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PAPER

Synthesis of internal fluorinated alkenes *via* facile aryloxylation of substituted phenols with aryl trifluorovinyl ethers†

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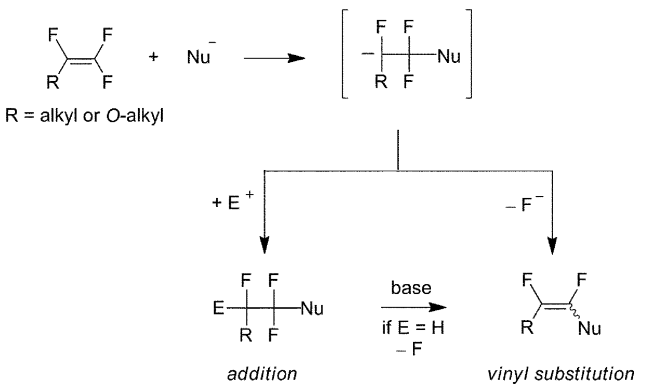
Nucleophilic addition–elimination of *ortho*- or *para*-substituted phenols to aryl trifluorovinyl ethers (TFVEs) in *N*,*N*-dimethylformamide was studied. Using sodium hydride as a base afforded vinyl substitution products R–Ar–O–CF═CF–O–Ar–R′, where R or R′ = H, Br, OMe, *tert*-Bu, or Ph. The vinyl substitution products produced mixtures of (*Z*)/(*E*)-isomers and this isomer ratio was influenced by substitution with more sterically encumbered phenol nucleophiles. Reactions using caesium carbonate afforded addition products R–Ar–O–$CHFCF_2$–O–Ar–R′ whereas upon dehydrofluorination using sodium hydride produced vinyl substitution products. The preparation of vinyl substituted and addition products proceeded in overall good isolated yields and were elucidated using ^{1}H and ^{19}F NMR, GC-MS, and X-ray analysis. Vinyl substituted products were inert to UV light and chemical reactivity using common polymerization promoters. Thermal activation of the (*Z*)/(*E*)-fluoroolefin (-CF═CF-) was observed at an onset of 310 °C in nitrogen using differential scanning calorimetry (DSC) producing insoluble network material. The synthesis, characterization, and mechanism for stereoselectivity are discussed.

Introduction

Nucleophilic addition to perfluorinated alkenes is a well known organofluorine transformation and continues to garner academic and commercial interest.[1–3] As a result, this methodology has led to the development of next-generation hydrofluoroethers (HCFCs) as leading alternatives to chlorofluorocarbons (CFCs),[4,5] perfluorinated polyethers (PFPEs) for high service temperature fluids,[6] processable ring-containing fluoropolymers,[7] intermediates/monomers for fluorinated polymers,[8–11] and latent thermally cross-linkable fluorinated aryl ether oligomers/polymers as additives for fluoroelastomers.[12] Further utility of fluorinated alkenes has more recently extended toward the development of quantitative chemisorption of chemical warfare agents in environmental samples.[13] The design of peptide mimics for the development of emerging biologically-active drug candidates has employed the internal fluoroolefin moiety to enhance membrane transport.[14] Use of internal fluorinated alkenes as a linking group for single molecule liquid crystals (LC) has been shown to enhance nematic phase stability, which is one of the main goals for maintaining a vibrant LC display market.[15,16] Continuing interest in these broad areas warrants investigating new strategies for the development functionalized of fluorinated alkenes.

The strong electron-withdrawing character of the fluorine atoms on terminal perfluorinated alkenes exposes their adjacent carbons to nucleophilic attack. The carbanion intermediate that results from the nucleophilic addition to a trifluoroalkene is either trapped by an accompanying electrophile or, in the absence of an electrophile, eliminates a fluoride ion, resulting in vinyl or allyl substitution (Scheme 1). In the case where the carbanion is trapped by a proton source (E = H), dehydrofluorination with



Scheme 1 Nucleophilic addition to terminal fluorinated alkenes affording addition or vinyl substitution products.

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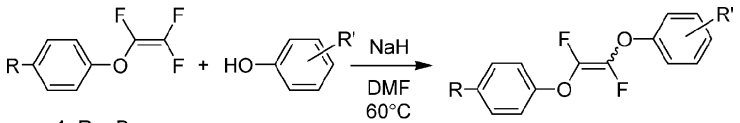
Table 1 Aryloxylation of substituted phenols with aryl TFVEs



1 R = Br
2 OCH_3

3–9

R	R′	Product[a]	(*Z*)/(*E*)[b]	Yield [%][c]
Br	*p*-Br	(*Z*)/(*E*)-**3**	1.26/1	75
Br	H	(*Z*)/(*E*)-**4**	1.31/1	72
Br	*p*-OCH_3	(*Z*)/(*E*)-**5**	1.26/1	60
OCH_3	*p*-Br	(*Z*)/(*E*)-**5**	1.28/1	86
OCH_3	*p*-OCH_3	(*Z*)/(*E*)-**6**	1.27/1	64
Br	*o*-Br	(*Z*)/(*E*)-**7**	1.41/1	69
Br	*o*-$C(CH_3)_3$	(*Z*)/(*E*)-**8**	1.69/1	50
Br	*o*-Ph	(*Z*)/(*E*)-**9**	1.95/1	67

[a] Average of two runs. [b] Determined by ^{19}F NMR. [c] Isolated yield of (*Z*)/(*E*)-mixture.

a base can also result in vinyl substitution by elimination *via* a similar carbanion intermediate.[17]

