# Stereo- and Regiospecific Syntheses of α- and β-Substituted Vinyl and Dienyl Triflones via the Stille Reaction[1]

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**Abstract:** Acetylenic anions undergo efficient sulfonylation with trifluoromethanesulfonic anhydride to provide acetylenic triflones. These materials are stereospecifically converted to (*Z*)-β-iodovinyl triflones in one step via the addition of hydrogen iodide. Access to (*Z*)-α-iodovinyl triflones is also possible via a two-step process involving tributyltin hydride addition to the acetylenic triflones to generate (*Z*)-α-(tributylstannyl)vinyl triflones followed by an iododestannylation reaction. Both classes of iodovinyl triflones smoothly undergo palladium (0)-mediated Stille reactions with vinyl, aryl, heteroaryl, and acetylenic stannanes to stereospecifically provide trisubstituted vinyl and dienyl triflones.

## Introduction

The seminal contributions of the Hendrickson research group have established that the trifluoromethyl sulfone (triflone) is an essentially unique amphoteric functional group; the potent electron-withdrawing properties of this moiety engender powerful polarization of a conjugated olefin toward conjugate-addition reactions (**1** → **2**, Scheme 1) as well as subsequently strongly enhancing the leaving-group ability of the resultant adduct (**2** → **3**).[2,3] Unfortunately, the same inductive effect which renders the triflone moiety so useful often strongly mitigates against efficient synthesis where the carbon−sulfur bond is constructed via nucleophilic protocols.[2]

In connection with our interest in extending the synthetic potential of the sulfone moiety, we have recently expanded our focus to include the synthetic chemistry of trifluoromethyl sulfones (triflones).[4] While we were recently successful at divising a one-pot Peterson protocol for synthesis of simple vinyl (**7a,b**) and dienyl (**8a,b**) triflones from addition of α-silylated triflone anion **6** to aldehydes (Scheme 2), all efforts to effect similar reactions with ketones was thwarted by the poor nucleophilicity (and steric congestion) of intermediate **6**.[4b]

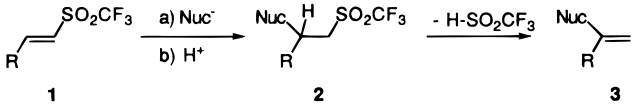
Faced with the substantial limitations described above, we decided to explore the potential of transition metal catalyzed reactions to effect construction of more highly functionalized vinyl and dienyl triflones (**12**−**15**, Scheme 3). This analysis suggested that β-and α-iodovinyl triflones **10** and **11** would constitute ideal substrates in Stille reactions with a variety of vinyl, aryl, and acetylenic stannane reagents.

## Results and Discussion

Acetylenic triflones have traditionally been prepared in 50−70% yield by addition of triflic anhydride to a solution of an acetylenic anion.[5] This approach is partially compromised by the tendency of the intermediate acetylenic triflone to undergo subsequent chemistry under the conditions of its formation. Fortunately, we have found that *inverse addition* minimizes the formation of diacetylenes as well as other unwanted polycondensation products. For example, model acetylenic triflones **9a**,**b** can be prepared in 75−87% yield by this simple modification. While acetylenic triflones have seen relatively little use in organic synthesis,[4d,5] we find that lithium iodide in acetic acid[6] effects stereo- and regiospecific addition to acetylenic triflones **9a** and **9b** to provide excellent yields of β-iodovinyl triflones **Z-10a** and **Z-10b**, respectively (Scheme 4). Testament to the inductive effect of the triflone moiety is the finding that the HI addition reaction occurs within minutes at 0 °C as compared to the same reaction with acetylenic esters, which require 12 h at 70 °C.[6] Perhaps even more amazing is the observation that aqueous lithium iodide, in the absence of any acid catalysis, will also afford β-iodovinyl triflones **10a**,**b** albeit in substantially reduced yields (∼40%).

Unambiguous definition of the olefin geometry of **Z-10a,b** required the preparation of the isomeric trisubstituted vinyl triflone **E-10a,b**. This was accomplished by photolysis of **Z-10a** at 254 nm for 2 h in deuterated acetonitrile at 30 °C using a Rayonet reactor. The resultant photostationary equilibrium consisted of 60% **Z-10a** and 40% of **E-10a**, which were separated by chromatography. Similar photolysis of **Z-10b** resulted in conversion to a mixture of **E-10b** and acetylenic triflone **9b**. Chromatography of the mixture easily provided a pure sample of **E-10b**. The indicated structural assignments were principally the result of a pair of equilibrium NOE experiments.[7] The first of these experiments involved irradiation

**Scheme 1**




**1** **2** **3**

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

(1) Syntheses via Vinyl Sulfones. 62. Triflone Chemistry. 4. For previous triflone papers: see footnote 4c.

(2) For excellent reviews discussing the chemistry of triflones, see: (a) Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306. (b) Hendrickson, J. B.; Bair, K. W.; Bergeron, R.; Giga, A.; Skipper, P. L.; Sternbach, D. D.; Wareing, J. *Org. Prep. Proced. Int.* **1977**, *9*, 173. (c) Hendrickson, J. B.; Judelson, D. A.; Chancellor, T. *Synthesis* **1984**, 320.

(3) Cumyl triflone undergoes solvolysis 170 times more slowly than cumyl chloride but $10^7$ times more rapidly than cumyl phenyl sulfone: Creary, X. *J. Org. Chem.* **1985**, *50*, 5080.

(4) (a) Magar, S. S.; Fuchs, P. L. *Tetrahedron Lett.* **1992**, *33*, 745. (b) Mahadevan, A.; Fuchs. P. L. *Tetrahedron Lett* **1994**, *35*, 6025. (c) Mahadevan, A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1995**, *117*, 3272.

(5) (a) Glass, R. S.; Smith, D. L. *J. Org. Chem.* **1974**, *39*, 3712. (b) Berk, H. C.; Franz, J. E. *Synth. Commun.* **1981**, *11*, 267. (c) Massa, F.; Hanack, M.; Subramanian, L. R. *J. Fluorine Chem.* **1982**, 601. (d) Hanack. M.; Subramanian, L. R. *Synthesis* **1988**, 592. (e) Hanack, M.; Willhelm, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1057.

(6) (a) Ma, S.; Lu, X. *J. Chem. Soc., Chem. Commun.* **1990**, 1643. (b) Marek, I.; Alexakis, A.; Normant, J.-F. *Tetrahedron Lett.* **1991**, *32*, 5329. (c) Lu, X.; Huang, X.; Ma, S. *Tetrahedron Lett.* **1992**, *33*, 2535. (d) Meyer, C.; Marek, I.; Normant, J. -F. *Synlett* **1993**, 386.

