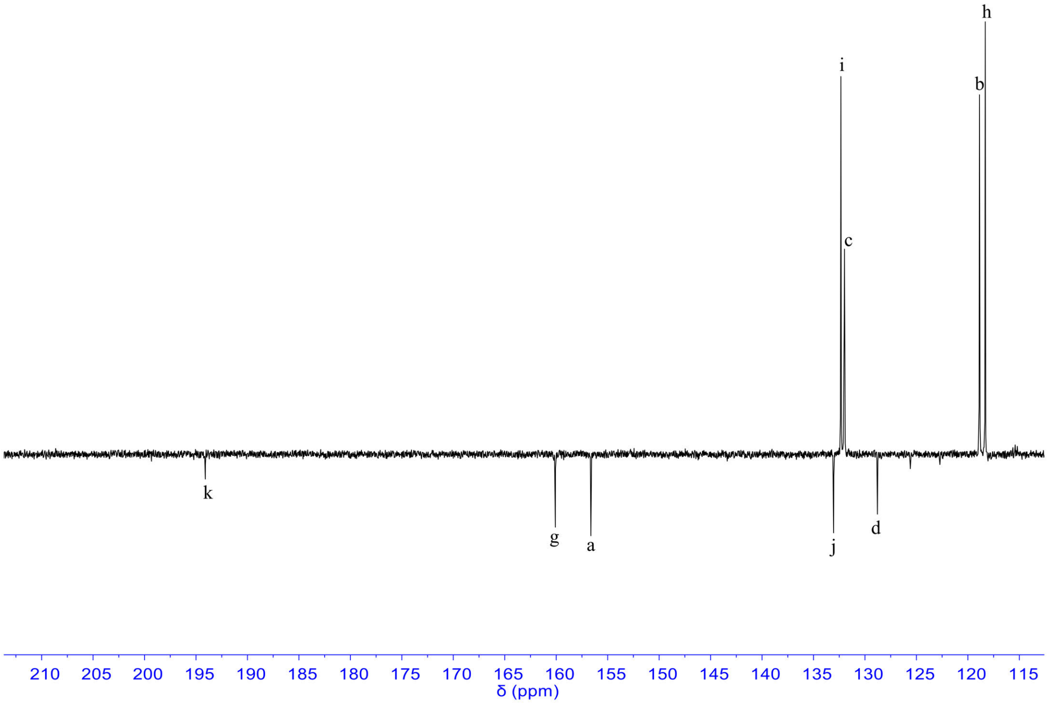


Figure S21. ^{13}C NMR (DEPT-135) spectrum of poly(ether ketone) **1** (100 MHz, CDCl$_3$).

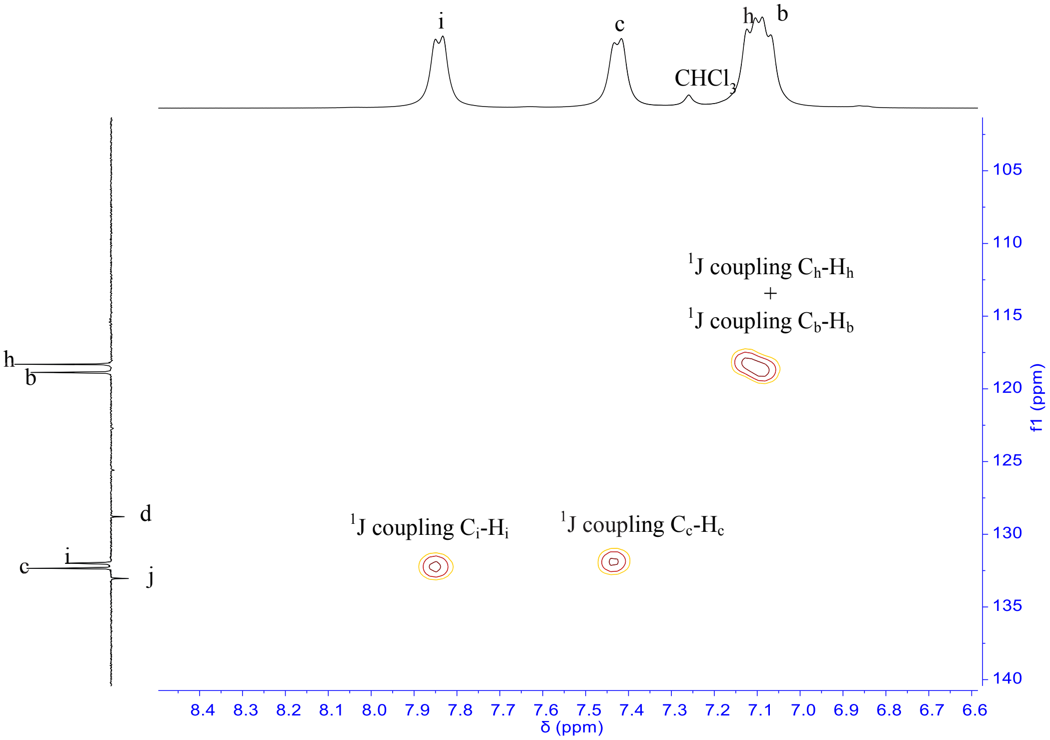


Figure S22. HSQC (^{1}H-^{13}C) NMR spectrum of poly(ether ketone) **1** (CDCl$_3$).

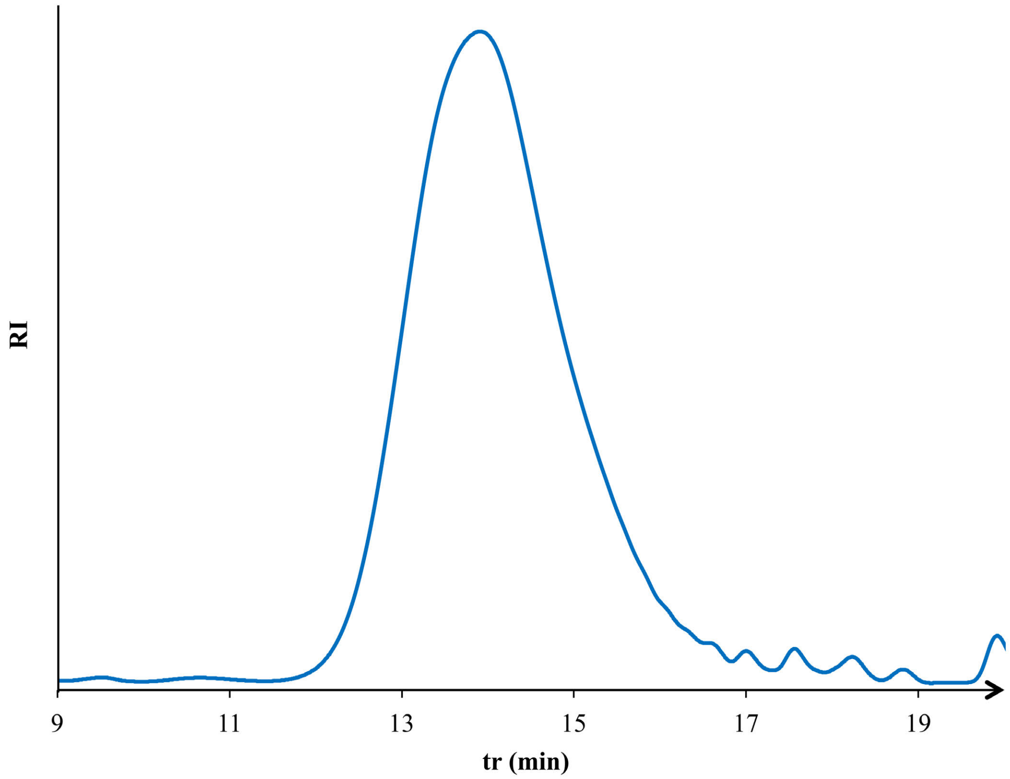


Figure S23. GPC trace for poly(ether ketone) **1** (in THF).

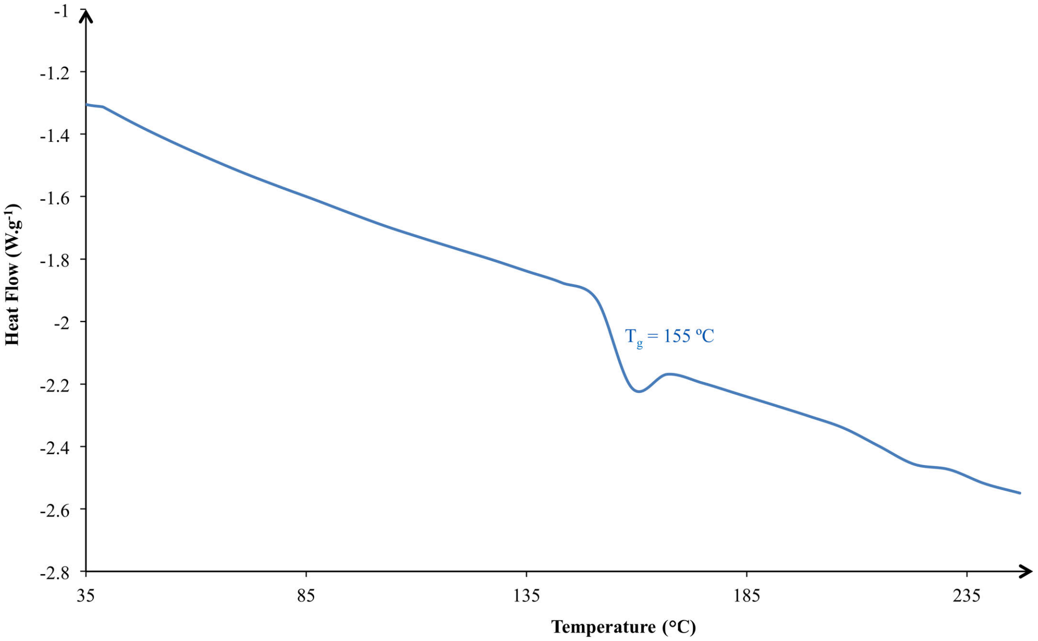
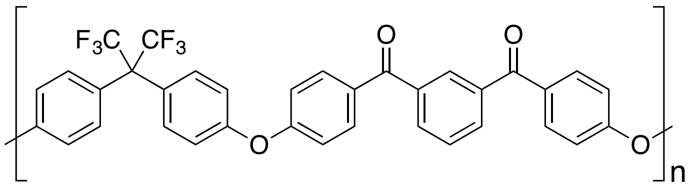
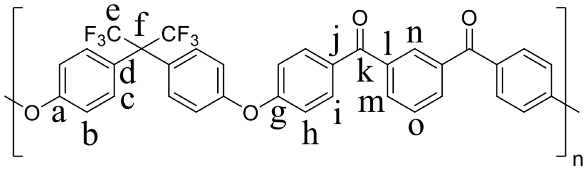


Figure S24. DSC thermogram (second heating scan) for poly(ether ketone) **1**.

Poly(ether ketone) 2:



Poly(ether ketone) **2** was obtained from monomers **6** and **7** using the method described above for poly(ether ketone) **1**, and was isolated in 80% yield.



^{1}H NMR (CDCl$_3$, 400 MHz): 7.09 (H_b, d, $^3J_{bc}$ = 9 Hz), 7.12 (H_h, d, $^3J_{hi}$ = 9 Hz), 7.43 (H_c, d, $^3J_{cb}$ = 9 Hz), 7.62 (H_o, t, $^3J_{om}$ = 8 Hz), 7.87 (H_i, d, $^3J_{ih}$ = 9 Hz), 7.99 (H_m, d, $^3J_{mo}$ = 8 Hz), 8.17 (H_n, s) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): 118.3 (C_h), 119.1 (C_b), 128.5 (C_o), 129.0 (C_d), 130.8 (C_n), 132.0 (C_c), 132.2 (C_j), 132.6 (C_i), 133.2 (C_m), 138.0 (C_l), 156.4 (C_a), 160.7 (C_g), 194.5 (C_k) ppm.

FTIR (ATR/ν max) υ(C=O) ketone = 1658 cm^{-1}, υ(C=C) = 1591 cm^{-1}, 1497 cm^{-1}, υ(C-O) aryl ether = 1236 cm^{-1}, υ(C-F) = 1170, 1157 cm^{-1}.

T_g (mid-point) = 158 °C. M_n = 20.4; M_w = 57.0 kDa; $Đ$ = 2.80; η_{inh} = 0.74 dL g^{-1} (NMP).

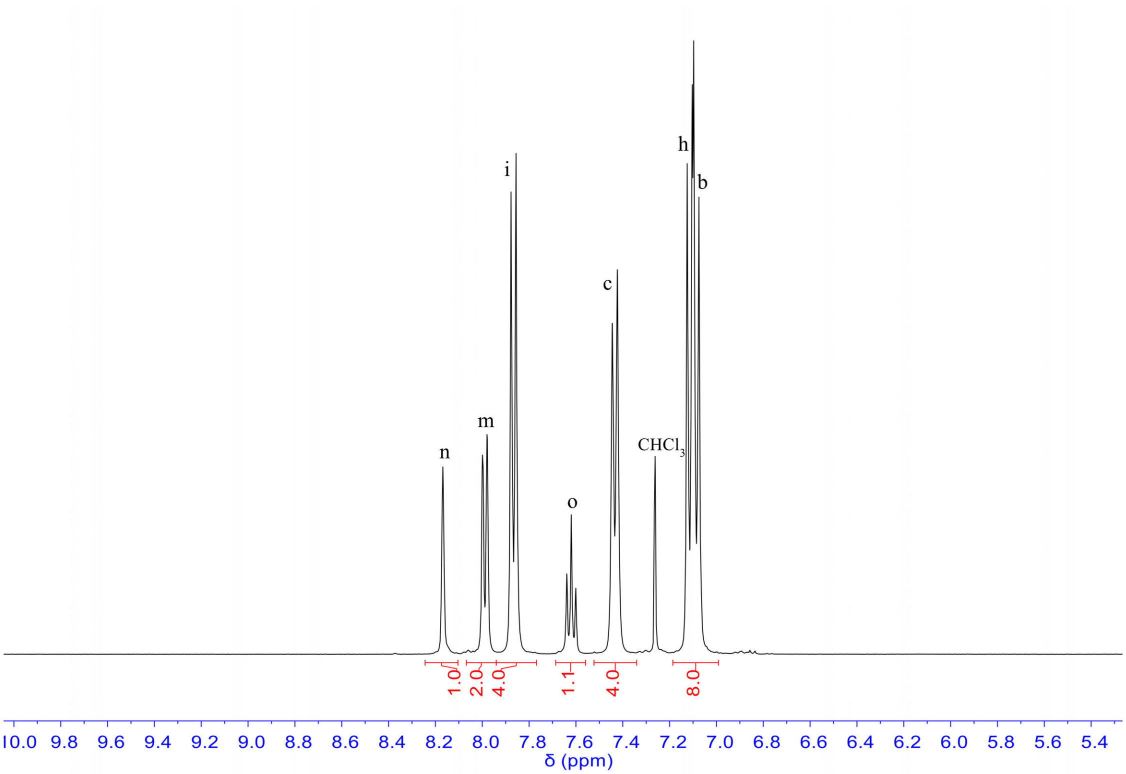


Figure S25. ^1H NMR spectrum of poly(ether ketone) **2** (400 MHz, $CDCl_3$).

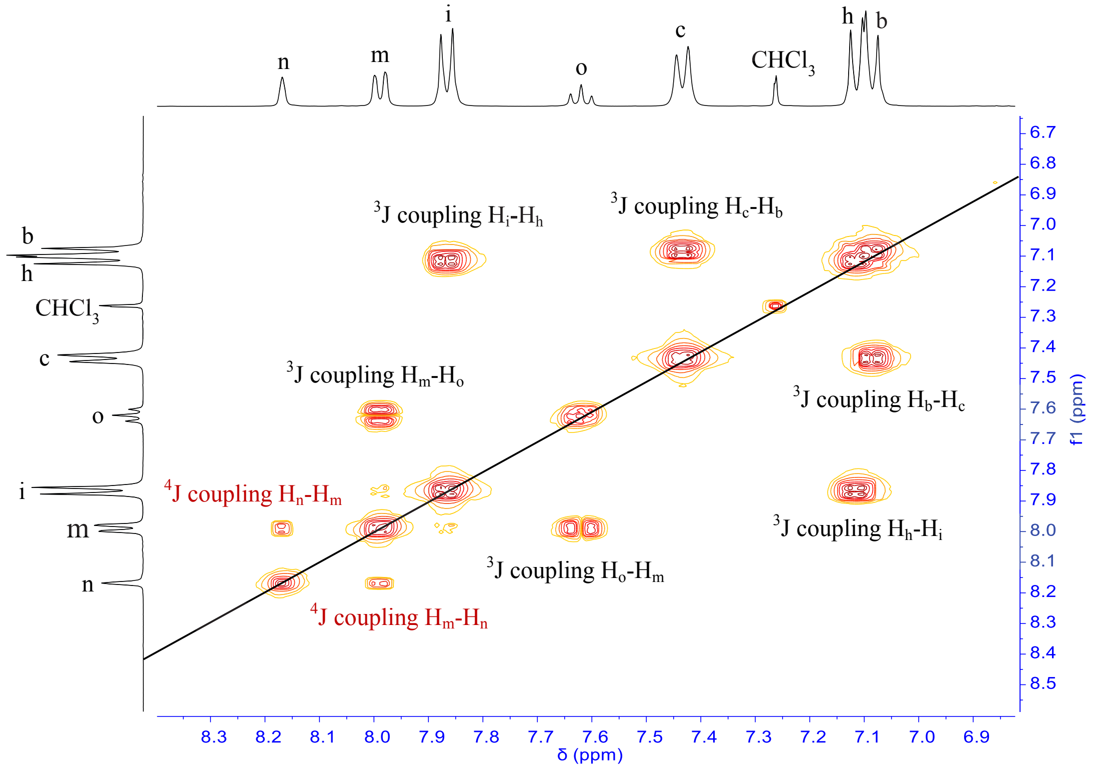


Figure S26. COSY (^1H-^1H) NMR spectrum of poly(ether ketone) **2** (400 MHz, $CDCl_3$).

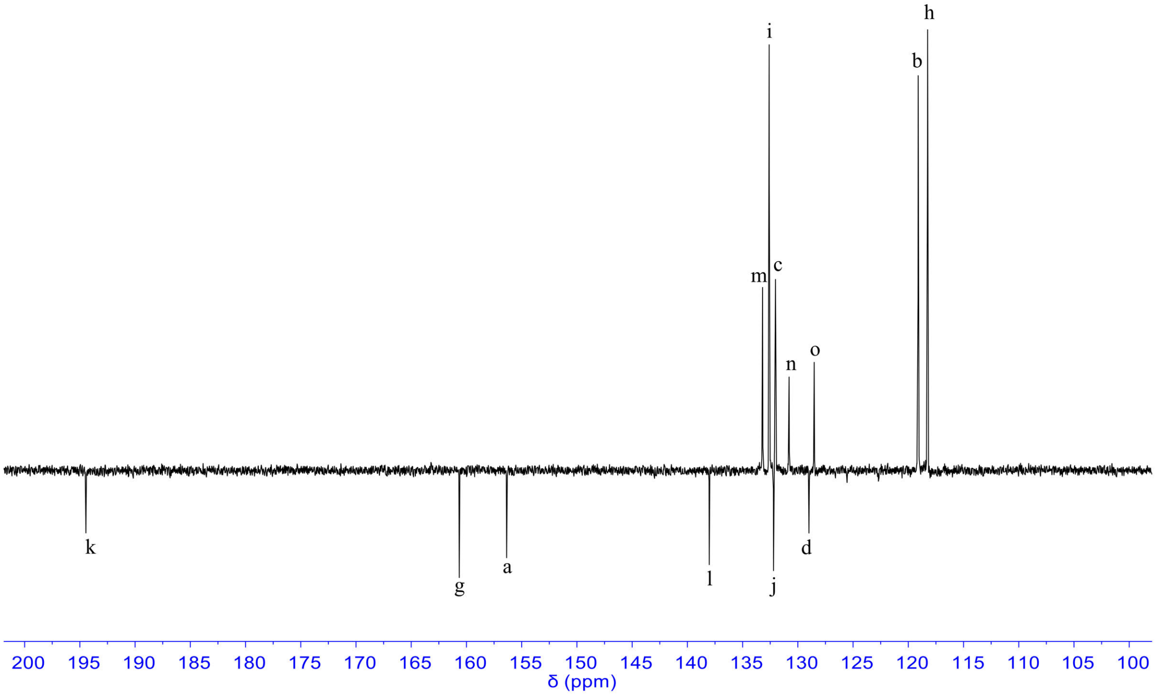


Figure S27. ^{13}C NMR (DEPT-135) spectrum of poly(ether ketone) **2** (100 MHz, $CDCl_3$).

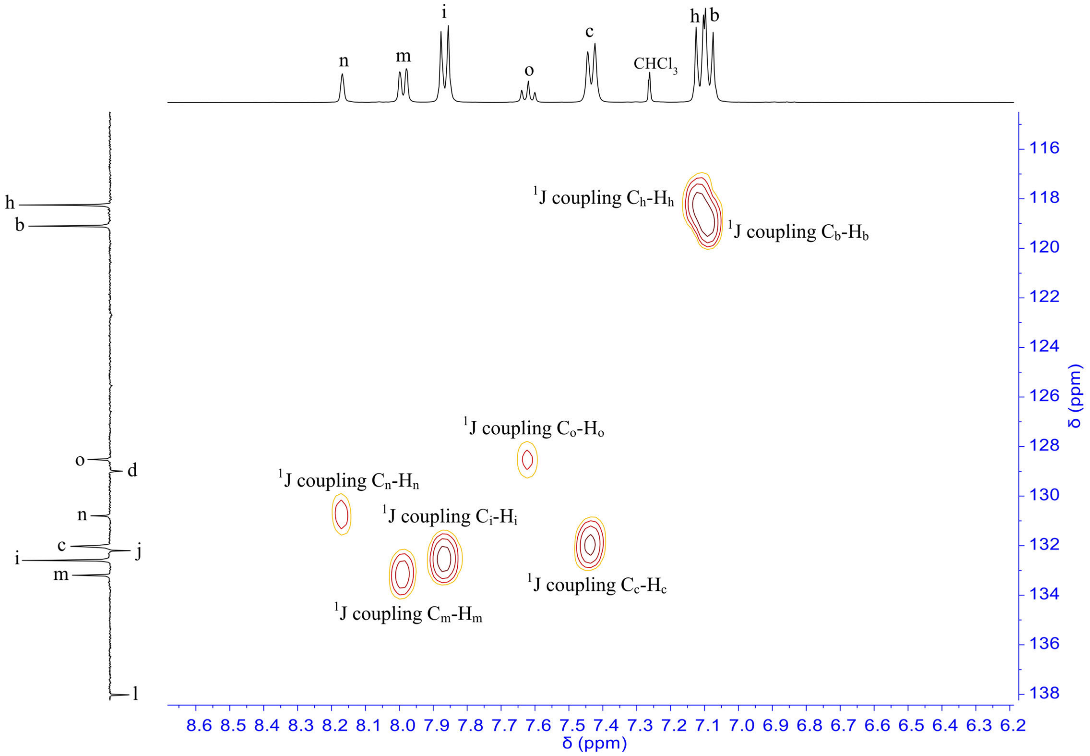


Figure S28. HSQC (^{1}H-^{13}C) NMR spectrum of poly(ether ketone) **2** ($CDCl_3$).

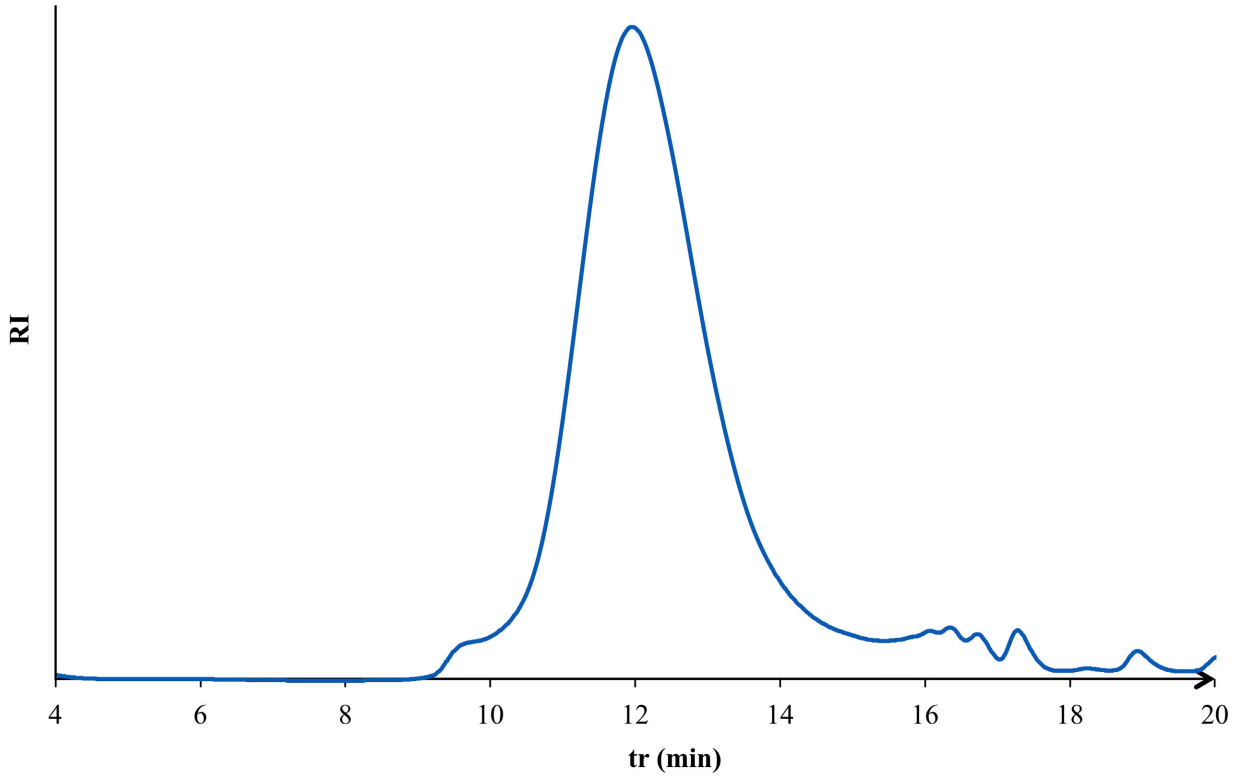
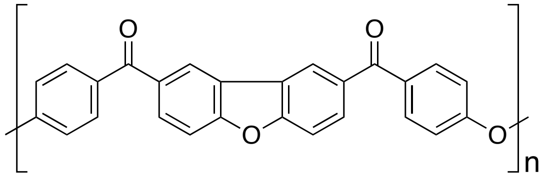


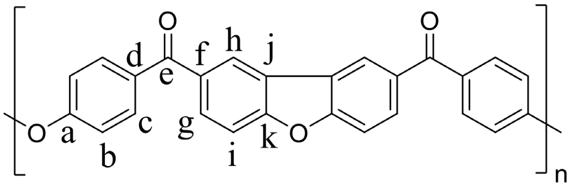
Figure S29. GPC trace for poly(ether ketone) **2** (in THF).

Poly(ether ketone) 3:



In a Schlenk flask were placed 2-(4'-fluorobenzoyl)-7-(4''-hydroxybenzoyl)-dibenzofuran (Monomer **3**, 1.53 g, 3.73 mmol), anhydrous potassium carbonate (0.27 g, 2.0 mmol), 4-fluorobenzophenone (0.0073 g, 3.6 x 10^{-5} mol), and diphenylsulfone (6.598 g). The mixture was stirred under a gentle flow of nitrogen and heated using a sandbath set to 200 ° C. After 30 min at 200 °C, the set-temperature was raised to 220 °C and then, after a further 30 min, to 250 °C. After an hour at 250 °C the temperature was raised steadily, over a further hour, to 320 °C. The reaction mixture was stirred at 320 °C for a further 4 h and then removed from the sandbath and the viscous polymer solution poured onto an aluminium foil tray.

