

Supporting Information for:

**Copolymerization of Ethylene and Vinyl Fluoride by (Phosphine-sulfonate)Pd(Me)(py)
Catalysts**

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I. Experimental Procedures

General procedures. All experiments were performed using dry box or Schlenk techniques under a nitrogen atmosphere. Nitrogen was purified by passage through columns containing activated molecular sieves and Q-5 oxygen scavenger. CH₂Cl₂ and CD₂Cl₂ were distilled from P₂O₅. Hexane and toluene were purified by passage through columns of activated alumina and BASF R3-11 oxygen scavenger. Catalysts **1a** and **1b** were prepared as described previously.¹ (TMEDA)PdMe₂ was prepared by a literature procedure.² Ethylene (Polymer grade) was purchased from Matheson and used as received. Vinyl fluoride (VF) of >98% purity was purchased from SynQuest Laboratories, Inc. and used as received.

NMR spectra of organometallic complexes were recorded at ambient temperature unless otherwise indicated. ¹H and ¹³C chemical shifts are reported relative to SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent resonances. ¹⁹F{¹H} NMR spectra were referenced externally with trifluoroacetic acid in CDCl₃ at δ -78.5. Coupling constants are given in Hz.

Polymer characterization. Gel permeation chromatography was performed with a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C. A set of three PLgel 10 μm Mixed-B LS columns was used. Samples were prepared at 160 °C. Molecular weights were determined by GPC using narrow polystyrene standards and are corrected for linear polyethylene by universal calibration using the Mark-Houwink parameters of Rudin: K = 1.75 × 10⁻² cm³/g and α = 0.67 for polystyrene and K = 5.90 × 10⁻² cm³/g and α = 0.69 for polyethylene.³

DSC measurements were performed on a TA Instruments DSC 2920 instrument. Samples (5 mg) were annealed by heating to 150 °C at 20 °C/min, cooled to 40 °C at 40 °C/min, and then analyzed while being heated to 150 °C at 20 °C/min.

¹H and ¹⁹F{¹H} NMR spectra for polymers were obtained as follows. A mixture of polymer (30-60 mg) and CDCl₂CDCl₂ (0.7 g) in an NMR tube was heated to 120 °C (≤ 15 min) affording a homogeneous solution. The tube was inserted into a pre-heated NMR probe at 120 °C and NMR spectra were obtained after a 5 min temperature equilibration period. ¹³C{¹H} NMR spectra were obtained from solutions of the copolymer (80 mg) in 1,2-dichlorobenzene-*d*₄ (0.8 g) at 110 °C.

Ortho-(Diphenylphosphino)toluenesulfonic acid ([PO-H]H). A flask was charged with

p-toluenesulfonic acid (2.10 g, 12.2 mmol, dehydrated) and THF (60 mL). The mixture was cooled to 0 °C, stirred for 10 min, and *n*-hexyllithium (10.6 mL of a 2.3 M solution in hexane, 24.4 mmol) was added dropwise over 3 min. The mixture was warmed to 50 °C for 10 min and then cooled to –78 °C. A second flask was charged with THF (60 mL), Ph₂PCl (2.25 mL, 12.2 mmol) was added by syringe, and the solution was cooled to –78 °C. The dilithiated *p*-toluenesulfonic acid solution was cannula-transferred to the Ph₂PCl solution to afford a pale yellow slurry, which was stirred at –78 °C for 1 h, warmed to room temperature and stirred for 3 h. Upon warming, the slurry became a pale brown solution which turned red and finally yellow. The volatiles were removed under vacuum and the residue was taken up in deionized water (50 mL). The aqueous mixture was acidified with dilute HCl to pH~2. The mixture was extracted with CH₂Cl₂ (3 × 60 mL). The extracts were combined, dried over MgSO₄, and evaporated under vacuum to yield a pale yellow solid. The solid was washed with THF and Et₂O to afford a white powder. The powder was dried under vacuum. Yield 3.03 g (70.3% based on *p*-toluenesulfonic acid). ¹H NMR (CD₂Cl₂): δ 9.49 (d, *J*_{PH} = 400, 1H, P-*H*), 8.14 (dd, *J*_{HH} = 6.5, *J*_{PH} = 5.5, 1H, *H*³-ArSO₃), 7.77 (m, 2H, *H*⁴-Ph), 7.66 – 7.58 (m, 10H, *H*⁴-ArSO₃, *H*²-Ph, *H*³-Ph), 7.07 (d, *J*_{PH} = 15, 1H, *H*⁶-ArSO₃), 2.33 (s, 3H, CH₃ArSO₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 151.0 (d, *J*_{PC} = 8.2, C²-ArSO₃), 141.2 (d, *J*_{PC} = 20, C⁵-ArSO₃), 136.6 (d, *J*_{PC} = 2.8, C⁴-ArSO₃), 135.2 (d, *J*_{PC} = 15, C⁶-ArSO₃), 135.1 (s, C⁴-Ph), 134.2 (d, *J*_{PC} = 11, C²-Ph), 130.5 (d, *J*_{PC} = 13, C³-Ph), 129.2 (d, *J*_{PC} = 9.8, C⁵-ArSO₃), 119.2 (d, *J*_{PC} = 90, C¹-ArSO₃), 113.5 (d, *J*_{PC} = 86, C¹-Ph), 21.5 (s, CH₃ArSO₃). ³¹P{¹H} NMR (CD₂Cl₂): δ 4.07 (br s).

[PO-H]Pd(Me)(py) (1c). A solution of [PO-H]H (0.354 g, 1.00 mmol) and (TMEDA)PdMe₂ (0.252 g, 1.00 mmol) in CH₂Cl₂ (15 mL) was cooled to –78 °C and stirred for 20 min. Pyridine (0.41 mL, 5.0 mmol) was added dropwise over 2 min. The mixture was stirred at –78 °C for 30 min, warmed to room temperature, and stirred for 45 min. A pale yellow solution formed. The volatiles were removed under vacuum to afford a pale yellow solid. The solid was washed with hexanes and dried under vacuum to afford a white solid. This compound was further purified by recrystallization from CH₂Cl₂ and hexane. Yield 0.297 g, 51%. ¹H NMR (CD₂Cl₂): δ 8.76 (m, 2H, *H*²-py), 8.03 (dd, *J*_{HH} = 6.2, *J*_{PH} = 4.4, 1H, *H*³-ArSO₃), 7.90 (m, 1H, *H*⁴-py), 7.63 – 7.58 (m, 4H, *H*³-py, *H*⁴-Ph), 7.54-7.43 (m, 8H, *H*²-Ph, *H*³-Ph), 7.35 (d, *J*_{HH} = 8.0, 1H, *H*⁴-ArSO₃), 6.83 (d, *J*_{PH} = 10, 1H, *H*⁶-ArSO₃), 2.24 (s, 3H, CH₃ArSO₃), 0.49 (d, *J*_{PH} = 2.8, 3H, Pd-CH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 150.7 (s, *o*-py), 147.2 (d, *J*_{PC} = 14, C²-ArSO₃), 140.9 (d,

