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Synthesis and Electronic Factors in Thermal Cyclodimerization of Functionalized Aromatic Trifluorovinyl Ethers

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Abstract: A series of 19 *p*-substituted aromatic trifluorovinyl ether compounds were prepared from versatile intermediate *p*-Br−C_6H_4−O−CF=CF_2 and underwent thermal radical mediated cyclodimerization to new difunctional compounds containing the 1,2-disubstituted perfluorocyclobutyl (PFCB) linkage. The synthetic scope demonstrates the functional group transformation tolerance of the fluorovinyl ether, and the dimers are useful as monomers for traditional step-growth polymerization methods. ^{19}F NMR spectra confirmed that *p*-substitution affects the trifluorovinyl ether group chemical shifts. The first kinetic studies and substituent effects on thermal cyclodimerization were performed, and the results indicated that electron-withdrawing groups slow the rate of cyclodimerization. The data were further analyzed using the Hammett equation, and reaction constants (ρ) of −0.46 at 120 °C and −0.59 at 130 °C were calculated. This study presents the first liner free energy relationship reported for the cyclodimerization of aromatic trifluorovinyl ethers to PFCB compounds.

1. Introduction

Trifluorovinyl ether (TFVE) chemistry drives an important enabling materials industry focused primarily on high value plastics and elastomers from perfluoro(alkoxyvinyl) copolymers (PFAs)[1] and membrane copolymers based on sulfonic acid containing perfluorovinyl ethers.[2] In contrast to predominant radical chain growth copolymerization of perfluoroalkyl TFVE monomers, aromatic TFVE derivatives undergo exclusive thermal cycloaddition to give perfluorocyclobutane (PFCB) containing compounds and polymers.[3−7] Multifunctional aromatic TFVE monomers have recently experienced a dramatic surge in interest as a variety of thermally stable and exceptionally processable PFCB polymers have been prepared, including: optical polymers and copolymers,[5] polyimide and sulfonimide polymers,[6] phosphine oxide polymers,[15,20] and unique hexabenzocoronene materials,[7] most of which originate from versatile precursor 4-bromo(trifluorovinyloxy)benzene (**1**).[8] From this intermediate and the remarkable tolerance of the aromatic TFVE group to functional group transformation, a variety of functional compounds can be realized, and due to their ability to undergo cyclodimerization, a host of new difunctional materials can be prepared (Figure 1).

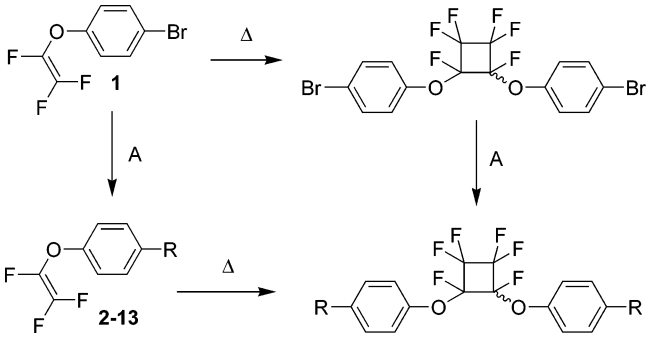

Figure 1. Dimerization strategy for aromatic trifluorovinyl ether (TFVE) compounds. A = Synthetic transformation.

Previous kinetic experiments have been reported for the cycloaddition of fluoroolefins. Early work relied on measuring pressure differentials in order to determine rates of conversion.[9]

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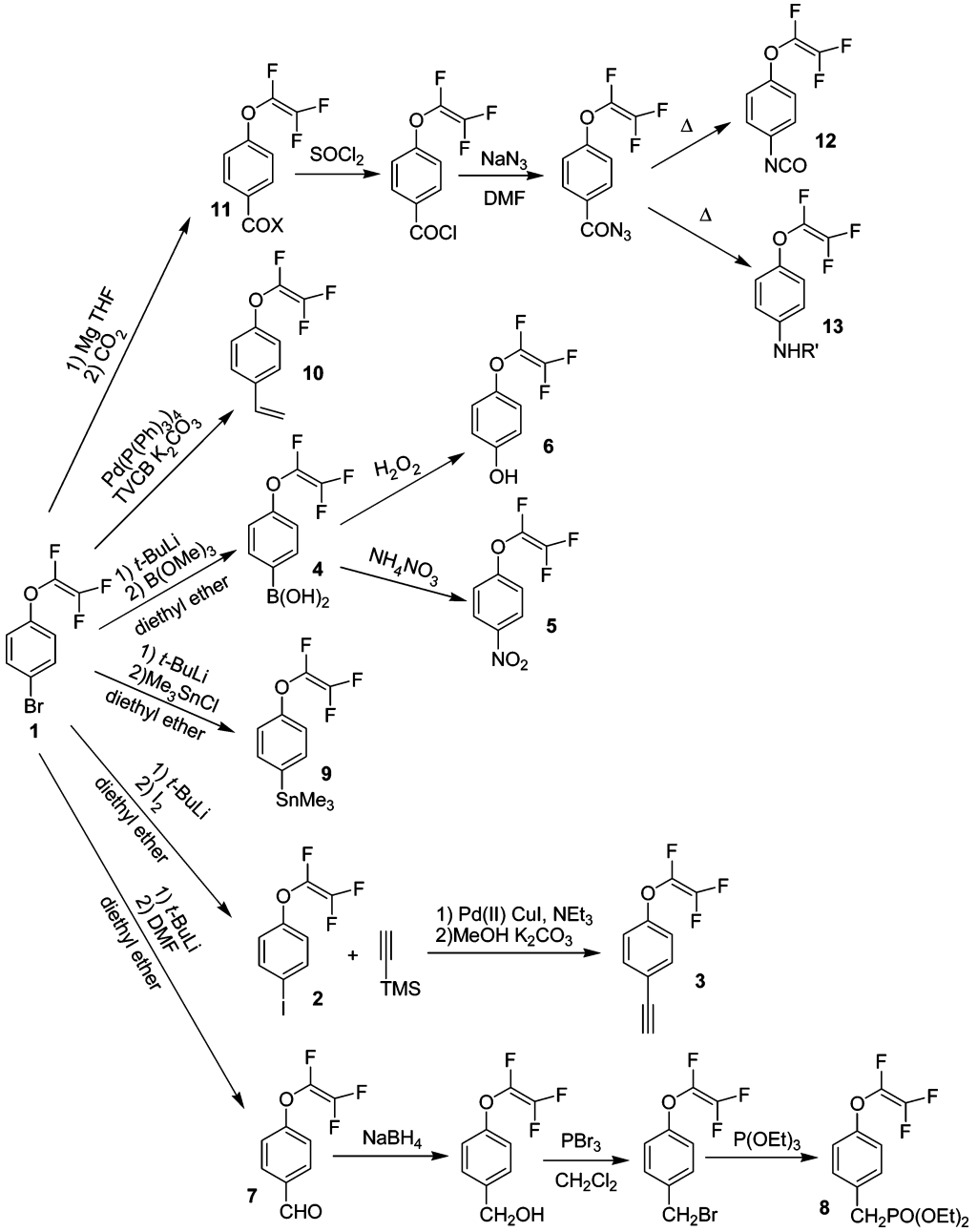

Figure 2. Synthesis of substituted trifluorovinyl phenyl ethers from bromo intermediate **1**.

Later work utilized Raman scattering,[10] differential scanning calorimetry,[11] and gas phase ^{19}F NMR spectroscopy.[12]

More recently, Wlassics probed the effect of substitution directly on fluoroolefins and fluorovinyl ether cyclodimerization.[13] This work demonstrated that substitution does have an effect on cycloaddition rates, and the more electronegative substituents gave lower energies of activation. In the quest to develop a versatile and accessible range of intermediates for PFCB aromatic ether polymer chemistry, here we describe a versatile synthetic strategy for the preparation of aromatic TFVE intermediates and report for the first time how electron donating and withdrawing groups affect the rate of aromatic TFVE cycloaddition. The PFCB dimers produced, furthermore, represent a new class of monomers that can be polymerized using traditional step growth polymerization techniques.

2. Results and Discussion

2.1. Synthesis. A wide range of substituted aromatic trifluorovinyl ether (TFVE) compounds can be accessed from versatile aromatic bromide **1** (Figure 1). Aromatic TFVE compounds are remarkably stable under typical lithiation and Grignard conditions,[15−17] thereby enabling the synthesis of useful intermediates for dimerization and polymerization studies. Table 1 lists the compounds prepared from **1** in a few steps and in reasonable unoptimized yields. The synthetic transformations for compounds **2**−**13** are summarized in Figure 2.

