Supporting Information

Vinylbenzenesulfonyl fluoride (VBSF) based binary, ternary copolymer and selective post-polymerization modification via SuFEx click chemistry

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Materials

Styrene (St) and 1-(chloromethyl)-4-vinylbenzene ($StCH_2Cl$) were purchased from TCI chemicals and purified by passing it through a plug of aluminum oxide (activated, basic) to remove the inhibitor, deoxygenized by freeze-pump-thaw cycle three times, backfilled with argon and sealed up. Methyl methacrylate (MMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) were purchased from TCI chemicals and distilled over CaH_2 under an argon atmosphere and deoxygenized by freeze-pump-thaw cycle three times and stored in Schlenk bar under argon atmosphere. Perfluorophenyl methacrylate (PFPMA), perfluorophenyl acrylate (PFPA), and oxygen-doped anthanthrene (ODA) were synthesized according to literature procedures[1, 2]. Diethyl 2-bromo-2-methylmalonate (DBMM) was purchased from Alfa Aesar Chemical and distilled over CaH_2 under an argon atmosphere and deoxygenized by freeze-pump-thaw cycle three times and stored in a brown bottle inside a freezer below 5°C. N, N-dimethylacetamide (DMA; 99.8%, SuperDry, with molecular sieves, J&K), N, N-dimethylformamide (DMF; 99.9%, SuperDry, with molecular sieves, J&K), Acetonitrile (CH_3CN; 99.9%, SuperDry, J&K) were used as received.

Sodium 4-vinylbenzenesulfonate (NaVBS; 90%, Energy chemical), Thionyl chloride ($SOCl_2$; 99%, Energy chemical), Potassium Hydrogenfluoride (KHF_2; 99%, Energy chemical), Phenol (99%, Energy chemical), 4-Cyanophenol (99%, Energy chemical), 4-tert-Butylphenol (98%, Energy chemical), 4-Methoxyphenol (98%, Energy chemical), 4-Fluorophenol (99%, Energy chemical), 2-Methylphenol (98%, Energy chemical), tert-Butyldimethylsilyl chloride (TBS-Cl; 99%, Energy chemical), 4-Dimethylaminopyridine (DMAP; 98%, Energy chemical), Imidazole (99%, Energy chemical), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 98%, Energy chemical), Butylamine (99%, Energy chemical), Pentafluorophenol(98%, Energy chemical), Triethylamine (TEA; 99.5%, Energy chemical), methacryloyl chloride (97%, Energy chemical), and acryloyl chloride (98%, Energy chemical) were used as received. All the tert-butyldimethylsilyl ethers were prepared according to the literature procedure[3]. All other chemicals and solvents were purchased from Energy chemical, J&K, Adamas or TCI chemicals, and were used as received unless otherwise specified.

Characterization

^1H NMR, ^{13}C NMR and ^{19}F NMR were used to demonstrate the structure of synthesized substances, conversions for polymerization and nuclear magnetic molecular weight of polymers, and tracing reaction, which were recorded on a Bruker AVIII 400 MHz or Bruker AVANCE NEO 500 (500 MHz) nuclear magnetic resonance instrument, and used $CDCl_3$ or DMSO-*d*6 as deuterium solvent for testing samples and tetramethylsilane as the internal standard. The number-average molecular weight (M_n) and molecular weight distributions ($Đ$) of the synthesized polymers were characterized by a Waters 1515 series gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive index detector, using a Styragel HR4 5 μm 7.8×300 mm (DMF) Column and a Styragel HR4 5 μm 7.8×300 mm (DMF) Column with measurable molecular weights ranging from 10^2 to 10^6 g/mol. DMF was used as eluent at a flow rate of 1.0 mL/min at 35 °C. GPC samples were injected manually and Shodex Polystyrene standards were used for calibration. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray ionization in Positive/Negative ion detection (ESI^+ / ESI^-) mode, and the significant fragments are reported in the following fashion: m/z (relative intensity).

Photoreaction Setup

As shown above (Figure S1), all polymerization reactionswere conducted in a 6 W blue photo-reactor placed 1 cm from light, which was purchased from http://www.geaochem.com/ (Model: H106062, GEAO CHEMICAL). The reactor has a fan for cooling and its light intensity to be ~30 mW/cm^2.

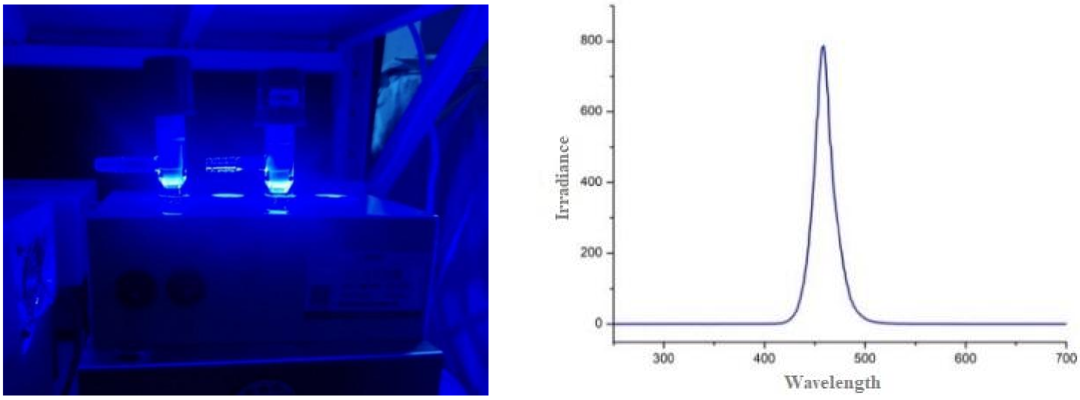
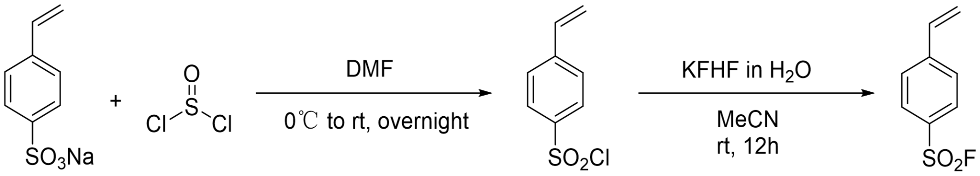


Figure S1. The reaction setup of photocatalytic ATRP polymerization with 6 W blue LEDs (λmax = 460 nm).

Synthesis of 4-vinylbenzenesulfonyl fluoride (VBSF)



Under an atmosphere of argon, Sodium 4-vinylbenzenesulfonate (18 g, 87.5mmol, 1 eq.) was poured into 100 mL dry N, N-dimethylformamide (DMF) at 0°C, followed by 40 mL $SOCl_2$ dropwise added to the solution. After the above system was stirred at 0°C for 2 h, it was allowed to warm to room temperature and stirred overnight. Finally, the system is poured onto crushed ice and extracted with ether. The separated organic phase was washed with saturated aqueous NaCl and dried with Na_2SO_4, and evaporated in vacuo to give 4-vinylbenzenesulfonyl chloride (VBSCl) as yellow liquid (15.59 g, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.99 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 6.78 (dd, J = 20.0, 12.0 Hz, 1H), 5.97 (d, J = 20.0 Hz, 1H), 5.54 (d, J = 12.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.56, 143.01, 134.89, 127.53, 127.26, 119.52.

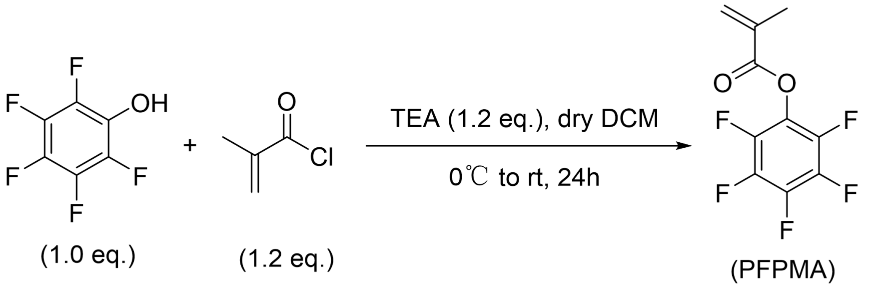
HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_8H_8ClO_2S^+$: 202.9928; found: 202.9927.

Sodium 4-vinylbenzenesulfonate (4.88 g, 24 mmol, 1 eq.) was poured into 48 mL CH_3CN, and aqueous solution of potassium hydrogenfluoride (KHF_2) (3.75 g KHF_2, $[KHF_2]$ = 5 mol/L) was dropwise added to the solution under agitation. The reaction mixture was stirred vigorously at room temperature for 12h. The resulting crude mixture was extracted with ethyl acetate (EA), then the separated organic phase was washed with saturated aqueous NaCl and dried with Na_2SO_4.

After evaporation in vacuo, the crude product was purified by silica gel column chromatography with petroleum ether and ethyl acetate (30:1, v/v) to give 4-vinylbenzenesulfonyl fluoride (VBSF) as colorless liquid (3.49 g, 78% yield).

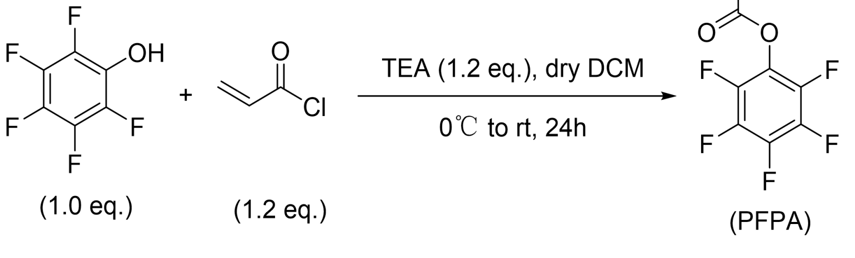
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 6.78 (dd, *J* = 20.0, 12.0 Hz, 1H), 5.97 (d, *J* = 20.0 Hz, 1H), 5.54 (d, *J* = 8.0 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.89, 134.91, 131.68, 131.44, 128.92, 127.25, 119.46.
^{19}F NMR (376 MHz, Chloroform-*d*): δ 66.30.
HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_8H_8FO_2S^+$: 187.0224; found: 187.0224.

Synthesis of perfluorophenyl methacrylate (PFPMA)



Pentafluorophenol (20.0 g, 109 mmol, 1 eq.) was poured into 100 mL dry dichloromethane at 0°C, and triethylamine (TEA) (18.2 mL, 131 mmol, 1.2 eq.) was slowly added, followed by methacryloyl chloride (12.7 mL, 131 mmol, 1.2 eq.) dropwise added to the solution. After the above system was stirred at 0°C for 1 h, it was allowed to warm to room temperature and stirred 24 h. Filtered to move the precipitate of triethyl amine hydrochloride salt and washed thoroughly with dichloromethane. The filtrate was extracted with aqueous solution of HCl, aqueous solution of Na_2CO_3, and deionized water, and the separated organic phase was dried with Na_2SO_4. After evaporation in vacuo, the crude product was purified by silica gel column chromatography with petroleum ether to give perfluorophenyl methacrylate as colorless liquid (22.5703 g, 82% yield).
^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.45 (s, 1H), 5.91 (s, 1H), 2.09 (s, 3H).
^{13}C NMR (125 MHz, Chloroform-*d*): δ 163.21, 142.56, 142.47, 140.74, 140.65, 140.54, 140.46, 139.23, 139.11, 139.00, 138.74, 138.63, 138.52, 137.22, 137.10, 136.99, 133.96, 129.88, 125.70, 125.58, 125.47, 18.17.
^{19}F NMR (470 MHz, Chloroform-*d*): δ -152.85, -152.90, -158.32, -158.37, -158.41, -162.60, -162.65, -162.69.

Synthesis of perfluorophenyl acrylate (PFPA)



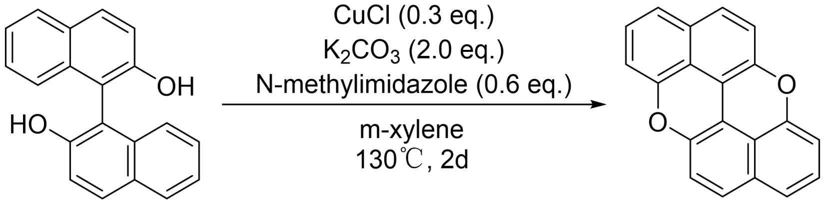
Pentafluorophenol (20.0 g, 109 mmol, 1 eq.) was poured into 100 mL dry dichloromethane at 0°C, and triethylamine (TEA) (18.2 mL, 131 mmol, 1.2 eq.) was slowly added, followed by acryloyl chloride (10.6 mL, 131 mmol, 1.2 eq.) dropwise added to the solution. After the above system was stirred at 0°C for 1 h, it was allowed to warm to room temperature and stirred 24 h. Filtered to move the precipitate of triethyl amine hydrochloride salt and washed thoroughly with dichloromethane. The filtrate was extracted with aqueous solution of HCl, aqueous solution of Na_2CO_3, and deionized water, and the separated organic phase was dried with Na_2SO_4. After evaporation in vacuo, the crude product was purified by silica gel column chromatography with petroleum ether to give perfluorophenyl acrylate as colorless liquid (23.3675 g, 90% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.72 (d, J = 17.2 Hz, 1H), 6.37 (dd, J = 17.2, 10.4 Hz, 1H), 6.18 (d, J = 10.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.82, 142.72, 142.68, 142.60, 142.55, 141.08, 140.95, 140.22, 140.17, 140.13, 140.09, 140.05, 139.49, 139.44, 139.33, 139.27, 139.21, 139.13, 138.57, 138.43, 138.30, 136.99, 136.91, 136.85, 136.80, 136.72, 136.66, 135.62, 125.50.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -152.58, -152.59, -152.62, -152.63, -157.96, -157.99, -158.06, -162.35, -162.39, -162.40, -162.43.

Synthesis of oxygen-doped anthanthrene (ODA)

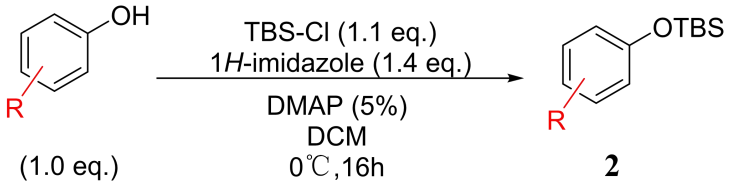


1,1'-bi-2-naphthol (143 mg, 0.5 mmol), K_2CO_3 (138 mg, 1 mmol) and CuCl(I) (15.0 mg, 0.15 mmol) were poured into a round-bottomed flask, followed by solvent (m-xylene, 3 mL) and N-methylimidazole (24 µL, 0.30 mmol), making the reaction system expose to air. The reaction mixture was stirred vigorously at 130 °C for 48h. After evaporation in vacuo, the crude product was filtered by silica gel column chromatography with $CHCl_3$ and recrystallized from toluene to afford oxygen-doped anthanthrene (organic photocatalyst) as yellow solid (98 mg, 70% yield).

^{1}H NMR (500 MHz, Dichloromethane-*d*2): δ 7.33 (d, J = 9.0 Hz, 2H), 7.14-7.10 (m, 4H), 6.93 (d, J = 9.0 Hz, 2H), 6.65 (dd, J = 5.5, 3.0 Hz, 2H).

^{13}C NMR (125 MHz, Dichloromethane-*d*2): δ 152.68, 144.30, 131.39, 127.22, 126.43, 121.53, 120.15, 117.35, 111.44, 108.66, 53.94, 53.73, 53.51, 53.29, 53.08.

General procedure for synthesis of tert-butyldimethylsilyl (TBS) ethers



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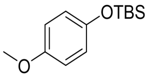
To a three-neck round-bottom flask (250 mL) equipped with a magnetic stirrer, phenol (4.0 g, 42.5 mmol), tert-butylchlorodimethylsilane (TBS-Cl) (7.1 g, 46.8 mmol), 1H-imidazole (4.05 g, 59.5 mmol), 4-Dimethylaminopyridine (DMAP) (0.26 g, 2.12 mmol) and CH_2Cl_2 (35 mL), were added respectively. The reaction mixture was stirred vigorously at 0 °C for 16 h. The reaction solvent (DCM) was removed via rotary evaporation and the resulting crude mixture was diluted and extracted with EA. The separated organic phase was washed with saturated aqueous NaCl and dried with Na_2SO_4. After evaporation in vacuo, the crude product was purified by silica gel column chromatography with petroleum ether and ethyl acetate (10: 1, v/v) to give white crystalline solid as the desired product **f** (3.46 g, 78% yield).

tert-butyl(4-methoxyphenoxy)dimethylsilane (a)

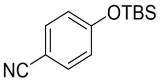


^{1}H NMR (500 MHz, DMSO-*d6*): δ6.79 (d, J=9.2, 2H), 6.74 (d, J=9.2, 2H), 3.68 (s, 3H), 0.93 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (125 MHz, DMSO-*d6*): δ153.78, 148.58, 120.30, 114.45, 55.11, 25.49, 17.80, -4.74.

HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_{13}H_{23}O2Si^+$: 239.1462; found: 239.1459.

4-((tert-butyldimethylsilyl)oxy)benzonitrile (b)

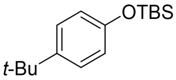


^{1}H NMR (400 MHz, Chloroform-d): δ7.53 (d, J=8.7, 2H), 6.88 (d, J=8.7, 2H), 0.98 (s, 9H), 0.23 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d): δ159.83, 134.14, 120.99, 119.34, 104.78, 25.65, 18.35, -4.27.

HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_{13}H_{20}NOSi^+$: 234.1309; found: 234.1306.

tert-butyl(4-(tert-butyl)phenoxy)dimethylsilane (c)

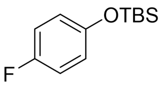


^{1}H NMR (400 MHz, DMSO-*d6*): δ7.25 (d, J=8.5, 2H), 6.75 (d, J=8.5, 2H), 1.24 (s, 9H), 0.94 (s, 9H), 0.16 (s, 6H).

^{13}C NMR (100 MHz, DMSO-*d6*): δ152.65, 143.43, 126.15, 119.12, 33.80, 31.33, 25.58, 17.91, -4.49.

HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_{16}H_{29}OSi^+$: 265.1982; found: 265.1982.

tert-butyl(4-fluorophenoxy)dimethylsilane (d)

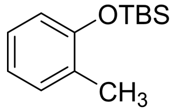


^{1}H NMR (500 MHz, DMSO-*d6*): δ7.04 (t, J=8.8, 2H), 6.82 (dd, J=9.0, 4.5, 2H), 0.92 (s, 9H), 0.15 (s, 6H).

^{13}C NMR (125 MHz, DMSO-*d6*): δ157.88, 156.00, 151.29, 151.27, 120.96, 120.89, 115.94, 115.76, 25.46, 17.84, -4.76.

^{19}F NMR (470 MHz, DMSO-*d6*): δ-122.81.

tert-butyldimethyl(o-tolyloxy)silane (e)

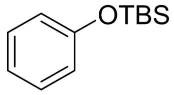


^{1}H NMR (500 MHz, DMSO-*d6*): δ7.13 (d, J=7.4, 1H), 7.06 (t, J=7.7, 1H), 6.83 (t, J=7.4, 1H), 6.77 (d, J=8.0, 1H), 2.14 (s, 3H), 0.98 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (125 MHz, DMSO-*d6*): δ153.24, 130.84, 127.97, 126.80, 121.07, 118.30, 25.57, 17.88, 16.41, -4.42.

HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_{13}H_{23}OSi^+$:223.1513; found: 223.1507.

tert-butyldimethyl(phenoxy)silane (f)

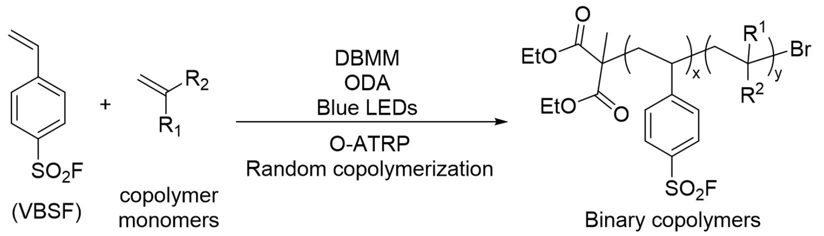


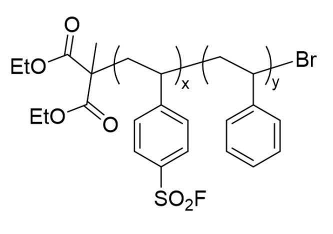
^{1}H NMR (400 MHz, DMSO-*d6*): δ7.25 (t, J=8.0, 2H), 6.95 (t, J=7.3, 1H), 6.83 (d, J=7.5, 2H), 0.95 (s, 9H), 0.17 (s, 6H).

^{13}C NMR (100 MHz, DMSO-*d6*): δ155.03, 129.49, 121.33, 119.76, 25.46, 17.85, -4.61.

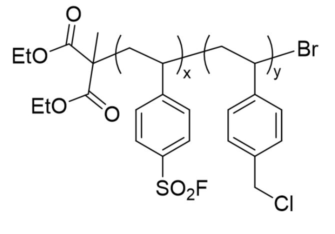
HRMS (ESI$^+$): m/z $[M + H]^+$ Calc. for $C_{12}H_{21}OSi^+$: 209.1356; found: 209.1355.

General method for synthesis of binary random copolymers

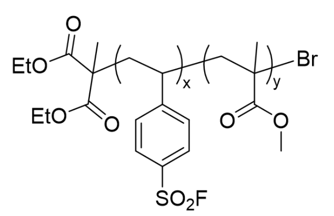




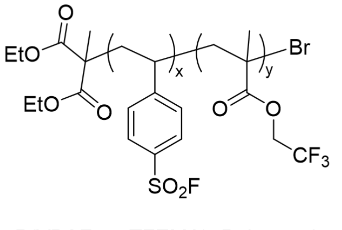
P(VBSF-co-St), Polymer 1



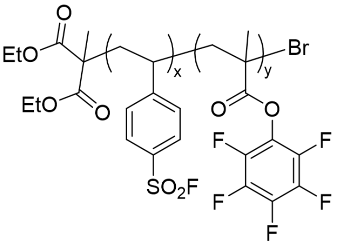
P(VBSF-co-StCH$_2$Cl), Polymer 2



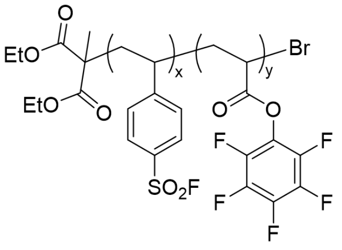
P(VBSF-co-MMA), Polymer 3



P(VBSF-co-TFEMA), Polymer 4



P(VBSF-co-PFPMA), Polymer 5



P(VBSF-co-PFPA), Polymer 6

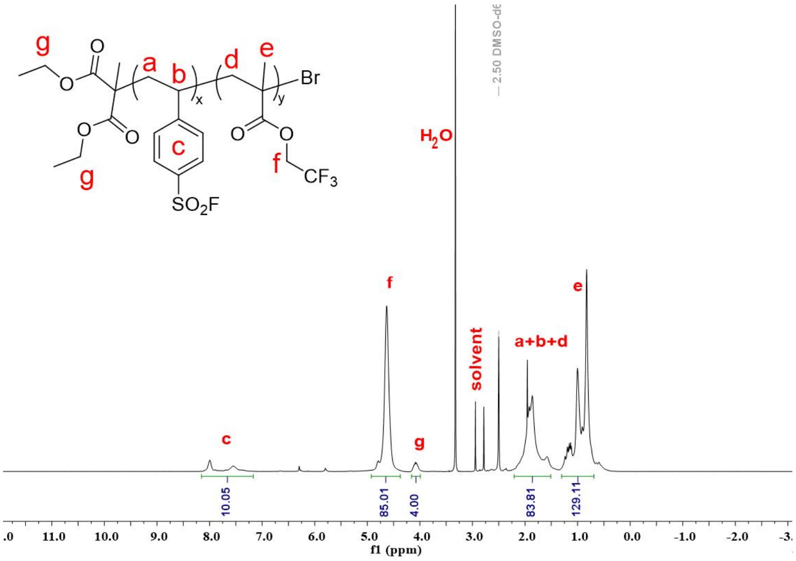
The molar ratio of [VBSF + comonomers]$_0$: [DBMM]$_0$: [ODA]$_0$ = 50: 1: 0.005 was showed as follows, wherein the molar ratio of [VBSF]$_0$: [St]$_0$= 5: 95. The polymerization was conducted with VBSF (50 uL, 0.34 mmol) and St (782 uL, 6.8 mmol) as the comonomers, DBMM (27 μL, 0.14 mmol, 1.0 eq.) as the ATRP initiator, ODA (0.2 mg, 7.0×10^{-4} mmol, 0.005eq.) as catalyst and DMA (1.4 mL) as solvent in a Schlenk tube with a PTFE stirring bar. The mixture was deoxygenized by freeze-pump-thaw cycle three times, backfilled argon and sealed up subsequently. And then the polymerization was occurred under blue LED irradiation at room temperature. After stopping the reaction, the tube was opened under argon and 30.0 μL of mixture were syringed out and quenched into DMSO-*d*6 or Chloroform-*d* to determine the respective conversion of two comonomers by ^{1}H NMR. The reaction mixture dripped into 100 mL methanol and stirred for 2 hours. The precipitates were then collected by suction filtration with a Buchner funnel and dried in vacuum at 50 °C to give binary random copolymer poly(VBSF-*co*-St). The composition of random binary copolymer was determined by ^{1}H NMR, and the M_n and M_w/M_n were analysed by GPC. With other different monomers copolymerization, in addition to the ratio of VBSF and another monomer is different, the method and ingredient ratio are the same, and the detailed values are in Table S1. And beyond that, study on different component proportions of copolymers, the synthesis method is the same as previous step, and only feeding ratio of two comonomers is changed.

Table S1. Binary random copolymerization

Entry	Comonomers[a]	x_0/y_0[b]	Time (h)	Conv.[c] (VBSF)	Conv.[c] (comonomers)	x/y[d] (copolymers)	$M_{n,theo}$[g] (kg/mol)	$M_{n,NMR}$[h] (kg/mol)	$M_{n,GPC}$[i] (kg/mol)	Đ[i]
1	St	05/95	18	/	/	/	5.7	/	12.0	1.44
2	StCH$_2$Cl	60/40	16	>99%	84%	67/33[e]	8.9	8.6	23.0	1.51
3	MMA	20/80	18	>99%	>99%	24/76[e]	6.1	8.7	24.1	1.28
4	TFEMA	05/95	24	>99%	>99%	6/94[e]	8.7	8.0	22.6	1.33
5	PFPMA	10/90	29	>99%	>99%	10/90[f]	12.5	12.0	15.2	1.23
6	PFPA	05/95	29	>99%	>99%	5/95[f]	12.0	16.3	22.3	1.39

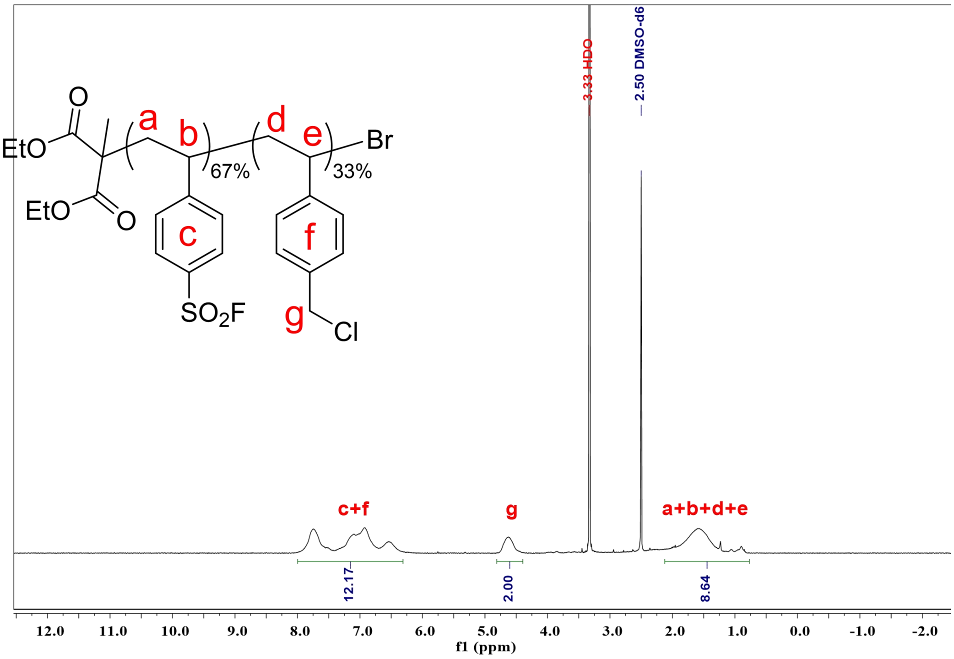
[a] Comonomers include styrene (St), 1-(chloromethyl)-4-vinylbenzene (StCH$_2$Cl), methyl methacrylate (MMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), perfluorophenyl methacrylate (PFPMA) and perfluorophenyl acrylate (PFPA). [b] Feeding ratio of VBSF to comonomers (x_0/y_0). [c] Monomer conversions are determined by ^{1}H NMR of reaction system. [d] Component proportions of VBSF to comonomer in copolymers were determined by ^{1}H NMR or ^{19}F NMR. The peaks of VBSF and St overlap, making it impossible to distinguish, so the copolymer composition cannot be calculated (Entry 1). [e] Determined by ^{1}H NMR. [f] Determined by ^{19}F NMR. [g] Calculation method: $M_{n,theo}$ = (50*x_0% × MW of VBSF × conv. %) + (50*y_0% × MW of comonomers × conv. %) + MW of DBMM. [h] Measured by ^{1}H NMR. [i] Measured by GPC using polystyrene standards in DMF.