$J_{\text{PC}} = 7.0$, $\text{C}^5\text{-ArSO}_3$), 139.1 (s, $\text{C}^4\text{-ArSO}_3$), 135.8 (s, *p*-py), 134.8 (d, $J_{\text{PC}} = 12$, $\text{C}^2\text{-Ph}$), 132.2 (s, *m*-py), 131.5 (d, $J_{\text{PC}} = 6.2$, $\text{C}^4\text{-Ph}$), 130.5 (d, $J_{\text{PC}} = 55$, $\text{C}^1\text{-Ph}$), 129.1 (d, $J_{\text{PC}} = 11$, $\text{C}^3\text{-Ph}$), 128.7 (d, $J_{\text{PC}} = 8.1$, $\text{C}^3\text{-ArSO}_3$), 128.5 (d, $J_{\text{PC}} = 44$, $\text{C}^1\text{-ArSO}_3$), 125.8 (s, $\text{C}^6\text{-ArSO}_3$), 21.6 (s, CH_3ArSO_3), 0.82 (d, $J_{\text{PC}} = 2.0$, Pd-CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 28.4 (s). Calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_3\text{PSPd}$: C, 54.01; H, 4.35; N, 2.52. Found: C, 53.84; H, 4.37; N, 2.68.

Standard procedure for Ethylene/VF copolymerization. Copolymerizations of ethylene and VF were performed in 300 mL stainless steel Parr autoclave equipped with a water cooling loop, thermocouple and magnetically coupled stirrer, and controlled by a Parr 4842 controller. In the glove box, the catalyst (6 mg, 10 μmol) was weighed into a glass autoclave liner. Toluene (50 mL) was added. The liner was placed in the autoclave, and the autoclave was assembled and brought out of the box. The autoclave was exposed to vacuum briefly, pressurized with VF to the desired pressure and ethylene was added until the total pressure reached 300 psi. The pressure was maintained at 300 psi by addition of ethylene on demand. The reactor was heated to the desired temperature (80 $^\circ\text{C}$) and stirring (170 rpm) was started. After 2 h, the ethylene flow was terminated and the pressure was released into a well-ventilated fume hood. **Caution:** Vinyl fluoride is anticipated to be a human carcinogen.⁴ The mixture was cooled to room temperature and MeOH (100 mL) was added. The polymer was collected by filtration, washed with MeOH (20 mL), and dried under high vacuum overnight.

Representative homopolymerization and copolymerization results are summarized in Table S-1. Note that entry 3-5 are replicates to demonstrate the reproducibility of the polymerization reactions.

Table S-1. Representative ethylene/VF polymerization results.^a

Exp #	ww069	ww064	ww061	ww062	ww063	ww065	ww072	ww070	ww071	ww091	ww097
Entry	1	2	3	4	5	6	7	8	9	10	11
Cat	1a	1a	1a	1a	1a	1a	1a	1b	1c	1a^f	AIBN^g
P_{VF} (psi) ^b	0	40	80	80	80	160	240	80	80	80	80
$P_{CH_2CH_2}$ (psi) ^b	300	260	220	220	220	140	60	220	220	220	220
Yield (g)	5.93	0.77	0.48	0.47	0.44	0.17	0.10	0.22	0.41	0.53	0.02
M_n (10 ³) ^c	16.6	14.5	13.7	12.1	12.4	8.6	6.8	6.2	4.5	13.2	11.2
M_w (10 ³) ^c	56.3	43.6	38.8	36.1	35.4	23.8	17.7	17.0	11.2	38.5	19.0
M_w/M_n ^c	3.4	3.0	2.8	3.0	2.9	2.7	2.6	2.7	2.5	2.9	1.7
Me /10 ³ C	0.3	1.3	1.2	1.0	0.9	1.1	2.4	2.7	4.7	1.0	70
VF Incorp (mol %) ^d	NA	0.09	0.16	0.13	0.17	0.37	0.45	0.15	0.14	0.15	8
VF per chain	NA	0.9	1.1	0.6	1.2	2.2	1.3	0.4	0.4	2.1	NA
T_m (°C) ^e	133.6	132.6	132.2	132.6	132.6	131.7	130.7	130.2	129.6	131.7	116.5

^a Conditions: toluene, 50 mL, [cat] = 0.2 mM, 80 °C, 2 h, total pressure 300 psi. ^b The reactor was charged with the given pressure of VF at 25 °C, pressurized with ethylene (on demand) to achieve a total pressure of 300 psi, and then heated to 80 °C. ^c GPC. ^d mol % VF incorporation in copolymer determined by NMR. ^e DSC. ^f contains galvinoxyl (21 mg, 0.05 mmol, 5 equiv. vs. Pd). ^g 5 mg (0.03 mmol) AIBN was used.

Attempted homopolymerization of VF by 1a. In the glove box, **1a** (6 mg, 10 μmol) was weighed into a glass autoclave liner. Toluene (50 mL) was added. The liner was placed in the autoclave, and the autoclave was assembled and brought out of the box. The autoclave was pressurized with VF to 160 psi, heated to 80 °C and stirring at 170 rpm was initiated. After 2 h, the reactor was vented and the volatiles were removed under vacuum. Only ~3.8 mg residue was obtained. ¹H and ¹⁹F{¹H} NMR spectra showed that no poly(vinyl fluoride) had formed. The ³¹P{¹H} NMR spectrum contained signals at δ 16.0, 11.8 and -2.1, suggesting that this material contains catalyst decomposition products.

Removal of volatile compounds from copolymer. A flask was charged with copolymer (28 mg, Table S-1, entry 3) and toluene (10 mL). The mixture was heated with a heat gun until all of the polymer dissolved. The flask was heated in an oil bath (140 °C) to evaporate all volatiles. This procedure was repeated twice. The flask was then exposed to high vacuum

overnight. The ^1H and ^{19}F spectra of the copolymer were unchanged by this procedure.