Reported additions to terminal trifluorovinyl perfluoroolefins have included F-,[18] AgF,[19] N_3-,[20] and C-,[21,22] O-,[23–25] N-,[21,24,26] or S-alkyl/aryl nucleophiles.[21,24,27] Such nucleophilic additions are primarily facilitated in basic conditions; other additions have also included radical[28,29] and Pd-catalyzed addition.[4] Most of the aforementioned reported examples have been limited to nucleophile additions to fluoroalkyl or fluoroalkyl ether substituted fluoroolefins. Herein, we describe the new synthesis of aryl 1,2-difluorodioxyethylenes by the facile nucleophilic addition of substituted phenols to aryl trifluorovinyl ethers (TFVEs). Aryl TFVEs are well known to undergo thermal [2 + 2] cyclodimerizations[30] whereby difunctional aryl TFVEs afford perfluorocyclobutyl (PFCB) aryl ether polymers used for a multitude of high-performance material applications.[31–34] Aryl TFVEs are commercially available and can also be prepared in two steps starting from phenolic precursors *via* alkylation with 1,2-dibromotetrafluoroethane ($BrCF_2CF_2Br$), followed by zinc-mediated dehalogenation.[32]

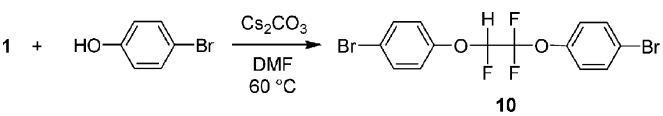
We have previously reported the polymerization of bisphenols to bis(trifluorovinyloxy)biphenyls affording high molecular weight, solution processable condensation polymers and oligomers possessing hydro-1,2,2-fluoroethane (-$CHFCF_2$-) or 1,2-difluoroethylene (-CF=CF-) enchainment.[12,35,36] In single molecule studies, we have discovered that substituted phenol additions to monofunctionalized aryl TFVEs showed stereoselectivity for the preparation of vinyl substituted isomers. This operationally simple, modularly tailorable methodology afforded substituted internal perfluorinated alkenes possessing functionalizable moieties on the *ortho*/*para* positions on the aromatic ring. Their synthesis, characterization, electronic/steric factors contributing to stereoselectivity, and reactivity will be discussed.

Results and discussion

Synthesis and characterization of vinyl substitution products

Vinyl substitution products **3–9** were prepared by the stoichiometric addition of substituted sodium phenoxides to aryl TFVEs 1-bromo-4-(trifluorovinyloxy)benzene (**1**) and 1-methoxy-4-(trifluorovinyloxy)benzene (**2**) in anhydrous DMF at 60 °C for 1 h (Table 1). Excess NaH (4 equiv.) was used to deprotonate substituted phenols in order to avoid the formation of addition products (*e.g.*, Ar–O–$CHFCF_2$–O–Ar′) by protonation from adventitious water from the solvent or unreacted phenol. The optimized preparation of vinyl substituted products **3–9** proceeded in quantitative conversion as observed by ^{19}F NMR and in modest to good isolated yields (50–86%) as a mixture of (*E*)- and (*Z*)-isomers.

The preparation of the hydrofluorinated addition product **10** was achieved by the addition of *p*-bromophenol to 1-bromo-4-(trifluorovinyloxy)benzene **1** in the presence of Cs_2CO_3 (0.5 equiv.) in DMF for 1 h (Scheme 2). As previously observed, the conversion was quantitative based on ^{19}F NMR and **10** was isolated in 73% yield. It was shown that aliphatic and aromatic alcohols, particularly phenol, proceed *via* Pd-catalyzed addition to perfluorinated alkenes to afford hydrofluorinated ethers.[4] Attempts to employ this strategy did not produce the desired addition product **10**, but rather afforded only unreacted starting materials. The general utility of this methodology is realized that by the choice of either NaH or Cs_2CO_3 as a base selectively affords either vinyl substituted or addition products, respectively. This is in agreement with previous studies for the preparation of step-growth polymers from difunctional phenols and aryl TFVEs.[12]



10

Scheme 2 Carbonate-catalyzed addition of 1,4-bromophenol with 1-bromo-4-(trifluorovinyloxy)benzene **1** affording hydrofluorinated ether **10**.

Fig. 1 shows the ^{19}F NMR patterns in $CDCl_3$ of the aryl TFVE **1** starting material, vinyl substituted products (*Z*)/(*E*)-**3** and (*Z*)/(*E*)-**5**, and the addition product **10**. Aryl TFVEs typically produce a diagnostic AMX pattern, and in the case of **1**, with peaks at −120.5 ppm (dd, J = 95.5, 55.4 Hz, *cis*-CF=CF_2, F_A), −126.4 ppm (dd, J = 111.9, 95.5 Hz,

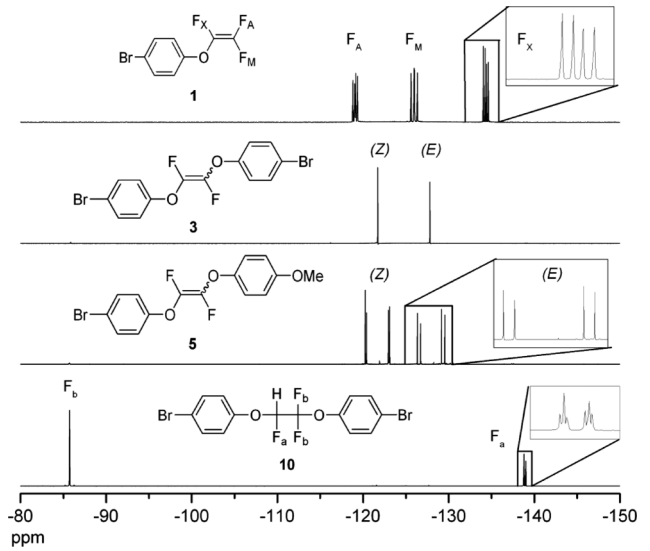


Fig. 1 ^{19}F NMR spectra (in $CDCl_3$) overlay of aryl TFVE **1**, vinyl substituted products (*Z*)/(*E*)-**3** and (*Z*)/(*E*)-**5**, and hydrofluorinated addition product **10**.