Example of $M_{n,NMR}$ calculation method, poly(VBSF-*co*-TFEMA): As shown in the figure below, the integration of the initiator characteristic peak (***g***) was set to 4.00. The integration of the benzene ring protons (***c***) was 10.05, corresponding to a DPn of 3 for VBSF (10.05/4). Meanwhile, the integration of peak ***f*** was 85.01, giving a DPn of 43 for TFEMA (85.01/2). Thus, the $M_{n,NMR}$ was calculated as: DPn$_{(VBSF)}$ × MW of VBSF + DPn$_{(TFEMA)}$ × MW of TFEMA + MW of initiator = 3 × 186.2 + 43 × 168.12 + 253.09 = 8.0 kg/mol.



Calculation method for component ratios of copolymers

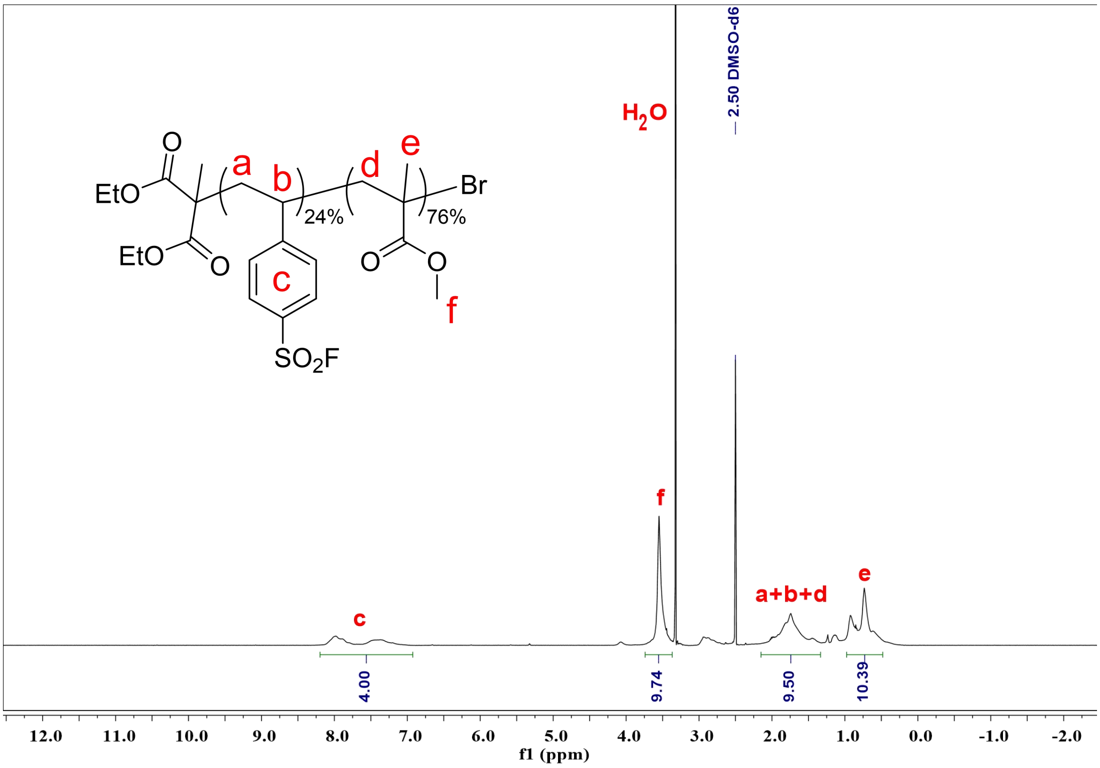
(1). ^{1}H NMR of poly(VBSF-*co*-StCH$_2$Cl), Polymer 2



The number of StCH$_2$Cl in poly(VBSF-*co*-StCH$_2$Cl) is set as N_{StCH2Cl}=1, then the characteristic peak (-CH$_2$Cl) of StCH$_2$Cl is integrated by 2 (I_{g}=2). Based on this, the total integral of benzene ring region is 12.17 ($I_{\mathrm{c+f}}$=12.17) and the integral of benzene ring in StCH$_2$Cl should be 4 (I_{f}=4), then the integral of VBSF on the benzene ring is I_{c}=8.17 (I_{c}=$I_{\mathrm{c+f}}$ - I_{f}), so the number of VBSF is N_{VBSF}=I_{c}/4=2.0425. The proportion of VBSF in poly(VBSF-*co*-StCH$_2$Cl) is

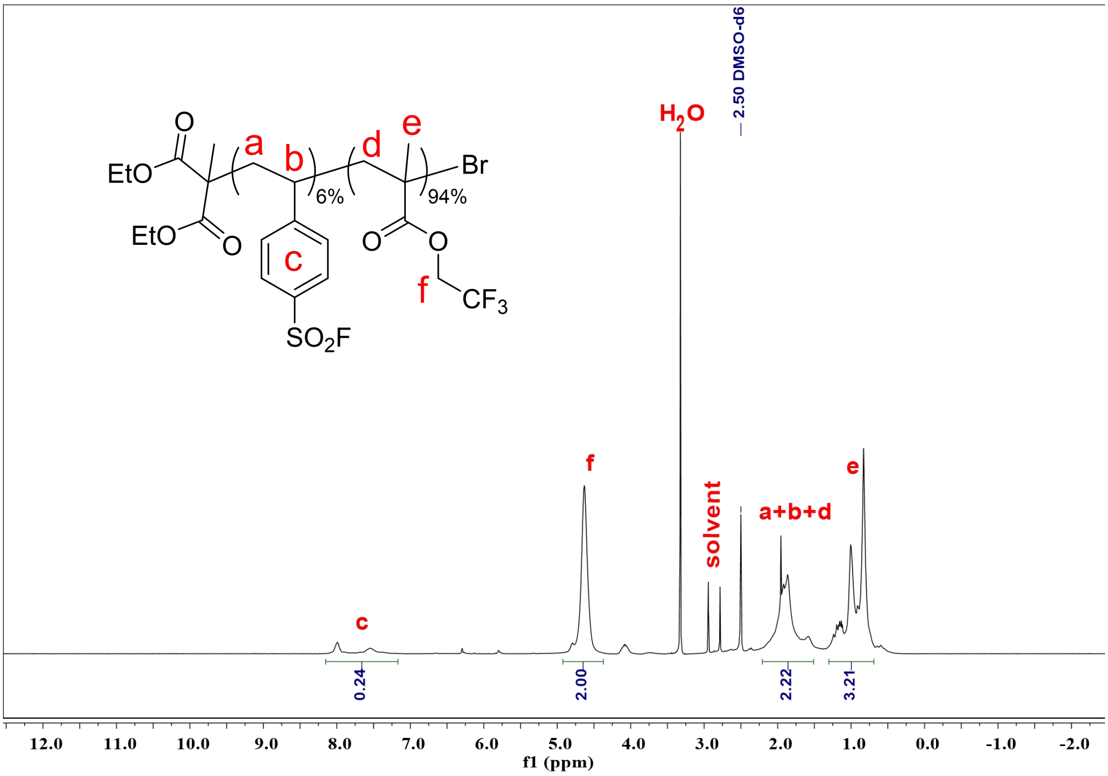
$N_{\mathrm{VBSF}}/(N_{\mathrm{StCH2Cl}}+N_{\mathrm{VBSF}})$*100%=2.0425/3.0425*100%=67%, and the proportion of StCH$_2$Cl in poly(VBSF-*co*-StCH$_2$Cl) is $N_{\mathrm{StCH2Cl}}/(N_{\mathrm{StCH2Cl}}+N_{\mathrm{VBSF}})$*100%=1/3.0425*100%=33%, x/y=67/33.

(2). ^{1}H NMR of poly(VBSF-*co*-MMA), Polymer 3



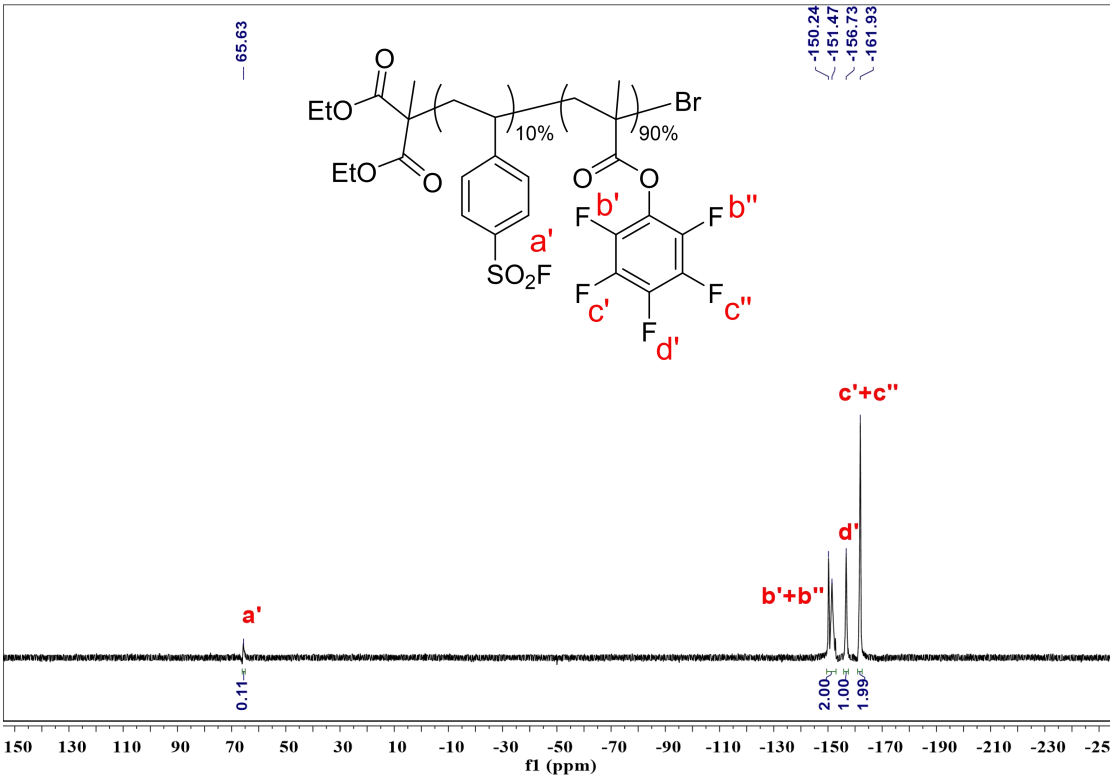
The number of MMA in poly(VBSF-*co*-MMA) is set as N_{VBSF}=1, the integral of VBSF on the benzene ring is I_c=4.00. Based on this, the characteristic peak (-OCH$_3$) of MMA is integrated by 9.74 (I_f =9.74), so the number of MMA is $N_{\mathrm{MMA}}=I_f/3$=3.247. The proportion of VBSF in poly(VBSF-*co*-MMA) is $N_{\mathrm{VBSF}}/(N_{\mathrm{MMA}}+N_{\mathrm{VBSF}})$*100%=1/4.247*100%=24%, and the proportion of MMA in poly(VBSF-*co*-MMA) is $N_{\mathrm{MMA}}/(N_{\mathrm{MMA}}+N_{\mathrm{VBSF}})$*100%=3.247/4.247*100%=76%, x/y=24/76.

(3). ^{1}H NMR of poly(VBSF-*co*-TFEMA), Polymer 4



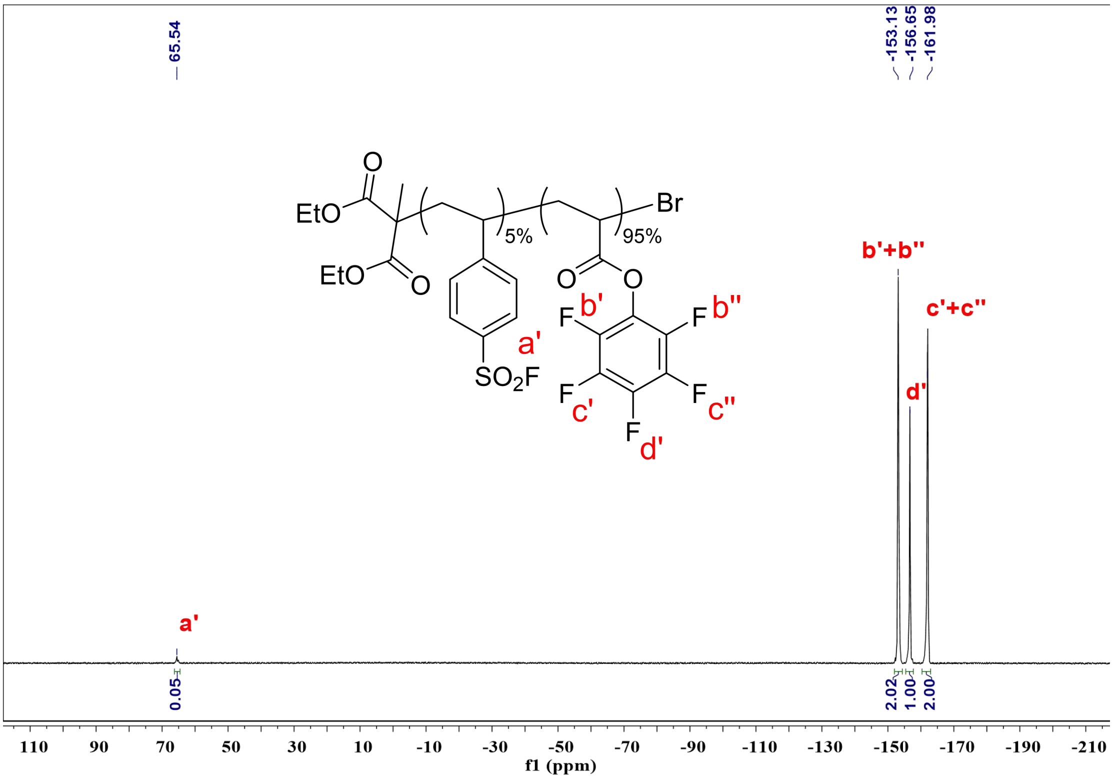
The number of TFEMA in poly(VBSF-*co*-TFEMA) is set as N_{TFEMA}=1, then the characteristic peak (-OCH$_2$CF$_3$) of MMA is integrated by 2 (I_f=2). Based on this, the integral of VBSF on the benzene ring is I_c=0.24, so the number of VBSF is $N_{\mathrm{VBSF}}=I_c/4$=0.06. The proportion of VBSF in poly(VBSF-*co*-TFEMA) is $N_{\mathrm{VBSF}}/(N_{\mathrm{TFEMA}}+N_{\mathrm{VBSF}})$*100%=0.06/1.06*100%=6%, and the proportion of TFEMA in poly(VBSF-*co*-TFEMA) is $N_{\mathrm{TFEMA}}/(N_{\mathrm{TFEMA}}+N_{\mathrm{VBSF}})$*100%=1/1.06*100%=94%, x/y=6/94.

(4). ^{19}F NMR of poly(VBSF-*co*-PFPMA), Polymer 5



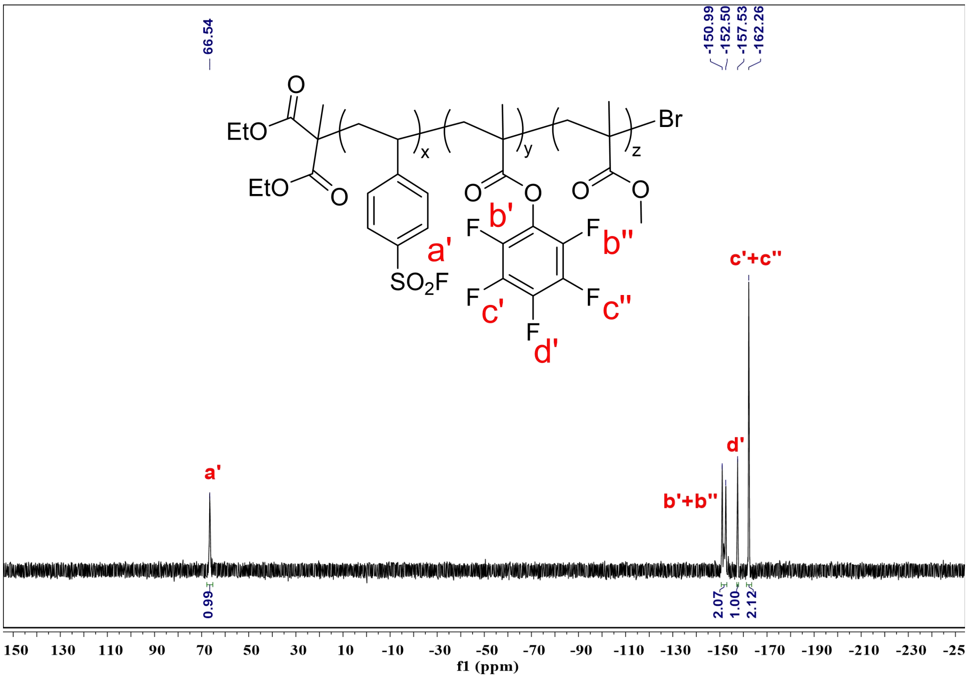
The number of PFPMA in poly(VBSF-*co*-PFPMA) is set as N_{PFPMA}=1, then the peak d' of PFPMA is integrated by 1 ($I_{\text{d'}}$=1). Based on this, the integral of peak a' in VBSF is $I_{\text{a'}}$=0.11, so the number of VBSF is N_{VBSF}=$I_{\text{a'}}$/1=0.11. The proportion of VBSF in poly(VBSF-*co*-PFPMA) is N_{VBSF}/(N_{PFPMA}+N_{VBSF})*100%=0.11/1.11*100%=10%, and the proportion of PFPMA in poly(VBSF-*co*-PFPMA) is N_{PFPMA}/(N_{PFPMA}+N_{VBSF})*100%=1/1.11*100%=90%, x/y=10/90.

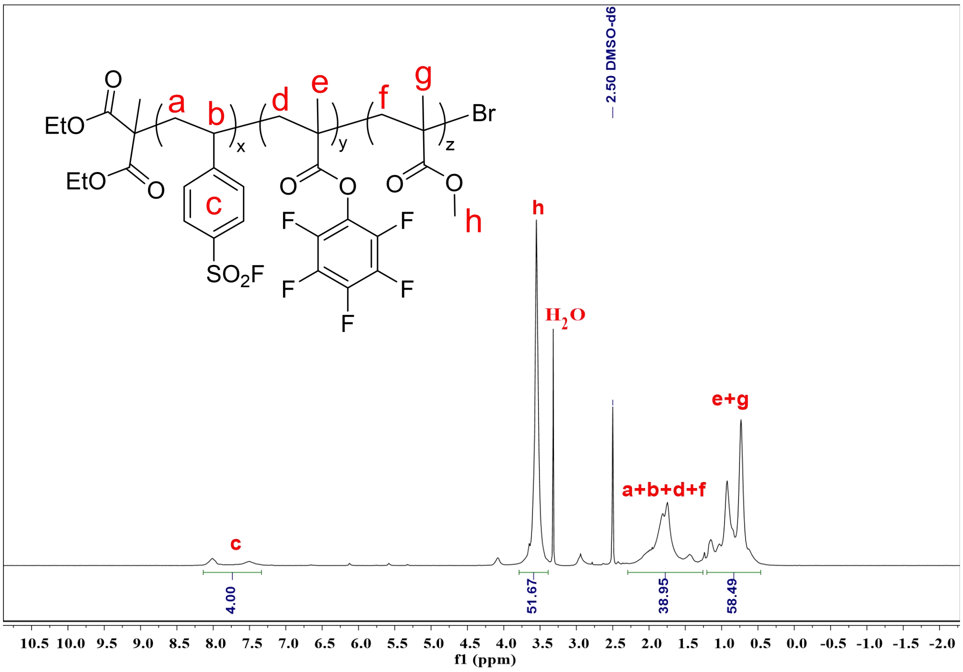
(5). ^{19}F NMR of poly(VBSF-*co*-PFPA), Polymer 6



The number of PFPA in poly(VBSF-*co*-PFPA) is set as $N_{\mathrm{PFPA}}=1$, then the peak d' of PFPA is integrated by 1 ($I_{\mathrm{d'}}=1$). Based on this, the integral of peak a' in VBSF is $I_{\mathrm{a'}}=0.05$, so the number of VBSF is $N_{\mathrm{VBSF}}=I_{\mathrm{a'}}/1=0.05$. The proportion of VBSF in poly(VBSF-*co*-PFPA) is $N_{\mathrm{VBSF}}/(N_{\mathrm{PFPA}}+N_{\mathrm{VBSF}})*100\%=0.05/1.05*100\%=5\%$, and the proportion of PFPA in poly(VBSF-*co*-PFPA) is $N_{\mathrm{PFPA}}/(N_{\mathrm{PFPA}}+N_{\mathrm{VBSF}})*100\%=1/1.05*100\%=95\%$, x/y=5/95.

(6). ^{19}F and ^{1}H NMR of poly(VBSF-*co*-PFPMA-*co*-MMA), Polymer 13

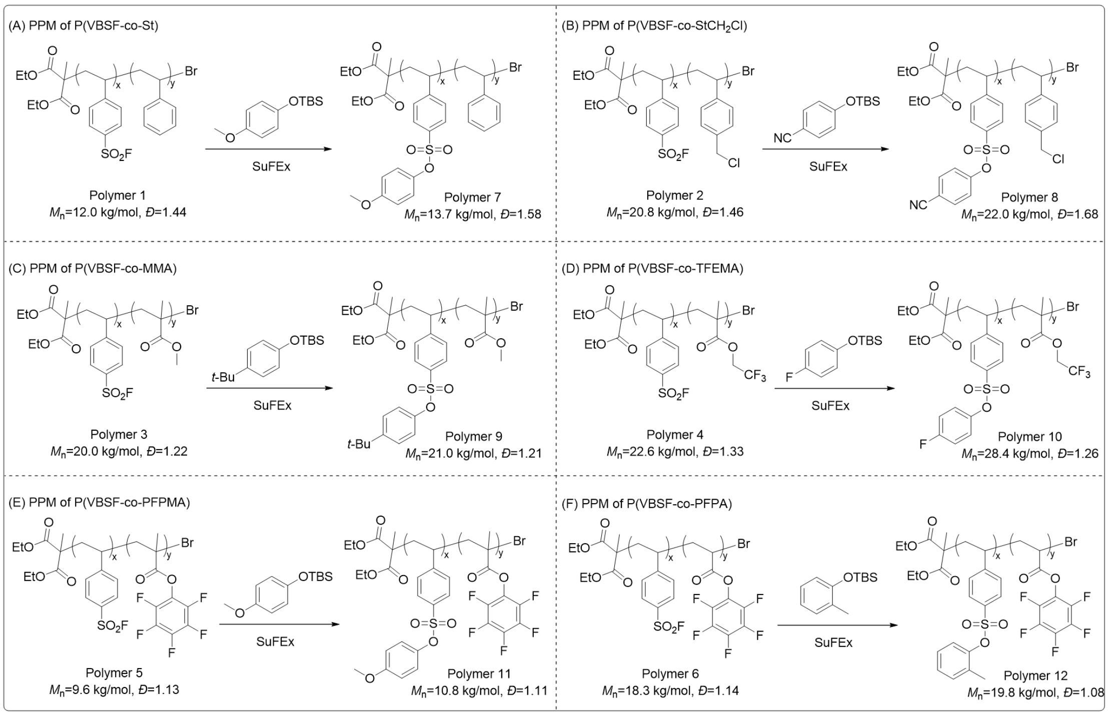




1). ^{19}F NMR: The number of PFPMA in poly(VBSF-*co*-PFPMA-*co*-MMA) is set as $N_{\mathrm{PFPMA}}=1$, then the peak d' of PFPMA is integrated by 1 ($I_{\mathrm{d'}}=1$). Based on this, the integral of peak a' in VBSF is $I_{\mathrm{a'}}=0.99$, so the number of VBSF is $N_{\mathrm{VBSF}}=I_{\mathrm{a'}}/1=0.99$. So, x/y=$N_{\mathrm{VBSF}}/N_{\mathrm{PFPMA}}=0.99/1=1/1$ (integer).

2). ^{1}H NMR: The number of VBSF in poly(VBSF-*co*-PFPMA-*co*-MMA) is set as $N_{\mathrm{VBSF}}=1$, the integral of VBSF on the benzene ring is $I_{\mathrm{c}}=4.00$. Based on this, the characteristic peak (-OCH$_3$) of MMA is integrated by 51.67 ($I_{\mathrm{f}}=51.67$), so the number of MMA is $N_{\mathrm{MMA}}=I_{\mathrm{f}}/3=17.223$. Because x/y=1/1, $N_{\mathrm{PFPMA}}=N_{\mathrm{VBSF}}=1$. Therefore, the proportion of VBSF in poly(VBSF-*co*-PFPMA-*co*-MMA) is $N_{\mathrm{VBSF}}/(N_{\mathrm{VBSF}}+N_{\mathrm{PFPMA}}+N_{\mathrm{MMA}})*100\%=1/19.223*100\%=5\%$ (integer), the proportion of PFPMA is $N_{\mathrm{PFPMA}}/(N_{\mathrm{VBSF}}+N_{\mathrm{PFPMA}}+N_{\mathrm{MMA}})*100\%=1/19.223*100\%=5\%$ (integer), and the proportion of MMA is $N_{\mathrm{MMA}}/(N_{\mathrm{VBSF}}+N_{\mathrm{PFPMA}}+N_{\mathrm{MMA}})*100\%=17.223/19.223*100\%=90\%$ (integer), x/y/z=5/5/90.

General procedure for PPM of binary random copolymers



Binary random copolymers (50 mg, 1.0 eq., the total polymer moles multiplied by the VBSF fraction) were added to a Schlenk tube vial equipped with PTFE stirring bar and dissolved in 1.5 mL DMF/MeCN. TBS ethers (2.0 eq.) were added followed by addition of DBU (0.6 eq.). The reaction was stirred at 60 °C and 20.0 µL of mixture were syringed out and quenched into DMSO-*d*6 tomonitor reaction by ^{19}F NMR. The reaction mixture dripped into 80 mL methanol and stirred for 2 hours. The precipitates were then collected by suction filtration with a Buchner funnel and dried in vacuum at 50 °C to give the modified copolymers, and the M_n and M_w/M_n were analysed by GPC, as shown in Table S2. The reaction steps and feeding ratio of different modified substrates are the same.

Table S2. PPM of binary copolymers

Entry	Copolymers	x/y	TBS ethers	Time (h)	Before PPM $M_{n,\,\mathrm{GPC}}$[a] (kg/mol)	Before PPM Đ[a]	After PPM $M_{n,\,\mathrm{GPC}}$ (kg/mol)	After PPM Đ	Gravimetric yields
1	Polymer 1	/	a	3	12.0	1.44	13.7	1.58	89.1%
2	Polymer 2	9/91	b	3	20.8	1.46	22.0	1.68	96.4%
3	Polymer 3	5/95	c	3	20.0	1.22	21.0	1.21	90.5%

4	Polymer 4	6/94	d	3	22.6	1.33	28.4	1.26	95.1%
5	Polymer 5	10/90	a	3	9.6	1.13	10.8	1.11	90.3%
6	Polymer 6	5/95	e	3	18.3	1.14	19.8	1.08	90.9%

[a]Determined by GPC using polystyrene standards.

