Supporting Information

Synthesis and Cationic Polymerization of Halogen Bonding Vinyl Ether Monomers

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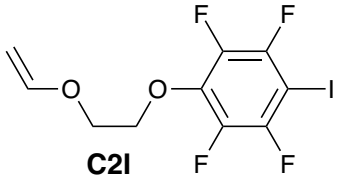
SI 2. Supplemental Experimental

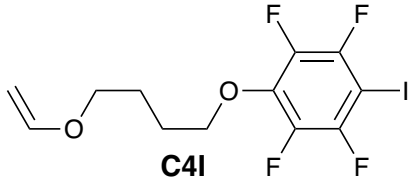
1.1 *Monomer Synthesis*



C2I

2,3,5,6-Tetrafluoro-4-iodophenoxyethyl vinyl ether（C2I）

First, 0.48 g (12 mmol) of sodium hydride (NaH, Aldrich, 60% dispersion in mineral oil) was placed in a 300 mL round bottom flask and washed with approximately 2 mL hexane (Wako Guaranteed Reagent, >96 %) three times. Next, 80 mL of tetrahydrofuran (THF, Wako Guaranteed Reagent, 99.5%, stabilizer: 2,6-di-*tert*-butyl-4-methylphenol about 0.03%) was added to the flask and the solution was cooled to -10 ˚C. Once cool, 1.80 mL (20 mmol) of ethylene glycol monovinyl ether (EGVE, TCI, >98.0%, stabilized with KOH) was added to the round bottom flask via a dry syringe and stirred for an additional 1.5 hours. Then 1.33 mL (10 mmol) of pentafluoroiodobenzene (TCI, >99.0%, stabilized with copper chip) was added and stirred for 10 minutes. After this the temperature was raised to room temperature and it was left to react overnight. Approximately 150 mL of diethyl ether (Wako 1st Grade, >99%) was added to the resulting supernatant and washed once with water and then 3 times with 10 wt% sodium hydroxide solution (formed using NaOH Wako 1st Grade, 93% and purified water). After drying the, monomers were purified with silica gel chromatography (Wakogel® C-300) using hexane as an eluent.

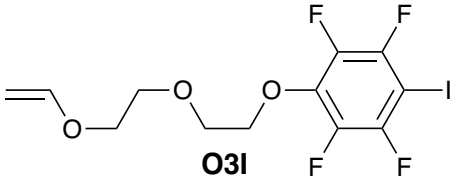


C4I

2,3,5,6-Tetrafluoro-4-iodophenoxybutyl vinyl ether (C4I)

First, 1.60 g (40 mmol) of NaH was placed in a 300 mL round bottom flask and washed with approximately 2 mL hexane three times. Next, 150 mL of THF was added to the flask and the solution was cooled to -10 ˚C. Once cool, 4.89 mL (40 mmol) of tetramethylene glycol monovinyl ether (TGVE, TCI, >97.0%, stabilized with KOH) was added to the round bottom flask via a dry

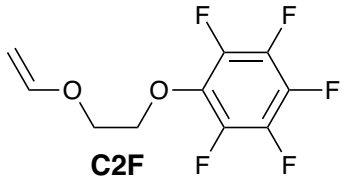
syringe and stirred for an additional hour. After this, 5.32 mL (40 mmol) of pentafluoroiodobenzene was added and stirred for 10 minutes. After this the temperature was raised to room temperature and it was left to react overnight. Approximately 150 mL of diethyl ether was added to the resulting supernatant and washed once with water and then 3 times with 10 wt% NaOH solution. After drying the, monomers were purified with silica gel chromatography using hexane as an eluent.



O3I

2-(2,3,5,6-Tetrafluoro-4-iodophenoxyethoxy)ethyl vinyl ether (O3I)

First, 1.60 g (40 mmol) of NaH was placed in a 300 mL round bottom flask and washed with approximately 2 mL hexane three times. Next, 150 mL of THF was added to the flask and the solution was cooled to -10 ˚C. Once cool, 5.13 mL (40 mmol) of diethylene glycol monovinyl ether (DGVE, TCI, >96.0%, stabilized with KOH) was added to the round bottom flask via a dry syringe and stirred for an additional hour. After this, 5.32 mL (40 mmol) of pentafluoroiodobenzene was added and stirred for 10 minutes. After this the temperature was raised to room temperature and it was left to react overnight. Approximately 150 mL of diethyl ether was added to the resulting supernatant and it was washed once with water and then 3 times with a 10 wt% NaOH solution and then two more times with pure water. After drying the, monomers were purified with silica gel chromatography using either hexane or hexane/ethyl acetate (Wako 1st Grade, >99%) 200:1 v/v as an eluent.

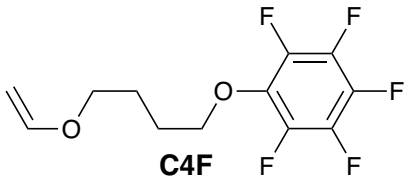


C2F

Pentafluorophenoxyethyl vinyl ether (C2F)

First, 1.60 g (40 mmol) of NaH was placed in a 300 mL round bottom flask and washed with approximately 2 mL hexane three times. Next, 150 mL of THF was added to the flask and the

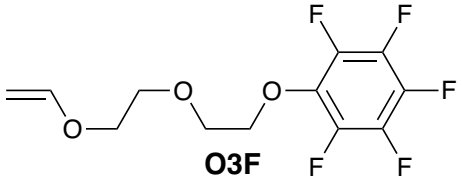
solution was cooled to -10 ˚C. Once cool, 4.88 mL (40 mmol) of ethylene glycol monovinyl ether was added to the round bottom flask via a dry syringe and stirred for an additional hour. After this, 4.60 mL (40 mmol) of hexafluorobenzene (Aldrich, 99.0%) was added and stirred for 10 minutes. After this the temperature was raised to room temperature and it was left to react overnight. Approximately 150 mL of diethyl ether was added to the resulting supernatant and was washed once with water and then 3 times with a 10 wt% NaOH solution and then three more times with pure water. After drying the, monomers were purified with silica gel chromatography using hexane/ethyl acetate 250:1 v/v as an eluent.



C4F

Pentafluorophenoxybutyl vinyl ether (C4F)

First, 0.80 g (20 mmol) of NaH was placed in a 300 mL round bottom flask and washed with approximately 2 mL hexane three times. Next, 75 mL of THF was added to the flask and the solution was cooled to -10 ˚C. Once cool, 2.44 mL (20 mmol) of tetramethylene glycol monovinyl ether was added to the round bottom flask via a dry syringe and stirred for an additional hour. After this, 2.30 mL (20 mmol) of hexafluorobenzene was added and stirred for 90 minutes. After this the temperature was raised to room temperature and it was left to react overnight. Approximately 150 mL of diethyl ether was added to the resulting supernatant and was washed once with water and then 3 times with 10 wt% NaOH and then three more times with pure water. After drying the, monomers were purified with silica gel chromatography using hexane/ethyl acetate 250:1 v/v as an eluent.



O3F

2-(Pentafluorophenoxyethoxy)ethyl vinyl ether (O3F)

First, 0.80 g (20 mmol) of NaH was placed in a 300 mL round bottom flask and washed with approximately 2 mL hexane three times. Next, 75 mL of THF was added to the flask and the

solution was cooled to -10 ˚C. Once cool, 2.44 mL (20 mmol) of diethylene glycol monovinyl ether was added to the round bottom flask via a dry syringe and stirred for an additional hour. After this, 2.30 mL (20 mmol) of hexafluorobenzene was added and stirred for 10 minutes. After this the temperature was raised to room temperature and it was left to react overnight. Approximately 150 mL of diethyl ether was added to the resulting supernatant and was washed once with water and then 3 times with 10 wt% NaOH and then 2 more times with pure water. After drying the, monomers were purified with silica gel chromatography using hexane/ethyl acetate 250:1 v/v as an eluent.

1.2 Infrared (IR) Measurements

Infrared (IR) spectra were measured using a JASCO FT/IR-4600 spectrometer equipped with an ATR-PRO-ONE attachment and a PKS-D1 diamond stage. When investigating the interactions in the mixture of two compounds, samples in the desired molar ratio were first dissolved in a common solvent and then allowed to dry together.

SI 2. NMR Spectra of Monomers (^{1}H NMR, ^{13}C NMR and ^{19}F NMR)

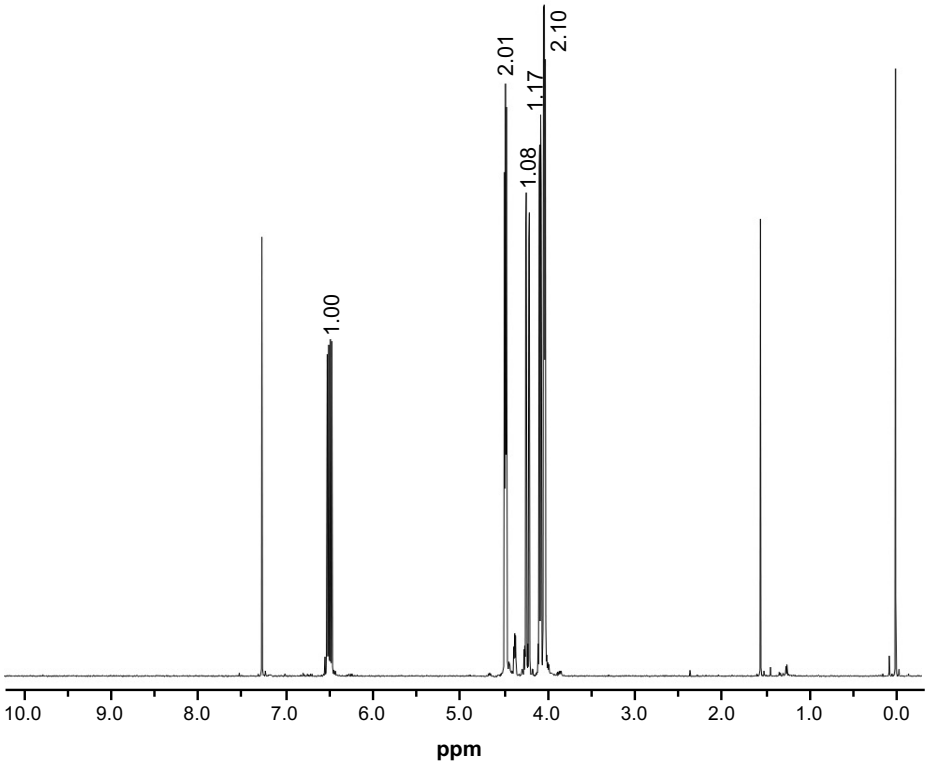


Figure S1. ^{1}HNMR spectra of monomer **C2I** in $CDCl_3$ (TMS standard). Integration values are shown.

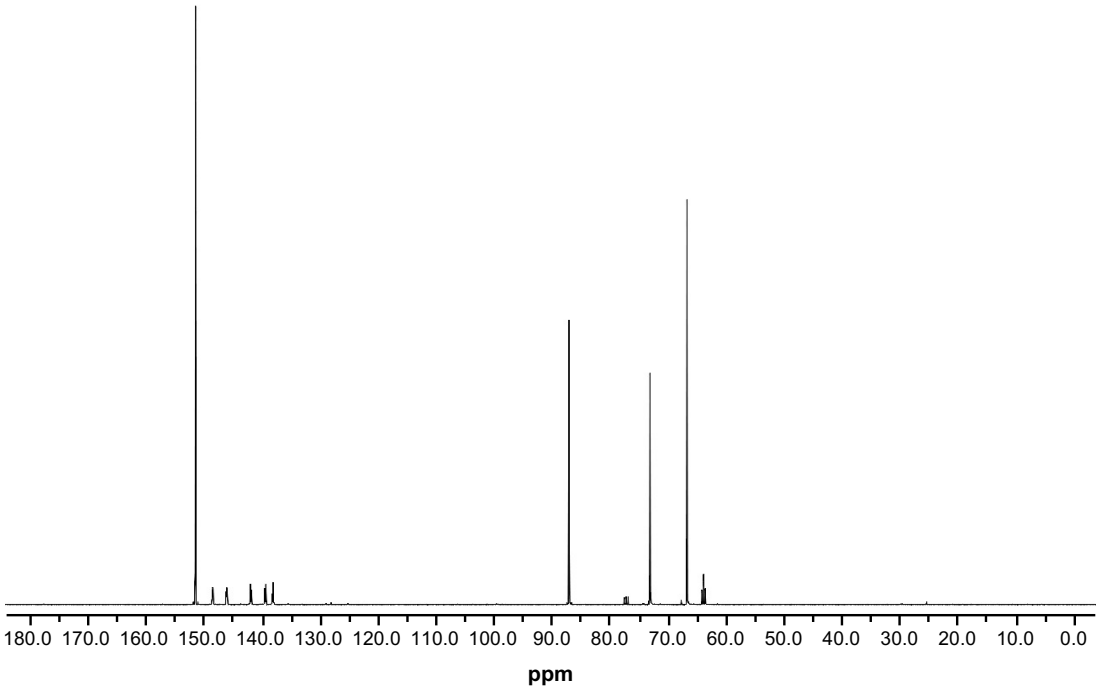


Figure S2. ^{13}CNMR spectra of monomer **C2I** in $CDCl_3$.

