Stereospecific Alkenylation of C−H Bonds via Reaction with β-Heteroatom-Functionalized Trisubstituted Vinyl Triflones[1]

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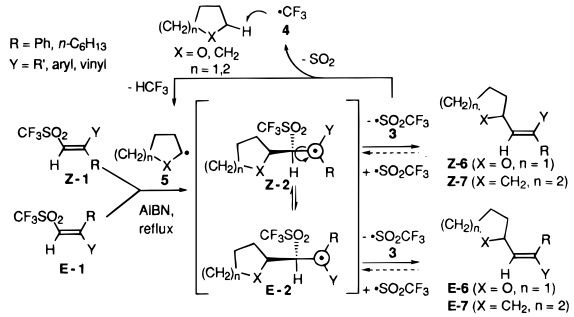
Abstract: Aryl and alkyl β-heteroatom-trisubstituted vinyl triflones react with THF and cyclohexane to undergo trifluoromethyl radical-mediated C−H functionalization reactions to afford *E* and *Z* β-heteroatom-trisubstituted olefins. Most reactions proceed with both high yield and high stereospecificity (retention of configuration). β-Substituents which have been employed in this study are iodine, bromine, fluorine, benzoate, ethylcarbonate, and phthalimide. β-Substituents bearing powerful electron-releasing groups such as alkoxy or amino render the vinyl triflone unreactive.

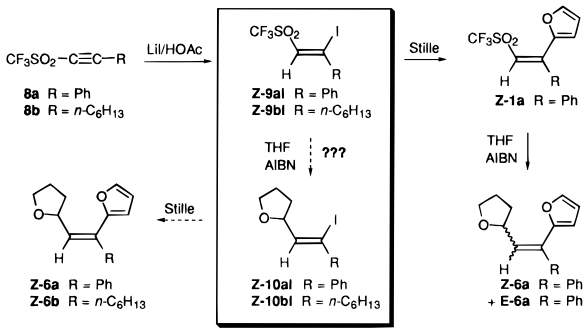
We recently reported that reaction of ethers and hydrocarbons with di- and trisubstituted vinyl and dienyl triflones such as **(*Z*)-1** and **(*E*)-1** provides ready access to trisubstituted olefins and dienes (Scheme 1).[2] The reaction proceeds through radical C−H abstraction[3] by the very electrophilic trifluoromethyl radical (**4**)[4,5] in a process involving addition of the thus-generated alkyl radical **5** to the α-carbon of the vinyl triflone **1** followed by elimination of the (trifluoromethyl)sulfonyl radical (**3**) to afford alkenes **6** and **7** by a unimolecular chain transfer process (UMCT[6]). Entropy-promoted fragmentation[7] of **3** to sulfur dioxide and the highly reactive trifluoromethyl radical (**4**) (a second UMCT reaction) efficiently propagates the chain.[8] The stereospecificity of the sequence is related to both the stability of the intermediate radical **(*Z*)-2** or **(*E*)-2** and the possibility of *reversible addition* of **3** to the olefinic product. Unfortunately, the reactions exhibited only modest (∼3−5:1) stereospecificity in favor of retention of the vinyl triflone stereochemistry.

Since the synthesis of trisubstituted vinyl triflones used in the above study involved the *trans*-addition of HI[9] (also facile and high-yielding for addition of HBr and HF[10]) to acetylenic triflones **8a**,**b**[8a] followed by Stille coupling, we considered the possibility of achieving a stereospecific C−H alkenylation reaction by *inversion of the reaction order*. If β-iodovinyl triflones **(*Z*)-9aI** and **(*Z*)-9bI** would afford vinyl iodides **(*Z*)-10aI** and **(*Z*)-10bI** (Scheme 2), the synthesis of trisubstituted olefins could then be achieved with a final Stille coupling.

Scheme 1



Scheme 2



Reaction of β-iodovinyl triflone **(*Z*)-9aI** with tetrahydrofuran or cyclohexane generates vinyl iodide **(*Z*)-10aI**[11] or **(*Z*)-11aI**[11] in high yield and with superb stereospecificity as assayed by HPLC (Scheme 3 and Table 1, entries 1 and 2). As expected from our observations with acetylenic triflone chemistry, where phenylethynyl triflone (**8a**) is about a factor of 5 more reactive than *n*-octynyl triflone (**8b**),[8a] treatment of alkyl-substituted β-iodovinyl triflone **(*Z*)-9bI** more slowly generates vinyl iodides **(*Z*)-10bI**[12] and **(*Z*)-11bI**,[12] but the stereospecificity remains very good (Scheme 3 and Table 1, entries 5 and 6). Reaction of the isomeric β-iodovinyl triflones **(*E*)-9aI**[9] and **(*E*)-9bI**[9] is more problematic due to competitive deiodination of the product vinyl iodides **(*E*)-10aI**, **(*E*)-10bI**,[12] **(*E*)-11aI**, and **(*E*)-11bI**[12] by reaction of the products with tetrahydrofuranyl and cyclohexyl radicals (Schemes 3 and 4 and Table 1, entries 3, 4, 7, and 8). This difficulty is especially severe in the case of alkenylation

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(2) Xiang, J., Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 11986.

(3) Medebielle, M.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 6872.

(4) The bond dissociation energy of HCF_3 is 107 kcal/mol: In *Handbook of Chemistry and Physics*, 74th ed.; Lide, D. R., Ed.; CRC Press, Inc.: Boca Raton, FL, 1993−1994, pp 9−137.

(5) For a comprehensive review on the chemistry of fluoroalkyl radicals, see: Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557.

(6) For an excellent discussion of the advantage of exploiting radical reactions which involve unimolecular propagation steps, see: Curran, D. P.; Xu, J.; Lazzarini, E. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3049.

(7) (a) Langlois, B. R.; Laurent, E.; Roidot, N. *Tetrahedron Lett.* **1992**, *33*, 1291. (b) Hu, C. -M.; Qing, F. -L.; Huang, W. -Y. *J. Org. Chem.* **1991**, *56*, 2801. (c) Huang, W. -Y.; Hu, L. -Q. *J. Fluorine Chem.* **1989**, *44*, 25. (d) Langlois, B. R.; Laurent, E.; Roidot, N. *Tetrahedron Lett.* **1991**, *32*, 7525.

(8) For mechanistic studies and C−H functionalization reactions of alkynyl triflones, see: (a) Gong, J.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 4486. (b) Xiang, J.; Fuchs, P. L. *Tetrahedron Lett.* **1996**, *37*, 5269. (c) For aldehyde C−H functionalization reactions with alkynyl triflones, see: Gong, J.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 787.

(9) Xiang, J.; Mahadevan, A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 4284.

(10) See the Experimental Section for the preparation of bromides **(*Z*)-9aBr** and **(*Z*)-9bBr** and fluorides **(*Z*)-9aF** and **(*Z*)-9bF**.