Metal halogen exchange with tertiary butyllithium was used for most transformations and gave fewer side products compared

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Table 1. Functional Groups (R) and Yields for the Synthesis of Aromatic Trifluorovinyl Ether (TFVE) Compounds

compound	steps from 1	overall yield (%)	R =
2	1	100	I
3	2	70	CCH
4	1	72	$B(OH)_2$
5	2	59	NO_2
6	2	60	OH
7	1	65	CHO
8	4	34	$CH_2PO(OEt)_2$
9	1	85	$SnMe_3$
10	1	95	$CHCH_2$
11[a]	3	53	COOX
12	3	53	NCO
13[b]	4	45	NHR

[a] X = H, R, or Cl. [b] R′ = H or COOEt.

to the corresponding Grignard reagent. As found earlier, the reaction should be performed in diethyl ether as reactions with **1** in THF do not undergo efficient metal halogen exchange.[16] The lithium reagent is a useful route to the boronic acid (**4**),[15,18] from which both phenol **6** and nitro compound **5**[19] were prepared. These compounds are not easily accessible from their respective phenolic starting materials via traditional TFVE chemistry (i.e., phenoxy fluoroalkylation with $BrCF_2CF_2Br$ followed by Zn mediated elimination),[3,4] since fluoroalkylation of hydroquinones, in general, are difficult and Br−F elimination of nitro intermediates or other deactivated aromatic derivatives does not proceed well as similarly found by Harris.[6] Lithiation chemistry also allowed for the synthesis of iodo (**2**) or trimethyl tin (**9**) derivatives, which proceeded cleanly with minimal side products. Aryl iodide **2** proved more reactive in Sonogashira coupling than did **1** as expected. Sonogashira coupling with trimethylsilylacetylene gave aryl acetylene **3** after deprotection with potassium carbonate.[7] Finally, quenching the lithium reagent with anhydrous DMF afforded aldehyde **7**;[20] however yields for this reaction were modest. The reaction was repeated using *N*-formylmorpholine in place of DMF, with no improvement in yield. Aldehyde **7** was used to prepare methylene phosphonate **8** useful for Wittig-Horner condensation. This transformation was carried out via reduction of the aldehyde to the benzyl alcohol with $NaBH_4$, followed by bromination with PBr_3 and Arbuzov reaction with triethyl phosphite. All reactions proceeded in reasonable to excellent yield (34−90+ %); however bromination with PBr_3 resulted in 30% bromination of the fluoroolefin.

Grignard chemistry proved adequate for the synthesis of benzoic acid **11**, which was purified by sublimation and gave the acyl chloride upon treatment with $SOCl_2$. Reaction of the acyl chloride with aqueous NaN_3 gave the acyl azide which underwent Curtis rearrangement to isocyanate **12** upon heating at 90−100 °C. In the presence of HCl, **12** gave the primary amine (**13**, R′ = H) or treatment with EtOH gave the ethyl carbamate (**13**, R′ = COOEt). Formation of the amine through this route was complicated, as extensive heating in aqueous HCl resulted in addition of HCl to the vinyl ether. Finally, bromo compound **1** itself underwent Pd catalyzed Heck coupling with 2,4,6-trivinylcyclotriboroxane (TVCB) pyridine complex to give styryl derivative **10** in good yield.[21]

2.2. NMR Characterization. The effect of *para* substitution on the ^{19}F NMR chemical shifts for compounds **2**−**13** is illustrated in Figure 3 by the correlation of vinyl fluorine signal (dd average) and the substituent. Chemical shifts of the specified fluorine (cis to O) move downfield with increasing electron withdrawing character of the substituent.

This trend is observed in both the cis and trans (to O) fluorine signals; however the *geminal* fluorine signals move upfield with increasing electron-withdrawing character as previously recognized for other fluorovinyl ethers (Table 2).[22] This effect on the *geminal* fluorine contradicts what is observed in ^1H NMR for nonfluorinated substituted phenyl vinyl ethers.[23] A plot of

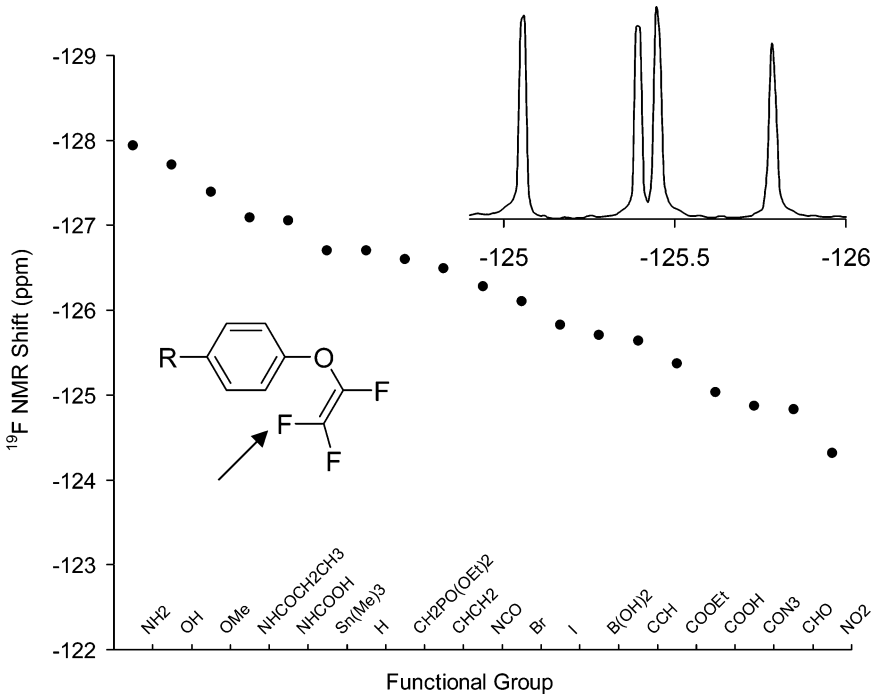

Figure 3. Effect of *p*-substitution on ^{19}F NMR shifts for TFVE compounds and representative dd pattern (inset). Shifts are reported as the average of the dd pattern for the cis to O fluorine (inset).

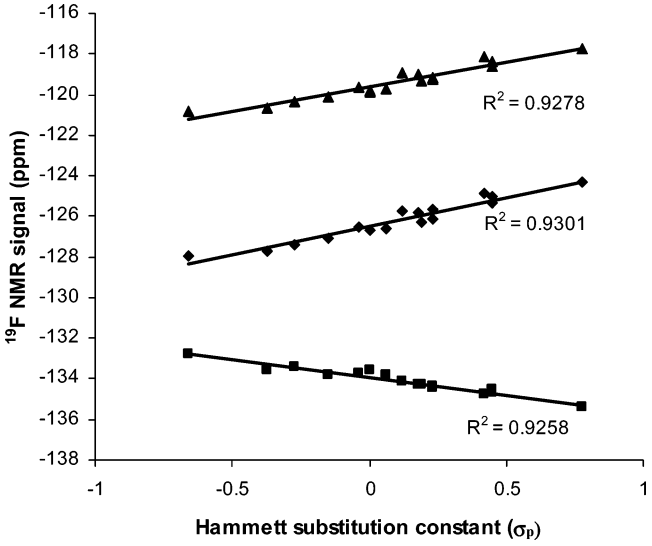

Figure 4. Plot of ^{19}F NMR vinyl F signals trans to O (▲), cis to O (◆), and gem to O (■) (average of dd) for compounds in Table 3.1 versus Hammett substitution constant σ_p.

Table 2. ^{19}F NMR Chemical Shifts for Substituted TFVE Compounds

	^{19}F NMR Chemical Shifts in $CDCl_3$		
p-substitution (R)	geminal to O	cis to O	trans to O
NH_2	−132.7	−127.9	−120.8
OH	−133.5	−127.7	−120.6
OMe	−133.3	−127.3	−120.3
$NHCOCH_2CH_3$	−133.7	−127.0	−120.1
$Sn(Me)_3$	−133.6	−126.6	−119.8
H	−133.5	−126.6	−119.8
$CH_2PO(OEt)_2$	−133.8	−126.6	−119.7
$CHCH_2$	−133.7	−126.4	−119.6
NCO	−134.3	−126.2	−119.3
Br	−134.4	−126.1	−119.1
I	−134.3	−125.8	−119.0
$B(OH)_2$	−134.1	−125.7	−118.9
CCH	−134.3	−125.6	−119.2
COOEt	−134.5	−125.3	−118.6
COOH	−134.6	−125.0	−118.3
CON_3	−134.7	−124.8	−118.4
CHO	−134.7	−124.8	−118.1
NO_2	−135.4	−124.3	−117.7

the average ^{19}F NMR shift versus the Hammett substitution constant σ_p[14] shows a linear relationship (Figure 4).

NMR chemical shifts can be a useful indication of substitution effects at a particular location and has been used frequently as a means of estimating Hammet substituent constants. For example, the effects of substitution were shown to transmit better through nonfluorinated vinyl ethers than for analogous allyl or styryl systems.[23] In addition to NMR shifts, the pK_a of a substituted phenoxyacrylic acid was measured and the Hammett relationship determined.[24] More recently, as mentioned earlier, Brey[22] and Wlassics[13] reported the effect of fluoroolefin substitution on NMR shifts and reactivity, respectively. While Brey focused primarily on ^{19}F NMR coupling constants, Wlassics reported coreactions of different triflurovinyl compounds and the effect of substitution on 2 + 2 cycloaddition. These results indicated that electronegativity of the substituent α to the vinyl group influenced reactivity.

