Facile generation of polyfluoro-1-(tosyloxy)prop-1-enyllithiums and their reaction with electrophiles. A new, efficient and convenient access to (*Z*)-1,1-di- and 1,1,1-tri-fluoro-3-(tosyloxy)alk-3-en-2-ones[1]

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Polyfluoro-1-(tosyloxy)prop-1-enyllithiums, generated by the reaction of polyfluoropropyl toluene-*p*-sulfonates or polyfluoroprop-1-enyl toluene-*p*-sulfonates with *n*-butyllithium, readily react with a variety of electrophiles, such as aldehydes, ketones, methyl trifluoromethanesulfonate, chlorotrimethylsilane and chlorotributylstannane, to give the corresponding coupling products in good yields. In particular, polyfluoro-2-(tosyloxy)but-2-enyl alcohols, obtained from the vinyllithiums and carbonyl compounds, undergo hydrolysis with concentrated sulfuric acid at room temperature or 70 °C to afford the corresponding (*Z*)-1,1-di- or 1,1,1-tri-fluoro-3-(tosyloxy)alk-3-en-2-ones in good to excellent yields.

Introduction

Considerable attention is currently being focused on fluorine-containing compounds, because they often bring about unique biological and physiological activities.[2] On account of their scarce occurrence in nature,[3] these compounds must be prepared artificially, so it is necessary to develop expedient and convenient chemical processes to introduce a fluorine atom or a fluorine-containing group into ordinary organic molecules.[4,5] In this connection, fluorinated organometallic reagents occupy a central position in highly regio- and/or stereo-selective synthesis of organofluorine compounds.[5]

On the other hand, fluorinated ketones are not only useful and versatile building blocks for the construction of biologically active substances,[6,7] but are also potent as enzyme inhibitors.[8] Therefore, it is important to develop a new efficient synthetic approach to functionalized fluorinated ketones.[6,7,9,10]

In our continuing studies on the synthesis and uses of new polyfluorinated building blocks,[11] we have succeeded in the efficient generation of polyfluoro-1-(tosyloxy)prop-1-enyllithiums[12] (**5a** and **5b**) from polyfluoropropyl toluene-*p*-sulfonates (**1a** and **1b**) or polyfluoroprop-1-enyl toluene-*p*-sulfonates (**2a** and **2b**), and have found that these new vinyllithiums readily react with various electrophiles to lead to the corresponding 1-substituted polyfluoroprop-1-enyl toluene-*p*-sulfonates (**3** and **4**) in good yields. Furthermore, we have applied this methodology successfully to the synthesis of functionalized di- or tri-fluoromethyl ketones.

In this paper we would like to describe in full detail a facile and stereoselective route to the synthesis of (*Z*)-1,1-di- and 1,1,1-tri-fluoro-3-(tosyloxy)alk-3-en-2-ones (**6** and **7**), based on the reaction of fluorinated vinyllithiums (**5a** and **5b**) with various carbonyl compounds providing the corresponding alcohols (**3** and **4**).

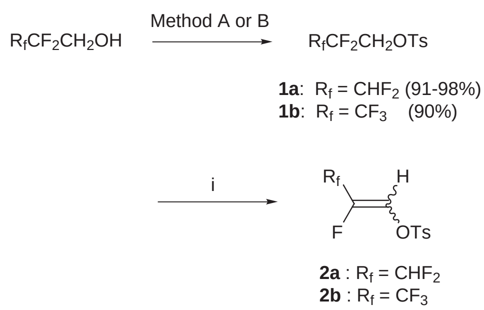
Results and discussion

Preparation of polyfluoroprop-1-enyl toluene-*p*-sulfonates (2)

2,2,3,3-Tetrafluoropropyl (**1a**) and 2,2,3,3,3-pentafluoropropyl toluene-*p*-sulfonate (**1b**) were prepared in high yields by the reaction of 2,2,3,3-tetrafluoropropan-1-ol or 2,2,3,3,3-pentafluoropropan-1-ol with toluene-*p*-sulfonyl chloride in the presence of NaOH in H_2O at 50 °C for 1 h (Method A) or in the presence of triethylamine in CH_2Cl_2 at room temperature for 3 h (Method B), as described in the Experimental section.

At first, we examined the reaction conditions for the dehydrofluorination of 2,2,3,3-tetrafluoropropyl toluene-*p*-sulfonate (**1a**) with bases. The results are compiled in Table 1.