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Scheme 3

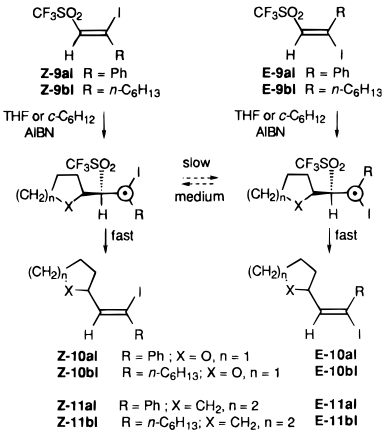
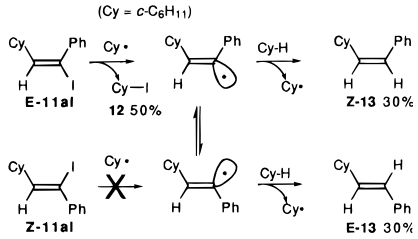


Table 1. C−H Alkenylation Reactions of β-Halovinyl Triflones

run	substrate	conditions[a]	products	yield (%)	*Z*:*E* ratio[b]
1	**(*Z*)-9aI**	THF, 1 d	**(*Z*)-10aI** + **(*E*)-10aI**	91	67:1
2	**(*Z*)-9aI**	c-C_6H_{12}, 2 d	**(*Z*)-11aI** + **(*E*)-11aI**	74	79:1
3	**(*E*)-9aI**	THF, 1 d	**(*Z*)-10aI** + **(*E*)-10aI**	49[c]	1:6[c]
4	**(*E*)-9aI**	c-C_6H_{12}, 20 h	**(*Z*)-11aI** + **(*E*)-11aI**	30[d]	>25:1[d]
5	**(*Z*)-9bI**	THF, 6 d	**(*Z*)-10bI** + **(*E*)-10bI**	55	177:1
6	**(*Z*)-9bI**	c-C_6H_{12}, 4 d	**(*Z*)-11bI** + **(*E*)-11bI**	81	13:1
7	**(*E*)-9bI**	THF, 6 d	**(*Z*)-10bI** + **(*E*)-10bI**	59[e]	1:>100[e]
8	**(*E*)-9bI**	c-C_6H_{12}, 4 d	**(*Z*)-11bI** + **(*E*)-11bI**	50[f]	1:9[f]
9	**(*Z*)-9aBr**	THF, 5 h	**(*Z*)-10aBr** + **(*E*)-10aBr**	90	75:1
10	**(*Z*)-9aBr**	c-C_6H_{12}, 8 h	**(*Z*)-11aBr** + **(*E*)-11aBr**	93	38:1
11	**(*E*)-9aBr**	THF, 8 h	**(*Z*)-10aBr** + **(*E*)-10aBr**	82	1:21
12	**(*E*)-9aBr**	c-C_6H_{12}, 5 h	**(*Z*)-11aBr** + **(*E*)-11aBr**	80	1:32
13	**(*Z*)-9aF**	THF, 13 h	**(*Z*)-10aF** + **(*E*)-10aF**	82	77:1
14	**(*Z*)-9aF**	c-C_6H_{12}, 2 d	**(*Z*)-11aF** + **(*E*)-11aF**	98	>100:1
15	**(*E*)-9aF**	THF, 8 h	**(*Z*)-10aF** + **(*E*)-10aF**	91	1:3
16	**(*E*)-9aF**	c-C_6H_{12}, 15 h	**(*Z*)-11aF** + **(*E*)-11aF**	96	1:8
17	**(*Z*)-9bF**	c-C_6H_{12}, 2 d	**(*Z*)-11bF** + **(*E*)-11bF**	0	NR
18	**(*E*)-9bF**	c-C_6H_{12}, 2 d	**(*Z*)-11bF** + **(*E*)-11bF**	0	NR

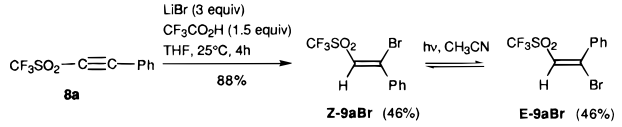
[a] AIBN (15 mol %), solvent at reflux. [b] Product ratios of >10:1 were assigned by analytical HPLC. Product ratios of <10:1 were assigned by NMR integration of the crude reaction mixture. NR = no reaction. [c] The *trans*-cinnamyl derivative of THF (deiodinated **10a**) was also isolated in 25% yield from this reaction (cf. Scheme 4). [d] A 60% yield of a 1:1 mixture of ***Z*-13** and **(*E*)-13** admixed with 50% cyclohexyl iodide (**12**) was also isolated from this reaction (see Scheme 4). [e] Yield based upon 30% recovered starting triflone **(*E*)-9bI**. [f] 30% cyclohexyl iodide (**12**) also isolated from this reaction (cf. Scheme 4).

Scheme 4



of **(*E*)-9aI**, which gives a 30% yield of **(*Z*)-11aI** with no trace of the expected isomeric iodide **(*E*)-11aI**. Analysis of the reaction byproducts reveals the presence of cyclohexyl iodide (**12**) (50%) accompanied by a 60% yield of a 1:1 mixture of isomeric styrenes **(*Z*)-13** and **(*E*)-13** (Schemes 3 and 4 and Table 1, entry 3). This observation reveals that the incipient cyclohexyl radicals react with the initially-produced vinyl iodide **(*E*)-11aI** in preference to the substrate vinyl triflone **(*E*)-9aI**, resulting in stereospecific radical deiodination. The aforementioned result stands in stark contrast to the chemistry of vinyl triflone **(*Z*)-9aI** which is sufficiently reactive so as to render

Scheme 5

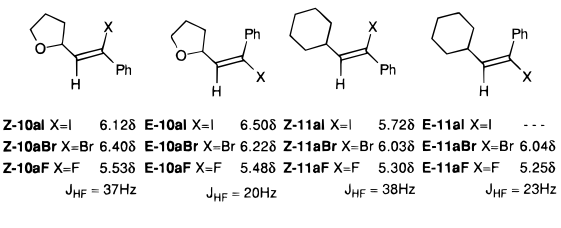


the product vinyl iodide **(*Z*)-11aI** kinetically inert toward deiodination (Schemes 3 and 4 and Table 1, entry 1).

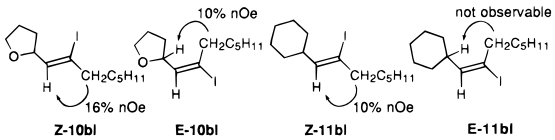
Reasoning that the unwanted radical-mediated deiodination of the (*E*)-vinyl iodides **(*E*)-10aI**, **(*E*)-10bI**, **(*E*)-11aI**, and **(*E*)-11bI** was a consequence of the relatively weak carbon−iodine bond, we briefly examined the stereospecificity of C−H alkenylation reactions of β-bromovinyl triflones **(*Z*)-9aBr** and **(*E*)-9aBr**. Synthesis of **(*Z*)-9aBr** was smoothly and stereospecifically accomplished in 88% yield by reaction of phenylacetylenic triflone **8a** (the analogous chemistry of *n*-octynyl triflone (**8b**) was not explored) in THF with lithium bromide and trifluoroacetic acid (similar reactions of acetic acid being too slow). Preparation of a sample of the isomeric β-bromovinyl triflone **(*E*)-9aBr** was easily achieved by separating a 1:1 mixture of the two isomers which was established via photochemical equilibration (Scheme 5). As expected, radical-mediated dehalogenation was not a problem with either (*Z*)- or (*E*)-β-bromovinyl triflone, as both **(*Z*)-9aBr** and **(*E*)-9aBr** smoothly underwent the alkenylation reaction in uniformly high yield with stereospecificities ranging from 21:1 to 75:1 for retention of stereochemistry (Scheme 6 and Table 1, entries 9−12).