Recrystallization of copolymer from $\text{CHCl}_2\text{CHCl}_2$. A test tube was charged with copolymer (25 mg, Table 1, entry 3) and $\text{CHCl}_2\text{CHCl}_2$ (5 mL). The mixture was heated with a heat gun until all of the polymer dissolved. The solution was allowed to cool to room temperature and kept still in a test tube rack for 3 days. The copolymer precipitated and floated to the top of solvent. The $\text{CHCl}_2\text{CHCl}_2$ was removed carefully using a syringe. This procedure was repeated. The $\text{CHCl}_2\text{CHCl}_2$ fractions were combined, passed through a pad of celite and evaporated, leaving a trace amount of residue (1.2 mg). ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR analysis of the residue (in $\text{CDCl}_2\text{CDCl}_2$) showed no signals for the copolymer. The purified copolymer was dried under vacuum (~20 mg solid was obtained). The ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were unchanged by this procedure.

Copolymerization of ethylene and VF by **1a in the presence of galvinoxyl (Table S-1, entry 10).** The standard copolymerization procedure was used except galvinoxyl (21 mg, 50 μmol , 5 equiv. vs. Pd) was also added. After the polymerization period, the mixture was cooled to room temperature and 100 mL MeOH was added. The polymer was collected by filtration, washed with Toluene (25 mL) and MeOH (20 mL), and dried under high vacuum overnight. Yield: 530 mg. The ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were similar to the spectra of copolymer obtained by **1a** in the absence of galvinoxyl (Table S-1, entry 3-5). The presence of unreacted galvinoxyl was confirmed by GC/MS as well as UV/Vis (absorbance at 428 nm).^{5,6} An estimate of amount of galvinoxyl (19.7 mg) was obtained from comparison of the galvinoxyl integral to that of added internal standard – 1,3,5– trisopropylbenzene. Similar results were obtained on repeated runs.

Copolymerization of ethylene and VF by AIBN (Table S-1, entry 11). The standard copolymerization procedure was used. After the polymerization period, the volatiles were removed under vacuum. The remaining solid (24 mg) was analyzed without further purification.

Attempted copolymerization of ethylene and VF by AIBN in the presence of galvinoxyl. The copolymerization procedure in Table S-1, entry 11 was followed except galvinoxyl (64 mg, 150 μmol) were also added. After the polymerization period, the volatiles were removed under vacuum. The remaining solid was analyzed without further purification. The yield was estimated by subtraction of the weight of galvinoxyl (64 mg) from the total solid product remaining (Yield: < 5 mg). ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR analysis of the residue (in 1,2-DCB- d_4)

showed no signals for the copolymer. The presence of unreacted galvinoxyl was confirmed by GC/MS and UV/Vis (absorbance at 428 nm).

Recrystallization of 1a-produced copolymer from 1,2-dichlorobenzene. A test tube was charged with copolymer (29 mg, Table S-1, entry 3) and 1,2-dichlorobenzene (5 mL). The mixture was heated with a heat gun until all of the polymer dissolved. The solution was allowed to cool to room temperature and kept still in a test tube rack for 2 days. The copolymer precipitated and floated to the top of solvent. The 1,2-dichlorobenzene solution was removed carefully using a syringe. This procedure was repeated. The 1,2-dichlorobenzene fractions were combined, passed through a pad of celite and evaporated. ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR analysis of the residue showed no signals for the copolymer.

Recrystallization of a mixture of 1a-produced copolymer and AIBN-produced copolymer. A test tube was charged with 1a-produced copolymer (24 mg, Table 1, entry 3), AIBN produced copolymer (20 mg, Table S-1, entry 11) and 1,2-dichlorobenzene (5 mL). The mixture was heated with a heat gun until all of the polymer dissolved. The solution was allowed to cool to room temperature and kept still in a test tube rack for 2 days. The copolymer precipitated and floated to the top of solvent. The 1,2-dichlorobenzene solution was removed carefully using a syringe. This procedure was repeated. The 1,2-dichlorobenzene fractions were combined, passed through a pad of celite and evaporated. ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR analysis of the residue showed signals for the copolymer produced by AIBN.

II. Representative NMR spectra of copolymers.

1,2-DCB

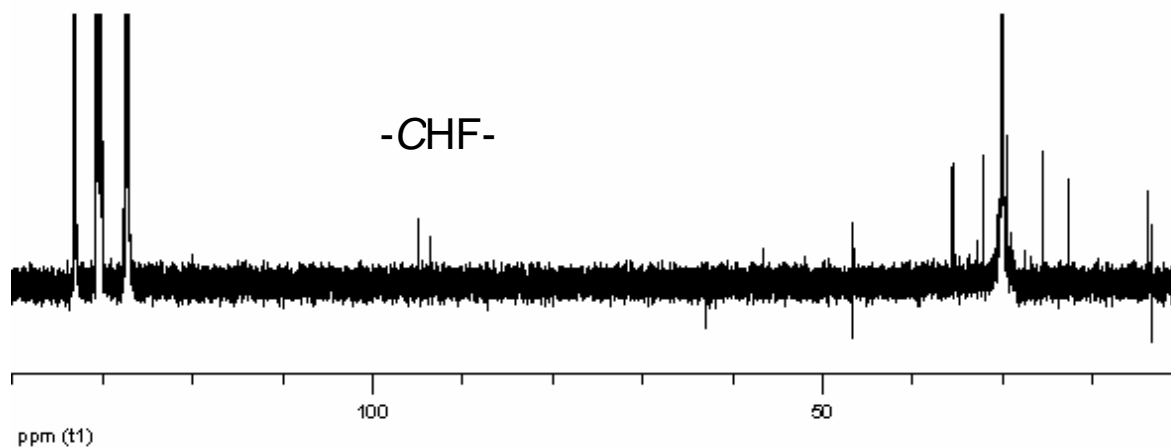


Figure S-1a. $^{13}\text{C}\{^1\text{H}\}$ NMR (1,2-DCB- d_4 , 110 °C) of ethylene/VF copolymer (Table S-1, entry 10).