After cooling, the solid was broken up and then ground to a coarse powder using an ultracentrifuge mill. The powder was extracted at reflux with methanol (60 mL x 3), water (60 mL x 3), methanol (60 mL x 1), and tetrahydrofuran (60 mL x 3), the solid being filtered off and washed with the same solvent after each extraction. The product polymer was finally dried at 100 °C in *vacuo* to afford poly(ether ketone) **3** as a pale brown solid (1.38 g, 90% yield).



^{1}H NMR ($CDCl_3$, 400 MHz): 7.19 (H_b, br. s), 7.67 (H_i, br. s), 7.67 (H_i, br. s), 7.89 (H_c, br. s), 7.99 (H_g, br. s), 8.44 (H_g, br. s) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): 111.9 (C_i), 118.8 (C_b), 123.5 (C_h), 123.9 (C_j), 130.4 (C_g), 132.5 (C_c), 133.3 and 133.4 (C_d+C_f), 159.1 (C_k), 159.8 (C_a), 194.6 (C_e) ppm.

T$_g$ (mid-point) = 226 °C. η_{inh} = 0.64 dL g^{-1} in H_2SO_4 (96%). GPC analysis was not obtained, owing to the insolubility of this polymer in THF.

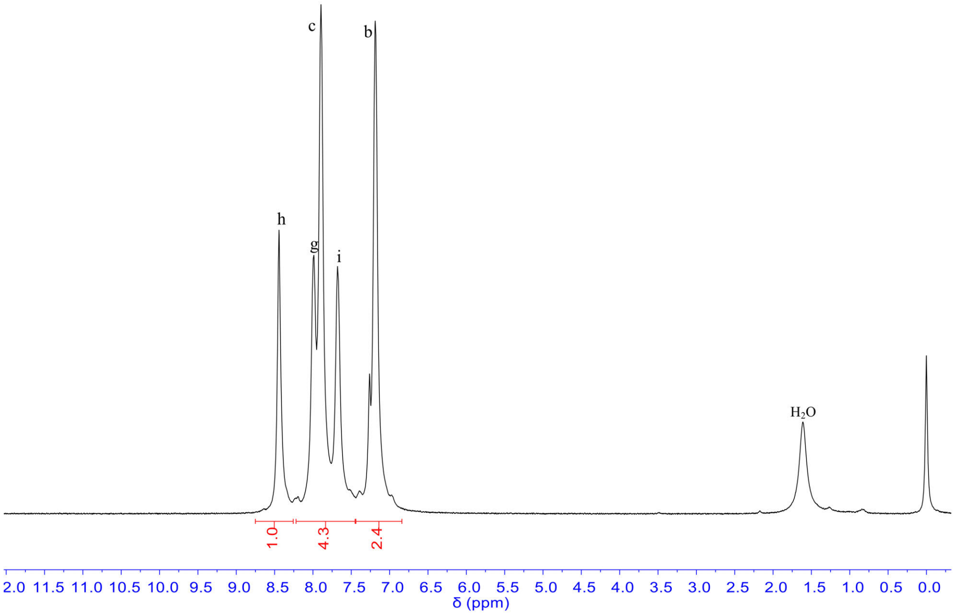


Figure S30. ^{1}H NMR spectrum of poly(ether ketone) **3** (400 MHz, $CDCl_3$).

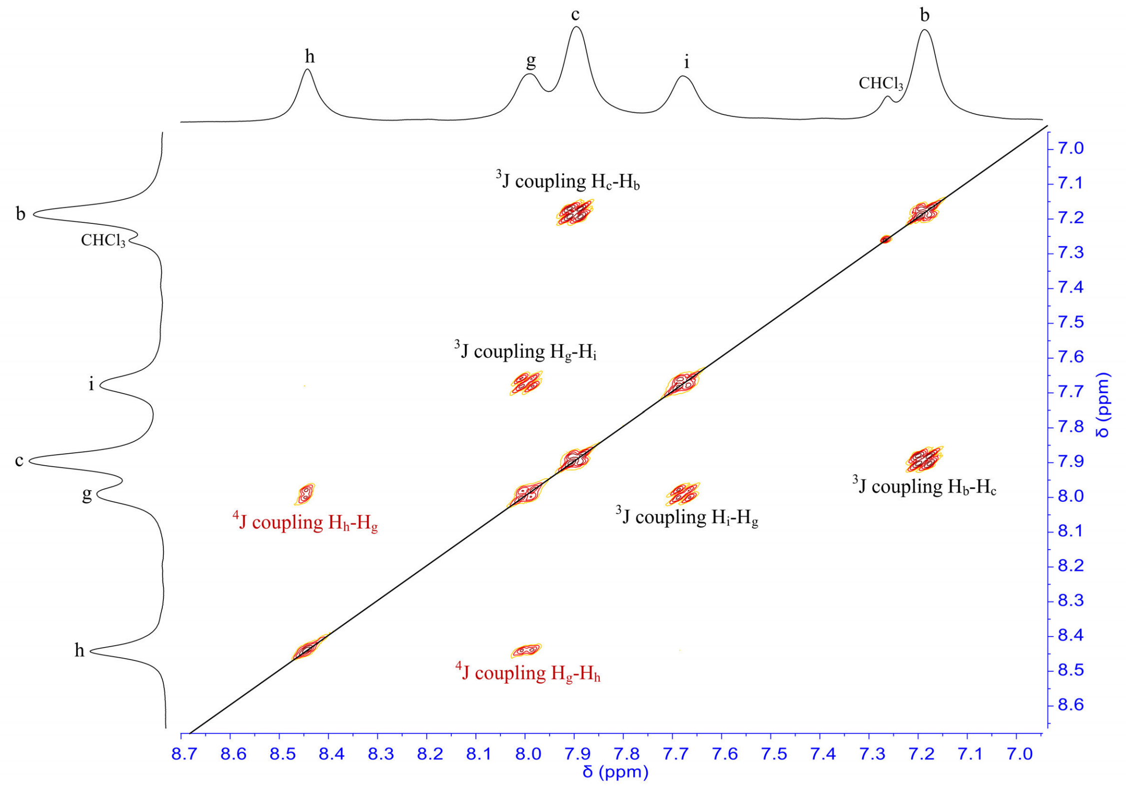


Figure S31. COSY (^{1}H-^{1}H) NMR spectrum of poly(ether ketone) **3** (400 MHz, $CDCl_3$).

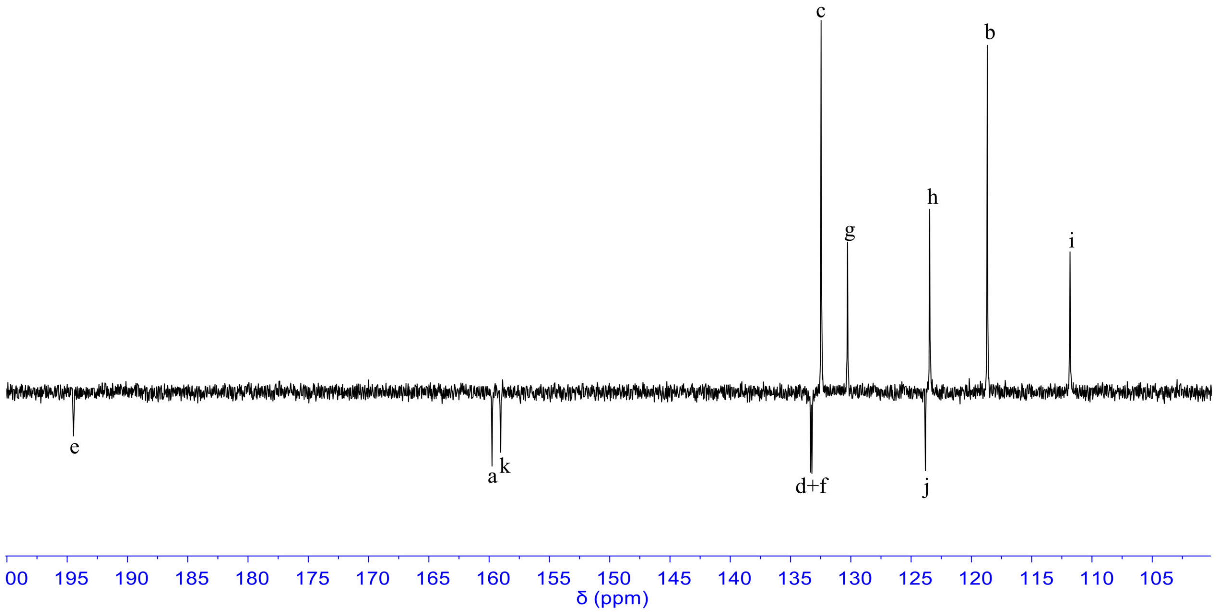


Figure S32. ^{13}C NMR (DEPT-135) spectrum of poly(ether ketone) **3** (100 MHz, $CDCl_3$).

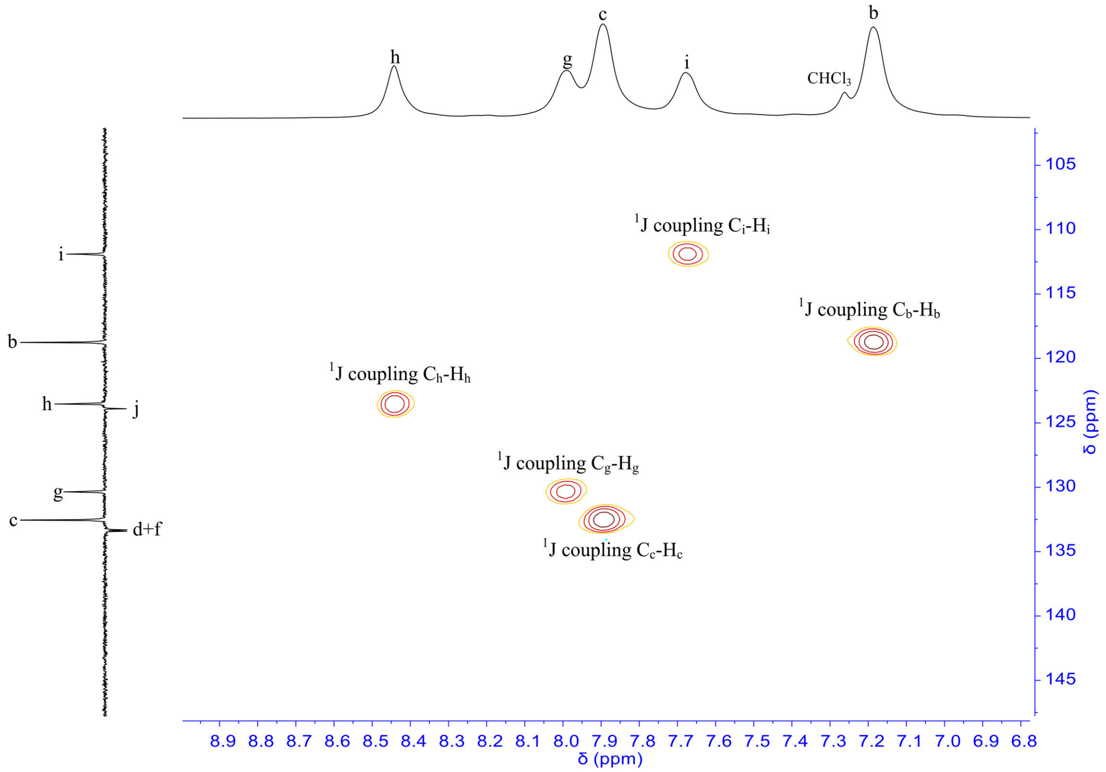
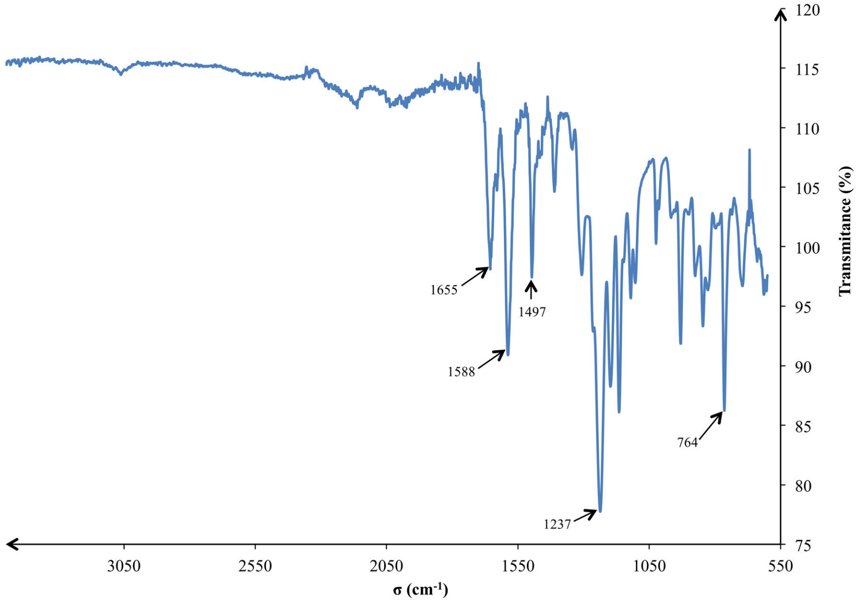
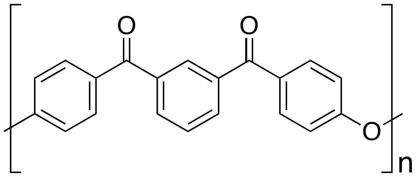


Figure S33. HSQC (^{1}H-^{13}C) NMR spectrum of poly(ether ketone) **3** (CDCl$_3$).

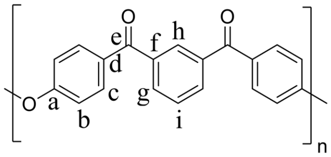


υ (C=O) ketone = 1655 cm^{-1}, υ (C=C) = 1588 cm^{-1}, 1497 cm^{-1}, υ (C-O) aryl ether = 1237 cm^{-1}, δ (C-H) = 764 cm^{-1}

Figure S34. Infra-red spectrum of poly(ether ketone) **3** (film from CHCl$_3$).

Poly(ether ketone) 4: 

Poly(ether ketone) **4** was obtained from monomers **7** and **9** using the method described above for poly(ether ketone) **3**, but with a maximum sand bath set temperature of 310 °C. Polymer **4** was isolated in 82% yield.



^{1}H NMR (CDCl$_3$/TFA: 9/1, 400 MHz): 7.23 (H$_b$, d, $^3J_{bc}$= 8 Hz), 7.74 (H$_i$, t, $^3J_{ig}$ = 8 Hz), 7.93 (H$_c$, d, $^3J_{cb}$ = 8 Hz), 8.08 (H$_g$, d, $^3J_{gi}$ = 8 Hz), 8.19 (H$_h$, s) ppm.

^{13}C NMR (CDCl$_3$/TFA: 9/1, 100 MHz): 119.2 (C$_b$), 129.1 (C$_i$), 131.4 (C$_d$), 131.4 (C$_h$), 131.6 (C$_c$), 133.6 (C$_g$), 134.6 (C$_f$), 137.3 (C$_a$), 198.3 (C$_e$) ppm.

T_g (mid-point) = 160 °C; T_m (1st DSC scan) = 258 °C. η_{inh} = 1.13 dL g^{-1} in H$_2$SO$_4$ (96%). GPC analysis was not obtained, owing to the insolubility of this polymer in THF.

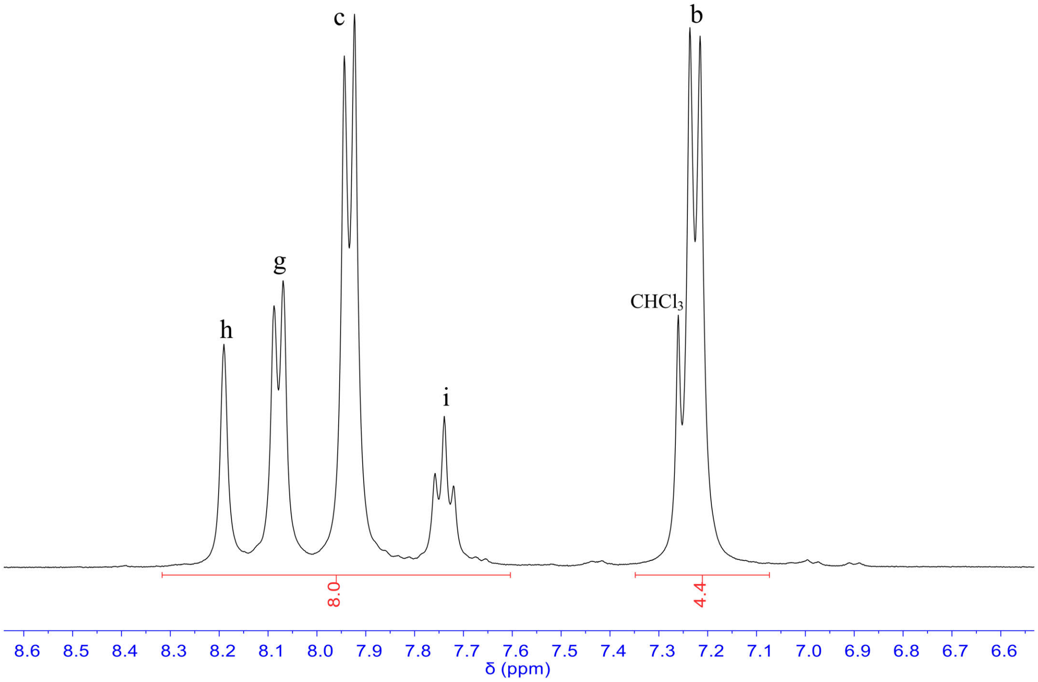


Figure S35. ^{1}H NMR spectrum of poly(ether ketone) **4** (400 MHz, $CDCl_3$/TFA).

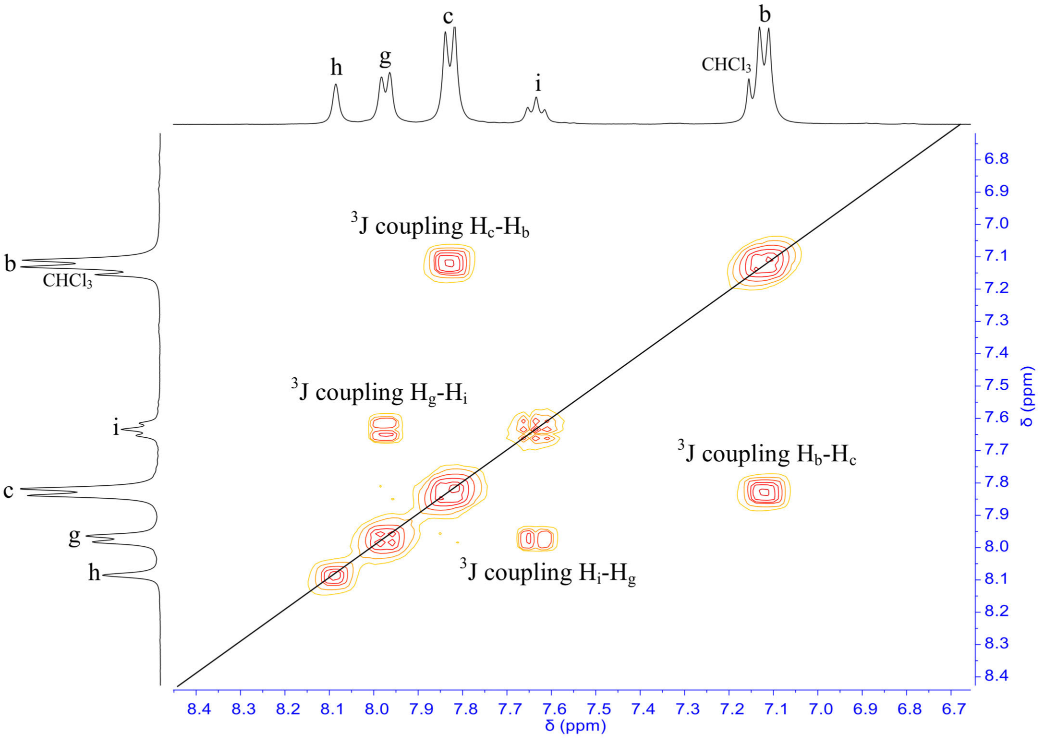


Figure S36. COSY (^{1}H-^{1}H) NMR spectrum of poly(ether ketone) **4** (400 MHz, $CDCl_3$/TFA).

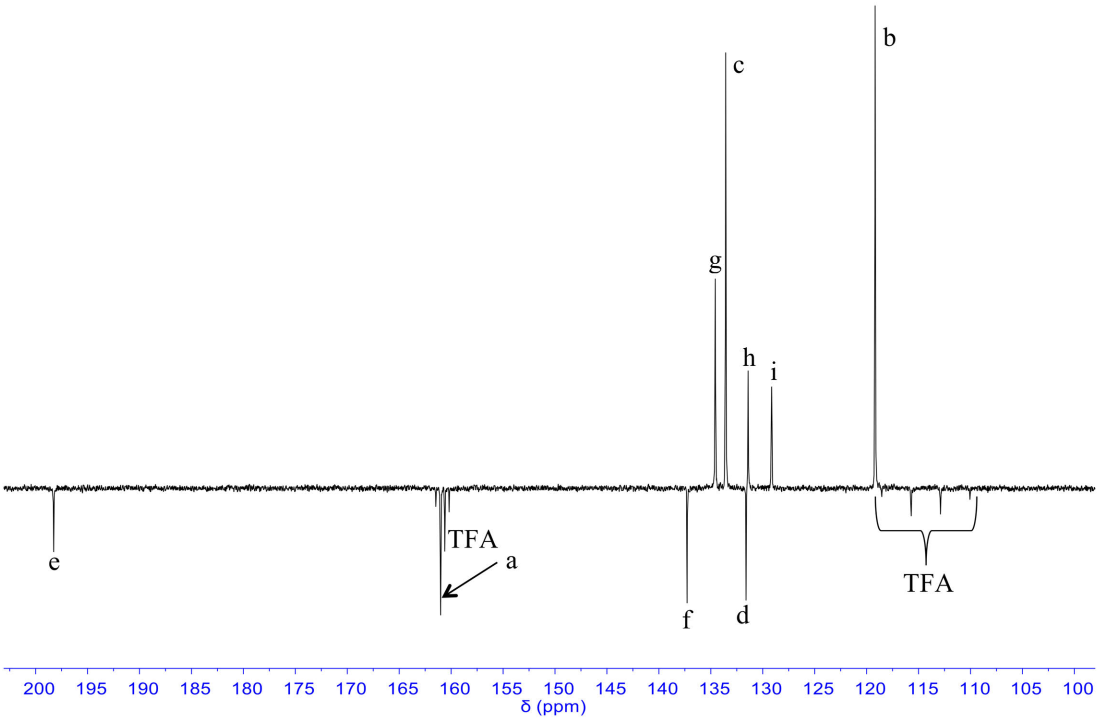


Figure S37. ^{13}C NMR (DEPT-13) spectrum of poly(ether ketone) **4** (100 MHz, $CDCl_3$/TFA).

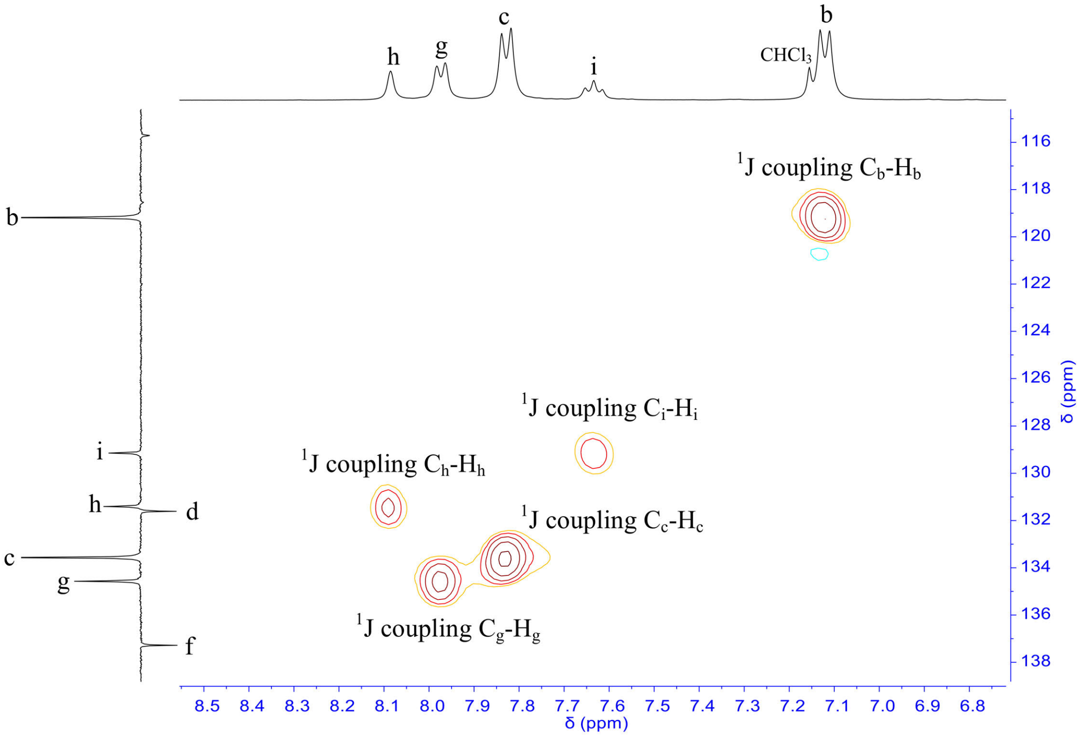
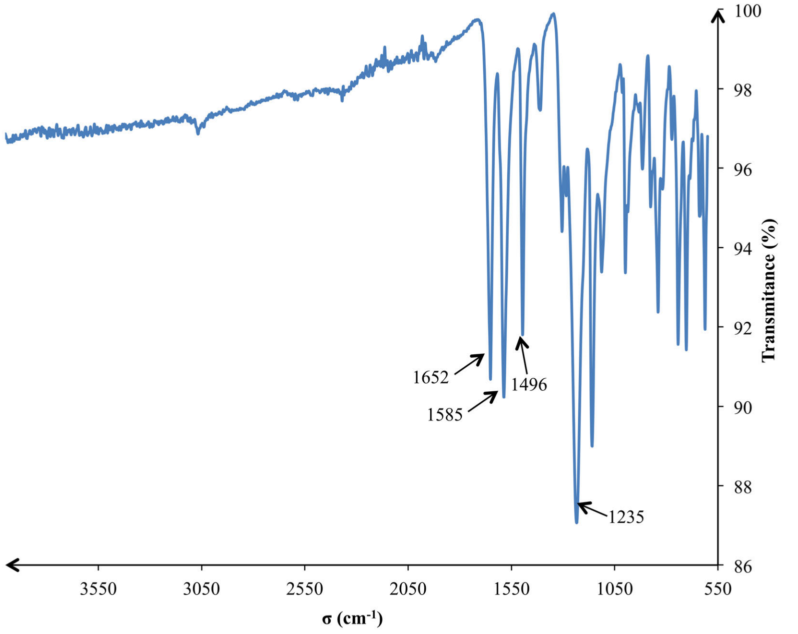
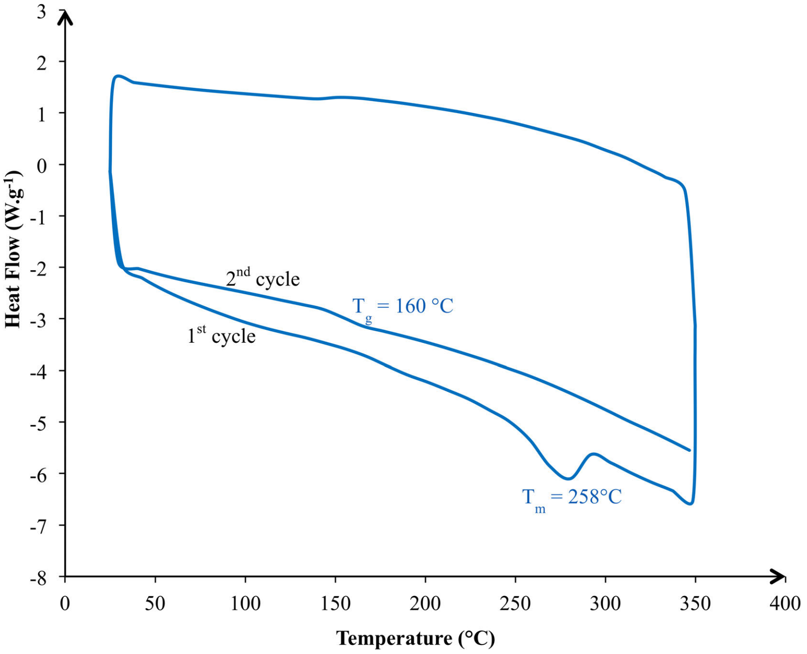


Figure S38. HSQC (^{1}H-^{13}C) NMR spectrum of poly(ether ketone) **4** ($CDCl_3$/TFA).