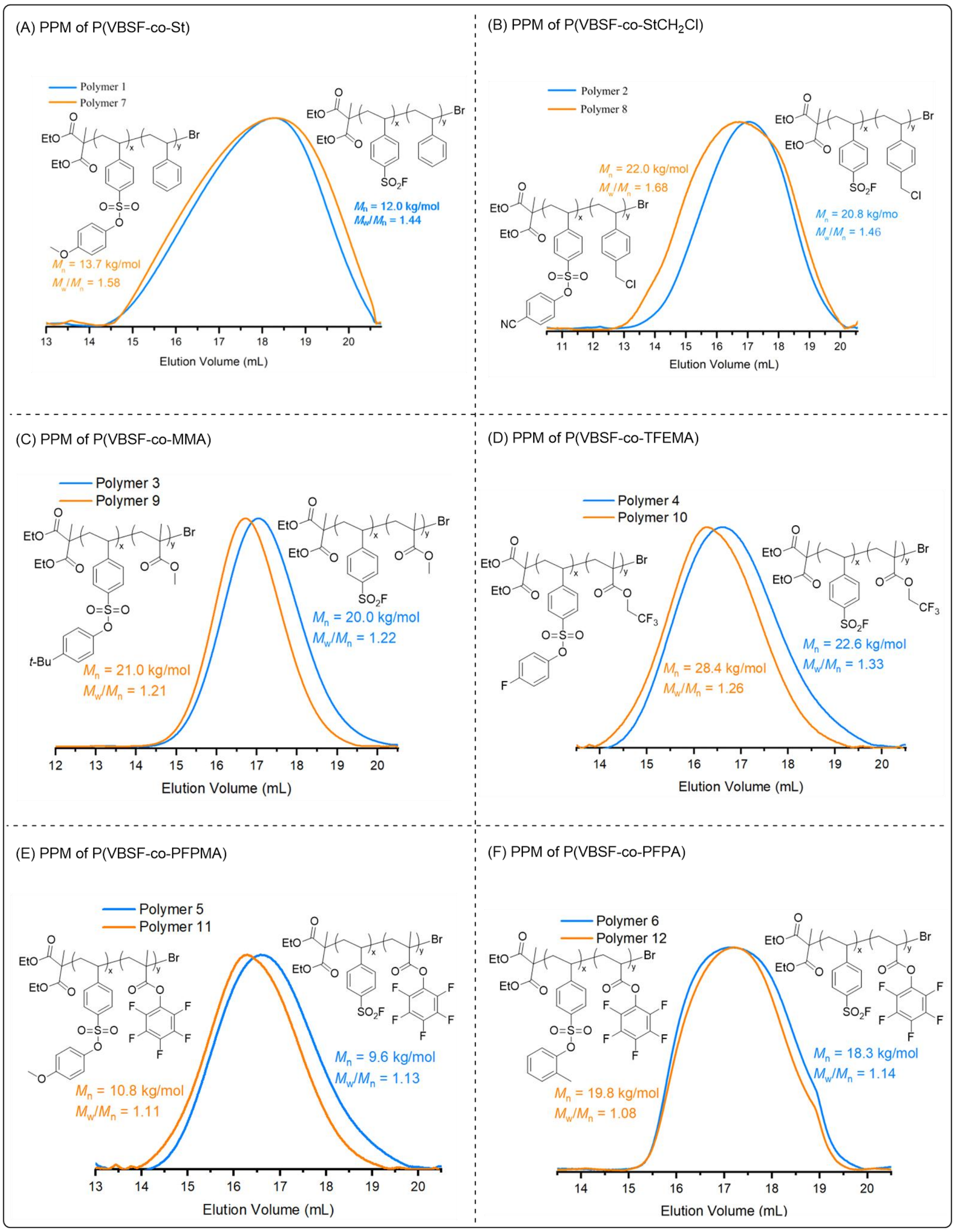
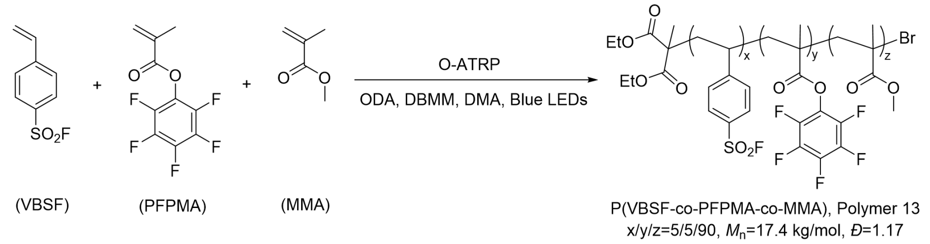


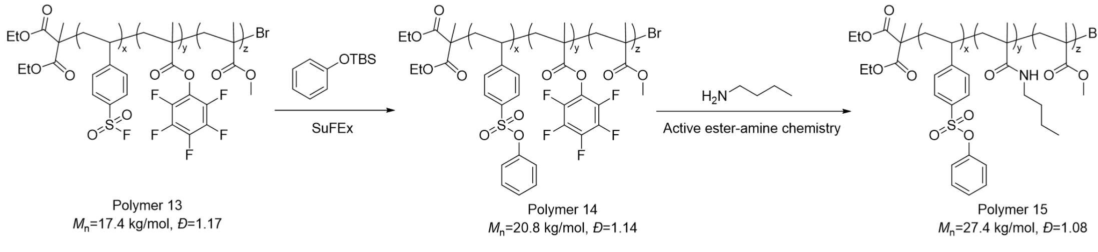
Figure S2. The overlaid GPC traces of the binary copolymers and its PPM products.

Synthesis method for random terpolymerization



The molar ratio of $[\mathrm{VBSF+PFPMA+MMA}]_0/[\mathrm{initiator}]_0/[\mathrm{catalyst}]_0=20/1/0.005$ were showed as follows, where in the molar ratio of $[\mathrm{VBSF}]_0/[\mathrm{PFPMA}]_0/[\mathrm{MMA}]_0=5/5/90$. The polymerization was conducted with VBSF (50 uL, 0.34 mmol) and PFPMA (62 uL, 0.34 mmol) and MMA (650 uL, 6.12 mmol) as the comonomers, DBMM (27 μL, 0.14 mmol, 1.0 eq.) as the ATRP initiator, ODA (0.17 mg, 6.8×10^{-4} mmol, 0.005 eq.) and DMA (1.4 mL) as the solvent in a Schlenk tube with a PTFE stirring bar. The mixture was deoxygenized by freeze-pump-thaw cycle three times, backfilled argon and sealed up subsequently. And then the polymerization was occurred under blue LED irradiation at room temperature for 28h. The reaction mixture dripped into 120 mL methanol and stirred for 4 hours. The precipitates were collected by suction filtration with a Buchner funnel and dried in vacuum at 50 °C to give the poly(VBSF-co-PFPMA-co-MMA) (white powder). The M_n (17.4 kg/mol) and M_w/M_n ($Đ$=1.17) were analysed by GPC.

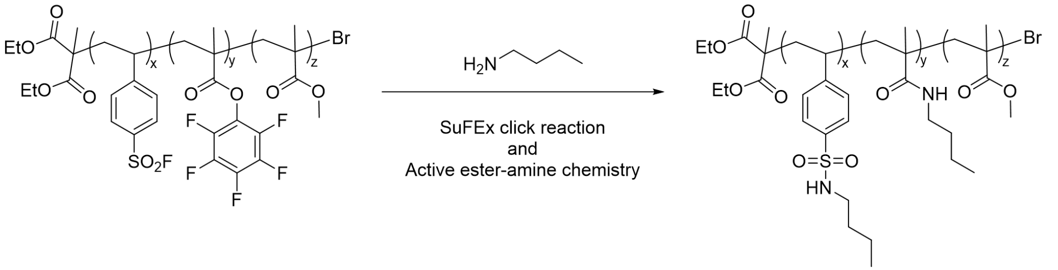
Method for PPM of random terpolymer, P(VBSF-co-PFPMA-co-MMA)



poly(VBSF-*co*-PFPMA-*co*-MMA) (Polymer 13, 50 mg, 1.0 eq., the total polymer moles multiplied by the VBSF fraction) was added to a Schlenk tube vial equipped with PTFE stirring bar and dissolved in 1.5 mL CH_3CN. Tert-butyldimethyl(phenoxy)silane (2.0 eq.) was added followed by addition of DBU (0.6 eq.). The reaction was stirred at 30 °C for 1 h and 20.0 μL of mixture were syringed out and quenched into DMSO-*d*6 tomonitor reaction by ^{19}F NMR. The reaction mixture dripped into 80 mL methanol and stirred for 3 h. The precipitates were then collected by suction filtration with a Buchner funnel and dried in vacuum at 50 °C to give the modified polymer (Polymer 14, white powder, 97.1% gravimetric yields), and the M_n and M_w/M_n were analysed by GPC.

Polymer 14 (50 mg, 1.0 eq., the total polymer moles multiplied by the PFPMA fraction) was added to a Schlenk tube vial equipped with PTFE stirring bar and dissolved in 1.5 mL CH_3CN. Butylamine (3.0 eq.) was added followed by the addition of DBU (0.6 eq.). The reaction was stirred at 30 °C for 24 h and 20.0 μL of mixture were syringed out and quenched into DMSO-*d*6 tomonitor reaction by ^{19}F NMR. The reaction mixture dripped into 80 mL methanol and stirred for 3 h. The precipitates were then collected by suction filtration with a Buchner funnel and dried in vacuum at 50 °C to give the modified polymer (Polymer 15, white powder, 93.9% gravimetric yields), and the M_n and M_w/M_n were analysed by GPC.

One-step dual functionalization reaction of Polymer 13 with butylamine



P(VBSF-co-PFPMA-co-MMA)
Polymer 13

Polymer 16

poly(VBSF-*co*-PFPMA-*co*-MMA) (Polymer 13, 50 mg, 1.0 eq., the total polymer moles multiplied by the VBSF fraction) was added to a Schlenk tube vial equipped with PTFE stirring bar and dissolved in 1.5 mL CH_3CN. Butylamine (6.0 eq.) was added followed by the addition of DBU (0.6 eq.). The reaction was stirred at 30 °C and 20.0 μL of mixture were syringed out and quenched into DMSO-*d*6 tomonitor reaction by ^{19}F NMR. The reaction mixture dripped into 80 mL methanol and stirred for 3 hours. The precipitates were then collected by suction filtration with a Buchner funnel and dried in vacuum at 50 °C to give the modified polymer (Polymer 16, white powder).

Because Polymer 13 (x/y/z, 5/5/90) exhibits significant fluorine signals, we monitored the reaction process by ^{19}F NMR spectroscopy. ^{19}F NMR spectrum of the reaction process of Polymer 13 with dimethylamine, as follows. First, before the reaction, the ^{19}F NMR spectrum only showed the peaks of VBSF (***a***, 1.00) and PFPMA (***b, b', c, c', d***, total 5.31) in Polymer 13, with the ratio of component [VBSF]/[PFPMA] was 1/1. Second, after 6 h of reaction, the ^{19}F NMR spectrum of the reaction mixture revealed the simultaneous presence of fluorine signals from VBSF, PFPMA, and pentafluorophenol (HF was not detected), indicating that PFPMA had partially reacted with butylamine to generate pentafluorophenol. Furthermore, the integration values for VBSF (***a***) and PFPMA (***b, b', c, c', d***) were 1.00 and 4.76, respectively, meaning that their component ratio remained was 1/1, which demonstrated that VBSF also reacted with butylamine and that both groups reacted at the same rate. Subsequently, after 36 h of reaction, the ^{19}F NMR spectrum of the reaction mixture showed only the pentafluorophenol signal (***e, e', f, f', g***), and the signals of VBSF and PFPMA completely absent, indicating that both VBSF and PFPMA had fully reacted with butylamine. Finally, after precipitation with methanol, the new modified product, Polymer 16, showed no fluorine signals, confirming that the post-modification of Polymer 13 with butylamine enables complete conversion of both VBSF and PFPMA without mutual interference.

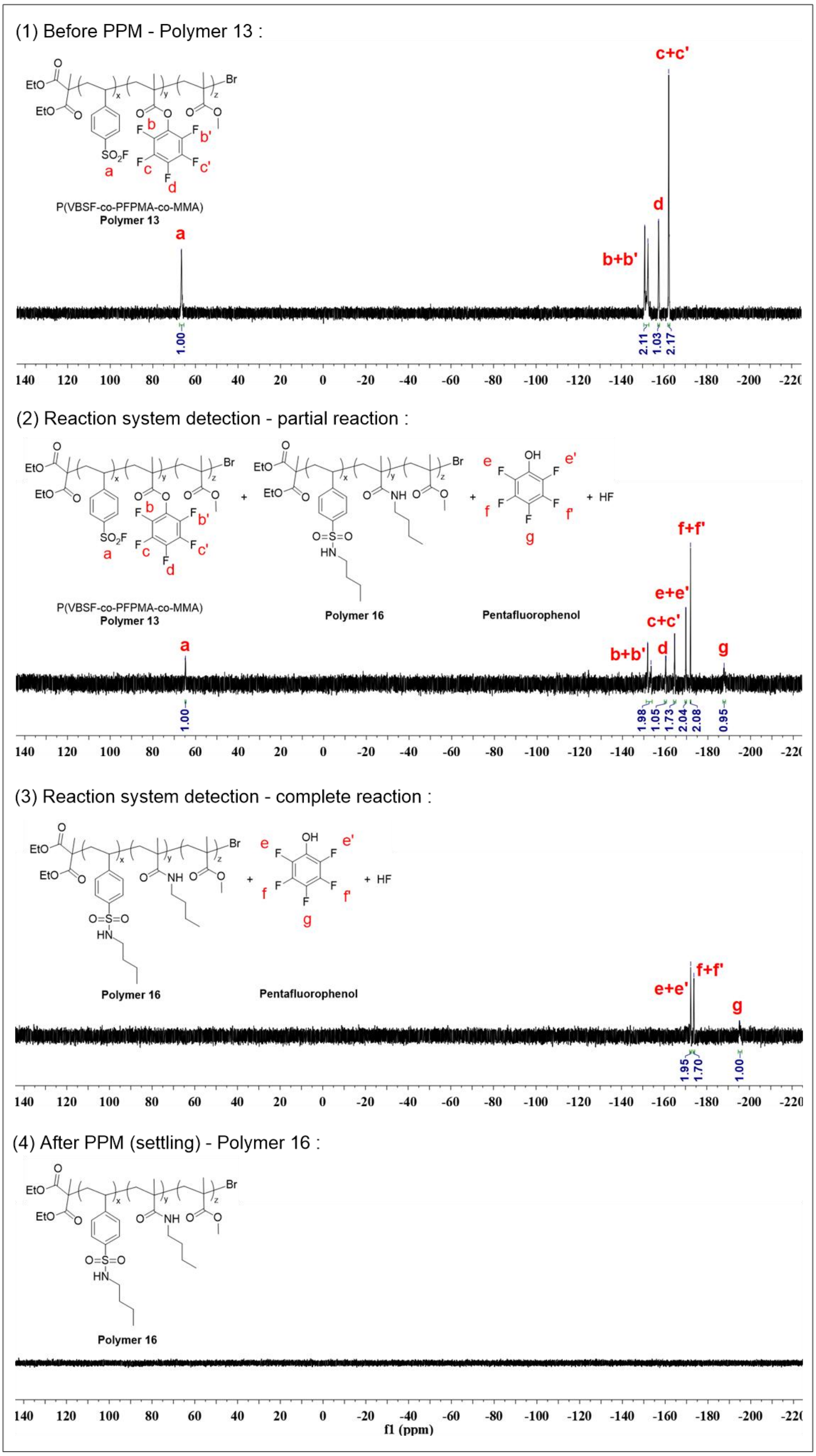


Figure S3. ^{19}F NMR spectrum of the reaction process of Polymer 13 with butylamine.

Supplementary nuclear magnetic spectra

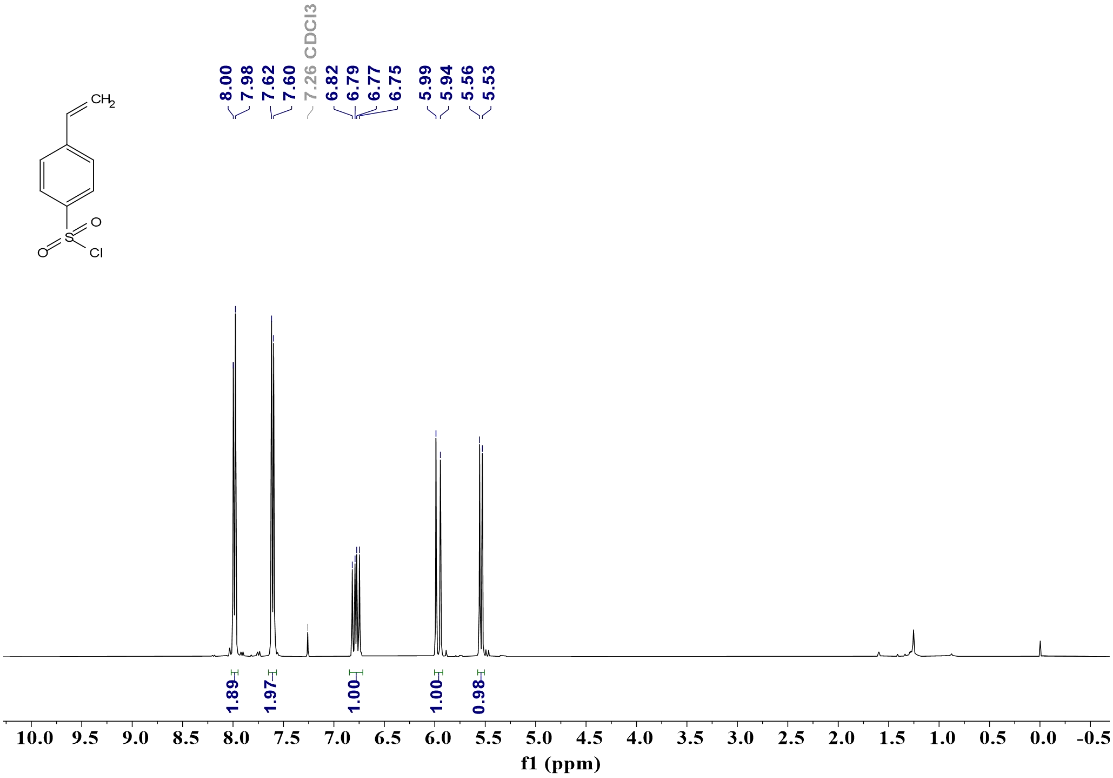


Figure S4. ^{1}H NMR spectrum of 4-vinylbenzenesulfonyl chloride (in $CDCl_3$).

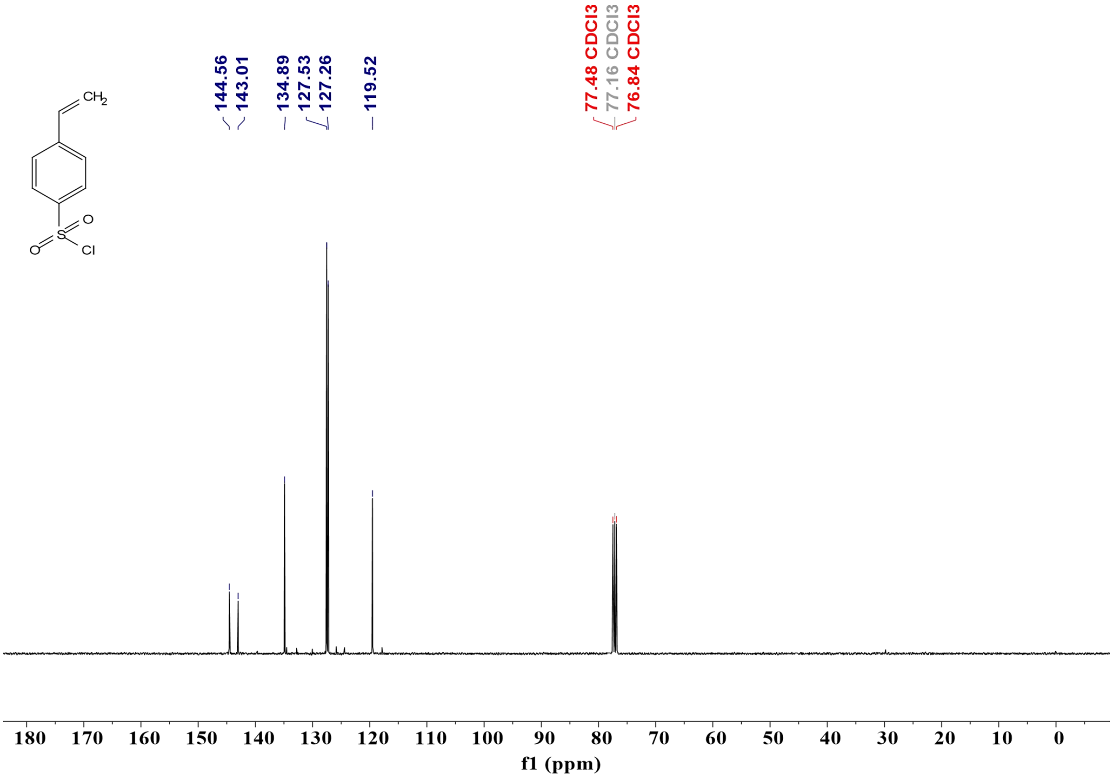


Figure S5. ^{13}C NMR spectrum of 4-vinylbenzenesulfonyl chloride (in $CDCl_3$)

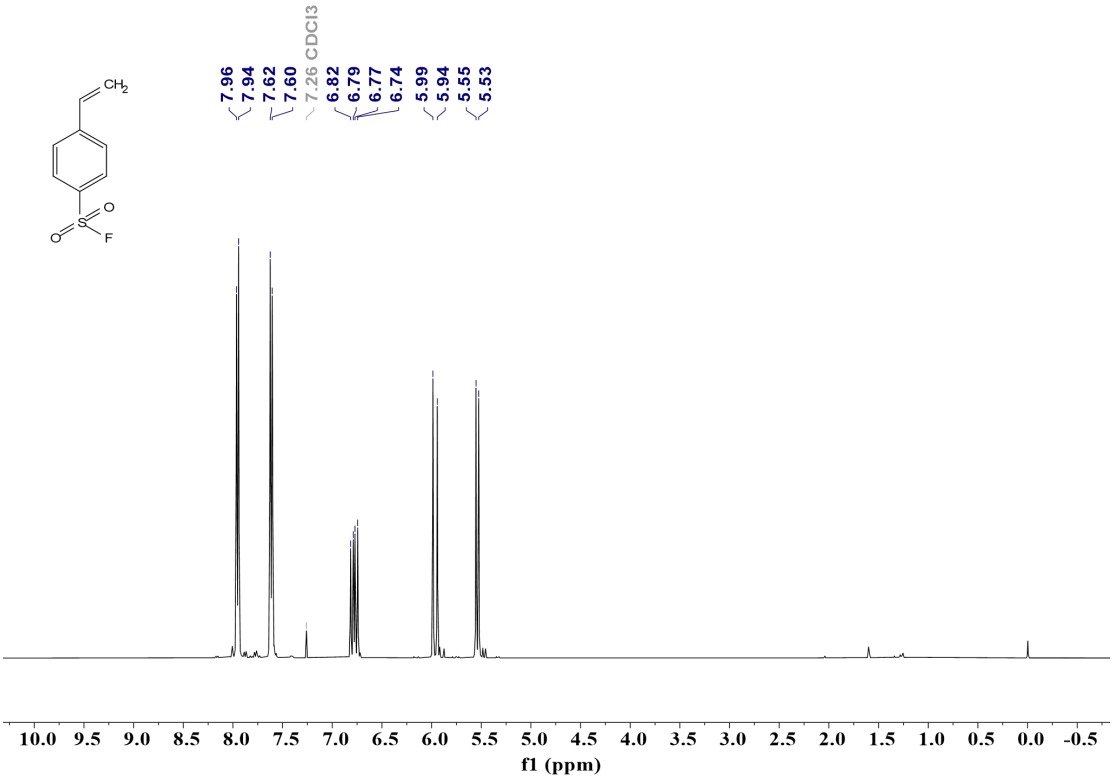


Figure S6. ^{1}H NMR spectrum of 4-vinylbenzenesulfonyl fluoride (in CDCl$_3$)

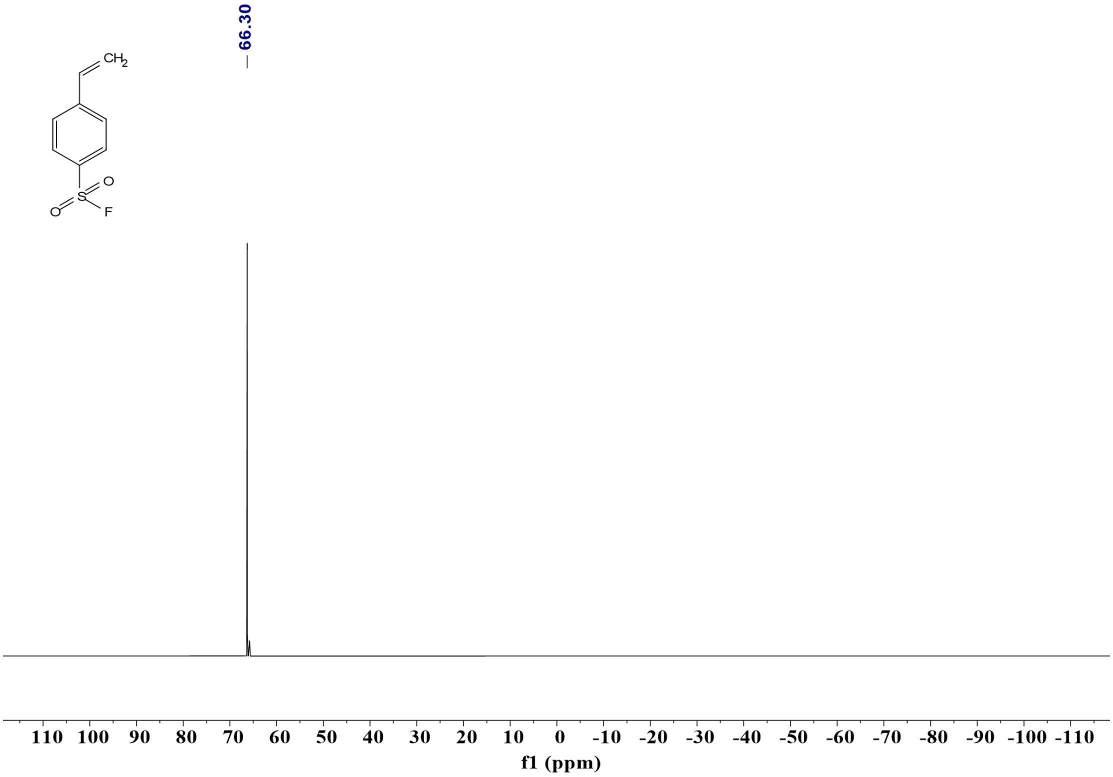


Figure S7. ^{19}F NMR spectrum of 4-vinylbenzenesulfonyl fluoride (in CDCl$_3$)

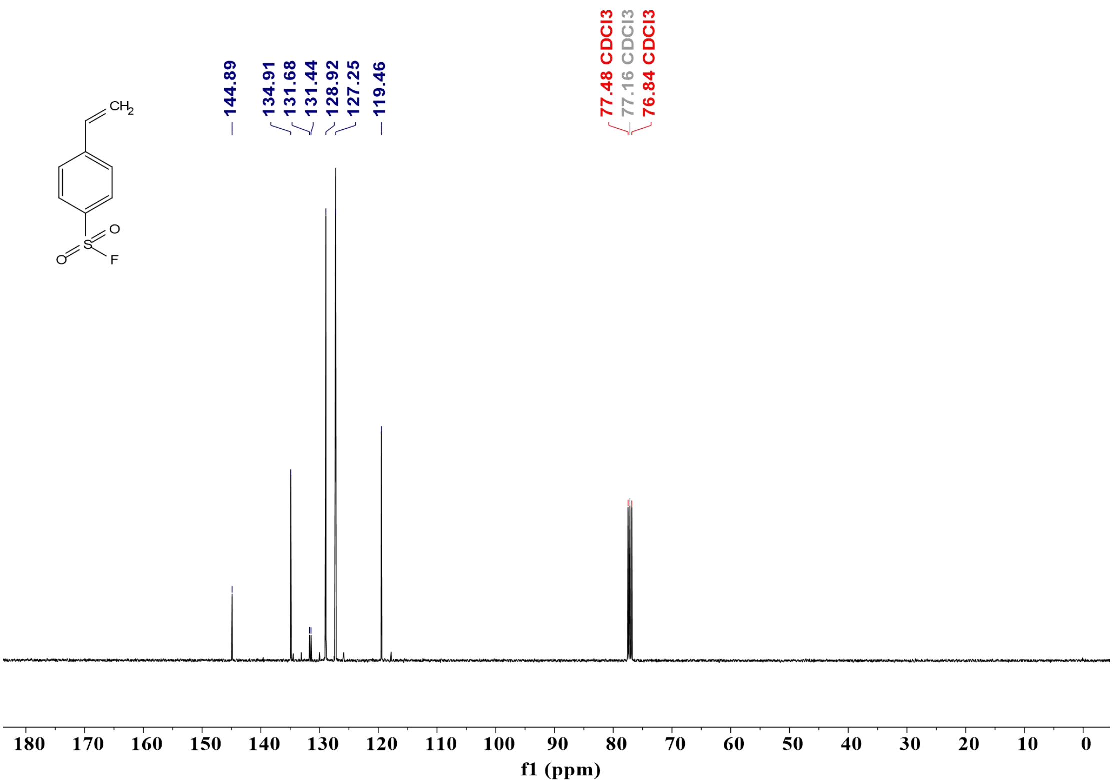


Figure S8. ^{13}C NMR spectrum of 4-vinylbenzenesulfonyl fluoride (in $CDCl_3$)

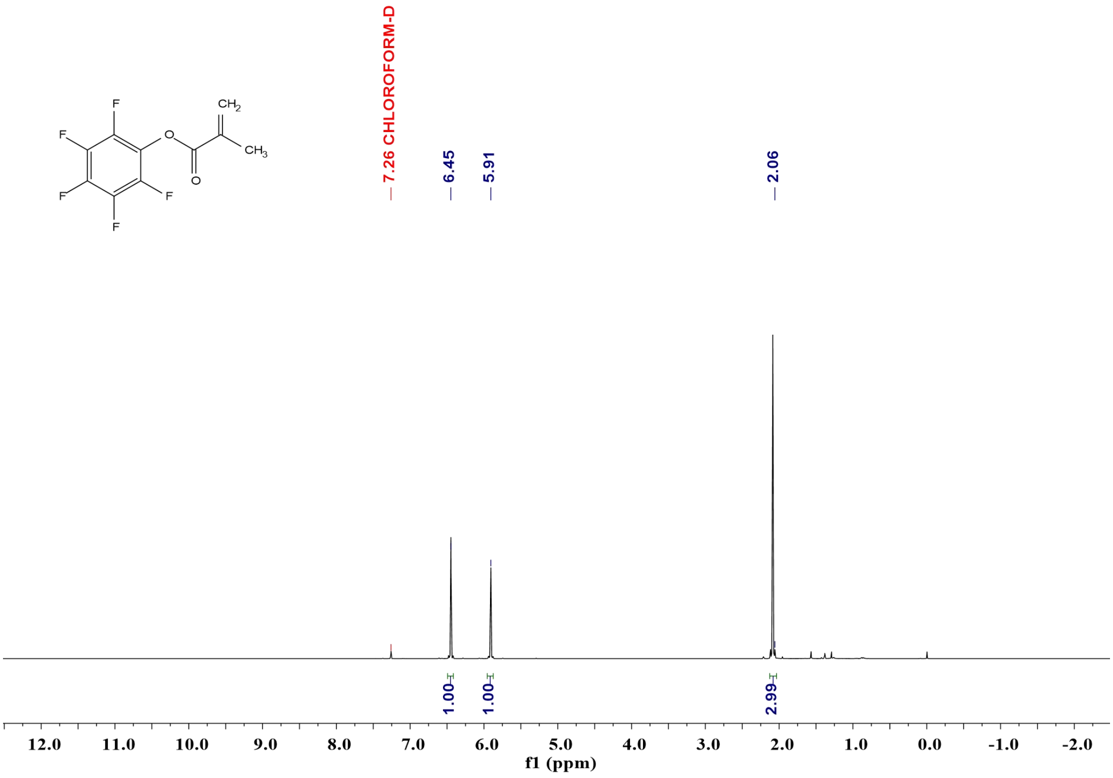


Figure S9. ^{1}H NMR spectrum of PFPMA (in $CDCl_3$).