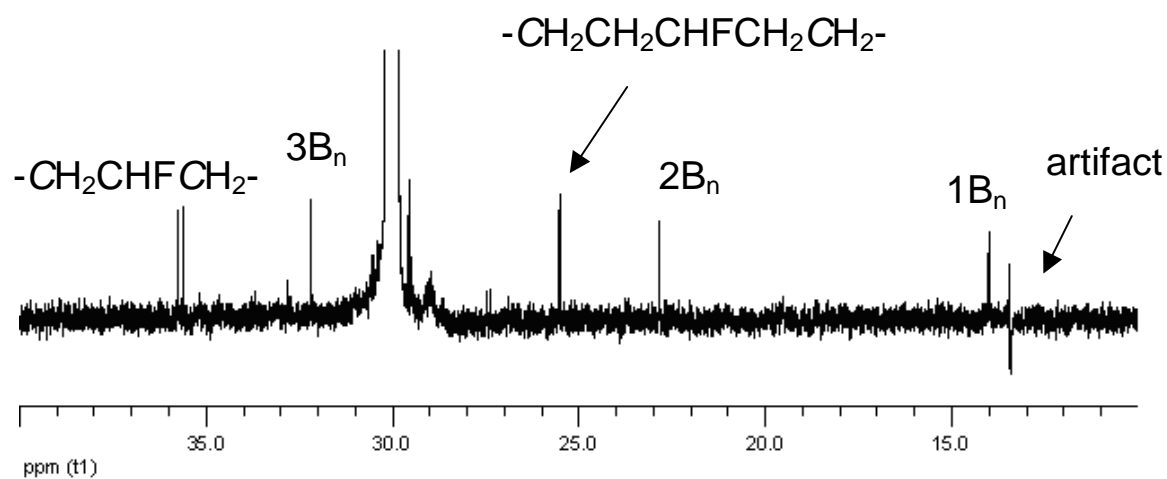


Figure S-1b. $^{13}\text{C}\{^1\text{H}\}$ NMR (1,2-DCB- d_4 , 110 °C) of ethylene/VF copolymer (Table S-1, entry 10). Expansion of the δ 40 to 10 region.

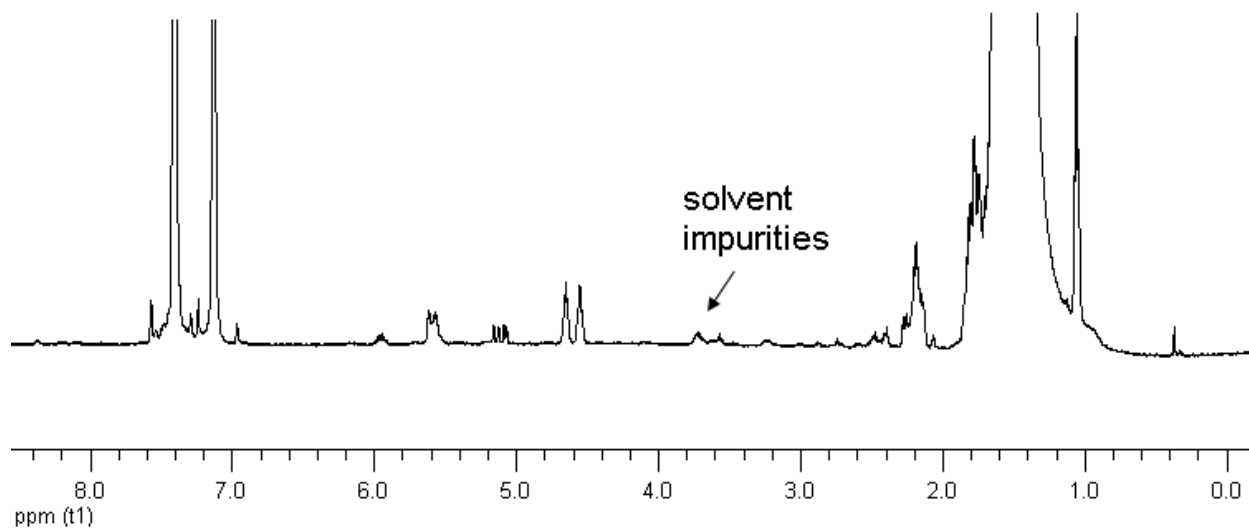


Figure S-1c. ^1H NMR (1,2-DCB- d_4 , 110 °C) of ethylene/VF copolymer (Table S-1, entry 10).

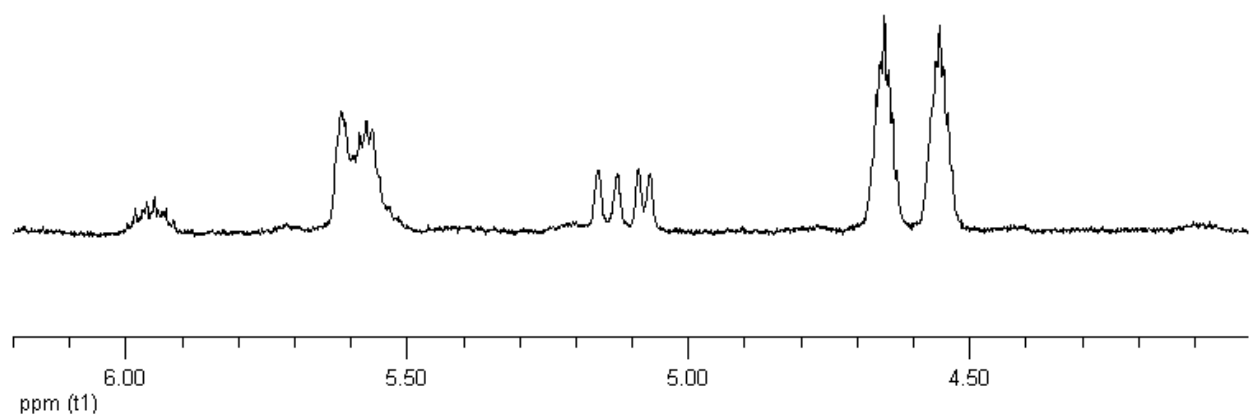


Figure S-1d. ^1H NMR (1,2-DCB- d_4 , 110 °C) of ethylene/VF copolymer (Table S-1, entry 10).
Expansion of the δ 6.2 to 4.0 region.