When toluene-*p*-sulfonate **1a** was treated with 2.2 equiv. of *n*-butyllithium (Bu^nLi) in tetrahydrofuran (THF) at −78 °C for 10 min, 2,3,3-tri-fluoroprop-1-enyl toluene-*p*-sulfonate (**2a**) was obtained in 70% yield as a mixture of geometrical isomers whose *Z*:*E* ratio was 86:14 (Scheme 1, Table 1, Entry 4).



Scheme 1 *Reagents and conditions*: i, base, THF (DMPU)

Among the bases employed, such as Bu^nLi, lithium diisopropylamide (LDA), potassium *tert*-butoxide (Bu^tOK), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), only Bu^nLi and LDA were effective for the reaction (Entries 1–5). Neither Bu^tOK nor DBU allowed the reaction to proceed at all, even by the use of a prolonged reaction time and elevated temperature (Entries 6 and 7). Bu^nLi was the most suitable base for the dehydrofluorination of **1a**. It was found that the ratio of Bu^nLi to **1a** as well as the reaction time were crucial for the reaction: the use of a stoichiometric amount (1.1 equiv.) of Bu^nLi did not result in complete reaction, giving **2a** (*Z*:*E* = 86:14) in low (36%) yield together with the unchanged sulfonate **1a** (38%) (Entry 3). Longer reaction time (30 min) substantially reduced the yield (32%) of **2a** (*Z*:*E* = 84:16) (Entry 5). Note that the *Z* to *E* isomer ratios of the products are essentially the same, irrespective of either the stoichiometry of Bu^nLi or the reaction periods employed (Entries 3–5). The geometrical assignments for **2a** were unambiguously made from its ^1H and ^{19}F NMR spectra, based on the relative magnitudes of the vicinal coupling constants between vinylic fluorine and hydrogen; the isomer

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Table 1 Screening for the preparation of polyfluoroprop-1-enyl toluene-*p*-sulfonates **2** from **1**

Entry	R_f	Base (equiv.)	DMPU (equiv.)	*T*/°C	Time	Ratio[a] of **1**:**2** (*Z*:*E*)	Yield[b] (%) of **2**
1	CHF_2	LDA (1.1)	None	−78	30 min	58:42 (74:26)	27 (37)
2	CHF_2	LDA (2.2)	None	−78	10 min	25:75 (83:17)	49 (16)
3	CHF_2	Bu^nLi (1.1)	None	−78	10 min	51:49 (86:14)	36 (38)
4	CHF_2	Bu^nLi (2.2)	None	−78	10 min	0:100 (86:14)	70
5	CHF_2	Bu^nLi (2.2)	None	−78	30 min	0:100 (84:16)	32
6	CHF_2	Bu^tOK (1.1)	None	rt	24 h	100:0 —	0 (74)
7[c]	CHF_2	DBU (1.1)	None	rt	24 h	100:0 —	0 (99)
8	CF_3	Bu^nLi (2.2)	None	−78	10 min	1:99 (>98:<2)	17 (2)
9	CF_3	Bu^nLi (2.2)	2.2	−78	10 min	0:100 (>98:<2)	67
10[d]	CF_3	Bu^nLi (2.2)	2.2	−78	10 min	0:100 (>98:<2)	44

[a] Determined by ^{19}F NMR. [b] Isolated yields. Values in parentheses are recovery of **1**. [c] Carried out in CH_2Cl_2. [d] DMI was used, instead of DMPU.

Table 2 Deuteration of fluorinated vinyllithiums **5** generated from **1** with D_2O

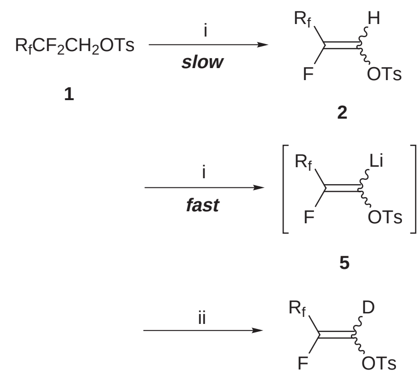
Entry	R_f	Bu^nLi (equiv.)	DMPU (equiv.)	Ratio[a] of **1**:[^{2}H]**2** (*Z*:*E*)	Yield[b] (%) of **2**
1	CHF_2	1.0	None	52:48 (83:17)	41 (44)
2	CHF_2	2.2	None	0:100 (85:15)	65
3	CF_3	1.0	1.0	49:51 (>98:<2)	40 (38)
4	CF_3	2.2	2.2	0:100 (98:2)	67

[a] Determined by ^{19}F NMR. [b] Isolated yields. Values in parentheses are recovery of **1**.

having a larger coupling constant (18.0 Hz) was assigned to the *Z* geometry with a *trans* relationship between fluorine and hydrogen, and the other isomer possessing a smaller coupling constant (4.4 Hz) to the *E* geometry.