υ (C=O) ketone = 1652 cm^{-1}, υ (C=C) = 1585 cm^{-1}, 1496 cm^{-1}, υ (C-O) aryl ether = 1235 cm^{-1}

Figure S39. Infra-red spectrum of poly(ether ketone) **4**.

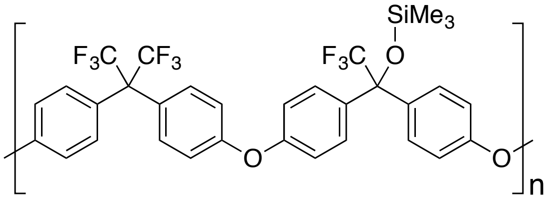


Heating rate: 5 °C min^{-1}: No recrystallization observed on cooling or on second scan

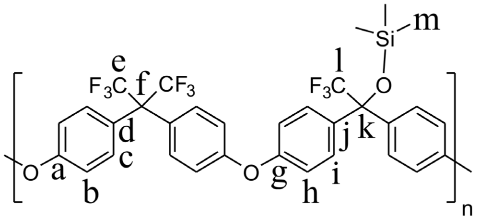
Figure S40. DSC thermograms (1st and 2nd heating) for the semi-crystalline poly(ether ketone) **4**.

4. Synthesis and characterization of poly[(trifluoromethyl)(trimethylsilylether)]s 10 – 13

Polymer 10:



To a stirred solution of poly(ether ketone) **1** (1.04 g, 1.96 mmol of repeat units) in THF (40 mL) was added, at 0 °C under nitrogen, trifluoromethyltrimethylsilane (2.91 mL, 20.0 mmol) and tetrabutylammonium fluoride (80 mg in 1 mL of THF, 0.31 mmol). The reaction mixture was allowed to warm to room temperature over three hours. After 16 h, the volatiles were removed in *vacuo* and the polymer was dissolved in the minimum amount of dichloromethane and reprecipitated in methanol (200 mL). After filtering off the polymer and drying at 100 °C in *vacuo* for 2 h, it was re-precipitated twice in methanol (200 mL) from solution in the minimum amount of dichloromethane. After finally drying at 100 °C in *vacuo,* the trifluoromethylated poly(ether) **10** was obtained as a white solid (1.09 g, 82% yield).



^{1}H NMR (CDCl$_3$, 400 MHz): -0.02 (H$_m$, s), 7.00 (H$_b$+H$_h$, m), 7.36 (H$_c$, d, $^3J_{cb}$ = 8 Hz), 7.41 (H$_i$, d, $^3J_{ih}$= 8 Hz) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): 0.0 (C$_m$), 116.6 (C$_b$), 117.4 (C$_h$), 126.6 (C$_d$), 128.6 (C$_i$), 130.5 (C$_c$), 135.0 (C$_j$), 154.8 (C$_g$), 156.2 (C$_a$) ppm.

T_g (mid-point) = 152 °C. M_n = 21.1; M_w = 48.8 kDa; $Đ$ = 2.32.

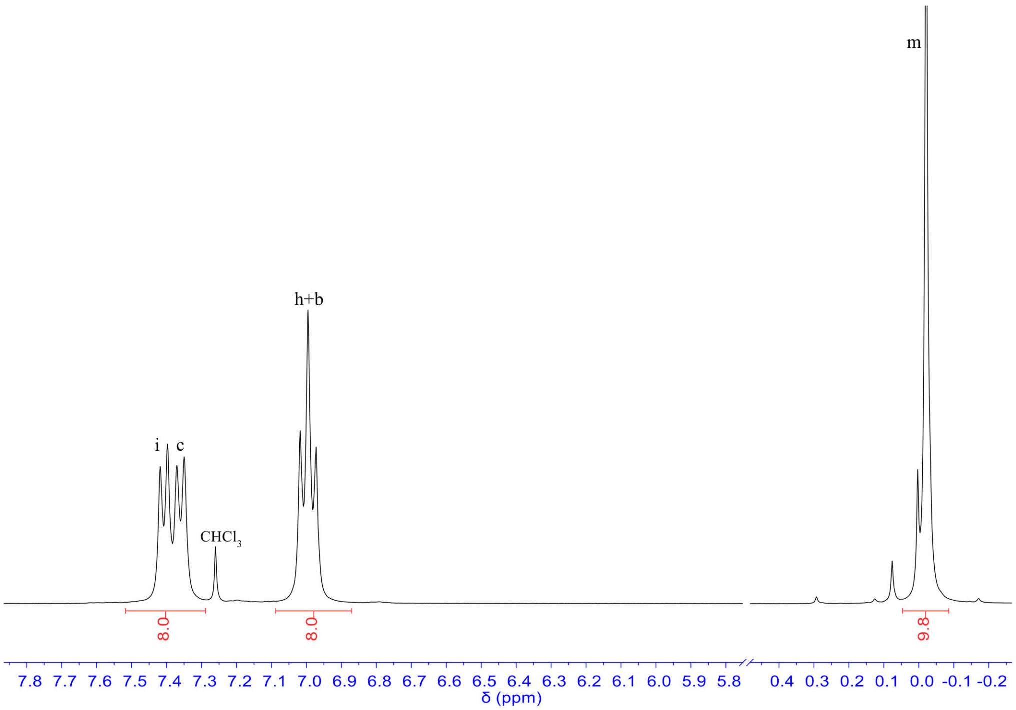


Figure S41. ^{1}H NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **10** (400 MHz, CDCl$_3$).

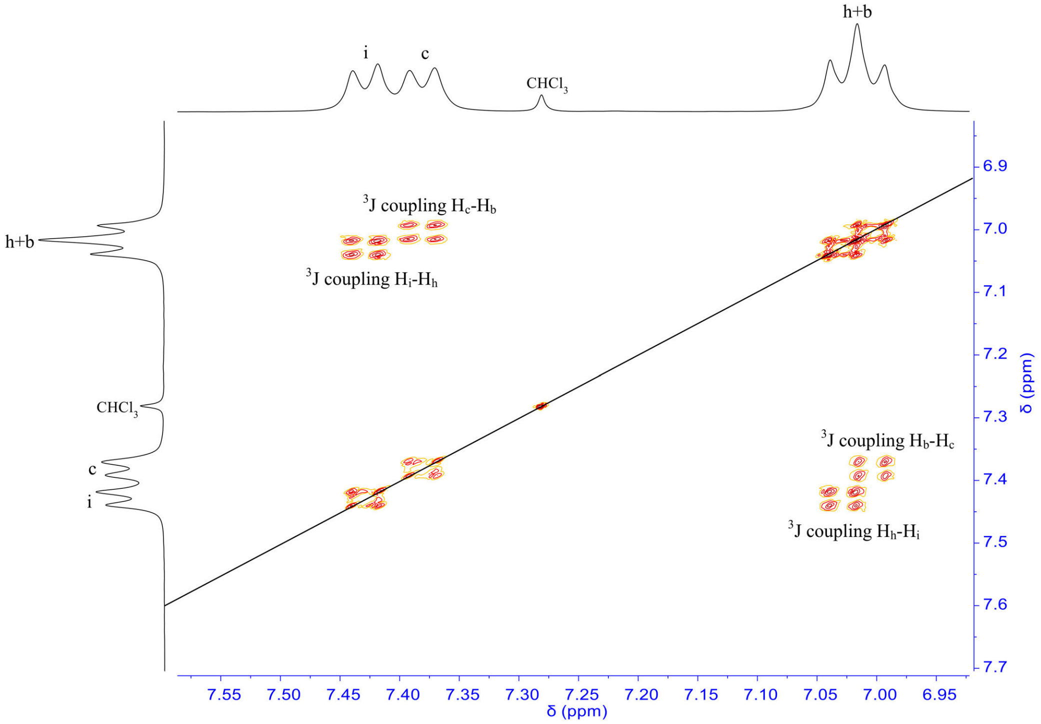


Figure S42. COSY (^{1}H-^{1}H) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **10** (400 MHz, CDCl$_3$).

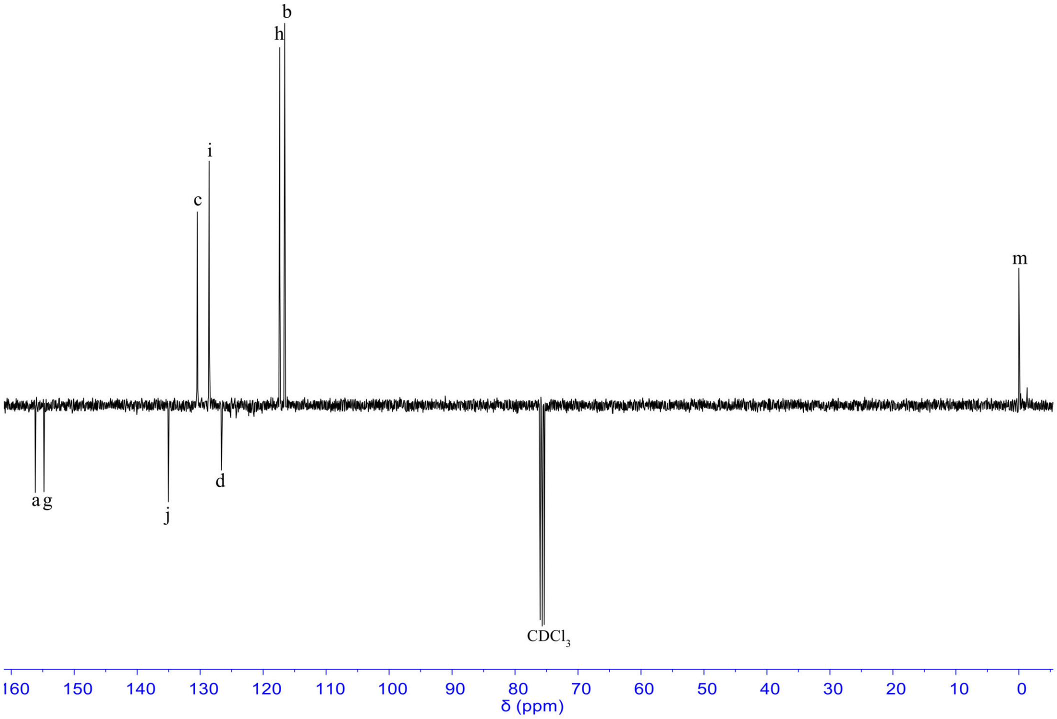


Figure S43. ^{13}C NMR (DEPT-135) spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **10** (100 MHz, CDCl$_3$).

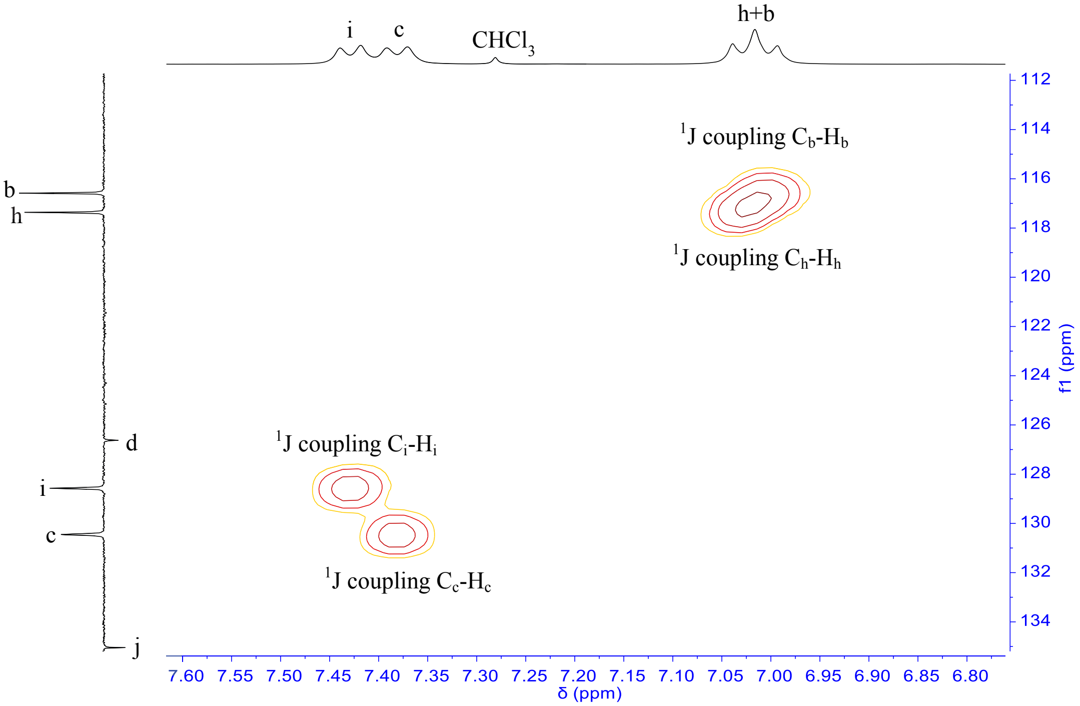


Figure S44. HSQC (^{1}H-^{13}C) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **10** (CDCl$_3$).

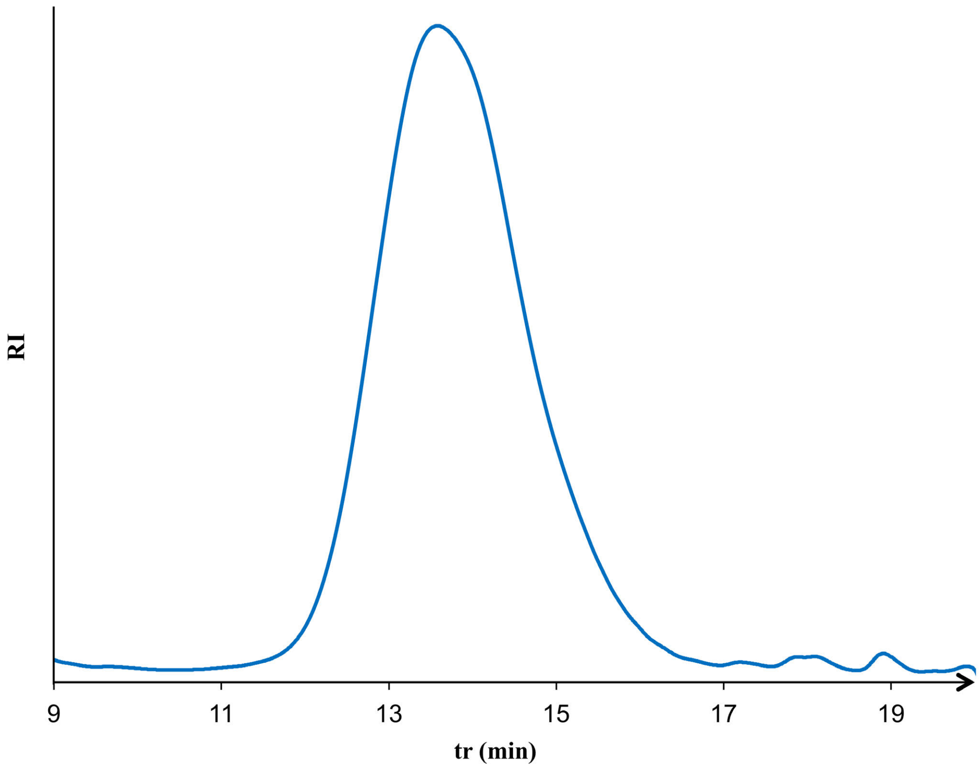
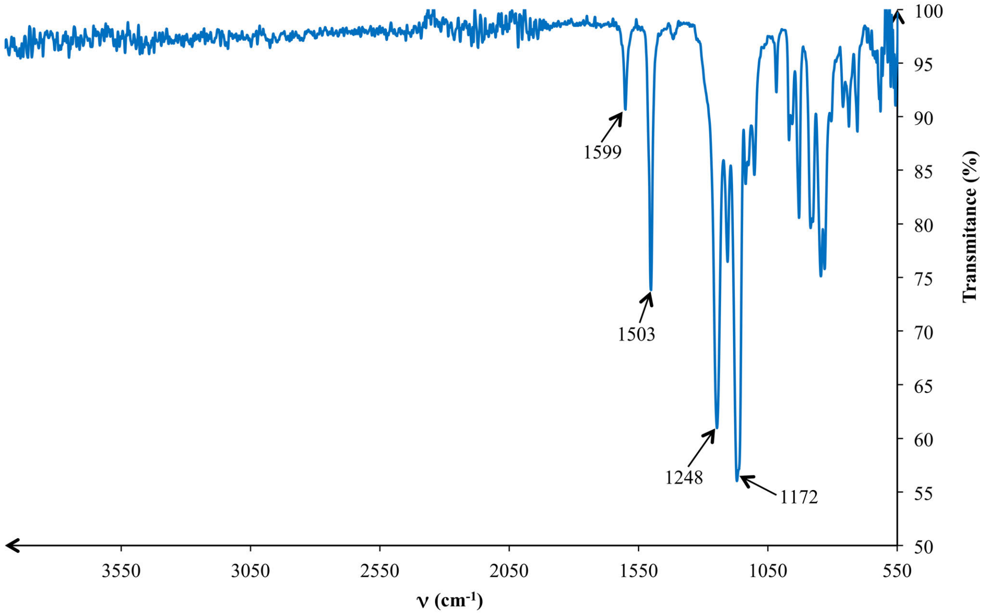


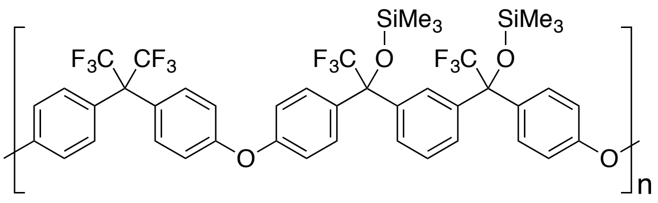
Figure S45. GPC trace for poly[(trifluoromethyl)(trimethylsilylether)] **10** (in THF).



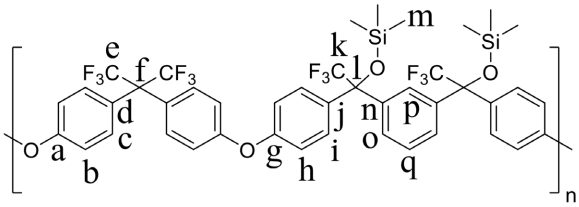
υ (C=C) = 1599 cm^{-1}, 1503 cm^{-1}, υ (C-O) aryl ether = 1248 cm^{-1}, υ (C-F) = 1172 cm^{-1}

Figure S46. Infra-red spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **10** (film from $CHCl_3$).

Polymer 11:



Polymer **11** was obtained from poly(ether ketone) **1** using the method described above for polymer **10**, and was isolated in 70% yield.



^{1}H NMR ($CDCl_3$, 400 MHz): -0.096 (H_m, s), 6.89-7.04 (H_b+H_h, m), 7.24-7.44 (H_c+H_i+H_o+H_q, m), 7.52 and 7.63 (H_p, s) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): 0.0 (C_m), 116.7 (C_b), 117.6 (C_h), 126.3 -126.6 -126.8 -127.1 (C_p+ C_o+ C_q), 126.7 (C_d), 128.7 (C_i), 130.6 (C_c), 135.1 (C_j), 139.5 (C_n), 154.9 (C_g), 156.4 (C_a) ppm.

T_g (mid-point) = 127 °C. M_n = 59.0; M_w = 136 kDa; $Đ$ = 2.31.

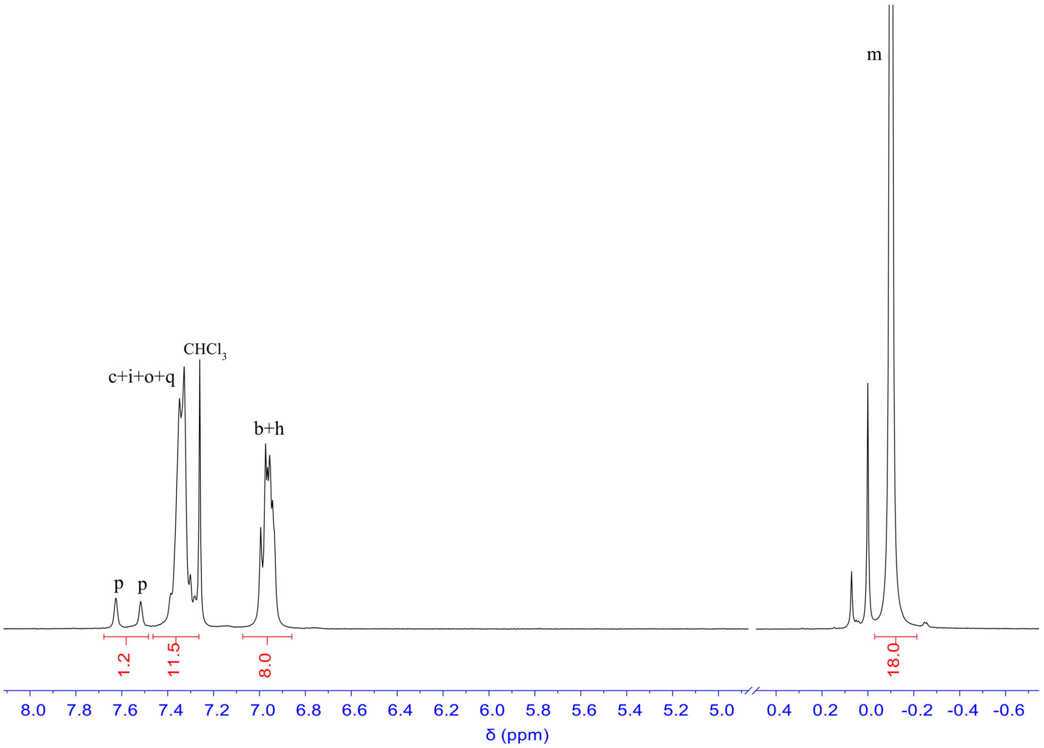


Figure S47. ^{1}H NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **11** (400 MHz, CDCl$_3$). Note the splitting of resonance "p" due to the diastereomeric character of the *m*-substituted aromatic unit.

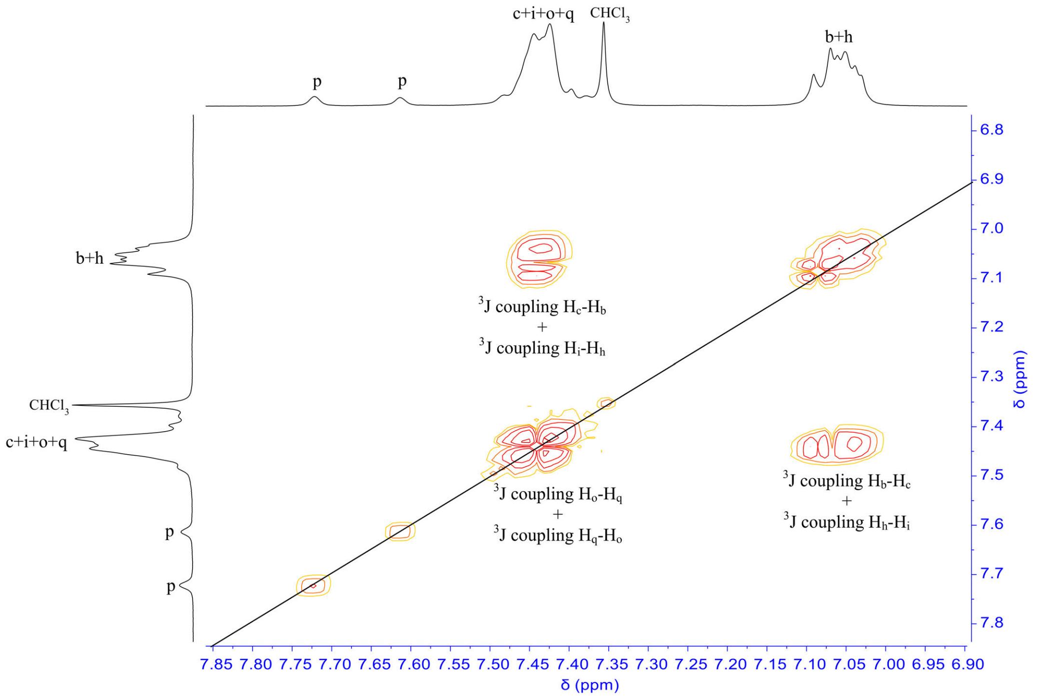


Figure S48. COSY (^{1}H-^{1}H) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **11** (400 MHz, CDCl$_3$).

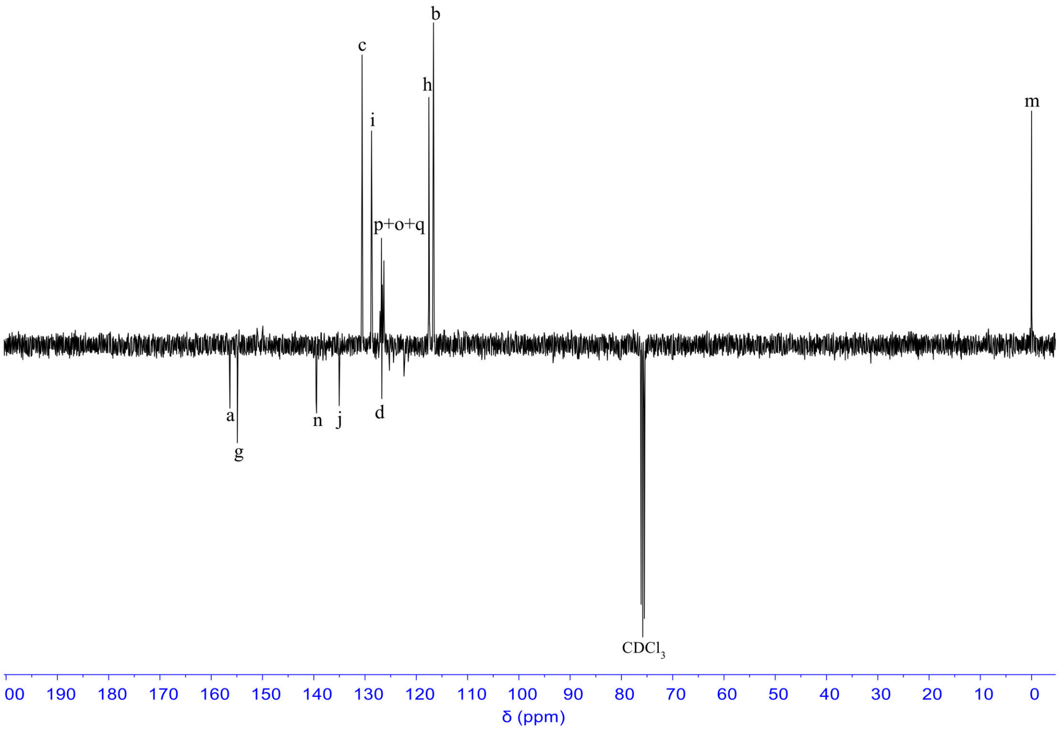


Figure S49. ^{13}C NMR (DEPT-135) spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **11** (100 MHz, CDCl$_3$).