2.3. Cyclodimerization Kinetics. With an obvious electronic substituent effect established by ^{19}F NMR, kinetics of substituted TFVE thermal cyclodimerization were studied. Selected monomers were heated neat in NMR tubes, and the conversion of the TFVE group to the sole perfluorocyclobutane (PFCB) product was measured as a function of time by ^{19}F NMR (Figure 5). The three TFVE fluorine signals appear as three sets of doublets of doublets, and the new PFCB fluorine signals appear between −127 ppm and −133 ppm.

TFVE cyclodimerization conversion for selected compounds vs time at 130 °C is shown in Figure 6 where, clearly, electron-donating substituents increase the rate of conversion. Cycloaddition of aromatic TFVE compounds has been previously shown to follow second-order kinetics.[10] Given the general rate law: $dx/dt = k(1 - x)^n$ for $n = 2$, integration gives $x/(1 - x) = kt$, for x the fractional conversion and k the rate constant. Using the data in Figure 6, a plot of $x/(1 - x)$ versus time (t) affords a linear slope k as shown in Figure 7.

Table 3 lists the rate constants and linear fit R^2 values for two cyclodimerization temperatures. In terms of ^{19}F NMR chemical shift for the selected TFVE compounds, every 1 ppm upfield shift in the fluoroolefin signal represents an increase in cyclodimerization rate by 1.5×10^{-2} h^{-1} at 120 °C and 3.1×10^{-2} h^{-1} ppm^{-1} at 130 °C.

A fit of the data using the Hammett equation $\log(k/k_0) = \sigma\rho$ (Figure 8) yielded a reaction constant $\rho = -0.46$ and $k_0 = 4.37 \times 10^{-2}$ h^{-1} at 120 °C and $\rho = -0.59$ and $k_0 = 6.8 \times 10^{-2}$ h^{-1} at 130 °C. The negative ρ value confirms for the first time that electron donation increases the rate of cycloaddition of aromatic trifluorovinyl ether compounds. As mentioned earlier, substitution effects for nonfluorinated phenyl vinyl ether compounds have been studied and the reaction constant for the ionization of phenoxyacrylic acids has been determined to be $\rho = 0.439$.[24] Therefore, and remarkably, the effect of phenyl substitution on radical mediated cycloaddition of these aromatic TFVE compounds is at least comparable to that reported for similar effects on ionic equilibrium.

2.4. Cis/Trans Isomerization. While reactivity was influenced, the resulting regioselectivity (1,3- vs 1,2-disubsitution) and stereochemistry of the 1,2-disubstituted hexafluorocyclobutyl ring was not affected by the electron-donating or -withdrawing nature of *para* substitution. Representative X-ray crystal structures of the cis and trans isomers are shown in Figure 9 for R = COOEt. Only the 1,2-regioisomer was detected, and both diastereomers of the perfluorocyclobutane were formed in essentially equal amounts for dimers from **2**−**13** as determined by ^{19}F NMR as well as GC/MS.

2.5. Competition Experiments. These results further confirm the recent qualitative observation of electronic effects on

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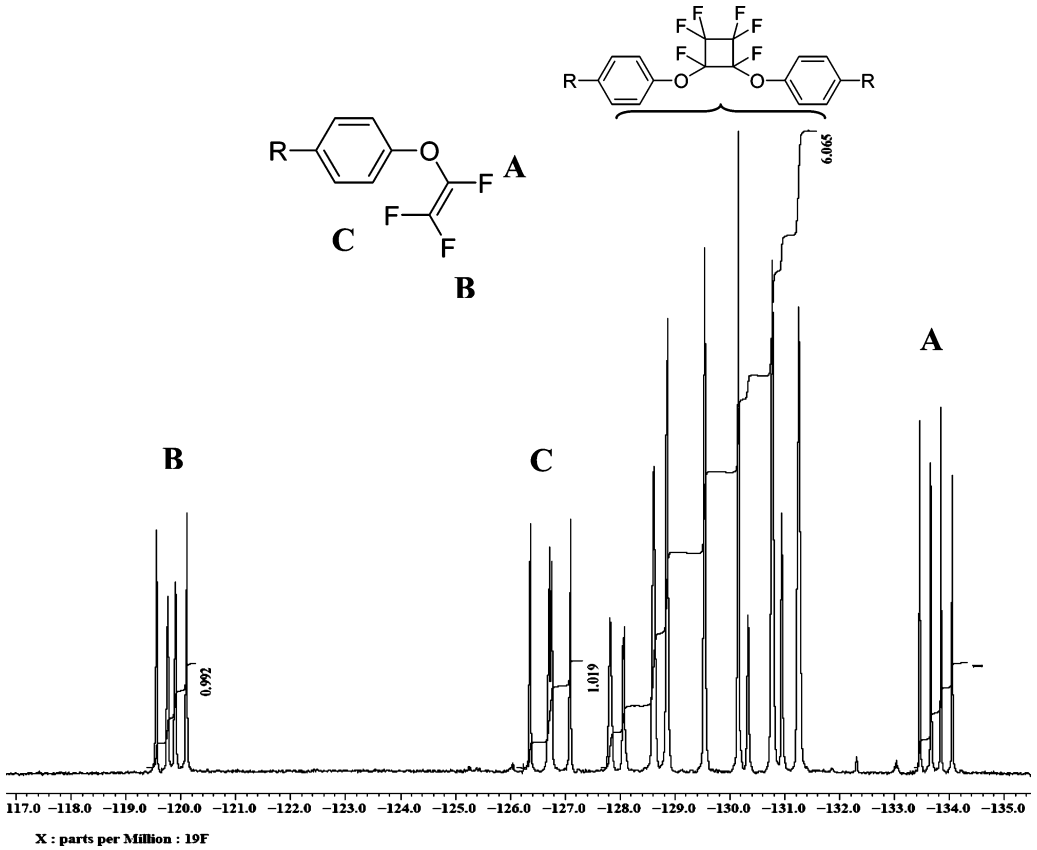

Figure 5. Representative ^{19}F NMR spectra of dimerization reaction mixture (R = H) showing three dd signals for the TFVE group and new signals representing the hexafluorocylcobutyl group.

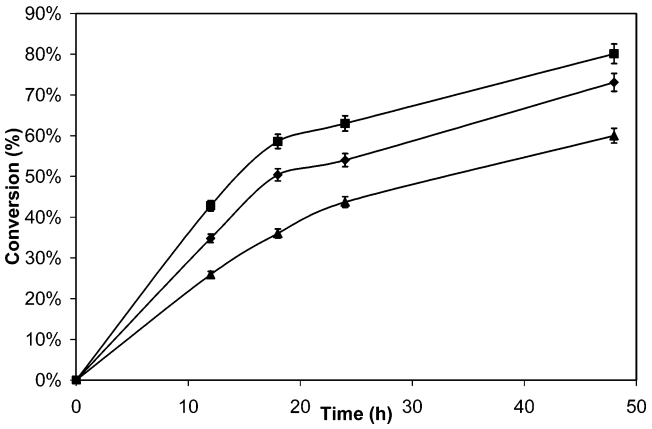

Figure 6. Conversion plot for the dimerization of selected TFVE compounds where R = NHCOOEt (◆), R = Br (■), and R = COOEt (▲) versus time at 130 °C.

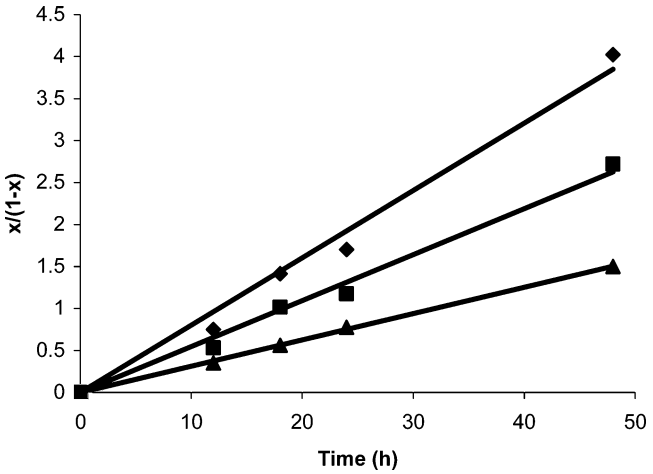

Figure 7. Second-order kinetic plot for the dimerization of selected TFVE compounds where R = NHCOOEt (◆), R = Br (■), and R = COOEt (▲).

polymerization reactivity during the thermal copolymerization of bisphenol A derived monomers, **6F** and **6H** (Figure 10).[26] The **6F** monomer with withdrawing CF_3 groups was less reactive toward cyclopolymerization, and the difference in their respective rates was found to be $\Delta k = 7.3 \times 10^{-2}$ h^{-1} at 135 °C. Copolymerization of the two monomers shows an enrichment of **6H** monomer, and complete results will be reported elsewhere. Likewise, a simple competitive rate study between **11** (R = NHCOOEt) and **13** (R = COOEt) indicated that while **11** reacted faster, the sums of the two homoproducts were equal to the amount of cross-product.