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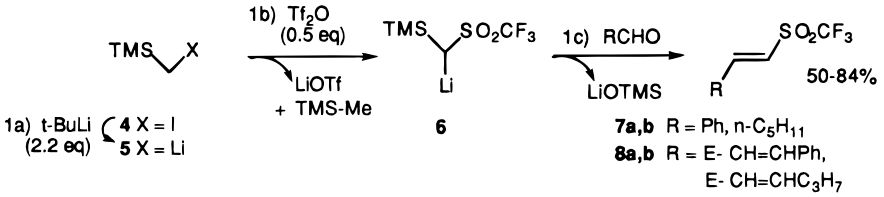
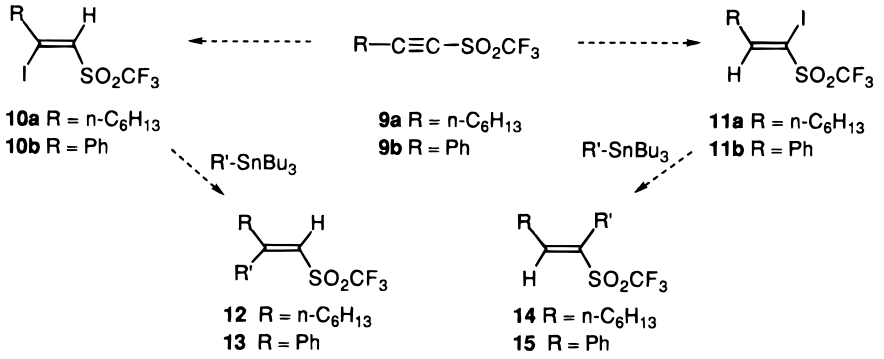
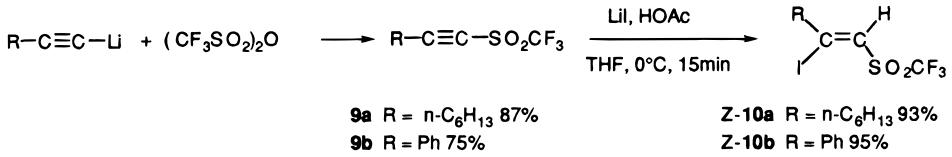
**Scheme 2**



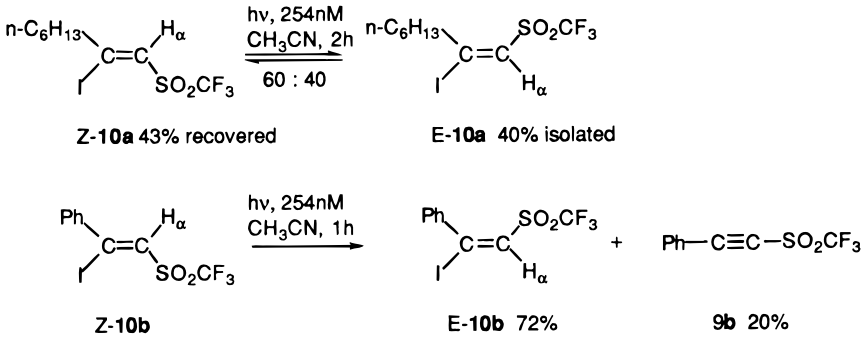

**Scheme 3**




**Scheme 4**




**Scheme 5**




of the allylic methylene group for both isomers of the octynyl triflones with observation of the enhancement of the vinyl proton $H_\alpha$. The finding of 23% and 6% enhancement for **Z-10a** and **E-10a** is uniquely consistent with the assigned stereochemistry of the olefin isomers (Scheme 5; Table 1). Delineation of the β-phenylvinyl triflones **Z-10b** and **E-10b** involved irradiation of the vinylic hydrogen and observation of the NOE for the *o*-aryl hydrogens. In this instance the *Z* isomer showed 4.5% enhancement, while the *E* isomer revealed no interaction (Scheme 5; Table 1).

Stille coupling[8] of β-iodovinyl triflones **Z-10a** and **E-10a** with vinyl tributylstannane **16** in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (**17**) stereospecifically provides trisubstituted dienyltriflones **Z-12a** and **E-12a** in high yield (Scheme 6).

A variety of stannane reagents were surveyed in the palladium-mediated Stille reaction using the now readily available β-iodovinyl triflones **Z-10a** and **Z-10b** as substrates. These reactions smoothly provided the trisubstituted unsaturated triflones **12b**−**f** and **13a**,**b**,**f** as detailed in Table 2.

**Table 1.** NMR Data for **10a** and **10b** ***Z*** and ***E*** Isomers

| observable | Z-10a | E-10a | Z-10b | E-10b |
|---|---|---|---|---|
| $^1$H chemical shift Hα (δ) | 6.9 | 7.0 | 7.15 | 7.25 |
| width at half-height Hα (Hz) | 3.6 | 3.3 | | |
| $^{13}$C chemical shift allylic $CH_2$ (δ) | 50 | 42 | | |
| $^1$H chemical shift allylic $CH_2$ (δ) | 2.88 | 3.05 | | |
| equilibrium NOE[a] (%) | 23 | 6 | 4.5 | none |
| relaxation time $\tau_1$ (s) | 8 | 20 | 7 | 5.5 |

[a] The allylic $CH_2$ was irradiated with observation of the vinylic $H_\alpha$ for **Z,E-10a**; the vinylic $H_\alpha$ was irradiated with observation of the *o*-aryl hydrogens for **Z,E-10b**.

While most of the examples in Table 2 are straightforward, the reaction of **Z-10a** with *trans*-1,2-distannylethylene **19** merits further discussion. The reaction of these two compounds is very poor using tetrakis(triphenylphosphine)palladium(0) **17** (Table 2, entries 2.2, 2.1), but using 1.7 equiv of distannylethylene **19** in the presence of bis(benzonitrile)palladium dichloride provides a 70% yield of δ-stannyldienyl triflone **12c** in addition to 20% of the expected bis coupling product **20** (Table 2, entry 2.3

(7) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press, New York, 1987; pp 121−122.

(8) (a) Reviews: Mitchell, T. N. *Synthesis* **1992**, 803. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138. (c) Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813.

**Scheme 6**

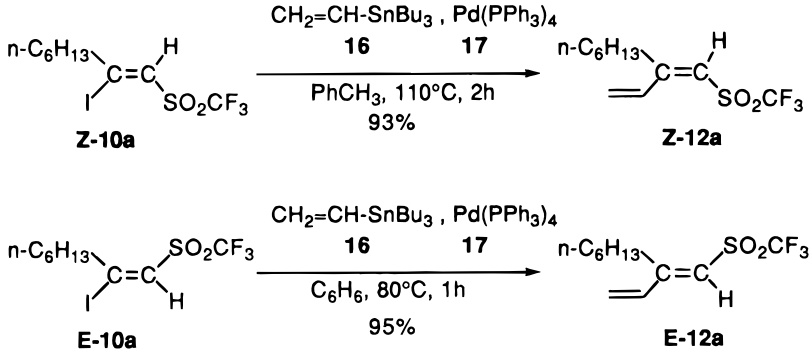
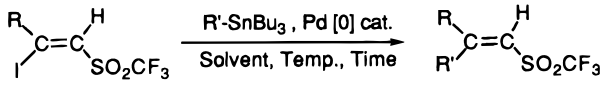
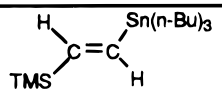
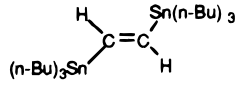
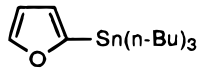
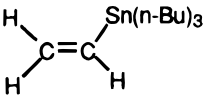