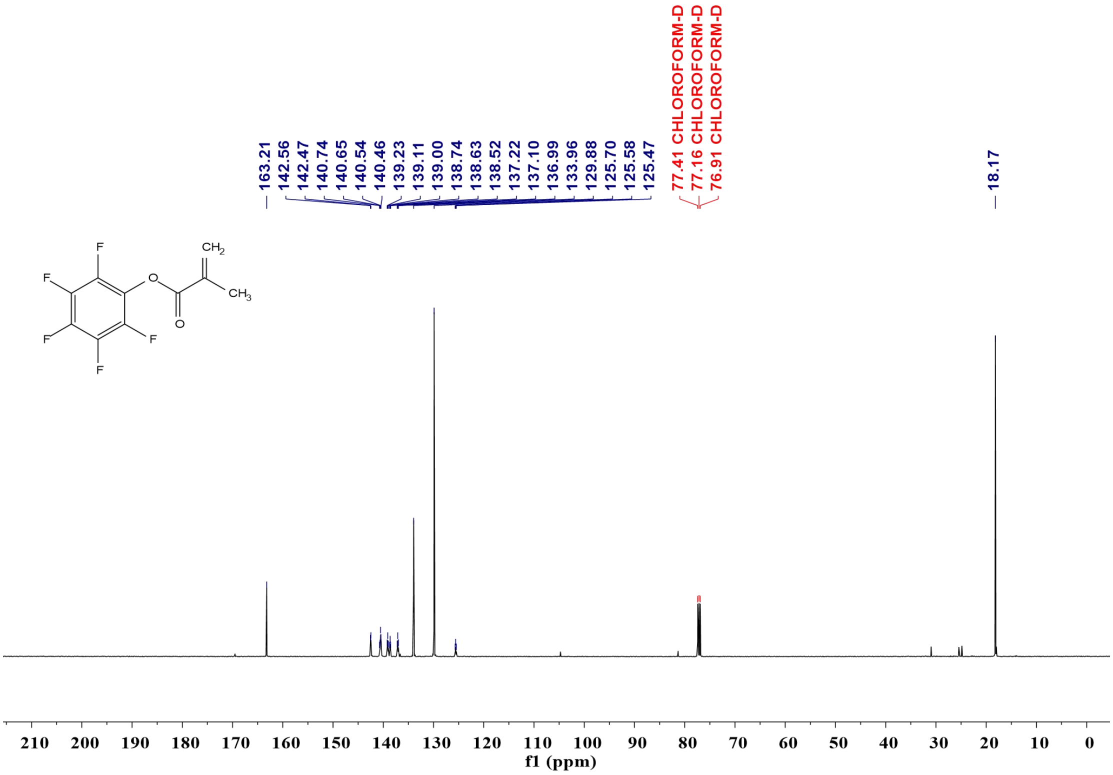


Figure S10. ^{13}C NMR spectrum of PFPMA (in CDCl$_3$).

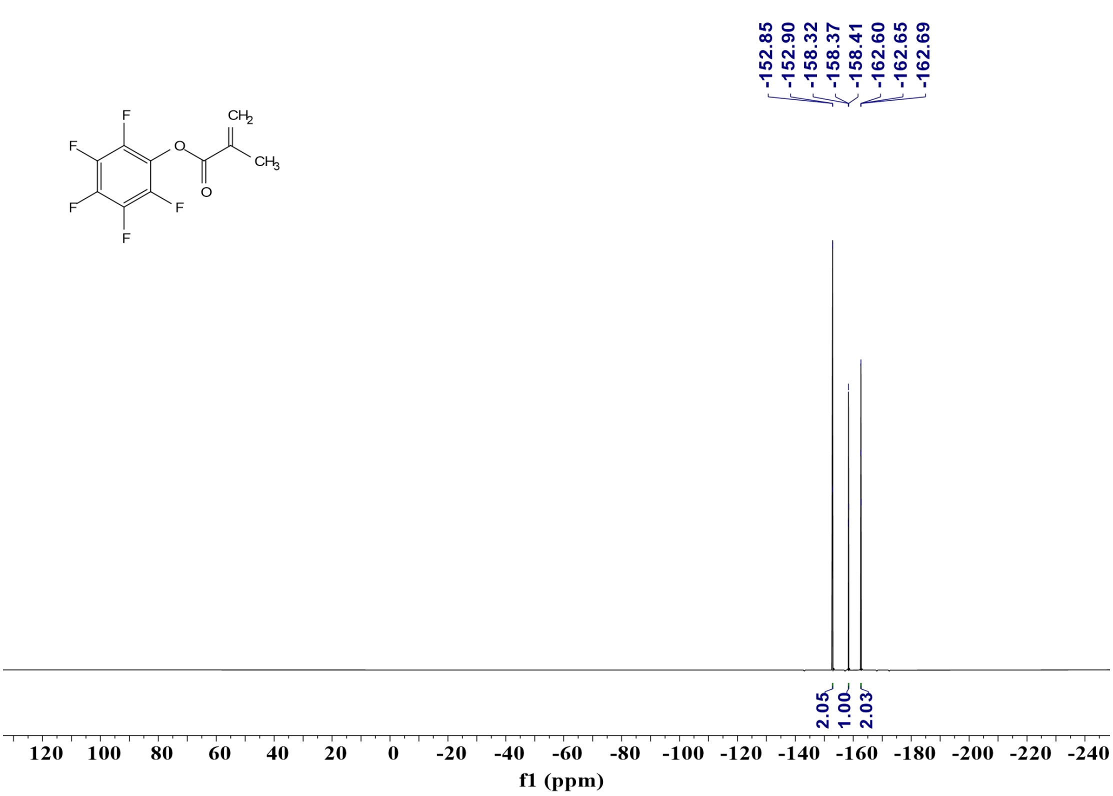


Figure S11. ^{19}F NMR spectrum of PFPMA (in CDCl$_3$).

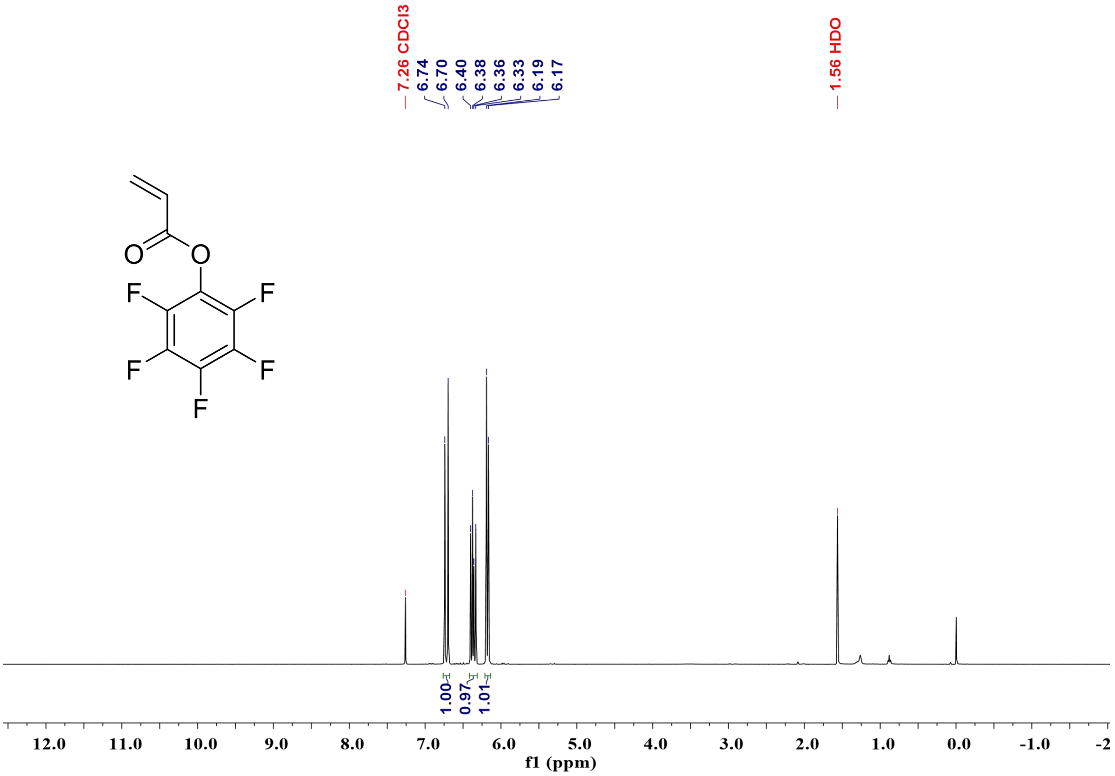


Figure S12. ^{1}H NMR spectrum of PFPA (in $CDCl_3$).

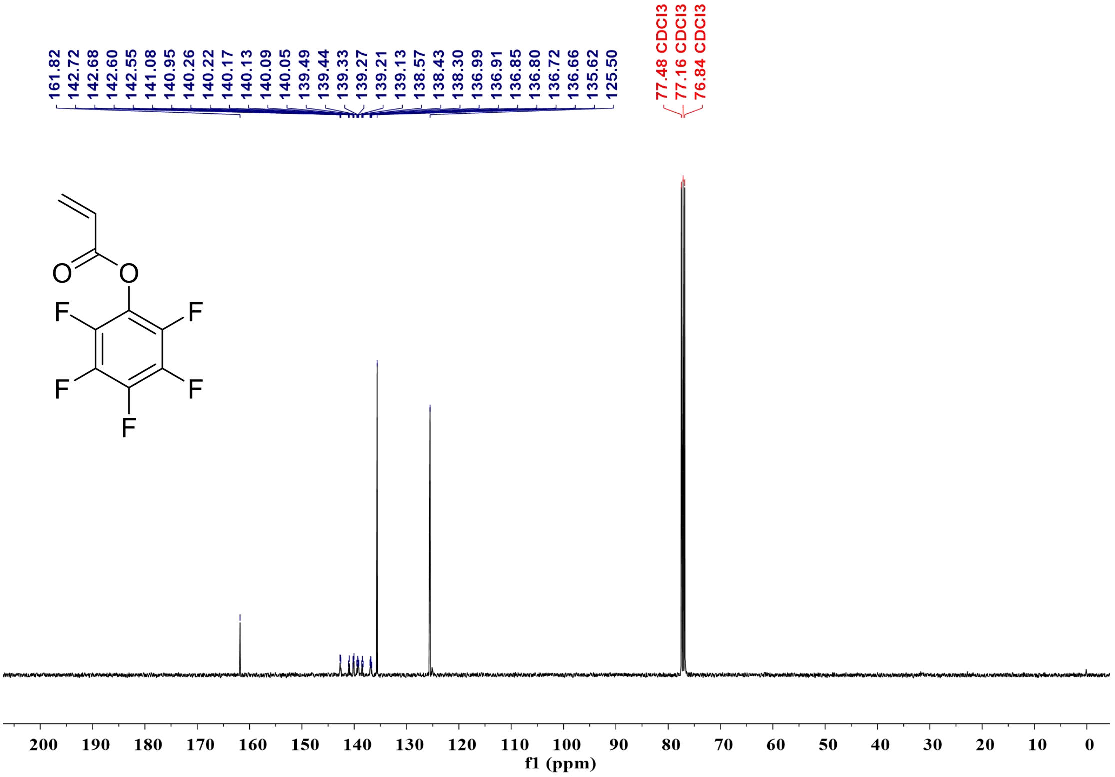


Figure S13. ^{13}C NMR spectrum of PFPA (in $CDCl_3$).

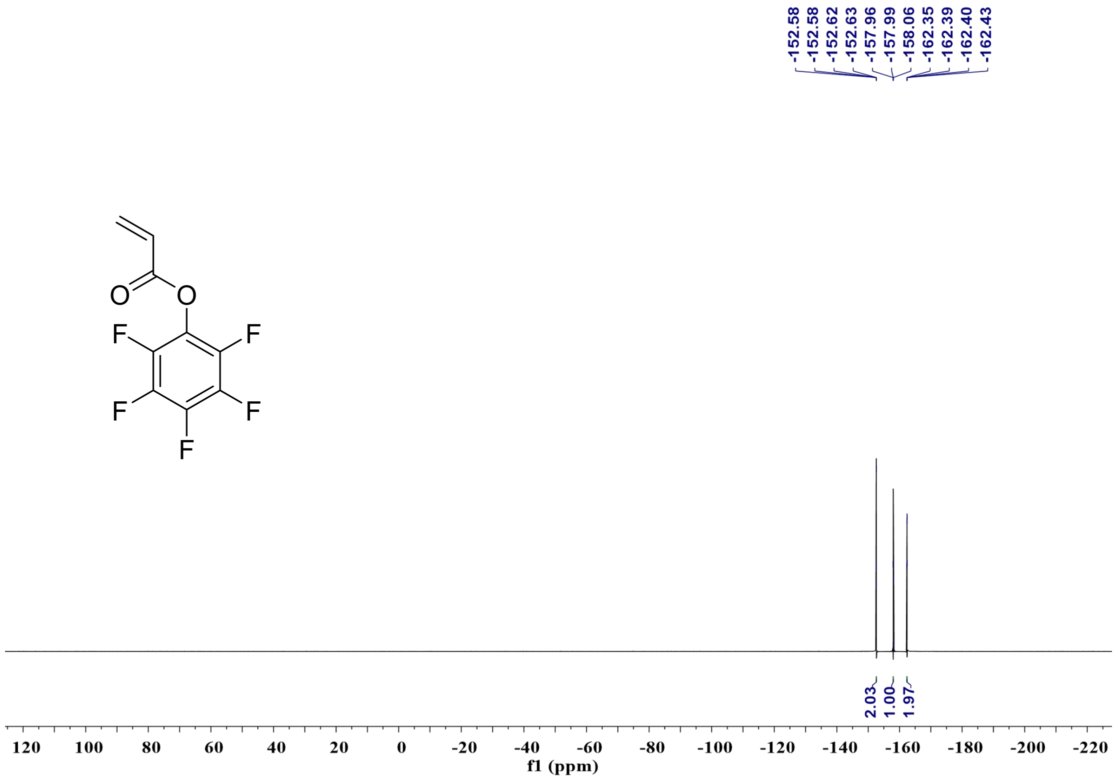


Figure S14. ^{19}F NMR spectrum of PFPA (in $CDCl_3$).

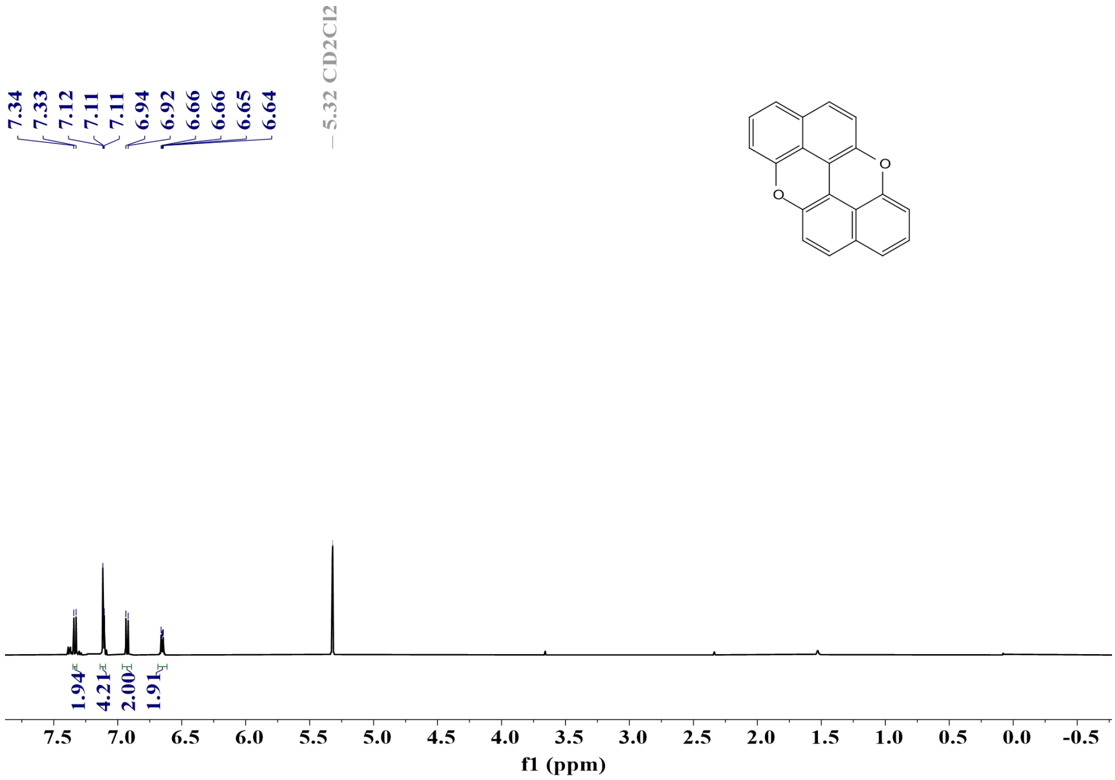


Figure S15. ^{1}H NMR spectrum of ODA (in CD_2Cl_2)

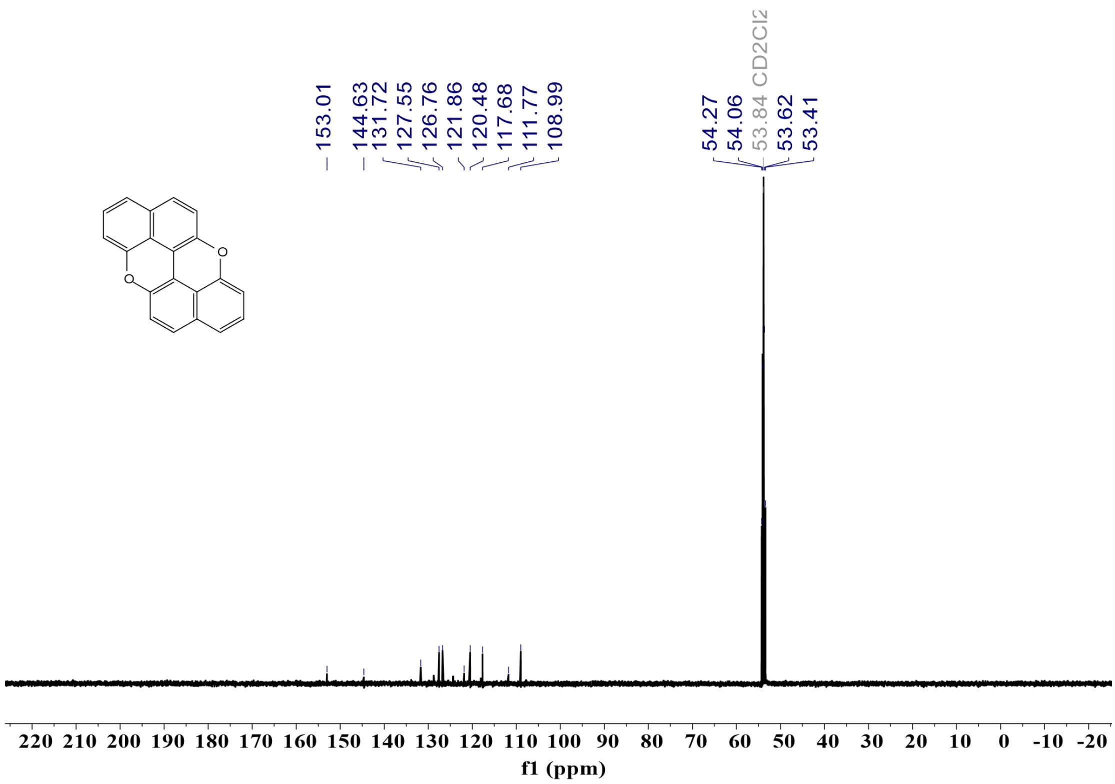


Figure S16. ^{13}C NMR spectrum of ODA (in CD_2Cl_2)

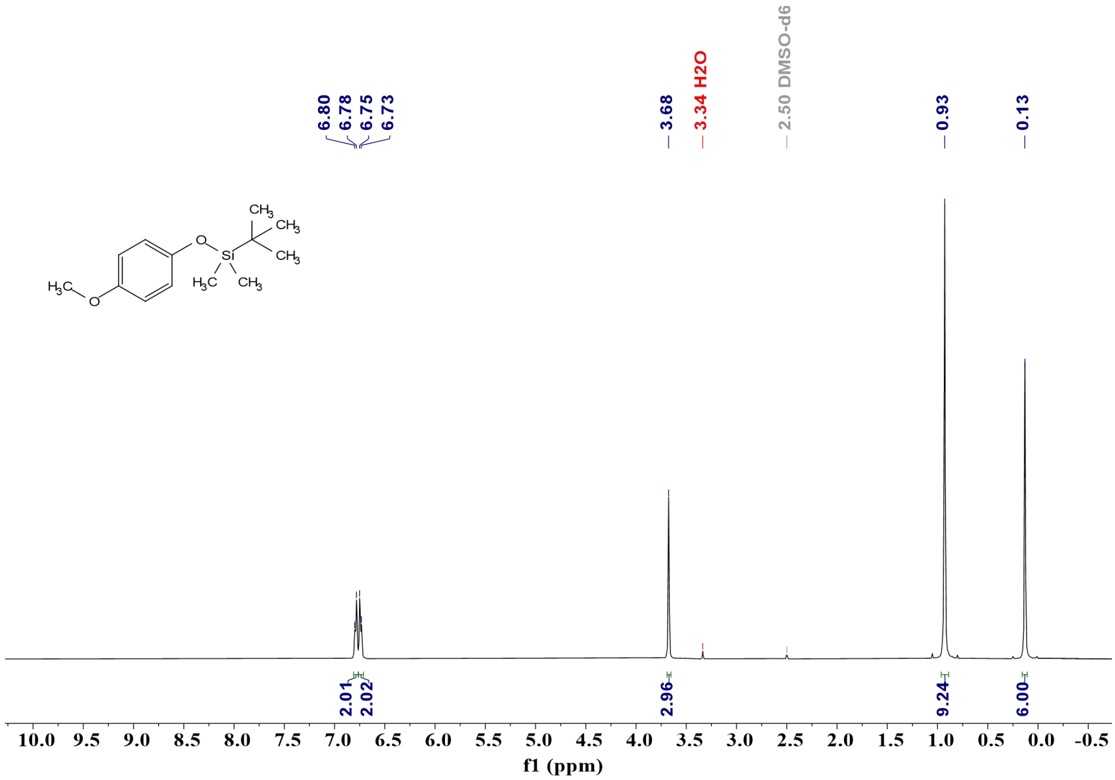


Figure S17. ^{1}H NMR spectrum of a (in DMSO-*d6*).

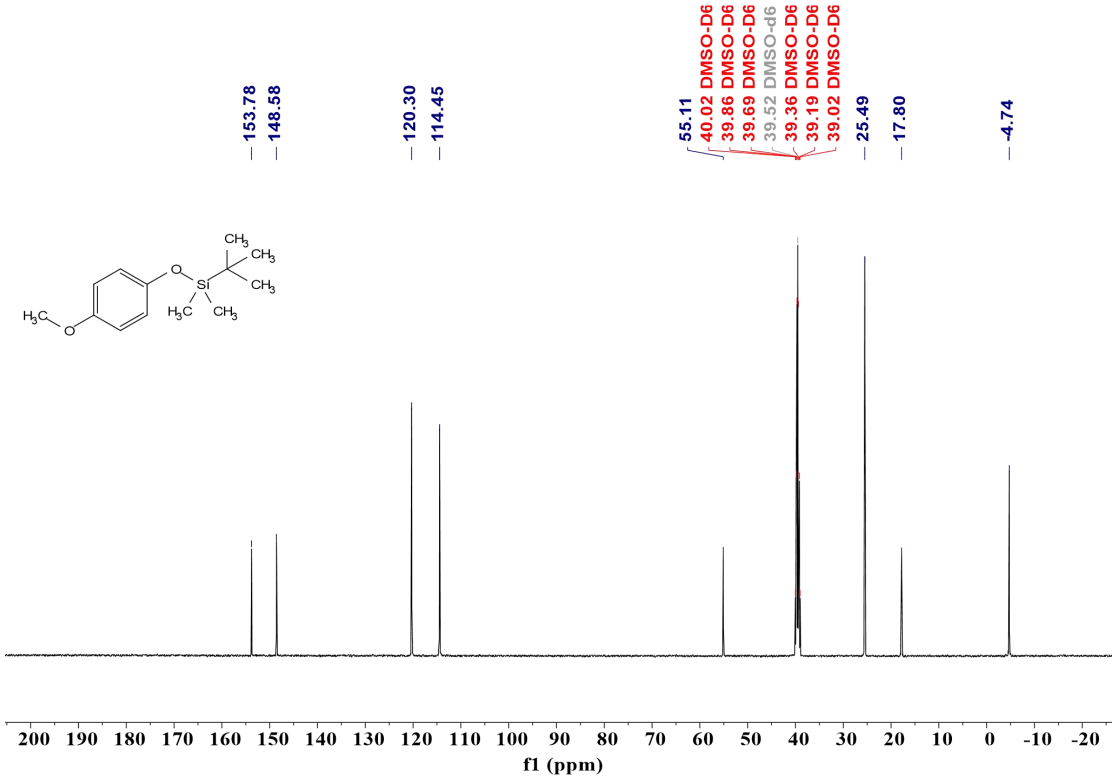


Figure S18. ^{13}C NMR spectrum of a (in DMSO-*d6*).