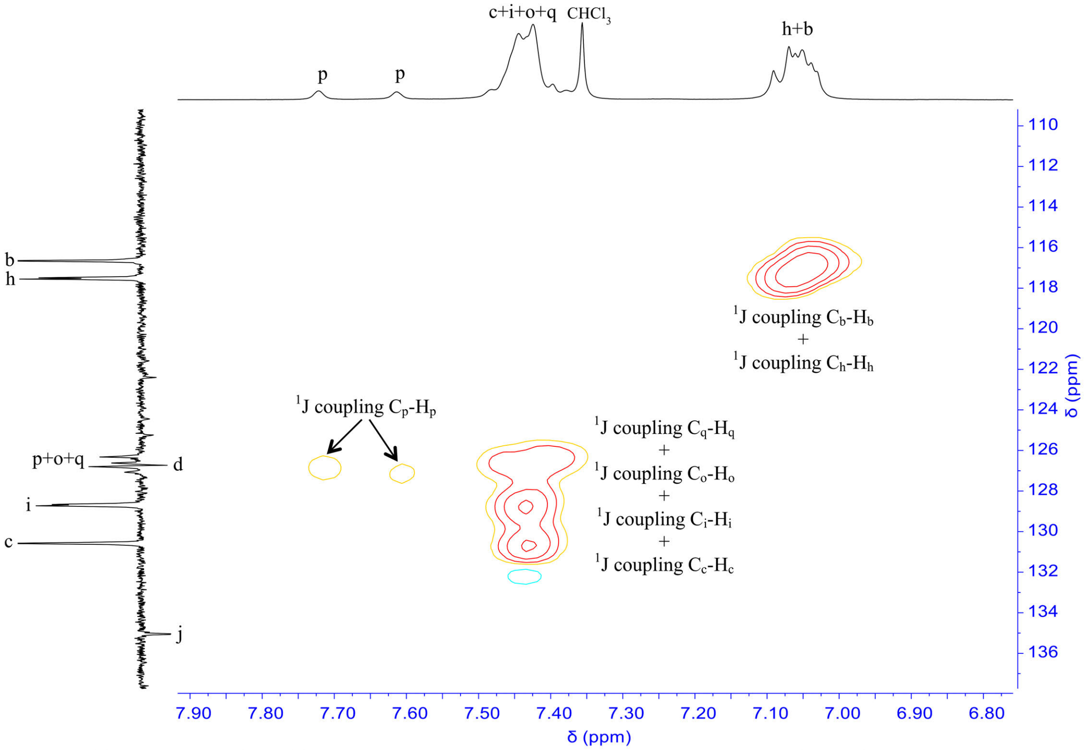


Figure S50. HSQC (^{1}H-^{13}C) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **11** (CDCl$_3$).

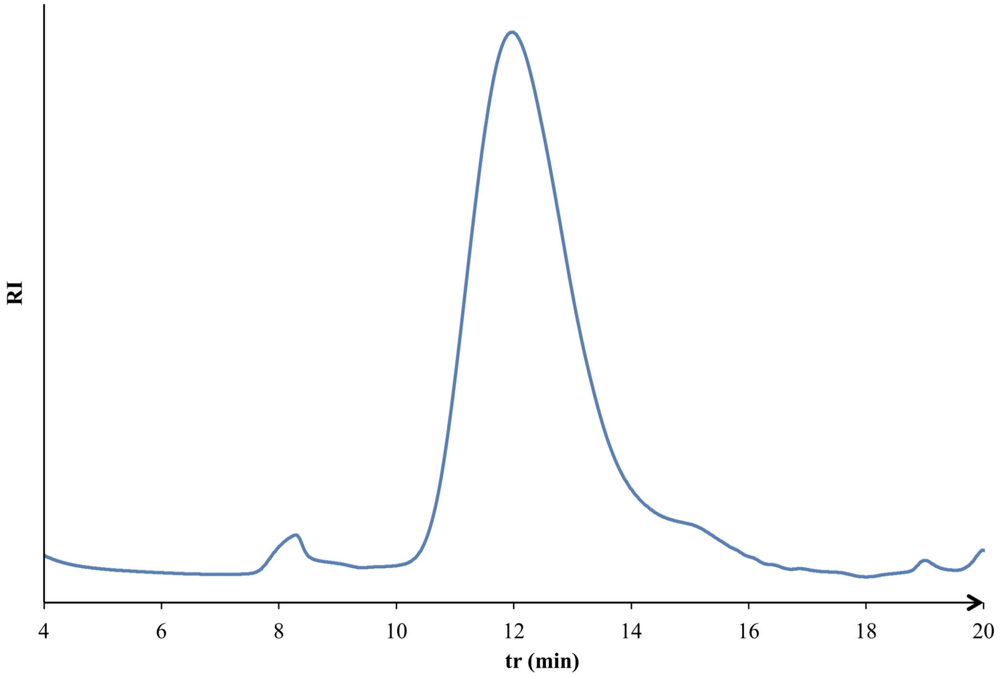
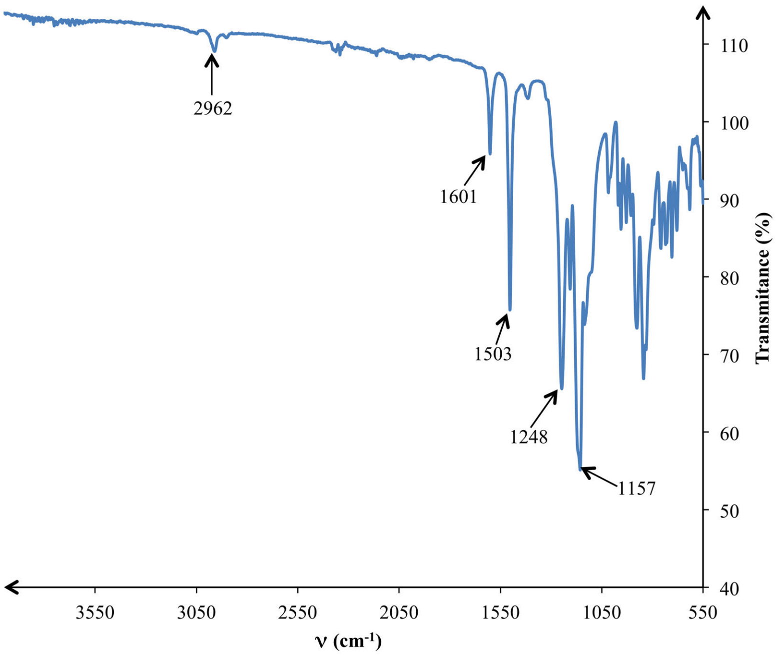
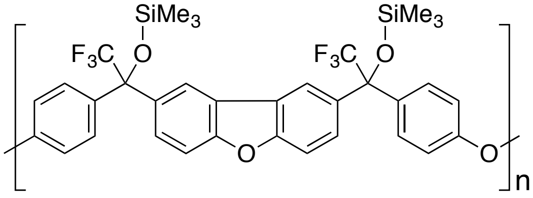


Figure S51. GPC trace for poly[(trifluoromethyl)(trimethylsilylether)] **11** (in THF).

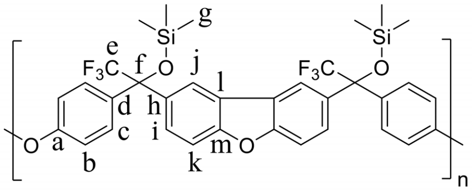


υ (C-H) alkane = 2962 cm^{-1}, υ (C=C) = 1601 cm^{-1}, 1503 cm^{-1}, υ (C-O) aryl ether = 1248 cm^{-1}, υ (C-F) = 1157 cm^{-1}

Figure S52. Infra-red spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **11** (film from $CHCl_3$).

Polymer 12: 

To a stirred suspension of poly(ether ketone) **3** (1.00 g, 2.56 mmol of repeat units) in THF (40 mL) was added, at 0 °C under nitrogen, trifluoromethyltrimethylsilane (13.0 mL, 89.3 mmol) followed by tetrabutyl-ammonium fluoride (220 mg in 2 mL of THF, 0.84 mmol). The reaction mixture was allowed to warm to room temperature over three hours and then stirred at 20 ºC for 120 h, with further additions of 13.0 mL of trimethyl(trifluoromethyl)silane and 220 mg of tetrabutylammonium fluoride hydrate at 24h intervals. Ultimately a clear, homogeneous solution was obtained. The volatiles were removed in *vacuo* and the polymer was dissolved in a minimum amount of dichloromethane and reprecipitated in methanol (200 mL). After filtering off and drying at 100 °C in *vacuo* for 2 h, the polymer was re-precipitated twice in methanol (200 mL) from solution in the minimum amount of dichloromethane. After drying at 100 °C in *vacuo*, the trifluoromethylated poly(ether) **12** was obtained as a pale brown solid (1.38 g, 80% yield).



^{1}H NMR (CDCl$_3$, 400 MHz): -0.027 (H_g, s), 6.97 (H_b, d, $^3J_{bc}$ = 8 Hz), 7.40 (H_c, d, $^3J_{hi}$ = 8 Hz), 7.48 (H_i+H_k, m), 8.07 (H_j, s) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): 0.0 (C_g), 109.9 (C_k) 116.8 (C_b), 118.8 (C_j), 122.2 (C_l), 126.6 (C_i), 128.6 (C_c), 134.5 (C_h), 134.8 (C_d), 155.0 (C_m), 155.4 (C_a) ppm.

T_g (mid-point) = 172 °C. M_n = 15.4; M_w = 44.0 kDa; $Đ$ = 2.86.

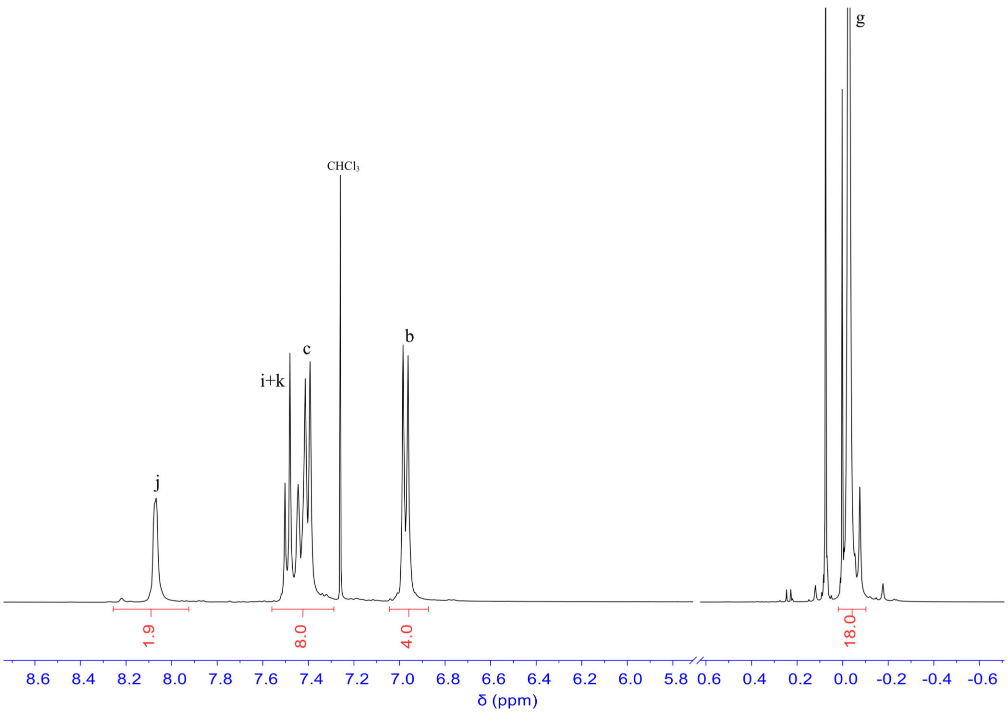


Figure S53. ^{1}H NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **12** (400 MHz, CDCl$_3$).

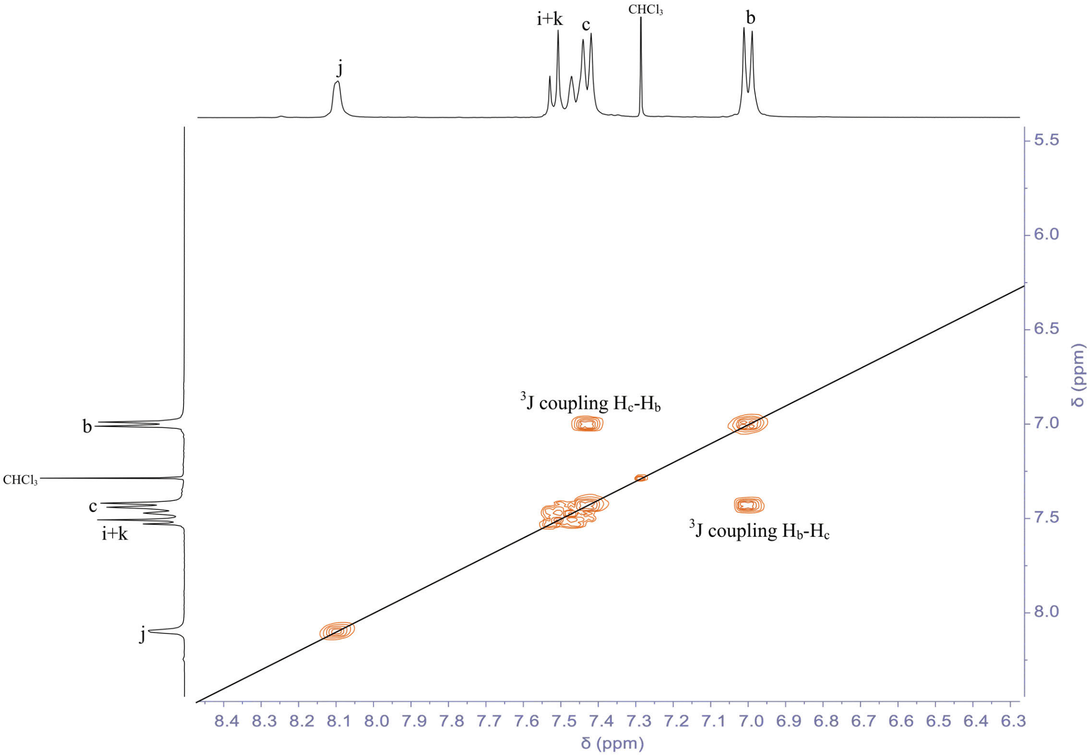


Figure S54. COSY (^{1}H-^{1}H) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **12** (400 MHz, CDCl$_3$).

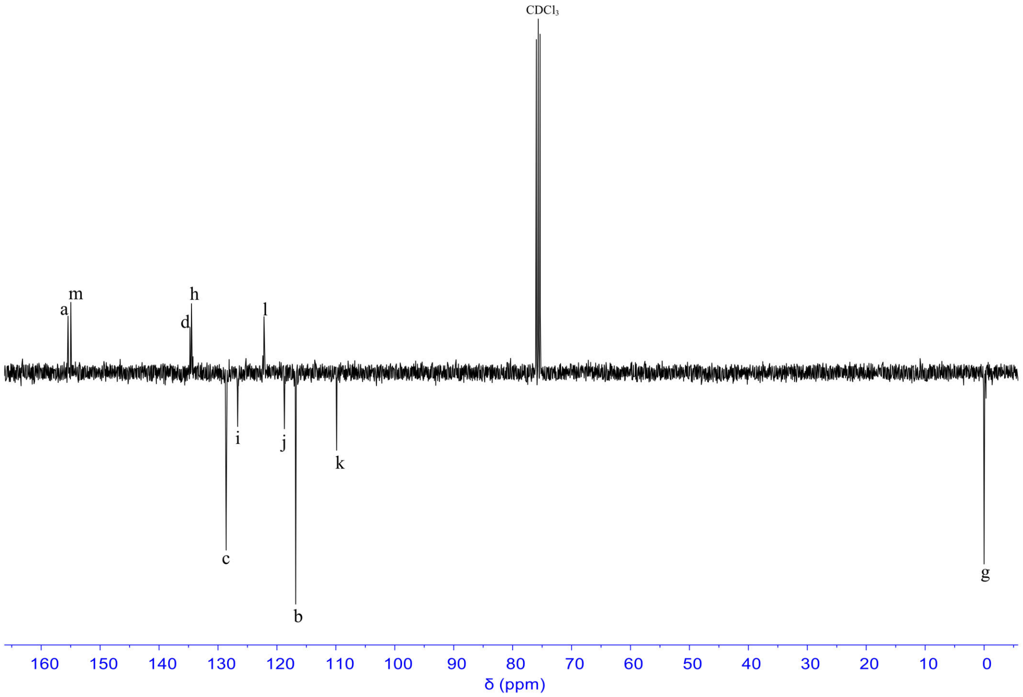


Figure S55. ^{13}C NMR (DEPT-135) spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **12** (100 MHz, $CDCl_3$).

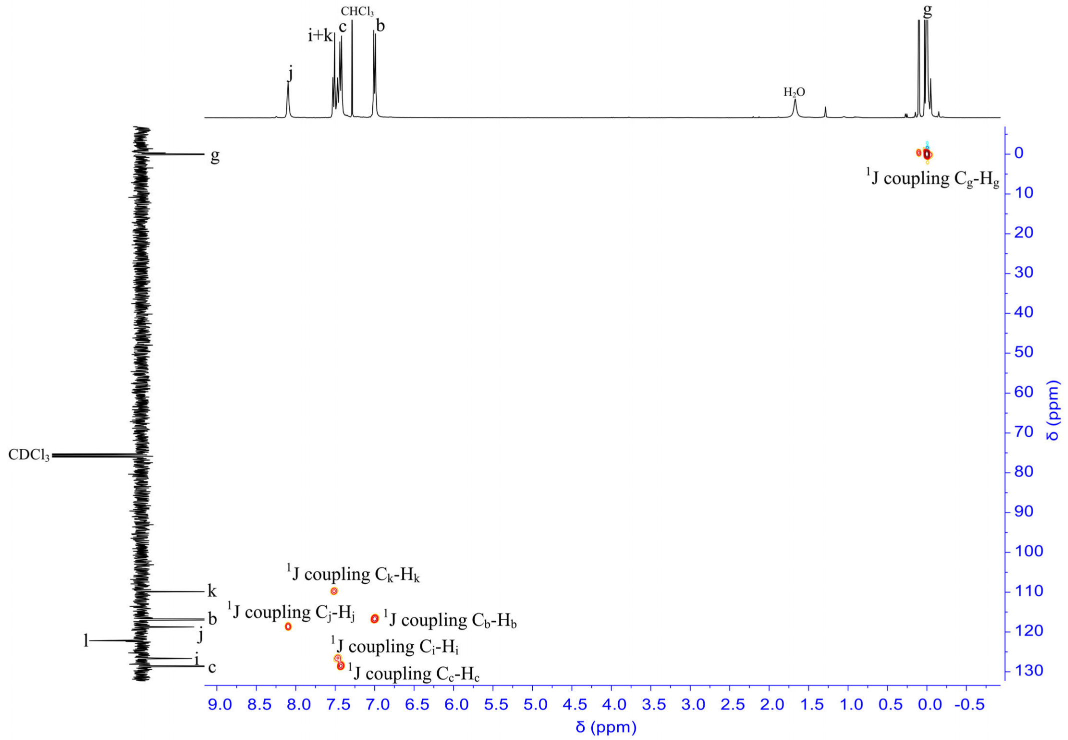


Figure S56. HSQC (^{1}H-^{13}C) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **12** ($CDCl_3$).

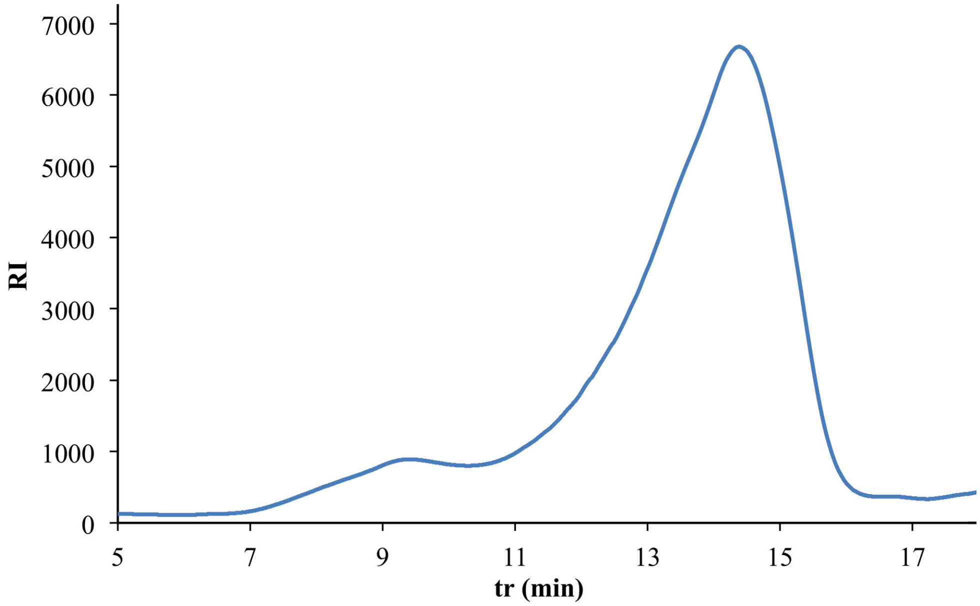
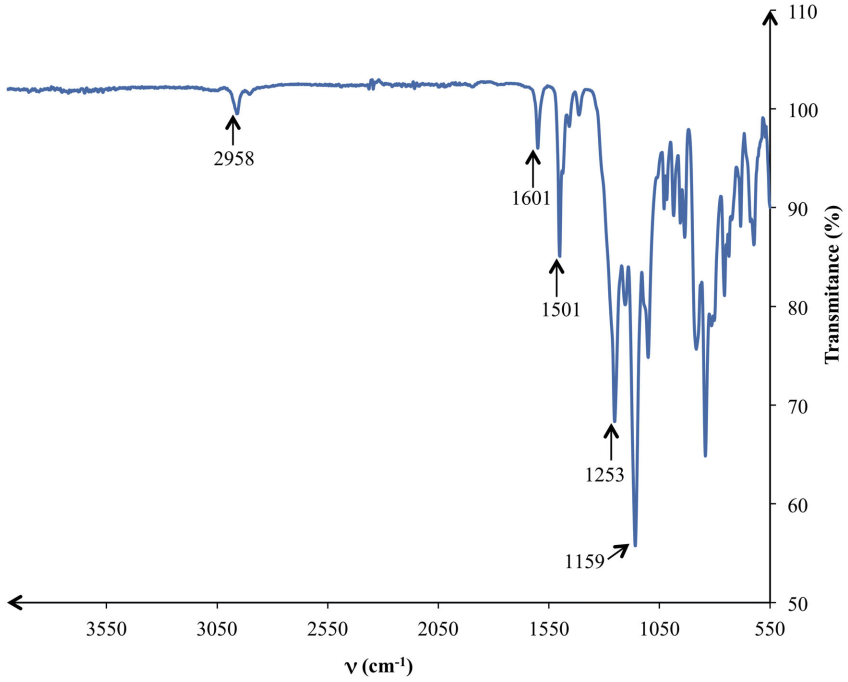


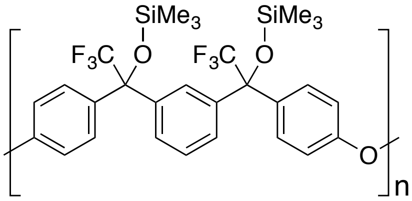
Figure S57. GPC trace for poly[(trifluoromethyl)(trimethylsilylether)] **12** (in THF).



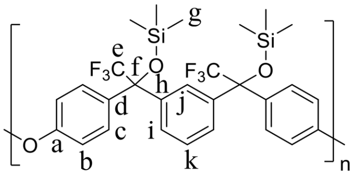
υ (C-H) alkane = 2958 cm^{-1}, υ (C-C) = 1601 cm^{-1}, 1501 cm^{-1}, υ (C-O) aryl ether = 1253 cm^{-1}, υ (C-F) = 1159 cm^{-1}

Figure S58. Infra-red spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **12** (film from $CHCl_3$).

Polymer 13:



Polymer **13** was obtained from poly(ether ketone) **4**, using the method described above for polymer **12**, and was isolated in 75% yield.



^{1}H NMR (CDCl$_3$, 400 MHz): -0.11 (H$_g$, s), 6.92 (H$_b$, t, $^3J_{bc}$ = 7 Hz), 7.48 (H$_c$+H$_i$+H$_k$, m), 7.54 and 7.64 (H$_j$, s) ppm.

^{13}C NMR (CDCl$_3$, 100 MHz): 0.0 (C$_g$),116.9 (C$_h$), 122.4 and 125.3 (C$_e$), 126.3-126.6-126.8-127 (C$_i$+C$_j$+C$_k$), 128.6 (C$_c$), 134.5 (C$_d$), 139.5 (C$_h$), 155.6 (C$_a$) ppm.

T_g (mid-point) = 90 °C. M_n = 21.2; M_w = 39.6 kDa; $Đ$ = 1.87.

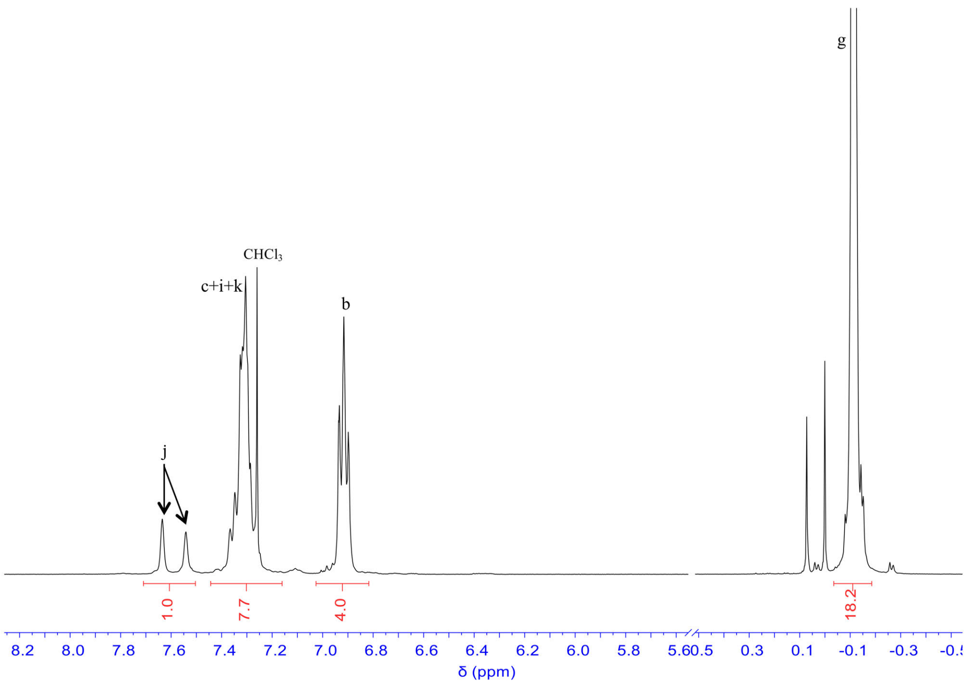


Figure S59. ^{1}H NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **13** (400 MHz, $CDCl_3$). Note the splitting of resonance "j" due to the diastereomeric character of the *m*-substituted aromatic unit.

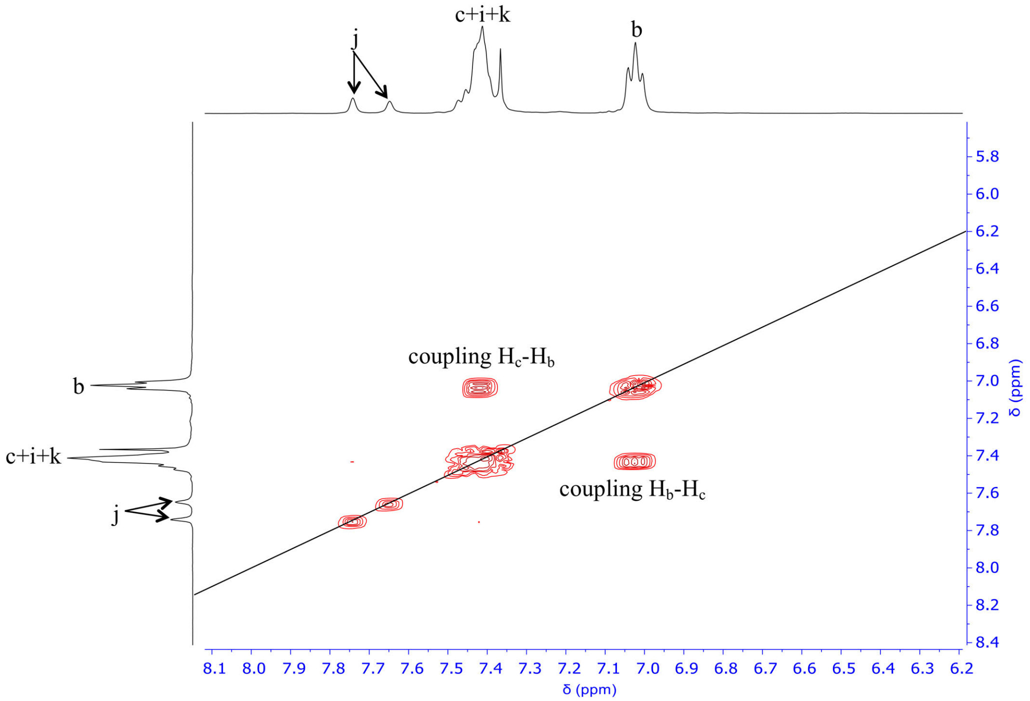


Figure S60. COSY (^{1}H-^{1}H) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **13** (400 MHz, $CDCl_3$).