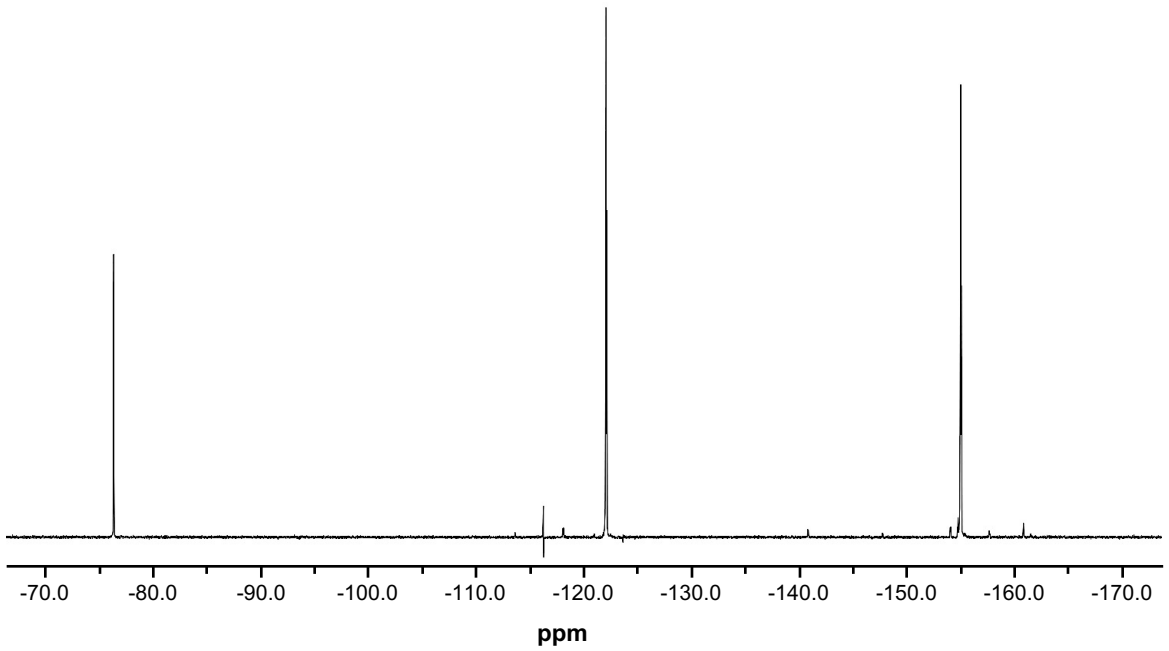


Figure S3. [19]FNMR spectra of monomer **C2I** in chloroform with trifluoroacetic acid (-76.5 ppm) as the internal standard.

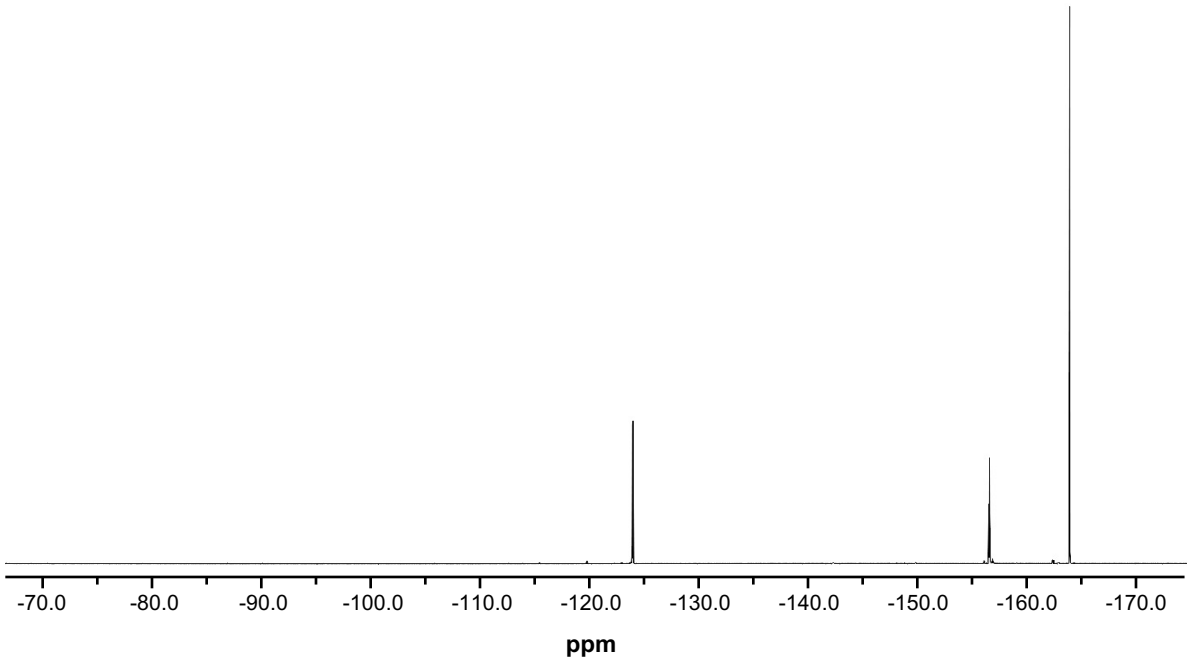


Figure S4. [19]FNMR spectra of monomer **C2I** in toluene with hexafluorobenzene (-163.9 ppm) as the internal standard.

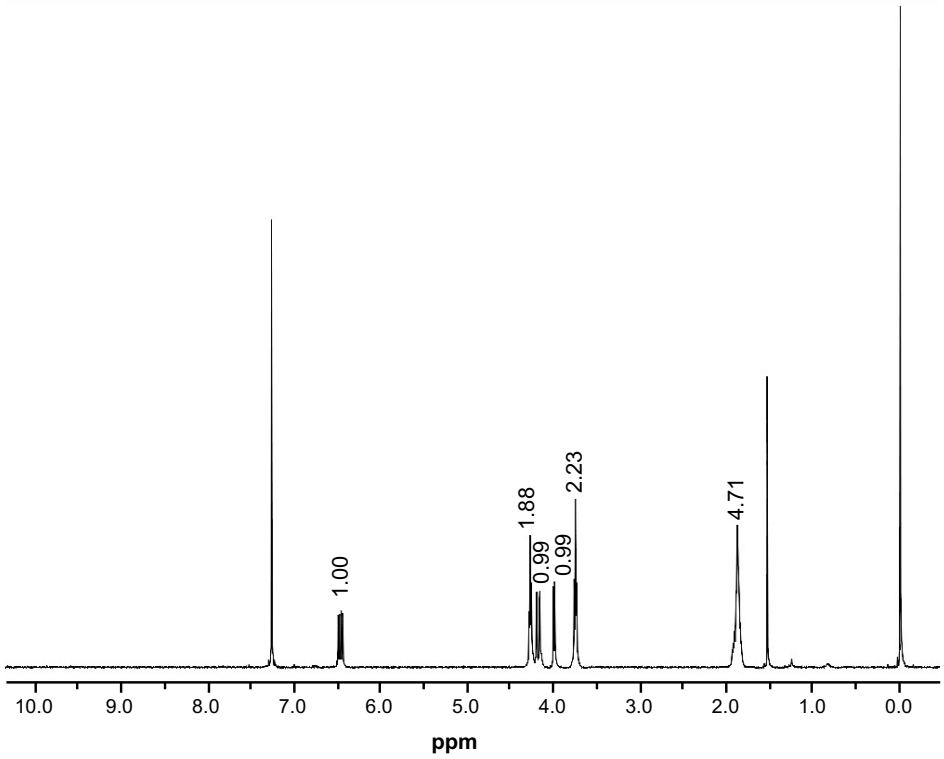


Figure S5. ^{1}HNMR spectra of monomer **C4I** in $CDCl_3$ (TMS standard). Integration values are shown.

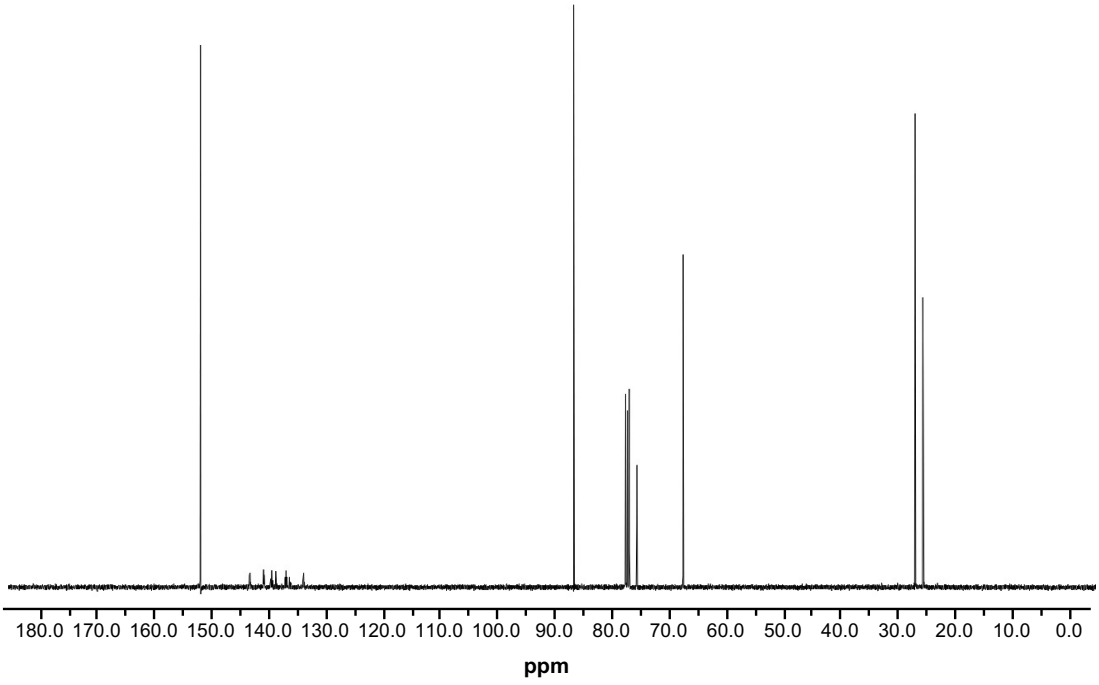


Figure S6. ^{13}CNMR spectra of monomer **C4I** in $CDCl_3$.