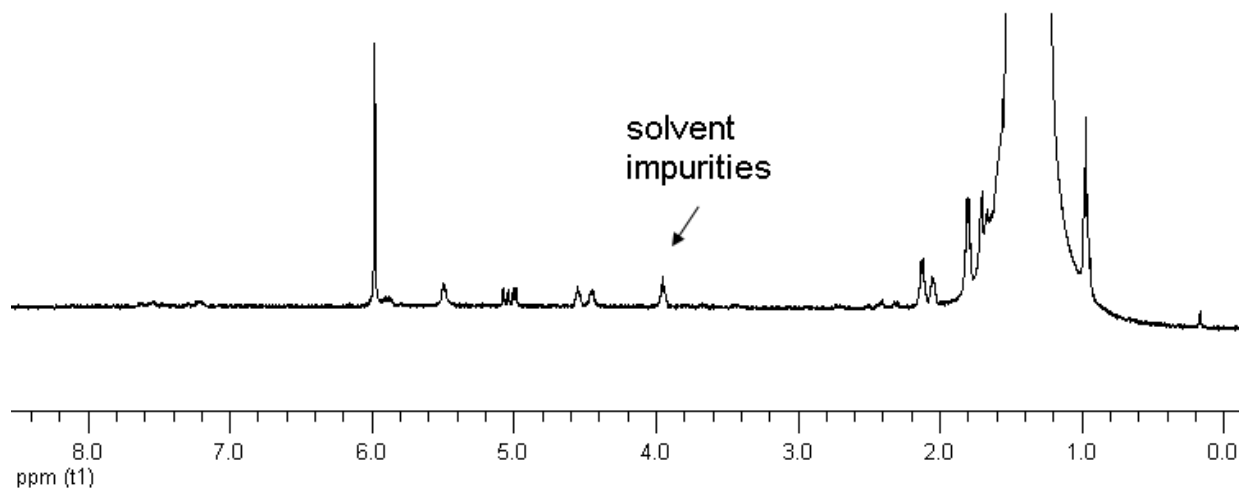


Figure S-2a. ^1H NMR ($\text{CDCl}_2\text{CDCl}_2$, 120°C) of ethylene/VF copolymer (Table S-1, entry 2).

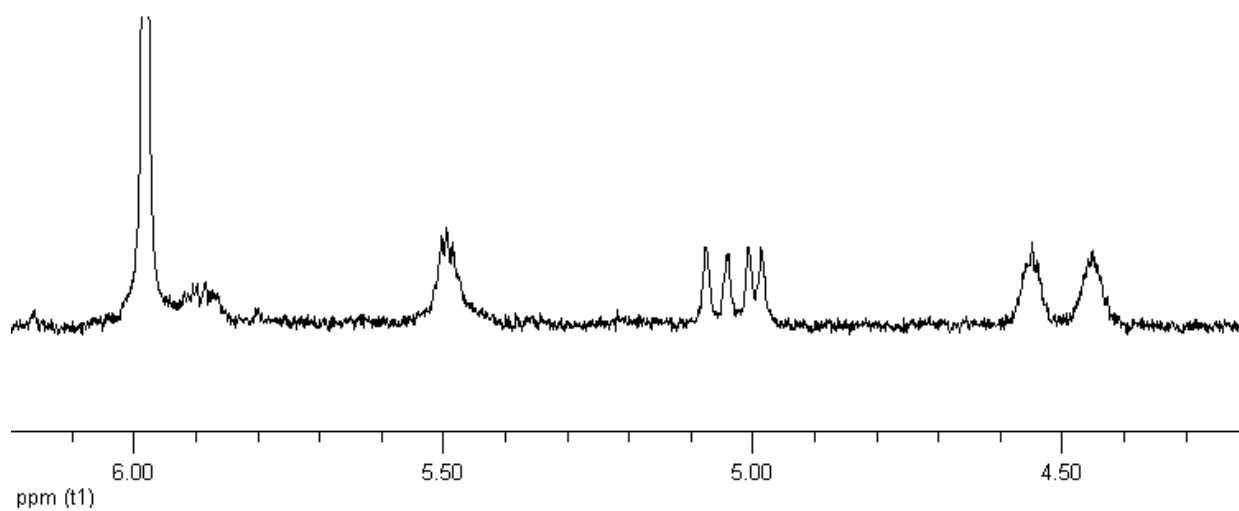


Figure S-2b. ^1H NMR ($\text{CDCl}_2\text{CDCl}_2$, 120°C) of ethylene/VF copolymer (Table S-1, entry 2).
Expansion of the δ 6.2 to 4.2 region.

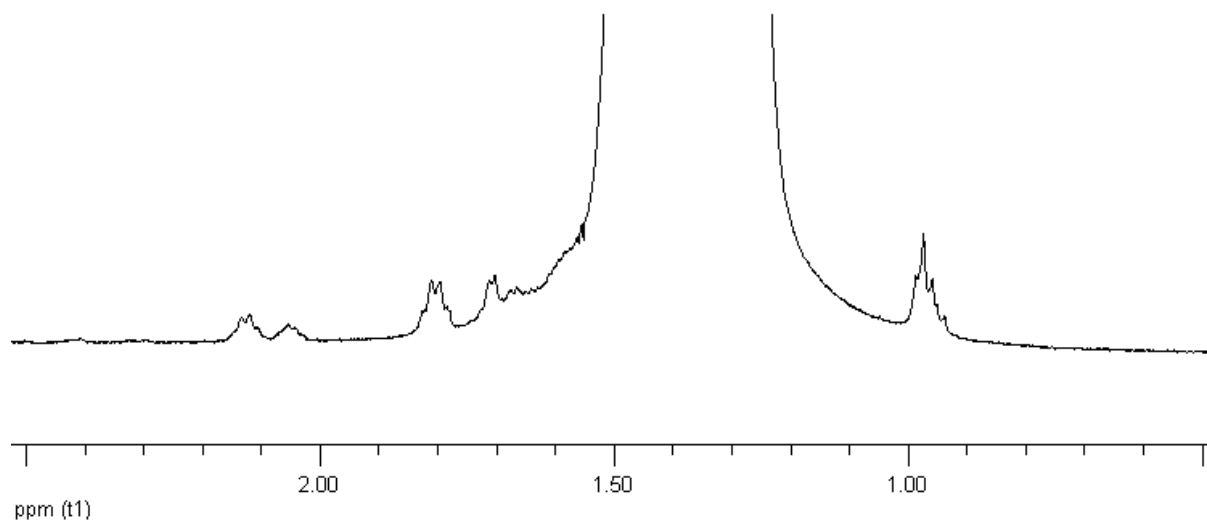


Figure S-2c. ^1H NMR ($\text{CDCl}_2\text{CDCl}_2$, 120°C) of ethylene/VF copolymer (Table S-1, entry 2). Expansion of the δ 2.5 to 0.5 region.