**Table 2.** Stille Coupling Reactions of $\beta$-Iodovinyl triflones



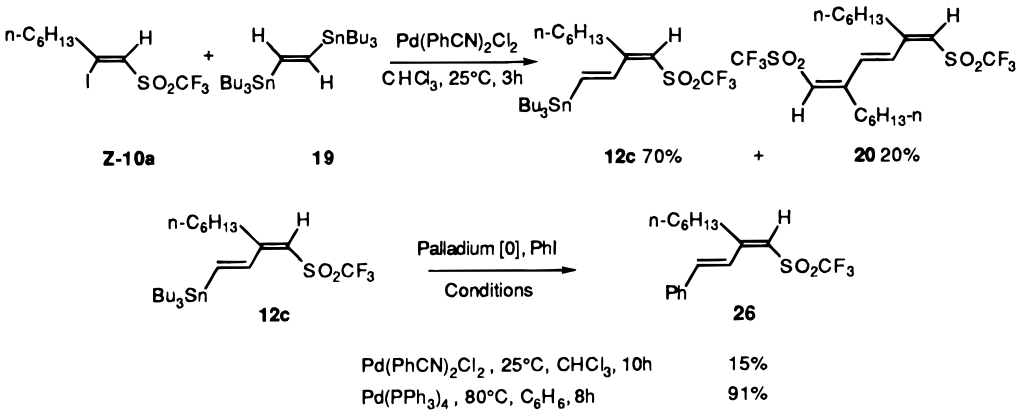

**Z-10a** R = n-$C_6H_{13}$
**Z-10b** R = Ph

**12** R = n-$C_6H_{13}$
**13** R = Ph

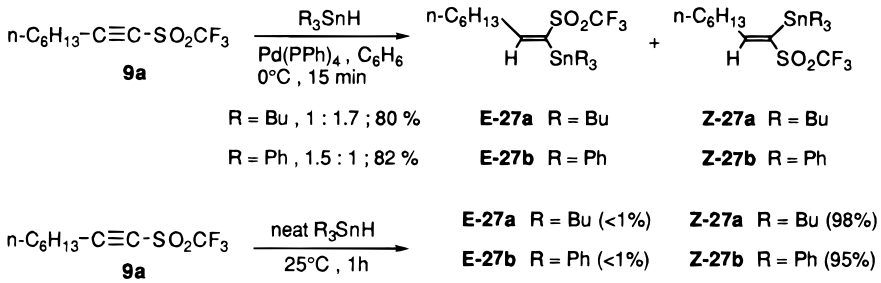
| Entry | triflone | Stannane | | Pd catalyst & Solvent | Temp. Time | Product R' = , Yield |
|---|---|---|---|---|---|---|
| 1 | **Z-10a** |  | **18** [12] | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 2h | **12b** R' = E-TMSCH=CH, 81% |
| 2.1 | **Z-10a** |  | **19** [13] | $Pd(PPh_3)_4$ **17** THF | 25°C 48h | **12c** R' = E-(n-$Bu_3$SnCH=CH), 10% |
| 2.2 | **Z-10a** | | **19** | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 2h | **12c** R' = E-(n-$Bu_3$SnCH=CH), tr. + **20**, 10% |
| 2.3 | **Z-10a** | | **19** | $Pd(PhCN)_2Cl_2$ **21** $CHCl_3$ | 25°C 3h | **12c** R' = E-(n-$Bu_3$SnCH=CH), 70% + **20**, 20% (See Scheme 7) |
| 3 | **Z-10a** | TMS—C≡C—Sn(n-Bu)3 | **22** [14] | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 55°C 9h | **12d** R' = TMS-C≡C, 77% |
| 4 | **Z-10a** | Ph-Sn(n-Bu)3 | **23** | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 3h | **12e** R'= Ph, 80% |
| 5 | **Z-10a** |  | **24** | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 2h | **12f** R' = 2-furyl 85% |
| 6 | **Z-10b** |  | **16** | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 3h | **13a** (R' = $CH_2$=CH), 81% |
| 7.1 | **Z-10b** | | **18** | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 6h | **13b** R' = E-TMSCH=CH, 72% |
| 7.2 | **Z-10b** | | **18** | $Pd(MeCN)_2Cl_2$ **25** $C_6H_6$ | 25°C 10h | **13b** R' = E-TMSCH=CH, 83% |
| 8 | **Z-10b** | | **24** | $Pd(PPh_3)_4$ **17** $C_6H_6$ | 80°C 2.5h | **13f** R' = 2-furyl, 90% |

Scheme 7). This allows for the possibility of construction of even more complex dienyl triflones. For example, subsequent palladium-catalyzed reaction of **12c** with iodobenzene affords $\delta$-phenyldienyl triflone **26** in 91% yield (Scheme 7).

**Scheme 7**




**Scheme 8**




Attention was next directed to the synthesis of trisubstituted α-iodovinyl triflones **14** and **15**. These compounds cannot be prepared by classical olefination methods such as the Peterson olefination or the Wadsworth−Emmons reaction. Because of the success enjoyed in the synthesis of **12** and **13**, we were drawn to consider palladium-catalyzed hydrostannylation of acetylenes **9a**,**b**, a reaction which had been shown to proceed with excellent regio- and stereoselectivity, and good overall yields in the case of other polarized acetylenic substrates.[9] In the event, hydrostannylation of acetylenic triflone **9a** with tributyltin hydride in the presence of tetrakis(triphenylphosphine)palladium(0) (**17**) rapidly provided α-stannylated vinyl triflones **E-27a** and **Z-27a** regiospecifically, but the reaction was not stereospecific, affording a 1:1.7 ratio of *E* and *Z* stereoisomers. Attempts were made to improve the stereospecificity of the palladium-catalyzed hydrostannylation reaction by using the more sterically demanding triphenyltin hydride. Surprisingly, this modification served to reverse the stereochemical ratio (**E-27b**/**Z-27b** = 1.5:1); nevertheless, it was clear that a better protocol was needed. Fortunately, it was found that simply allowing neat tributyltin hydride to react with the acetylenic triflone **9a** for 1 h at 25 °C stereospecifically produced **Z-27a** in 98% yield. Repeating the process with triphenyltin hydride also stereospecifically afforded the triphenylstannyl analog **Z-27b** in 95% yield (Scheme 8).