On the other hand, dehydrofluorination of 2,2,3,3,3-pentafluoropropyl toluene-*p*-sulfonate (**1b**) did not proceed cleanly under the same conditions, and resulted in the formation of complex products, with only a trace amount of dehydrofluorinated product **2b** being obtained (Entry 8). Careful examination of the reaction conditions revealed that the addition of 1,3-dimethyl-3,4,5,6-perhydropyrimidin-2-one (DMPU) to the reaction mixture was extremely effective for the dehydrofluorination of **1b** (Entry 9). The use of 1,3-dimethylimidazolidin-2-one (DMI) was also efficient for the reaction, the yield of **1b** being slightly reduced (Entry 10). It should be noted that the dehydrofluorination of **1b** proceeds with high (*Z*)-stereoselectivity. This (*Z*)-stereoselectivity may be considered to result from preferential occurrence of the *trans*-elimination toward the most stable conformer of **1b**, in which the bulky trifluoromethyl and tosyloxy groups are situated *anti* to each other.

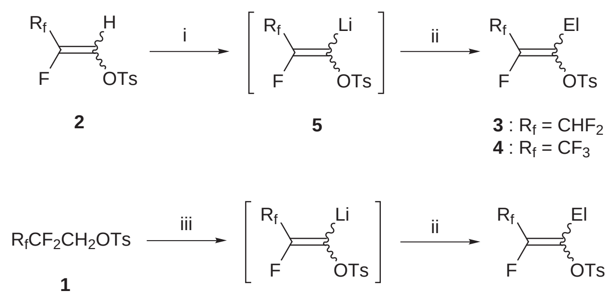
The presence of intermediary vinyllithium **5** was confirmed by the following deuteration experiments. Thus, the treatment of **1a** with 1.0 or 2.2 equiv. of Bu^nLi at −78 °C for 10 min followed by quenching with deuterium oxide (D_2O) gave rise to 1-deuterio-2,3,3-trifluoroprop-1-enyl toluene-*p*-sulfonate ([^{2}H]**2a**) in 41 or 65% yield, respectively, as shown in Table 2 (Entries 1 and 2). Similar treatment of **1b** in the presence of DMPU led to 1-deuterio-2,3,3,3-tetrafluoroprop-1-enyl toluene-*p*-sulfonate ([^{2}H]**2b**) in 40 or 67% yield (Entries 3 and 4). In either case, 2.2 equiv. of Bu^nLi was needed for complete consumption of the sulfonate **1**. These results strongly suggest that the rate of lithiation of **2** leading to vinyllithium **5** is much faster than that of dehydrofluorination of **1** (Scheme 2).



1 **2** **5**

[^{2}H]**2a**: R_f = CHF_2
[^{2}H]**2b**: R_f = CF_3

Scheme 2 *Reagents and conditions*: i, Bu^nLi, −78 °C; ii, D_2O, −78 to 10 °C



2 **5** **3** : R_f = CHF_2 **4** : R_f = CF_3

1 **5** **3** : R_f = CHF_2 **4** : R_f = CF_3

Scheme 3 *Reagents and conditions*: i, 1.1 equiv., Bu^nLi (1.1 equiv., DMPU), THF, −78 °C, 10 min; ii, electrophile, THF, −78 °C, 30 min; iii, 2.2 equiv., Bu^nLi (2.2 equiv., DMPU), THF, −78 °C

Reaction of polyfluoro-1-(tosyloxy)prop-1-enyllithiums (5) with electrophiles

The fluorinated vinyllithiums **5** were generated either by the reaction of the sulfonate **2** with 1.1 equiv. of Bu^nLi or by the reaction of **1** with 2.2 equiv. of Bu^nLi (in the presence of DMPU in the case of **1b** and **2b**) in THF at −78 °C. *In situ* generated vinyllithiums **5** were allowed to react with various electrophiles to give the corresponding products **3** or **4** in good yields, as shown in Table 3 and Scheme 3.