trans-CF=CF_2, F_M), and −136.8 ppm (dd, J = 111.9, 52.4 Hz, CF=CF_2, F_X). The vinyl substituted product isomer mixture of (*E*)/(*Z*)-**3** produced two singlet signals due to the asymmetry of the isomers at −121.7 and −127.8 ppm for the (*E*)- and (*Z*)-isomer, respectively. In comparison, the substitution of R = Br with R = OMe desymmetrized the stereochemical environment and produced peak signals for (*E*)/(*Z*)-**5** at −120.5 and −122.3 ppm (d, J = 42.8 Hz, (*Z*)-CF=CF) and −126.7 and −129.6 ppm (d, J = 110.3 Hz, (*E*)-CF=CF). Lastly, the addition hydro-1,2,2-fluoroethane ether containing product **10** produced an AB pattern at −85.4 and −85.9 ppm (d, J = 148.1 Hz) for the geminal fluorines (CHFCF_2) and −138.9 ppm (dt, J = 59.3 Hz, 8.2 Hz) for the fluorine coupled with the proton (CHFCF_2).

(*Z*)- and (*E*)-isomers were difficult to separate using column chromatography or vacuum distillation. However, in some cases vinyl substituted (*Z*)- and (*E*)-isomers were easily separated by fractional solvent precipitation. Specifically, dispersion of vinyl substituted products **3** and **6** in methanol or hexanes resulted in the exclusive precipitation of the (*E*)-isomer. Recrystallization of the precipitated (*E*)-isomer from the slow evaporation of diethyl ether at room temperature afforded X-ray quality crystalline solids. Fig. 2 shows the ORTEP structures of (*E*)-**3** and (*E*)-**6**. Crystalline solids of the respective (*Z*)-isomers of **3** and **6** were difficult to obtain; attempts to crystallize from a multitude of polar and non-polar solvents produced only an amorphous solid or oil. Differential scanning calorimetry (DSC) showed a broad melting point range of 120–147 °C for (*Z*)/(*E*)-**3** isomers. Broad melting point ranges were similar for all other isomers with no distinct melting endotherm of individual isomers. Finally, X-ray quality crystalline solids of addition product **10** were elucidated from the slow evaporation of diethyl ether.

Selected bond length (Å) mean values and bond angles for (*E*)-**3**, (*E*)-**6**, and **10** are shown in Table 2. (*E*)-isomers of **3** and **6** showed nearly identical C(1)–O(1) bond lengths. However, the C(7)–C(7A) unsaturated bond length for (*E*)-**6** was shorter by nearly 0.1, which profoundly influences the F(1)–C(7)–C(7A) and O(1)–C(7)–C(7A) bond angles compared with (*E*)-**3**. The

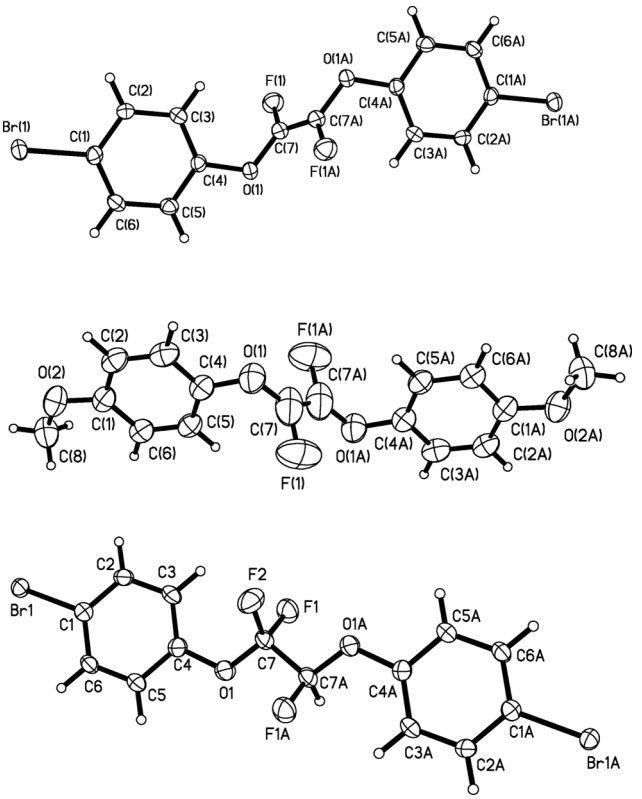


Fig. 2 ORTEP representations (50% probability) of vinyl substituted product (*E*)-**3** (top), (*E*)-**6** (middle), and addition product **10** (bottom). The crystal of **10** produced a mixture of conformers which cause intermixing of F- and H-atoms. The F-atoms are each given occupancy of 0.75.

unsaturated double bond lengths of these isomers are considerably contracted compared to typical hydrocarbon alkene bonds and are comparable to triple bond lengths. The result showed the F(1)–C(7)–C(7A) bond angle for (*E*)-**6** was decreased by 9.06° and the O(1)–C(7)–C(7A) bond angle was increased by nearly the same magnitude at 9.35° compared with bromine substituted (*E*)-**3**. This may be due to the electron donation of the *para*-methoxy substituted aryl groups to the fluorines low lying 2p orbitals.[37] In all cases, the structures demonstrated that the O(1)–C(7)–C(7A) bond angles were larger than the F(1)–C(7)–C(7A) angle due to oxygen lone pair repulsions. Bond angles for both (*E*)-isomers and the hydrofluorinated solid state structures indicate relatively consistent sp^2 and sp^3 fluorocarbon C(7) hybridization, respectively, compared with homoanalogous hydrocarbons.