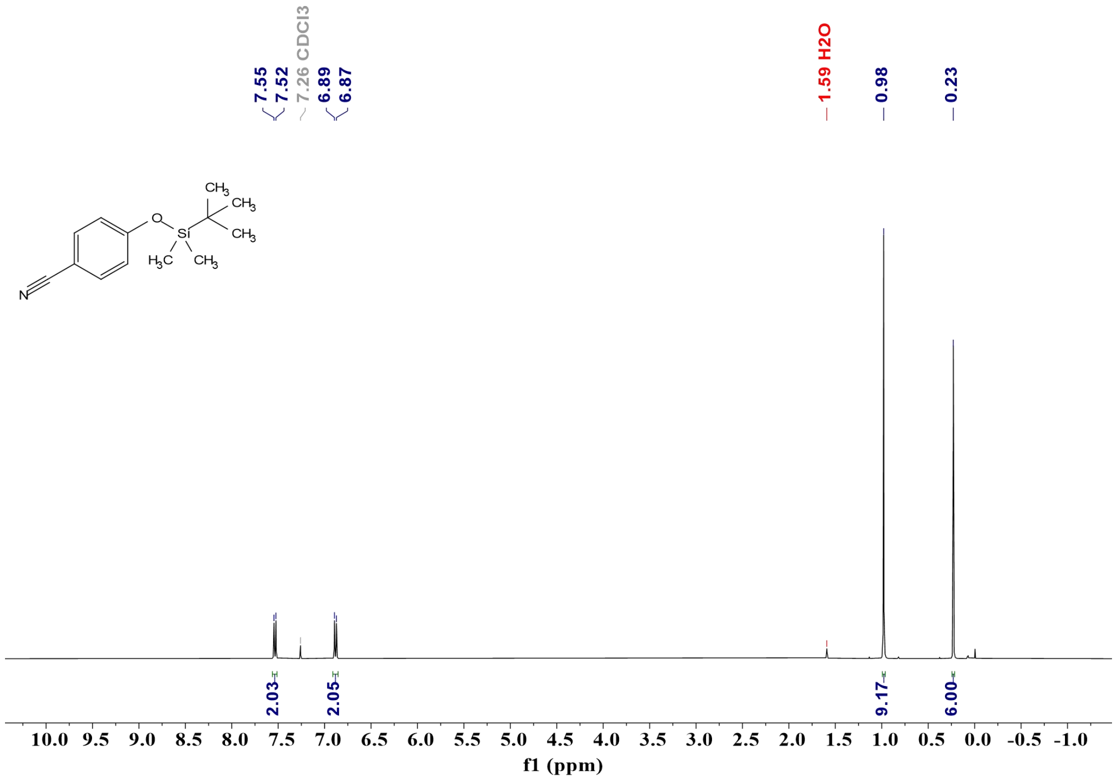


Figure S19. ^{1}H NMR spectrum of b (in DMSO-*d6*).

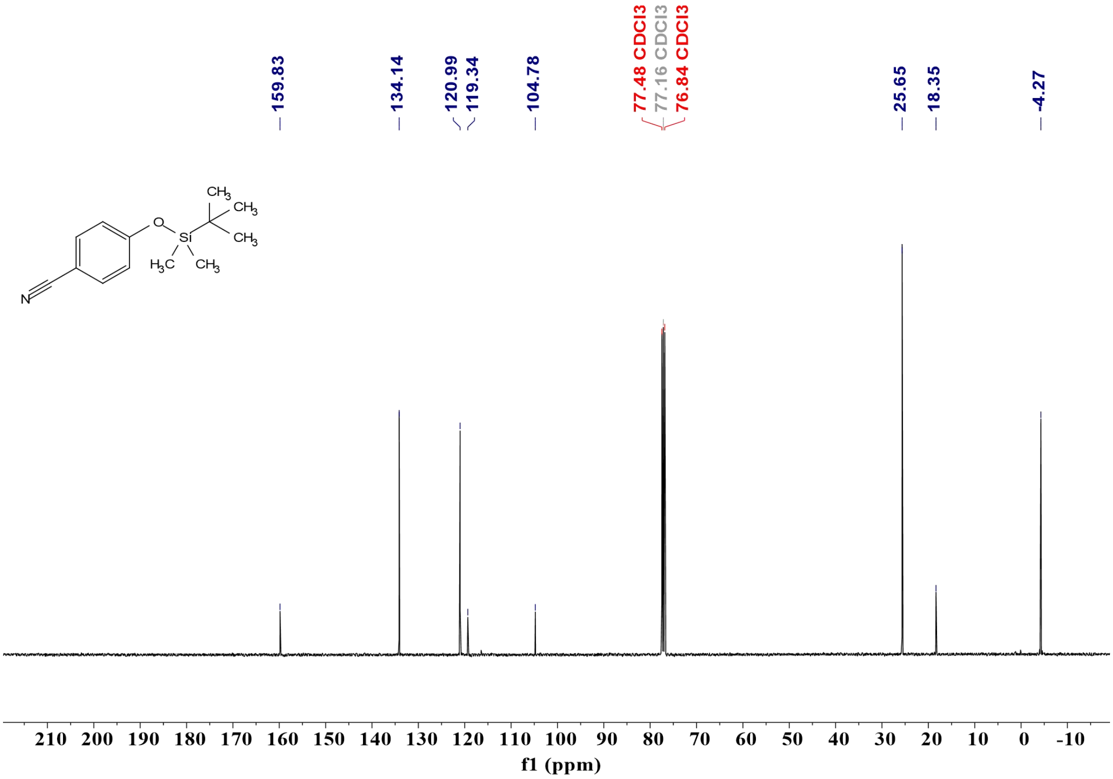


Figure S20. ^{13}C NMR spectrum of b (in DMSO-*d6*).

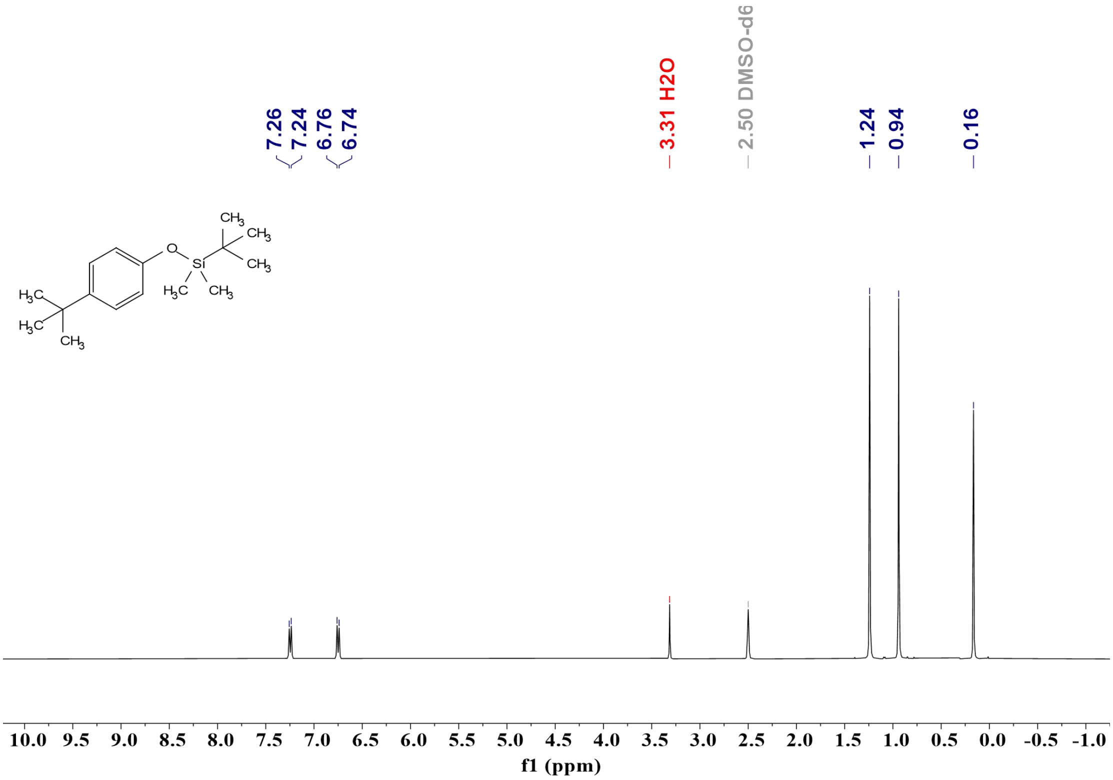


Figure S21. ^{1}H NMR spectrum of c (in DMSO-*d6*).

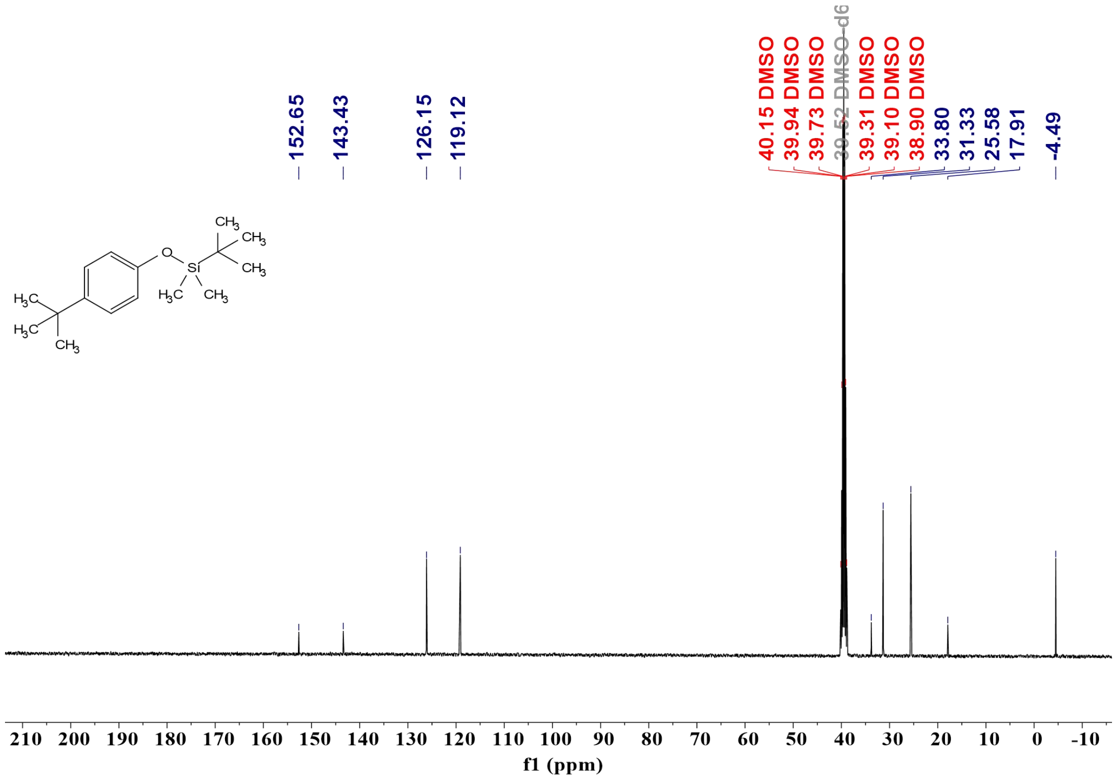


Figure S22. ^{13}C NMR spectrum of c (in DMSO-*d6*).

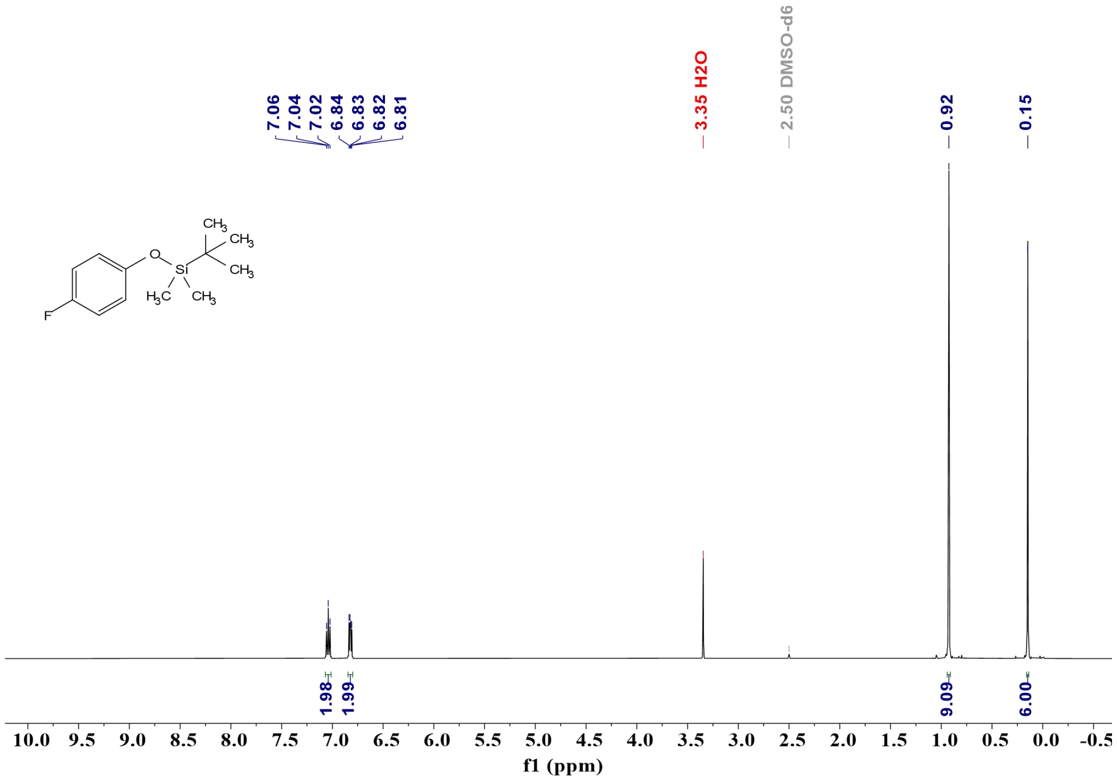


Figure S23. ^{1}H NMR spectrum of d (in DMSO-*d6*).

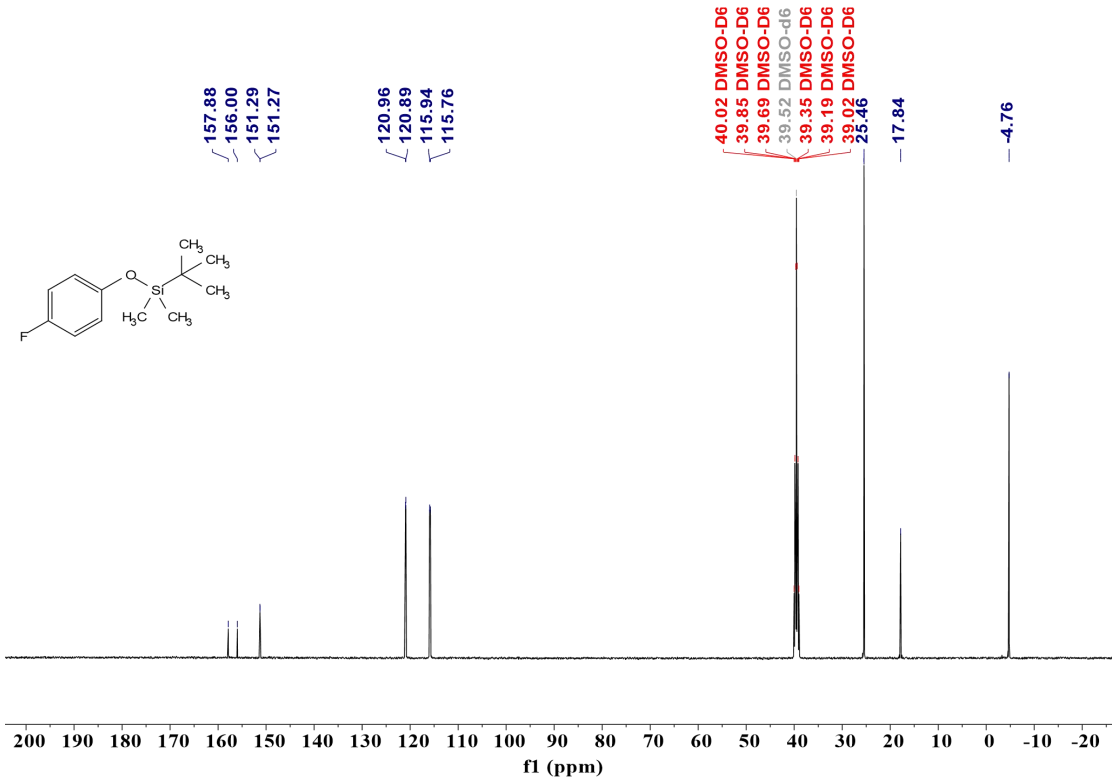


Figure S24. ^{13}C NMR spectrum of d (in DMSO-*d6*).

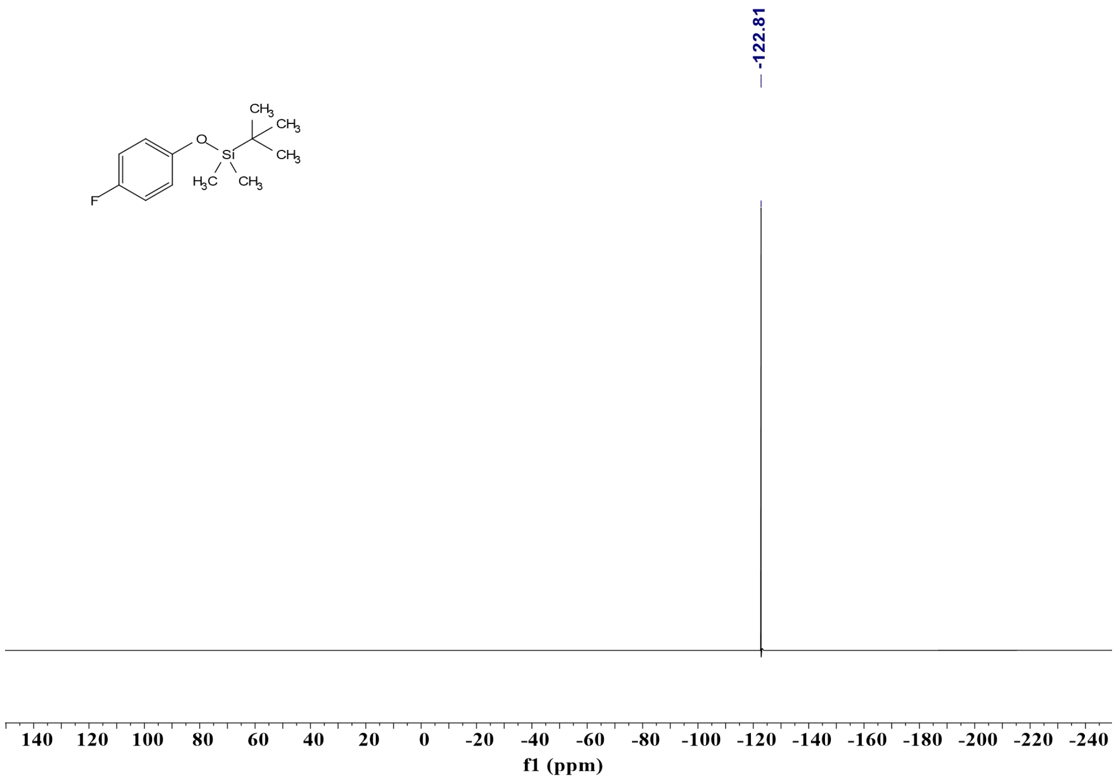


Figure S25. ^{19}F NMR spectrum of d (in DMSO-*d6*).

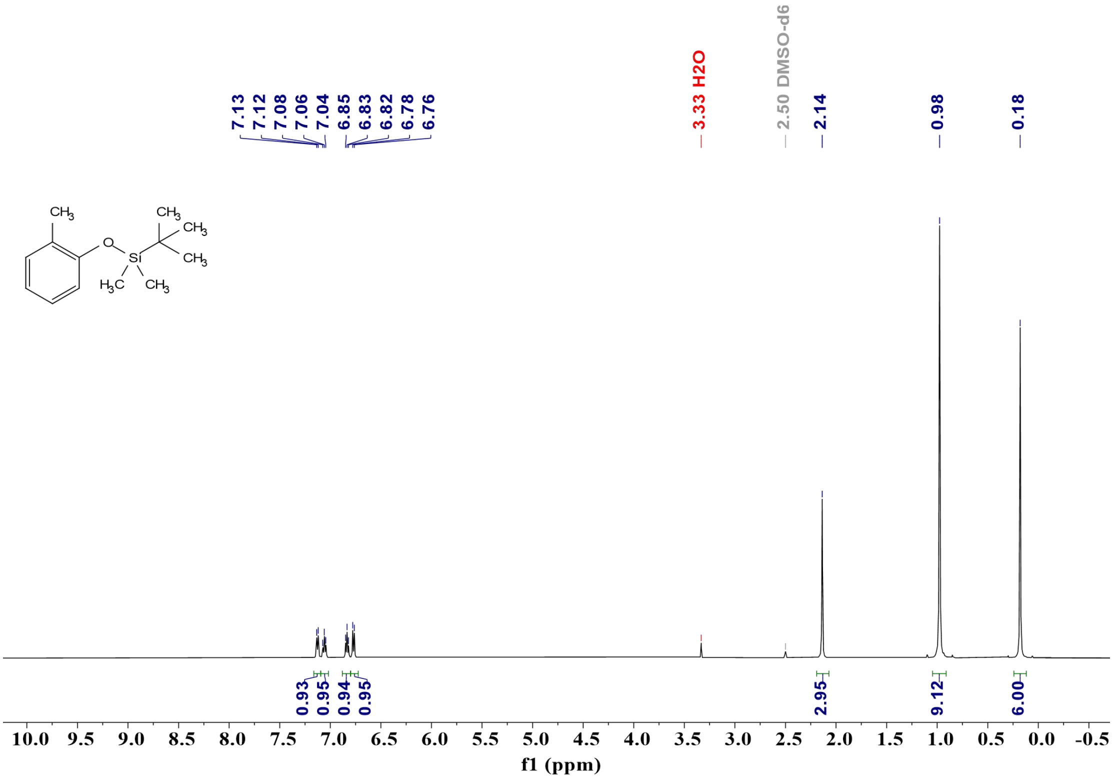


Figure S26. ^{1}H NMR spectrum of e (in DMSO-*d6*).

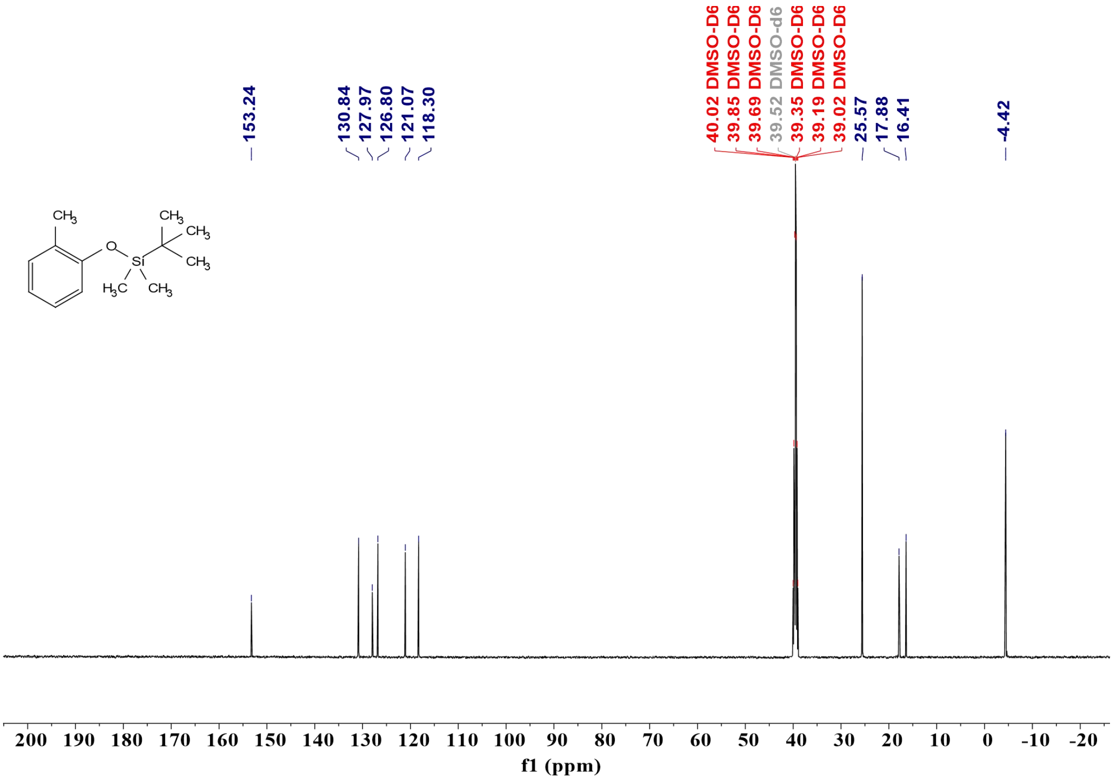


Figure S27. ^{13}C NMR spectrum of e (in DMSO-*d6*).

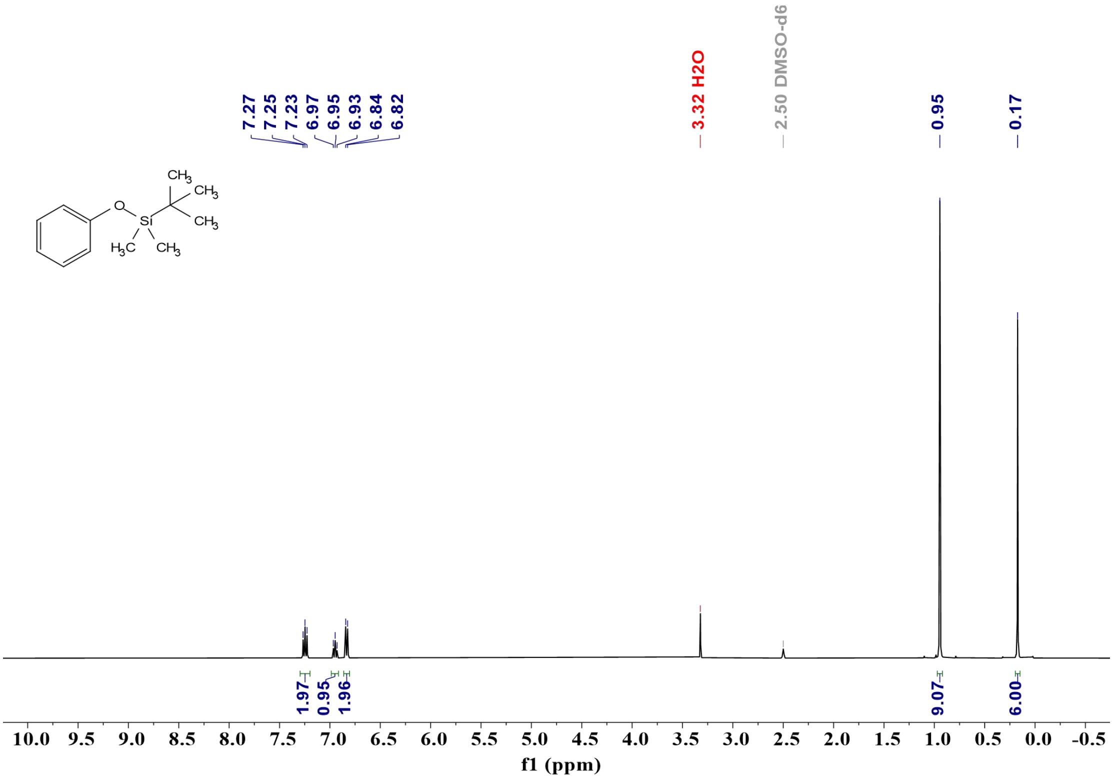


Figure S28. ^{1}H NMR spectrum of f (in DMSO-*d6*).