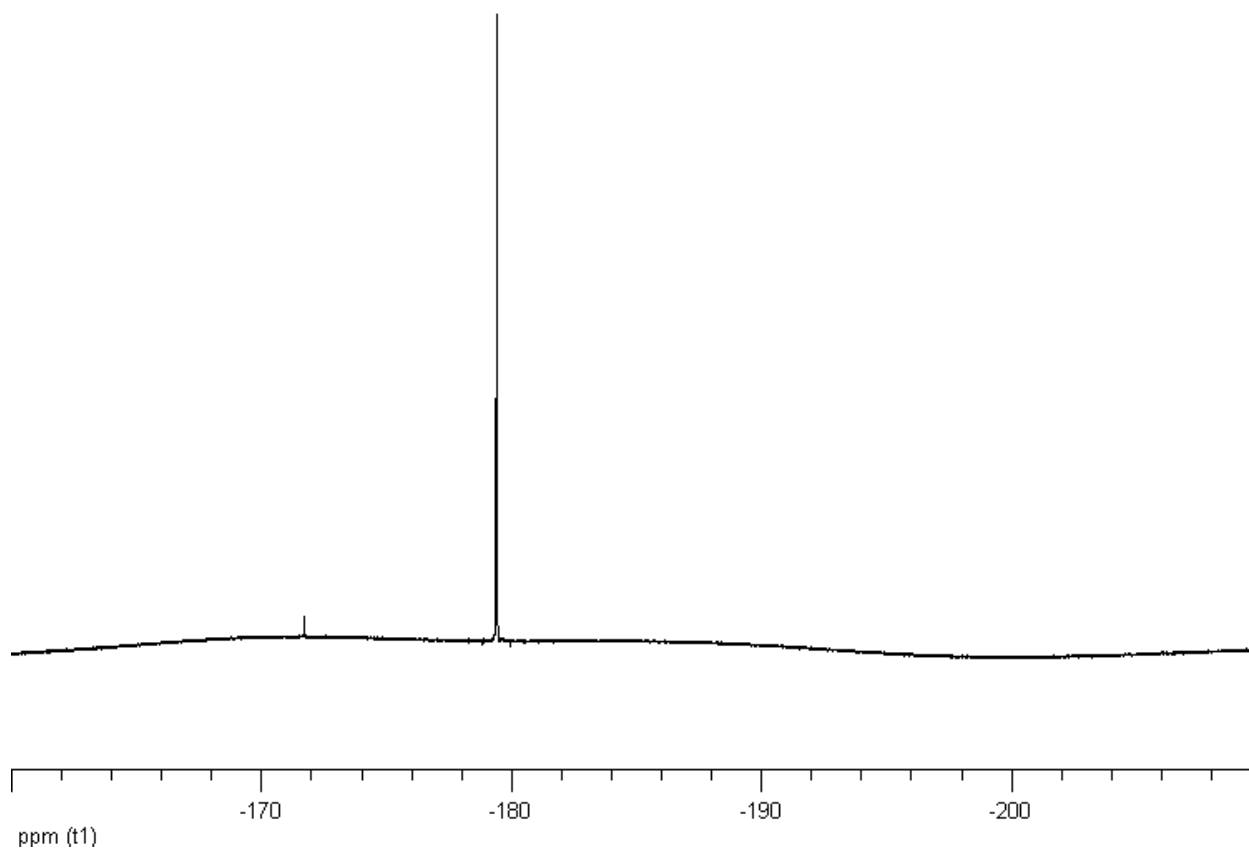


Figure S-3. ^{19}F NMR ($1,2\text{-DCB-}d_4$, 110°C) of ethylene/VF copolymer (Table S-1, entry 3). Expansion of the δ -160 to -200 region.

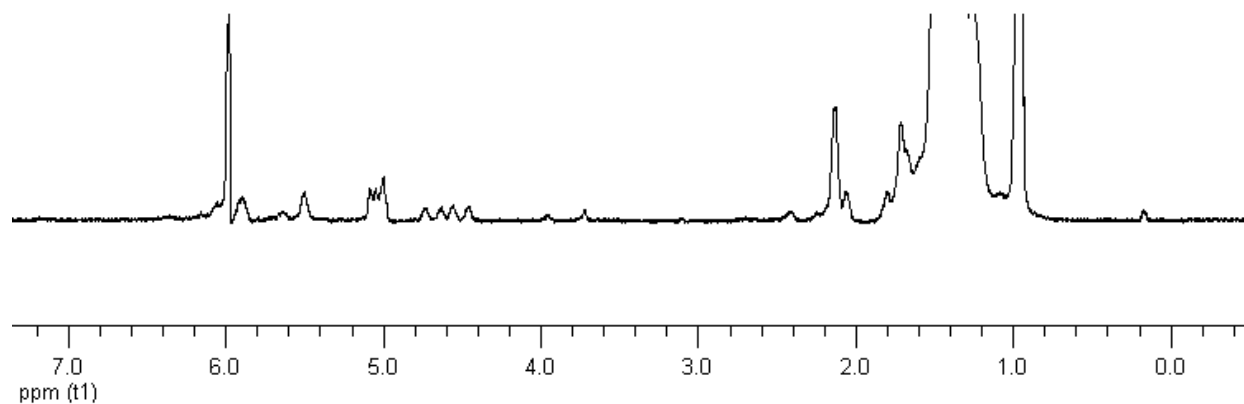


Figure S-4a. ^1H NMR ($\text{CDCl}_2\text{CDCl}_2$, 120°C) of ethylene/VF copolymer clearly showing $-\text{CH}_2\text{CHFMe}$ chain end. This copolymer was produced by **1a** from a mixture of 80 psi VF and 120 psi ethylene at 100°C .