Electronic and steric effects on the stereoisomeric ratio of vinyl substituted products

The results in Table 1 indicated a preference for the formation of the (*Z*)-isomer of the vinyl substituted products **3–9** as indicated by ^{19}F NMR. Substituted phenol additions to the aryl TFVEs producing **3–6** showed quantitative conversion at room temperature or 60 °C in DMF; however, the (*Z*)/(*E*)-isomer ratios were unaffected. Furthermore, cation substitution did not influence the stereoisomer outcome when using either LiH or NaH as the base. Solvent effects were then investigated facilitating sodium phenoxide additions to aryl TFVE **1** in THF and benzene. These reactions produced lower conversions of the

Table 2 Selected bond lengths (Å) and angles (°) of (*E*)-**3**, (*E*)-**6**, and **10**

Entry	C(7)–C(7A)	C(7)–O(1)	C(7)–F(1)	F(1)–C(7)–C(7A)	O(1)–C(7)–C(7A)
(*E*)-**3**	1.288(7)	1.343(4)	1.358(4)	118.8(4)	126.2(5)
(*E*)-**6**	1.189(11)	1.321(5)	1.449(7)	109.7(6)	135.7(8)
10	1.513(7)	1.349(4)	1.381(4)	107.10(3)	111.3(5)

vinyl substituted product **4** in 60–88% and 15%, respectively. Although conversions were not quantitative, the (*Z*)/(*E*)-isomer ratio of the vinyl substituted product **4** was unaffected. Electronic effects due to the donating/withdrawing ability of aryl ethers have been shown to influence the formation of (*Z*)/(*E*) isomers.[38] This was not the case in our observations as the nature of the *para*-functionalized vinyl substituted products **3–6** also showed no indication of preference of the respective (*Z*)- or (*E*)-isomer. However, installing bromine, *tert*-butyl, and phenyl functional groups in the *ortho* position of the phenol nucleophile produced vinyl substituted products **7–9** with preferential formation of the (*Z*)-isomer. The most pronounced effect was observed for the case where R = Ph, where up to 54% more *ortho*-substituted (*Z*)-isomer was formed of **9** compared with the *para*-substituted **3**.

In order to elucidate the mechanistic rationale for the preference of (*Z*)-isomer formation, these results possibly indicate that a steric effect is influencing their formation. It has been reported most addition–elimination reactions to fluoroolefins proceed *via* a $E1_{CB}$-like mechanism[1] and occur initially either by the formation of a sp^2-hybridized planar[39,40] or sp^3-hybridized tetrahedral[41,42] carbanion. A competitive addition pathway *via* single-electron transfer (SET) was ruled out based on previous reports[43] and given the fact that aryl TFVEs are benign to chemical radical initiation.[44] In most cases, fluorocarbanion hybridization is predominately influenced by repulsion or inductive effects.[1,45] We initially invoke the generation of the sp^3-hybridized intermediate **I** shown in Fig. 3 as a result of *anti*-addition of the phenol nucleophile. *Syn*-addition of the nucleophile is possible due to anion hyperconjugation by the stabilizing interaction of the carbanion 2p orbital with the σ* C_β–F orbital.[39] The anionic intermediates generated would then facilitate *syn*-elimination of NaF to form the (*Z*)/(*E*)-vinyl substituted products. However, *syn*-elimination may be unlikely as the hyperconjugative stabilization would not overcome the eclipsing steric interactions by initial addition followed by ensuing elimination.[41]

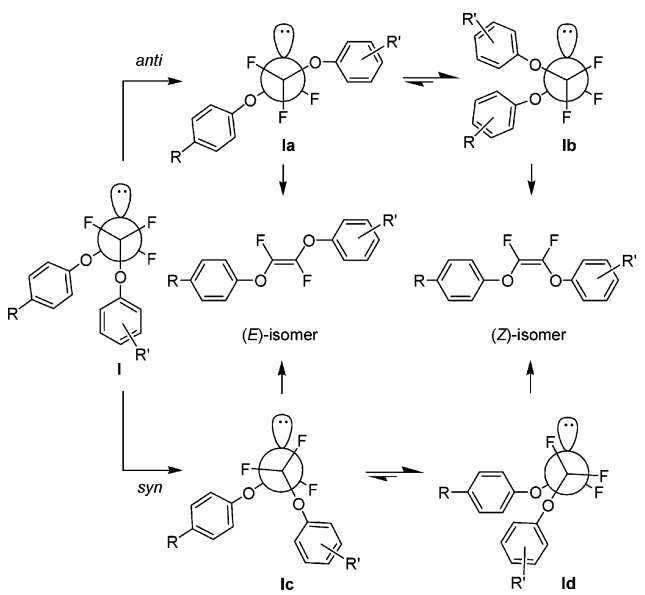
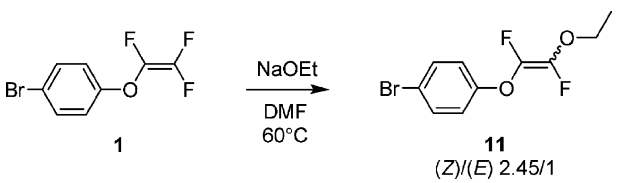


Fig. 3 Proposed mechanism of the addition–elimination of aryl TFVEs by substituted phenols affording vinyl substituted (*Z*)- and (*E*)-isomers.

Anti-elimination would involve comparing rotational energy barriers of the intermediate **I**. Our observations pointing to the formation of the preferred (*Z*)-isomer indicates the kinetically favored intermediate is **Ib**. This elimination pathway involves clockwise rotation of **I** between the two aryl ethers. Such a rotation in **Ib** may be favored because of greater flexibility of the adjoining aryl ether linkages compared with rotation by a more sterically encumbered, shorter C–F bond shown as the proposed intermediate **Ia**. This steric effect would be more pronounced if *ortho*-substituted groups on the phenol nucleophile are present; we have shown this to be experimentally the case as shown with *ortho*-substituted vinyl addition products **7–9** (*vide supra*). The intermediate **Ib** may be further stabilized by the *gauche* effect whereby the σ C–O bonding orbitals delocalize electron density to the antibonding σ* C_β–F orbitals.[46] *Syn*-elimination can also be considered since it would involve no rotation. If *syn*-elimination were to occur, this would be indicative of favorable eclipsing of the aryl ethers (**Id**) rather than the aryl ether eclipsing with fluorine atoms (**Ic**).