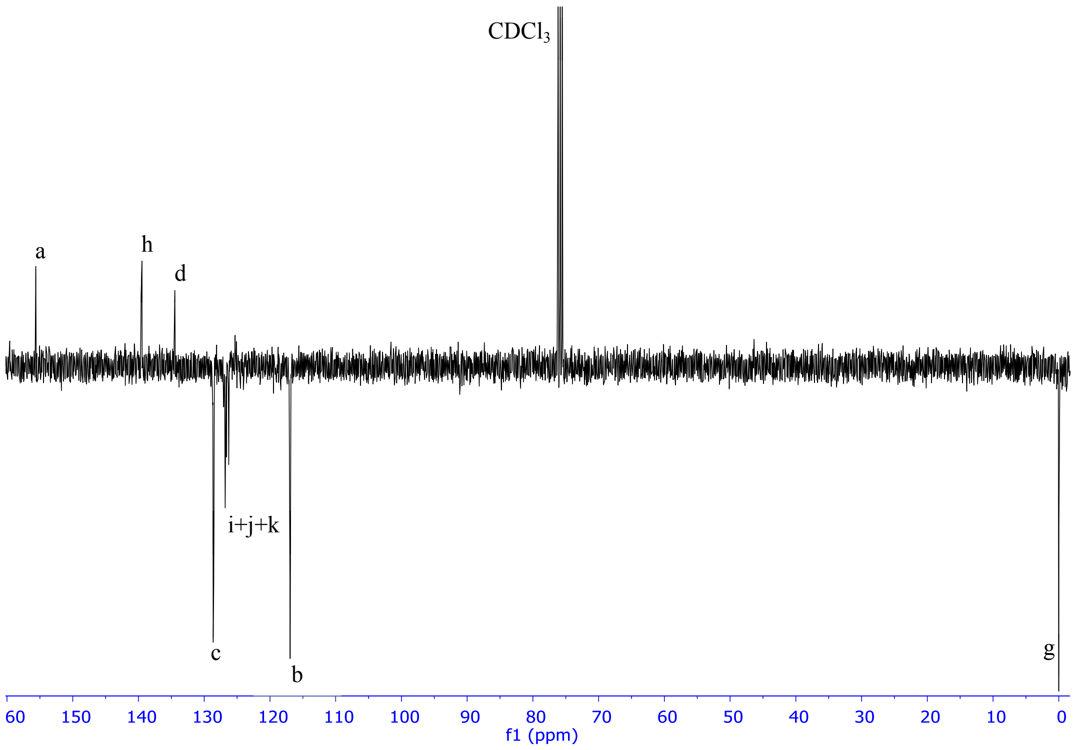


Figure S61. ^{13}C NMR (DEPT-135) spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **13** (100 MHz, CDCl$_3$).

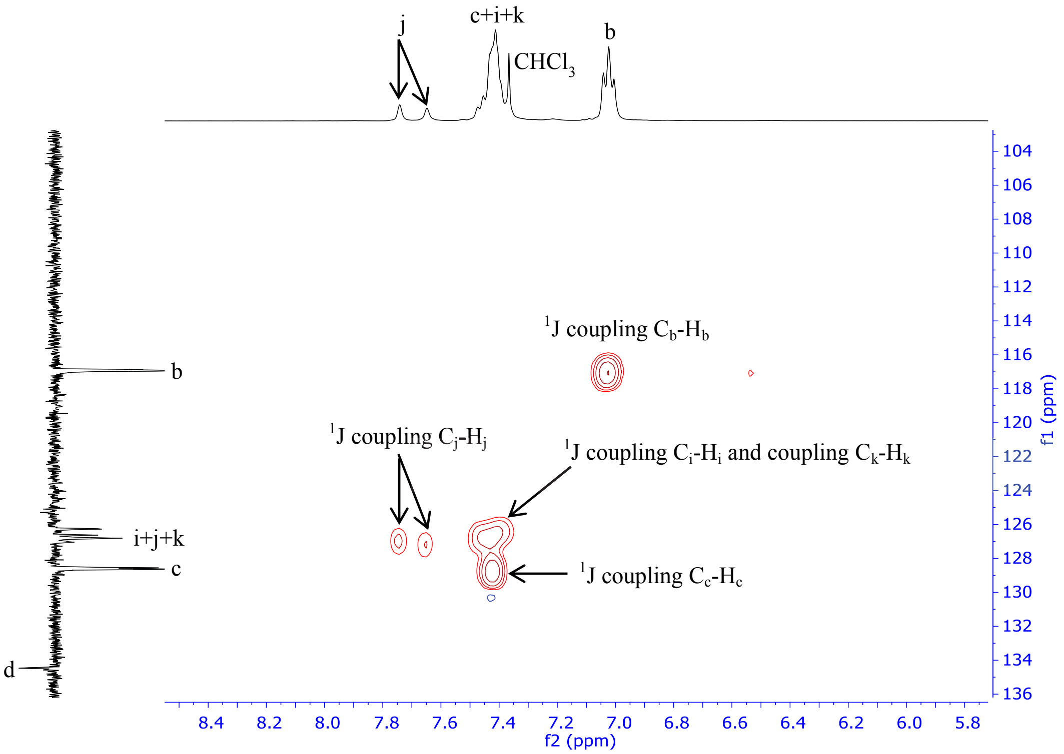


Figure S62. HSQC (^{1}H-^{13}C) NMR spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **13** (CDCl$_3$).

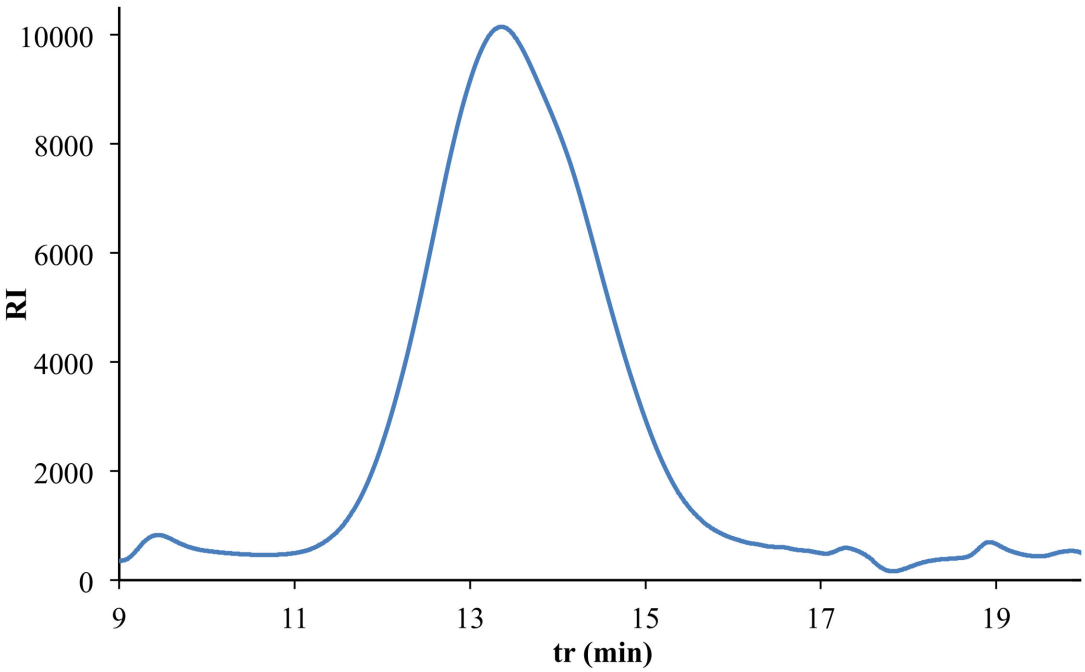
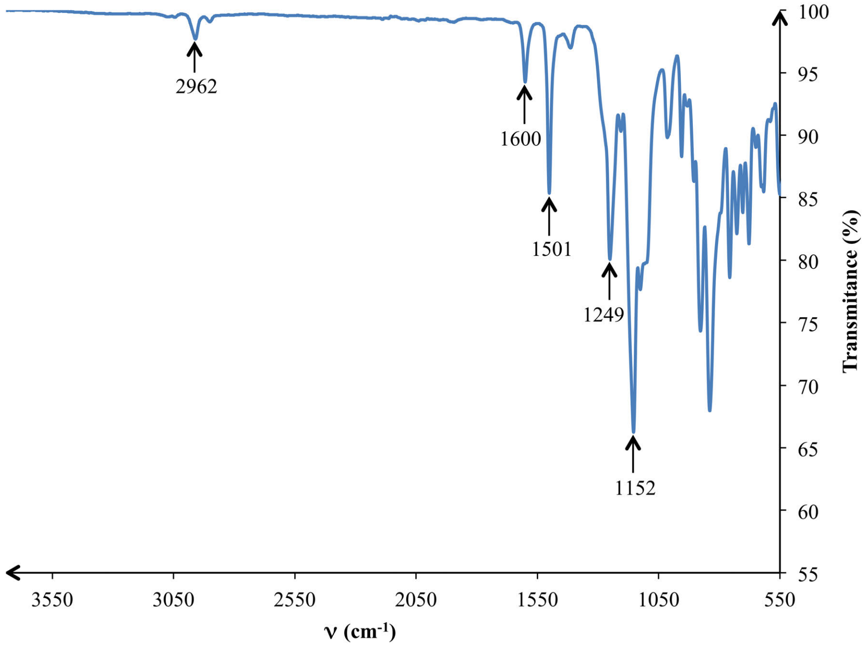


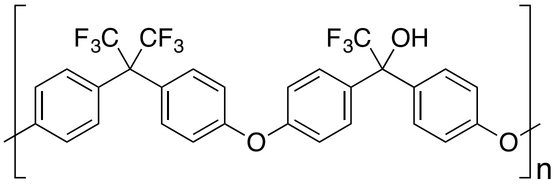
Figure S63. GPC trace for poly[(trifluoromethyl)(trimethylsilylether)] **13** (in THF).



υ (C-H) alkane = 2962 cm^{-1}, υ (C-C = 1600 cm^{-1}, 1501 cm^{-1}, υ (C-O) aryl ether = 1249 cm^{-1}, υ (C-F) = 1152 cm^{-1}

Figure S64. Infra-red spectrum of poly[(trifluoromethyl)(trimethylsilylether)] **13** (film from $CHCl_3$).

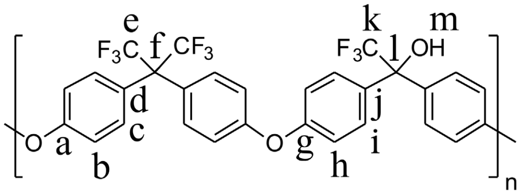
5. Synthesis and characterization of poly(trifluoromethylcarbinol)s 14 – 17



Polymer 14:

To a stirred solution of the silyl poly(ether) **10** (1.00 g, 1.52 mmol of repeat units) in dry THF (85 mL) was added tetrabutylammonium fluoride (1.59 g, 6.10 mmol, in 5 mL of THF) under nitrogen. After 24 h the volatiles were removed in *vacuo* and the polymer was dissolved in the minimum amount of acetone and precipitated in water (300 mL). After drying at 100 °C in *vacuo* over 2 hours, the polymer was reprecipitated twice in water (300 mL), from solution in the minimum amount of acetone. After drying at 100 °C in *vacuo*, the poly(trifluoromethyl)carbinol **14** was obtained as a white solid (0.67 g, 75 % yield).

Solvent	Acetone	THF	$CHCl_3$	CH_2Cl_2	MEK	MeOH	EtOH	i-PrOH
Solubility at 20 °C	Yes	Yes	Yes	Yes	Yes	No	No	No



14

^{1}H NMR ($CDCl_3$, 400 MHz): 2.90 (H_m, s), 6.97 (H_b, d, $^3J_{bc}$ = 8 Hz), 7.02 (H_h, d, $^3J_{hi}$ = 8 Hz), 7.35 (H_c, d, $^3J_{cb}$ = 8 Hz), 7.47 (H_i, d, $^3J_{ih}$ = 8 Hz) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): 118.1 (C_b), 119.0 (C_h), 128.1 (C_d), 129.2 (C_i), 131.8 (C_c), 134.7 (C_j), 156.5 (C_g), 157.3 (C_a) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz): -74.6 (2F), -64.1 (1F) ppm.

T_g (mid-point) = 155 °C. M_n = 15.4; M_w = 29.8 kDa; $Đ$ = 1.94.

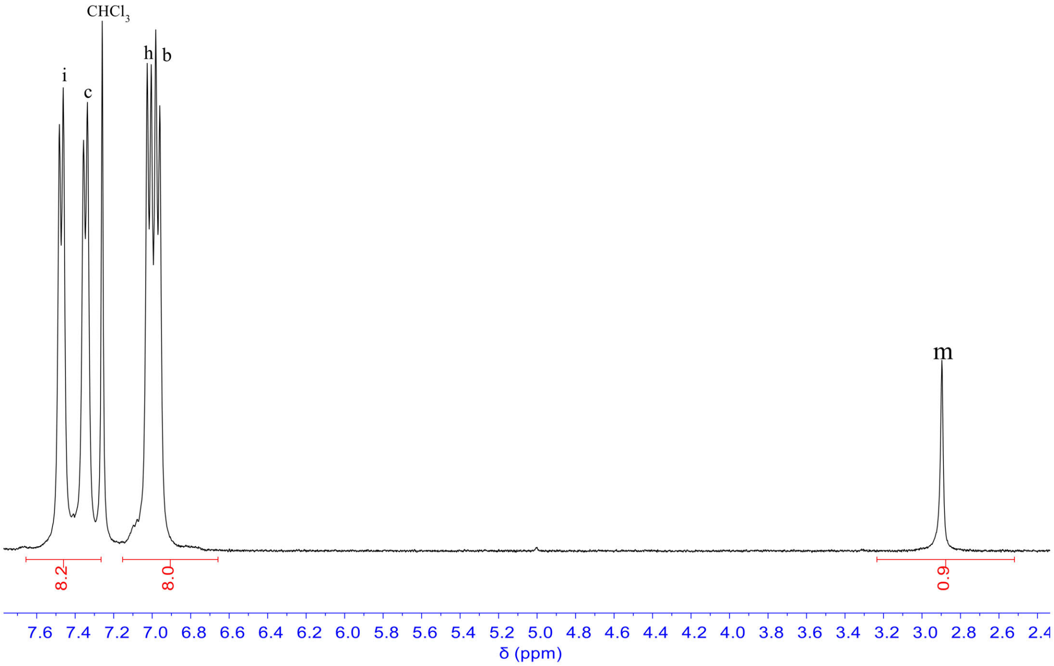


Figure S65. ^{1}H NMR spectrum of poly(trifluoromethylcarbinol) **14** (400 MHz, CDCl$_3$).

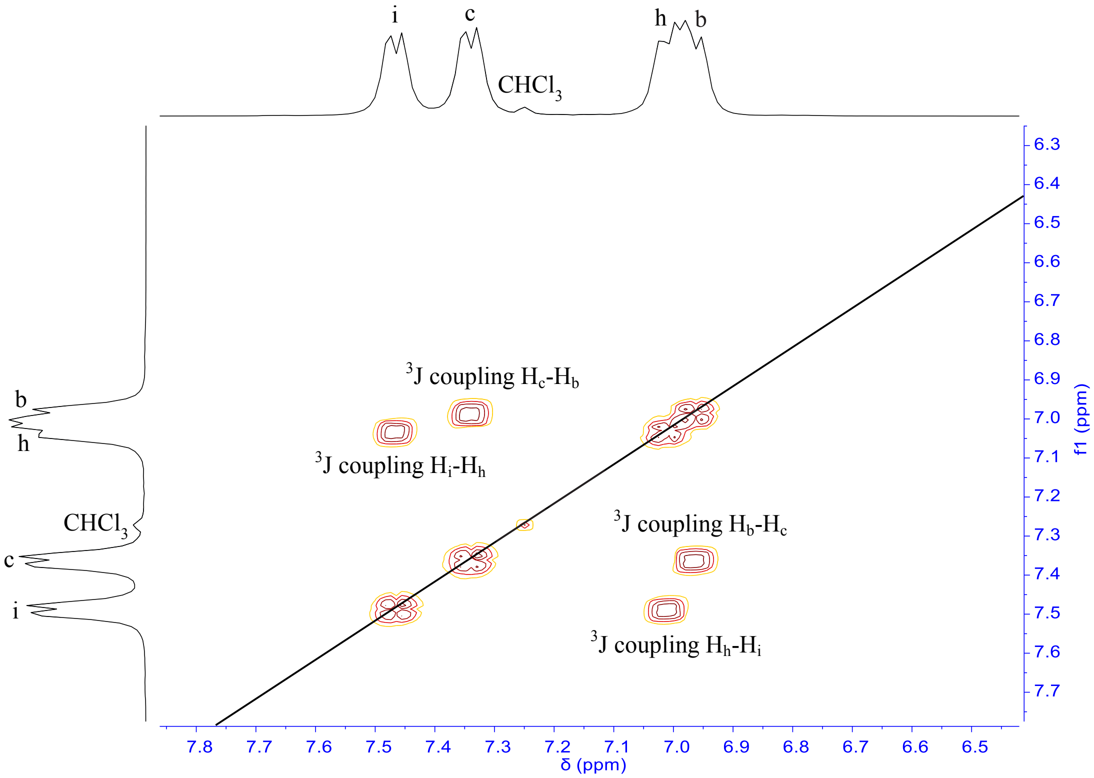


Figure S66. COSY (^{1}H-^{1}H) NMR spectrum of poly(trifluoromethylcarbinol) **14** (400 MHz, CDCl$_3$).

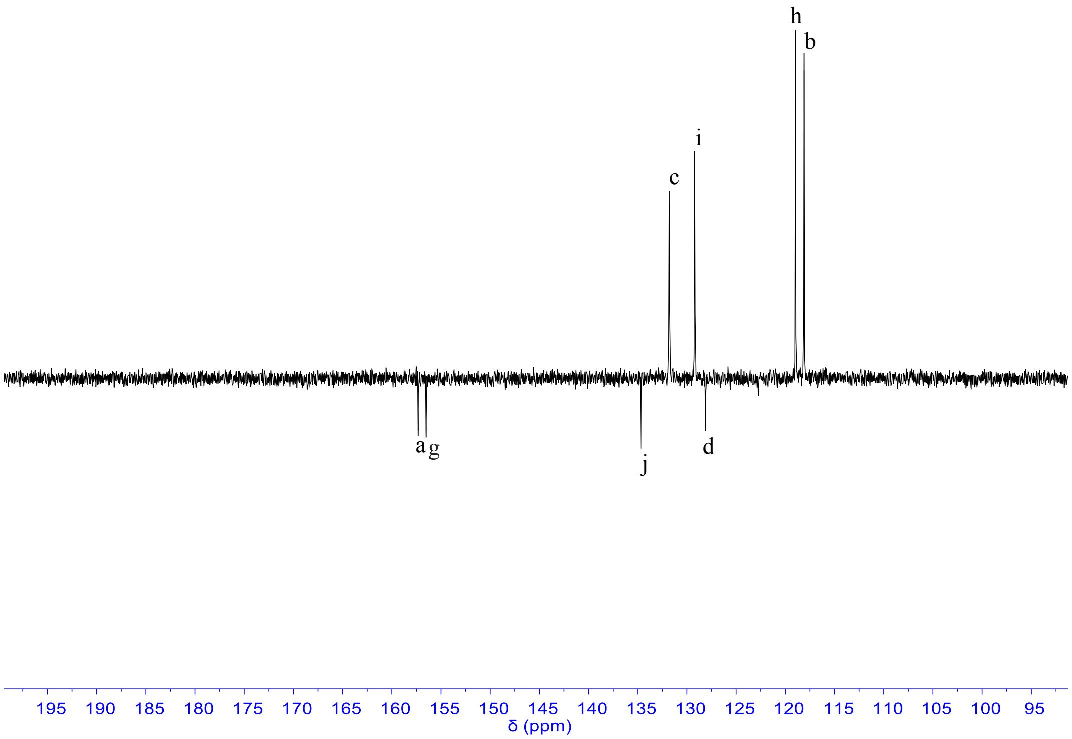


Figure S67. ^{13}C NMR (DEPT-135) spectrum of poly(trifluoromethylcarbinol) **14** (100 MHz, $CDCl_3$).

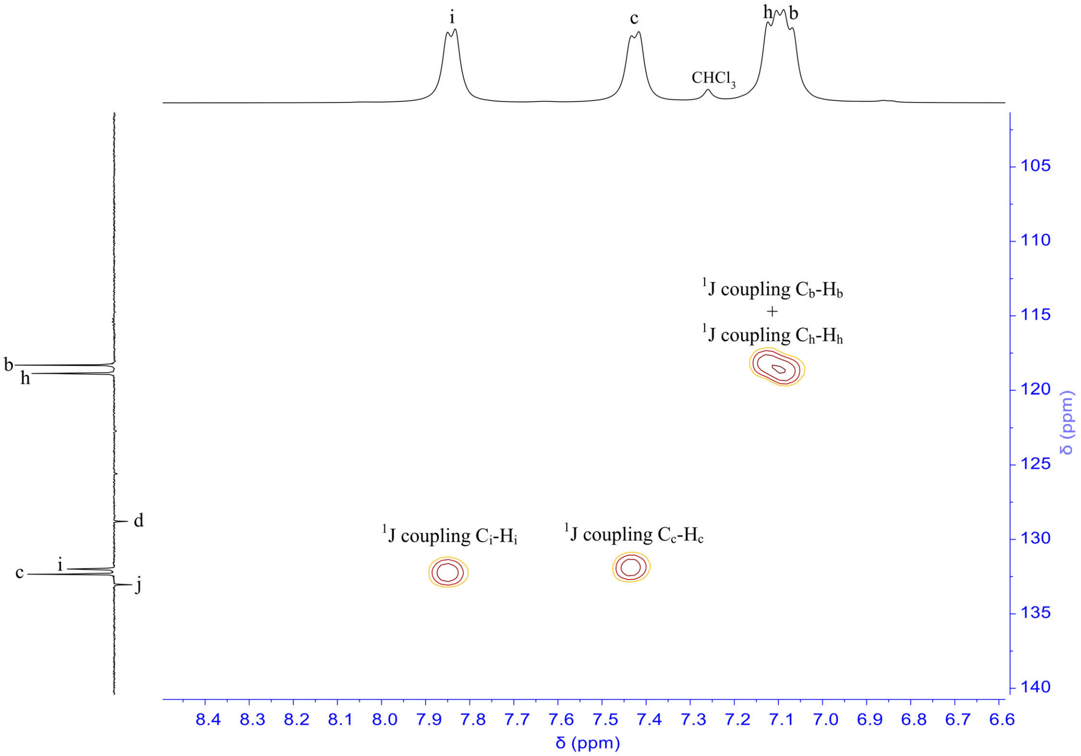
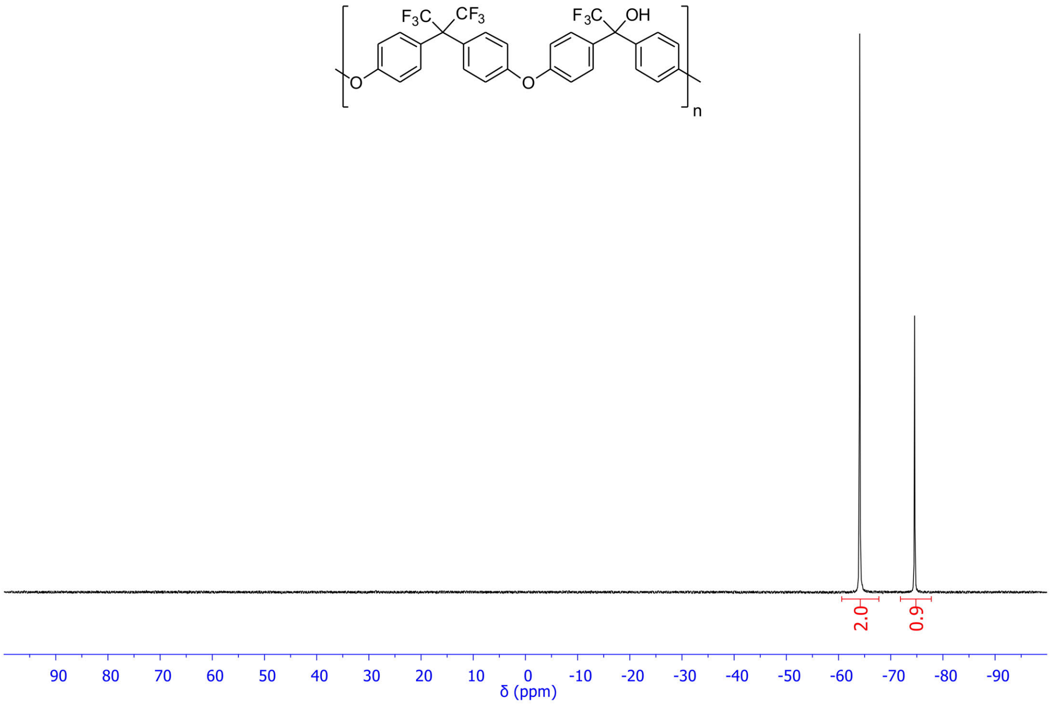


Figure S68. HSQC (^{1}H-^{13}C) NMR spectrum of poly(trifluoromethylcarbinol) **14** ($CDCl_3$).



^{19}F NMR (CDCl$_3$, 376 Mhz) δ$_F$ -64.1, -74.6 ppm.

Figure S69. ^{19}F NMR spectrum of poly(trifluoromethylcarbinol) **14** (376 MHz, CDCl$_3$).