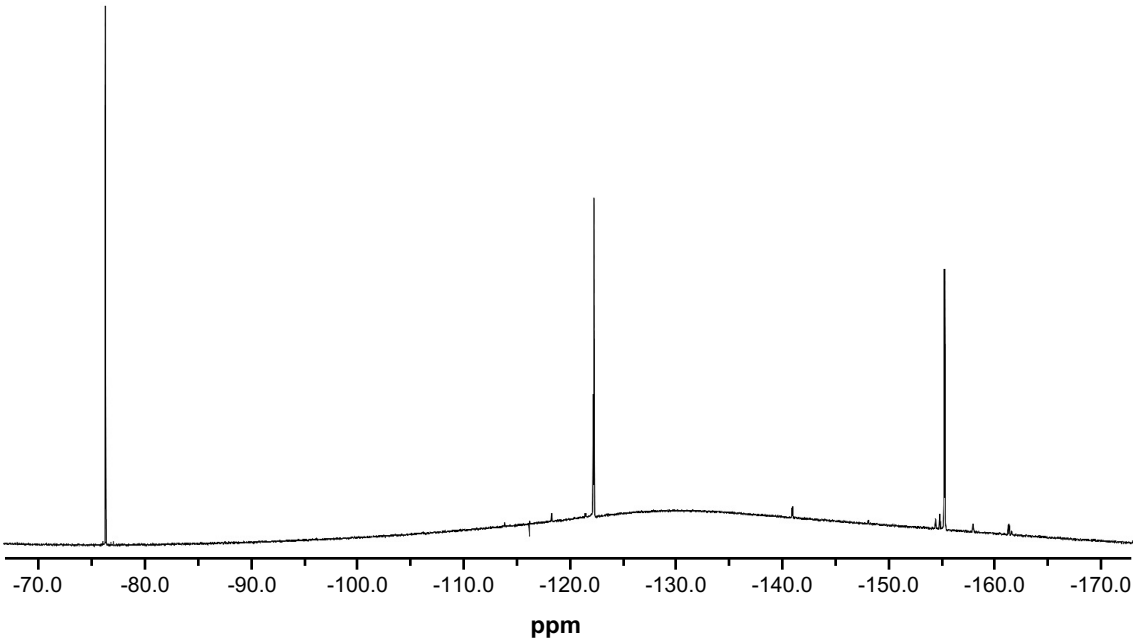


Figure S7. ^{19}FNMR spectra of monomer **C4I** in chloroform with trifluoroacetic acid (-76.5 ppm) as the internal standard.

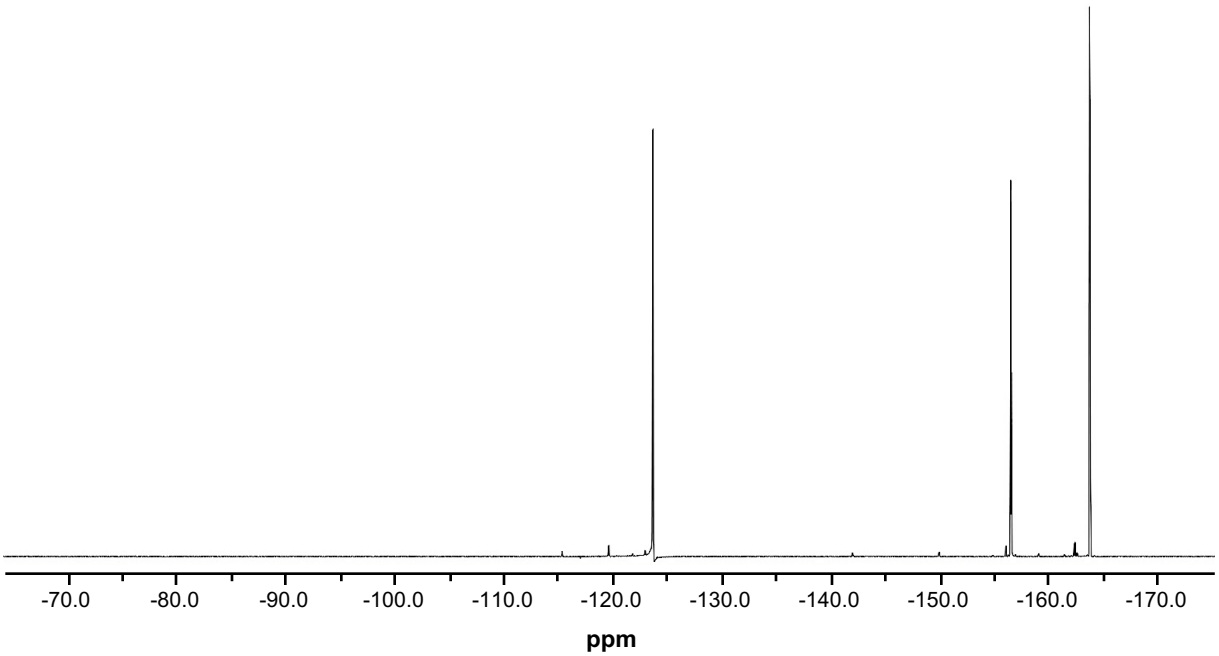


Figure S8. ^{19}FNMR spectra of monomer **C4I** in toluene with hexafluorobenzene (-163.9 ppm) as the internal standard.

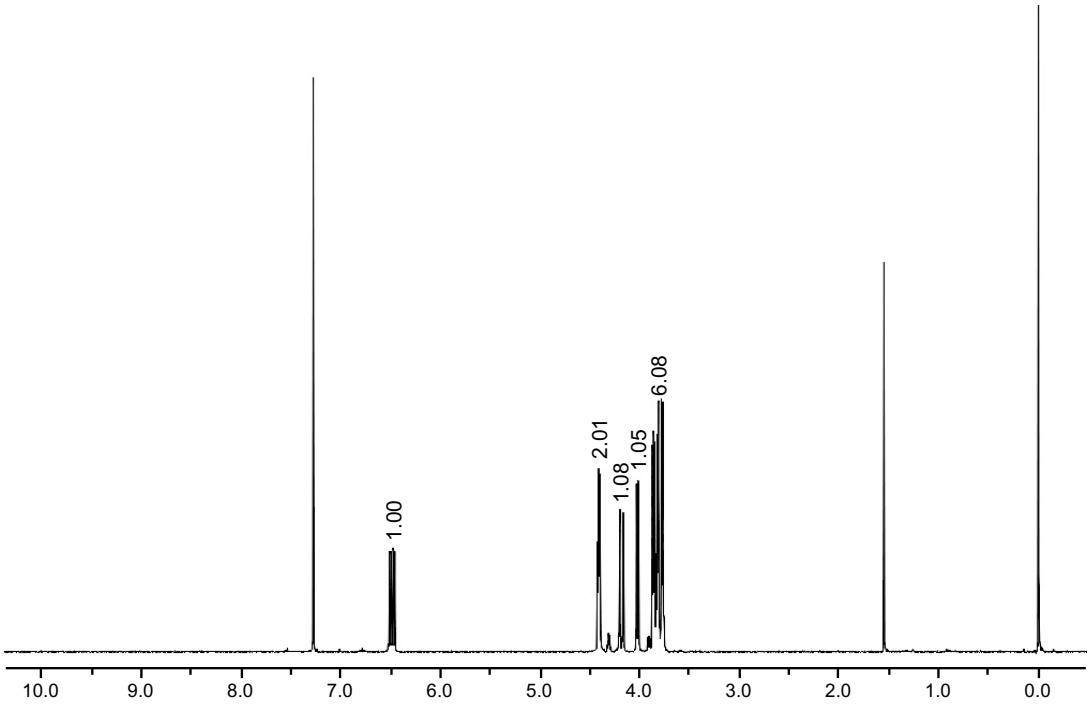


Figure S9. ^{1}HNMR spectra of monomer **O3I** in $CDCl_3$ (TMS standard). Integration values are shown.

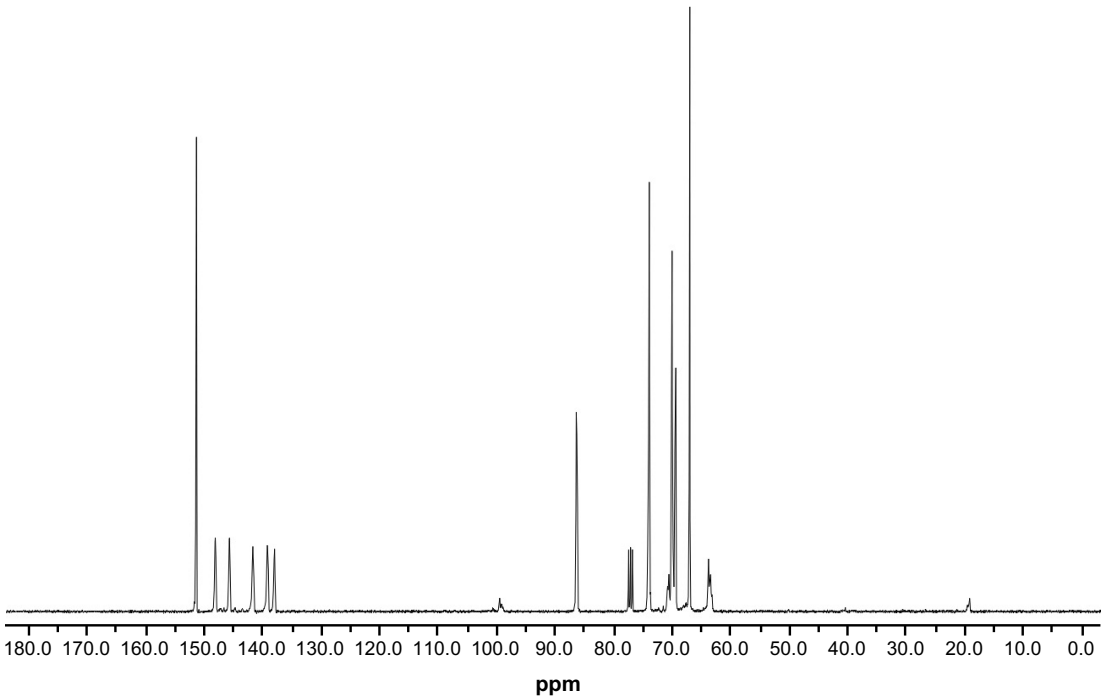


Figure S10. ^{13}CNMR spectra of monomer **O3I** in $CDCl_3$.

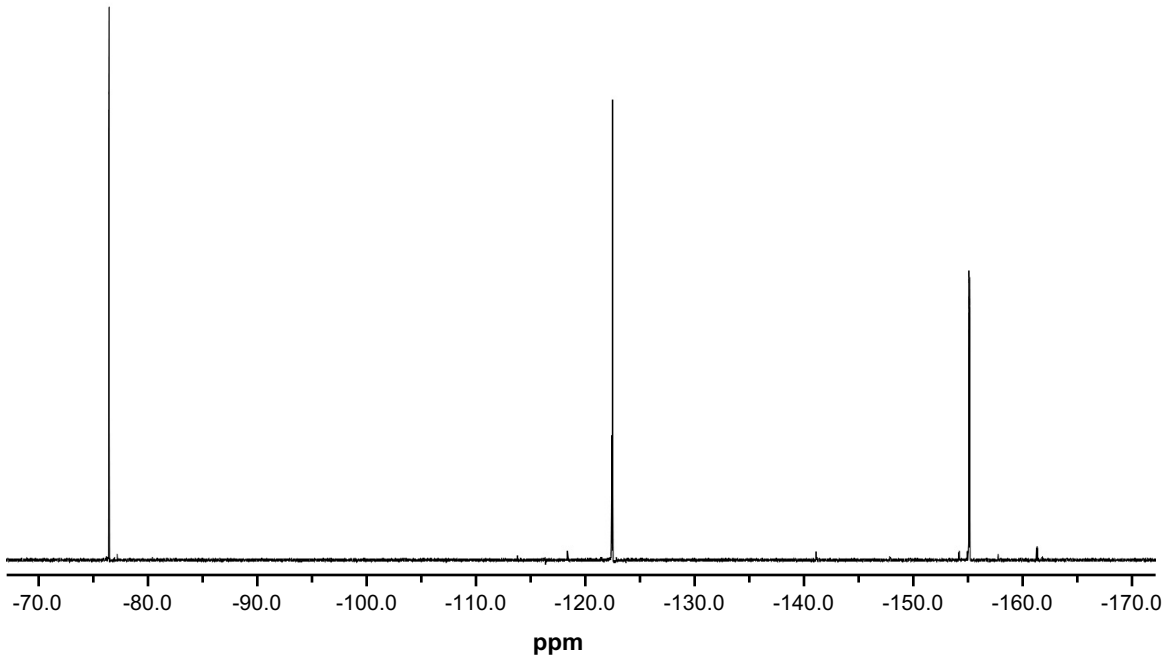


Figure S11. ^{19}FNMR spectra of monomer **O3I** in chloroform with trifluoroacetic acid (-76.5 ppm) as the internal standard.