Since fluorine-substituted materials are highly prized in the realm of medicinal chemistry,[13] we next turned our attention to

(11) Since there was no clear relationship between the vinyl proton chemical shift of the vinyl halides as a function of their stereochemistry (see below), we based the stereochemical assignment of the phenyl-substituted vinyl halides shown below upon *t*-BuLi metalation−H_2O quenching reactions of **(*Z*)-10aI**, **(*Z*)-11aI**, and **(*E*)-10aI** which quantitatively and stereospecifically afforded the disubstituted styrene derivatives with J_{HCCH} = 16, 16, and 11.5 Hz, respectively. Such metalations are known to occur with retention of stereochemistry (Davis, F. A.; Lal, G. S.; Wei, J. *Tetrahedron Lett.* **1988**, *29*, 4269 and references cited therein). The vinyl bromide and vinyl fluoride stereochemistry was assigned by mechanistic analogy, but was further verified in the case of the vinyl fluorides by noting the three-bond J_{HCCF} coupling constants shown below (for typical fluoroolefin assignments using J_{HCCF} coupling constants, see: Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Oxford, 1969; pp 348−350 and references cited therein).

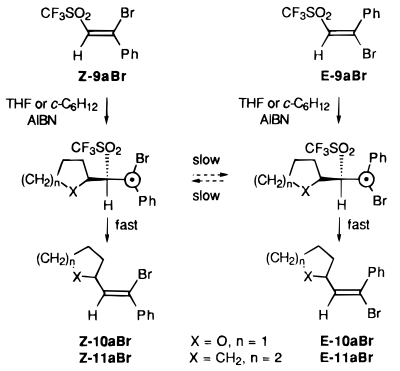


(12) The trisubstituted vinyl iodides **(*Z*)-10bI** and **(*Z*)-11bI** showed 16% and 10% NOEs, respectively, for the vinyl proton upon irradiation of the allylic CH_2 moiety; the complementary experiment revealed a 10% NOE in the methine hydrogen of **(*E*)-10bI** upon irradiation of the allylic CH_2 moiety; a similar conformation experiment was not possible for **(*E*)-11bI** since both allylic methylene and methine were not sufficiently separated in chemical shift.

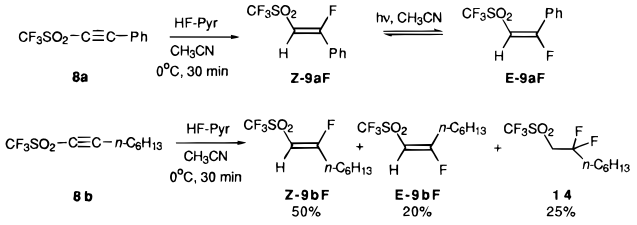


(13) For a set of recent references describing the value of fluorinated organics, see: Umemoto, T.; Adachi, K. *J. Org. Chem.* **1994**, 59, 5692.

Scheme 6



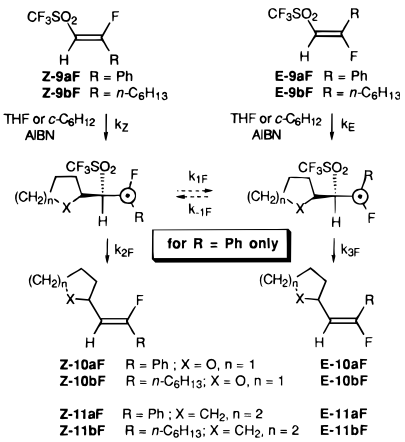
Scheme 7



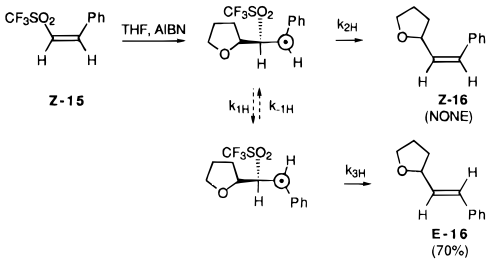
the preparation of vinyl triflones substituted in the β position with a fluorine atom. Reaction of phenylethynyl triflone **8a** with HF·pyridine in acetonitrile stereospecifically produced (*Z*)-vinyl fluoride **(*Z*)-9aF** in 80% yield. Photochemical equilibration of **(*Z*)-9aF** at 254 nm in acetonitrile at 25 °C for 1.5 h afforded a ~1:1 *Z*/*E* mixture from which a sample of **(*E*)-9aF** was obtained by silica gel chromatography (Scheme 7). Hydrofluorination of *n*-octynyl triflone **8b** was not as simple as expected; for the first time, a hydrohalogenation reaction had failed to stereospecifically effect a *trans*-addition to the acetylenic triflone. In this instance a mixture of both (*Z*)- and (*E*)-vinyl triflones **(*Z*)-9bF** and **(*E*)-9bF** was formed, accompanied by a significant quantity of the bis addition product **14**. Although the point was not experimentally tested, one can speculate that difluoride **14** is the progenitor of the unexpected vinyl triflone **(*E*)-9bF** by a pyridine-promoted β-elimination reaction (Scheme 7). No further effort at optimization of the synthesis of the alkyl-substituted β-fluorovinyl triflones **(*Z*)-9bF** and **(*E*)-9bF** was undertaken as these substrates were found to be inert to the conditions of the C−H alkenylation reaction.

The alkyl-substituted β-fluorovinyl triflones **(*Z*)-9bF** and **(*E*)-9bF** were unreactive with cyclohexane (or THF) even when heated for extended periods of time (Scheme 8 and Table 1, entries 17 and 18). The deactivation observed is likely a consequence of the optimal 2p-π resonance for fluorine which accompanies carbon in the second row of the periodic table, an observation which presaged difficulties which lay ahead with vinyl triflones bearing oxygen and nitrogen substituents. Fortunately, at least the phenyl-substituted β-fluorovinyl triflones **(*Z*)-9aF** and **(*E*)-9aF** were still able to undergo exceptionally high-yielding reactions with THF and cyclohexane. As expected, the transformation of **(*Z*)-9aF** was essentially stereospecific, affording fluoroolefins **(*Z*)-10aF** and **(*Z*)-11aF** with 77:1 and >100:1 selectivity, respectively (Scheme 8 and Table 1, entries 13 and 14). The isomeric β-fluorovinyl triflone **(*E*)-9aF** saw substantially decreased stereoselectivity, providing the fluoroolefins **(*E*)-10aF** and **(*E*)-11aF** with 3:1 and 8:1 selectivity, respectively (Scheme 8 and Table 1, entries 15 and 16). While the modest selectivity exhibited with β-fluorovinyl triflone **(*E*)-9aF** seems unimpressive compared to the earlier examples, these results are quite informative when contrasted with the previously reported reaction of disubstituted β-phenylvinyl triflone **(*Z*)-15** (Scheme 9).[2] In this latter instance, reaction of **(*Z*)-15** with THF afforded an initial adduct which possessed a sufficient lifetime to enable bond rotation in preference to elimination of the (trifluoromethyl)sulfonyl radical (Scheme 9, $k_{1H} \gg k_{2H}$), resulting in the exclusive formation of **(*E*)-16** with no trace of **(*Z*)-16**, the product of retained stereochemistry. Since we know from the fluoro series shown in Scheme 8 that $k_{-1F} < k_{3F}$ (**(*E*)-9aF** gives a 3:1 ratio of **(*E*)-10aF:(*Z*)-10aF**), this fixes the composite electronic and steric destabilization of replacing a hydrogen with a fluorine atom on the incipient β-(trifluoromethyl)sulfonyl radical as being worth a factor of at least 200 (>70 × 3).