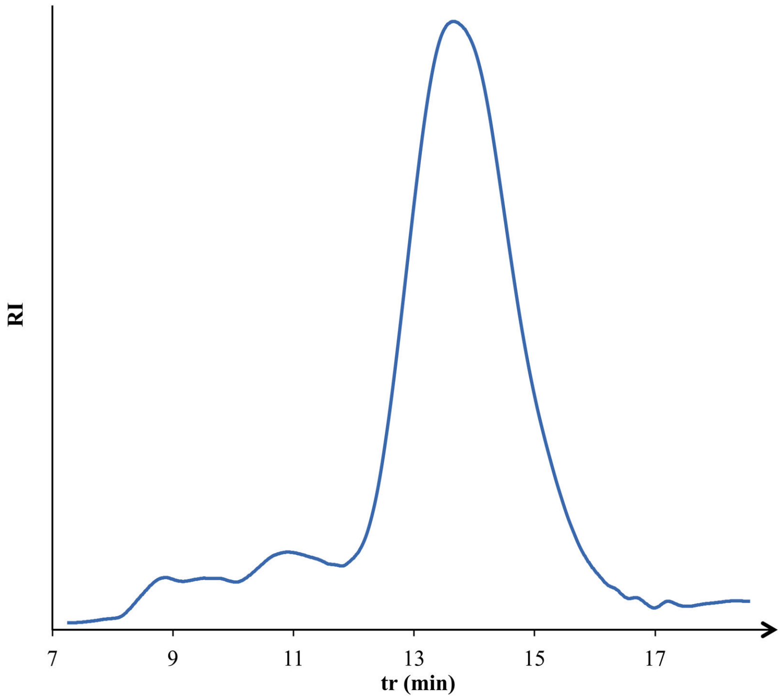
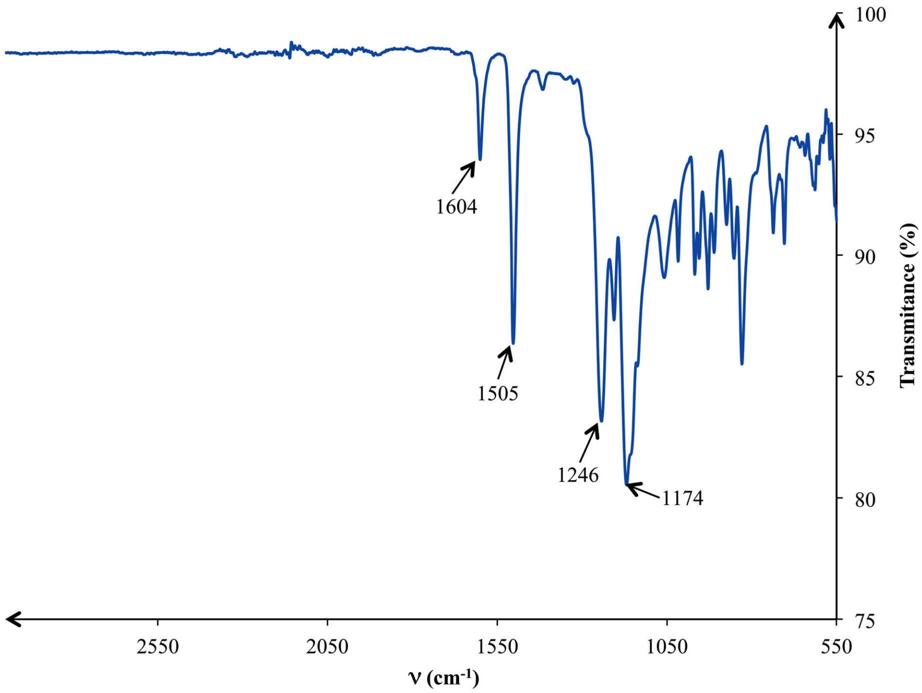


Figure S70. GPC trace for poly(trifluoromethylcarbinol) **14** (in THF).



υ (C=C) = 1604 cm^{-1}, 1505 cm^{-1}, υ (C–O) aryl ether = 1246 cm^{-1}, υ (C-F) = 1174 cm^{-1}

Figure S71. Infra-red spectrum of poly(trifluoromethylcarbinol) **14** (film from $CHCl_3$).

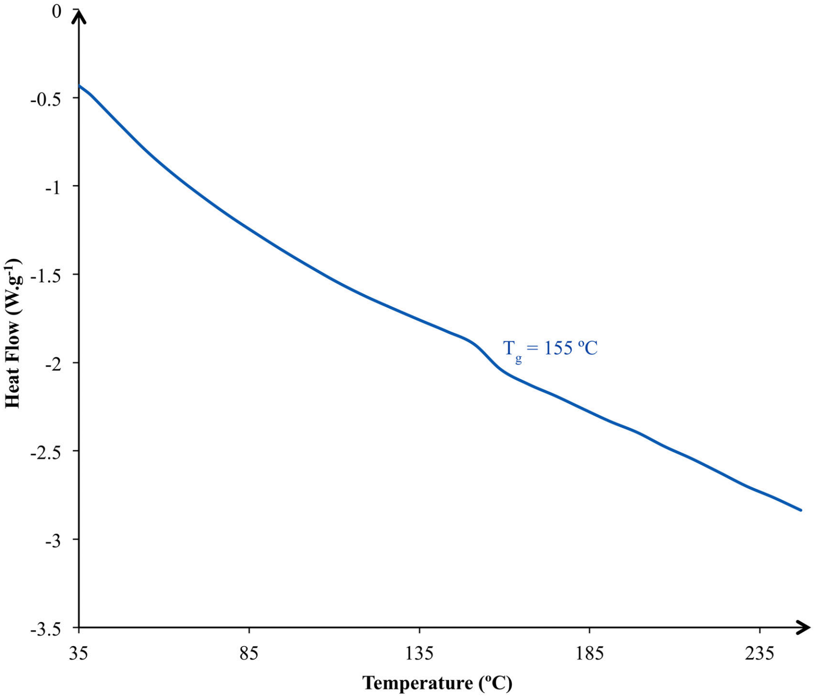
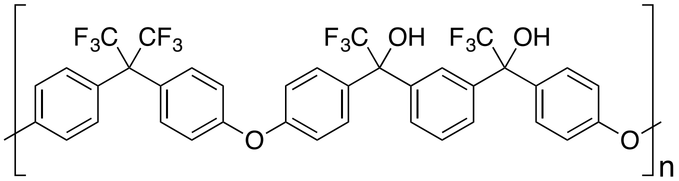


Figure S72. DSC thermogram (second heating scan) for poly(trifluoromethylcarbinol) **14**.

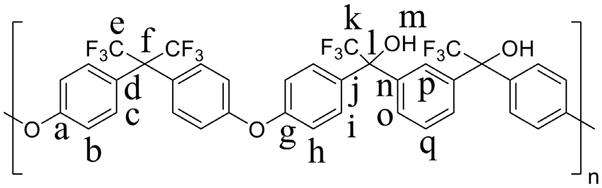
Polymer 15:



Polymer **15** was obtained from the poly(silyl ether) **11** using the method described above for the synthesis of polymer **14**, and was isolated in 79% yield.

T_g (mid-point) = 143 °C. M_n = 420; M_w = 1,640 kDa; $Đ$ = 3.90.

Solvent	Acetone	THF	$CHCl_3$	CH_2Cl_2	MEK	MeOH	EtOH	i-PrOH
Solubility at 20 °C	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes



15

^{1}H NMR ($CDCl_3$, 400 MHz): 2.96 (H_m, s), 6.94 (H_b, d, $^3J_{bc}$ = 8 Hz), 6.98 (H_h, d, $^3J_{hi}$ = 8 Hz), 7.33 (H_c+H_q, m, $^3J_{cb}$ = 8 Hz), 7.41 (H_i, m, $^3J_{ih}$ = 8 Hz), 7.46 (H_o, m, $^3J_{oq}$ = 7 Hz), 7.67 and 7.70 (H_p, s) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz): 118.1 (C_b), 119.0 (C_h), 126.5 (C_p), 127.9 (C_o), 128.1(C_d), 128.3 (C_q), 129.2 (C_i), 131.8 (C_c), 134.5 (C_j), 139.3 (C_n), 156.5(C_g), 157.3 (C_a) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz): -74.5 (2F), -64.1 (2F) ppm.

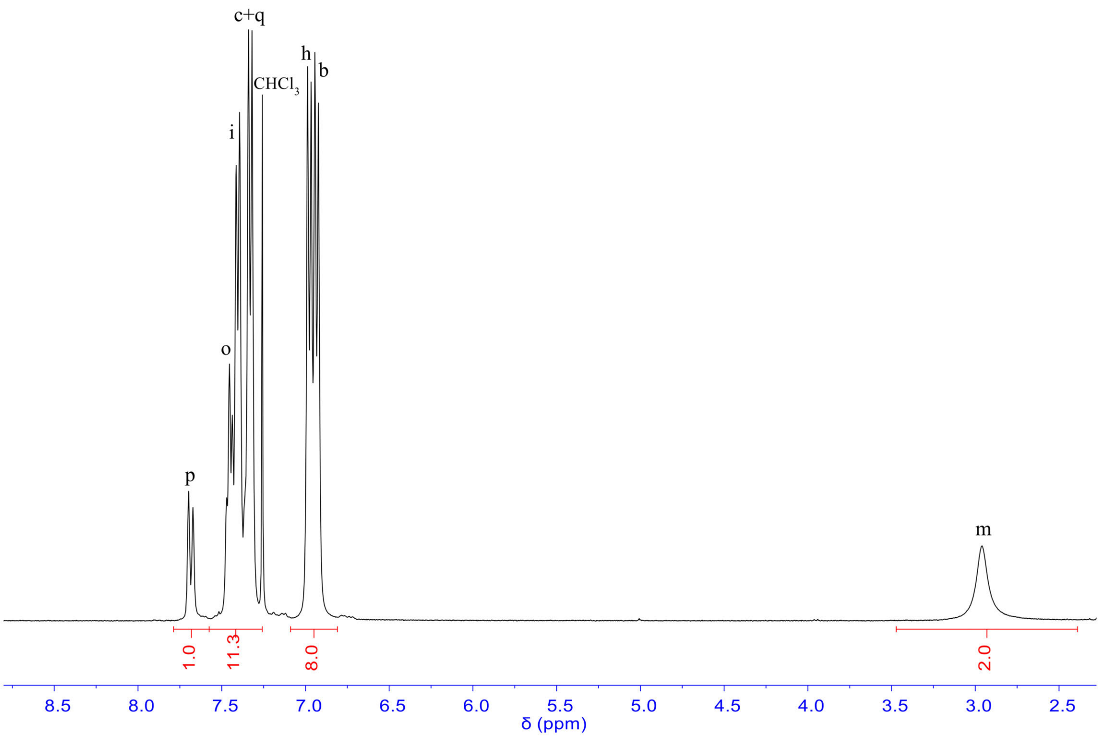


Figure S73. ^{1}H NMR spectrum of poly(trifluoromethylcarbinol) **15** (400 MHz, CDCl$_3$).

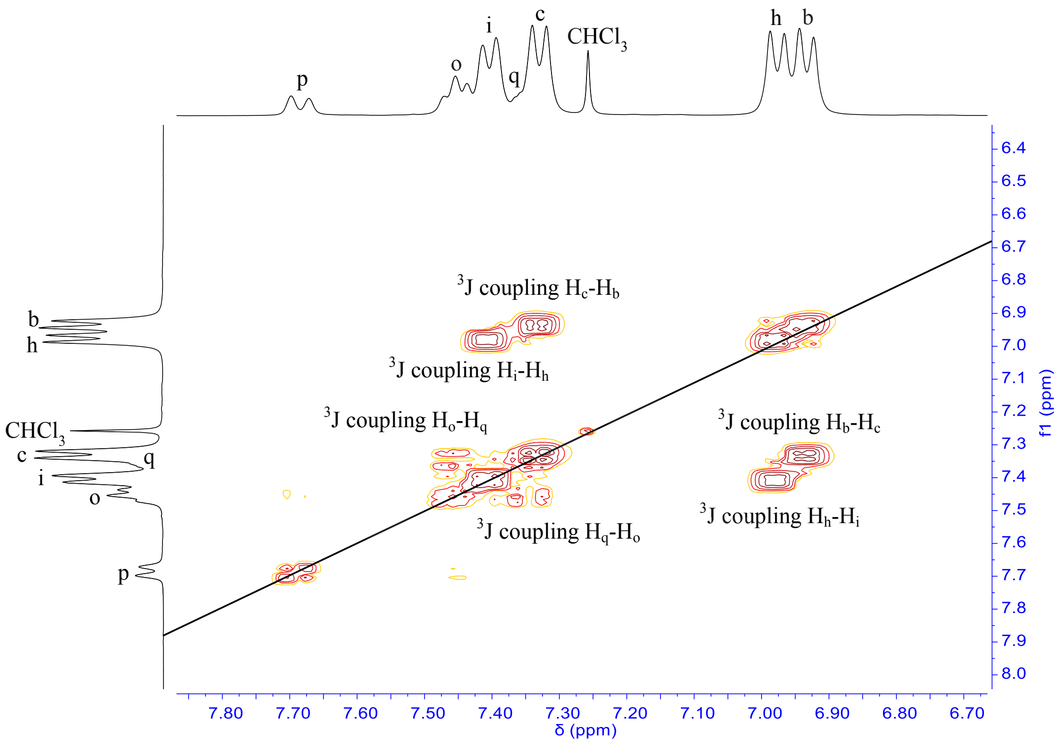


Figure S74. COSY (^{1}H-^{1}H) NMR spectrum of poly(trifluoromethylcarbinol) **15** (400 MHz, CDCl$_3$).

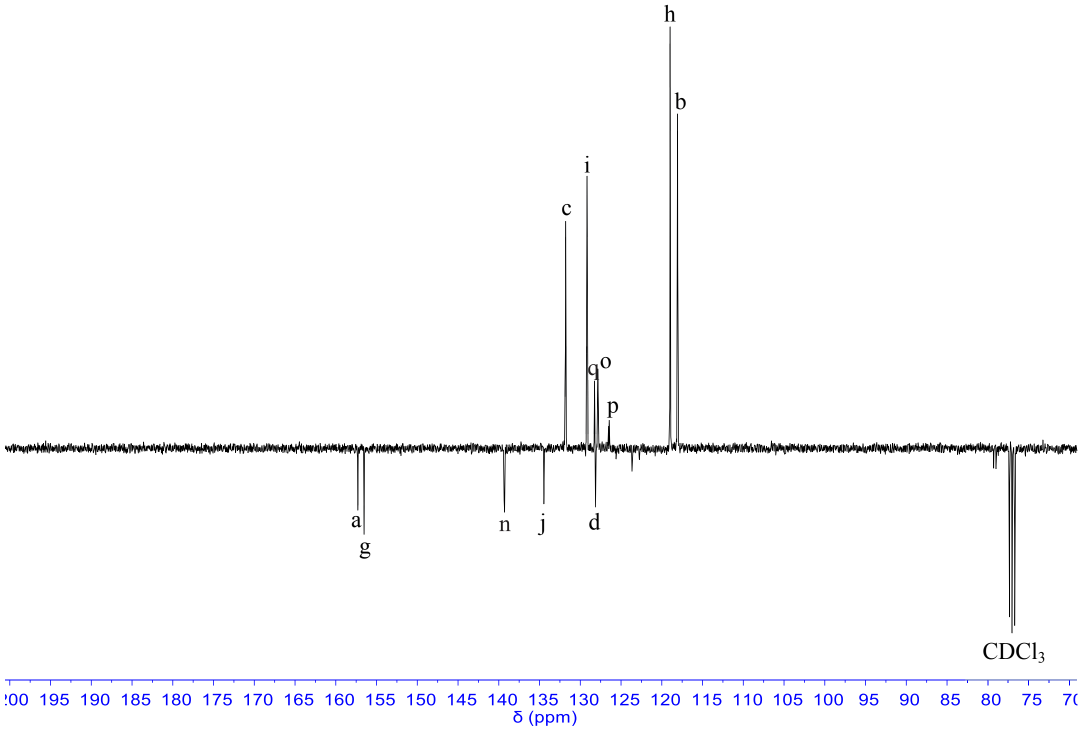


Figure S75. ^{13}C NMR (DEPT-135) spectrum of poly(trifluoromethylcarbinol) **15** (100 MHz, CDCl$_3$).

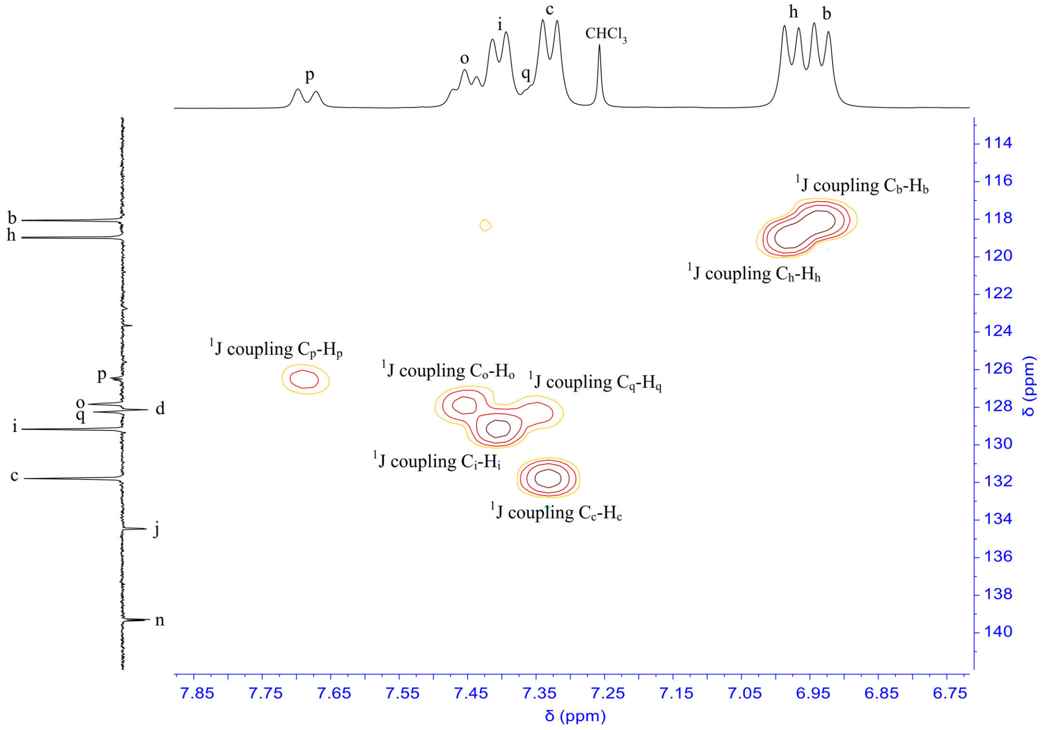
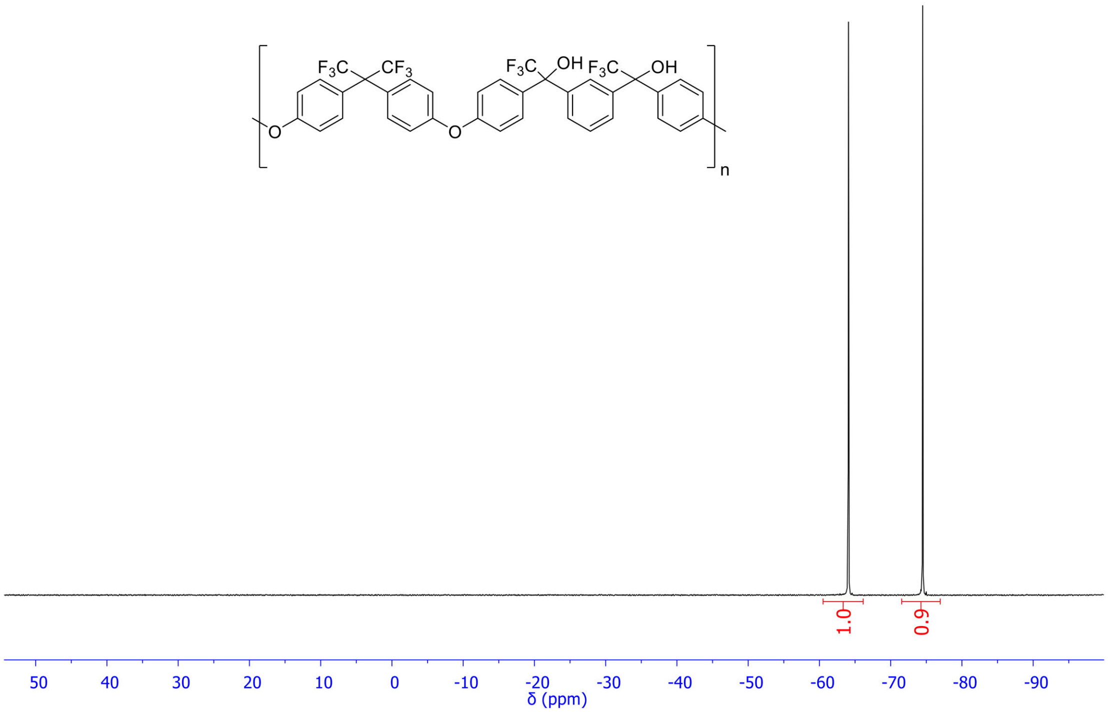


Figure S76. HSQC (^{1}H-^{13}C) NMR spectrum of poly(trifluoromethylcarbinol) **15** (CDCl$_3$).



^{19}**F NMR** (CDCl$_3$, 376 Mhz) δ_F -64.1, -74.5 ppm.

Figure S77. ^{19}F NMR spectrum of poly(trifluoromethylcarbinol) **15** (376 MHz, CDCl$_3$).

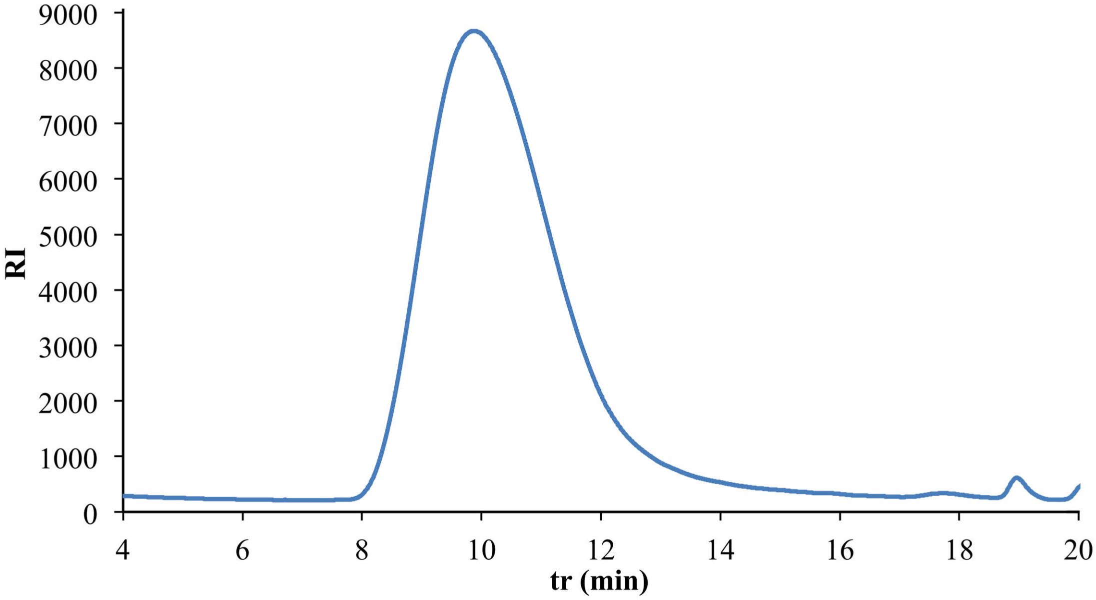
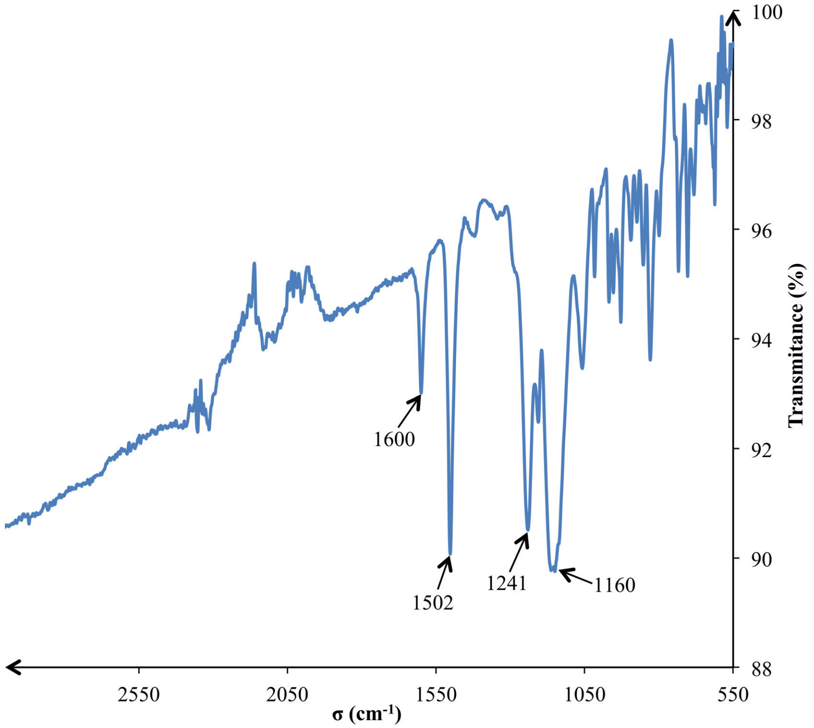


Figure S78. GPC trace for poly(trifluoromethylcarbinol) **15** (in THF).



υ (C=C) = 1600 cm^{-1}, 1502 cm^{-1}, υ (C-O) aryl ether = 1241 cm^{-1}, υ (C-F) = 1160 cm^{-1}

Figure S79. Infra-red spectrum of poly(trifluoromethylcarbinol) **15** (film from $CHCl_3$).

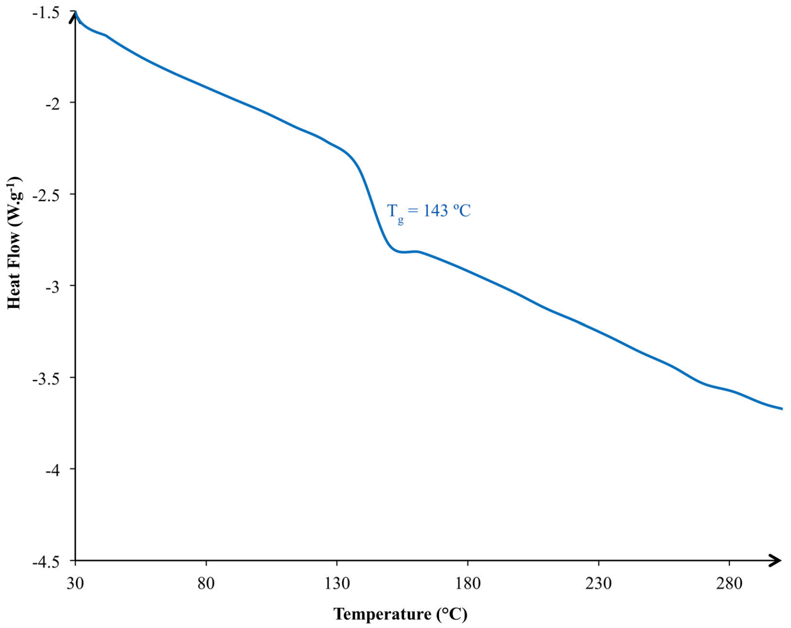
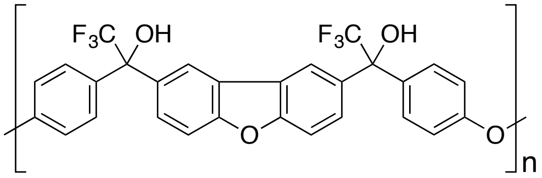


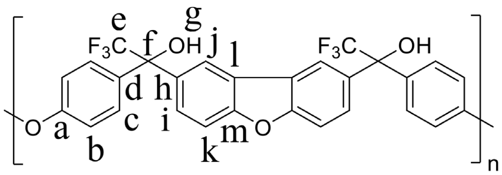
Figure S80. DSC thermogram (second heating scan) for poly(trifluoromethylcarbinol) **15**.

Polymer 16:



Polymer **16** was obtained from the poly(silyl ether) **12** using the method described above for the synthesis of polymer **14**, and was isolated in 52% yield.

Solvent	Acetone	THF	$CHCl_3$	CH_2Cl_2	MEK	MeOH	EtOH	i-PrOH
Solubility at 20 °C	Yes	Yes	No	No	Yes	Yes	Yes	Yes



^{1}H NMR (Acetone-d_6, 400 MHz): 6.41 (H_g, s), 7.05 (H_b, d, $^3J_{bc} = 8$ Hz), 7.59 (H_c, d, $^3J_{cb} = 8$ Hz), 7.65 (H_i+H_k, m), 8.39 (H_j, s) ppm.

^{13}C NMR (Acetone-d_6, 100 Mhz): 79.6 (C_f), 112.1 (C_k), 119.2 (C_b), 121.0 (C_j), 124.5 (C_l), 128.4 (C_i), 130.3 (C_c), 136.4-136.6 (C_d+C_h), 157.1 (C_m), 157.7 (C_a) ppm.

^{19}F NMR (Acetone-d_6, 376 MHz): 103.1 ppm.

T_g (mid-point) = 216 °C. $M_n = 23.1$; $M_w = 86.6$ kDa; $Đ = 3.75$.