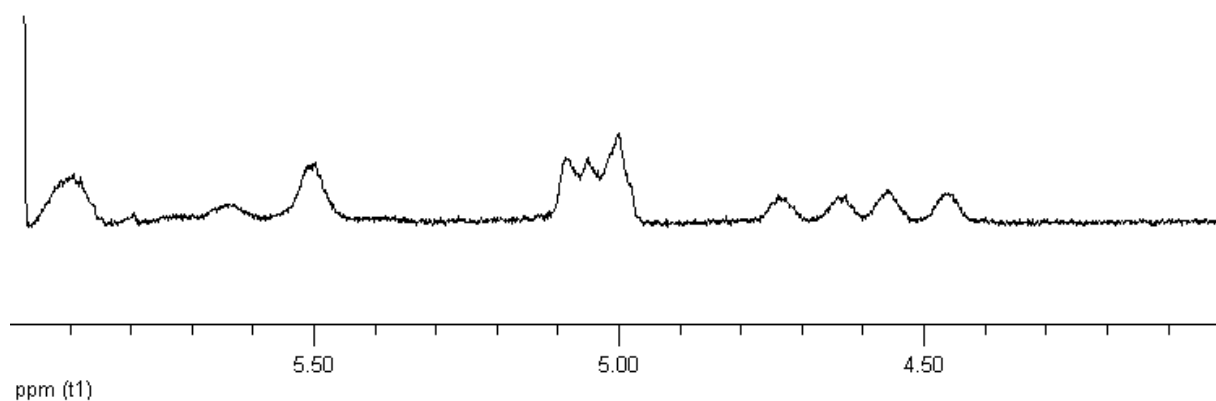


Figure S-4b. ^1H NMR ($\text{CDCl}_2\text{CDCl}_2$, 120°C) of ethylene/VF copolymer clearly showing $-\text{CH}_2\text{CHFMe}$ chain end. Expansion of the δ 6.0 to 4.0 region.

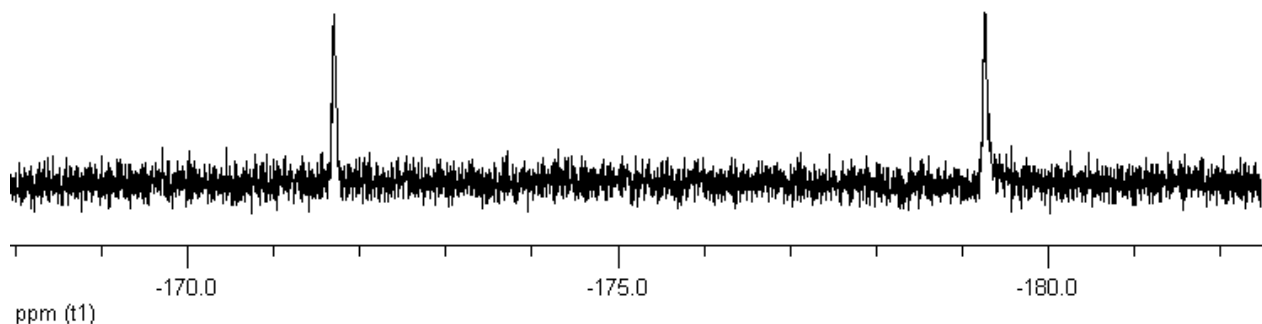


Figure S-4c. ^{19}F NMR ($\text{CDCl}_2\text{CDCl}_2$, 120°C) of ethylene/VF copolymer clearly showing $-\text{CH}_2\text{CHFMe}$ chain end. Expansion of the δ -168.0 to -182.5 region.

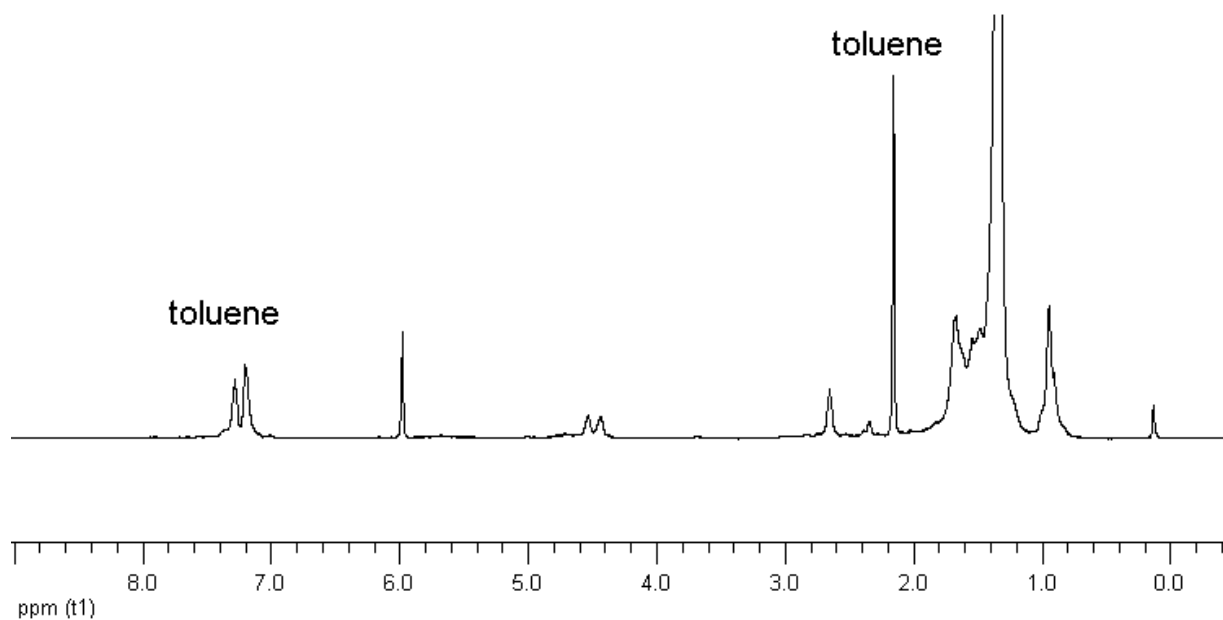


Figure S-5a. ^1H NMR ($\text{CDCl}_2/\text{CDCl}_2$, 120 $^\circ\text{C}$) ethylene/VF copolymer made by AIBN (Table S-1, entry 11).