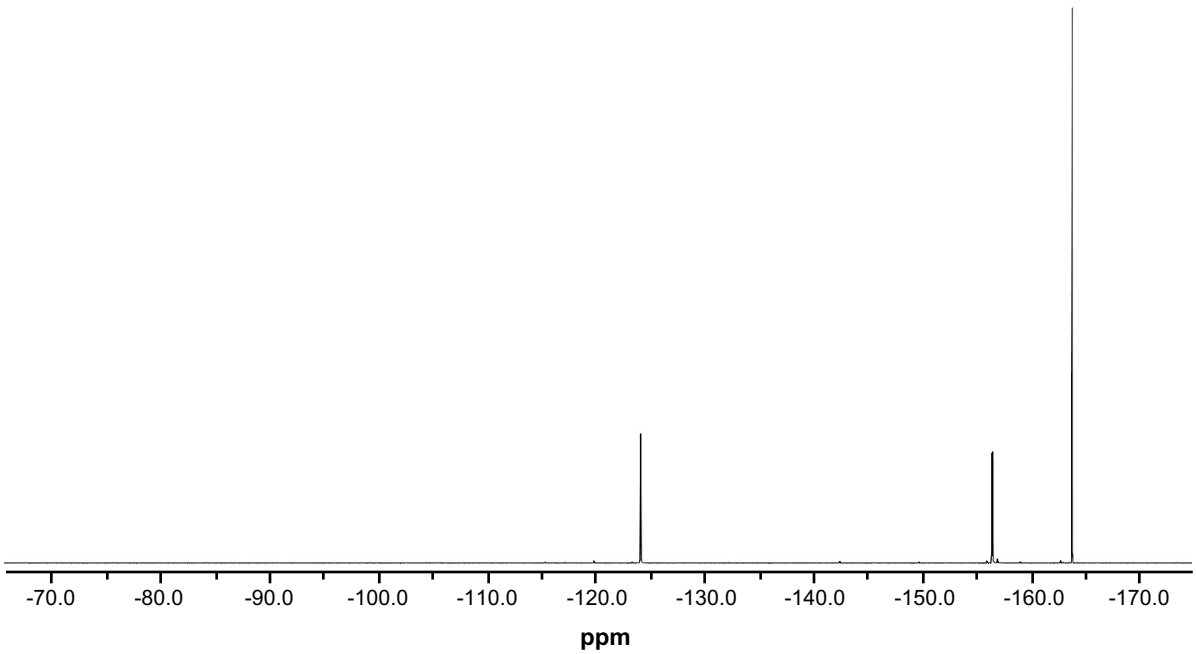


Figure S12. ^{19}FNMR spectra of monomer **O3I** in toluene with hexafluorobenzene (-163.9 ppm) as the internal standard.

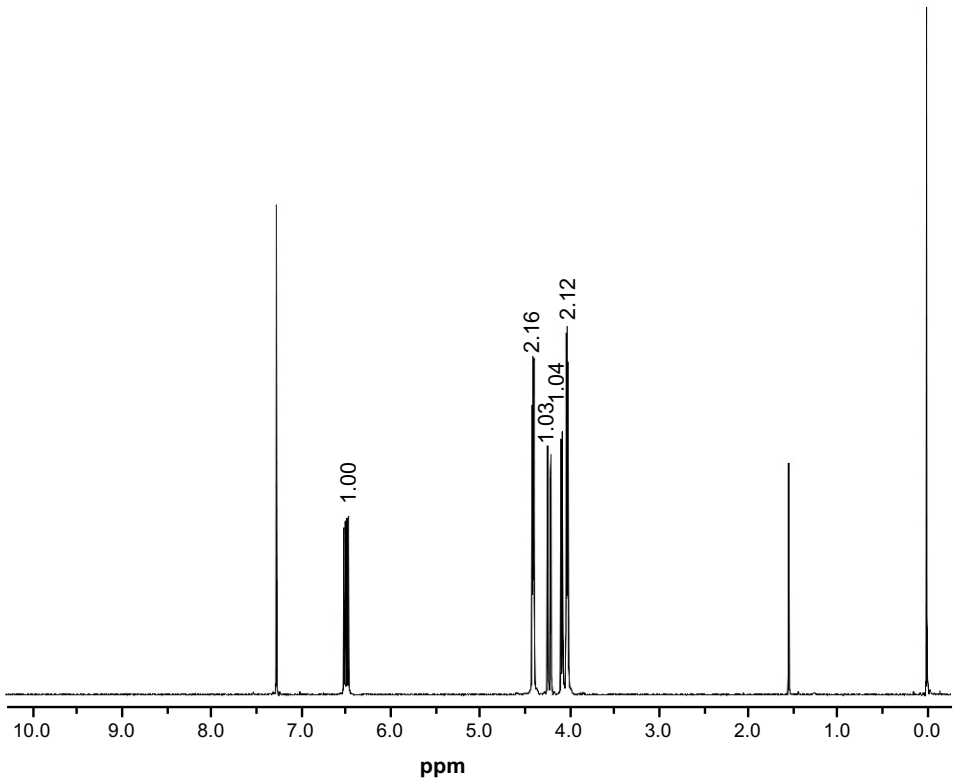


Figure S13. ^{1}HNMR spectra of monomer **C2F** in $CDCl_3$ (TMS standard). Integration values are shown.

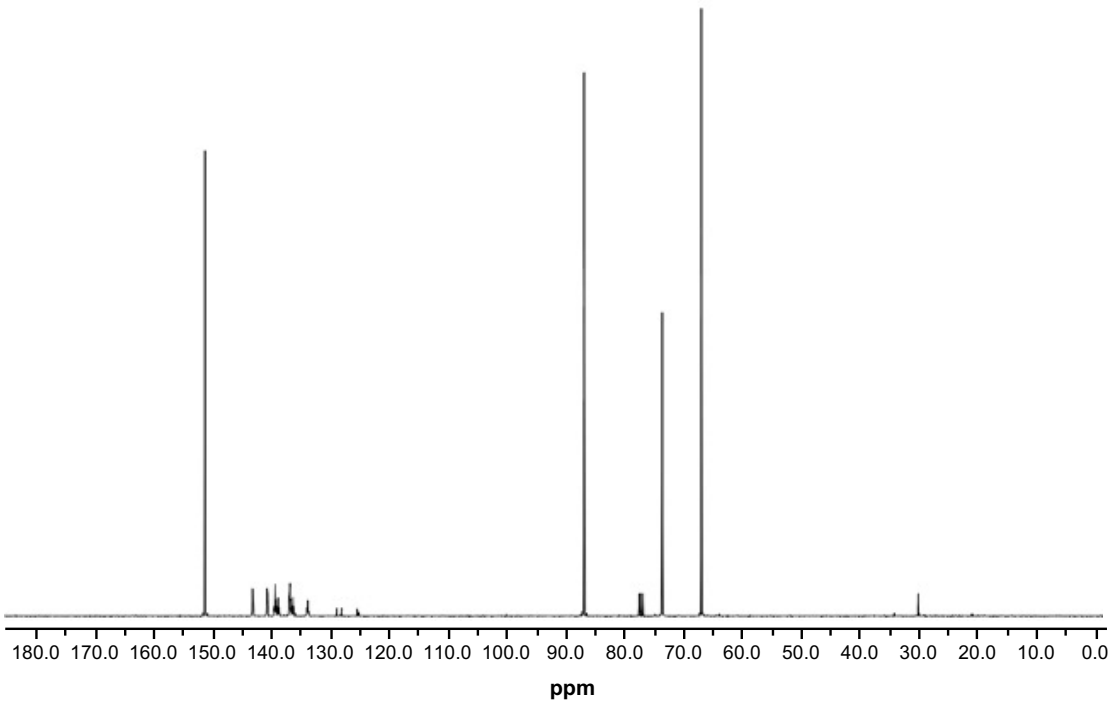


Figure S14. ^{13}CNMR spectra of monomer **C2F** in $CDCl_3$.

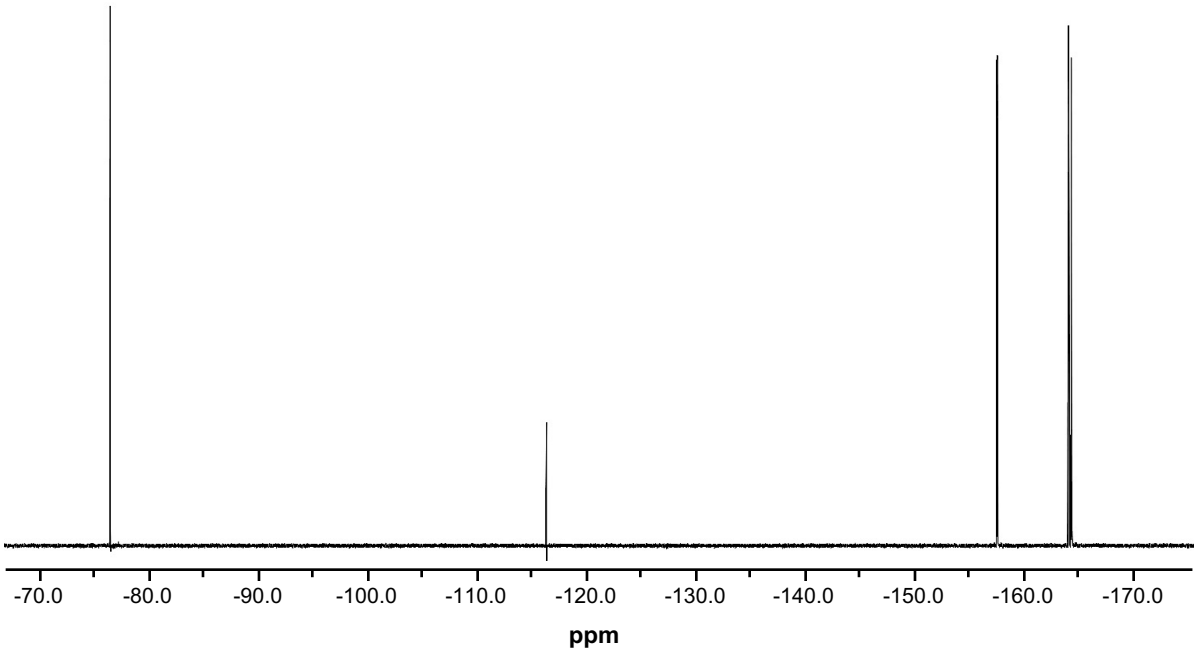


Figure S15. ^{19}FNMR spectra of monomer **C2F** in chloroform with trifluoroacetic acid (-76.5 ppm) as the internal standard.

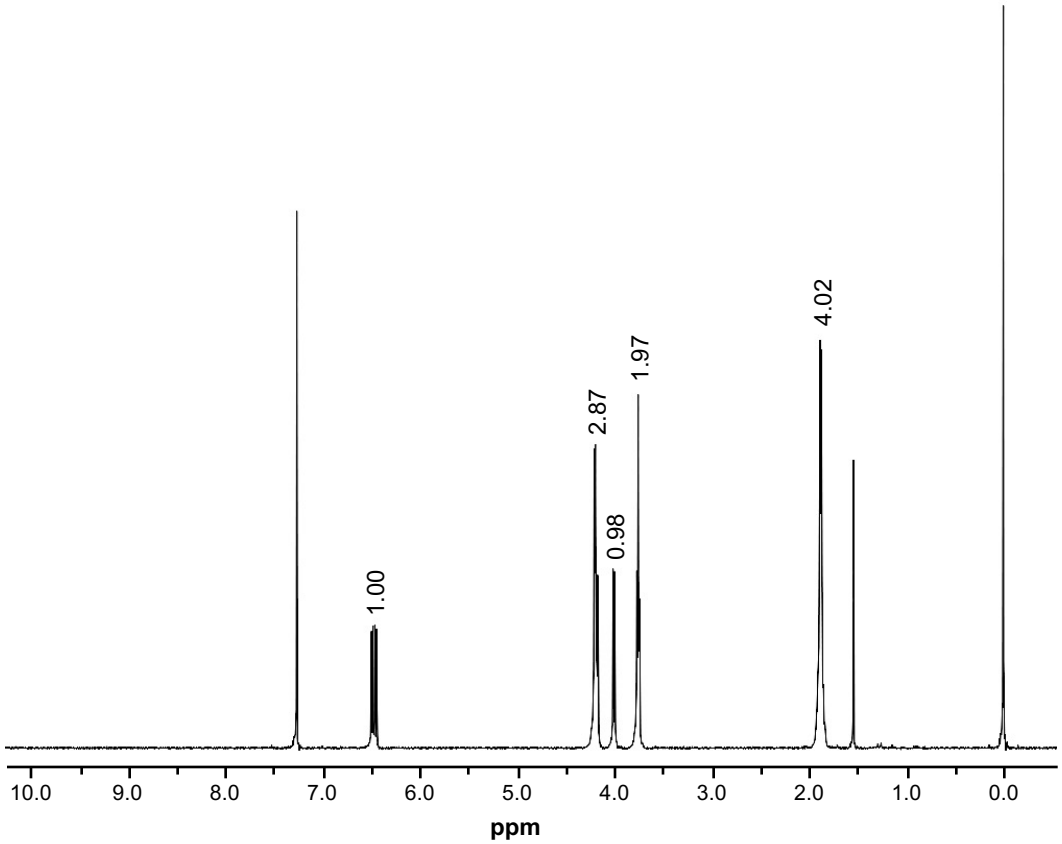


Figure S16. ^{1}HNMR spectra of monomer **C4F** in $CDCl_3$ (TMS standard). Integration values are shown.