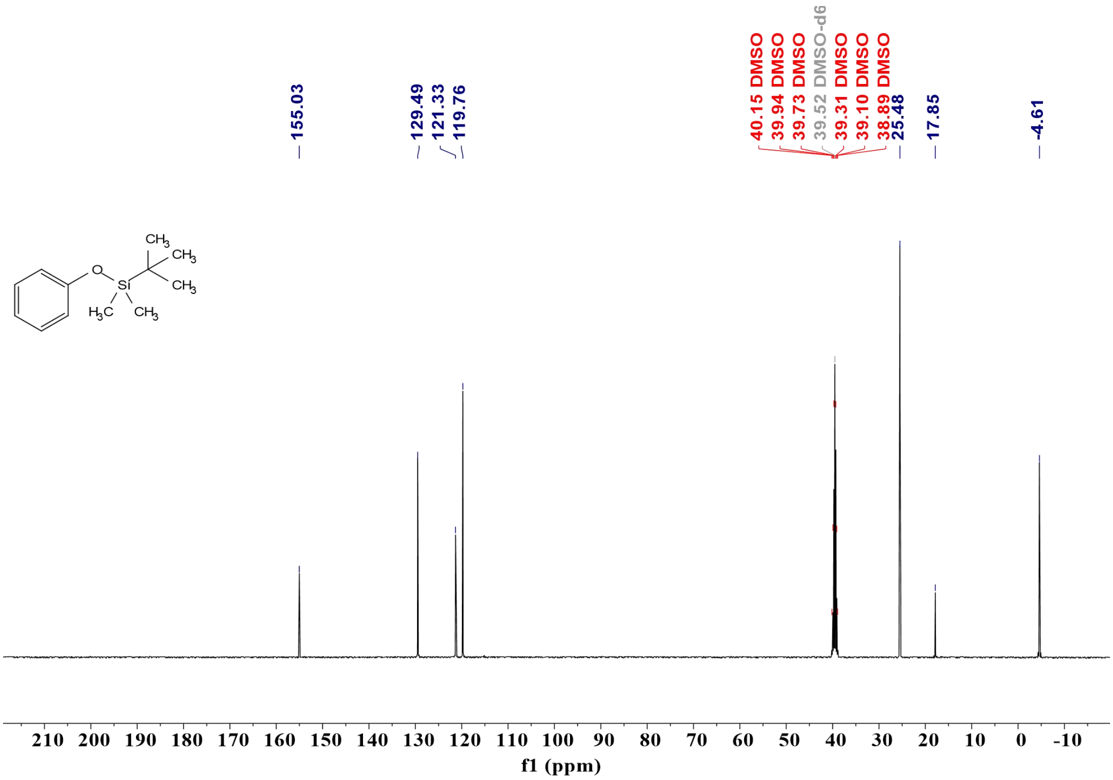


Figure S29. ^{13}C NMR spectrum of f (in DMSO-*d6*).

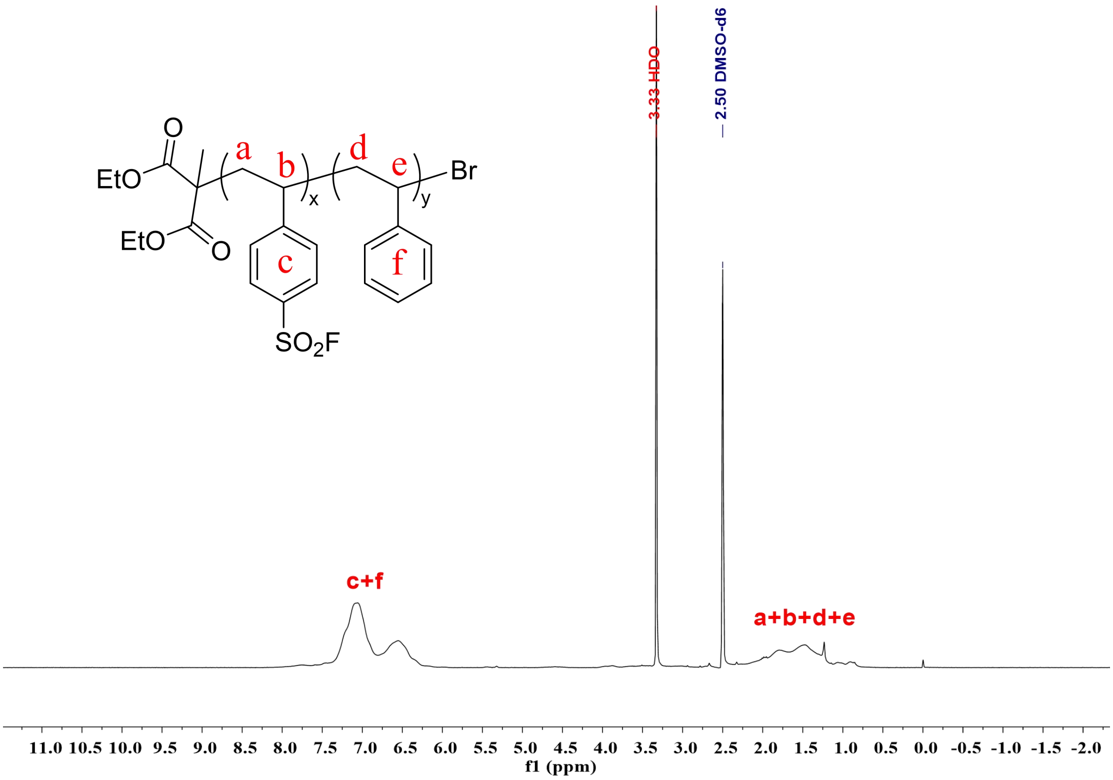


Figure S30. ^{1}H NMR spectrum of poly(VBSF-*co*-St) (in DMSO-*d6*).

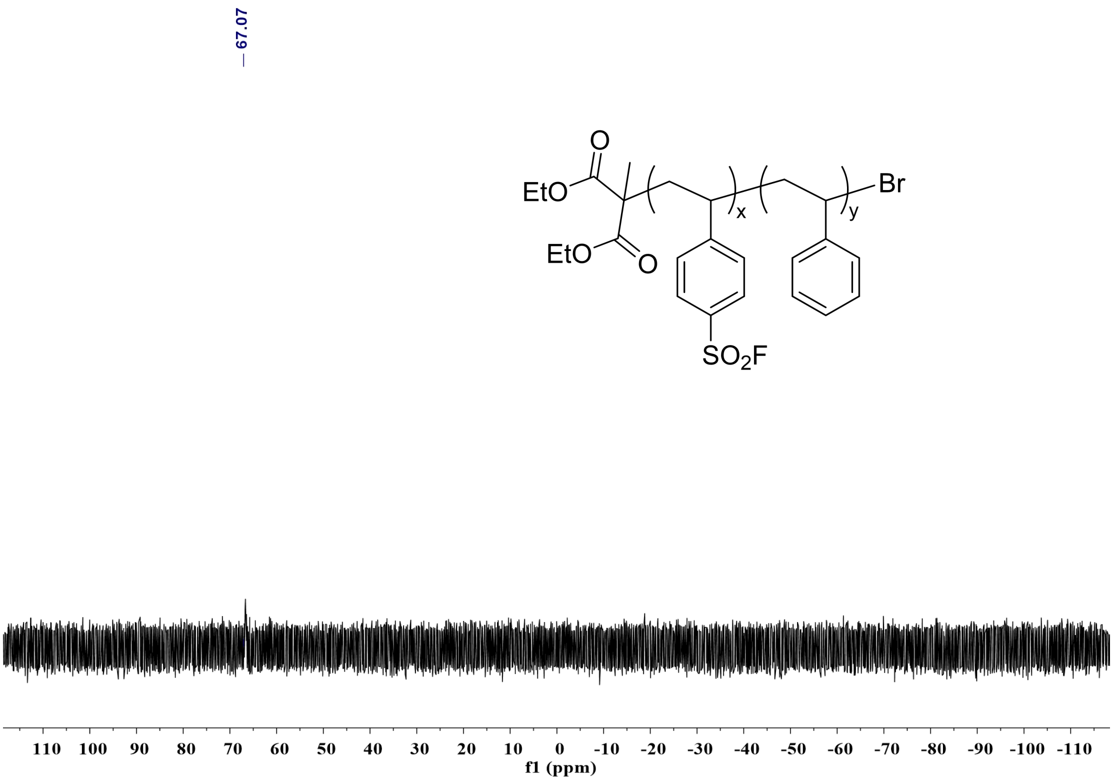


Figure S31. ^{19}F NMR spectrum of poly(VBSF-*co*-St) (in DMSO-*d6*).

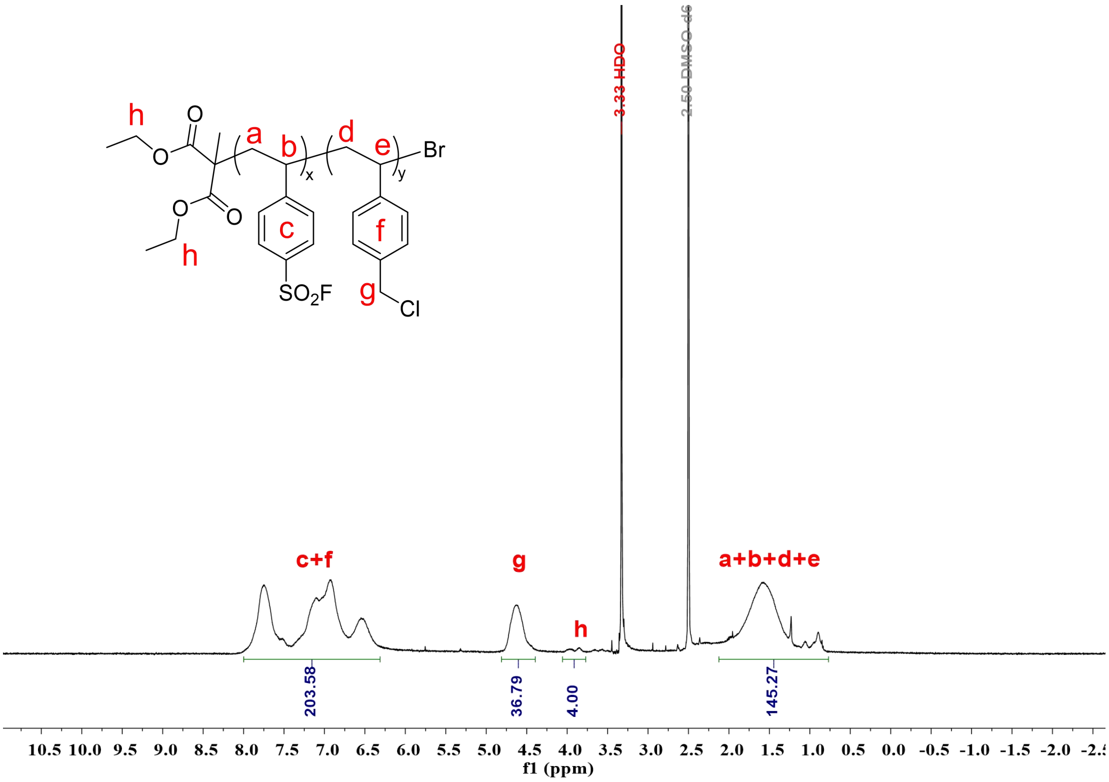


Figure S32. ^{1}H NMR spectrum of poly(VBSF-*co*-StCH$_2$Cl), x/y=67/33 (in DMSO-*d6*).

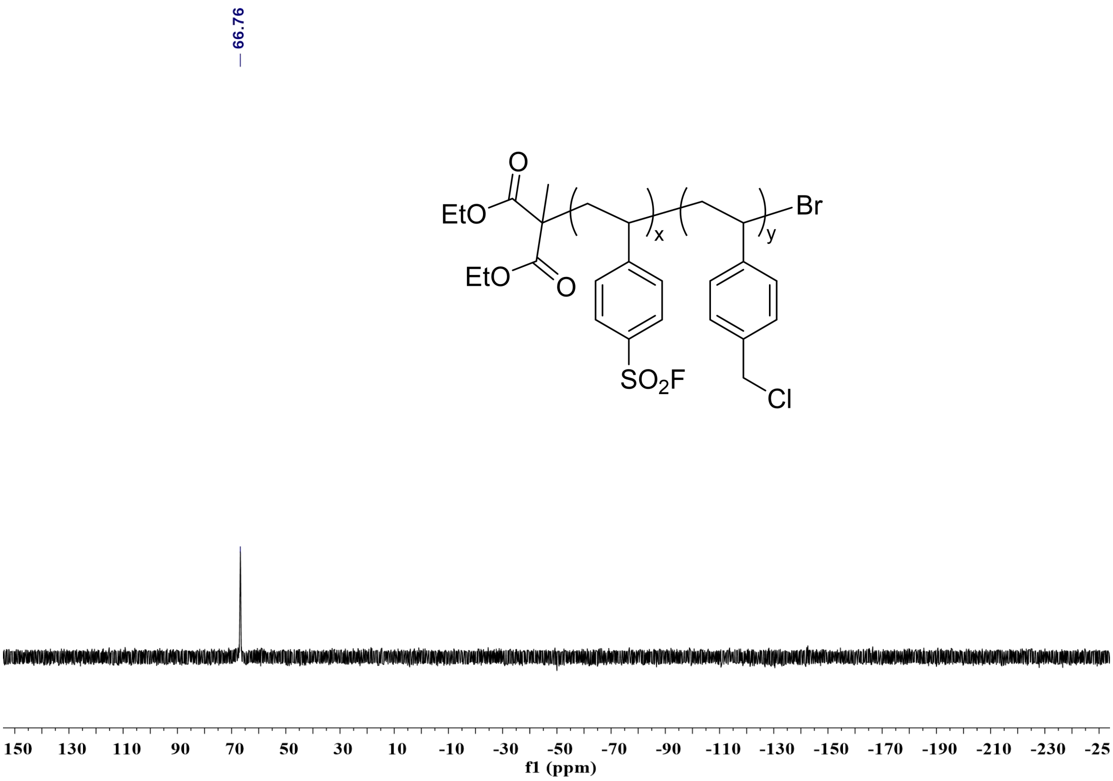


Figure S33. ^{19}F NMR spectrum of poly(VBSF-*co*-StCH$_2$Cl) (in DMSO-*d6*).

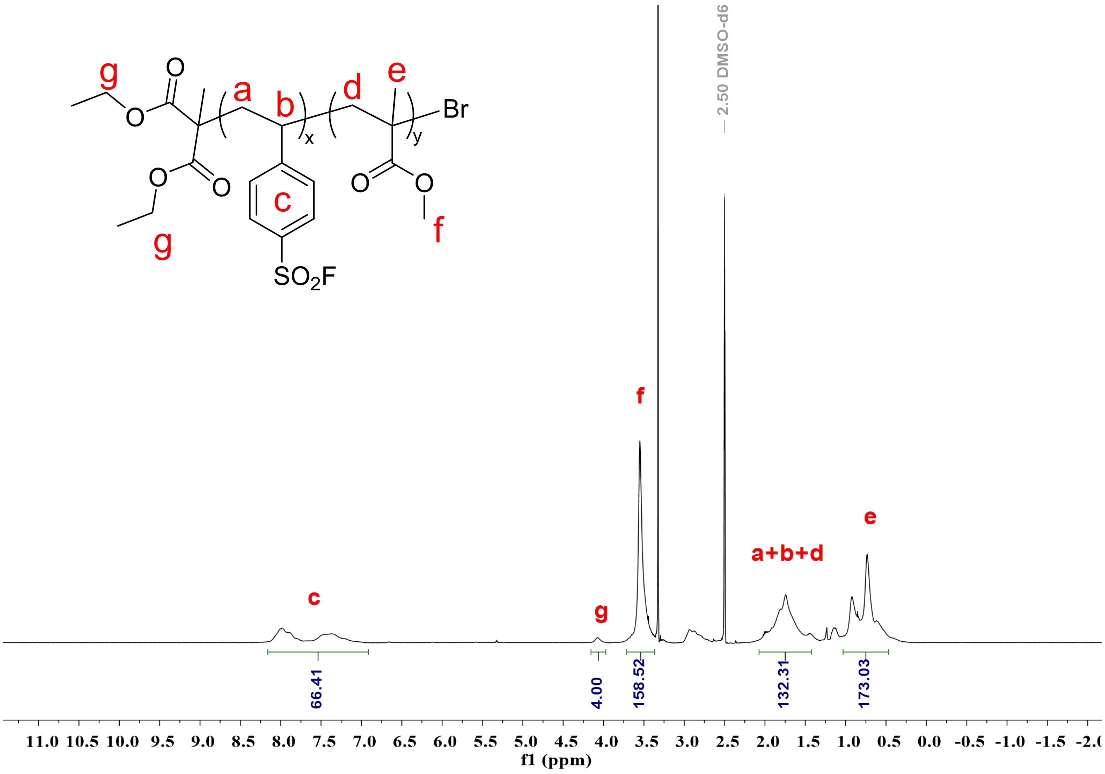


Figure S34. ^{1}H NMR spectrum of poly(VBSF-*co*-MMA), x/y=24/76 (in DMSO-*d6*).

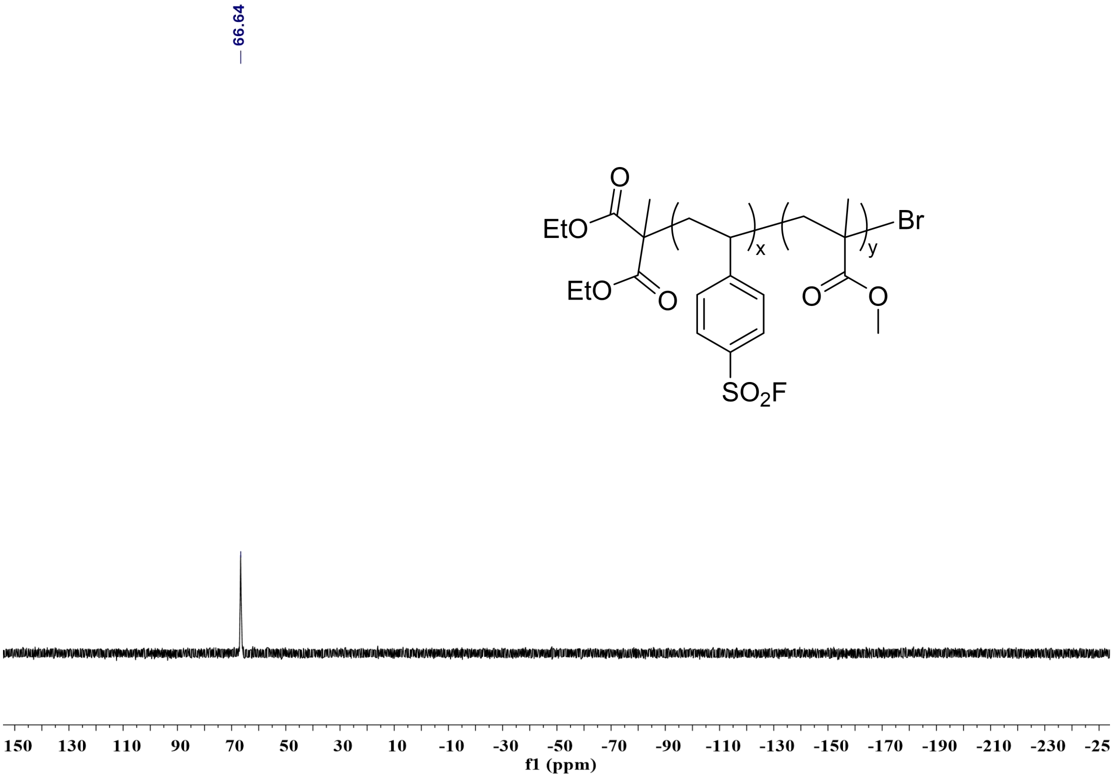


Figure S35. ^{19}F NMR spectrum of poly(VBSF-*co*-MMA) (in DMSO-*d6*).

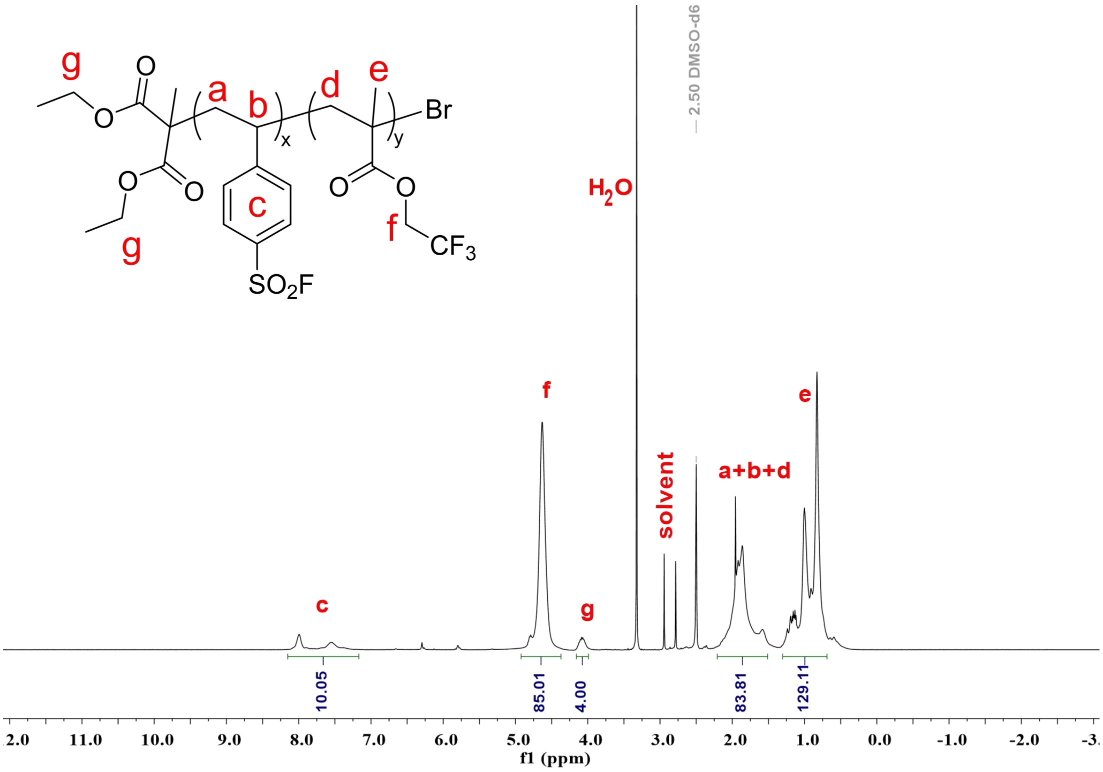


Figure S36. ^{1}H NMR spectrum of poly(VBSF-*co*-TFEMA), x/y=6/94 (in DMSO-*d*6).

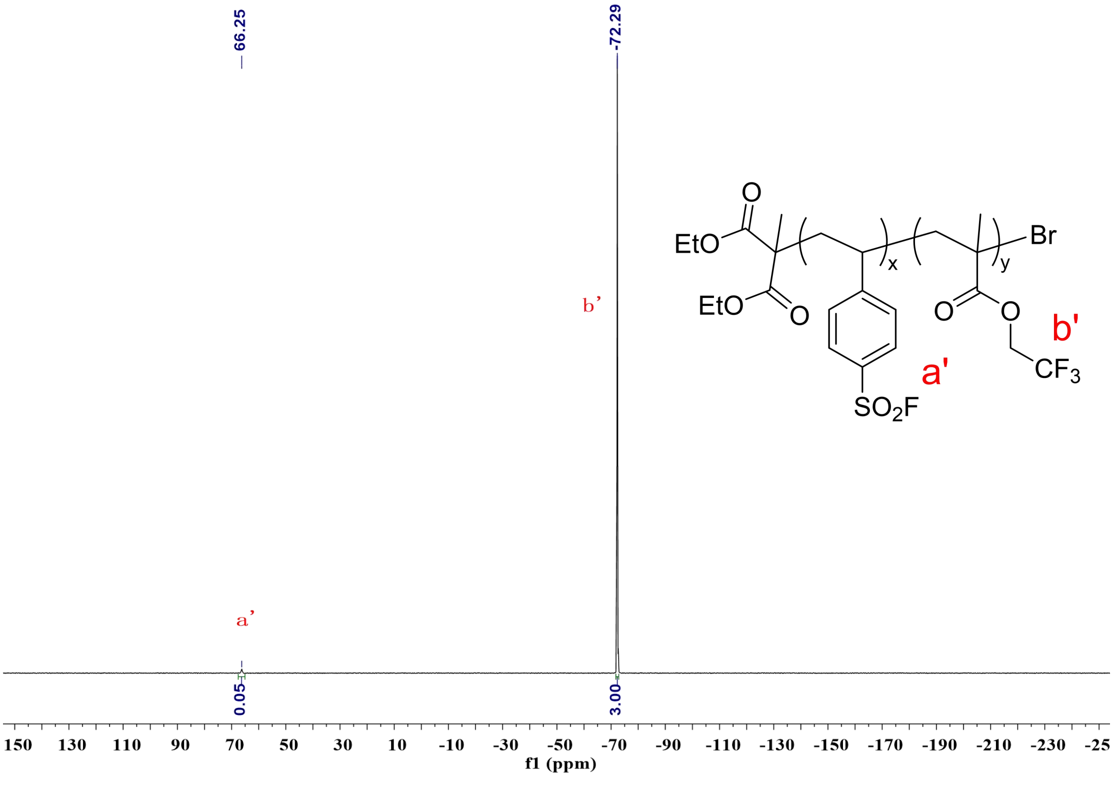


Figure S37. ^{19}F NMR spectrum of poly(VBSF-*co*-TFEMA) (in DMSO-*d*6).

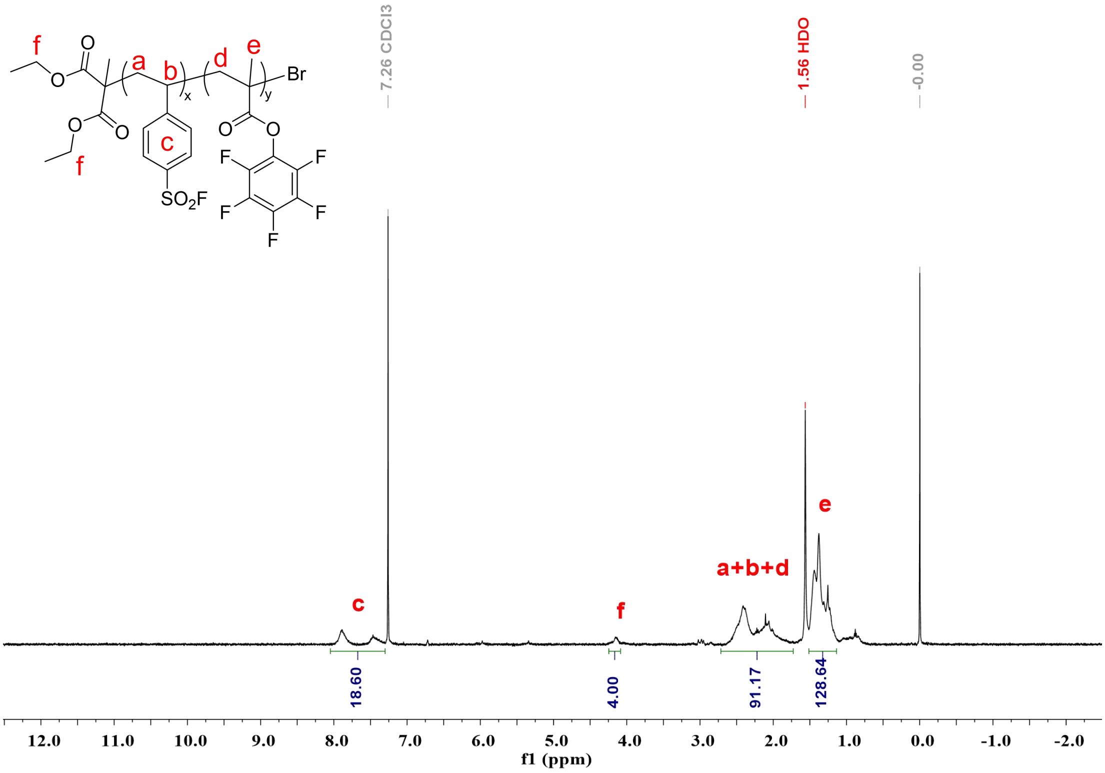


Figure S38. ^{1}H NMR spectrum of poly(VBSF-*co*-PFPMA) (in $CDCl_3$).

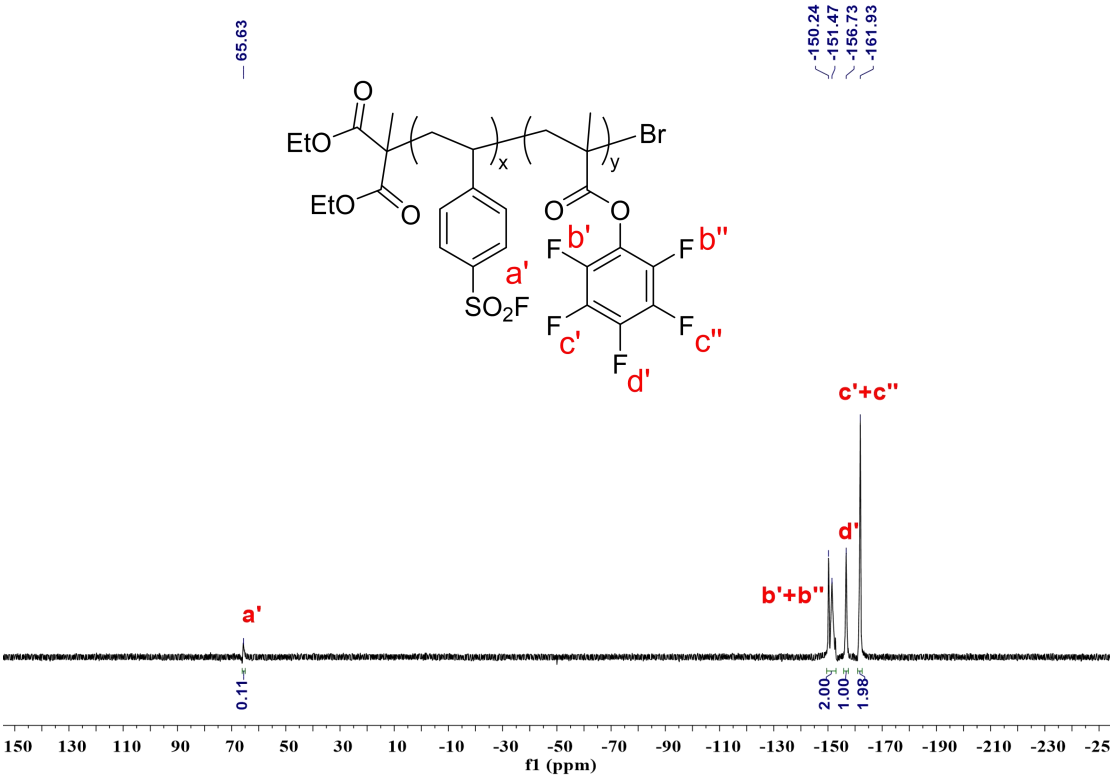


Figure S39. ^{19}F NMR spectrum of poly(VBSF-*co*-PFPMA), x/y=10/90 (in $CDCl_3$).