Assignment of stereochemistry for these trisubstituted α-stannylvinyl triflones was readily accomplished by proton NMR based upon the three-bond coupling between the tin atom and the terminal vinyl hydrogen. Specifically it was found that **E-27a,b** exhibited $^3J_{Sn-H}$ values of 42 and 55 Hz, while **Z-27a,b** had coupling constants of 67 and 90 Hz, respectively.[10]

Attempts at direct coupling of α-stannylvinyl triflone **Z-27a** with iodobenzene or vinyl iodide **28**[11] using tetrakis(triphenylphosphine)palladium(0) (**17**) or bis(acetonitrile)palladium dichloride (**25**) were unavailing. Therefore, **Z-27a** was reacted with iodine in dichloromethane at 25 °C to provide an 88% yield of α-iodovinyl triflone **11a**. By way of contrast, α-iodovinyl triflone **11a** undergoes efficient Stille reaction with vinyltributylstannane (**16**) and 2-furylstannane **24** to afford cross-conjugated dienyl triflone **E-14a** and trisubstituted vinyl triflone **E-14f**, respectively (Scheme 9).

## Experimental Section

Starting materials were obtained either from Aldrich Chemicals or from other commercial suppliers. Solvents were purified as follows: diethyl ether and tetrahydrofuran, by distillation from benzophenone ketyl under argon; methylene chloride, benzene, and toluene, by distillation from calcium hydride.

$^1$H NMR (300 and 200 MHz) and $^{13}$C NMR (75 and 50 MHz) spectra were recorded on General Electric QE-300 and Varian Gemini 200 instruments, respectively. $^1$H chemical shifts are reported in parts per million (ppm) from the internal chloroform (7.26 ppm); TMS (0 ppm); or benzene (7.15 ppm) standard. Coupling constants (*J* ) are reported in hertz. $^{13}$C chemical shifts are reported in parts per million relative to chloroform (77 ppm); $^{19}$F NMR (283 MHz) spectra were recorded on a General Electric QE-300 instrument. $^{19}$F chemical shifts are reported in parts per million relative to $CFCl_3$ (0 ppm) standard.

Melting points reported are uncorrected and were obtained on a Mel-Temp apparatus. Low-resolution EI and CI mass spectra were obtained on a Finnigan 400 mass spectrometer. High-resolution mass spectra (HRMS) were obtained on a Kratos MS-50 instrument.

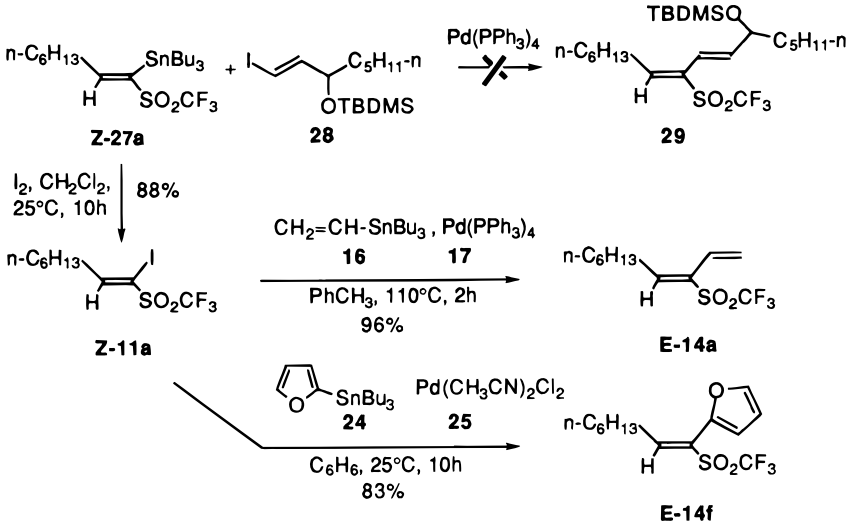
All reactions described were carried out under an atmosphere of argon unless otherwise indicated. All yields reported are isolated yields of material. TLC was performd on Merck glass silica gel plates. Column chromatography was performed using Merck silica gel 60 (60−200 mesh).

(9) (a) Cochran, J. C.; Bronk, B. S.; Terrence, K. M.; Phillips, H. K. *Tetrahedron Lett*. **1990**, *31*, 6621. (b) Rossi, R.; Carpita, A.; Cossi, P. *Tetrahedron Lett*. **1992**, *33*, 4495.

(10) (a) Delmas, M; Maire, J. C.; Santamaria, J. *J. Organomet. Chem.* **1969**, *16*, 405. (b) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem*. **1983**, *241*, C45. (c) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem*. **1986**, *51*, 3561. (d) Cochran, J. C.; Williams, L. E.; Bronk, B. S.; Calhoun, J. A.; Fassberg, J.; Clark, K. G. *Organometallics* **1989**, *8*, 804.

(11) Donaldson, R. E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1981**, *103*, 2108.

**Scheme 9**




**1-Octynyl Trifluoromethyl Sulfone (9a).** 1-Octyne (0.500 g, 4.5 mmol) was added dropwise to a stirred solution of *n*-BuLi (4.8 mmol, 2 mL, 2.4 M in hexane) in diethyl ether (50 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h followed by slow cannula transfer of the lithium acetylide to a solution of triflic anhydride (1.280 g, 4.5 mmol) in 20 mL of ether at −78 °C. After the addition, the temperature was maintained at −78 °C for 30 min and then slowly warmed to 0 °C, and the reaction mixture was quenched with water. The aqueous layer was extracted with ether, and the combined organic extracts were washed with brine. Drying and concentration afforded a yellow oil, which was purified by column chromatography (silica gel deactivated with acetone, pentane eluent) to yield 0.95 g (87%) of pure 1-octynyl trifluoromethyl sulfone **9a** as a colorless oil ($R_f$ 0.50, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.55 (t, 7.0 Hz, 2H), 1.66 (m, 2H), 1.38 (m, 6H), 0.90 (t, 6.6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.81, 19.19, 22.29, 26.48, 28.31, 30.92, , 70.19, 105.93, 118.84 (q, $J_{C,F}$ = 323 Hz); $^{19}$F NMR (283 MHz, $CFCl_3$) $\delta$ −81.6; mass spectrum (CI), 243 (M + $H^+$, 1.00), 109 (0.09); HRMS calcd for $C_9H_{14}F_3O_2S$ 243.0667, found 243.0667.