Table 3. Second-Order Reaction Rate Constants for the Cyclodimerization of Selected TFVE Compounds

R =	k (h^{-1})[a] at 120 °C	k (h^{-1})[a] at 130 °C
NHCOOEt	5.2×10^{-2}	8.0×10^{-2}
H	4.1×10^{-2}	
Br	3.9×10^{-2}	5.5×10^{-2}
COOEt	2.4×10^{-2}	3.1×10^{-2}

[a] Conversion calculated using ^{19}F NMR.

These results would suggest that the effective reactivity of an unactivated TFVE monomer could be increased by the

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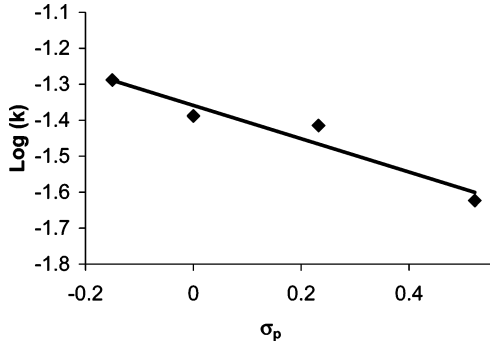

Figure 8. Rate constants (Table 3.2) versus Hammett substitution constant σ_p with best fit line. $R^2 = 0.93$

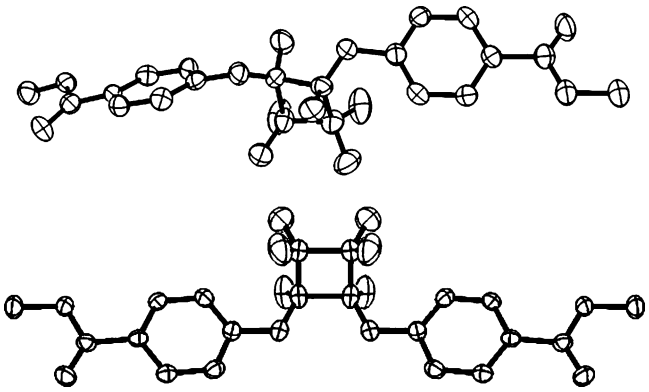

Figure 9. Single-crystal structure perspective drawings (50% thermal ellipsoids) for dimer **11** (R = −COOMe) diastereomers.

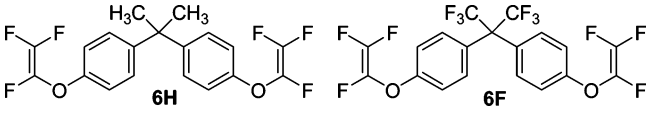

Figure 10. Activated (**6H**) and deactivated (**6F**) TFVE monomers.

introduction of an activated monomer to the system. The implications for the preparation of tailored copolymers is significant in that random copolymers can be produced even from monomers of contrasting reactivity.

3. Conclusions

The synthetic scope for the preparation and dimerization of aromatic TFVE intermediates has been demonstrated for a range of useful functional groups. Thermal dimerization of TFVE compounds produced difunctional monomers containing the perfluorocyclobutyl (PFCB) linkage and represent a new class of monomers that can be polymerized using traditional step-growth polymerization techniques. The first kinetic studies and aromatic substituent effects on trifluorovinyl ether cyclodimerization were performed and confirmed using the Hammett equation. This result represents the first linear free energy relationship measured for aromatic trifluorovinyl ether cyclodimerization and should contribute to the broader understanding and use of TFVE compounds in general.

4. Experimental Section

Chemicals and solvents used were purchased from Sigma Aldrich and Alfa Aesar and used without purification. 4-Bromo(trifluorovinyloxy)benezene (**1**), 4-iodo(trifluorovinyloxy)benezene (**2**), 4-ethynyl-(trifluorovinyloxy)benzene (**3**), 4-(trifluorovinyloxy)phenylboronic acid (**4**), 4-(trifluorovinyloxy)benzoic acid **11** (X = H), 4-(trifluorovinyloxy)-benzoyl chloride **11** (X = Cl), and bis(4-bromophenoxyl)hexafluorocyclobutane were prepared as described previously.[7,15−17,25] TFVE compound **1** and selected monomers are commercially available from Tetramer Technologies, L.L.C. (Pendelton, SC, www.tetramertechnologies.com) and distributed by Oakwood Chemicals, Inc. (Columbia, SC, www.oakwoodchemical.com). House nitrogen was passed over $CaSO_4$ and used for all synthetic reactions. ^{1}H NMR 500 MHz, proton decoupled ^{13}C NMR 125 MHz, and ^{19}F NMR 470.6 MHz spectra were obtained using a JEOL Eclipse$^+$ 500 or Bruker AF-300 spectrometer system, respectively. Chloroform-*d* or pyridine-d_5 was used as solvent, and chemical shifts reported were internally referenced to tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C, and ^{19}F nuclei, respectively. Yields refer to isolated yields of compounds estimated to be greater than 95% pure as determined by NMR. Infrared

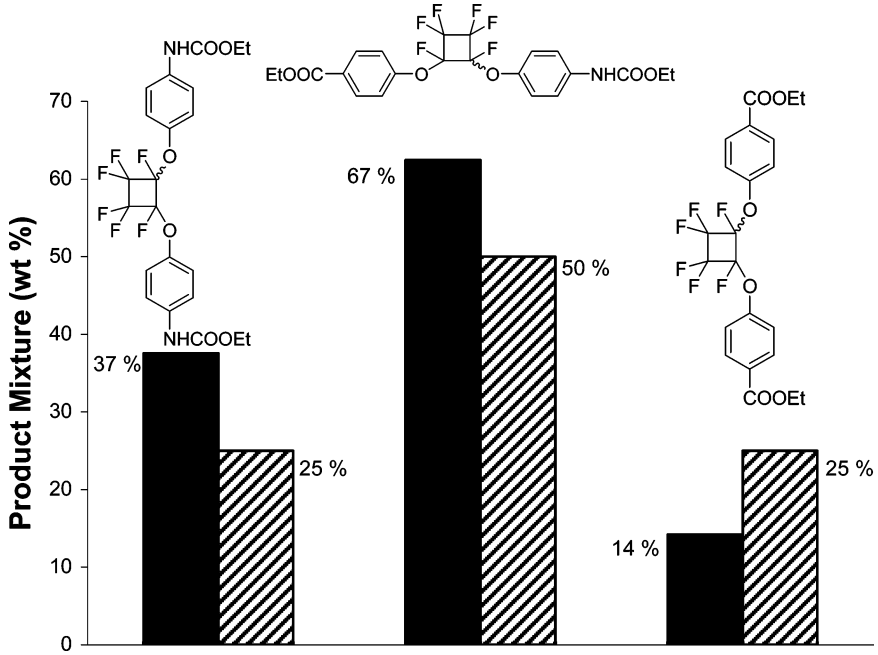

Figure 11. Competition cyclodimerization reaction mixture distribution of products (black) and expected statistical outcome (hashed) for TFVE compounds determined by HPLC.

analyses were performed on thin films on ZnSe plates or KBr disks using a ThermoNicolet Magna-IR 550 FTIR spectrometer. Gas chromatography/mass spectrometry (GC/MS) data were obtained using a HP 5890A gas chromatograph coupled with an HP 5970 mass spectrometer or a Shimadzu 17A gas chromatograph coupled with a Shimadzu QP5000 mass spectrometer.

4.1. Synthesis. 4.1.1. 1,2-Bis(4-iodophenoxy)hexafluorocyclobutane. 4-Iodo(trifluorovinyloxy)benzene (**2**) (0.25 g, 0.83 mmol) was heated neat at 150 °C for 2 days in a 25 mL single-neck round-bottom flask under N_2 to yield 0.25 g (100%) of the dimer of **2** as white solid. GC-EI-MS *m*/*z* (% relative intensity): 76 (100), 203 (58), 300 (30). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.85 (d, J = 9 Hz, 1H), 6.91 (d, J = 8 Hz, 1H), 7.62 (d, J = 11 Hz, 2H). ^{19}F (470 MHz, $CDCl_3$, δ): −131.37, −131.25, −130.63, −130.16, −129.89, −129.41, −128.57, −128.45, −128.09, −127.97, −126.54. HRMS Calculated (Found) for $C_{16}H_8F_6I_2O_2$ 599.8518 (599.8523).