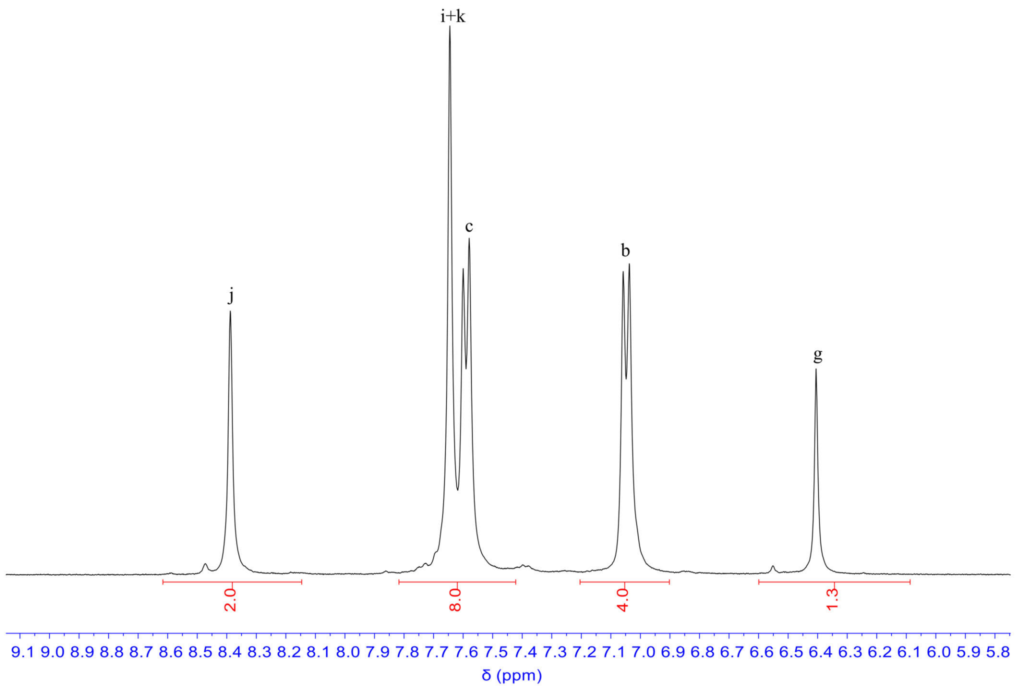


Figure S81. ^{1}H NMR spectrum of poly(trifluoromethylcarbinol) **16** (400 MHz, acetone-*d*$_6$).

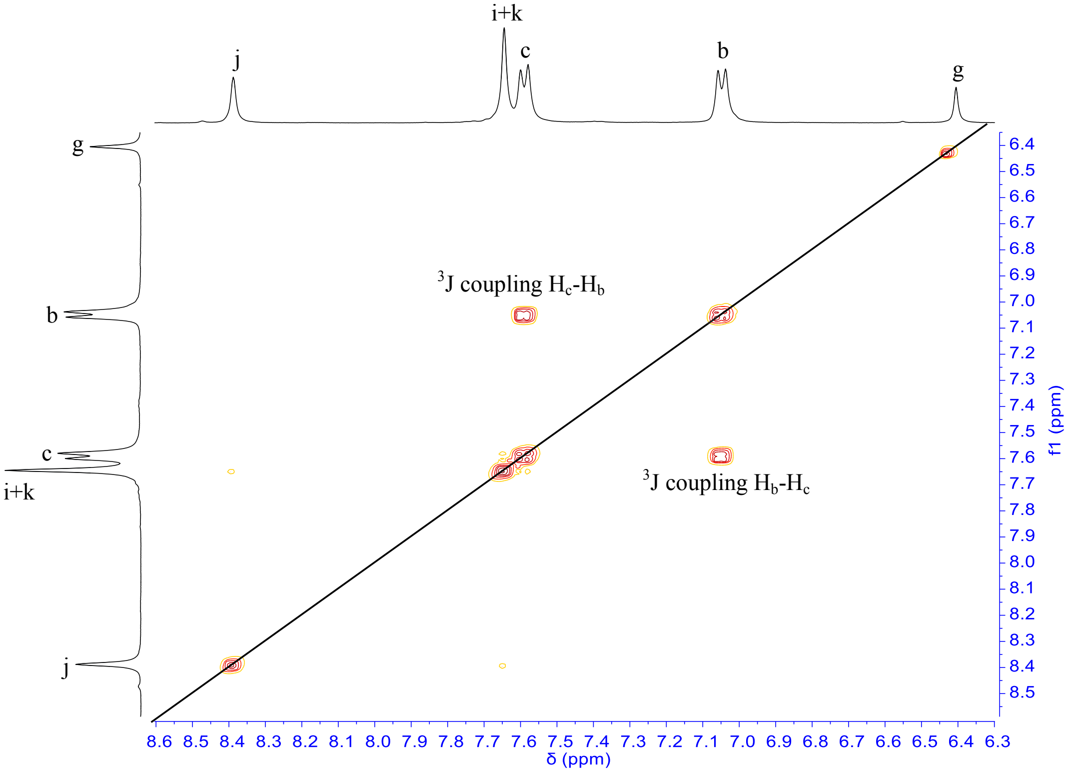


Figure S82. COSY (^{1}H-^{1}H) NMR spectrum of poly(trifluoromethylcarbinol) **16** (400 MHz, acetone-*d*$_6$).

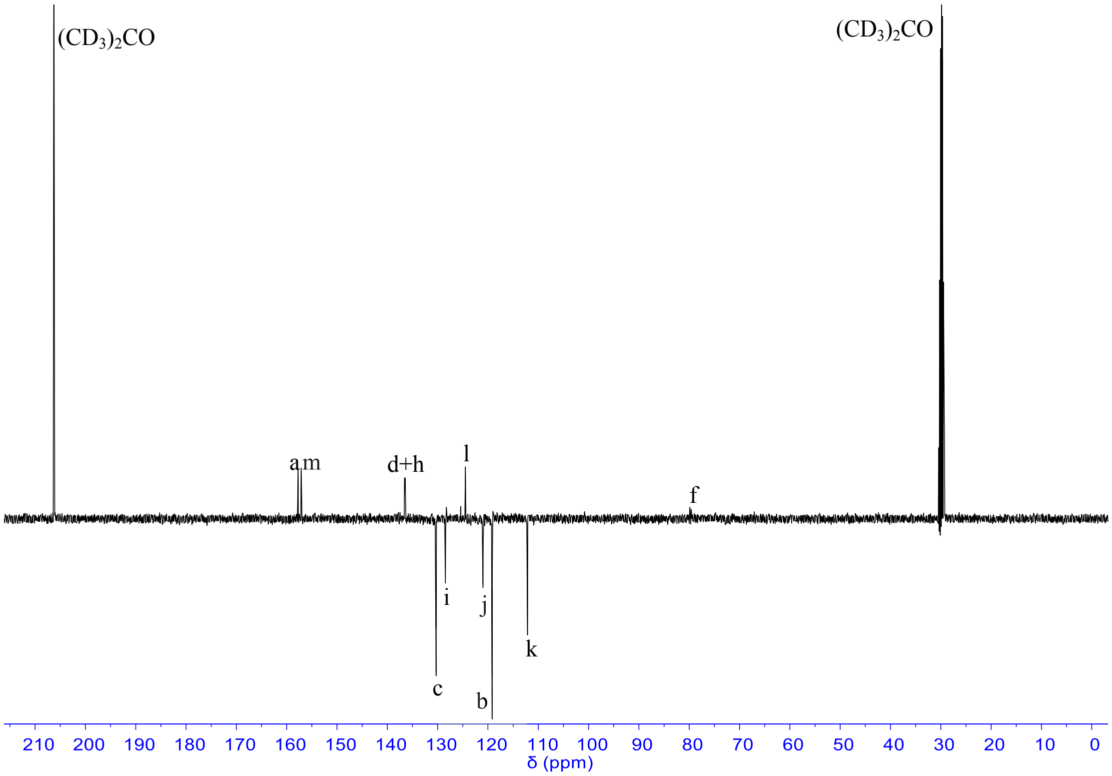


Figure S83. ^{13}C NMR (DEPT-135) spectrum of poly(trifluoromethylcarbinol) **16** (100 MHz, acetone-*d*$_6$).

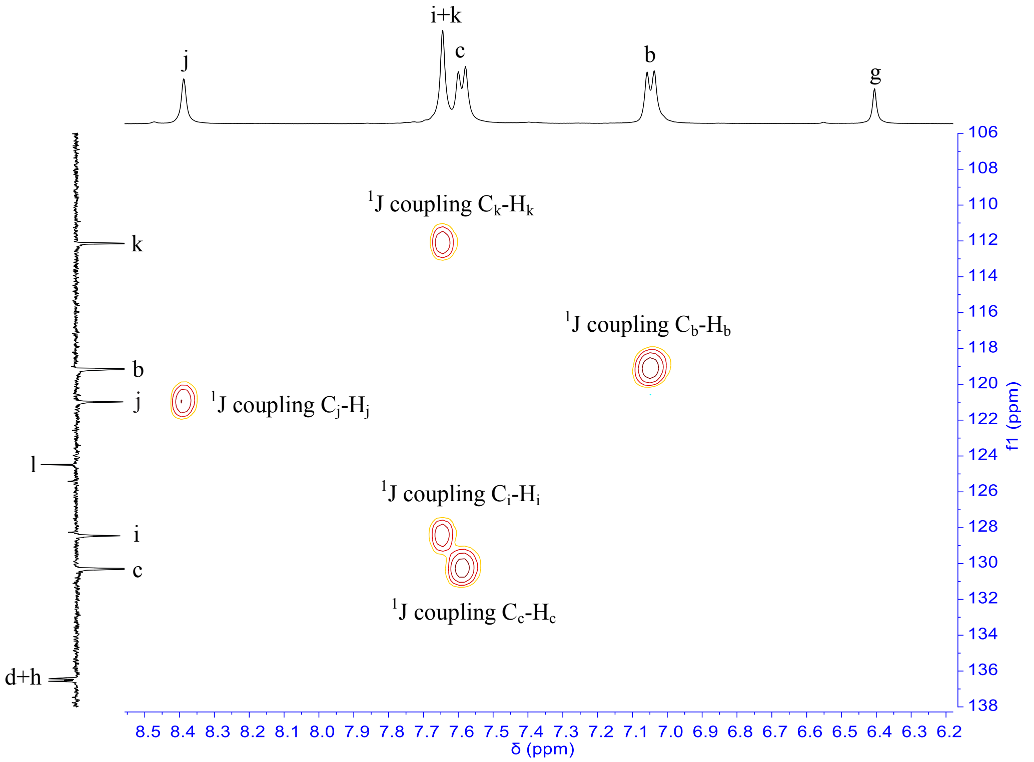


Figure S84. HSQC (^{1}H-^{13}C) NMR spectrum of poly(trifluoromethylcarbinol) **16** (acetone-*d*$_6$).

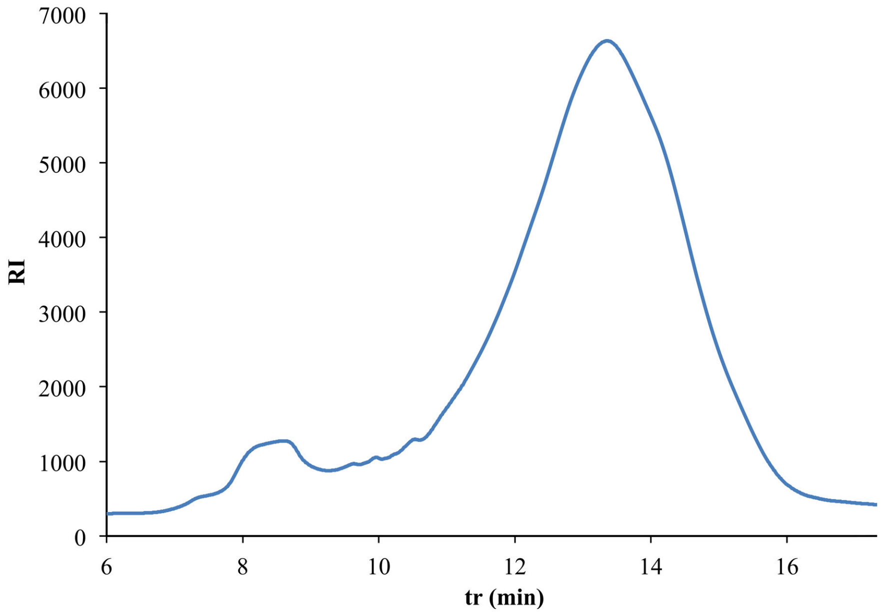
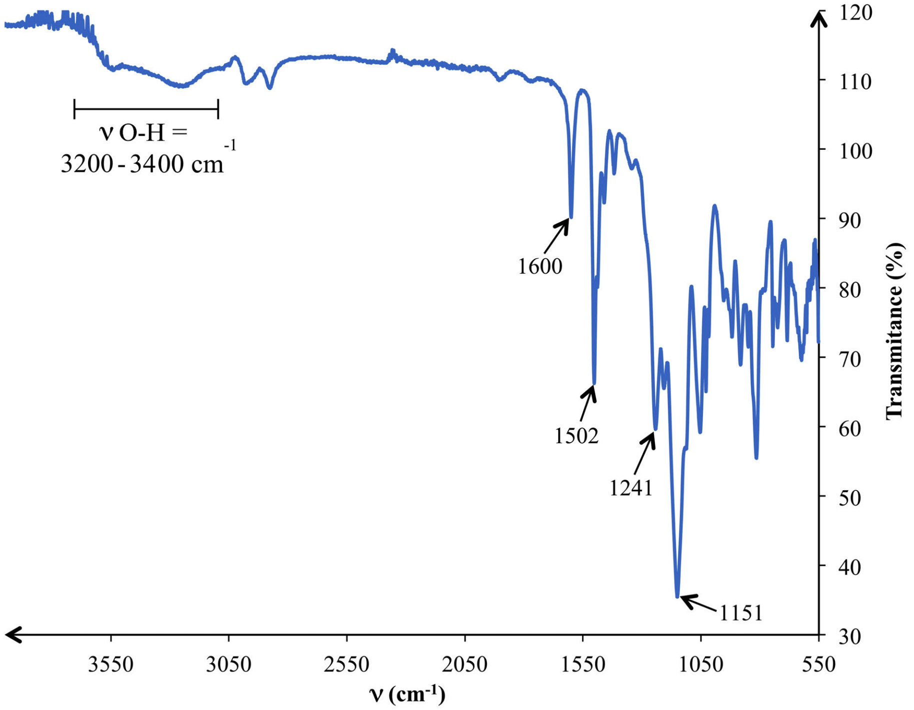


Figure S85. GPC trace for poly(trifluoromethylcarbinol) **16** (in THF).



υ (C=C) = 1600 cm^{-1}, 1502 cm^{-1}, υ (C-O) aryl ether = 1241 cm^{-1}, υ (C=F) = 1151 cm^{-1}

Figure S86. Infra-red spectrum of poly(trifluoromethylcarbinol) **16** (film from CHCl$_3$).

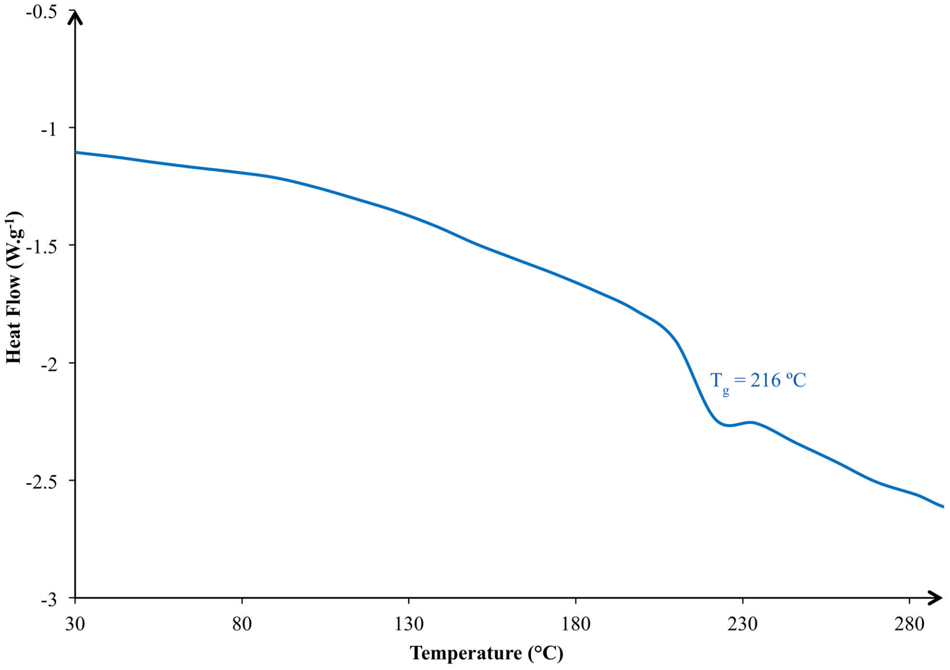
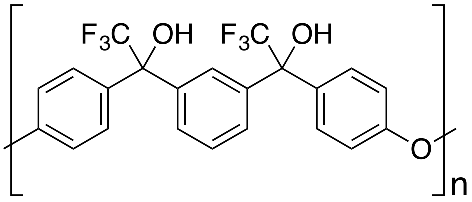


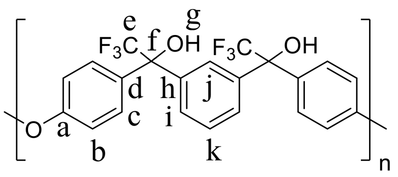
Figure S87. DSC thermogram (second heating scan) for poly(trifluoromethylcarbinol) **16**.

Polymer 17:



Polymer **17** was obtained from the poly(silyl ether) **13** using the method described above for the synthesis of polymer **14**, and was isolated in 51% yield.

solvent	Acetone	THF	$CHCl_3$	CH_2Cl_2	MEK	MeOH	EtOH	isoPrOH
Solubility at 20 °C	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes



^{1}**H NMR** (Acetone-d_6, 400 MHz): 6.39 (H_g, s), 7.02 (H_b, d, $^{3}J_{bc} = 9$ Hz), 7.43 (H_k, m, $^{3}J_{ki} = 8$ Hz), 7.52 (H_c+H_i, m), 7.88 (H_j, s) ppm.

^{13}**C NMR** (Acetone-d_6, 100 MHz): 79.2 (C_f), 79.5 (C_f), 79.7(C_f), 80.0 (C_f), 119.1 (C_b), 122.3 (C_e), 125.3 (C_e), 127.6 (C_i), 128.1 (C_e), 128.4 (C_k), 128.7 (C_j), 130.2 (C_c), 131.0 (C_e), 136.1 (C_d), 141.0 (C_h), 157.8 (C_a) ppm.

^{19}**F NMR** (Acetone-d_6, 376 MHz): 103.9 ppm.

T_g (mid-point) = 120 °C. M_n = 25.0; M_w = 224 kDa; $Đ$ = 8.96.

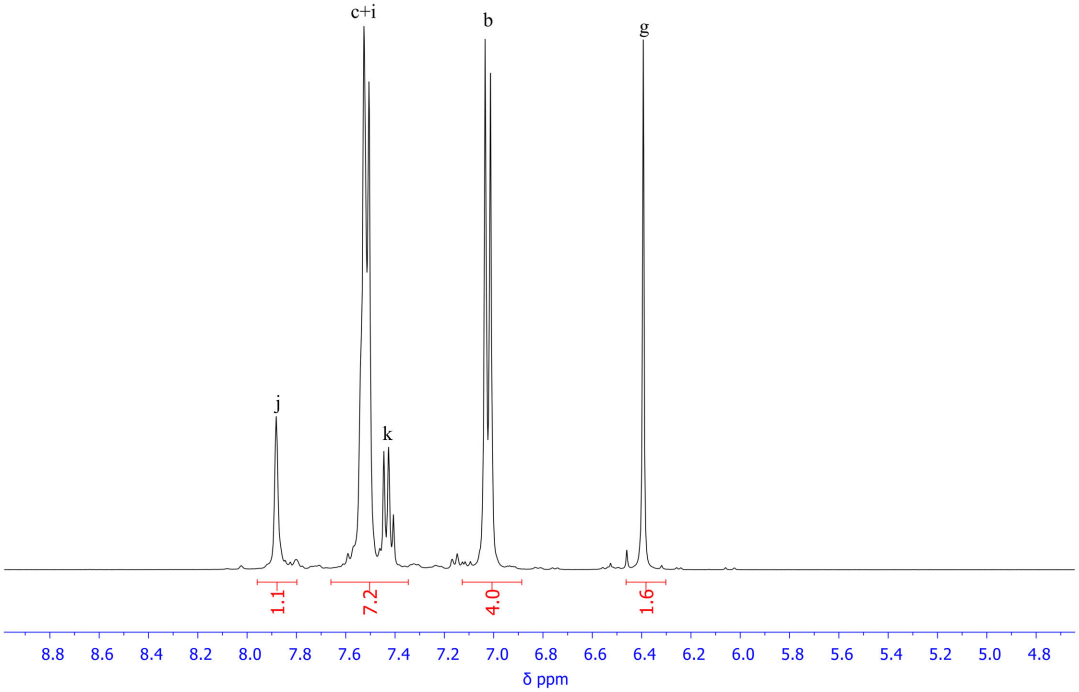


Figure S88. ^{1}H NMR spectrum of poly(trifluoromethylcarbinol) **17** (400 MHz, acetone-d_6).

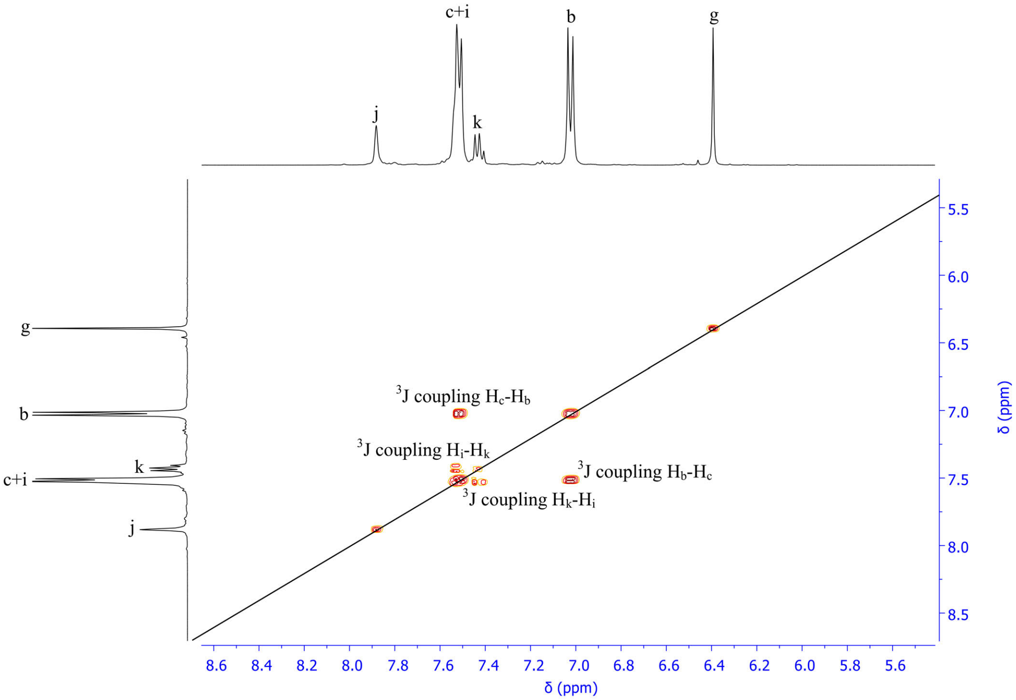


Figure S89. COSY (^{1}H-^{1}H) NMR spectrum of of poly(trifluoromethylcarbinol) **17** (400 MHz, acetone-d_6).

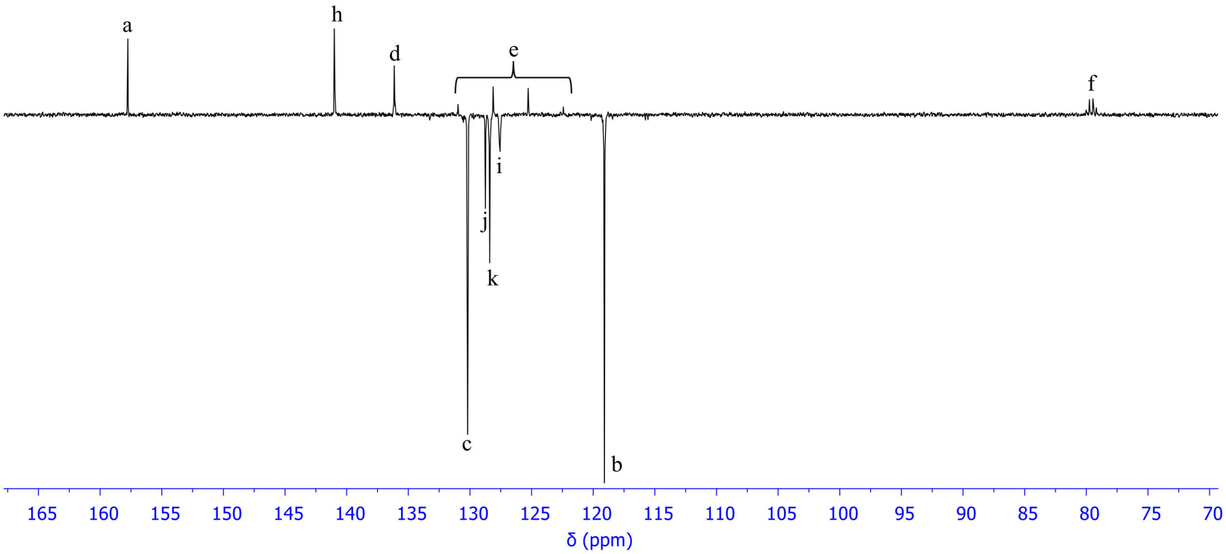


Figure S90. ^{13}C NMR (DEPT 135) spectrum of poly(trifluoromethylcarbinol) **17** (100 MHz, acetone-*d*$_6$).

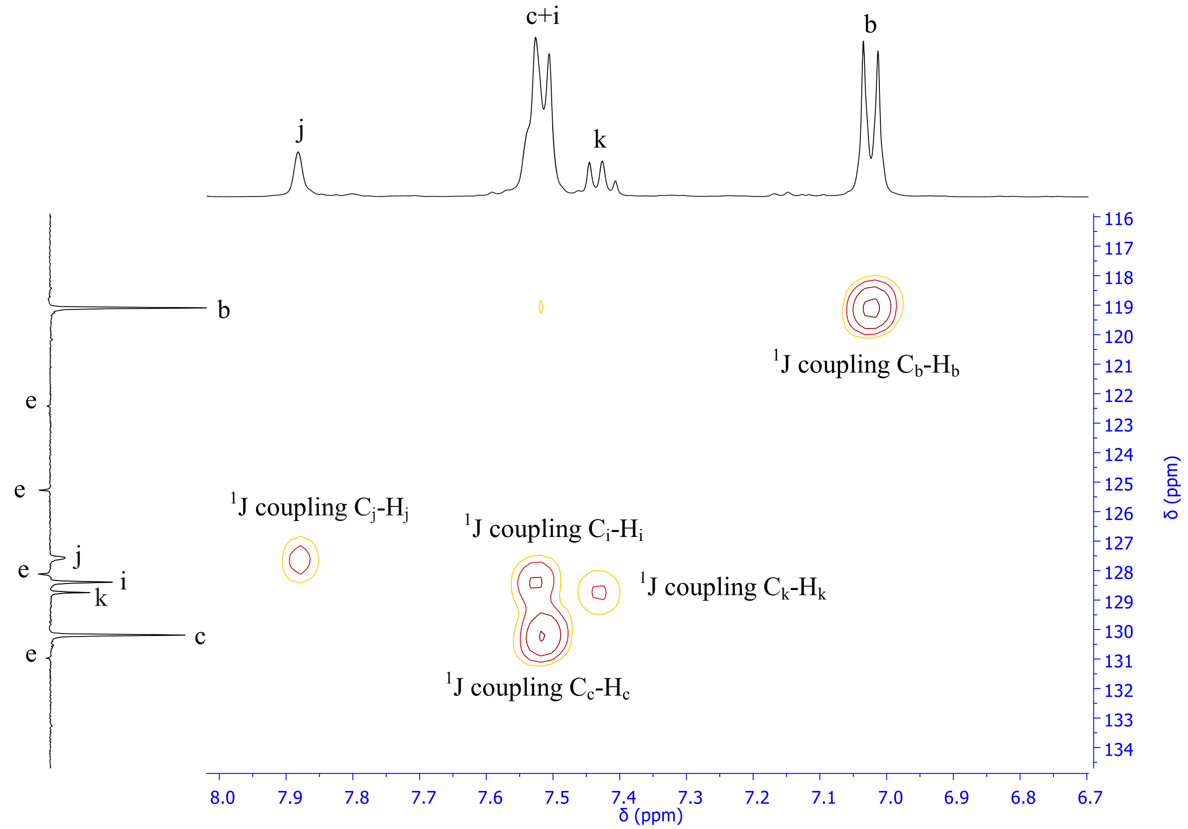


Figure S91. HSQC (^{1}H-^{13}C) NMR spectrum of poly(trifluoromethylcarbinol) **17** (acetone-*d*$_6$).