**Phenylethynyl Trifluoromethyl Sulfone (9b).** This triflone was prepared from phenylacetylene, using a procedure similar to that described above. Product **9b** was obtained as a yellow solid in 75% yield ($R_f$ 0.40, $SiO_2$, 0.05:1 ether/hexane): mp 29.0−31.5 °C (hexane); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35−7.76 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 77.6, 101.3, 116.1, 119.4 (q, $J_{C,F}$ = 322 Hz), 129.4, 133.8, 134.1; $^{19}$F NMR (283 MHz, $CFCl_3$) $\delta$ −81.1; mass spectrum (EI), 234 (0.25), 165 (0.97), 89 (1.00); mass spectrum (CI), 235 (M + $H^+$, 0.99); HRMS calcd for $C_9H_5F_3SO_2$ 233.9962, found 233.9969. The $^1$H and $^{13}$C NMR are consistent with those reported.[5d]

**(*Z*)-2-Iodo-1-[(trifluoromethyl)sulfonyl]oct-1-ene (Z-10a).** To a solution of octynyl trifluoromethyl sulfone **9a** (0.570 g, 2.35 mmol) in 10 mL of THF at 0 °C was added lithium iodide (0.330 g, 2.47 mmol, 1.05 equiv) followed by glacial acetic acid (0.14 mL, 2.35 mmol, 1 equiv). The reaction was complete within 15 min. THF was removed *in vacuo*, and the residue was partitioned between ether and water. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The resulting yellow oil was purified by column chromatography (silica gel deactivated with acetone, eluted with 2% ether/pentane) to afford 0.808 g (93%) of **10a** as a colorless oil ($R_f$ 0.40, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.90 (t, 4.7 Hz, 3H), 1.31 (m, 6H), 1.65 (m, 2H), 2.87(t, 7.1 Hz, 2H), 6.88 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.85, 22.34, 27.62, 29.15, 31.21, 49.62, 119.04 (q, $J_{C,F}$ = 325 Hz), 125.86, 133.92; $^{19}$F NMR (283 MHz, $CFCl_3$) $\delta$ −76.8; mass spectrum (EI), 371(0.14), 167(0.26), 109(1.00) ; mass spectrum (CI), 371(M + $H^+$, base peak); HRMS calcd for $C_9H_{15}F_3IO_2S$ 370.9790, found 370.9779.

**(*Z*)-1-Iodo-1-phenyl-2-[(trifluoromethyl)sulfonyl]ethene (Z-10b).** This vinyl triflone was prepared from phenylethynyl trifluoromethyl sulfone, using a procedure similar to that described above. The reaction was complete within 45 min. Product **Z-10b** was obtained as a yellow oil in 85% yield ($R_f$ 0.35, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.14 (s, 1H), 7.42−7.59 (m, 5H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 119.69(q, $J_{C,F}$ = 327 Hz), 127.39, 128.43, 129.29, 129.49, 132.69, 142.23; mass spectrum (EI), 362 (0.01), 235 (0.42), 105 (0.52), 102 (1.00); mass spectrum (CI), 363 (1.00), 235 (0.10); HRMS calcd for $C_9H_6F_3IO_2S$ 361.9085, found 361.9081.

**(*E*)-2-Iodo-1-[(trifluoromethyl)sulfonyl]oct-1-ene (E-10a).** Acetonitrile was purged with argon for 15 min before use. Vinyl iodide **Z-10a** (0.230 g, 0.62 mmol) dissolved in acetonitrile (5 mL) was added into a quartz tube under argon. The reaction mixture was irradiated with 254 nm ultraviolet light in a Rayonet reactor for 2 h. The mixture was then partitioned between pentane and water. Usual work-up and column chromatography afforded 0.092 g (40%) of **E-10a** as a colorless oil ($R_f$ 0.45, $SiO_2$, 0.05:1 EtOAc/hexane) in addition to 43% recovered **Z-10a**. In a separate experiment monitored by NMR, it was found that longer exposure time to UV led to the formation of significant amounts of side products. **E-10a**: $^1$H NMR (200 MHz) $\delta$ 0.91 (m, 3H), 1.37 (m, 6H), 1.66 (m, 2H), 3.09 (t, 7.5 Hz, 2H), 7.01 (s, 1H); $^{13}$C NMR (50 MHz) $\delta$ 14.47, 22.90, 28.59, 31.02, 31.83, 41.75, 119.97 (q, $J_{C,F}$ = 326 Hz), 128.92, 141.00; mass spectrum (EI), 237 (0.01), 236 (0.01), 173 (0.02), 167 (0.08), 109 (M − $SO_2CF_3$ − HI, 0.97); mass spectrum (CI), 371 (M + $H^+$, base peak), 212 (0.17); HRMS calcd for $C_9H_{15}F_3IO_2S$ 370.9790, found 370.9786.

**(*Z*)-1-Iodo-1-phenyl-2-[(trifluoromethyl)sulfonyl]ethene (E-10b).** This vinyl iodide was prepared from **Z-10b**, using a procedure similar to that described for **E-10a**. The reaction was complete within 1 h. Product **E-10b** was obtained as a yellow oil in 72% yield ($R_f$ 0.40, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz) $\delta$ 7.27(s, 1H), 7.35−7.44 (m, 5H); $^{13}$C NMR (50 MHz) $\delta$ 119.64 (q, $J_{C,F}$ = 333 Hz), 127.76, 128.44, 128.59, 129.42, 131.43, 134.27, 139.52; mass spectrum (CI), 363 (M + $H^+$, base peak); HRMS calcd for $C_9H_6F_3IO_2S$ 361.9085, found 361.9090.

**(*Z*)-1-Iodo-1-[(trifluoromethyl)sulfonyl]oct-1-ene (Z-11a).** To a stirred solution of vinylstannane **Z-27a** (0.455 g, 0.85 mmol) in 10 mL of $CH_2Cl_2$ was added $I_2$ (0.217 g, 0.85 mmol) at 25 °C. After stirring for 2 h, an additional amount of $I_2$ (0.087 g, 0.34 mmol) was added and the resulting solution was stirred overnight. Reaction was complete as determined by TLC ($SiO_2$, 0.05:1 EtOAc/hexane). The resulting solution was diluted with $CH_2Cl_2$, washed with $Na_2S_2O_3$ (aqueous) and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The crude mixture was purified by column chromatography (silica gel, pentane) to afford **Z-11a** (0.262 g, 88%) as a yellow oil ($R_f$ 0.50, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (m, 3H), 1.30 (m, 6H), 1.58 (m, 2H), 2.42 (q, 7.2 Hz, 2H), 7.59 (t, 7.2 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.45, 22.92, 27.40, 29.28, 31.88, 37.76, 88.53, 120.02 (q, $J_{C,F}$ = 327 Hz), 165.39; mass spectrum (CI), 371 (M + $H^+$, base peak); HRMS calcd for $C_9H_{15}F_3IO_2S$ 370.9790, found 370.9786.