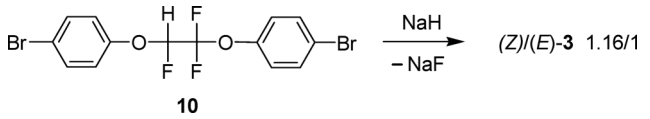
To rule out π–π electronic interactions or the presence of phenonium ion intermediates,[47] addition to **1** with sodium ethoxide (NaOEt) was performed. This afforded vinyl substituted product **11** with a higher 2.45/1 (*Z*)/(*E*) isomer ratio compared to phenol nucleophiles (Scheme 3). This result indicates that smaller linear aliphatic nucleophiles such as ethoxide desire rotation (for *anti*-elimination) or eclipsing (for *syn*-elimination) with the carbanion possessing the aromatic ether.



Scheme 3 Addition of aliphatic alcohol, sodium ethoxide, with aryl TFVE **1**.

Dehydrofluorination of addition product 10

Facile dehydrofluorination of addition product **10** proceeds using an equivalent amount of base. In this case, elimination of NaF using NaH in DMF at 60 °C produced **3** in nearly quantitative yield (Scheme 4). The vinyl substituted product produced slightly preferential formation of the (*Z*)-isomer in a (*Z*)/(*E*) ratio of

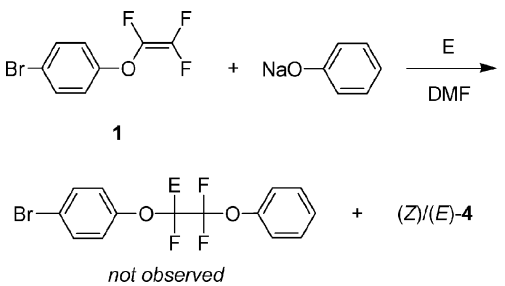


Scheme 4 Dehydrofluorination of **10** using NaH affording isomeric mixture (*Z*)/(*E*)-**3**.

1.16/1. This indicates the carbanion is relatively long-lived in order to facilitate rotation in order to expel fluorine *via syn*- or *anti*-elimination. Based on the single X-ray structure of **10** (Fig. 2, bottom image), the most stable conformation indicates the aromatic ethers are pseudo-*trans*. Therefore, less (*Z*)-isomer **3** formation by dehydrofluorination (*i.e.*, (*Z*)/(*E*) = 1.16/1) compared with sodium *p*-bromophenoxide addition–elimination (*i.e.*, (*Z*)/(*E*) = 1.26/1) may be due to competitive *syn*- and *anti*-elimination pathways.

Attempted fluorocarbanion trapping

The sequential trapping of carbanions with electrophiles upon initial nucleophilic addition to fluoroolefins has been extensively reported.[39,41,48] This is evident by the inevitable formation of trace amounts of hydro-1,1,2-trifluoroethane inevitable due to adventitious water or from free hydroxyl (-OH) species. It would seem obvious that the trapping of electrophiles could produce a functionally diverse pool of fluorinated compounds from a tandem, two-step addition–substitution methodology. As a model system, initial attempts were performed in order to trap the carbanion intermediate generated from the addition of sodium phenoxide to **1** with labile electrophiles (denoted E) to produce compounds with the general structure shown in Scheme 5. Trapping with D_2O or CF_3SO_2Cl failed to produce any substituted product, where E = D or CF_3SO_2. ^{19}F NMR spectroscopy revealed only the formation of the vinyl ether product (*Z*)/(*E*)-**3** and trace amount of the hydro-1,2,2,-fluoroethane adduct. The addition of the electrophiles was performed in a sequential fashion, whereas addition of sodium phenoxide was added first to **1** at room temperature, allowed to stir for 5 min, wherein the electrophile was finally added. The evidence of trace amounts of hydro-1,2,2-fluoroethane that indicate the rate of the nucleophilic addition is quite rapid and the fluorocarbanion is short-lived, which is consistent with a previous report.[41] The lifetime of carbanions generated by nucleophilic additions to fluoroolefins has been shown to be very sensitive to the specific nature of nucleophile substrates.[39,48] Attempts to employ trapping at lower temperatures (*e.g.*, –78 °C) in THF or Et_2O failed to produce any trapped products in this study.



Scheme 5 Nucleophilic addition of phenol to aryl TFVE followed by attempted *in situ* trapping of electrophiles.

Reactivity of vinyl substitution products

The chemical reactivity of vinyl substitution products of (*Z*)/(*E*)-**3** was investigated using typical polymerization protocols.[49] Attempts to polymerize with 2,2-azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), boron trifluoride etherate, and *n*-butyl lithium resulted with retention of the unreacted (*Z*)/(*E*)-**3**. Reactions with *p*-toluenesulfonic acid, I_2, and UV radiation failed to promote any evidence of isomerization. However, thermal treatment of (*Z*)/(*E*)-**3** using DSC analysis in nitrogen revealed an exotherm at 310 °C, which produced an insoluble, black glassy solid. These results were consistent with reported crosslinking of aryl 1,2-difluorodioxyethylenes enchained in polymer systems produced insoluble crosslinked networks.[12] The mechanistic details of thermal crosslinking are currently under investigation.

Compound (*Z*)/(*E*)-**3** possesses dibromofunctionality that was found compatible with the Ni-catalyzed Yamamoto homocoupling protocol under mild conditions.[50] Polymers prepared by polymerizing aryl dihalides have produced a plethora of new conjugated polymer systems, which continue to gain interest.[50] ^{19}F NMR in DMSO-d_6 showed the fluoroolefins were still intact producing broad peaks associated with compound (*Z*)/(*E*)-**3** with no observed isomerization. Thermal calorimetry of the polymer using DSC produced an exotherm onset at 260 °C with its maximum at 310 °C that is consistent with the exotherms observed due to the thermal activation of 1,2-difluoroethylene moiety.