Scheme 8



Scheme 9

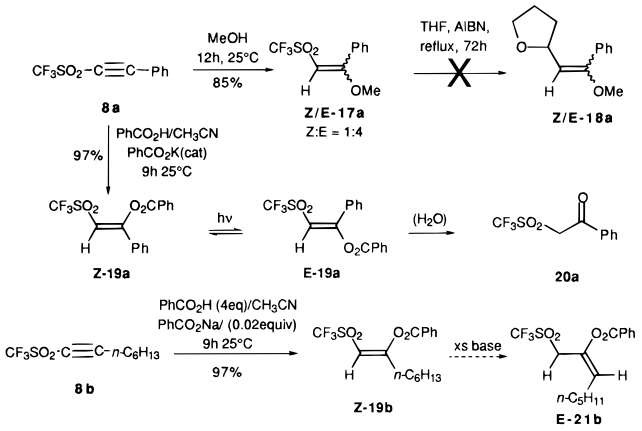


Having established the utility of β-halovinyl triflones in the C−H alkenylation reaction, we next turned to the synthesis of vinyl triflones bearing oxygen functionality. Simple base-catalyzed addition of methanol to acetylenic triflone **8a** was high-yielding but nonstereospecific, affording **(*Z*)-17a** and **(*E*)-17a** as a 1:4 mixture.[14] Further investigation of the methanol addition reaction of **8a** was not undertaken since attempted reaction of enol ether **(*Z*)-17a/(*E*)-17a** with THF at reflux for 72 h under the standard radical conditions returned the substrate unchanged. This observation is reminiscent of vinyl fluorides **(*Z*)-9bF** and **(*E*)-9bF**, except that in this case even the presence of the radical-stabilizing phenyl group was insufficient to overcome the strong resonance effect of the methoxy moiety (Scheme 10).

Armed with the hypothesis that substitution of a carboxylate group for the ether moiety might decrease the lone pair density on oxygen to a sufficient extent so as to engender alkenylation reactivity, we examined additions of benzoic acid to acetylenic triflones **8a,b**. Reaction of **8a** with benzoic acid in the presence of a small amount of sodium benzoate in acetonitrile smoothly afforded trisubstituted enol benzoate **(*Z*)-19a** as a single

(14) Hanack reports the addition of ethanol to **8a** to give the corresponding ethyl enol ether but does not define the stereochemistry of the process (Massa, F.; Hanack, M.; Subramanian, L. R. *J. Fluorine Chem.* **1982**, *19*, 601).

Scheme 10



stereoisomer. While photochemical isomerization of the (*Z*)-enol benzoate **(*Z*)-19a** in acetonitrile provided a ∼1:1 *Z*/*E* mixture, isolation of **(*E*)-19a** by silica gel chromatography was initially hampered by partial hydrolysis of the desired isomer **(*E*)-19a** to β-keto triflone **20a**. The *Z* isomer **(*Z*)-19a** was not appreciably degraded under these conditions. Fortunately, chromatography of the 1:1 *Z*/*E* photolysis mixture **(*Z*)-19a**/**(*E*)-19a** on acetone-deactivated silica gel was effective at affording a sample of **(*E*)-19a**, with only a trace of hydrolysis product **20a** being generated. Similar synthesis of alkyl-substituted enol carboxylate **(Z)-19b**[15] from *n*-octynyl triflone (**8b**) required use of minimal amounts of the basic catalyst in order to avoid isomerization of the vinyl triflone **(*Z*)-19b** to the deconjugated allyl triflone **(*E*)-21b**[15] (Scheme 10).

As the isolation of **(*E*)-19a** was initially problematical, we also explored the use of enol carbonates as more robust acyloxy substituents. In this approach, β-keto triflone **20a** was intentionally prepared in near-quantitative yield by reaction of **8a** with acetone and water.[16] Similar hydrolysis of octynyl triflone (**8b**) afforded a 93% yield of keto triflone **20b** provided that dilute (0.003 M) conditions were employed to prevent conjugate addition of **20b** to **8b**. Treatment of β-keto triflones **20a,b** under the conditions of Table 2 provided enol carbonates **(*Z*)-22a**/**(*E*)-22a** and **(*Z*)-22b**/**(*E*)-22b** which could be separated by chromatography on acetone-deactivated silica gel without hydrolytic difficulties (Scheme 11).

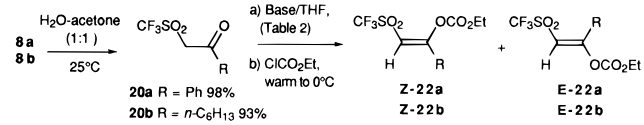
In marked contrast to the failure of **(*Z*)-17a**/**(*E*)-17a** to undergo the alkenylation reaction, benzoates **(*Z*)-19a,b** and **(*E*)-19a,b** and carbonates **(*Z*)-22a,b** and **(*E*)-22a,b** smoothly undergo the C−H alkenylation reaction with THF and cyclohexane to provide the alkenylated enol benzoates **(*Z*)-23a,b**, and **(*E*)-23a,b**, **(*Z*)-24a,b**, and **(*E*)-24a,b** and enolcarbonates **(*Z*)-25a,b**, **(*E*)-25a,b**, and **(*Z*)-26a,b**, and **(*E*)-26a,b** in excellent yields with good to outstanding stereocontrol[17] (Scheme 12 and Table 3).

Finally, the chemistry of nitrogen-substituted vinyl triflones was examined. Reaction of **8a** with diethylamine provides β-aminovinyl triflone **(*E*)-27a**, the *E* stereochemistry presumably a consequence of intramolecular proton transfer from the dipolar intermediate (Scheme 13). As anticipated, on the basis of the results from the fluorine and oxygen series, this substrate is completely unreactive in the C−H functionalization reaction. Base-catalyzed addition of phthalimide to acetylenic triflones **8a,b** stereospecifically affords the β-phthalimidovinyl triflones **(Z)-29a,b**. Photoisomerization of **(*Z*)-29a** in acetonitrile provides a sample of the isomeric vinyl triflone **(*E*)-29a**. As can be seen in Table 4, the phenyl-substituted phthalimides **(*Z*)-29a** and **(*E*)-29a** provide adducts **(*Z*)-30a**, **(*E*)-30a**, **(*Z*)-31a**, and

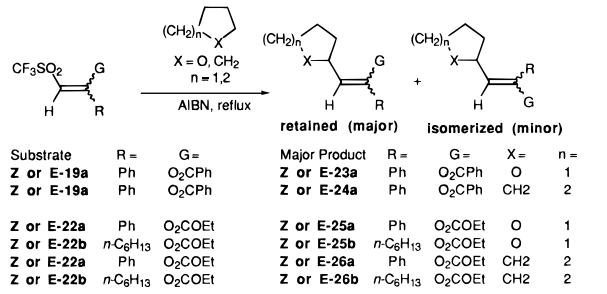
Table 2. Formation of β-Carbonates of Trisubstituted Vinyl Triflones

run	substrate	conditions	products	yield (%)	*Z*:*E* ratio
1	**20a**	Et_3N, −78 °C, 1 h	**(*Z*)-22a** + **(*E*)-22a**	85	2:1
2	**20a**	Et_3N, 0 °C, 1 h	**(*E*)-22a** + **(*E*)-22a**	86	14:1
3	**20b**	Et_3N, −78 °C, 1 h	**(*E*)-22b** + **(*E*)-22b**	77	1:11
4	**20b**	Et_3N, 0 °C, 1 h	**(*E*)-22b** + **(*E*)-22b**	71	1:10
5	**20b**	LDA, −78 → 0 °C, 1 h	**(*E*)-22b** + **(*E*)-22b**	70	1:4