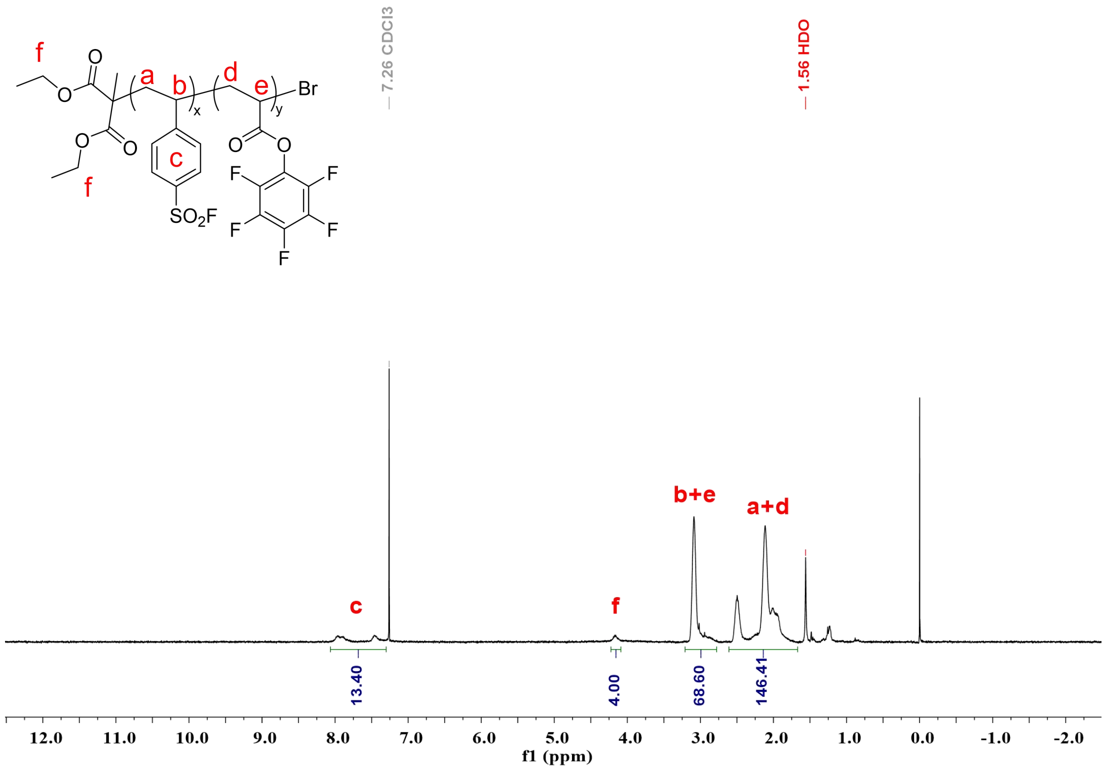


Figure S40. ^{1}H NMR spectrum of poly(VBSF-*co*-PFPA) (in CDCl$_3$).

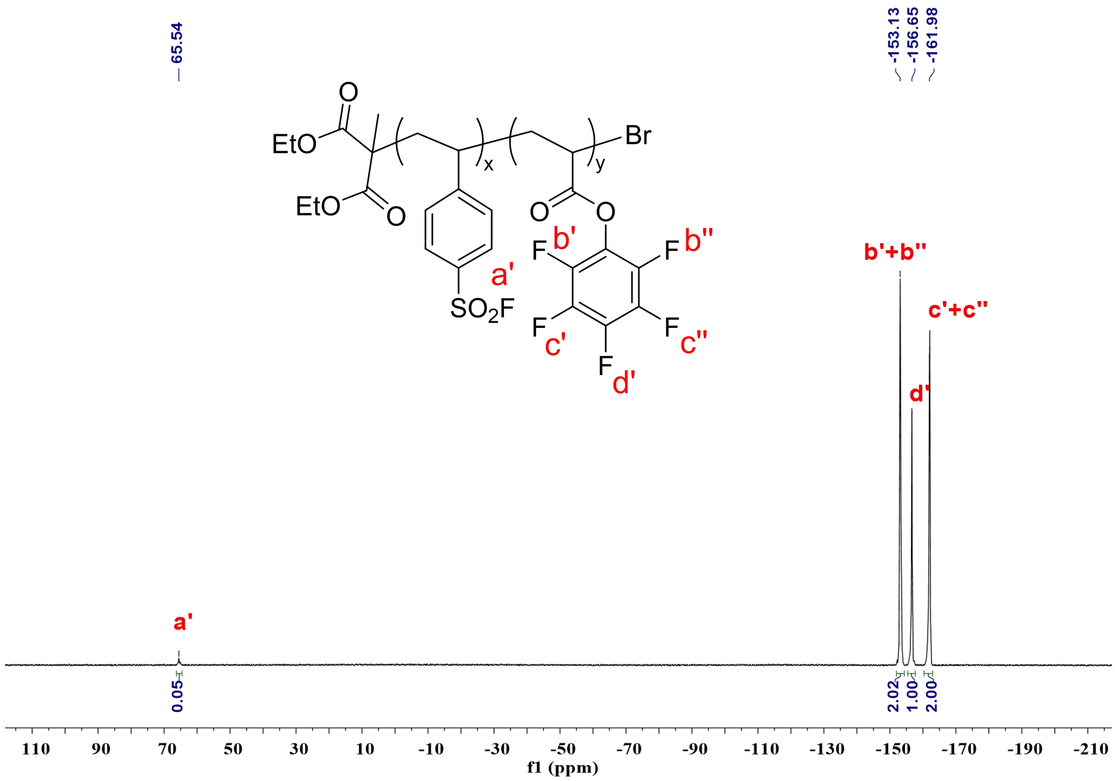


Figure S41. ^{19}F NMR spectrum of poly(VBSF-*co*-PFPA), x/y=5/95 (in CDCl$_3$).

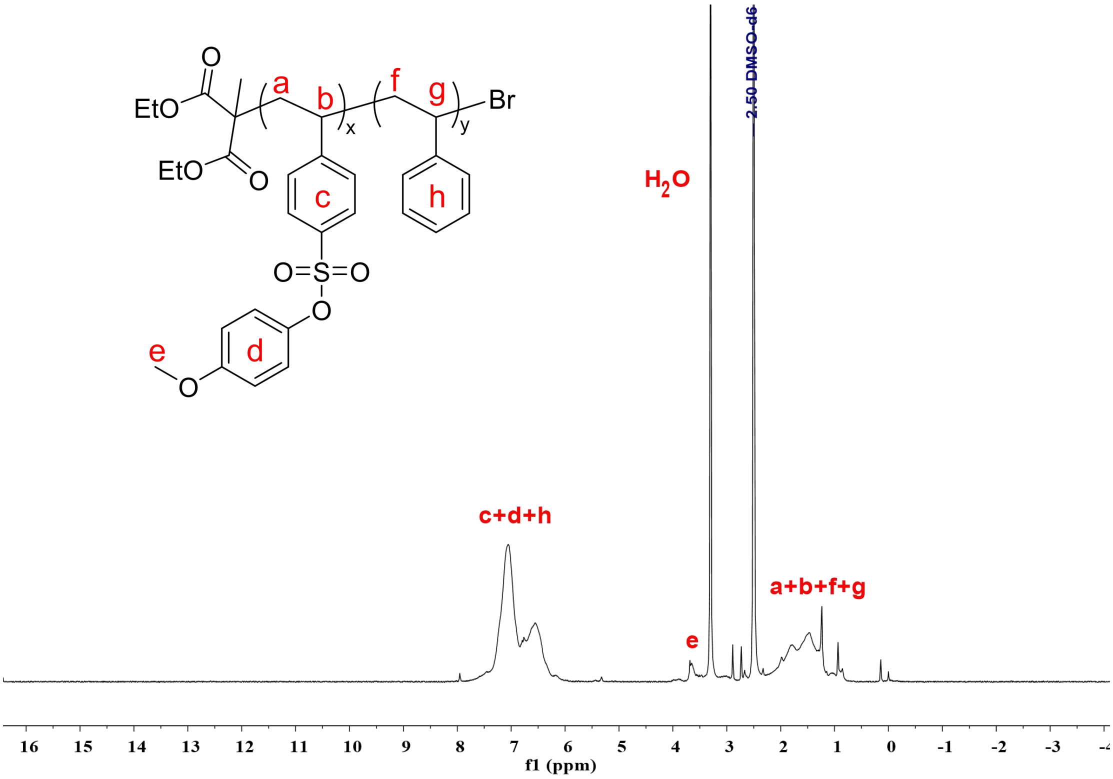


Figure S42. ^{1}H NMR spectrum of Polymer 7 (in DMSO-*d6*), PPM of poly(VBSF-*co*-St).

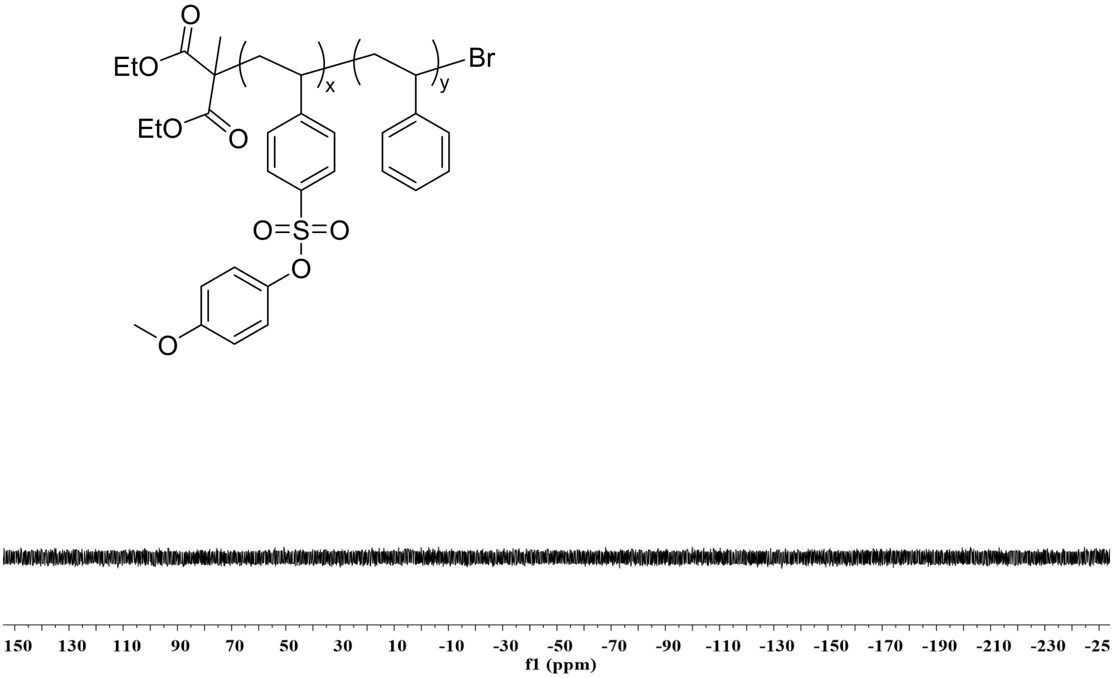


Figure S43. ^{19}F NMR spectrum of Polymer 7 (in DMSO-*d6*), PPM of poly(VBSF-*co*-St).

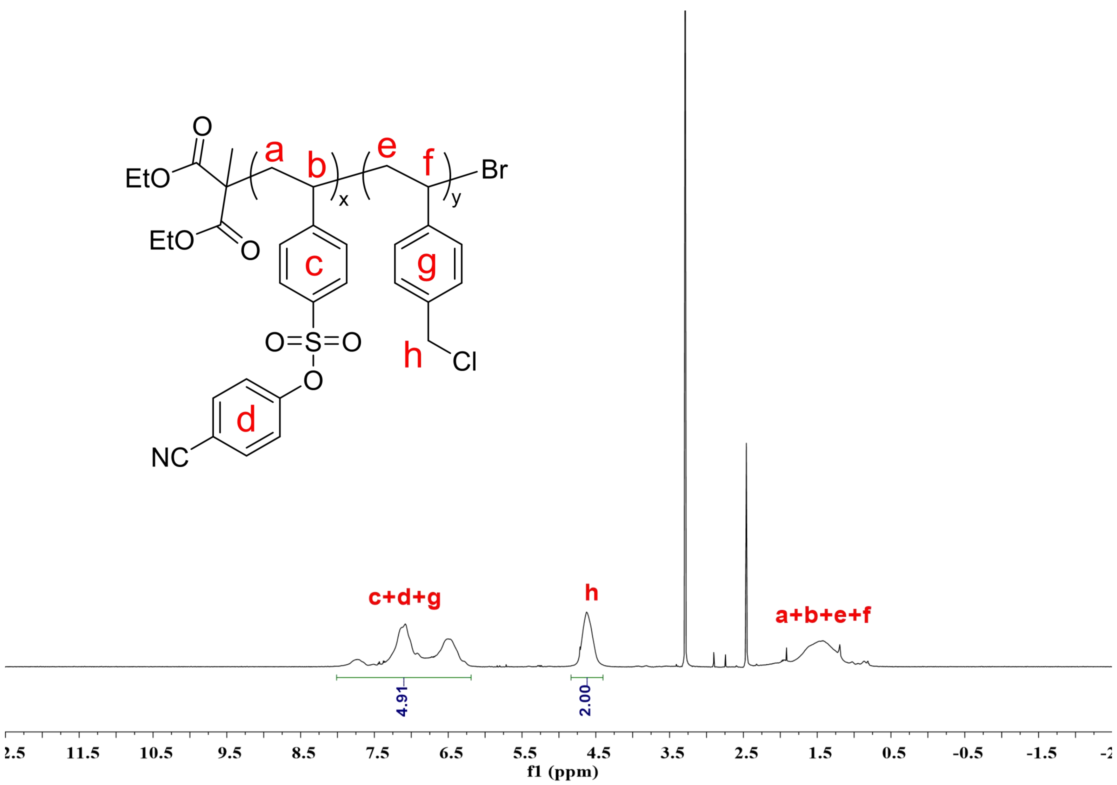


Figure S44. ^{1}H NMR spectrum of Polymer 8 (in DMSO-*d6*), PPM of poly(VBSF-*co*-StCH$_2$Cl).

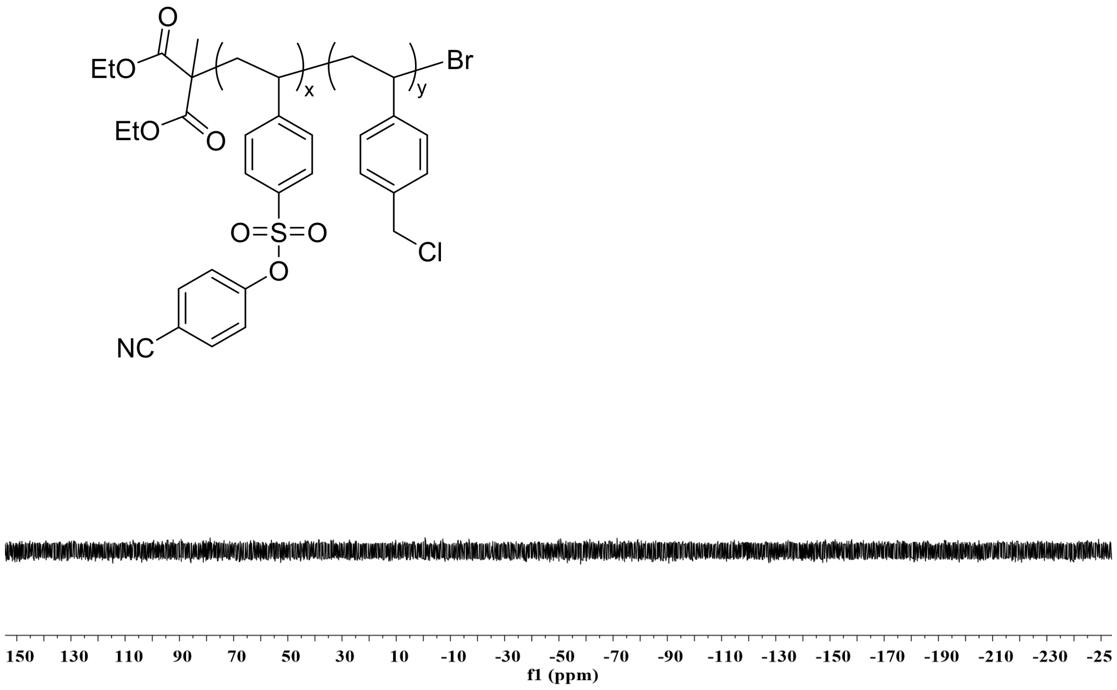


Figure S45. ^{19}F NMR spectrum of Polymer 8 (in DMSO-*d6*), PPM of poly(VBSF-*co*-StCH$_2$Cl).

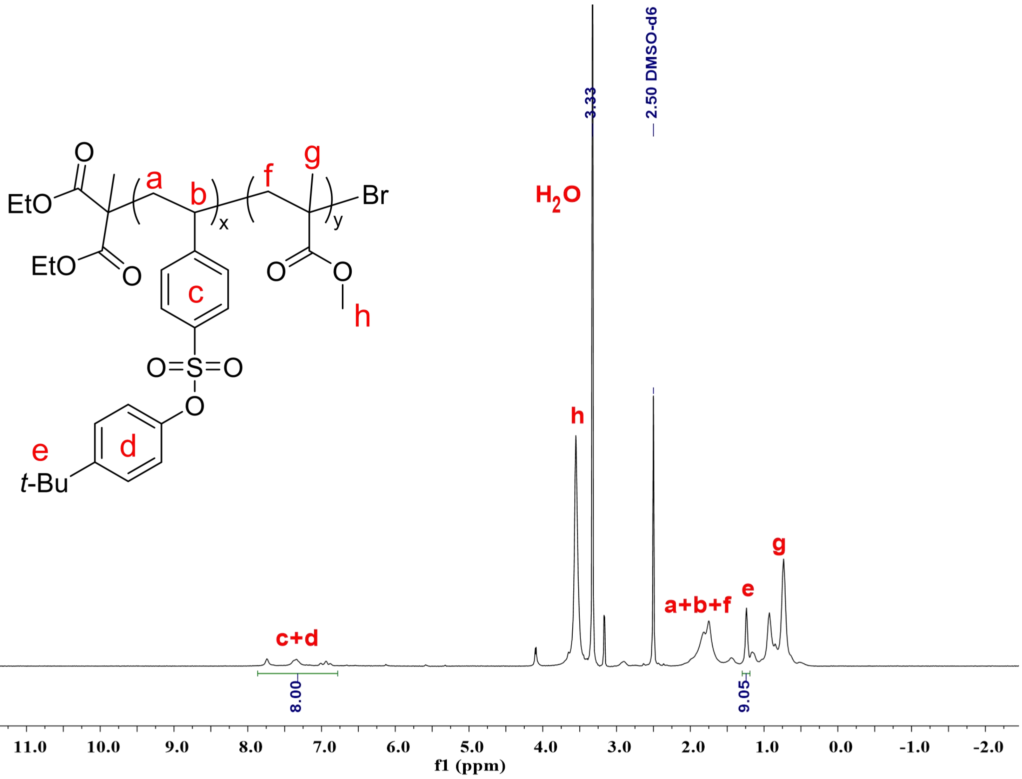


Figure S46. ^{1}H NMR spectrum of Polymer 8 (in DMSO-*d6*), PPM of poly(VBSF-*co*-MMA).

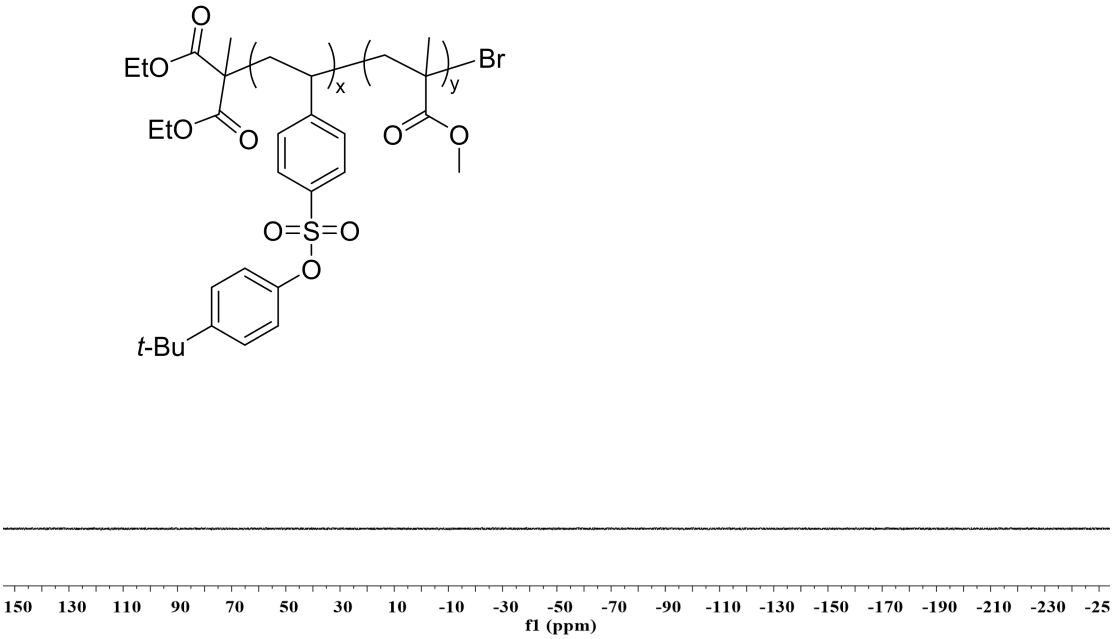


Figure S47. ^{19}F NMR spectrum of Polymer 8 (in DMSO-*d6*), PPM of poly(VBSF-co-MMA).

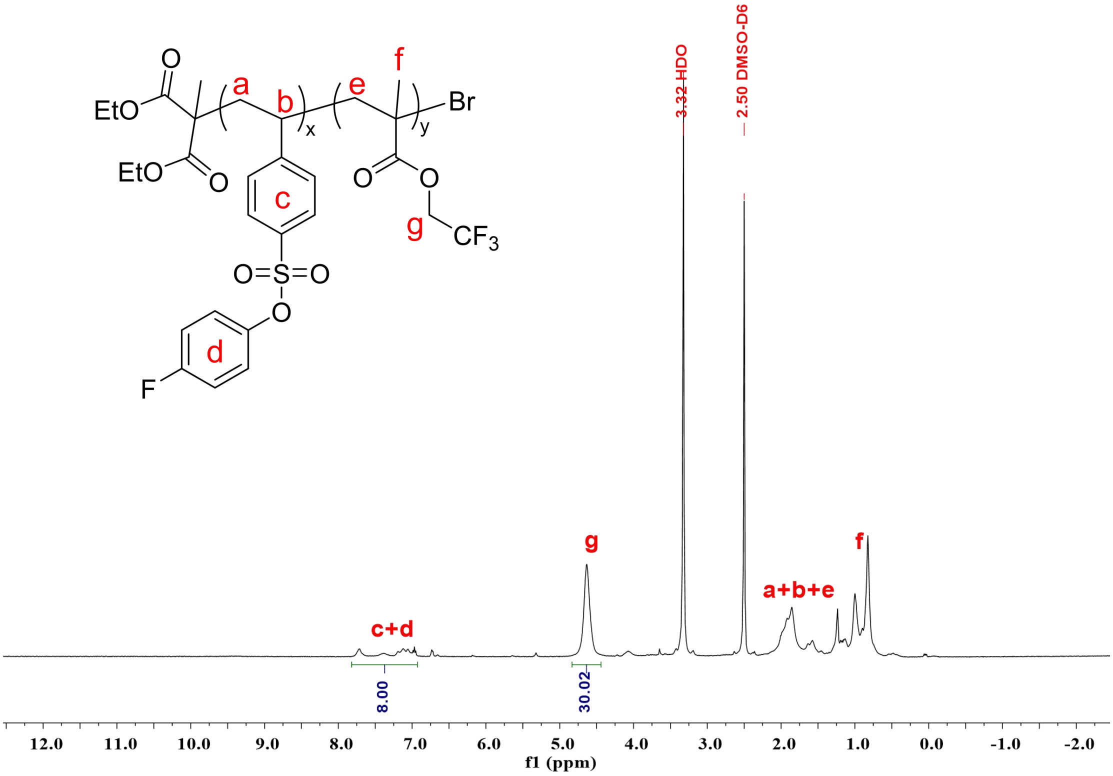


Figure S48. ^{1}H NMR spectrum of Polymer 10 (in DMSO-*d6*), PPM of poly(VBSF-*co*-TFEMA).

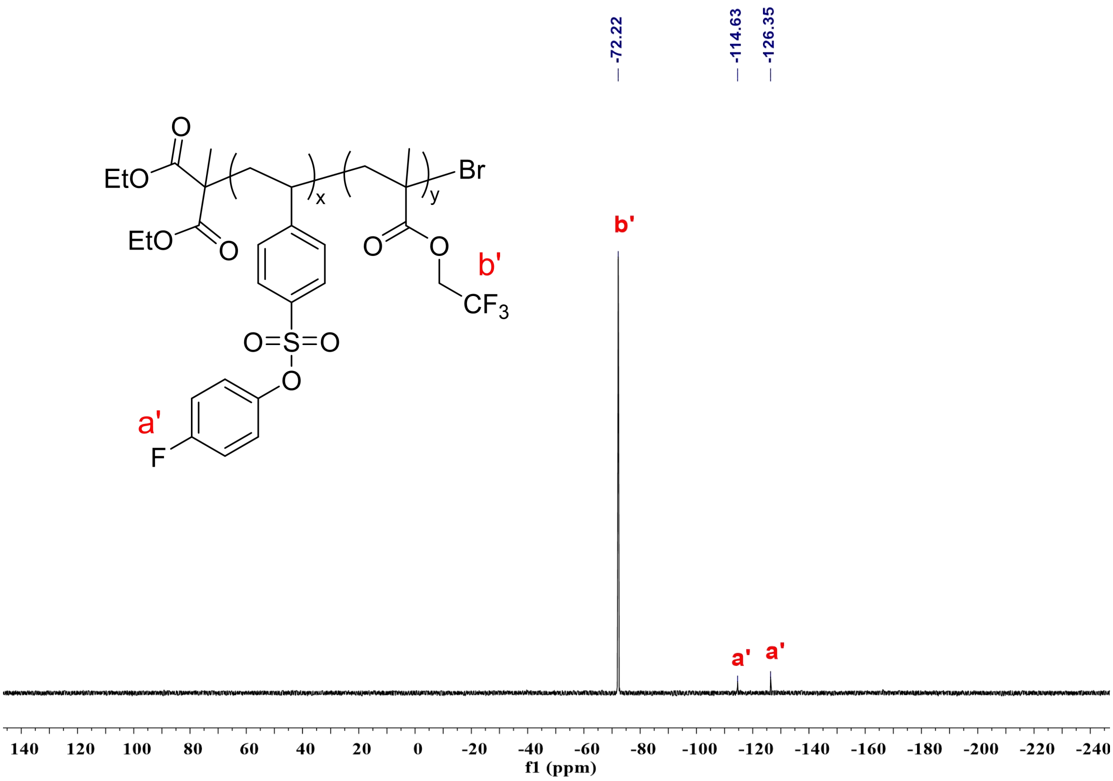


Figure S49. ^{19}F NMR spectrum of Polymer 10 (in DMSO-*d6*), PPM of poly(VBSF-*co*-TFEMA).