**2-*n*-Hexyl-(*Z*)-1,3-butadienyl Trifluoromethyl Sulfone (Z-12a).** Toluene was purged with argon for 15 min before use. To a solution

of β-iodovinyl triflone **Z-10a** (0.660 g, 1.78 mmol) in 10 mL of toluene was added tetrakis(triphenylphosphine)palladium (**17**) (Aldrich, 0.103 g, 0.09 mmol, 5 mol %) under argon. Vinyltributyltin (Aldrich, 0.564 g, 1.78 mmol, 1 equiv) was added via syringe, and the solution was heated to reflux. The reaction was complete within 2 h as determined by TLC ($SiO_2$, 1:10 EtOAc/hexane). The reaction mixture was cooled to room temperature and washed with water. The aqueous layer was extracted with ether. The extracts were combined, washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel deactivated with acetone, eluted with 2% ether/pentane) to afford 0.451 g (94%) of **Z-12a** as a colorless oil ($R_f$ 0.35, $SiO_2$, 1:10 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.9 (t, 6.7 Hz, 3H), 1.33 (m, 6H), 1.55 (m, 2H), 2.56 (t, 7.6 Hz, 2H), 5.75 (d, 11.1 Hz, 1H), 5.89 (d, 17.1 Hz, 1H), 6.03 (s, 1H), 7.46 (dd, 11.1 Hz, 17.4 Hz, 1H) . $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 13.94, 22.45, 28.85, 28.89, 31.37, 34.24, 115.83, 119.92 (q, $J_{C,F}$ = 324 Hz), 126.03, 129.68, 164.97; $^{19}$F NMR (283 MHz, $CFCl_3$) −80.8 $\delta$; mass spectrum (EI), 271 (0.49), 137 (0.07), 107 (0.13), 67 (1.00); mass spectrum (CI), 271 (M + $H^+$, base peak); HRMS calcd for $C_{11}H_{17}F_3O_2S$ 271.0980, found 271.0974.

**2-*n*-Hexyl-(*E*)-1,3-butadienyl Trifluoromethyl Sulfone (E-12a).** This dienyl triflone was prepared from vinyl iodide **E-10a**, using a procedure similar to that described for **Z-12a**. The product **E-12a** was obtained as a yellow oil in 95% yield ($R_f$ 0.45, $SiO_2$, 1:10 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.92 (m, 3H), 1.42 (m, 8H), 2.80 (t, 7.80 Hz, 2H), 5.69 (d, 10.62 Hz, 1H), 5.90 (d, 17.22 Hz, 1H), 6.10 (s, 1H), 6.36 (dd, 10.62 Hz, 17.36 Hz, 1H). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.57, 22.83, 28.10, 30.07, 31.14, 31.96, 117.83, 120.03 (q, $J_{C,F}$ = 330 Hz), 125.29, 136.81, 167.00; mass spectrum (CI), 271 (M + $H^+$, base peak); HRMS calcd for $C_{11}H_{18}F_3O_2S$ 271.0980, found 271.0983.

**(1*Z*,3*E*)-2-*n*-Hexyl-4-(trimethylsilyl)-1,3-butadienyl Trifluoromethyl Sulfone (12b).** To a solution of β-iodovinyl triflone **10a** (0.056 g, 0.15 mmol) in 2 mL of benzene was added tetrakis(triphenylphosphine)palladium (**17)** (Aldrich, 0.09 g, 5 mol %) under argon. (*E*)-1-(Tributylstannyl)-2-(trimetylsilyl)ethylene (**18**)[12] (0.065 g, 0.17 mmol) was slowly added via syringe to the above solution, and the mixture was heated to reflux. The reaction was complete within 2 h. Usual workup and column chromatography (silical gel deactivated with acetone, pentane eluent) afforded 0.042 g (81%) of **12b** as a yellow oil ($R_f$ 0.65, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.17 (s, 9H), 0.89 (m, 3H), 1.33 (m, 6H), 1.52 (m, 2H), 2.52 (t, 7.3 Hz, 2H), 6.02 (s, 1H), 6.70 (d, 19.0 Hz, 1H), 7.62 (d, 18.8 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ − 1.31, 14.47, 22.96, 29.38, 30.21, 31.88, 34.69, 115.65, 120.51 (q, $J_{C,F}$ = 326 Hz), 136.12, 145.80, 165.91; mass spectrum (EI), 343 (0.03), 327 (0.19), 277 (0.10), 191 (0.19), 141 (0.93); mass spectrum (CI), 343 (M + $H^+$, base peak); HRMS calcd for $C_{14}H_{26}F_3O_2SSi$ 343.1375, found 343.1368.

**(1*Z*,3*E*)-2-*n*-Hexyl-4-(tributylstannyl)-1,3-butadienyl Trifluoromethyl Sulfone (12c).** β-Iodovinyl triflone **10a** (0.02 g, 0.054 mmol) in 0.5 mL of $CDCl_3$ was added to a solution of (*E*)-1,2-bis-(tributylstannyl)ethylene (**19**)[13] (0.055 g, 0.092 mmol, 1.7 equiv) and solid $Pd(PhCN)_2Cl_2$ (Aldrich, 0.01 g, 0.003 mmol, 5 mol %) in 1 mL of dry $CDCl_3$. The solution turned brown immediately. The reaction was complete within 3 h at 25 °C as monitored by $^1$H NMR. After removal of solvent *in vacuo*, the residue was purified by column chromatography (silica gel deactivated with acetone, 5% ether/pentane) to afford 0.021 g (70%) of **12c** as a colorless oil ($R_f$ 0.50, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.90 (m, 18H), 1.32 (m, 12H), 1.53 (m, 8H), 2.51 (t, 7.4 Hz, 2H), 5.96 (s, 1H), 7.26 (d, 19.4 Hz, 1H), 7.66 (d, 19.3 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 10.29, 14.08, 14.43, 22.94, 27.70, 29.36, 29.48, 29.69, 31.92, 34.57, 114.18, 120.59 (q, $J_{C,F}$ = 326 Hz), 138.57, 149.61, 165.37; mass spectrum (EI), 503 (0.71), 369 (0.22), 313 (0.55), 253 (0.32), 177 (0.23); mass spectrum (CI), 561 (M + $H^+$, 0.03), 503 (M + $H^+$ − $C_4H_9$, 1.00); HRMS calcd for $C_{19}H_{34}F_3O_2S^{116}Sn$ 499.1249, found 499.1254.

Also isolated in the above experiment was bis coupling product **20**, 0.03 g (21%) as a yellow oil ($R_f$ 0.30, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.90 (t, 6.4 Hz, 6H), 1.32 (m, 12H), 1.57 (m, 4H), 2.58 (t, 7.6 Hz, 4H), 6.24 (s, 2H), 7.92 (s, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.44, 22.91, 29.33, 29.48, 31.81, 35.47, 120.20, 120.29 (q, $J_{C,F}$ = 326 Hz), 131.21, 163.85; mass spectrum (EI), 443 (0.08), 205 (0.16), 175 (0.47),121 (0.25); mass spectrum (CI), 513 (M + $H^+$, base peak); HRMS calcd for $C_{20}H_{31}F_6O_4S_2$ 513.1568, found 513.1563.