4.1.2. 1,2-Bis(4-ethynylphenoxy)hexafluorocyclobutane. 1,2-Bis-(4-iodophenoxy)hexafluorocyclobutane (2 g, 3.3 mmol) dissolved in NEt_3, dichlorobis(triphenylphosphine) palladium (23 mg, 0.03 mmol), and CuI (51 mg, 0.26 mmol) was added to a three-necked round-bottom flask. The solution was degassed, and trimethylsilylacetylene (979 mg, 9.9 mmol) was added dropwise at room temperature. The reaction was stirred for 15 h at which point a large quantity of NEt_3HCl salts appeared. The salts were removed by vacuum filtration, and the NEt_3 was removed under vacuum. The residue was dissolved in excess EtO_2, washed with water, dried in $MgSO_4$, and concentrated by rotary evaporation. The crude product was dissolved in CH_2Cl_2 (5 mL) and MeOH (12 mL), and K_2CO_3 (460 mg, 3.3 mmol) was added all at once. The reaction was allowed to stir for 2 h at room temperature. The solvent was removed by rotary evaporation, and the product was purified by column chromatography on silica gel using hexane/ethyl acetate (90:10) to afford 1.06 g (80%) of the dimer of **3** as a white solid. Mp 131 °C. GC/MS (EI) *m*/*z* (% relative intensity): 73 (100), 255 (45), 437 (17) 535 (43), 540 (92). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.05 (s, 2H), 7.03 (d, J = 8 Hz, 1H), 7.12 (d, J = 8 Hz, 1H) 7.44 (d, J = 9 Hz, 1H), 7.45 (d, J = 9 Hz, 1H); ^{19}F NMR (470 MHz, $CDCl_3$, δ): −131.44, −131.11, −130.11, −129.95, −129.49, −128.59, −128.26, −128.12, −127.78, −126.55. ^{13}C NMR (125 MHz, CD_3CN, δ) 77.8, 82.4, 118.3, 118.4, 119.4, 119.7, 133.9, 152.6. HRMS Calculated (Found) for $C_{20}H_{10}F_6O_2$ 396.0584 (396.0576).

4.1.3. 1,2-Bis(4-borophenoxy)hexafluorocyclobutane. 4-(Trifluorovinyloxy)phenylboronic acid (**4**) (98 mg, 2.24 mmol) was heated at 150 °C for 2 days in a single-neck round-bottom flask under N_2 to afford 98 mg (100%) of the dimer of **4** as white solid. ^{1}H NMR (500 MHz, CD_3CN, δ): 6.11 (s, 1H), 6.14 (s, 1H), 7.15 (d, J = 7 Hz, 1H), 7.22 (d, J = 7 Hz, 1H), 7.79 (d, J = 7 Hz, 1H), 7.81 (d, J = 7 Hz, 1H). ^{19}F NMR (470 MHz, CD_3CN, δ): −131.74, −131.51, −131.05, −131.04, −130.84, −130.36, −129.58, −129.11, −128.64.

4.1.4. 4-Nitro(trifluorovinyloxy)benzene (5). To a solution of 4-(1,2,2-trifluorovinyloxy)phenylboronic acid (**4**) (200 mg, 0.92 mmol) in CH_3CN (20 mL), trifluoroacetic anhydride (1 mL) was added dropwise at −35 °C. In a second 25 mL single-neck flask equipped with a stir bar, NH_4NO_3 (81 mg, 1.02 mmol) was mixed with CH_3CN (10 mL), and the mixture was cooled to −35 °C. Trifluoroacetic anhydride (3 mL) was added dropwise to the NH_4NO_3/CH_3CN mixture, until the NH_4NO_3 dissolved. The contents of the second flask were then added dropwise via syringe to the boronic acid solution. The reaction was stirred at −35 °C for 4 h and slowly warmed to room temperature. Water was then added to the reaction, and the organic phase was extracted into dichloromethane, separated, dried, and concentrated by rotary evaporation. The product was purified by column chromatography over silica gel using hexane/ethyl acetate (90:10) to afford 119 mg (59%) of **5** as light yellow oil. GC/MS (EI) *m*/*z* (% relative intensity): 50 (90), 76 (100), 92 (30), 122 (20), 172 (20), 219 (40). IR (cm^{-1}): 3120 (m), 3082 (m), 1833 (m), 1614 (m), 1534 (s), 1486 (s), 1107 (m), 1004 (w), 848 (s), 743 (s). ^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.21 (d, 2H, J = 5 Hz), 8.26 (d, J = 9 Hz, 2H). ^{19}F NMR (470 MHz,$CDCl_3$, δ): −135.6 (dd, 1F), −124.53 (dd, 1F), −117.89 (dd, 1F) (J_{gem} = 94, Hz, J_{cis} = 59 Hz, J_{trans} = 110 Hz); ^{13}C NMR (125 MHz $CDCl_3$): δ 116.2, 126.2, 133.0 (ddd, J = 42 Hz, 40 Hz, 264 Hz), 146.9 (ddd, J = 62 Hz, 279 Hz, 274 Hz), 144.8, 159.2. HRMS Calculated (Found) for $C_8H_4F_3NO_3$ 219.0143 (219.0134).

4.1.5. 1,2-Bis(4-nitrophenoxy)hexafluorocyclobutane. In a single-neck flask flask, 4-nitro(trifluorovinyloxy)benzene (**5**) (71 mg, 0.162 mmol) was heated at 150 °C for 2 days to afford 71 mg (100%) of the dimer of **5** as a white solid. Mp 120 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.23 (d, J = 9 Hz, 1H), 7.35 (d, J = 9 Hz, 1H), 8.27 (d, J = 11 Hz, 1H), 8.29 (d, J = 11 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −132.36, −132.08, −129.75, −129.28, −129.12, −128.64, −127.91, −127.43, −127.10, −126.63. ^{13}C NMR (125 MHz $CDCl_3$, δ): 118.2, 118.4, 126.0, 126.2, 14.0, 145.2, 156.7. HRMS Calculated (Found) for $C_{16}H_8F_6N_2O_6$ 438.0286 (438.0280).

4.1.6. 4-(Trifluorovinyloxy)phenol (6). In a 50 mL single-neck flask 4-(1,2,2-trifluorovinyloxy)phenylboronic acid (**4**) (2.0 g, 9.2 mmol) was mixed with 30% aqueous H_2O_2 (1.04 mL) and water (30 mL) under air for 24 h at room temperature. The crude product was extracted into ether and was washed with water. The organic layer was separated, dried, concentrated by rotary evaporation, and purified by column chromatography over silica gel, hexane/ethyl acetate (95:5) to afford 1.70 g (97%) of **6** as light yellow oil. GC/MS (EI) *m*/*z* (% relative intensity): 65 (52), 93 (45), 109 (20), 143 (20), 190 (20), 380 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.0 (s, 1H), 6.84 (d, J = 9 Hz, 2H), (d, J = 10 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −133.74 (dd, 1F), −127.93 (dd, 1F), −120.84 (dd, 1F) (J_{gem} = 99 Hz, J_{cis} = 57 Hz, J_{trans} = 110 Hz). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 116.1, 120.0, 120.7, 146.2, 143.1, 208.1. HRMS Calcd (Found) for $C_8H_5F_3O_2$ 190.0241 (190.0241).

4.1.7. 1,2-Bis(4-hydroxyphenoxy)hexafluorocyclobutane. 4-(Trifluorovinyloxy)phenol (**6**) (302 mg, 1.59 mmol) was heated in a single-neck 25 mL round-bottom flask at 105 °C for 4 days. Unreacted **6** was removed by column chromatography on silica gel hexane/ethyl acetate (90:10) to afford 211 mg (70%) of the dimer from **6** as light yellow oil. GC/MS (EI) *m*/*z* (% relative intensity): 65(60), 93(44), 109(20), 143(20), 190(19), 380(100). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 6.67−6.75 (m, 2H), 6.93−6.97 (m, 2H), 7.46 (d, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −132.36, −132.08, −129.75, −129.24, −129.12, −128.63, −127.91, −127.42, −127.10, −126.63. ^{13}C NMR (125 MHZ, $CDCl_3$, δ): 118.2 (s), 118.4, 126.0, 126.1, 145.0, 145.2, 156.7.

4.1.8. 4-(Trifluorovinyloxy)benzaldehyde (7). To a flame dried two-neck flask, a solution of **1** (300 mg, 1.18 mmol) and anhydrous Et_2O (5 mL) was charged. The flask was cooled to −78 °C, and *t*-BuLi (1.5M in pentane, 0.76 mL, 1.30 mmol) was added dropwise via syringe. After complete addition the reaction was maintained at −78 °C for 1 h. Anhydrous DMF (1 mL, 13.7 mmol) was then added, and the reaction mixture was allowed to warm to room temperature over a period of 1 h. Water was added to quench the reaction, and the product was extracted into ether and purified by column chromatography on silica gel hexane/ethyl acetate (85:15) to afford 155 mg (65%) of **7** as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.22 (d, J = 11 Hz, 1H), 7.91 (d, J = 9 Hz, 1H), 9.97 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$, δ): −135.04 (dd, 1F), −125.20 (dd, 1F), −118.43 (dd, 1H) (J_{gem} = 94 Hz, J_{cis} = 59 Hz, J_{trans} = 110 Hz). HRMS Calculated (Found) for $C_9H_5O_2F_3$ 202.0241 (202.0237).