Thus, a variety of aromatic (Entries 1–7 and 21–23) and aliphatic aldehydes (Entries 10–12 and 25), including α,β-unsaturated aldehydes (Entries 8, 9 and 24) smoothly underwent the addition reaction with the vinyllithiums **5** to afford the corresponding allyl alcohols **3** and **4** in good yields. α,β-Unsaturated aldehydes, such as crotonaldehyde and cinnamaldehyde, led to the exclusive formation of the 1,2-addition products, none of the 1,4-addition products being detected in the reaction mixture (Entries 8, 9 and 24). A hindered aldehyde

Table 3 Reactions of fluorinated vinyllithiums **5** with various electrophiles

Entry	R_f	Ratio[a] of **2** (Z:E)	Electrophile (equiv.)	Product	Yield[b] (%) of **3** or **4** (Z:E)[a]
1	CHF_2	—[c]	PhCHO (1.5)	**3a**	61 (87:13)
2	CHF_2	84:16	PhCHO (1.5)	**3a**	81 (83:17)
3	CHF_2	85:15	4-MeC_6H_4CHO (1.5)	**3b**	76 (84:16)
4	CHF_2	81:19	4-$MeOC_6H_4CHO$ (1.5)	**3c**	68 (81:19)
5	CHF_2	85:15	4-ClC_6H_4CHO (1.5)	**3d**	84 (87:13)
6	CHF_2	81:19	Naphthalene-1-carbaldehyde (1.5)	**3e**	69 (79:21)
7	CHF_2	79:21	Thiophene-2-carbaldehyde (1.5)	**3f**	69 (81:19)
8	CHF_2	81:19	(E)-MeCH=CHCHO (1.5)	**3g**	56 (80:20)
9	CHF_2	83:17	(E)-PhCH=CHCHO (1.5)	**3h**	55 (82:18)
10	CHF_2	—[c]	Pr^nCHO (1.5)	**3i**	55 (82:18)
11	CHF_2	81:19	Pr^nCHO (1.5)	**3i**	76 (80:20)
12	CHF_2	83:17	Bu^tCHO (1.5)	**3j**	49 (85:15)
13	CHF_2	—[c]	Et_2CO (1.5)	**3k**	48 (81:19)
14	CHF_2	86:14	Et_2CO (1.5)	**3k**	63 (85:15)
15	CHF_2	—[c]	Me_3SiCl (2.0)	**3l**	66 (18:82)
16	CHF_2	87:13	Me_3SiCl (2.0)	**3l**	79 (15:85)
17[d]	CHF_2	84:16	$Bu^n{}_3SnCl$ (2.0)	**3m**	68 (17:83)
18	CHF_2	—[c]	MeI (5.0)	**3n**	17[e]
19	CHF_2	—[c]	CF_3SO_3Me (2.0)	**3n**	60 (80:20)
20	CHF_2	83:17	CF_3SO_3Me (2.0)	**3n**	79 (81:19)
21[f]	CF_3	>98:<2	PhCHO (1.2)	**4a**	63 (>99:<1)
22[f]	CF_3	>98:<2	4-ClC_6H_4CHO (1.2)	**4b**	64 (>99:<1)
23[f]	CF_3	>98:<2	Thiophene-2-carbaldehyde (1.2)	**4c**	56 (>99:<1)
24[f]	CF_3	>98:<2	(E)-PhCH=CHCHO (1.2)	**4d**	54 (>99:<1)
25[f]	CF_3	>98:<2	Pr^nCHO (1.2)	**4e**	48 (>99:<1)
26[f]	CF_3	>98:<2	Et_2CO (1.2)	**4f**	Trace[g]
27[f]	CF_3	>98:<2	Me_3SiCl (1.2)	**4g**	64 (<1:>99)

[a] Determined by ^{19}F NMR. [b] Isolated yields. [c] Toluene-p-sulfonate **1** and 2.2 equiv. of Bu^nLi were employed. [d] Carried out at 0 °C for 1 h. [e] Ratio was not determined. Toluene-p-sulfonate **2a** was obtained in 31% yield. [f] DMPU (2.2 equiv.) was added. [g] Toluene-p-sulfonate **2b** was recovered in 38% yield.