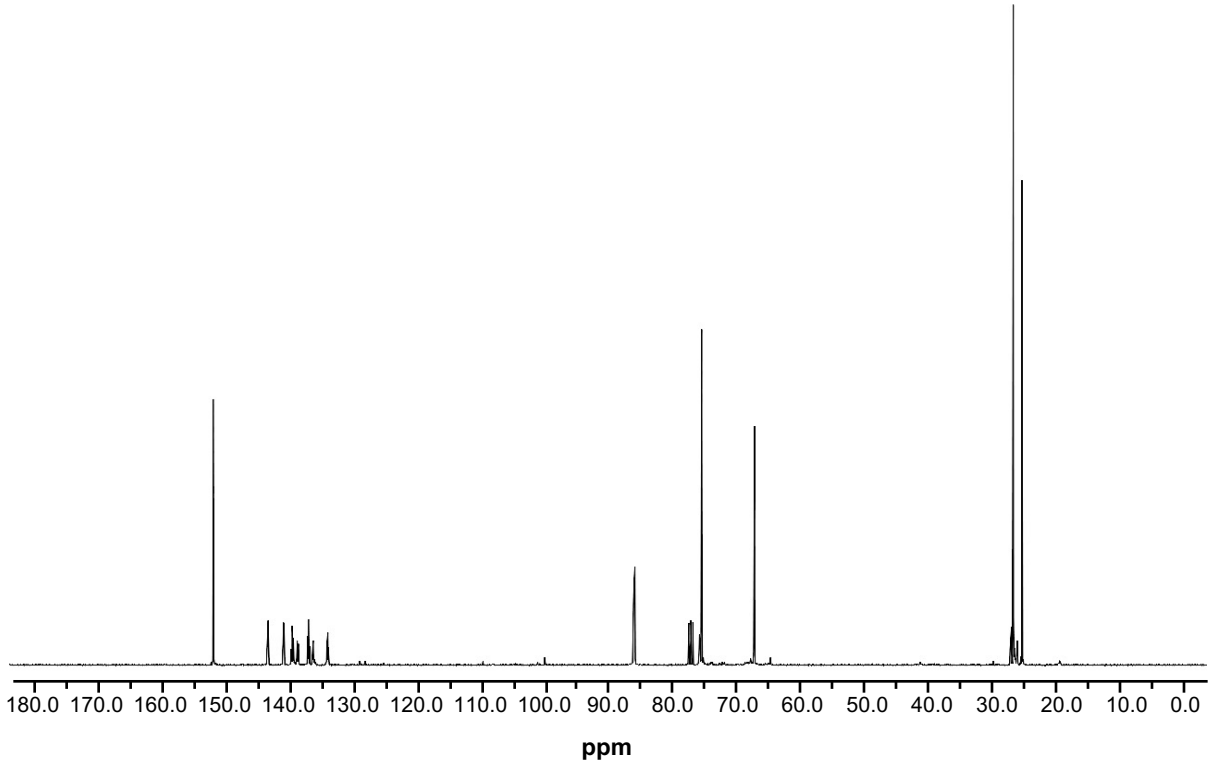


Figure S17. ^{13}CNMR spectra of monomer **C4F** in $CDCl_3$.

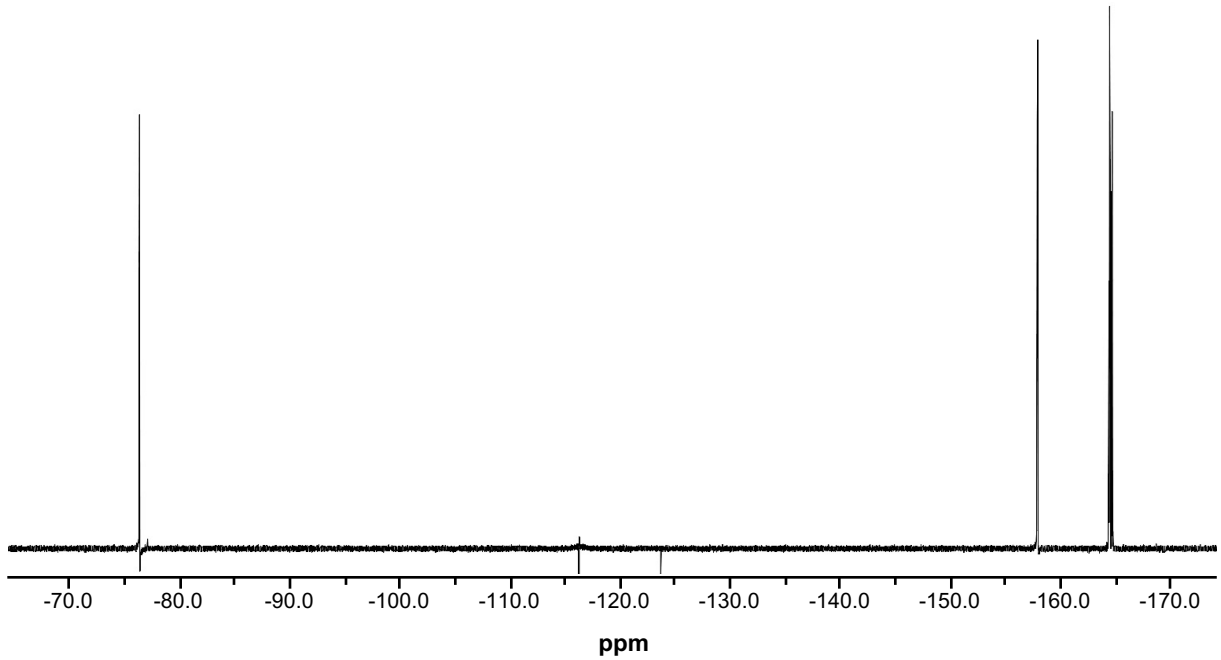


Figure S18. ^{19}FNMR spectra of monomer **C4F** in chloroform with trifluoroacetic acid (-76.5 ppm) as the internal standard.

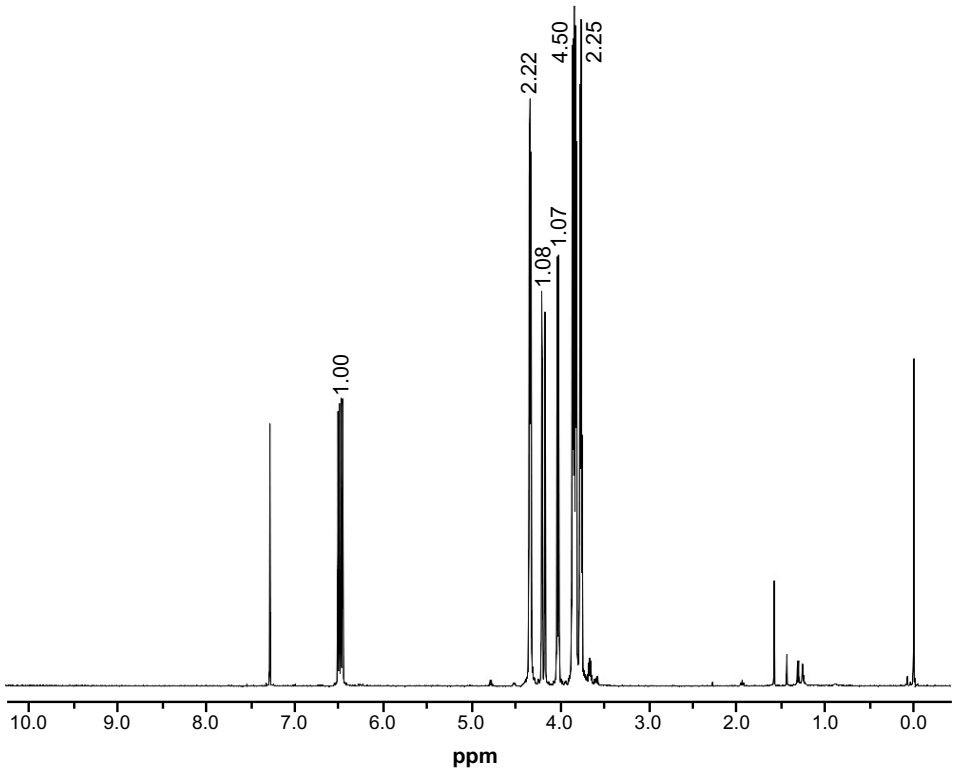


Figure S19. ^{1}HNMR spectra of monomer **O3F** in $CDCl_3$ (TMS standard). Integration values are shown.

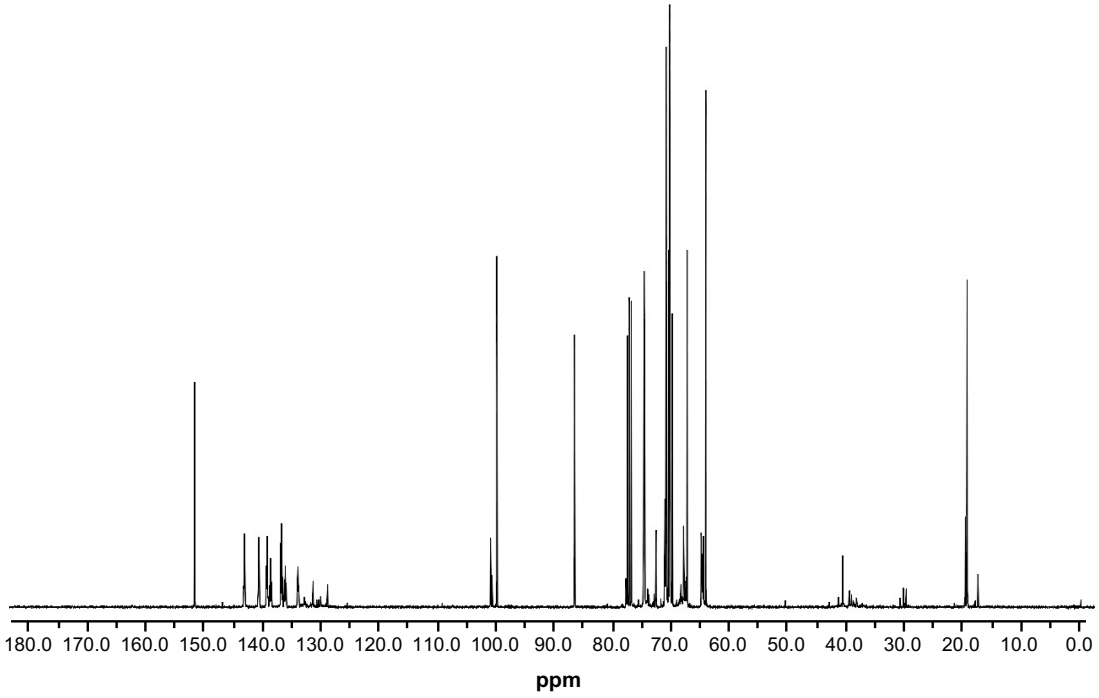


Figure S20. ^{13}CNMR spectra of monomer **O3F** in $CDCl_3$.