**(*Z*)-3-*n*-Hexyl-1-(trimethylsilyl)-4-[(trifluoromethyl)sulfonyl]but-3-en-1-yne (12d).** To a solution of β-iodovinyl triflone **10a** (0.107 g, 0.29 mmol) in benzene (4 mL) was added tetrakis(triphenylphosphine)-palladium (**17**) (Aldrich, 0.017 g , 0.014 mmol, 5 mol %) under argon. 1-(Tributylstannyl)-2-(trimethylsilyl)ethyne (**22**)[14] (0.123 g, 0.32 mmol) was added slowly via syringe, and the resulting solution was stirred at 50 °C under argon for 9 h. Analysis by TLC ($SiO_2$, 0.05:1 EtOAc/hexane) indicated that the reaction was complete. Usual workup and column chromatography (silica gel deactivated with acetone, pentane eluent) afforded **12d** (0.075 g, 77%) as a colorless oil ($R_f$ 0.60, $SiO_2$, 0.05:1 ether/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.25 (s, 9H), 0.90 (m, 3H), 1.30 (m, 6H), 1.64 (m, 2H), 2.41 (t, 7.5 Hz, 2H), 6.32 (s, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 0, 14.44, 22.89, 28.02, 28.71, 31.81, 40.16, 98.24, 116.89, 120.54 (q, $J_{C,F}$ = 327 Hz), 123.53, 151.25; mass spectrum (EI), 341 (0.02), 325 (0.41), 77 (1.00), 73 (0.93), mass spectrum (CI), 341 (M + $H^+$, base peak); HRMS calcd for $C_{14}H_{24}F_3O_2SSi$ 341.1218, found 341.1211.

**(*Z*)-2-*n*-Hexyl-2-phenyl-1-[(trifluoromethyl)sulfonyl]ethene (12e).** To a solution of β-iodovinyl triflone **10a** (0.170 g, 0.459 mmol) in 4 mL of benzene was added tetrakis(triphenylphosphine)palladium (**17**) (Aldrich, 0.028 g, 0.025 mmol, 5 mol %) under argon. Phenyltributylstannane (**23**) (Aldrich, 0.185 g , 0.505 mmol, 1.1 equiv) was added via syringe, and the solution was heated to reflux. The reaction was complete within 3 h. Usual workup and column chromatography (silica gel deactivated with acetone, eluted with 5% ether/pentane) afforded **12e** (0.117 g, 80%) as a colorless oil ($R_f$ 0.25, $SiO_2$, 0.05 ether/hexane): $^1$H NMR (200 MHz, $CDCl_3$) 7.40 (m,3H), 7.20 (m, 2H), 6.31 (s, 1H), 2.60 (t, 6.8 Hz, 2H), 1.26∼1.54 (m, 8H), 0.88 (t, 6.6 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.46, 22.94, 27.35, 29.00, 31.86, 42.73, 120.14 (q, $J_{C,F}$ = 326 Hz), 116.90, 127.45, 128.46, 129.78; mass spectrum (EI), 251 (0.02), 250 (0.17), 128 (0.07), 117 (1.00); mass spectrum (CI), 321 (M + $H^+$, base peak); HRMS calcd for $C_{15}H_{20}F_3SO_2$ 321.1136, found 321.1139.

**(*Z*)-2-*n*-Hexyl-2-(2-furyl)-1-[(trifluoromethyl)sulfonyl]ethene (12f).** To a solution of β-iodovinyl triflone **10a** (0.105 g, 0.28 mmol) in 3 mL of benzene was added tetrakis(triphenylphosphine)palladium (**17)** (Aldrich, 0.016 g, 0.014 mmol, 5 mol %) under argon. 2-Furyltributylstannane (**24**) (Aldrich, 0.106 g, 0.298 mmol, 1.05 equiv) was injected with a syringe, and the solution was heated to reflux. The reaction was complete within 2 h. Usual workup and column chromatography (silica gel deactivated with acetone, eluted with 5% ether/pentane) afforded **12f** (0.075 g, 85%) as a colorless oil ($R_f$ 0.30, $SiO_2$, 0.05 ether/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.64 (d, 1.71 Hz, 1H), 7.23 (d, 3.67 Hz, 1H), 6.57 (dd, 1.83 Hz, 3.67 Hz, 1H), 6.01 (s, 1H), 2.68 (t, 7.55 Hz, 2H), 1.58 (m, 2H), 1.32 (m, 6H), 0.89 (t, 6.45 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.45, 22.94, 29.21, 29.72, 31.86, 37.90, 112.47, 113.25, 119.33, 120.59 (q, $J_{C,F}$ = 327 Hz), 146.66, 148.12, 153.46; mass spectrum (EI), 311 (0.01), 310 (0.01), 240 (0.48), 107 (1.00), (CI), 311 (M + $H^+$, base peak); HRMS calcd for $C_{13}H_{17}F_3SO_3$ 311.0929, found 311.0920.

**2-Phenyl-(*E*)-1,3-butadienyl Trifluoromethyl Sulfone (13a).** Benzene was purged with argon for 15 min before use. To a solution of β-iodovinyl triflone **Z-10b** (0.05 g, 0.138 mmol) in 5 mL of benzene was added tetrakis(triphenylphosphine)palladium (**17**) (Aldrich, 0.08 g, 5 mol %) under argon. Vinyltributyltin (Aldrich, 0.048 g, 0.152 mmol) was added via syringe, and the solution was heat to reflux. The reaction was complete within 3 h. Usual workup and column chromatography (silica gel deactivated with acetone, eluted with 5% ether/hexane) afforded **13a** (0.029 g, 81%) as a colorless oil ($R_f$ 0.40, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.57 (d, 17.3 Hz, 1H), 5.94 (d, 10.74 Hz, 1H), 6.14 (s, 1H), 7.32−7.52 (m, 5H), 7.71 (dd, 17.1, 10.8 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 116.44, 120.6 (q, $J_{C,F}$ = 322 Hz), 129.22, 129.44, 131.09, 131.31, 132.31, 137.18, 164.56. Mass Spectrum (CI), 263 (M + $H^+$, base peak); HRMS calcd for $C_{11}H_{10}F_3O_2S$ 263.0354, found 263.0357.

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**2-Phenyl-4-(trimethylsilyl)-(E)-1,3-butadienyl Trifluoromethyl Sulfone (13b)** Dienyl triflone **13b** was prepared from vinyl iodide **Z-10b**, using a procedure similar to that described for **13a**. Product **13b** was obtained as a yellow oil in 72% yield ($R_f$ 0.50, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.15 (s, 9H), 6.12 (s, 1H), 6.40 (d, 19.3 Hz, 1H), 7.27−7.49 (m, 5H), 7.84 (d, 19.0 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ −1.35, 115.56, 120.59 (q, $J_{C,F}$ = 326 Hz), 129.16, 129.52, 130.95, 137.03, 137.55, 152.95, 164.88; mass spectrum (CI), 335 (M + H$^+$, base peak); HRMS calcd for $C_{14}H_{17}F_3O_2SSi$ 334.0671, found 334.0671.