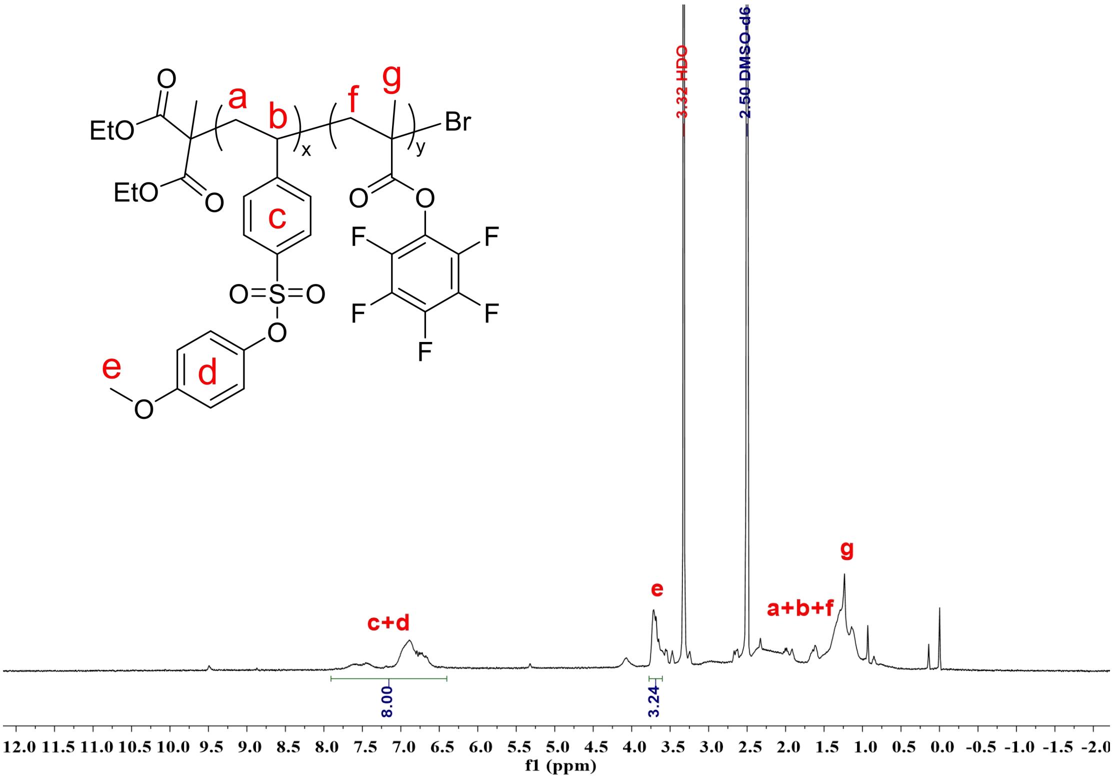


Figure S50. ^{1}H NMR spectrum of Polymer 11 (in DMSO-*d6*), PPM of poly(VBSF-*co*-PFPMA).

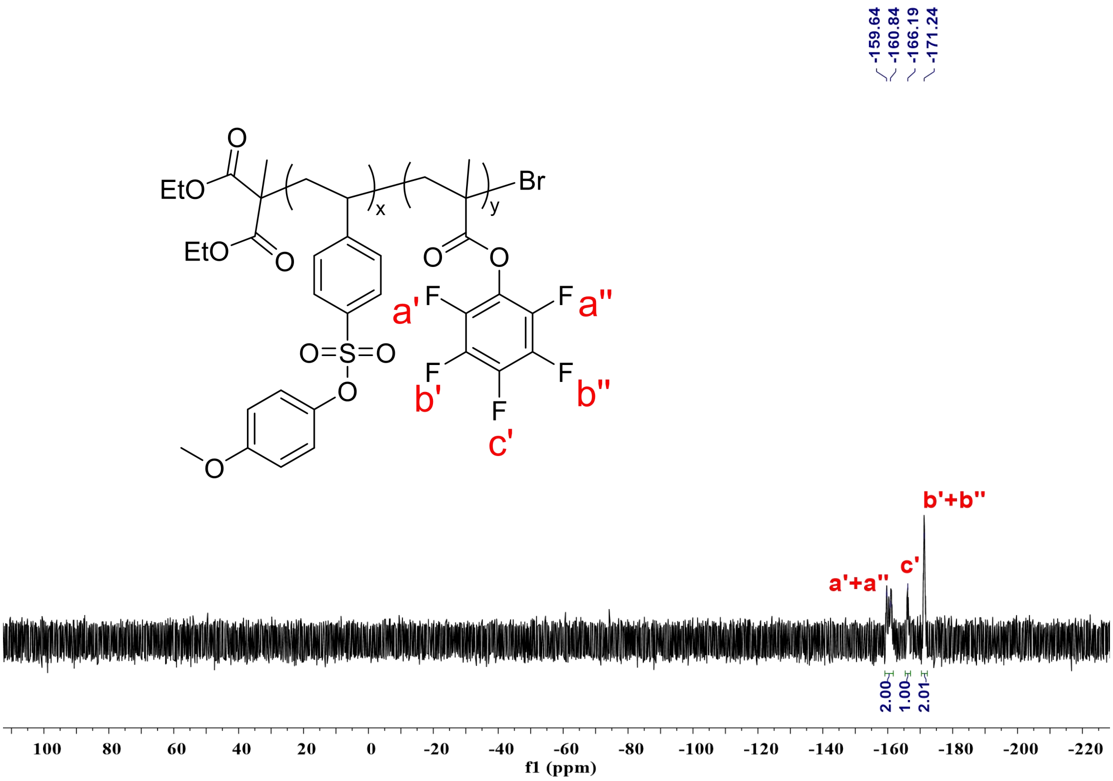


Figure S51. ^{19}F NMR spectrum of Polymer 11 (in DMSO-*d6*), PPM of poly(VBSF-*co*-PFPMA).

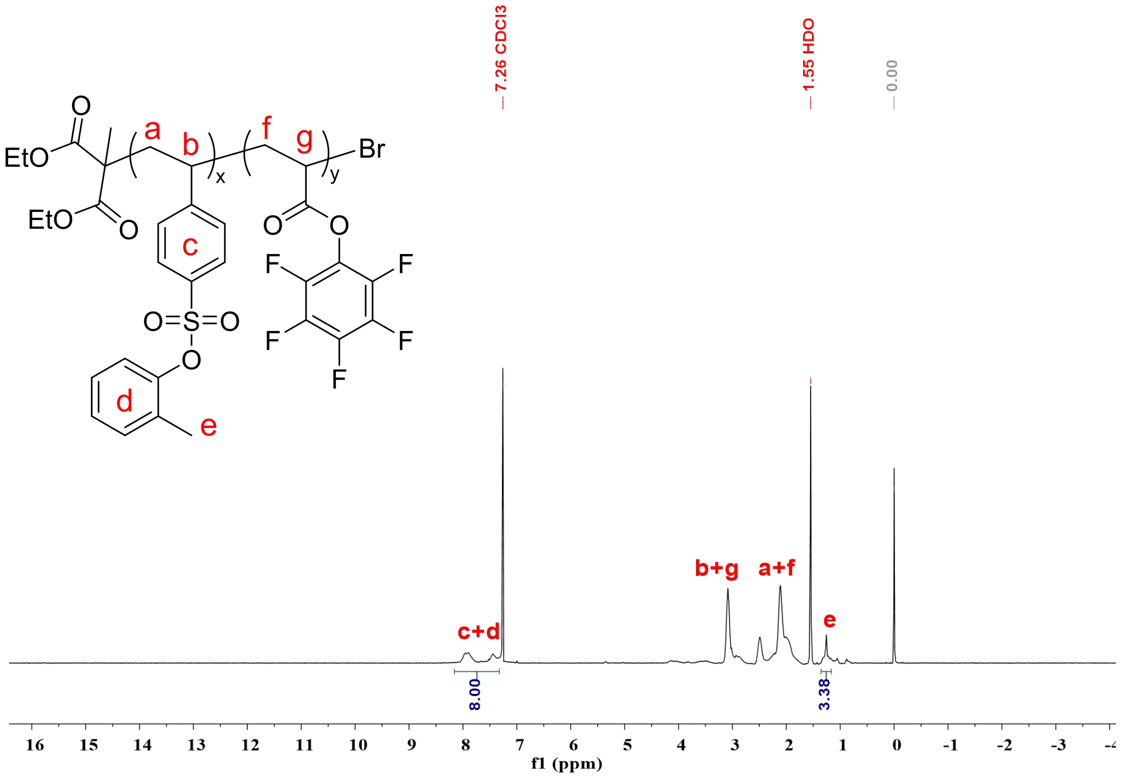


Figure S52. ^{1}H NMR spectrum of Polymer 12 (in $CDCl_3$), PPM of poly(VBSF-*co*-PFPA).

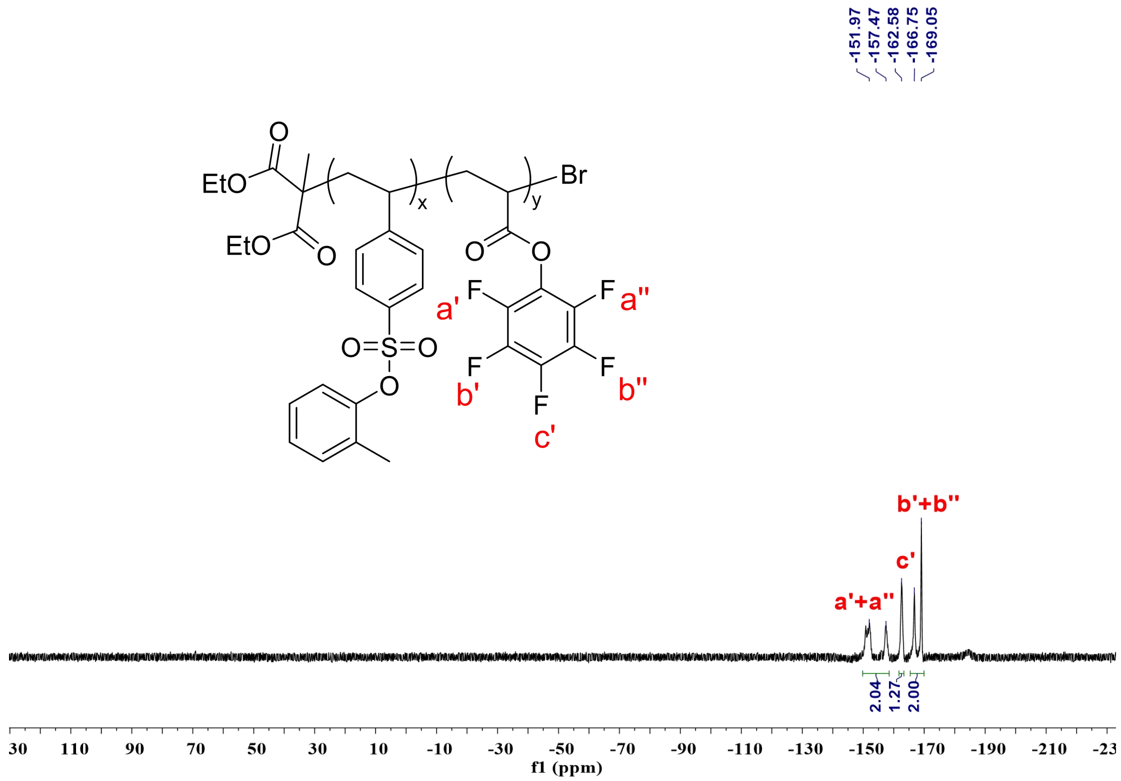


Figure S53. ^{19}F NMR spectrum of Polymer 12 (in $CDCl_3$), PPM of poly(VBSF-*co*-PFPA).

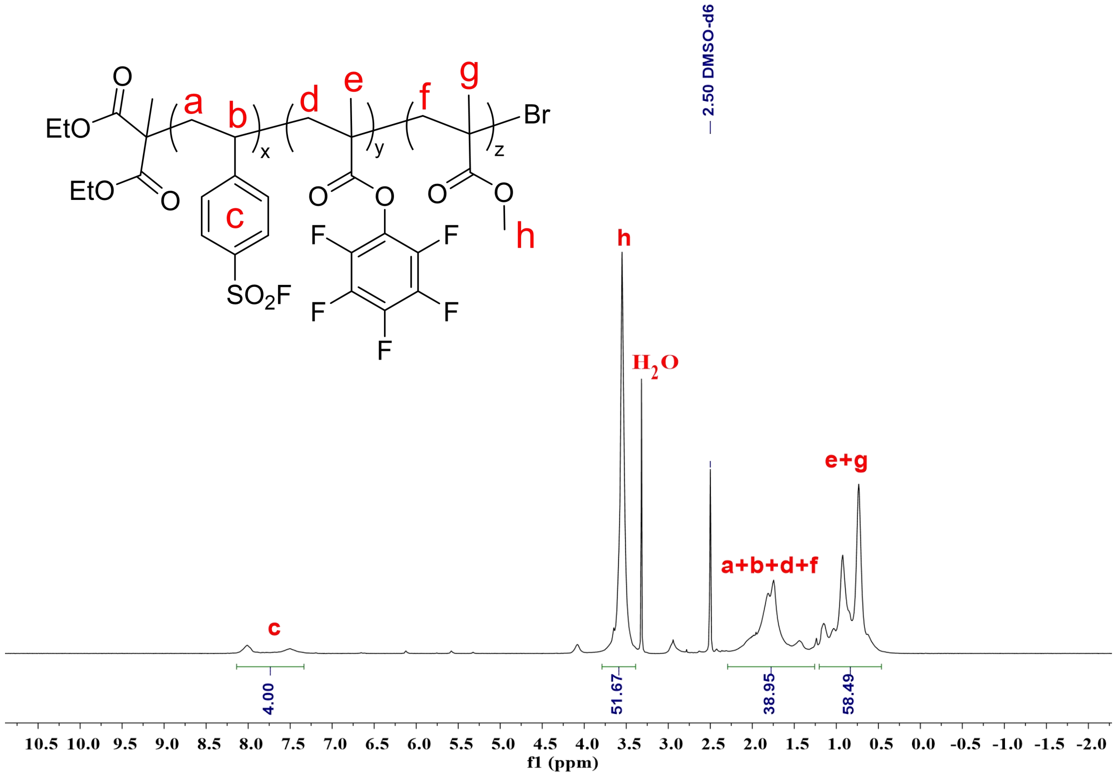


Figure S54. ^{1}H NMR spectrum of poly(VBSF-*co*-PFPMA-*co*-MMA), x/y/z=5/5/90, (in DMSO-*d*6).

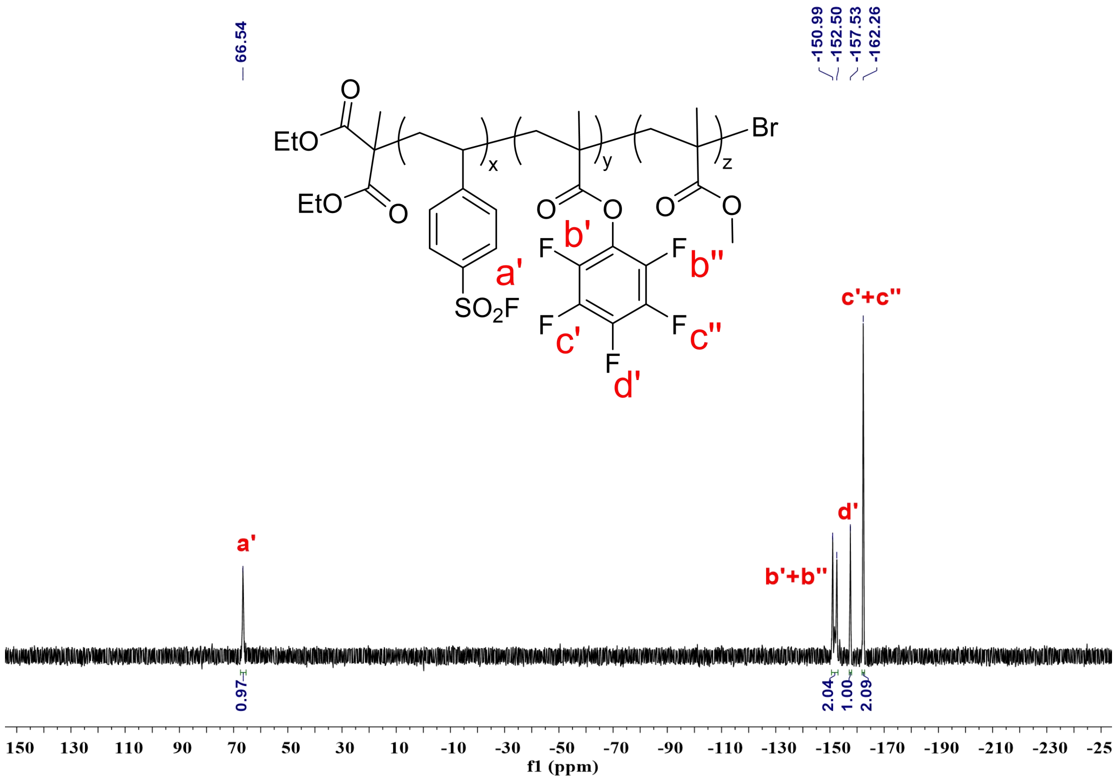


Figure S55. ^{19}F NMR spectrum of poly(VBSF-*co*-PFPMA-*co*-MMA), x/y/z=5/5/90, (in DMSO-*d*6).

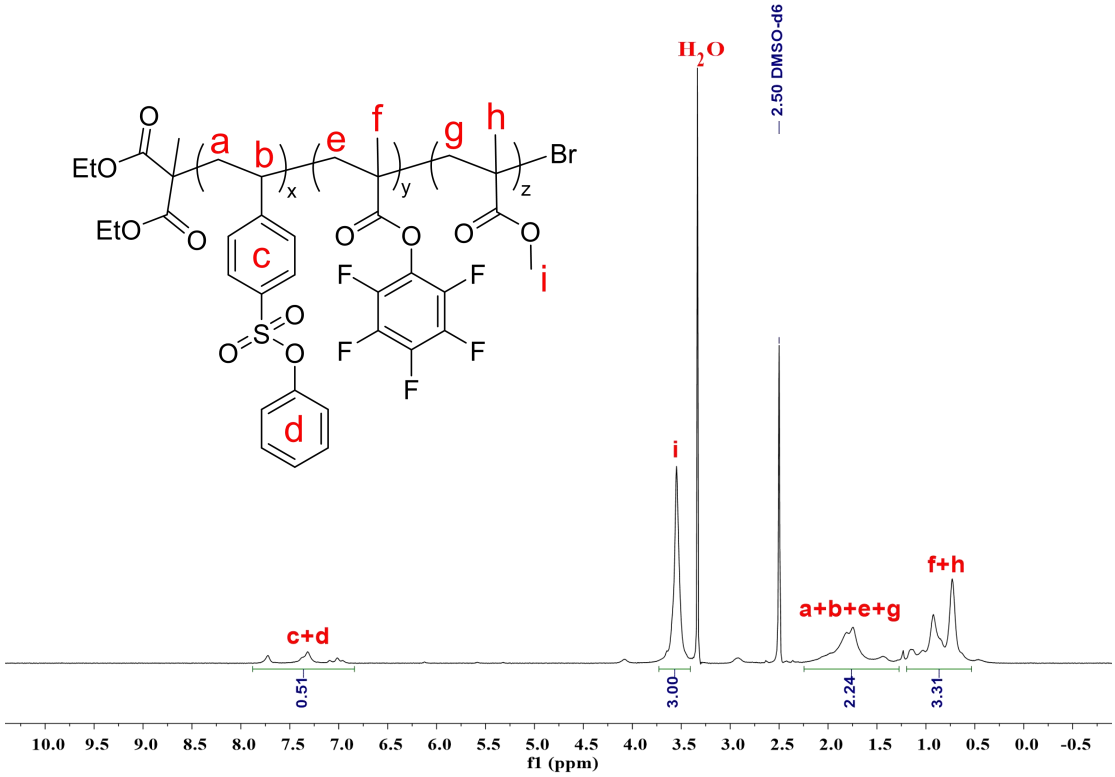


Figure S56. ^{1}H NMR spectrum of Polymer 14 (in DMSO-*d6*).

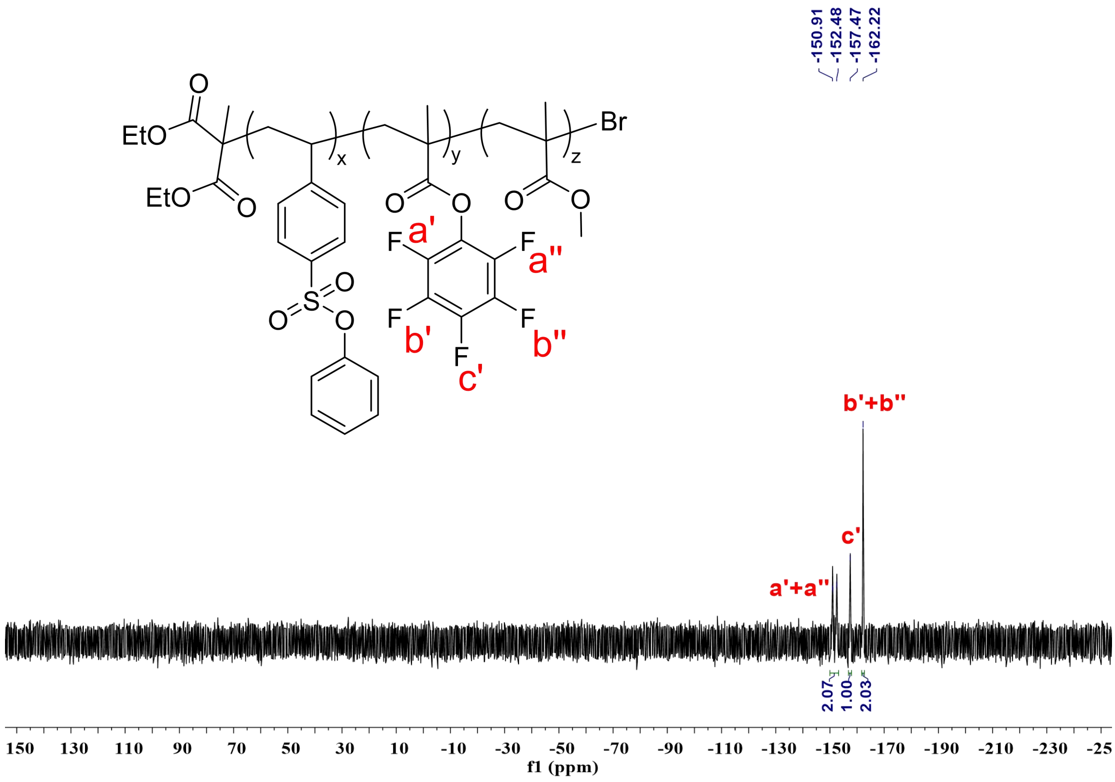


Figure S57. ^{19}F NMR spectrum of Polymer 14 (in DMSO-*d6*).

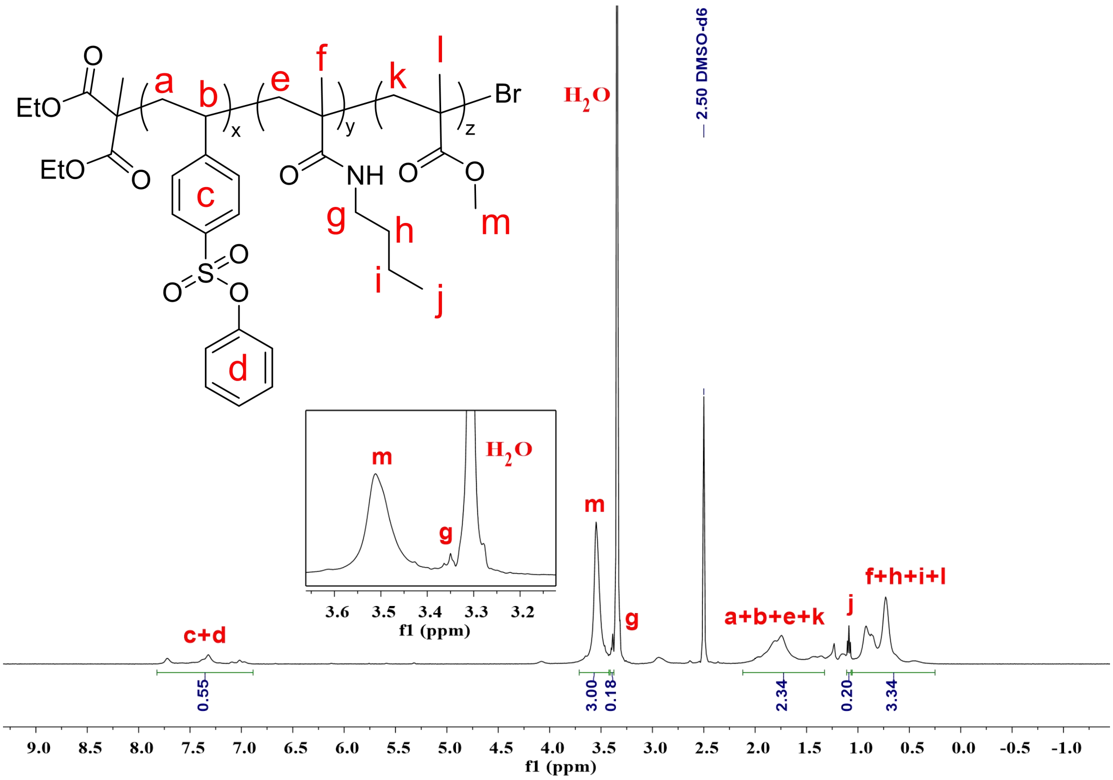


Figure S58. ^{1}H NMR spectrum of Polymer 15 (in DMSO-*d6*).

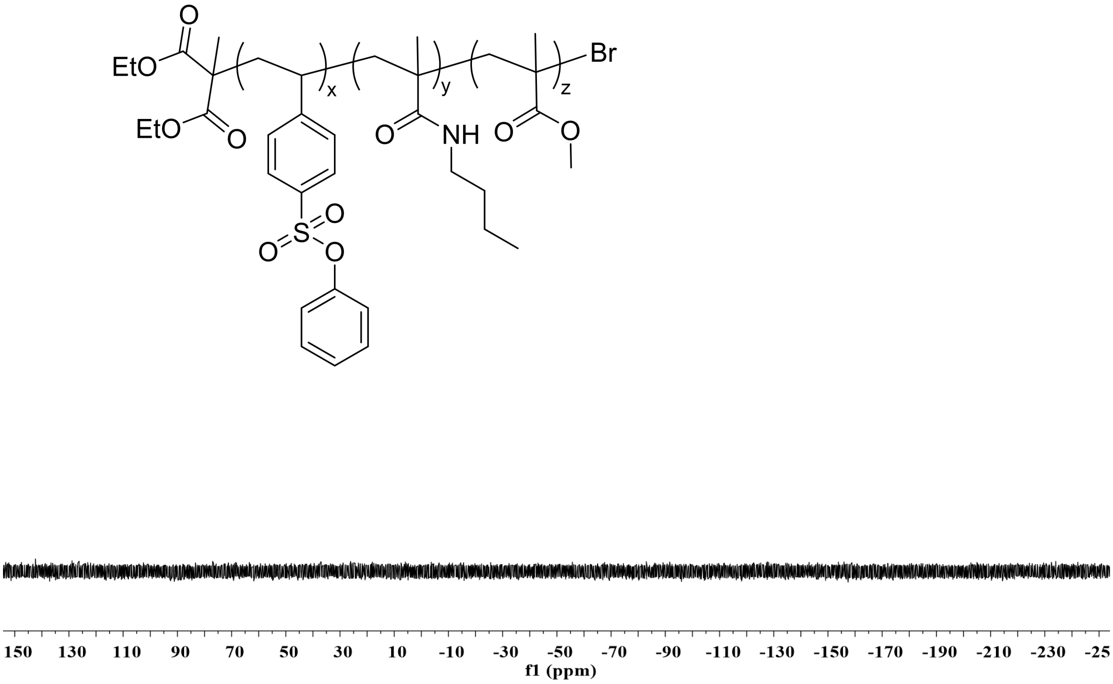


Figure S59. ^{19}F NMR spectrum of Polymer 15 (in DMSO-*d6*).

References

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(2) Jochum, F. D.; Theato, P. Temperature- and Light-Responsive Polyacrylamides Prepared by a Double Polymer Analogous Reaction of Activated Ester Polymers. *Macromolecules* **2009**, *42*, 5941-5945.

(3) Kim, H. T.; Kang, E.; Kim, M.; Joo, J. M. Synthesis of Bidentate Nitrogen Ligands by Rh-Catalyzed C-H Annulation and Their Application to Pd-Catalyzed Aerobic C-H Alkenylation. *Org. Lett.* **2021**, *23*, 3657-3662.