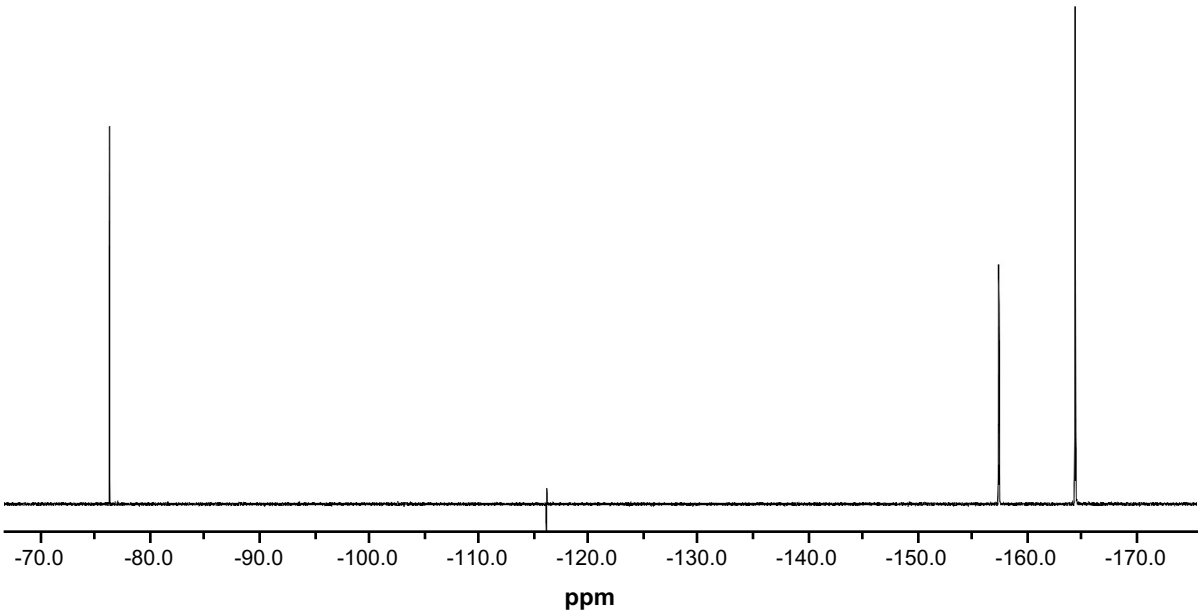


Figure S21. ^{19}FNMR spectra of monomer **O3F** in chloroform with trifluoroacetic acid (-76.5 ppm) as the internal standard.

SI 3. MS graphs

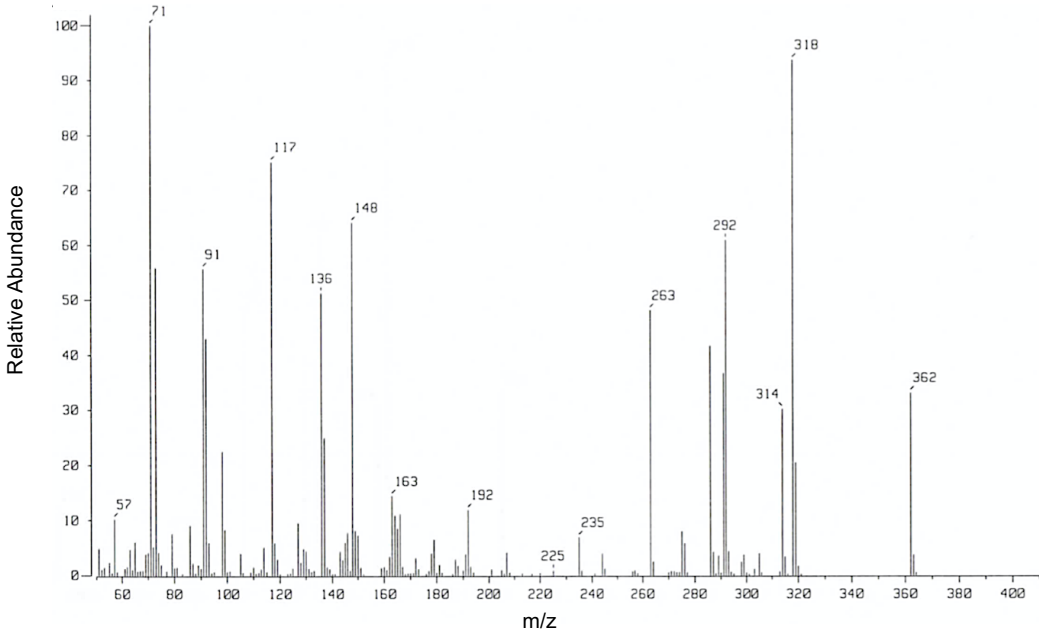


Figure S22. Mass spectra data for monomer **C2I** using electronic ionization mass spectrometry (EI-MS).

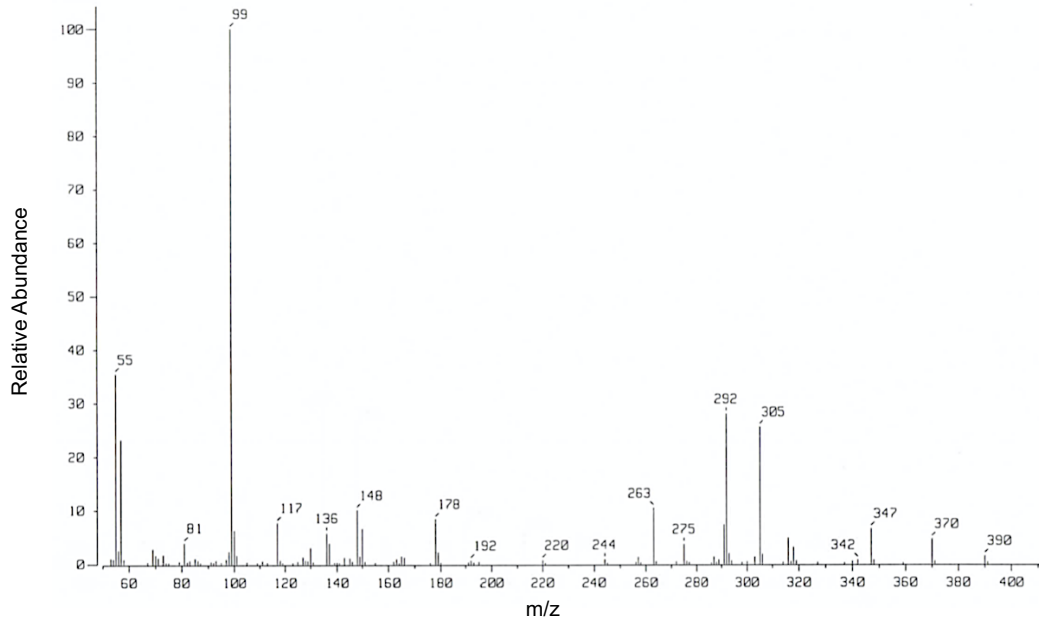


Figure S23. Mass spectra data for monomer **C4I** using EI-MS.

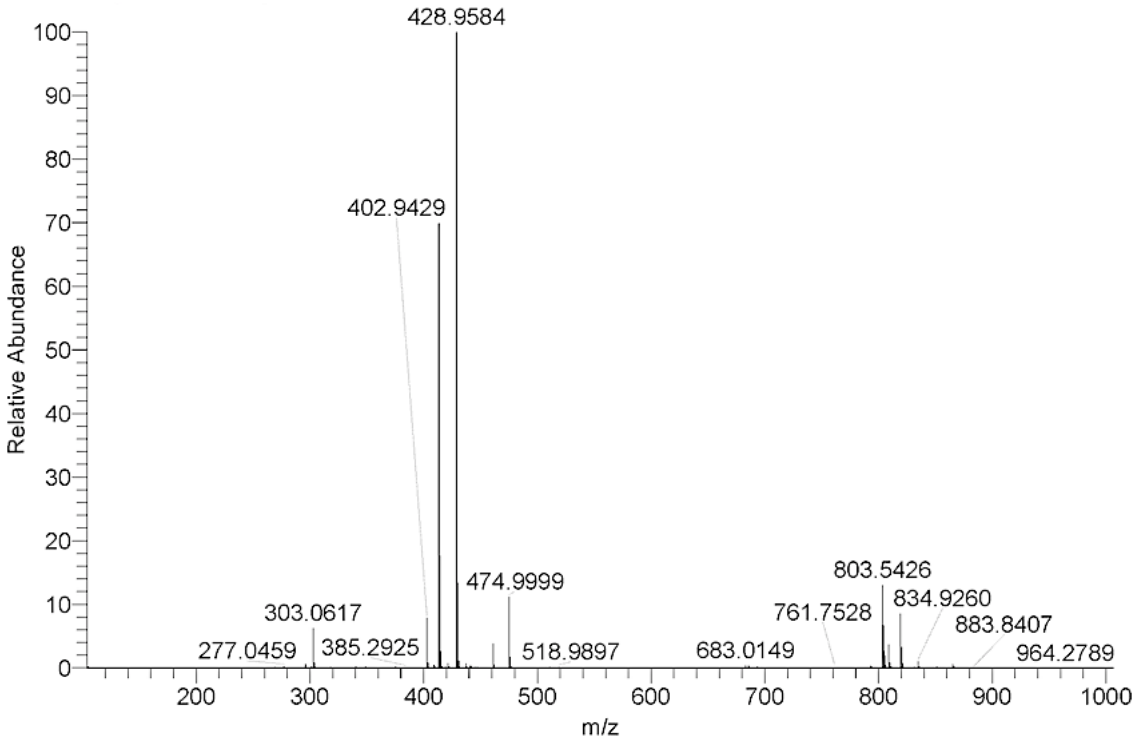


Figure S24. Mass spectra data for monomer **O3I** using ElectroSpray Ionization Orbitrap mass spectrometry (ESI-orbitrap MS).

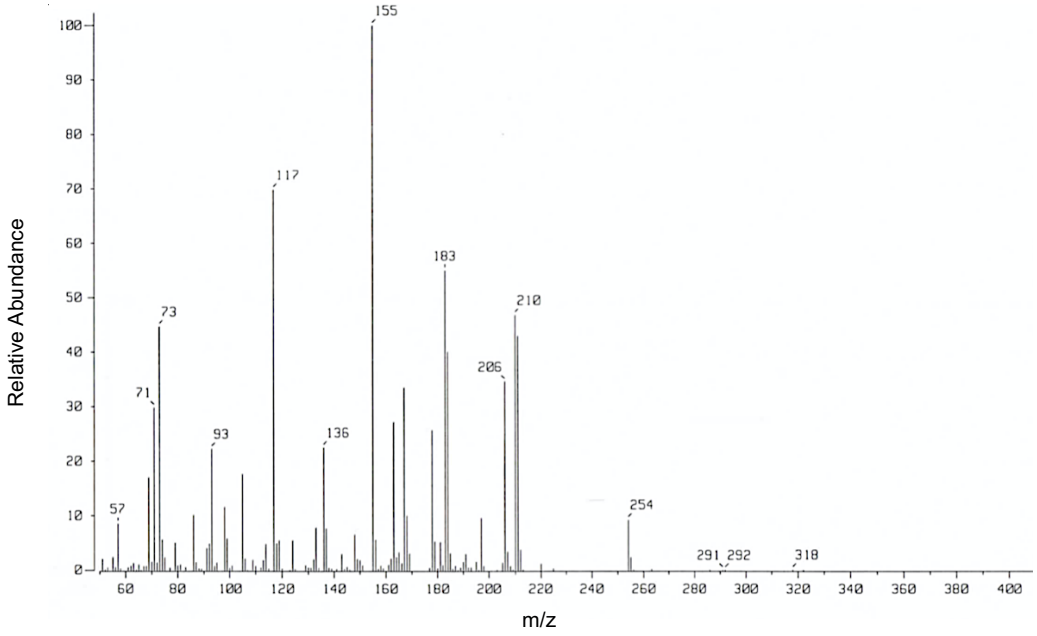


Figure S25. Mass spectra data for monomer **C2F** using EI-MS.