4.1.9. 1,2-Bis(4-formylphenoxy)hexafluorocyclobutane. To a flame dried two-neck flask, bis(4-bromophenoxyl)hexafluorocyclobutane (0.5 g, 0.98 mmol) and anhydrous Et_2O (10 mL) was added. The reaction mixture was cooled to −78 °C, and *t*-BuLi (1.28 mL, 2.17 mmol) was added dropwise. After complete addition the reaction was maintained at −78 °C for 1 h. Anhydrous DMF (1 mL) was then added, and the mixture was allowed to warm to room temperature over a period of 1 h. Water was added to quench the reaction, and the product was extracted into ether, washed with water, dried, and purified by column

chromatography on silica gel hexane/ethyl acetate (85:15) to afford 257 mg (65%) of the dimer of **7** as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.23 (d, J = 10 Hz, 1H), 7.34 (d, J = 9 Hz, 1H), 7.89−7.94 (m, 2H), 9.97 (s, 1H), 9.99 (s, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, δ) −132.08, −131.66, −130.09, −129.53, −129.49, −129.00, −128.24, −127.76, −127.51, −127.03. ^{13}C NMR (125 MHz, $CDCl_3$, δ): 118.3, 118.4, 131.8, 131.9, 133.6, 133.7, 156.8, 190.5. HRMS Calculated (Found) for $C_{18}H_{10}F_6O_4$ 404.0483 (404.0481).

4.1.10. 4-(Trifluorovinyloxy)benzyl Alcohol (Precursor to 8). In a two-neck flask, equipped with a nitrogen inlet adapter and magnetic stir bar, was added **7** (2.20 g, 11 mmol) dissolved in dry MeOH (20 mL). The solution was cooled to 0 °C, and $NaBH_4$ (413 mg, 11 mmol) was added in four portions at 15 min intervals. After stirring for 3 h, the reaction was allowed to warm to room temperature and stirred for an additional 15 h. The reaction mixture was then quenched with water, and the organic layer was extracted into diethyl ether, dried with $MgSO_4$, and concentrated by rotary evaporation to afford 1.84 g (82%) of 4-(trifluorovinyloxy)benzyl alcohol as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.63 (s, 1H), 4.48 (s, 2H), 7.06 (d, J = 10 Hz, 2H), 7.39 (d, J = 10 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −134.2 (dd, 1F), −126.30 (dd), −119.41 (dd, 1F) (J_{gem} = 99 Hz, J_{cis} = 56 Hz, J_{trans} = 108 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 115.9, 128.7, 133.8 (ddd, J = 41 Hz, 39 Hz, 262 Hz), 137.6, 147.0 (ddd, J = 60 Hz, 277 Hz, 272 Hz), 154.5.

4.1.11. 4-Bromomethyl(trifluorovinyloxy)benzene (Immediate Precursor to 8). In a two-neck 50 mL flask equipped with a nitrogen inlet adapter and magnetic stir bar, 4-(trifluorovinyloxy)benzyl alcohol (1.83 g, 8.95 mmol) was diluted in CH_2Cl_2 (12 mL) and cooled to 0 °C. PBr_3 (2.42 g, 8.95 mmol) was added dropwise to the reaction mixture at 0 °C. After complete addition the reaction was stirred at room temperature for 3 h. The organic layer was diluted with CH_2Cl_2 and washed several times with water. The organic layer was dried, concentrated by rotary evaporation, and purified by column chromatography on silica gel hexane/ethyl acetate (95:5) to afford 1.53 g (64%) of 4-bromomethyl(trifluorovinyloxy)benzene as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.47 (s, 1H), 7.05 (d, J = 8 Hz, 1H), 7.38 (d, J = 8, 1H Hz). ^{19}F NMR (470 MHz $CDCl_3$, δ): −134.24 (dd, 1H), −126.34 (dd, 1H), −119.46 (dd, 1H) (J_{gem} = 103 Hz, J_{cis} = 56 Hz, J_{trans} = 117 Hz). ^{13}C NMR (125 MHZ, $CDCl_3$, δ): 64.3, 115.9, 128.7, 133.8 (ddd, J = 44 Hz, 39 Hz, 266 Hz), 137.6, 144.6, 145.1, 146.7, 147.2, 148.9, 149.4 (ddd, J = 61 Hz, 280 Hz, 276 Hz), 154.5.

4.1.12. Diethyl(4-(trifluorovinyloxy)phenyl)methylphosphonate (8). In a one-neck flask, 4-bromomethyl(trifluorovinyloxy)benzene (770 mg, 2.88 mmol) and $P(OEt)_3$ (527 mg, 3.17 mmol) were combined and heated at 80 °C for 12 h under nitrogen. Excess $P(OEt)_3$ was removed by vacuum distillation to afford 924 mg (99%) of **8** as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.22 (t, 6H, J = 7 Hz), 3.07 (d, 2H, J = 20 Hz), 3.99 (q, 4H, J = 3 Hz), 7.01 (d, 2H, J = 5 Hz), 7.26 (d, 2H J = 9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −134.25 (dd, 1F), −126.33 (dd, 1F), −119.46 (dd, 1F) (J_{gem} = 94 Hz, J_{cis} = 57 Hz, J_{trans} = 109 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 16.3, 34.6 62.3, 116.3, 130.9, 133. 6 (ddd, J = 45 Hz, 40 Hz, 260 Hz), 134.6, 144.5, 147.2 (ddd, J = 64 Hz, 279 Hz, 271 Hz), 154.9. HRMS Calculated (Found) for $C_{13}H_{16}F_3O_4P$ 324.0738 (324.0730).

4.1.13. 1,2-Bis(4-diethyl(methylphosphonate)phenoxy)hexafluorocyclobutane. Diethyl (4-(trifluorovinyloxy)phenyl)methylphosphonate (**8**) (205 mg, 632 mmol) was heated in a single-neck round-bottom flask at 150 °C for 2 days to afford 205 mg (100%) of the dimer of **8** as a viscous yellow oil. GC/MS (EI) m/z (% relative intensity): 90 (80), 107 (80), 124 (45), 187 (100), 324 (30). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.18−1.28 (m, 12H), 3.07 (d, J = 5 Hz, 2H), 3.10 (d, J = 5 Hz, 2H), 3.94−4.03 (m, 8H), 7.04 (d, J = 8 Hz, 2H), 7.12 (d, J = 6 Hz, 2H), 7.23−7.28 (m, 4H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −131.30, −130.75, −130.63, −130.28, −130.12, −129.64, −128.68, −128.36, −128.20, −127.89. ^{13}C NMR (125 MHz, $CDCl_3$, δ): 16.25, 32.06, 62.18, 115.98, 118.2, 128.40, 128.67, 131.00, 151.46.

4.1.14. (4-(Trifluorovinyloxy)phenyl)trimethylstannane (9). To a flame dried two-neck flask, **1** (3 g, 11.85 mmol) and 30 mL of dry Et_2O were charged. The reaction mixture was cooled to −78 °C, and *t*-BuLi (1.5 M in pentane, 8.3 mL, 12.39 mmol) was added dropwise via syringe. After complete addition, the reaction was maintained at −78 °C for 1 h, and Me_3SnCl (2.35 g, 11.85 mmol) in ether (20 mL) was added. The reaction was allowed to warm and stir for 4 h at room temperature. Water was added to quench the reaction, and the organic layer was extracted into ether, dried with $MgSO_4$, concentrated by rotary evaporation, and purified by column chromatography on silica gel hexane/ethyl acetate (85:15) to afford 3.39 mg (85%) of **9** as a clear oil. GC/MS (EI) m/z (% relative intensity): 135 (15), 226 (14), 293 (12), 323 (100). FTIR (KBr, cm^{-1}): 3022 (m), 2983 (m), 2923 (m), 1831 (m), 1579 (s), 1492 (s) 1388 (w), 1284 (s), 1175 (s), 1072 (m), 766 (s). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 0.33 (s, 9H), 7.11 (d, J = 10 Hz, 2H), 7.51 (d, J = 10 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −133.78 (dd, 1F), −126.92 (dd 1F), −119.98 (dd, 1F) (J_{gem} = 97 Hz, J_{cis} = 58 Hz, J_{trans} = 111 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): −9.5, 115.6, 133.7 (ddd, J = 42 Hz, 38 Hz, 263 Hz), 137.4, 147.1 (ddd, J = 59 Hz, 276 Hz, 275 Hz), 155.8. HRMS Calculated (Found) for $C_{11}H_{13}F_3OSn$ 337.9940 (337.9938).