Conclusion

We have developed a methodology for the facile preparation of substituted aryl 1,2-difluorodioxyethylenes **3–9** and aryl hydro-1,2,2-fluorooxyethane **10** employing base-promoted nucleophilic additions of phenols to aryl trifluorovinyl ethers **1** and **2**. The transformation demonstrates general utility using commercially available materials that afforded either the vinyl substituted or addition products by simple choice of the base. As such, a diverse pool of functionalized internal fluoroolefins are now available that possess functionalizable synthetic handles. We were able to influence the selective formation of the (*Z*)-isomer upon addition of sterically encumbered phenol nucleophiles to aryl trifluorovinyl ether substrates. From this, we proposed that the formation of vinyl substituted products are due to either *syn*- or *anti*-elimination of fluorine from the generated carbanion intermediate which is influenced by the steric nature of the appended nucleophile. All other effects such as electronic, solvent, or temperature failed to promote selectivity of either (*Z*)/(*E*)-isomers. Finally, vinyl substituted products were benign to UV light exposure and chemical treatment using common polymerization initiators; thermal treatment using DSC analysis showed an exotherm at an onset of 310 °C producing an insoluble material. This may be due to the thermally activated self-initiation of the fluoroolefin moiety which undergoes further reaction with other fluoroolefins present ultimately producing network polymers. The robust nature of the prepared substrates would be attractive in the organic electronics whereby thermal stability is highly desired.

Experimental section

Reagents and general procedures

1-Bromo-4-(trifluorovinyloxy)benzene (**1**) is commercially available from Oakwood Products, Inc. and was donated along with 1-methoxy-4-(trifluorovinyloxy)benzene (**2**) by Tetramer Technologies, L.L.C. All other reagents and solvents were purchased from Aldrich and purified according to established procedures.[51] Anhydrous DMF was further dried by storage over anhydrous $MgSO_4$ under nitrogen atmosphere. All reactions and solvent transfers were carried out under nitrogen atmosphere. Glassware and syringes were flamed-dried and allowed to cool in a desiccator prior to use. Syringes fastened with needles were flushed with nitrogen prior to use. All reactions and solvent transfers were carried out under an atmosphere of nitrogen. Air- and moisture-free manipulations were carried out in a MBraun Labmaster glove box under nitrogen circulation.

Instrumentation

^{1}H, and ^{19}F NMR data were obtained on a JEOL Eclipse 300+ NMR Spectrometer and chemical shifts were reported in parts per million (δ ppm). ^{1}H NMR was internally referenced to tetramethylsilane (δ 0.0), ^{13}C NMR chemical shifts were reported relative to the center peak of the multiplet for $CDCl_3$ (δ 77.0 (t)), and ^{19}F NMR was referenced to $CFCl_3$. Gas chromatography (GC) coupled with electron ionization mass spectrometry (EIMS) was performed on a Shimadzu GC17A gas chromatograph coupled with a Shimadzu QP5000 mass spectrometer (EI at 70 eV) with initial temperature of 60 °C at a ramp of 10 °C min^{-1}. Melting points and thermal analysis was performed on a TA Q1000 differential scanning calorimetry (DSC) instrument at 10 °C min^{-1} in nitrogen.

Single crystal X-ray

Intensity data were collected using a Rigaku Mercury CCD detector and an AFC8S diffractometer. Data reduction including the application of Lp and absorption corrections used the CrystalClear program. The structure was solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by full-matrix least squares, on F^2 using SHELXTL 6.10.[52] Hydrogen atom positions were calculated from ideal geometry with coordinates riding on the parent atom. Crystallographic data for structures (*E*)-**3**, (*E*)-**6**, and **10** have been deposited in the Cambridge Crystallographic Data Center with publication numbers CCDC 656776, 656778, 656777, respectively.†

(*Z*)- and (*E*)-1,2-Bis(4-bromophenoxy)-1,2-difluoroethene ((*Z*)/(*E*)-3)

A solution of *p*-bromophenol (274 mg, 1.58 mmol) dissolved in DMF (4 mL) was added dropwise to a stirred suspension of NaH (152 mg, 6.32 mmol) in DMF (2 mL) at room temperature. The flask was placed in a preheated oil bath at 60 °C and sparged with nitrogen for 30 min. 1-Bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol) was transferred into the solution *via* syringe in a single portion. After 1 h, the mixture was treated with DI H_2O (25 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 25 mL). The combined organic layers were washed with water (2 50 mL), dried over $MgSO_4$, filtered over a pad of silica gel, and concentrated under vacuum affording the product mixture (*Z*)/(*E*)-**3** as an oily yellow solid (484 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.43 (m), 7.02 (d, J = 8.9 Hz), 6.95 (d, J = 8.9); ^{19}F NMR (283 MHz, $CDCl_3$) δ –121.7 (s, (*Z*)-CF═CF, 2F), –127.8 (s, (*E*)-CF═CF, 2F); GC-EIMS (70 eV) m/z (% relative intensity) (*Z*)-**3**: 408, 406, 404 (M^+, 10, 19, 11), 235, 233 (25, 26), 207, 205 (19, 19), 185, 183 (17, 17), 157, 155 (86, 91), 76, (89), 75 (89), 74 (24), 50 (100); (*E*)-**3**: 408, 406, 404 (M^+, 10, 18, 9), 235, 233 (25, 23), 207, 205 (18, 20), 185, 183 (17, 16), 176, 175 (9, 11), 157, 155 (82, 85), 76 (85), 75 (88), 50 (100).

(*Z*)- and (*E*)-1-(4-Bromophenoxy)-1,2-difluoro-2-phenoxyethene ((*Z*)/(*E*)-4)

Sodium phenoxide (184 mg, 1.58 mmol), sodium hydride (76 mg, 3.16 mmol) and 1-bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*E*)/(*Z*)-**4** as a yellow oil (373 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.39 (m), 7.20–7.01 (m); ^{19}F NMR (283 MHz, $CDCl_3$) δ –120.9 and –122.5 (d, J = 41.1 Hz, (*Z*)-CF═CF), –127.1 and –128.7 (d, J = 111.9 Hz, (*E*)-CF═CF); GC-EIMS (70 eV) m/z (% relative intensity) (*Z*)-**4**: 328, 326 (M^+, 22, 24), 157, 155 (31, 42), 77 (100), 76 (32), 75 (29), 51 (64), 50 (43); (*E*)-**4**: 328, 326 (M^+, 21, 21), 157, 155 (32, 42), 77 (100), 76 (32), 75 (29), 51 (61), 50 (44).