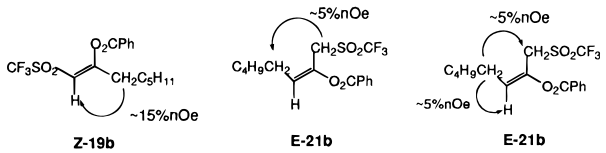
Scheme 11



Scheme 12

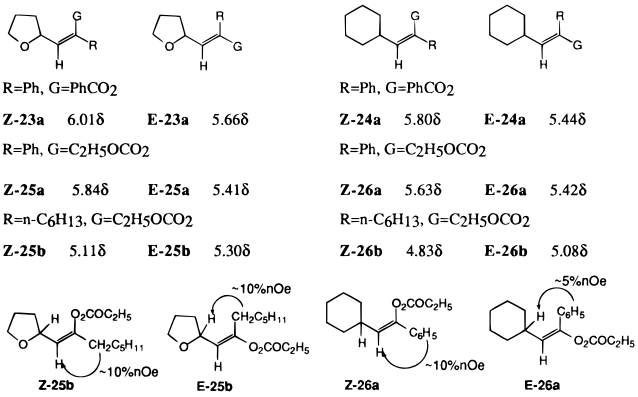


(15) The trisubstituted enol carboxylate **(Z)-19b** showed 15% NOE enhancement on the vinyl proton upon irradiation of the allylic CH_2 moiety. The allyl triflone **(*E*)-21b** showed 5% NOE on the allylic protons when the CH_2 α to the triflone group was irradiated; the same results were obtained on vinyl proton and methylene protons α to the triflone group when the allylic CH_2 moiety was irradiated.



(16) Compound **20a** has been previously prepared by Hanack et. al.,[14] who report a 47% yield for recrystallized material, prepared for securing an analytical sample. We find that the crude β-keto triflone may be routinely used for all synthetic purposes.

(17) Spectral information and stereochemical assignments are given below.



The trisubstituted enol carbonate **(Z)-25b** showed a 10% NOE increase of the vinyl proton when the allylic methylene was irradiated, while **(*E*)-25b** only showed a 10% NOE of the methine proton upon irradiation of the allylic CH_2 moiety. Similar results were obtained from NOE phenyl irradiation experiments with the trisubstituted enol carbonates **(*Z*)-26a** and **(*E*)-26a**.

Table 3. C−H Alkenylation Reactions of β-Oxygenated Vinyl Triflones

run	substrate	conditions[a]	products[b]	yield (%)	*Z*:*E* ratio[c]
1	**(*Z*)-17a/(*E*)-17a**	THF, 3 d	**(*Z*)-18a/(*E*)-18a**	0	NR
2	**(*Z*)-19a**	THF, 5 h	**(*Z*)-23a** + **(*E*)-23a**	91	28:1
3	**(*Z*)-19a**	*c*-C_6H_{12}, 12 h	**(*Z*)-24a** + **(*E*)-24a**	94	156:1
4	**(*E*)-19a**	THF, 8 h	**(*Z*)-23a** + **(*E*)-23a**	95	1:3
5	**(*E*)-19a**	*c*-C_6H_{12}, 1 d	**(*Z*)-24a** + **(*E*)-24a**	93	1:33
6	**(*Z*)-22a**	THF, 4.5 h	**(*Z*)-25a** + **(*E*)-25a**	97	16:1
7	**(*Z*)-22a**	c-C_6H_{12}, 12 h	**(*Z*)-26a** + **(*E*)-26a**	95[d]	49:1
8	**(*E*)-22a**	THF, 5 h	**(*Z*)-25a** + **(*E*)-25a**	89	1:22
9	**(*E*)-22a**	c-C_6H_{12}, 12 h	**(*Z*)-26a** + **(*E*)-26a**	96[d]	1:35
10	**(*Z*)-22b**	THF, 8 d	**(*Z*)-25b** + **(*E*)-25b**	85[d]	35:1
11	**(*Z*)-22b**	c-C_6H_{12}, 4 d	**(*Z*)-26b** + **(*E*)-26b**	83[d]	47:1
12	**(*E*)-22b**	THF, 8 d	**(*Z*)-25b** + **(*E*)-25b**	55[d]	1:3[e]
13	**(*E*)-22b**	c-C_6H_{12}, 4 d	**(*Z*)-26b** + **(*E*)-26b**	77[d]	1:28

[a] AIBN (20 mol %), solvent at reflux. [b] Product stereochemistry is assigned by NOE experiments. [c] Product ratios of >10:1 were assigned by analytical HPLC. Product ratios of <10:1 were assigned by NMR integration of the crude reaction mixture. NR = no reaction. [d] This reaction requires 1−3 additional portions of AIBN (0.3 equiv). [e] This reaction also produces 30% of the ketone from hydrolysis of enol carbonate **(*E*)-25b**, making the actual *Z*:*E* ratio 1:5.

Scheme 13

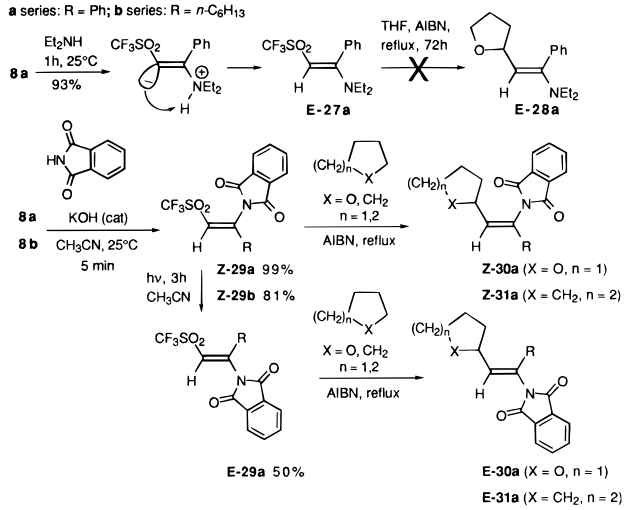


Table 4. C−H Alkenylation Reactions of β-Aminated Vinyl Triflones

run	substrate	conditions[a]	products[b]	yield (%)	*Z*:*E* ratio[c]
1	**(*E*)-27a**	THF, 3 d	**(*E*)-28a**	0	NR
2	**(*Z*)-29a**	THF, 6 h	**(*Z*)-30a** + **(*E*)-30a**	95	>100:1
3	**(*Z*)-29a**	c-C_6H_{12}, DCE,[d] 3 d	**(*Z*)-31a** + **(*E*)-31a**	82	>100:1
4	**(*E*)-29a**	THF, 6 h	**(*Z*)-30a** + **(*E*)-30a**	89	1:25
5	**(*E*)-29a**	c-C_6H_{12}, DCE,[d] 3 d	**(*Z*)-31a** + **(*E*)-31a**	81	1:10
6	**(*Z*)-29b**	THF, 120 °C, 1 d	**(*Z*)-30b** + **(*E*)-30b**	0	NR
7	**(*Z*)-29b**	c-C_6H_{12}, 3 d	**(*Z*)-31b** + **(*E*)-31b**	0	NR

[a] AIBN (20 mol %), solvent at reflux, except for run 6, which used a sealed tube. [b] Product stereochemistry is assigned by NOE experiments (see supplemental material). [c] Product ratios were assigned by reversed phase analytical HPLC. NR = no reaction. [d] This reaction requires addition of four additional portions of AIBN (0.3 equiv). This reaction was run in 1,2-dichloroethane as solvent because **(*Z*)-29a** and **(*E*)-29a** were insoluble in cyclohexane or acetonitrile.