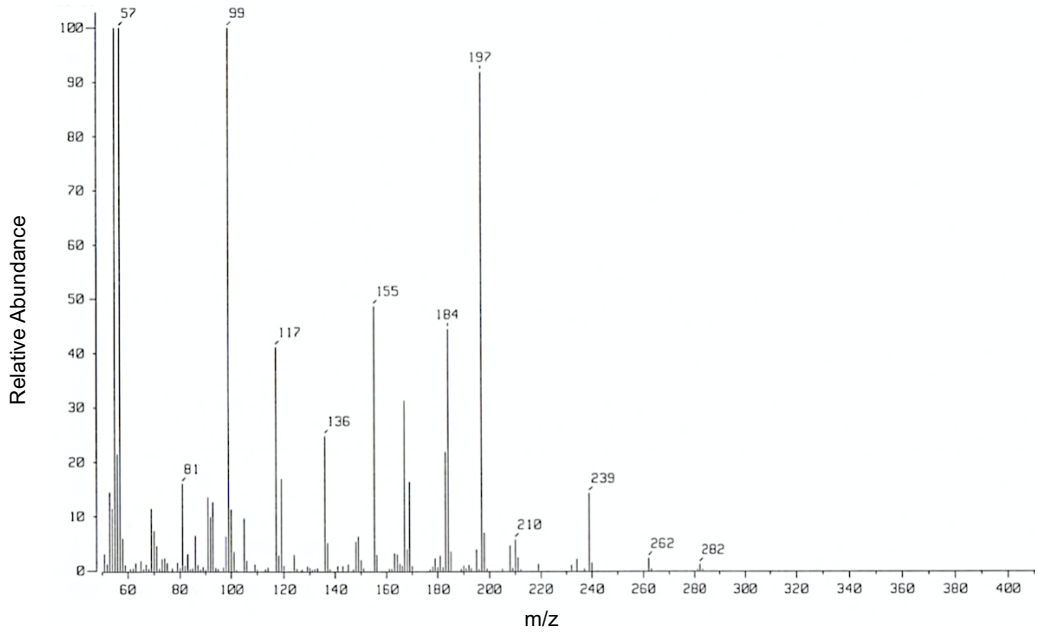


Figure S26. Mass spectra data for monomer **C4F** using EI-MS.

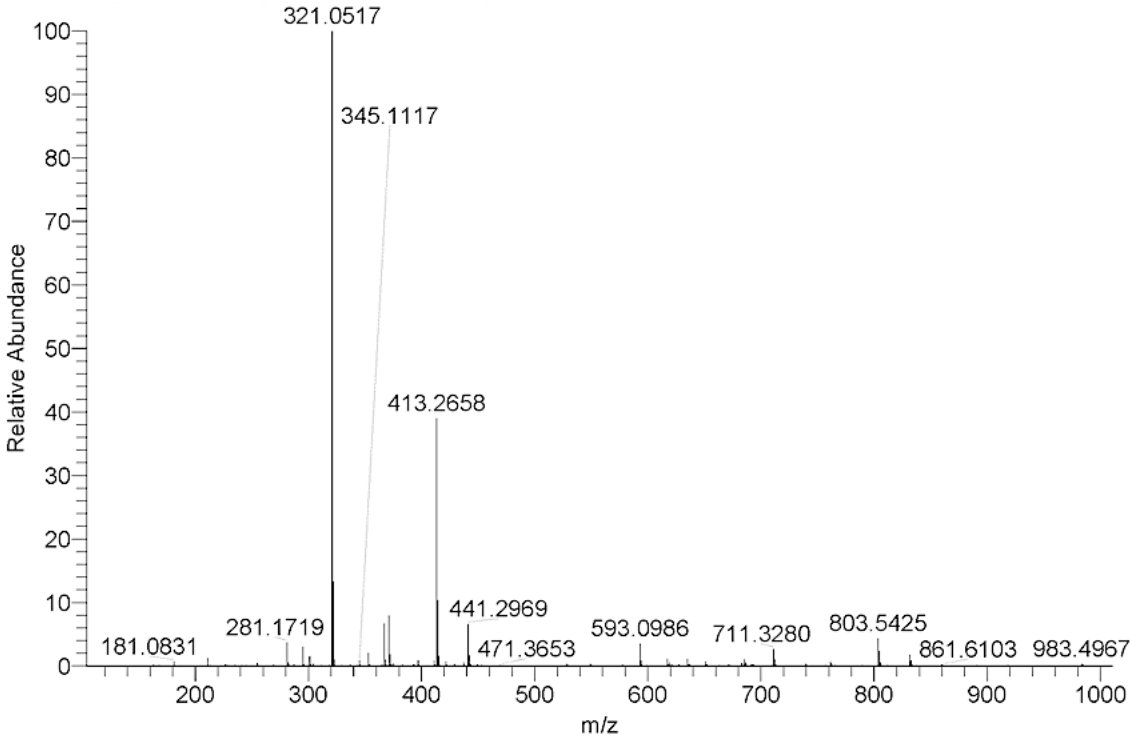


Figure S27. Mass spectra data for monomer **O3I** using ESI-orbitrap MS.

SI 4. Solubility of Monomers and Polymers

Table S1. Solubility of the monomers (left column) and polymers (right column) used in this study. A ○ indicates solubility in the given solvent, while a x indicates insolubility.

solvent	**C2I**		**C4I**		**O3I**		**C2F**		**C4F**		**O3F**	
toluene	○	○	○	○	○	○	○	○	○	○	○	○
tetrahydrofuran	○	○	○	○	○	○	○	○	○	○	○	○
hexane	○	○	○	○	○	○	○	○	○	○	○	○
dichloromethane	○	○	○	○	○	○	○	○	○	○	○	○
water	x	x	x	x	x	x	x	x	x	x	x	x

SI 5. Molecular Weight Estimation of Polymers

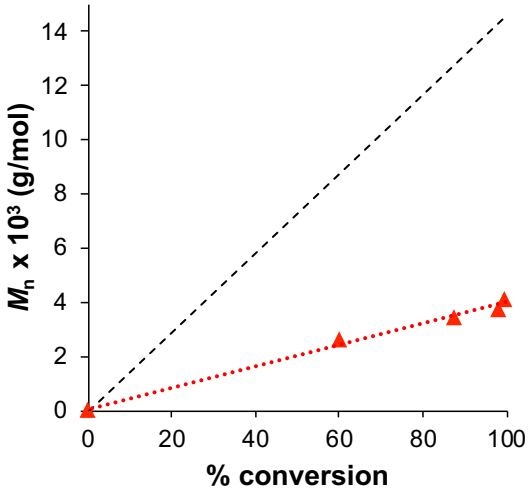


Figure S28. A comparison of the molecular weight of polymer **C2I** vs. % conversion. The predicted molecular weight is indicated by the black dashed line while the molecular weight as measured by SEC is shown by the red line.

A polystyrene standard was used for SEC analysis in this study. Due to the presence of fluorine and in some monomers iodine, the estimated densities of these samples were significantly different from the available polystyrene standard. As is apparent in Figure S28, while there is a linear relationship between the conversion and the molecular weight, it is lower than the predicted molecular weight expected based on the conversion.

An investigation of the molecular weight calculated from SEC as compared to the molecular weight determined from MALDI-TOF (Table S2) also shows that SEC produces a consistent underestimation in the calculated weight.

Table S2. A comparison of the molecular weights observed from both SEC analysis and MALDI-TOF analysis for the polymerization of **C4I**.

reaction time (min)	SEC peak top (g/mol)	calculated DP from SEC	MALDI-TOF peak top (g/mol)	calculated DP from MALDI-TOF
1	5.2 x 10^3	13	6.8 x 10^3	17
2	6.3 x 10^3	16	8.0 x 10^3	21
5	7.3 x 10^3	19	10.7 x 10^3	27
10	7.7 x 10^3	20	11.1 x 10^3	28

SI 6. Comparison of Halogen Bonding Acceptors

Table S3. A summary of initial tests on the halogen bonding ability of various donors and acceptors. 1,4-Diiodotetrafluorobenzene was used as received (Apollo Scientific, 97%).

donor (50 mM)	acceptor (50 mM)	peak shift (Δppm)
pentafluoroiodobenzene	triethylamine	0.246
1,4-diiodotetrafluorobenzene	triethylamine	0.241
C4I	triethylamine	0.144
C4I	1,4-dioxane	0.133
C4I	tetrahydropyran	0.007

SI 7. Infrared (IR) Spectra

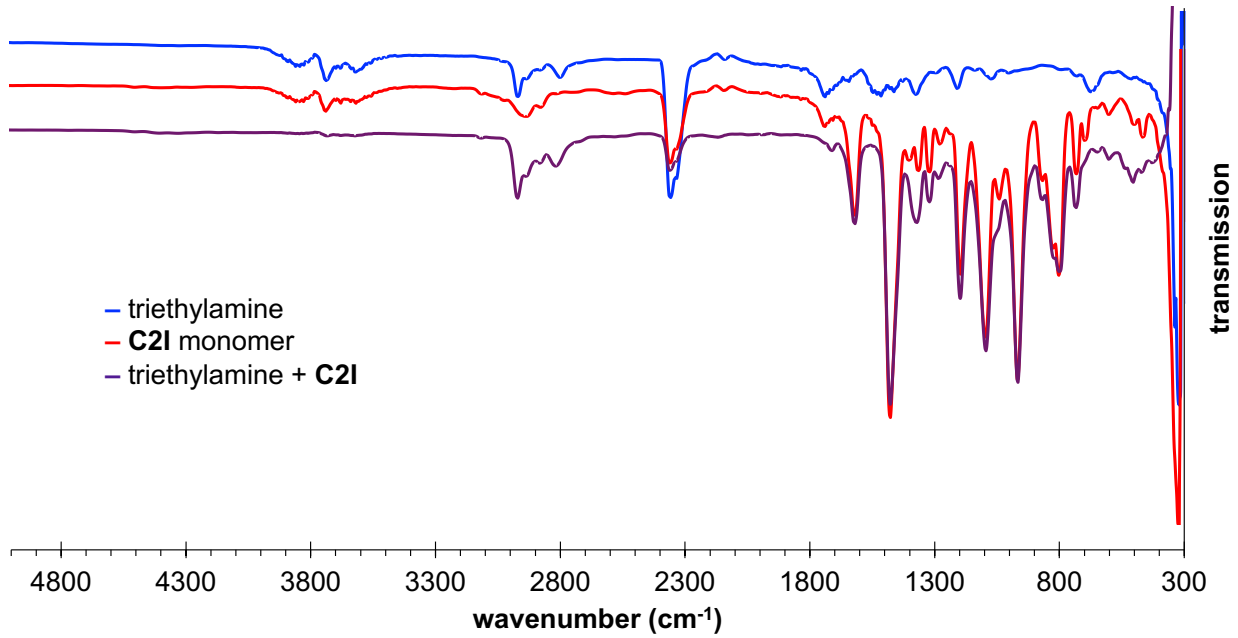


Figure S29. IR spectra for triethylamine, the **C2I** monomer and the 1:1 combination thereof.

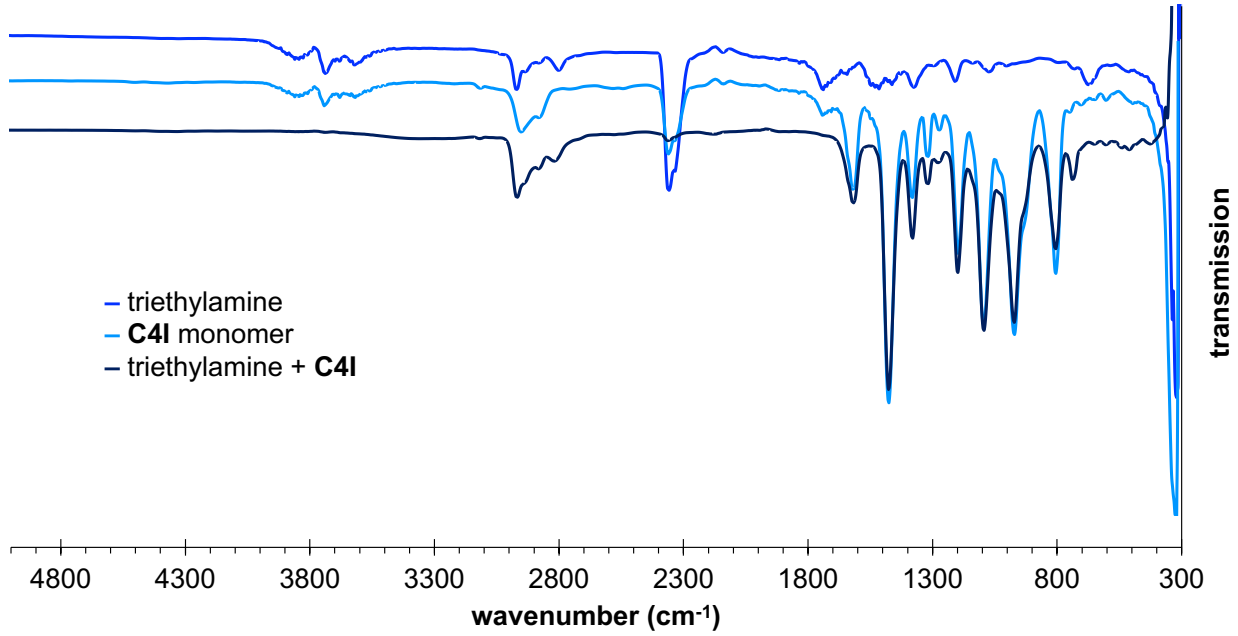


Figure S30. IR spectra for triethylamine, the **C4I** monomer and the 1:1 combination thereof.