4.1.15. 1,2-Bis(4-trimethylstannylphenoxy)hexafluorocyclobutane. To a flame dried two-neck flask, bis(4-bromophenoxyl)hexafluorocyclobutane (200 mg, 40 mmol) in dry Et_2O (5 mL) was added and cooled to −78 °C. At that temperature, *t*-BuLi (1.5 M in pentane, 0.58 mL, 0.87 mmol) was added dropwise via syringe. After the reaction stirred for 1 h, Me_3SnCl (165 mg, 0.83 mmol) in ether (3 mL) was added and the reaction mixture was allowed to warm and stir for 4 h at room temperature. The reaction mixture was quenched with water, and the product was extracted into ether. The organic layer was concentrated by rotary evaporation, and the product was purified by column chromatography on silica gel treated with NEt_3 to afford 108 mg (80%) of the dimer of **9** as a white crystalline solid. Mp 158 °C. GC/MS (EI) m/z (% relative intensity): 165(100), 306(38), 321(67), 477(33), 497(35). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 0.031 (s, 9 H), 7.11 (d, J = 8 Hz, 1H), 7.19 (d, J = 7 Hz, 1H), 7.45 (d, J = 10 Hz, 1H), 7.47 (d, J = 11 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −131.47, −130.87, −130.56−130.09, −129.92, −128.67, −128.16, −127.7. ^{13}C NMR (125 MHz, $CDCl_3$, δ): −10.7, 115.6, 118.3, 129.7, 129.9, 137.0, 137.2, 138.6, 138.9, 152.9, 153.0. HRMS Calculated (Found) for $C_{21}H_{23}F_6O_2Sn_2$ 660.9646 (660.9657).

4.1.16. 4-Vinyl(trifluorovinyloxy)benzene (10). To a three-neck flask, **1** (316 mg, 1.25 mmol) and DME (5 mL) were dissolved, degassed with N_2, and stirred for 20 min after which $Pd(PPh_3)_4$ (14 mg, 0.012 mmol) was added. The solution was degassed again and stirred under N_2 for 10 min. K_2CO_3 (172 mg, 1.25 mmol) was added followed by water (3 mL) and 2,4,6-trivinylcyclotriboroxane pyridine complex (301 mg, 1.25 mmol) prepared according to a published procedure.[21] The reaction was heated and stirred at 85 °C for 20 h. The solvent was then removed under vacuum, and the product was purified by column chromatography on silica hexane/ethyl acetate (95:5) to afford 185 mg (74%) of **10** as a clear oil. FTIR (KBr, cm^{-1}): 1831 (w), 1601 (w), 1503 (m), 1312 (m), 1269 (s),1186 (m), 1181 (m), 1142 (s). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 5.25 (d, J = 11 Hz, 1H), 5.69 (d, J = 18 Hz, 1H), 6.67 (dd J = 11 Hz, 17 Hz, 1H), 7.08 (d, J = 8 Hz, 2H), 7.42 (d, J = 6 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −133.92 (dd, 1F), −126.72 (dd, 1F), −119.77 (dd, 1F) (J_{gem} = 94 Hz, J_{cis} = 56 Hz, J_{trans} = 108 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 127.8, 133.5 (ddd, J = 40 Hz, 41 Hz, 262 Hz), 134.6, 135.6, 147.0 (ddd, J = 61 Hz, 277 Hz, 270 Hz), 154.7. HRMS Calculated (Found) for $C_{10}H_7O_1F_3$ 200.0449 (200.0446).

4.1.17. 1,2-Bis(4-vinylphenoxy)hexafluorocyclobutane. In a two-neck flask, bis(4-bromophenoxyl)hexafluorocyclobutane (200 mg, 0.40 mmol) and DME (5 mL) were added and degassed with 15 cycles of vacuum and N_2. The solution was allowed to stir under N_2 for 20 min after which $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) was added and the solution

was degassed again and stirred under N_2 for 10 min. K_2CO_3 (110 mg, 0.8 mmol) was added next followed by water (3 mL) and 2,4,6-trivinylcyclotriboroxane pyridine complex (192 mg, 0.8 mmol). The reaction was heated at 85 °C for 20 h. The solvent was removed under vacuum, and the product was purified by column chromatography on silica gel hexane/ethyl acetate (95:5) to afford 96 mg (60%) of the dimer of **10** as a clear oil. GC/MS (EI) *m*/*z* (% relative intensity): 77 (67), 103 (65), 153 (20), 200 (25), 400 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.22 (d, J = 11 Hz, 1H), 5.66 (d, J = 17 Hz, 1H), 6.63 (dd, J = 11 Hz, 17 Hz, 1H), 7.06 (d, J = 9 Hz, 1H), 7.12 (d, J = 10 Hz, 1H), 7.35 (d, J = 7 Hz, 2H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −131.14, −130.81,−130.76, −130.29, −130.05, −129.58, −128.65, −128.53, −128.18, −128.06. ^{13}C NMR (125 MHz, $CDCl_3$, δ): 114.2, 114.3, 118.2, 118.6, 127.5, 127.6, 134.8, 135.6, 152.2. HRMS Calculated (Found) for $C_{20}H_{14}F_6O_2$ 400.0897 (400.0902).

4.1.18. 4,4′-((1,2,3,3,4,4-Hexafluorocyclobutane-1,2-diyl)bis(oxy))-dibenzoic Acid. The thermal cyclodimerization 4-(trifluorovinyloxy)-benzoic acid **11** (X = H) (2.3 mmol, 0.5 g) was carried out at 180 °C in mesitylene for 24 h. The product precipitated during the reaction and was further purified by washing with hexane and MeOH to afford the dimer of **11** in 80% yield. GC/MS ($C_{18}H_{10}O_6F_6$, M^+ calcd as 436) *m*/*z*: 436, 299, 249, 218, 198, 171, 121. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, 2H), 7.38 (d, 2H), 8.2 (m, 4H). ^{19}F NMR (470 MHz, $CDCl_3$): δ −126.7, −127.2, −127.4, −127.9, −128.8, −129.3, −129.5, −130.0, −131.2.

4.1.19. Ethyl 4-(2-Bromo-1,1,2,2-tetrafluoroethyoxy))benzoate (Precursor to 11 (X = COOEt). To a flame dried nitrogen purged three-necked flask, NaH powder (2.16 g, 0.09 mol) was added followed by slow addition of anhydrous DMSO (20 mL) via addition funnel. After complete addition, the solution was cooled using an ice bath to just above the freezing point of the DMSO. In a separate 50 mL one-neck flask, ethyl-4 hydroxy benzoate (10 g, 0.06 mol) was dissolved in DMSO (40 mL). The benzoate solution was transferred to the addition funnel and added slowly over a 1 h time period. After complete addition of the benzoate solution, the reaction was warmed to room temperature, and dibromotetrafluoroethane (78 g, 0.3 mol) was added. The mixture was heated at 50 °C for 15 h. Water (50 mL) was then added to quench the reaction, and the contents were transferred to a separatory funnel, and the product was washed with water (500 mL) and extracted as an oil. The crude oil was purified by column chromatography on silica gel hexane/ethyl acetate (95:5) to afford 9.94 g (48%) of ethyl 4-(2-bromo-1,1,2,2-tetrafluoroethyoxy))benzoate (X = COOEt) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.86 (d, J = 10 Hz, 2H), 7.82 (d, J = 9 Hz, 2H), 4.40 (q, J = 10 Hz, 2H), 1.4 (t, J = 10 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −68.1 (s, 1F), δ −85.9 (s, 1F).

4.1.20. Ethyl 4-(trifluorvinyloxy)benzoate (11) (X = COOEt). In a flame dried three-neck flask, Zn (2 g, 30.6 mmol) was added and heated thoroughly with a flame under nitrogen. After cooling, CH_3CN (5 mL) was added and a solution of ethyl 4-(2-bromo-1,1,2,2-tetrafluoroethyoxy))benzoate (8 g, 23.1 mmol) in CH_3CN (18 mL) was added dropwise while heating with a hot air gun. After complete addition of the solution, the reaction was heated for 24 h at 95 °C. The reaction mixture was then filtered using vacuum filtration to remove any unreacted Zn and the Zn salts produced. The solvent was removed by rotary evaporation, and the product was purified by column chromatography over alumina hexane/ethyl acetate (95:5) to afford 5.40 g (95%) of **11** (X = COOEt) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): δ 8.05 (d, J = 8 Hz, 2H), 7.11 (d, J = 11 Hz, 2H), 4.34 (q, J = 8 Hz, 2H), 1.36 (t, J = 7 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −118.91 (dd, 1F), 125.74 (dd, 1F), 134.81 (dd, 1F) (J_{gem} = 95 Hz, J_{cis} = 55 Hz, J_{trans} = 108 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 165.6, 158.2, 148.9 (ddd, J = 60 Hz, 279 Hz, 274 Hz), 134.7 (ddd, J = 40 Hz, 41 Hz, 262 Hz), 131.9, 127.3, 115.5, 61.2, 14.1.