(*Z*)- and (*E*)-1-(4-Bromophenoxy)-1,2-difluoro-2-(4-methoxyphenoxy)ethene ((*Z*)/(*E*)-5)

p-Methoxyphenol (196 mg, 1.58 mmol), sodium hydride (152 mg, 6.32 mmol) and 1-bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*Z*)/(*E*)-**5** as a yellow oil (340 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.43 (m), 7.12–6.84 (m), 3.79 (d, J = 8.9 Hz, -OCH_3); ^{19}F NMR (283 MHz, $CDCl_3$) δ –120.5 and –122.3 (d, J = 42.8 Hz, (*Z*)-CF═CF), –126.7 and –129.6 (d, J = 110.3 Hz, (*E*)-CF═CF); GC-EIMS (70 eV) m/z (% relative intensity) (*Z*)-**5**: 358, 356 (M^+, 31, 31), 185 (37), 157 (54), 155 (32), 154 (37), 135 (36), 123 (52), 107 (44), 92 (63), 77 (100), 76 (37), 75 (31), 64 (45), 63 (31), 50 (43); (*E*)-**5**: 358, 356 (M^+, 31, 31), 185 (40), 157 (58), 155 (35), 154 (35), 135 (38), 123 (52), 107 (45), 92 (69), 77 (100), 76 (38), 75 (33), 64 (44), 63 (31), 50 (45). (*Z*)/(*E*)-**5** can also be prepared in 86% isolated yield using the above procedure using *p*-bromophenol (339 mg, 1.96 mmol), sodium hydride (152 mg, 6.32 mmol), and 1-methoxy-4-(trifluorovinyloxy)benzene (**2**) (400 mg, 1.96 mmol).

(*Z*)- and (*E*)-1,2-Difluoro-1,2-bis(4-methoxyphenoxy)ethene ((*Z*)/(*E*)-6)

p-Methoxyphenol (243 mg, 1.96 mmol), sodium hydride (152 mg, 6.32 mmol) and 1-methoxy-4-(trifluorovinyloxy)benzene (**2**) (400 mg, 1.96 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*Z*)/(*E*)-**6** as a yellow oil (384 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11–7.02 (m), 6.91–6.78 (m), 3.78 (d, J = 5.82 Hz, -OCH_3); ^{19}F NMR (283 MHz, $CDCl_3$) δ –122.2 (s, (*Z*)-CF═CF),

–128.5 (s, (*E*)-CF═CF); GC-EIMS (70 eV) *m*/*z* (% relative intensity) (*Z*)-**6**: 308 (M^+, 40), 185 (68), 157 (43), 135 (63), 126 (25), 123 (24), 107 (58), 92 (63), 77 (100), 64 (42), 63 (23); (*E*)-**6**: 308 (M^+, 35), 185 (66), 157 (41), 154 (20), 135 (61), 126 (24), 123 (23), 107 (58), 92 (66), 77 (100), 64 (44), 63 (25).

(*Z*)- and (*E*)-1-(2-Bromophenoxy)-2-(4-bromophenoxy)-1,2-difluoroethene ((*Z*)/*E*)-7)

o-Bromophenol (274 mg, 1.58 mmol), sodium hydride (152 mg, 6.32 mmol) and 1-bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*Z*)/(*E*)-**7** as a yellow oil (441 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.00 (m); ^{19}F NMR (283 MHz, $CDCl_3$) δ –120.9 and –121.2 (d, J = 42.8 Hz, (*Z*)-CF═CF), –126.9 and –127.8 (d, J = 111.9 Hz, (*E*)-CF═CF); GC-EIMS (70 eV) *m*/*z* (% relative intensity) (*Z*)-**7**: 408, 406, 404 (M^+, 12, 22, 12), 235, 233 (19, 18), 207, 205 (17, 18), 185, 183 (19, 19), 157, 155 (97, 100), 152 (14), 76 (83), 75 (91), 74 (21), 63 (13), 51 (15), 50 (96); (*E*)-**7**: 408, 406, 404 (M^+, 12, 23, 11), 235 (17, 18), 207, 205 (16, 16), 185, 183 (18, 19), 157, 155 (94, 100), 126 (12), 76 (86), 75 (85), 74 (20), 63 (12), 51 (14), 50 (95).

(*Z*)- and (*E*)-1-(4-Bromophenoxy)-2-(2-*tert*-butylphenoxy)-1,2-difluoroethene ((*Z*)/(*E*)-8)

o-*tert*-Butylphenol (238 mg, 1.58 mmol), sodium hydride (152 mg, 6.32 mmol) and 1-bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*Z*)/(*E*)-**8** as a yellow oil (304 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–6.97 (m), 1.45 (s, -$C(CH_3)_3$), 1.35 (s, -$C(CH_3)_3$); ^{19}F NMR (283 MHz, $CDCl_3$) δ –120.7 and –122.3 (d, J = 42.8 Hz, (*Z*)-CF═CF), –126.8 and –129.2 (d, J = 108.6 Hz, (*E*)-CF═CF); GC-EIMS (70 eV) *m*/*z* (% relative intensity) (*Z*)-**8**: 384, 382 (M^+, 6, 6), 157, 155 (4, 4), 117, 115 (4, 4), 105 (12), 92 (8), 91 (100), 77 (6), 76 (5), 75 (5), 65 (3), 55 (22), 51 (3), 50 (5); (*E*)-**8**: 384, 382 (M^+, 6, 7), 157, 155 (4, 4), 117, 115 (4, 4), 105 (11), 92 (8), 91 (100), 77 (5), 76 (5), 75 (5), 55 (22), 51 (3), 50 (6).