**(*Z*)-2-(2-Furyl)-2-Phenyl-1-[(trifluoromethyl)sulfonyl]ethene (13f).** Triflone **13f** was prepared from vinyl iodide **Z-10b**, using a procedure similar to that described for **13a**. Product **13f** was obtained as a yellow oil in 90% yield ($R_f$ 0.30, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.23 (s, 1H), 6.61 (dd, 1.8 Hz, 4.04 Hz, 1H), 6.80 (d, 3.5 Hz, 1H), 7.44−7.56 (m, 5H), 7.75 (d, 1.8, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 113.32, 113.88, 120.58 (q, $J_{C,F}$ = 327 Hz), 121.46, 129.34, 130.01, 131.98, 137.53, 147.74, 148.46, 150.79; mass spectrum (EI), 302 (M$^+$, 0.20), 233 (M − $CF_3$, 0.25), 169 (M − $SO_2CF_3$, 0.27); mass spectrum (CI), 303 (M + H$^+$, base peak); HRMS calcd for $C_{13}H_9F_3O_3S$ 302.0225, found 302.0224.

**3-[(Trifluoromethyl)sulfonyl]-(*E*)-deca-1,3-diene (E-14a).** Dienyl triflone **E-14a** was prepared from vinyl iodide **Z-11a**, using a procedure similar to that described for **Z-12a**. Product **E-14a** was obtained as a yellow oil in 96% yield ($R_f$ 0.45, $SiO_2$, 0.05:1 EtOAc/hexane): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.89 (m, 3H), 1.30 (m, 6H), 1.53 (m, 2H), 2.46 (q, 7.4 Hz, 2H), 5.71 (dd, 11.7, 6.0 Hz, 2H), 6.39 (dd, 11.7 Hz, 6 Hz, 1H), 7.14 (t, 7.5 Hz, 1H); $^{13}$ C NMR (75 MHz, $CDCl_3$) $\delta$ 14.07, 22.56, 28.34, 28.95, 29.79, 31.51, 120.04 (q, $J_{C,F}$ = 325 Hz), 124.45, 124.79, 148.09, 154.18; mass spectrum (CI), 271 (M + H$^+$, 0.14), 137 (M + H$^+$-$HSO_2CF_3$, 1.00); HRMS calcd for $C_{11}H_{18}F_3O_2S$ 271.0980, found 271.0983.

**(*E*)-1-(2-Furyl)-1-[(-2-trifluoromethyl)sulfonyl]oct-1-ene (E-14f).** Triflone **E-14f** was prepared from vinyl iodide **Z-11a**, using a procedure similar to that described for **12c**. Product **E-14f** was obtained as a colorless oil in 83% yield ($R_f$ 0.30, $SiO_2$, 0.05 ether/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.89 (m, 3H), 1.29 (m, 6H), 1.57 (m, 2H), 2.55 (q, 7.5 Hz, 2H), 6.51 (dd, 1.8 Hz, 3.6 Hz, 1H), 6.80 (d, 3.6 Hz, 1H), 7.32 (t, 7.7 Hz, 1H), 7.56 (d, 1.8 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.48, 22.94, 28.65, 29.35, 31.09, 31.88, 112.03, 115.03, 120.32 (q, $J_{C,F}$ = 327 Hz), 126.74, 142.72, 144.94, 156.93; mass spectrum (CI), 367 (M + $C_4H_9^+$, 0.74), 310 (M + H$^+$, 0.07), 177 (M + H$^+$ − $HSO_2CF_3$, 1.00); HRMS calcd for $C_{13}H_{17}F_3O_3S$ 310.0851, found 310.0854.

**(1*E*,3*E*)-2-*n*-Hexyl-4-phenyl-1-[(trifluoromethyl)sulfonyl]buta-1,3-diene (26).** Dienyl triflone **26** was prepared from the reaction of phenyl iodide and tin reagent **12c**, using a procedure similar to that described for **Z-12a**. Product **26** was obtained as a yellow oil in 91% yield ($R_f$ 0.35, $SiO_2$, 0.05 ether/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.92 (t, 6.5 Hz, 3H), 1.36 (m, 6H), 1.65 (m, 2H), 2.65 (t, 7.3 Hz, 2H), 6.02 (s, 1H), 7.19 (d, 16.2 Hz, 1H), 7.39−7.60 (m, 5H), 7.97 (d, 16.2 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$14.50, 23.00, 29.43, 29.82, 31.93, 35.20, 114.73, 120.60 (q, $J_{C,F}$ = 326 Hz), 121.39, 128.64, 129.52, 130.81, 135.68, 140.98, 165.59; mass spectrum (CI), 347 (M + H$^+$, base peak); HRMS calcd for $C_{17}H_{21}F_3O_2S$ 346.1214, found 346.1207.

**(*Z*)-1-(Tributylstannyl)-1-[(Trifluoromethyl)sulfonyl]oct-1-ene (Z-27a).** Under argon, tributyltin hydride (0.35 mL, 0.13 mmol) was added slowly to octynyl triflone **9a** (0.299 g, 0.12 mmol, neat) at 0 °C. Once the addition was complete, the reaction mixture was allowed to warm to 25 °C for 3 h. The reaction was complete as monitored by NMR. The resulting oil was purified with column chromatography (silica gel deactivated with acetone, eluent pentane) to afford **Z-27a** (0.553 g, 84%) as a colorless oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.91 (m, 12H), 1.12 (m, 6H), 1.29 (m, 12H), 1.50 (m, 8H), 2.35 (m, 2H), 7.68 (t, 7.32 Hz, $J_{Sn,H}$ = 67 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 12.82, 14.05, 14.45, 22.96, 27.60, 28.83, 29.11, 29.53, 32.03, 35.34, 120.63 (q, $J_{C,F}$ = 327 Hz), 137.96, 170.91; mass spectrum (EI), 477 (M − Bu, base peak); mass spectrum (CI), 477 (M + H$^+$ − HBu, base peak); HRMS calcd for $C_{17}H_{32}F_3O_2S^{116}Sn$ 473.1092, found 473.1093.

**(*Z*)-1-(Triphenylstannyl)-1-[(trifluoromethyl)sulfonyl]oct-1-ene (Z-27b).** This compound was prepared from the reaction of octynyl triflone **9a** and triphenyltin hydride (Aldrich), using a procedure similar to that described for **Z-27a**. Product **Z-27b** was obtained as a yellow oil in 95% yield ($R_f$ 0.40, $SiO_2$, 0.05:1 ether/hexane): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.82 (t, 7.0 Hz, 3H), 0.91−1.33 (m, 8H), 2.24 (dt, 7.4 Hz, 7.7 Hz, 2H), 7.35−7.76 (m, 15H), 7.97 (t, 7.7 Hz, $J_{Sn,H}$ = 90 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 14.37, 23.08, 28.16, 29.20, 31.94, 35.87, 120.53 (q, $J_{C,F}$ = 323 Hz), 129.41, 130.34, 137.00, 137.31, 137.72, 173.42; mass spectrum (CI), 517 (M + H$^+$ − $C_6H_5$, base peak); HRMS calcd for $C_{21}H_{24}F_3O_2S^{116}Sn$ 513.0466, found 513.0461.

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**Supporting Information Available:** $^1$H and $^{13}$C NMR spectra of all new compounds (48 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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