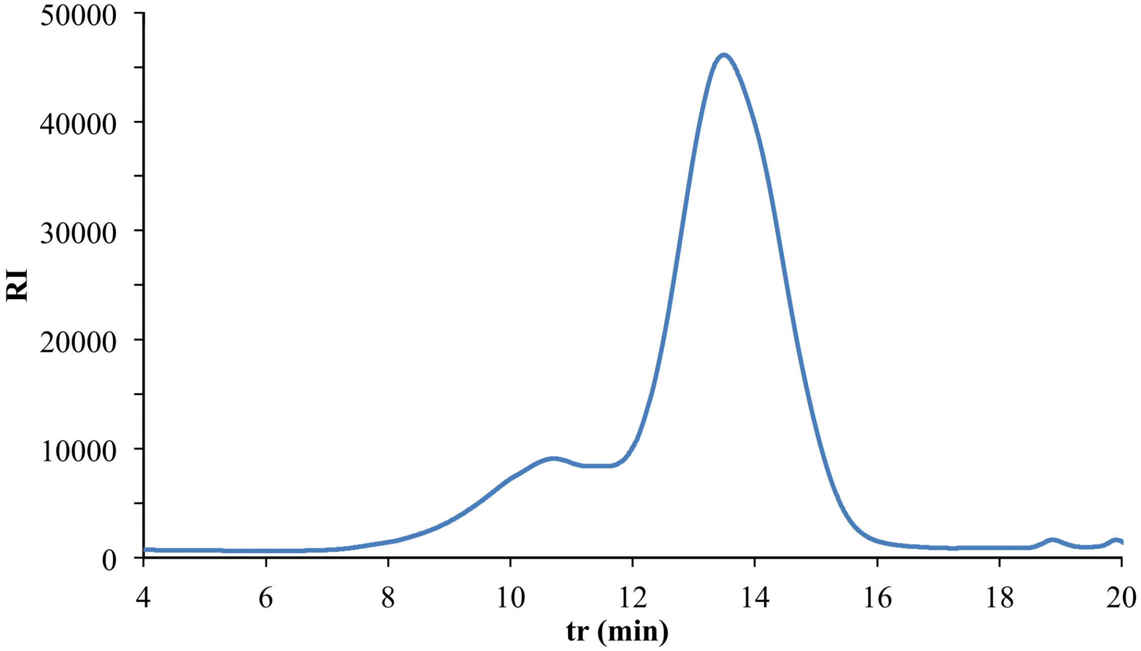
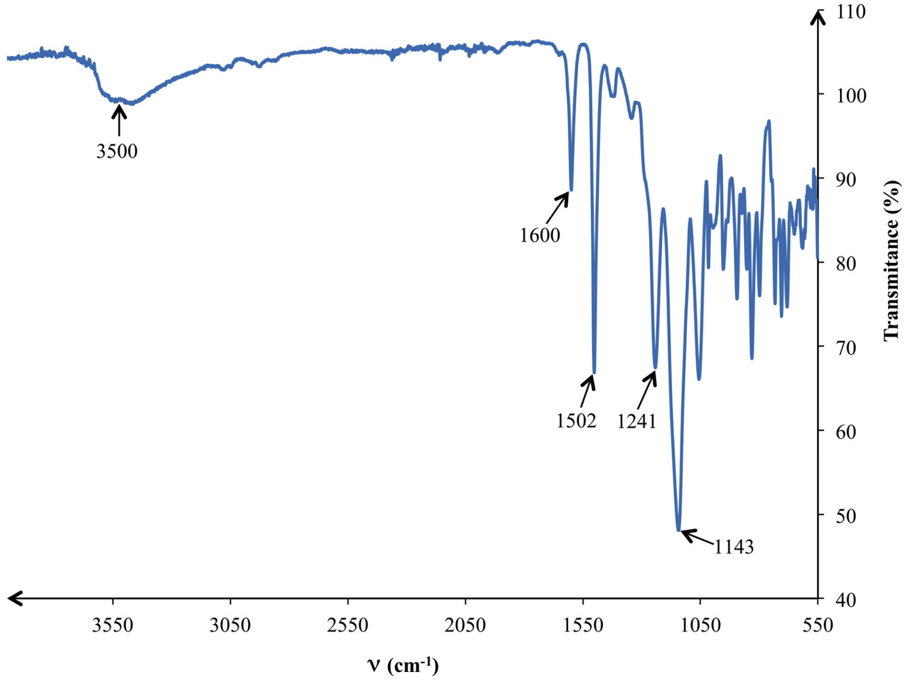


Figure S92. GPC trace for poly(trifluoromethylcarbinol) **17** (in THF).



υ (O-H) = 3500 cm^{-1}, υ (C=C) = 1600 cm^{-1}, 1502 cm^{-1}, υ (C-O) aryl ether = 1241 cm^{-1}, υ (C-F) = 1143 cm^{-1}

Figure S93. Infra-red spectrum of poly(trifluoromethylcarbinol) **17** (film from $CHCl_3$).

6. Contact angle measurements for polymers 2, 11 and 15

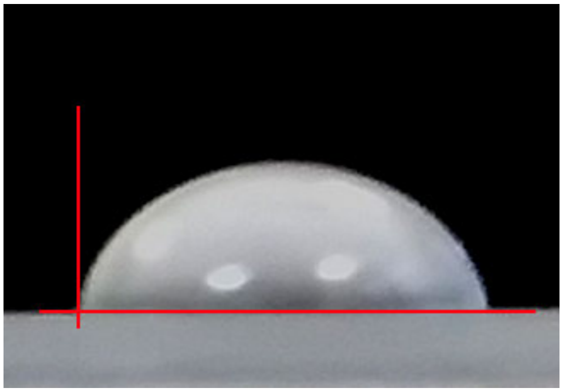


Figure S94. Contact angle (ca. 90°) for a 10 μL drop of DI water on the surface of poly(ketone) **2**.

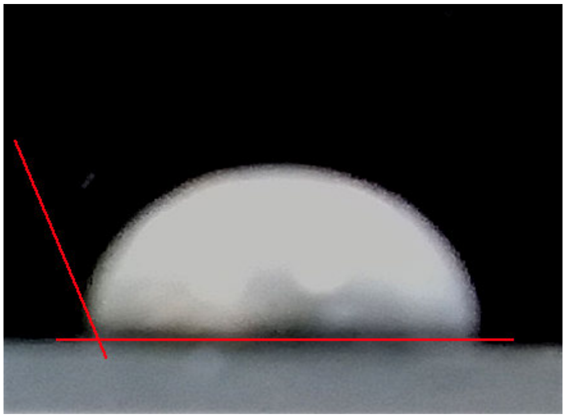


Figure S94. Contact angle (ca. 112°) for a 10 μL drop of DI water on the surface of poly(trimethylsilyl ether) **11**.

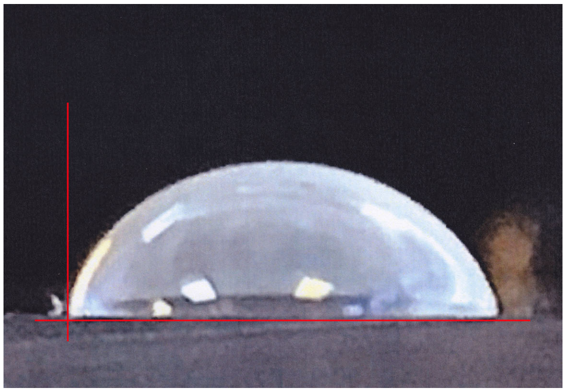


Figure S94. Contact angle (ca. 90°) for a 10 μL drop of DI water on the surface of polyol **15**.

7. XPS surface analyses

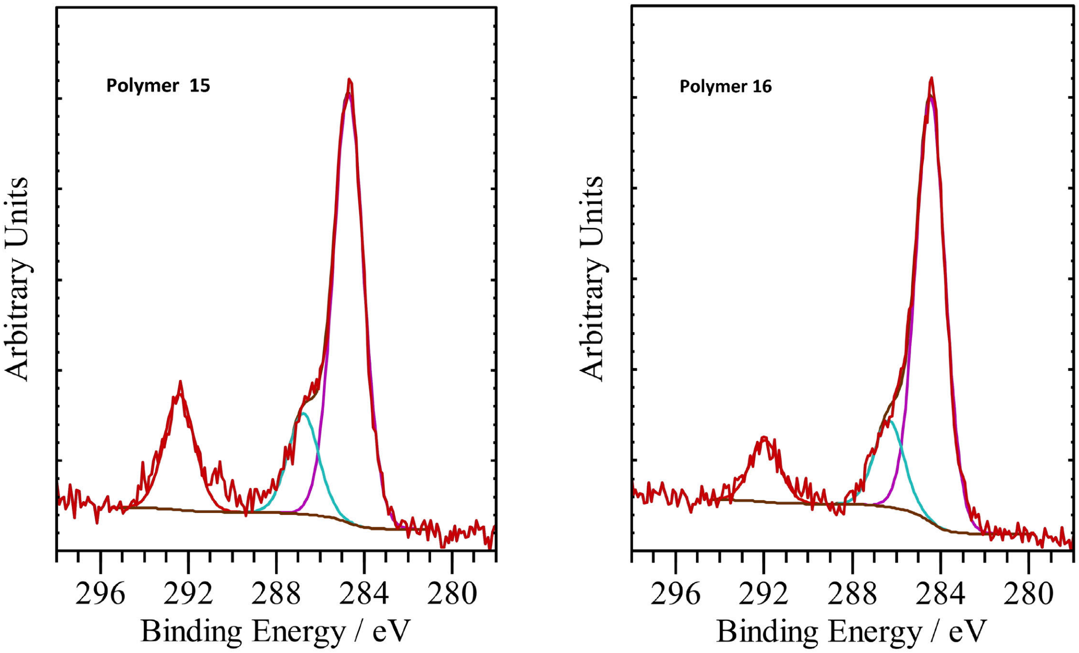
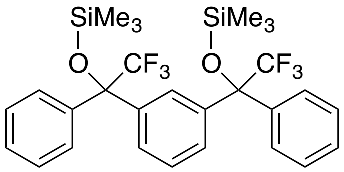


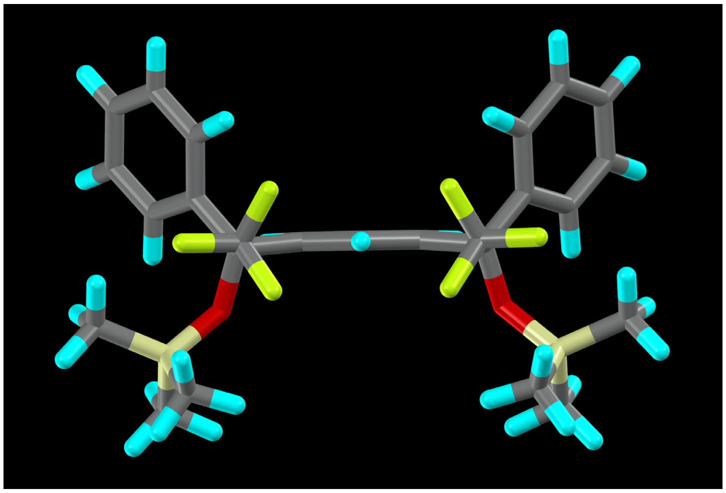
Figure S95. Deconvoluted XPS spectra (averaged over take-off angles of 25-60°) for polyols **15** and **16**. Assigments and measured/calculated surface-atom percentages are given in Table 2 of the main paper.

8. Molecular mechanics calculations for a diastereomeric model compound

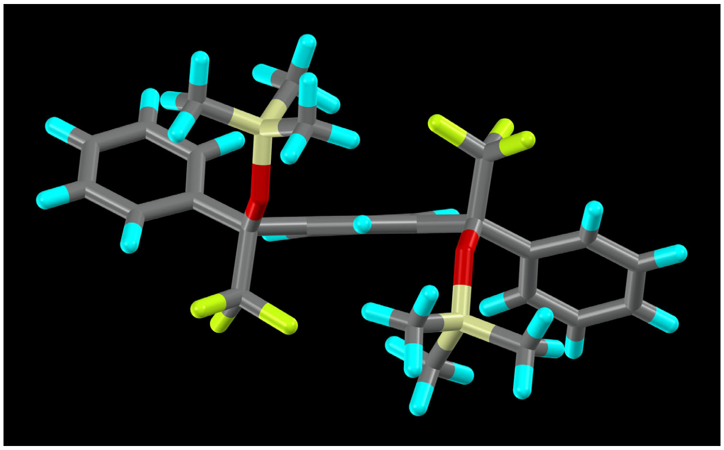
Calculations were carried out using the Dreiding-2 force field (with charge-equilibration), implemented in Cerius2 (v. 6.7, Accelrys, San Diego). The model compound shown below was constructed in both RS and SS configurations, and energy-minimisation was carried out on the two diastereomers. Structures are shown projected along the plane of the central aromatic ring.



Model compound for diastereomeric centres in polymers **11** and **13**



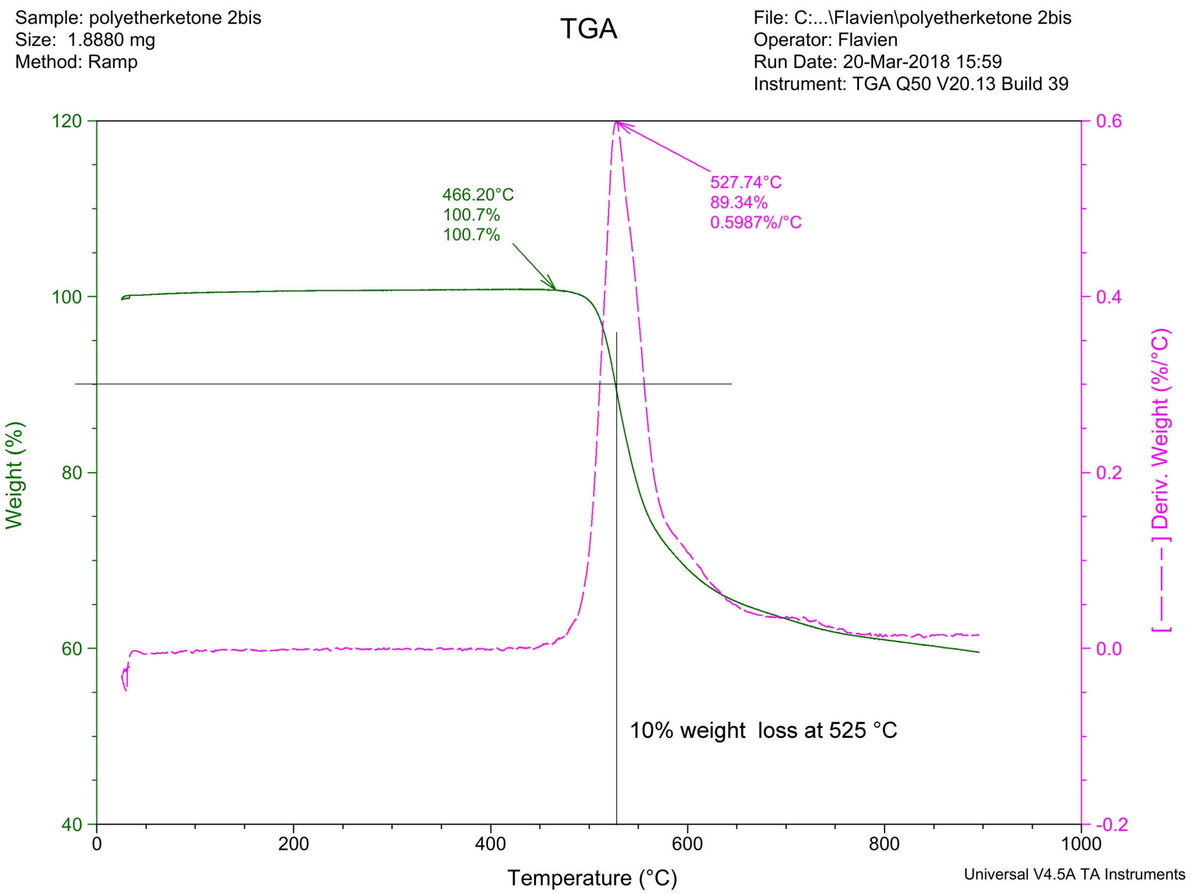
Energy-minimised conformation of the RS-diastereomer. Final energy = 64.5 kcal mol^{-1}.



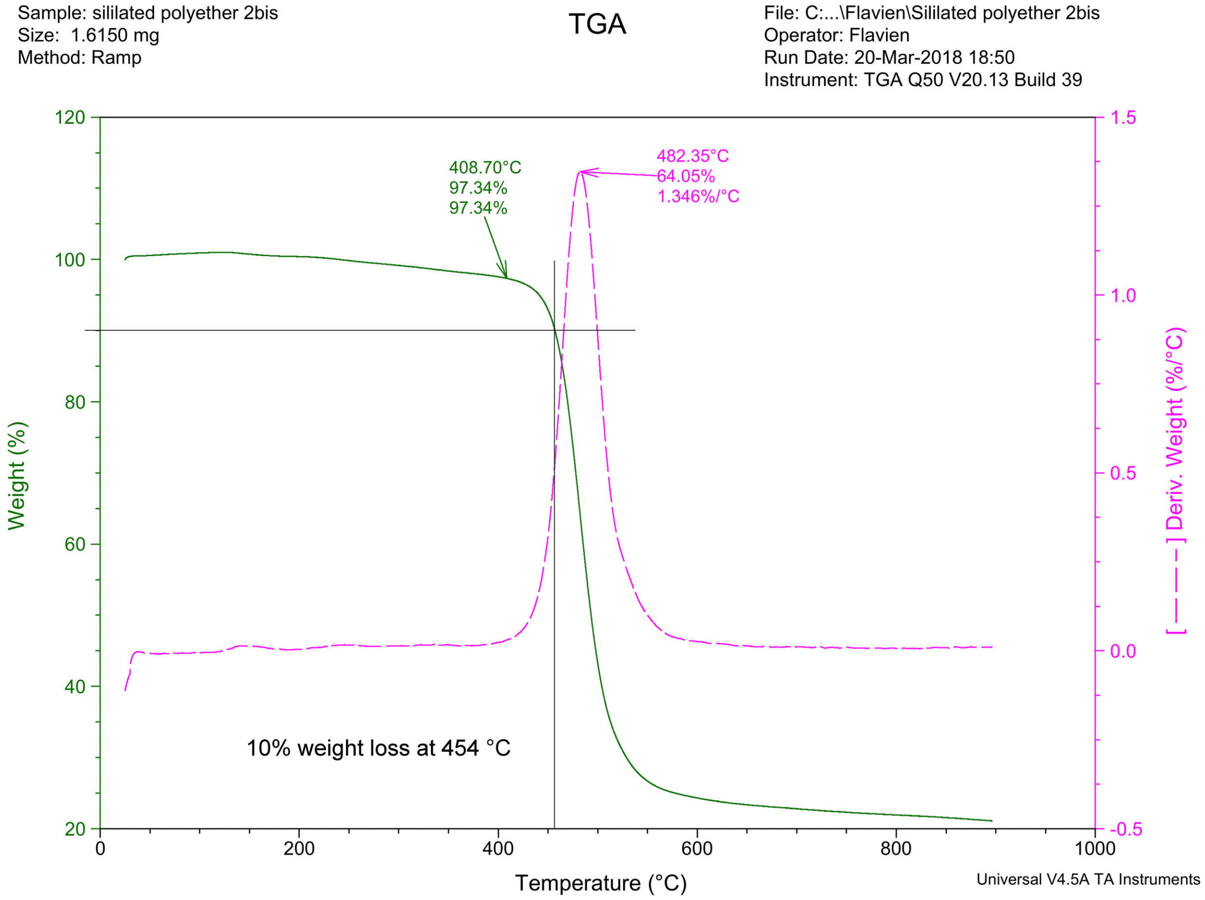
Energy-minimised conformation of the SS-diastereomer. Final energy = 70.4 kcal mol^{-1}.

9. Thermogravimetric analyses of polymers 2, 11 and 15

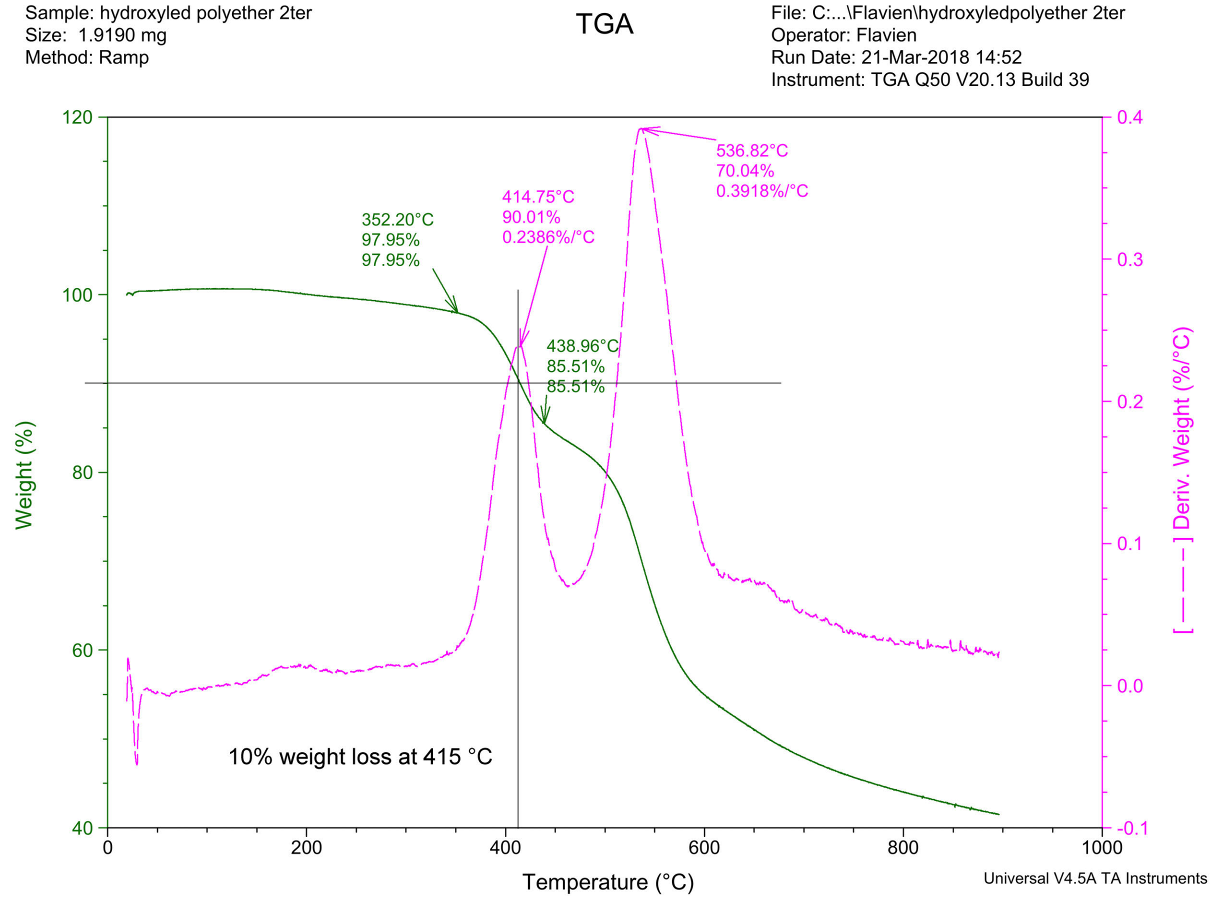
(a) Poly(ether ketone) **2**



(b) Poly(trimethylsilyether) **11**



(c) Poly(trifluoromethylcarbinol) **15**



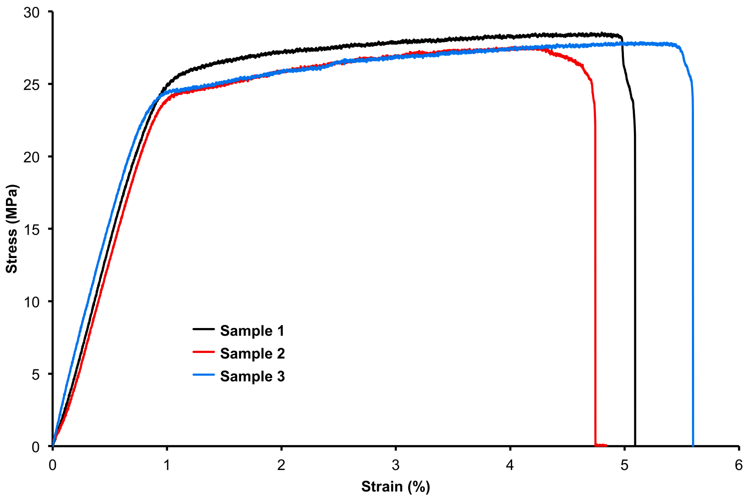
Sample: hydroxyled polyether 2ter
Size: 1.9190 mg
Method: Ramp

TGA

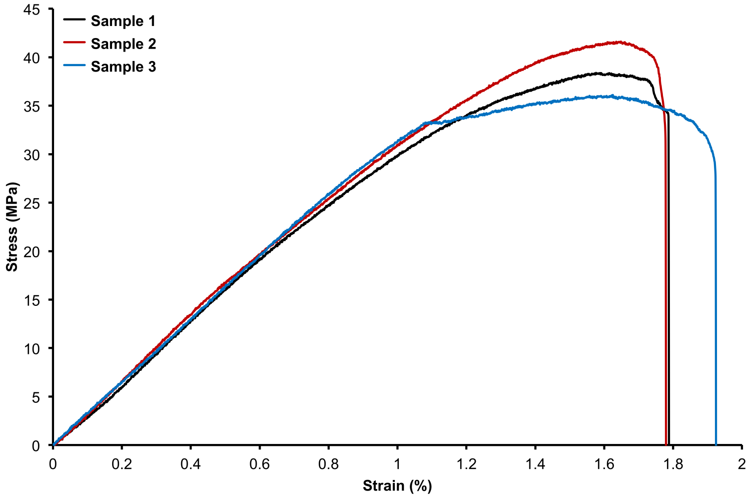
File: C:...\Flavien\hydroxyledpolyether 2ter
Operator: Flavien
Run Date: 21-Mar-2018 14:52
Instrument: TGA Q50 V20.13 Build 39

10. Tensile properties of polyols 15 and 16

A 50 μm film of polymer **15** was cast by evaporation of a 10% w/v solution in dry *N,N*-dimethylacetamide, and from this film were cut three test strips with dimensions 4.0 x 0.5 cm. Specimens were extended at 25 °C and a strain rate of 1 mm min^{-1} to obtain the tensile modulus, ultimate tensile strength, elongation at break and modulus of toughness (area under the stress-strain curve). This procedure was repeated for a 40 mm film of polymer **16**. Stress-strain curves and mean values of the derived parameters are given below.



Polymer **15**



Polymer **16**

Tensile Property	Polymer **15**	Polymer **16**
Tensile Modulus (GPa)	2.83 (0.41)	3.29 (0.25)
Modulus of Toughness (MJ m^{-3})	1.25 (0.12)	0.45 (0.02)
Elongation at Break (%)	5.19 (0.36)	1.83 (0.08)
Ultimate Tensile Strength (MPa)	28.00 (0.49)	38.70 (2.77)