(*E*)-31a with excellent stereocontrol, while surprisingly, the alkyl-substituted phthalimide **(*Z*)-29b** is unreactive under the standard conditions (Scheme 13).

In conclusion, it has been established that β-heteroatom-functionalized trisubstituted vinyl triflones undergo trifluoromethyl radical-promoted C−H alkenylation reactions with two test substrates, THF and cyclohexane. The reactions proceed with moderate to very high retention of the triflone stereochemistry, the 30 examples examined having an average stereospecificity of 48:1, over a range of 3:1 to 177:1. The most successful substrates in terms of both yield and stereospecificity were those with the greatest synthetic potential: vinyl iodides, vinyl bromides, and vinyl carbonates. Efforts at incorporating the synthetic potential of this new C−H alkenylation strategy into the arena of total synthesis are under active investigation.

Experimental Section

General Methods. Melting points were obtained on a MEL-TEMP apparatus and are uncorrected. Unless otherwise stated, reactions were carried out under argon in flame-dried glassware. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium−benzophenone ketyl. Dichloromethane and benzene were distilled from calcium hydride. Cyclohexane was stored over sodium metal. Deuterated NMR solvents ($CDCl_3$ and CD_3CN) were stored over 4 Å molecular sieves for several days prior to use. Flash chromatography on silica gel was carried out as described by Still[18] (230−400 mesh silica gel was used). ^1H and ^{13}C NMR spectra were obtained using GE QE-300 NMR and Varian Gemini 200 NMR spectrometers at 300 or 200 MHz and 75 or 50 MHz, respectively. ^1H NMR chemical shifts are reported in parts per million relative to the residual protonated solvent resonance: $CHCl_3$, δ 7.26; C_6D_5H, δ 7.15. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), br (broadened). Coupling constants (*J*) are reported in hertz. ^{13}C NMR chemical shifts are reported in parts per million relative to solvent resonance: $CDCl_3$, δ 77.00; C_6D_6, δ 128.00. Mass spectral data were obtained on a Finnigan 4000 mass spectrometer (low resolution) and a CEC 21 110 B high-resolution mass spectrometer, with the molecular ion designated as M.

Representative Experimental Procedures. See Supporting Information for the synthesis of the following compounds: **(*E*)-9aF**, **(*Z*)-9bF**, **(*E*)-9bF**, **(*E*)-10aBr**, **(*Z*)-11aBr**, **(*Z*)-19b**, **(*E*)-21b**, **(*Z*)-23a**, **(*E*)-23a**, **(*Z*)-24a**, **(*E*)-24a**, **(*Z*)-25a**, **(*E*)-25a**, **(*Z*)-25b**, **(*E*)-25b**, **(*Z*)-26a**, **(*E*)-26a**, **(*Z*)-26b**, and **(*E*)-26b**.

Synthesis of (*Z*)-2-Bromo-2-phenyl-1-ethenyl Trifluoromethyl Sulfone ((*Z*)-9aBr). To a solution of phenylethynyl triflone (**8a**) (0.303 g, 1.29 mmol) in 10 mL of THF at 0 °C was added lithium bromide (0.336 g, 3.87 mmol, 3 equiv) followed by trifluoroacetic acid (0.221 g, 1.94 mmol, 1.5 equiv). The addition is complete after stirring at room temperature for 4 h (as determined by TLC: SiO_2, 0.05:1 EtOAc/hexane). The THF was removed *in vacuo*, and the residue was partitioned between ether and water. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The resulting oil was purified by column chromatography (silica gel, 5% EtOAc/hexane) to afford 0.358 g (88%) of **(*Z*)-9aBr** as a yellow solid (R_f 0.25, SiO_2, 0.05:1 EtOAc/hexane): mp 46−48 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.47−7.72 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 119.74 (q, $J_{C,F}$ = 326 Hz), 120.48, 128.61, 129.25, 133.06, 137.09, 149.12; mass spectrum (CI) *m*/*z* 315 ($M + H^+$, base peak); HRMS *m*/*z* calcd for $C_9H_6BrF_3O_2S$ 313.9224, found 313.9217.

Synthesis of (*E*)-2-Bromo-2-phenyl-1-ethenyl Trifluoromethyl Sulfone ((*E*)-9aBr). Acetonitrile was purged with argon for 15 min. before use. Vinyl bromide **(*Z*)-9aBr** (0.302 g, 0.96 mmol) was dissolved in acetonitrile (24 mL) and placed in a quartz tube under argon. The reaction mixture was irradiated with 254 nm ultraviolet light in a Rayonet reactor for 1 h. The mixture was then partitioned between ether and water. Normal workup and column chromatography (silica gel, 5% CH_2Cl_2/hexane) afforded 0.139 g (46%) of **(*E*)-9aBr** as a yellow solid (R_f 0.40, SiO_2, 0.05:1 EtOAc/hexane) in addition to 46% recovered **(*Z*)-9aBr**. Data for **(*E*)-9aBr**: mp 81−83 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 1H), 7.45 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 119.50 (q, $J_{C,F}$ = 326 Hz), 122.30, 128.27, 128.44, 131.69, 135.29, 151.00; mass spectrum (CI) *m*/*z* 315 ($M + H^+$, base peak); HRMS *m*/*z* calcd for $C_9H_7BrF_3O_2S$ 314.9224, found 314.9225.

Synthesis of (*Z*)-2-Fluoro-2-phenyl-1-ethenyl Trifluoromethyl Sulfone ((*Z*)-9aF). Phenylethynyl triflone (**8a**) (40 mg, 0.17 mmol) dissolved in acetonitrile (1 mL) in a polyethylene vial was cooled to 0

(18) Still, W. C.; Kahn, M.;Mitra, A. *J. Org. Chem.* **1978**, *43*, 923.

°C. HF−pyridine (3 mL) was added, and the mixture was stirred at 0 °C for 30 min. The reaction mixture was diluted with chloroform (50 mL) and washed with water and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The resulting oil was purified by column chromatography (silica gel, 5% EtOAc/hexane) to afford 35 mg (80%) of **(*Z*)-9aF** as a light yellow solid (mp 75−77 °C) **Note:** More reproducible results were obtained by dilution of HF−pyridine (3 mL) with pyridine (2 mL): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.36 (d, $J_{F,H}$ = 29.6 Hz, 1H), 7.68 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 98.37 (d, $J_{F,C}$ = 10.9 Hz), 120.16 (q, $J_{F,C}$ = 324.0 Hz), 127.44 (d, $J_{F,C}$ = 8.5 Hz), 127.93 (d, $J_{F,C}$ = 24.5 Hz), 129.94, 134.96, 172.21 (d, $J_{F,C}$ = 287.0 Hz); mass spectrum (CI) *m/z* 255 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_9H_6F_4O_2S$ 254.0025, found 254.0033.