4.1.21. (4-(Trifluorovinyloxy)phenyl)azidomethanone (Precursor to 12 and 13). To a flame dried two-neck flask, 4-(trifluorovinyloxy)-benzoyl chloride **11** (X = Cl) (2 g, 8.47 mmol) and distilled THF (8 mL) were charged. The solution was cooled to 0 °C using an ice bath, and a solution of NaN_3 (1.82 g, 28 mmol) in water (6 mL) was added dropwise. The resulting solution was stirred at 0 °C for 1.5 h. Additional water was then added, and product was extracted into CH_2Cl_2 and concentrated by rotary evaporation to yield a light yellow oil which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 6 Hz, 1H), 7.15 (d, J = 6 Hz, 1H). ^{19}F NMR (470 MHz, $CDCl_3$) δ −118.04 (dd, 1F), −124.65 (dd, 1F), −134.60 (dd, 1F) (J_{gem} = 94 Hz, J_{cis} = 60 Hz, J_{trans} = 111 Hz).

4.1.22. 4-Isocyanato(trifluorovinyloxy)benzene (12). In a single-neck 100 mL flask, (4-(trifluorovinyloxy)phenyl)azidomethanone (1.0 g, 4.11 mmol) was disolved in toluene (10 mL) and heated at 100 °C until the evolution of N_2 was no longer apparent (about 1.5 h). The toluene was then removed under a vacuum, and the product was purified by vacuum distillation (0.1 Torr) at 78 °C to afford 468 mg (53%) of **12** as a clear oil. GC/MS (EI) *m*/*z* (% relative intensity): 63 (40), 90 (95), 118 (35), 189 (35), 215 (100). ^{1}H NMR (300 MHz $CDCl_3$, δ): 7.03 (d, J = 9 Hz, 1H), 7.07 (d, J = 5 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$, δ): −134.49 (dd, 1F), −126.50 (dd, 1F), −119.52 (dd, 1F) (J_{gem} = 94 Hz, J_{cis} = 56 Hz, J_{trans} = 108 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 117.2, 124.8, 126.1, 132.8 (ddd, J = 42 Hz, 40 Hz, 265 Hz), 147.0 (ddd, J = 59 Hz, 280 Hz, 275 Hz), 152.7.

4.1.23. 1,2-Bis(4-isocyanatophenoxy)hexafluorocyclobutane. In a single-neck flask, 4-isocyanato(trifluorovinyloxy)benzene (**12**) (240 mg, 1.12 mmol) was heated neat for 72 h at 120 °C. The starting material (**12**) was removed by vacuum distillation to afford 161 mg (67%) of the dimer as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.04−7.16 (m, 4 H). ^{19}F NMR (282 MHz, $CDCl_3$, δ): −131.27, −131.01, −130.32, −129.53, −128.77, −128.72, −127.98−126.75. ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.1, 149.9 (d), 131.1, 130.8, 126.0, 124.9, 119.8, 119.4.

4.1.24. 4-(Trifluorovinyloxy)benzenamine (13) (R′ = H). In a single-neck 100 mL flask (4-(trifluorovinyloxy)phenyl)azidomethanone (500 mg, 2.05 mmol) was dissolved in toluene (5 mL). Concentrated aq HCl (5 mL) was then added, and the reaction was stirred and heated at 100 °C for 2 h. The reaction was then cooled, and water (40 mL) was added. The water layer was washed twice with CH_2Cl_2 (50 mL) and neutralized to pH 7 with KOH after which the product was extracted into CH_2Cl_2. The organic layer was concentrated by rotary evaporation, and the product was purified by column chromatography on silica, with dichloromethane as the eluent to afford 194 mg (50%) of **13** as a brown oil. GC/MS (EI) *m*/*z* (% relative intensity): 189 (38), 142 (15), 92 (45), 65 (100). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.60 (s, 1H), 6.57 (d, J = 3 Hz, 1H), 6.59 (d, J = 3 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$, δ): −133.20 (dd, 1F), −128.16 (dd, 1F), −120.97 (dd, 1F) (J_{gem} = 99 Hz, J_{cis} = 57 Hz, J_{trans} = 110 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 148.1 (ddd, J = 60 Hz, 277 Hz, 269 Hz), 145.0, 144.5, 134.6 (ddd, J = 46 Hz, 43 Hz, 260 Hz), 123.3, 117.5.

4.1.25. 1,2-Bis(4-aminophenoxy)hexafluorocyclobutane. In a one-neck flask 1,2-bis(4-isocyanatophenoxy)hexafluorocyclobutane (200 mg, 0.46 mmol) was added to toluene (5 mL). Concentrated aq HCl (5 mL) was added, and the reaction was heated at 100 °C for 2 h. The reaction was cooled, and water (40 mL) was added and washed twice with CH_2Cl_2 (50 mL). The water layer was neutralized with KOH, and the product was extracted into CH_2Cl_2. The organic layer was concentrated by rotary evaporation, and the product was purified by column chromatography on silica gel, CH_2Cl_2/MeOH (95:5) to afford 156 mg (90%) of the dimer of **13** (R = H) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.63 (s, 1H), 6.58 (m 1H), 7.00 (d, 1H). ^{19}F NMR (282 MHz, $CDCl_3$, δ): −131.52, −130.74, −130.48, −130.16, −130.00, −129.67, −129.15, −128.89, −128.34. ^{13}C NMR (75 MHz, $CDCl_3$, δ): 115.7, 120.0, 120.4, 143.9, 144.2, 144.7, 144.9, 171.4.

4.1.26. Ethyl 4-(Trifluorovinyloxy)phenylcarbamate (13) (R′ = COOEt). To a flame dried one-neck flask, **12** (500 mg, 2.05 mmol) dissolved in ethanol (10 mL) was added, and the reaction was heated

at 100 °C for 2 h. Excess EtOH was removed by rotary evaporation and purified by column chromatography on silica with dichloromethane as the eluent to afford 411 mg (82%) of **13** (R = COOEt) as a light tan oil. GC/MS (EI) *m*/*z* (% relative intensity): 216 (100), 202 (36), 142 (25), 92 (48), 65 (50). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.40 (d, J = 8 Hz, 2H), 7.01 (d, J = 9 Hz, 2H), 4.23 (q, J = 7 Hz, 2H), 1.29 (t, J = 7 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −119.94 (dd, 1F), −126.86 (dd, 1F), −133.60 (dd, 1F) (J_{gem} = 97 Hz, J_{cis} = 58 Hz, J_{trans} = 111 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 154.1, 150.9, 148.9 (ddd, J = 46 Hz, 43 Hz, 260 Hz), 135.3 (ddd, J = 64 Hz, 275 Hz, 270 Hz), 135.1, 120.4, 116.3, 61.4, 14.5. HRMS Calcd (Found) for $C_{11}H_{10}N_1F_3O_3$ 261.0613 (261.0612).

4.1.27. 1,2-Bis(4-ethylcarbmatephenoxy)hexafluorocyclobutane. In flame dried one-neck flask under nitrogen, **13** (R = COOEt) (300 mg 1.23 mmol) was heated neat for 24 h at 150 °C. The product was purified by column chromatography on silica gel using hexane/ethyl acetate (90:10) to afford 285 mg (95%) of the dimer of **13** (R = COOEt) as a white powder. Mp 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.27−1.29 (m, 6H), 4.15−4.22 (m, 4H), 6.99−7.11 (m, 5H), 7.29−7.36 (m, 4 H). ^{19}F NMR (470 MHz, $CDCl_3$, δ): −131.4, −130.6, −129.8, −129.6, −129.0, −128.8, −128.2. HRMS Calcd (Found) for $C_{22}H_{20}N_2F_6O_6$ 522.1226 (522.1227).

4.2. Kinetic Rate Experiments. To separate 5 mm NMR tubes, the TFVE compounds (150 mg) dissolved in $CDCl_3$ were added and the tubes were purged with N_2 and sealed. The samples were then immersed in a stirred oil bath equilibrated at the desired temperature. Samples were removed at varying times, and the reaction was quenched by rapid cooling. Conversion was determined by ^{19}F NMR for which the TFVE fluorine signals appear as doublets of doublets for each vinyl fluorine and the new PFCB fluorine signals appear between −127 ppm and −133 ppm (Figure 5). The percent conversion was calculated by dividing the integration of the PFCB fluorine signals by the total fluorine integration (PFCB + TFVE) × 100.

4.3. Competitive Rate Study. To a 5 mm NMR tube, **11** (X = COOEt) and **13** (R = COOEt) (50 wt % of each, 100 mg total) were added, and the tube was purged with N_2 and then sealed. The samples were immersed in an equillibrated 130 °C stirred oil bath, heated for 18 h, and then quenched by cooling. The product distribution was determined by HPLC using pure standards as calibration and confirmed by ^{19}F NMR.

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Supporting Information Available: Data files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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