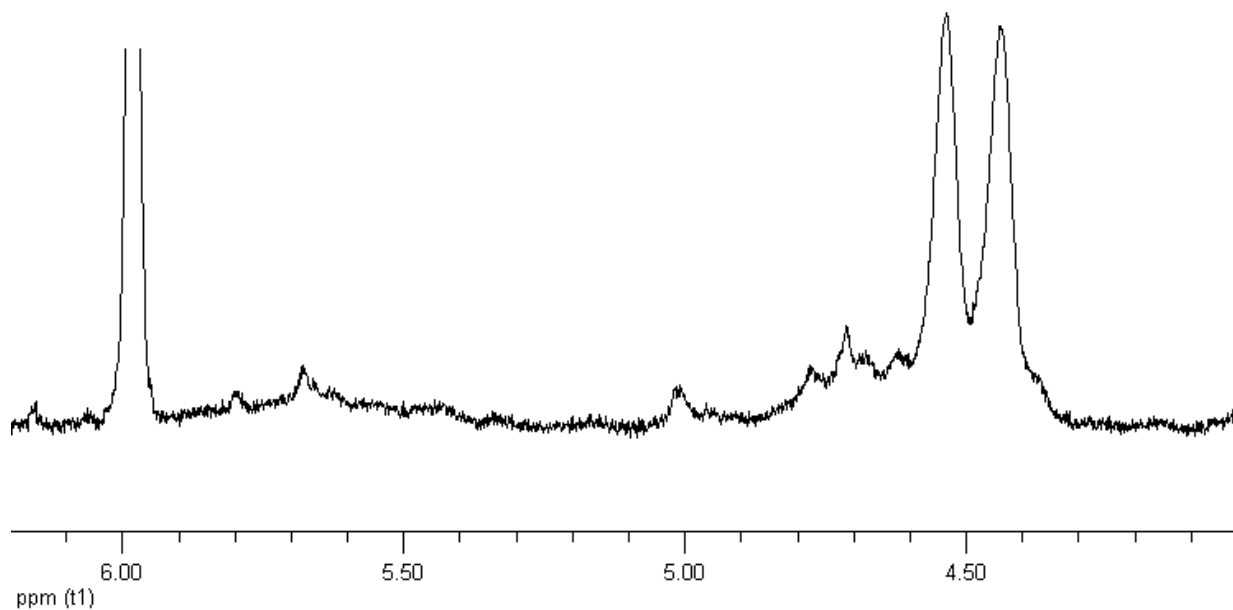


Figure S-5b. ^1H NMR ($\text{CDCl}_2/\text{CDCl}_2$, 120 $^\circ\text{C}$) ethylene/VF copolymer made by AIBN (Table S-1, entry 11). Expansion of the δ 6.2 to 4.0 region.

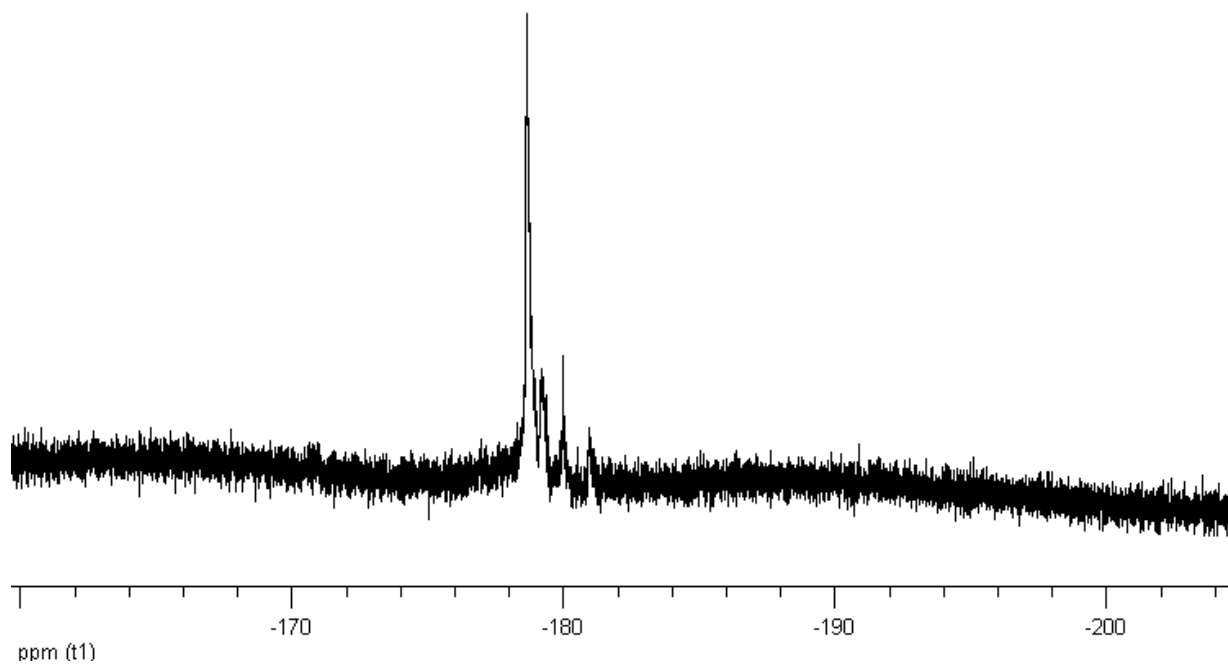


Figure S-5c. $^{19}\text{F}\{^1\text{H}\}$ NMR ($\text{CDCl}_2\text{CDCl}_2$, 120 °C) ethylene/VF copolymer made by AIBN (Table S-1, entry 11). Expansion of the δ -160 to -204 region.

References

- ¹ (a) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *129*, 8946. (b) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. manuscript submitted.
- ² De Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.
- ³ Grinshpun, V.; Rudin, A. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 219.
- ⁴ VF is “reasonably anticipated to be a human carcinogen” according to the Report on Carcinogens, Tenth Ed., 2002, which is available on the Internet and can be accessed from the Environmental Health Perspectives website at: <http://www.ehponline.org> or from the NTP website at: <http://ntp.niehs.nih.gov/ntp>.
- ⁵ Nakanishi, I.; Kawashima, T.; Ohkubo, K.; Kanazawa, H.; Inami, K.; Mochizuki, M.; Fukuhara, K.; Okuda, H.; Ozawa, T.; Itoh, S.; Fukuzumi, S.; Ikota, N. *Org. Biomol. Chem.* **2005**, *3*, 626.
- ⁶ Decomposition products of galvinoxyl were also detected by GC/MS. Autooxidation of galvinoxyl by molecular oxygen has been previously reported. See for example: Dubinskii, V. Z.; Belyakov, V. A.; Roginskii, V. A.; Miller, V. B. *Russ. Chem. Bull.* **1975**, *24*, 44.