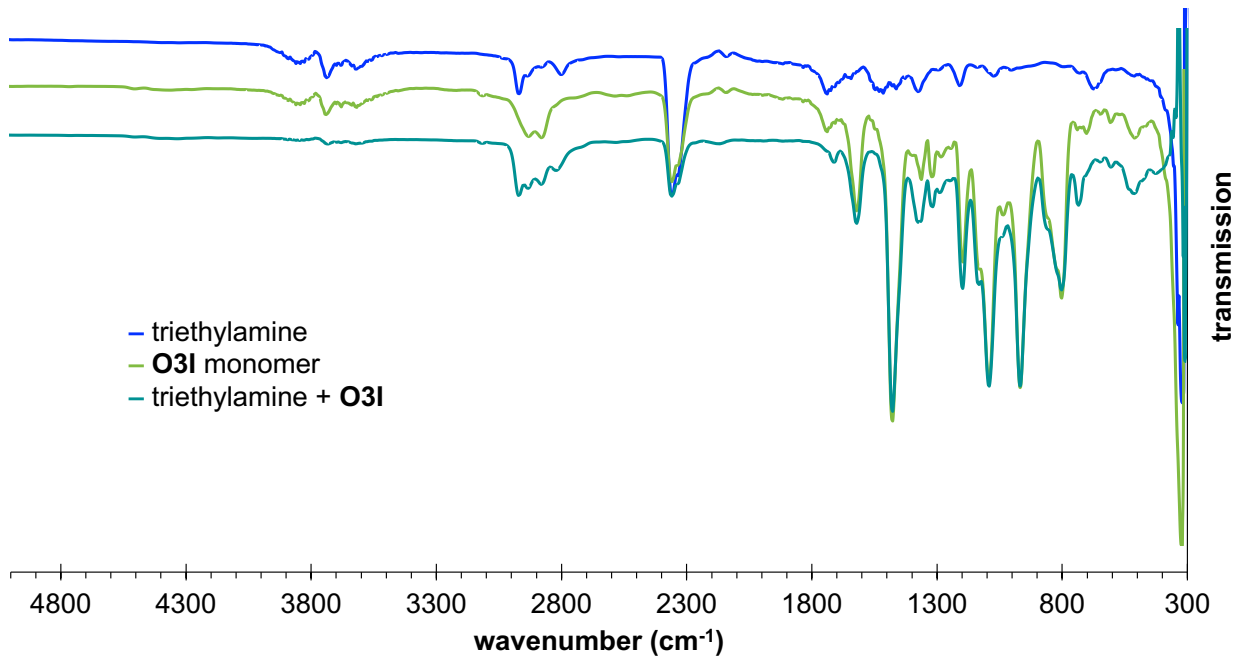


Figure S31. IR spectra for triethylamine, the **O3I** monomer and the 1:1 combination thereof.

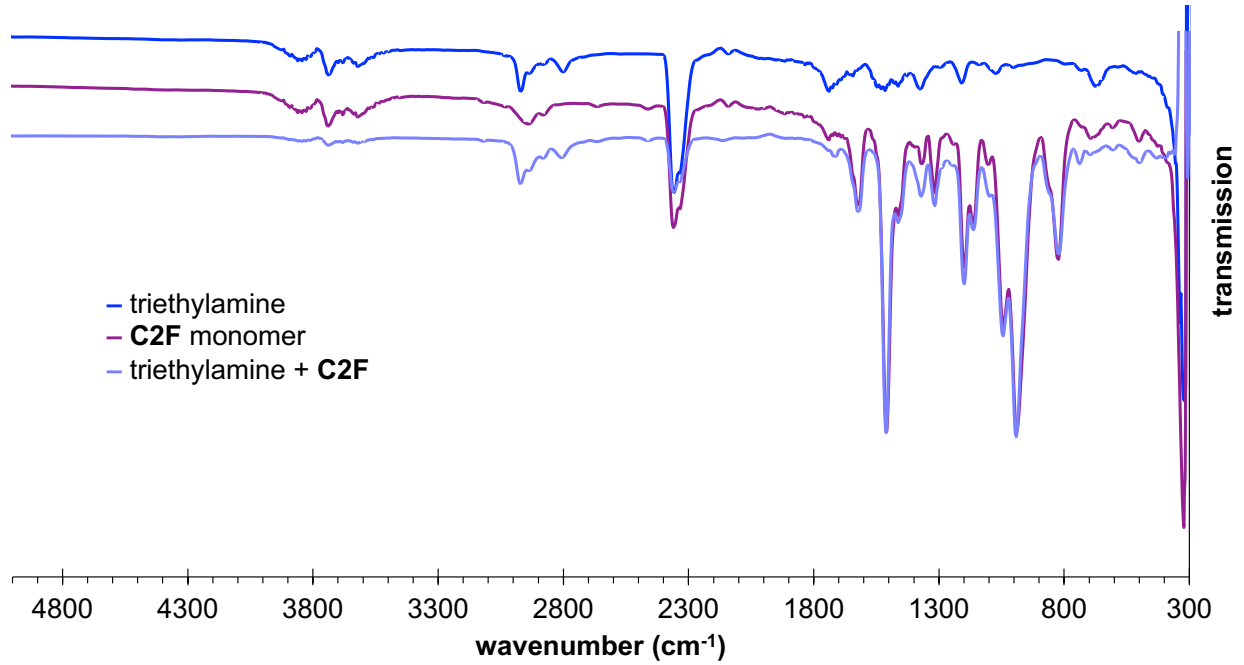


Figure S32. IR spectra for triethylamine, the **C2F** monomer and the 1:1 combination thereof.

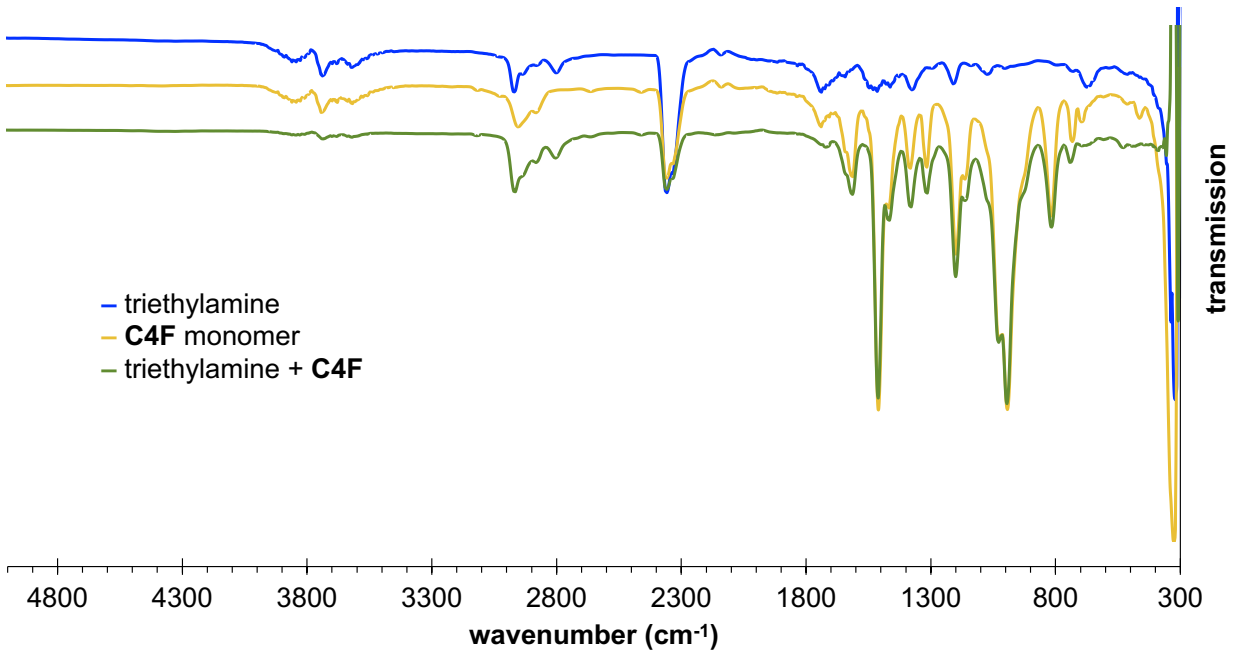


Figure S33. IR spectra for triethylamine, the **C4F** monomer and the 1:1 combination thereof.

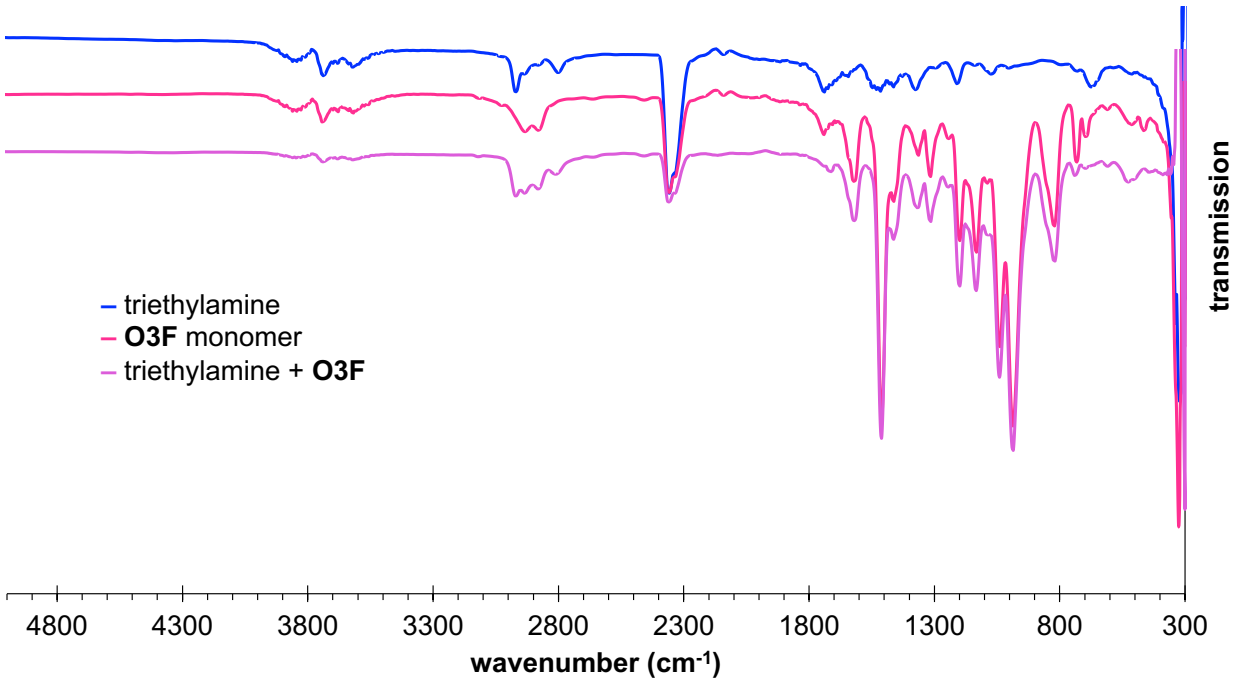


Figure S34. IR spectra for triethylamine, the **O3F** monomer and the 1:1 combination thereof.