Synthesis of (*Z*)-1-Bromo-2-(2-oxolanyl)-1-phenyl-1-ethene ((*Z*)-10aBr). To vinyl triflone **(*Z*)-9aBr** (0.104 g, 0.33 mmol) in 8 mL of dry THF was added AIBN (11 mg, 0.07 mmol, 0.2 equiv) under argon. The reaction mixture was heated to reflux. The reaction was complete within 5 h. After the mixture was cooled to room temperature, THF was removed *in vacuo*, and the residue was partitioned between ether and water. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The resulting oil was purified by column chromatography (silica gel, 5% EtOAc/hexane) to afford 75 mg (90%) of **(*Z*)-9aBr** as a colorless oil (R_f 0.25, SiO_2, 0.05:1 EtOAc/hexane): ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.70−2.32 (m, 4H), 3.92 (m, 2H), 4.81 (q, J = 7.1 Hz, 1H), 6.35 (d, J = 7.0 Hz, 1H), 7.30−7.57 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.16, 31.85, 68.47, 79.52, 125.54, 127.66, 128.37, 128.86, 132.96, 139.31; mass spectrum (CI) *m/z* 173 (M + H$^+$ − HBr, 1.00), 253 (M + H$^+$, 0.47); HRMS *m/z* calcd for $C_{12}H_{13}BrO$ 252.0150, found 252.0147.

Synthesis of (*Z*)-1-Iodo-2-(2-oxolanyl)-1-phenyl-1-ethene ((*Z*)-10aI). To vinyl triflone **(*Z*)-9aI** (45 mg, 0.12 mmol) in 5 mL of dry THF was added AIBN (3 mg, 0.15 equiv) under argon at room temperature. The reaction mixture was heated at reflux for 12 h. The mixture was cooled to 25 °C, THF was removed *in vacuo*, and the residue was partitioned between ether and water. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The resulting oil was purified by column chromatography (silica gel, 5% EtOAc/hexane) to afford 34 mg (91%) of **(*Z*)-10aI** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.70 (m, 1H), 2.02 (m,1H), 2.33 (m, 1H), 3.91 (m, 1H), 4.63 (q, J = 7.0 Hz, 1H), 6.09 (d, J = 7.0 Hz, 1H), 7.40 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.56, 32.08, 69.06, 84.46, 104.65, 128.70, 129.02, 140.00, 142.96; mass spectrum (CI) *m/z* 301 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_{12}H_{13}IO$ 300.0011, found 300.0014.

Synthesis of 1-[(*Z*)-1-[(Phenylcarbonyl)oxy]-2-[(trifluoromethyl)-sulfonyl]-1-ethenyl]benzene ((*Z*)-19a). Phenylethynyl triflone (**8a**) (50 mg, 0.21 mmol) was dissolved in acetonitrile (5 mL) at 25 °C. Two equivalents of benzoic acid and 0.1 equiv of sodium benzoate were added, and the mixture was stirred at 25 °C for 5 h. The reaction mixture was concentrated *in vacuo*, washed with saturated sodium bicarbonate solution, and extracted with ether. The extract was washed with brine, dried ($MgSO_4$), filtered, and concentrated. The resulting white solid was purified by column chromatography (silica gel, 8% EtOAc/hexane) to afford 71 mg (97%) of **(*Z*)-19a** mp 120−121 °C; $_1$H NMR (200 MHz, $CDCl_3$) δ 6.66 (s, 1H), 7.45−7.80 (m, 8H), 8.15−8.30 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 107.8, 120.3 (q, $^1J_{C,F}$ = 326 Hz), 127.4, 127.9, 128.9, 129.5, 130.0,131.2, 131.9, 133.9, 135.1, 163.6, 167.2; mass spectrum (EI) *m/z* 105 (PhCO$^+$, base peak), 287 (M$^+$ − CF_3, 0.06); mass spectrum (CI) *m/z* 105 (PhCO$^+$, base peak), 357 (M + H$^+$, 0.07); HRMS *m/z* calcd for $C_{16}H_{11}F_3O_4S$ 357.0408, found 357.0400.

Synthesis of 1-[(*E*)-1-[(Phenylcarbonyl)oxy]-2-[(trifluoromethyl)-sulfonyl]-1-ethenyl]benzene ((*E*)-19a). **(*Z*)-19a** (71 mg) dissolved in acetonitrile (50 mL) was irradiated with 254 nm ultraviolet light in a Rayonet reactor (internal temperature 35 °C) for 5.5 h. The reaction mixture was concentrated and separated by column chromatography (acetone-deactivated silica gel, 0−3% EtOAc/hexane) to afford 61 mg (85%) of a mixture of **(*Z*)-19a** (33 mg) and **(*E*)-19a** as a colorless oil (28 mg): ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.77 (s, 1H), 7.40−7.75 (m, 8H), 8.05−8.15 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 110.7, 120.1 (q, $^1J_{C,F}$ = 326 Hz), 127.7, 128.1, 128.6, 129.5, 129.9, 130.9, 132.6, 135.3, 163.4, 168.5; mass spectrum (EI) *m/z* 105 (PhCO$^+$, base peak), 223 (M$^+$ − SO_2CF_3, 0.04);mass spectrum (CI) *m/z* 105 (PhCO$^+$,base peak), 357(M + H$^+$, 0.04); HRMS *m/z* calcd for $C_{16}H_{11}F_3O_4S$ 357.0408, found 357.0397.

Synthesis of 1-Phenyl-2-[(trifluoromethyl)sulfonyl]-1-ethanone (20a) and 1-[(Trifluoromethyl)sulfonyl]-2-octanone (20b). Phenylethynyl triflone (**8a**) or *n*-octynyl triflone (**8b**) (0.30 mmol) was dissolved in 100 mL of 1:1 acetone/water and stirred at 25 °C for 2 days followed by removal of the acetone *in vacuo*. The residue was extracted with ether, washed with brine, dried ($MgSO_4$), filtered, and concentrated. The resulting oil (**20a**)[16] or white solid (**20b**) was purified by column chromatography (silica gel, 8% EtOAc/hexane) to afford a 98% yield of **20a** (colorless oil in our hands, but known to be a 36−37 °C mp solid[16]) or 93% yield of **20b** (mp 68−69 °C).

Data for **20a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.87 (s, 2H), 7.50−7.80 (m, 3H), 7.90−8.05 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 57.3, 119.7 (q, $^1J_{C,F}$ = 328 Hz), 129.7, 135.5, 135.8, 185.0; mass spectrum (EI) *m/z* 105 (PhCO$^+$, base peak), 183 (M$^+$ − CF_3, 0.10), 252 (M$^+$, 0.15); mass spectrum (CI) *m/z* 253 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_9H_7F_3O_3S$ 252.0068, found 252.0065.

Data for **20b**: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.89 (t, $^3J_{H,H}$ = 6.5 Hz, 3H), 1.20−1.40 (m, 6H), 1.50−1.75 (m, 2H), 2.74 (t, $^3J_{H,H}$ = 5.6 Hz, 2H), 4.25 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.4, 22.9, 23.5, 28.8, 31.9, 45.1, 60.3, 119.5 (q, $^1J_{C,F}$ = 327 Hz), 194.9; mass spectrum (CI) *m/z* 261 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_9H_{15}F_3O_3S$ 261.0772, found 261.0766.