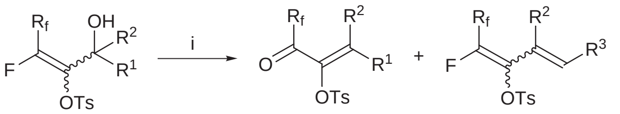
such as 2,2-dimethylpropanal also reacted with **5a** to give the corresponding allyl alcohol **3j** in 49% yield (Entry 12). The vinyllithium **5a** could react with pentan-3-one to give a good yield of the product **3k** (Entry 14), whereas the vinyllithium **5b** did not react at all, the starting **2b** being recovered in 38% yield.

Other electrophiles, such as chlorotrimethylsilane (Entries 15, 16 and 27), chlorotributylstannane (Entry 17) and methyl trifluoromethanesulfonate (Entries 19 and 20), participated well in the reaction with **5** affording good yields of the products. The reaction with an excess amount (5 equiv.) of methyl iodide did not occur sufficiently, giving 17% yield of the methylated product **3n**, along with **1a** in 31% yield (Entry 18). When vinyllithium **5a** was treated with allyl bromide or benzyl bromide, neither allylated nor benzylated products were formed at all in the reaction mixture. These facts suggest that the reactivity of **5a** is lower than that of fluorine-free vinyllithium.[12n] The low reactivity of **5a** may be attributed to the presence of the difluoromethyl and/or fluorine substituent.

The fluorinated vinyllithium species **5a**, generated from **2a** (Z:E = 84:16), was treated with deuterated ethyl alcohol (C_2H_5OD) to give 1-deuterio-2,3,3-trifluoroprop-1-enyl toluene-p-sulfonate ([^{2}H]**2a**) (Z:E = 82:18) in 79% yield. The stereochemistry of the product [^{2}H]**2a** was determined on the basis of comparison of coupling constants (J_{trans} = 2.2 Hz and J_{cis} = 0 Hz) between vinylic fluorine and deuterium (see Experimental section). In all the reactions, the isomer ratios of the products **3** and **4** were identical with those of the starting enol tosylates **2**, as shown in Table 3. This fact indicates that the fluorinated vinyllithiums **5** are generated and react with electrophiles with retention of configuration of the starting enol toluene-p-sulfonate **2**.

Synthesis of 1,1-di- and 1,1,1-tri-fluoro-3-(tosyloxy)alk-3-en-2-ones (6 and 7)

The hydrolysis of allyl alcohol **3a**, prepared from **2a** and benzaldehyde, with 3–5 equiv. of concentrated sulfuric acid (H_2SO_4) in THF at room temperature for 5–24 h was very sluggish giving (Z)-1,1-difluoro-4-phenyl-3-(tosyloxy)but-3-en-2-one (**6a**) in less than 27% yield (Scheme 4). However, when



3 : R_f = CHF_2
4 : R_f = CF_3

6 : R_f = CHF_2
7 : R_f = CF_3

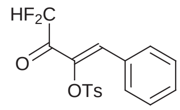
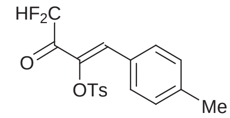
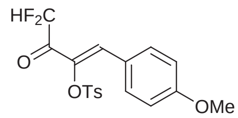
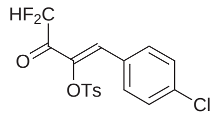
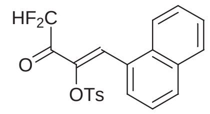
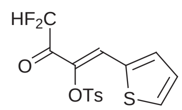
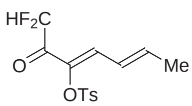
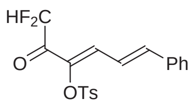
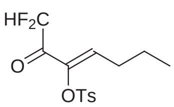
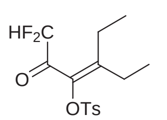
8 : R_f = CHF_2
9 : R_f = CF_3

Scheme 4 *Reagents and conditions*: i, conc. H_2SO_4, THF, rt, or 70 °C

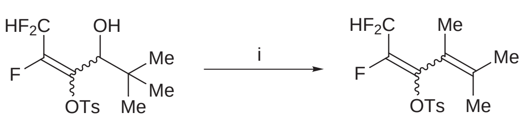
the alcohol **3a** was treated with 10 equiv. of conc. H_2SO_4 in THF at room temperature for 30 min, the hydrolysis smoothly occurred to afford difluoromethyl ketone **6a** in 82% yield as a single stereoisomer (Entry 1 in Table 4). The use of trifluoroacetic acid in place of H_2SO_4 was inefficient for the reaction to leave the alcohol **6a** remained in 77% yield.