(*Z*)- and (*E*)-1-(4-Bromophenoxy)-2-(2-phenylphenoxy)-1,2-difluoroethene ((*Z*)/(*E*)-9)

o-Phenylphenol (269 mg, 1.58 mmol), sodium hydride (152 mg, 6.32 mmol) and 1-bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*Z*)/(*E*)-**9** as a yellow oil (429 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.20 (m), 7.15–6.74 (m); ^{19}F NMR (283 MHz, $CDCl_3$) δ –120.2 and –122.3 (d, J = 42.8 Hz, (*Z*)-CF═CF), –127.3 and –128.8 (d, J = 111.9 Hz, (*E*)-CF═CF); GC-EIMS (70 eV) *m*/*z* (% relative intensity) (*Z*)-**9**: 404, 402 (M^+, 8, 9), 231 (13), 230 (26), 200 (42), 199 (54), 183 (10), 181 (17), 157, 155 (9, 9), 153 (51), 152 (100), 151 (26), 127 (8), 77 (7), 76 (15), 75 (15), 51 (8), 50 (13); (*E*)-**9**: 404, 402 (M^+, 9, 8), 231 (12), 230 (25), 200 (40), 199 (56), 183 (9), 181 (17), 157, 155 (8, 9), 153 (50), 152 (100), 151 (24), 127 (7), 76 (16), 75 (16), 51 (8), 50 (15).

1,2-Bis(4-bromophenoxy)-1,1,2-trifluoroethane (10)

1-Bromo-4-(trifluorovinyloxy)benzene (**1**) (400 mg, 1.58 mmol), *p*-bromophenol (274 mg, 1.58 mmol), and Cs_2CO_3 (258 mg, 0.79 mmol) in DMF (4 mL) and DI H_2O (10 L) were placed in a preheated oil bath at 60 °C and allowed to stir for 1 h. The mixture was then treated with DI H_2O (25 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 25 mL). The combined organic layers were washed with water (2 50 mL), dried over $MgSO_4$, filtered over a pad of silica gel, and concentrated under vacuum affording **10** as an oily yellow solid (493 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.48 (m), 7.13 (d, J = 8.9 Hz), 7.04 (d, J = 8.6 Hz), 5.84 (dt, J = 58.4 Hz, 3.1 Hz, C*H*FCF_2); ^{19}F NMR (283 MHz, $CDCl_3$) δ –85.4 and –85.9 (AB pattern, J_{ab} = 148.1 Hz, CHFC*F*$_2$), –138.9 (dt, J = 59.26 Hz, 8.2 Hz, CH*F*CF_2); GC-EIMS (70 eV) *m*/*z* (% relative intensity) 428, 426, 424 (M^+, 49, 100, 51), 205, 203 (54, 56), 157, 155 (92, 99), 145, 143 (35, 34), 76 (48), 75 (41), 64 (39), 63 (55), 50 (43).

(*Z*)- and (*E*)-1-(4-Bromophenoxy)-2-(ethyloxy)-1,2-difluoroethene ((*Z*)/(*E*)-11)

Anhydrous sodium ethoxide (57 mg, 0.830 mmol) and 1-bromo-4-(trifluorovinyloxy)benzene (**1**) (200 mg, 0.790 mmol) were used following the procedure outlined for the preparation of (*Z*)/(*E*)-**3** affording the product mixture (*Z*)/(*E*)-**11** as a yellow oil (190 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.9 Hz), 6.96 (d, J = 8.9 Hz), 4.10 and 3.99 (q, J = 6.8 Hz, -C*H*$_2$CH$_3$), 1.25 and 1.28 (q, J = 6.8 Hz, -CH$_2$C*H*$_3$); ^{19}F NMR (283 MHz, $CDCl_3$) δ –120.9 and –126.9 (d, J = 39.5 Hz, (*Z*)-CF═CF), –127.3 and –133.6 (d, J = 108.6 Hz, (*E*)-CF═CF); GC–EIMS (70 eV) *m*/*z* (% relative intensity) (*Z*)-**11**: 280, 278 (M^+, 19, 18), 252, 250 (28, 26), 158 (40), 156 (42), 157, 155 (96, 94), 77 (100), 76 (65), 75 (62), 74 (18), 50 (63); (*E*)-**11**: 280, 278 (M^+, 17, 17), 252, 250 (29, 29), 158 (40), 156 (43), 157, 155 (93, 100), 77 (98), 76 (63), 75 (64), 74 (17), 50 (62).

General procedure for the isolation of (*Z*)- and (*E*)-isomers

Dispersion of the vacuum dried (*Z*)- and (*E*)-isomer mixture in MeOH (10–20 mL) precipitated exclusively the (*E*)-isomer as a white or yellow solid, which was filtered and dried in vacuum. This process was typically repeated 5–10 times to separate the (*E*)-isomer affording >90% pure isolated (*Z*)-isomer as a yellow oil. X-ray quality white crystals were produced by recrystallization of the combined precipitates of the (*E*)-isomers of **3** and **6** from slow evaporation in diethyl ether at room temperature.

Dehydrofluorination of 10

1,2-Bis(4-bromophenoxy)-1,1,2-trifluoroethane (**10**) (100 mg, 1.58 mmol), sodium hydride (14 mg, 0.587 mmol) in DMF (3 mL) were placed in a preheated oil bath at 60 °C and allowed to stir for 24 h. The mixture was then treated with DI H_2O (10 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2 10 mL). The combined organic layers were washed with water (2 10 mL), dried over $MgSO_4$, filtered over a pad of silica gel, and concentrated under vacuum. ^{19}F NMR (283 MHz, $CDCl_3$) peak integration showed 71% conversion to (*Z*)/(*E*)-**3** in a 1.16 : 1 isomer ratio with the remaining as unreacted **10**.

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