Synthesis of Trisubstituted Vinyl Triflone Carbonates (*Z*)-22a and (*E*)-22a or (*Z*)-22b and (*E*)-22b. β-Keto triflone **20a** or **20b** (0.30 mmol) was dissolved in THF (10 mL) and cooled to −78 °C (or 0 °C in order to get different *Z*/*E* product ratios). A 1.1 equiv sample of triethylamine was added, and the mixture was stirred at −78 °C (or 0 °C) for 10−15 min followed by addition of 1.1 equiv of ethyl chloroformate, which produced a white precipitate. The reaction mixture was stirred for 1 h, warmed to 0 °C, and filtered through acetone-deactivated silica gel, followed by concentration of the filtrate. The resulting oil was purified and separated by column chromatography (acetone-deactivated silica gel, 0−3% EtOAc/hexane) to afford 70−86% yield of **(*Z*)-22a** and **(*E*)-22a** or **(*Z*)-22b** and **(*E*)-22b** (all compounds were colorless oils).

Data for [(*E*)-1-phenyl-2-[(trifluoromethyl)sulfonyl]-1-ethenyl]carbonic acid ethyl ester ((***Z*)-22a**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.37 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 4.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 6.51 (s, 1H), 7.43−7.70 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.5, 67.0, 107.6, 120.1 (q, $^3J_{C,F}$ = 326 Hz), 127.4, 128.8, 130.0, 131.6, 134.0, 151.1, 165.3; mass spectrum (CI) *m/z* 253 (M + H$^+$ − $CO_2C_2H_4$, base peak), 325 (M + H$^+$, 0.80); HRMS *m/z* calcd for $C_{12}H_{11}F_3O_5S$ 325.0358, found 325.0351.

Data for [(*E*)-1-phenyl-2-[(trifluoromethyl)sulfonyl]-1-ethenyl]carbonic acid ethyl ester ((***E*)-22a**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 4.27 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 6.69 (s, 1H), 7.40−7.60 (m,5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.4, 66.8, 109.5, 120.0 (q, $^1J_{C,F}$ = 326 Hz), 128.6, 130.0, 130.2, 132.7, 150.9, 168.0; mass spectrum (CI) *m/z* 253 (M + H$^+$ − $CO_2C_2H_4$, 0.68), 325 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_{12}H_{11}F_3O_5S$ 325.0358, found 325.0351.

Data for [(*Z*)-1-hexyl-2-[(trifluoromethyl)sulfonyl]-1-ethenyl]carbonic acid ethyl ester (**(*Z*)-22b**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, $^3J_{H,H}$ = 6.5 Hz, 3H), 1.22−1.40 (m, 6H), 1.38 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 1.50−1.70 (m,2H), 2.54 (t, $^3J_{H,H}$ = 7.5 Hz, 2H), 4.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 6.00 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.4, 14.5, 22.9, 26.1 28.8, 31.7, 35.8, 66.7, 109.3, 120.0 (q, $^1J_{C,F}$ = 326 Hz), 150.8, 172.2; mass spectrum (CI) *m/z* 333 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_{12}H_{19}F_3O_5S$ 333.0984, found 333.0990.

Data for [(*E*)-1-hexyl-2-[(trifluoromethyl)sulfonyl]-1-ethenyl]carbonic acid ethyl ester (**(*E*)-22b**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, $^3J_{H,H}$ = 6.5 Hz, 3H), 1.23−1.45 (m, 6H), 1.39 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 1.52−1.70 (m,2H), 2.80 (t, $^3J_{H,H}$ = 7.6 Hz, 2H), 4.33 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 6.62 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.5, 22.8, 27.7, 29.2, 31.7, 31.8, 66.6, 107.8, 120.0 (q, $^1J_{C,F}$ = 326 Hz), 150.8, 173.9; mass spectrum (CI) *m/z* 333 (M + H$^+$, base peak); HRMS *m/z* calcd for $C_{12}H_{19}F_3O_5S$ 333.0984, found 333.0977.

C−H Alkenylation Reactions of β-Oxygenated Vinyl Triflones (*Z*)-22a,b and (*E*)-22a,b. β-oxygenated trisubstituted vinyl triflones (0.20 mmol) were dissolved in THF or cyclohexane (10 mL), and 0.2

equiv of AIBN was added (when reaction times were longer than one day, additional portions of AIBN were periodically added as required). The reactions of Table 3 were conducted at reflux for 12 h to 8 days. The reaction mixtures were concentrated, and the resulting oil was purified by column chromatography (silica gel, 5% EtOAc/hexane) to afford the products in the yields indicated in Table 3. See the Supporting Information section for the spectra of the products (***Z***)-**23**−**26a**,**b** and (***E***)-**23**−**26a**,**b**.

Synthesis of 2-[(*Z*)-1-Phenyl-2-[(trifluoromethyl)sulfonyl]-1-ethenyl]-2,3-dihydro-1*H*-benz[*c*]azole-1,3-dione ((*Z*)-29a). To a solution of phenylethynyl triflone (**8a**) (1.0 g, 4.3 mmol) in acetonitrile (30 mL) was added phthalimide (0.63 g, 4.3 mmol) followed by a catalytic amount of potassium hydroxide. The reaction was complete within 1 h. Acetonitrile was removed by rotary evaporator. The residue was purified by column chromatography (silica gel, eluted with 2:1 hexane/ethyl acetate) to afford 1.6 g (99%) of **(*Z*)-29a** as white crystals: mp 118−120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 1H), 7.51 (m, 5H), 7.88 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.54, 119.65 (q, $J_{C,F}$ = 326 Hz), 124.71, 127.56, 129.55, 129.67, 131.72, 132.92, 133.39, 135.21, 150.25, 165.63; mass spectrum (CI) *m*/*z* 382 (M + H$^+$, base peak); HRMS *m*/*z* calcd for $C_{17}H_{11}F_3NO_4S$ 382.0361, found 382.0353.

Synthesis of 2-[(*Z*)-2-(2-Oxolanyl)-1-phenyl-1-ethenyl]-2,3-dihydro-1*H*-benz[*c*]azole-1,3-dione ((*Z*)-30a). A solution of **(*Z*)-29a** (40 mg, 0.105 mmol) and AIBN (1.7 mg, 0.021 mmol) in THF (2 mL) was heated to reflux for 10 h. THF was removed on a rotary evaporator. The resulting residue was purified by column chromatography (silica gel, eluted with 2:1 hexane/ethyl acetate) to afford 33.1 mg (99%) of **(*Z*)-30a** as a white solid: mp 110−125 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (m, 2H), 1.80 (m, 2H), 3.40 (m, 1H), 3.57 (m, 1H), 4.50 (q, J = 7.39 Hz, 1H), 6.41 (d, J = 7.79 Hz, 1H), 6.88 (m, 5H), 7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.10, 32.73, 67.22, 76.04, 124.01, 124.39, 125.86, 129.14, 130.95, 132.45, 133.23, 134.89, 136.33, 168.01; mass spectrum (CI) *m*/*z* 320 (M + H$^+$, base peak); HRMS *m*/*z* calcd for $C_{20}H_{17}O_3N$ 319.1208, found 319.1201.

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Supporting Information Available: Experimental procedures for the synthesis of **(*E*)-9aF, (*Z*)-9bF, (*E*)-9bF, (*E*)-10aBr, (*Z*)-11aBr, (*Z*)-19b, (*E*)-21b, (*Z*)-23a, (*E*)-23a, (*Z*)-24a, (*E*)-24a, (*Z*)-25a, (*E*)-25a, (*Z*)-25b, (*E*)-25b, (*Z*)-26a, (*E*)-26a, (*Z*)-26b,** and **(*E*)-26b**, as well as ^{1}H and ^{13}C NMR of all new compounds (118 pages). See any current masthead page for ordering and Internet access instructions.

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