The results of the hydrolysis of other alcohols **3** are summarized in Table 4. Allyl alcohols **3a-f,h**, derived from various aromatic aldehydes and cinnamaldehyde, were subjected to the reaction with conc. H_2SO_4 in THF at room temperature for 30 min to give the corresponding (Z)-difluoromethyl ketones **6a–f,h** in good to excellent yields (Entries 1–6 and 8). The hydrolysis of alcohol **3g** derived from crotonaldehyde proceeded readily to give the corresponding difluoromethyl ketone **6g** in 49% yield, along with 20% yield of fluorinated triene **8g** (R^2 = H, R^3 = CH=CH_2) which resulted from dehydration (Entry 7). The hydrolysis of alcohols **3i**, **3j** and **3k**, derived from butanal, 2,2-dimethylpropanal and pentan-3-one, respectively, did not take place under the same conditions. As a result of careful screening of the reaction conditions, such as reaction temperature and solvents, it was found that **3i** and **3k** underwent the hydrolysis in the presence of 5 equiv. of water without THF to provide (Z)-difluoromethyl ketones **6i** and **6k** in 47 and 24% yields, together with 24 and 62% yields of fluorodienes **8i** (R^2 = H, R^3 = Et) and **8k** (R^2 = Et, R^3 = Me), respectively (Entries 9 and 10). Interestingly, the alcohol **3j** derived from 2,2-dimethylpropanal did not give the corresponding difluoromethyl ketone at all but the Wagner–Meerwein rearrangement[13] product **10** in 72% yield, as shown in Scheme 5.

Table 4 Synthesis of (*Z*)-1,1-difluoro-3-(tosyloxy)alk-3-en-2-one **6**[a]

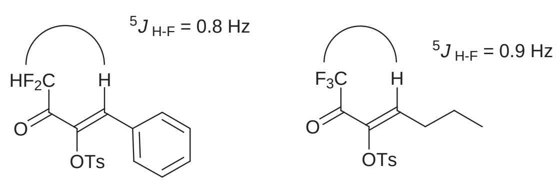
Entry	**3** (*Z*:*E*)[b]	Product **6**		Yield[c] (%) of **6** (*Z*:*E*)[b]
1	**3a** (83:17)		**6a**	82 (>97:<3)
2	**3b** (84:16)		**6b**	90 (>97:<3)
3	**3c** (81:19)		**6c**	89 (97:3)
4	**3d** (87:13)		**6d**	87 (>97:<3)
5	**3e** (79:21)		**6e**	81 (>97:<3)
6	**3f** (81:19)		**6f**	89 (>97:<3)
7	**3g** (80:20)		**6g**	49[d] (>97:<3)
8	**3h** (82:18)		**6h**	94 (>97:<3)
9[e]	**3i** (80:20)		**6i**	47[f] (>97:<3)
10[e]	**3k** (85:15)		**6k**	24[g]

[a] Unless otherwise noted, the reaction was carried out at room temperature for 30 min in THF. [b] Determined by ^{19}F NMR. [c] Isolated yields. [d] Fluorinated triene **8** was obtained in 20% yield. [e] Carried out in the presence of 5 equiv. of water without THF. [f] Fluorinated diene **8i** was obtained in 24% yield. [g] Fluorinated diene **8k** was obtained in 62% yield.



3j **10**

Scheme 5 *Reagents and conditions*: conc. H_2SO_4, H_2O, rt, 30 min



(*Z*)-**6a** (*Z*)-**7e**

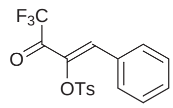
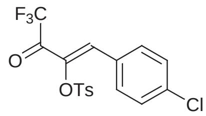
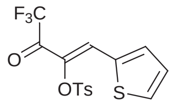
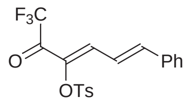
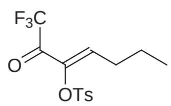
Fig. 1

On the other hand, the hydrolysis of alcohol **4a** carrying the trifluoromethyl group with conc. H_2SO_4 in THF did not proceed efficiently at room temperature, giving only 22% yield of the corresponding trifluoromethyl ketone **7a**, the starting alcohol **4a** being recovered in 56% yield. Raising the reaction temperature to 70 °C completed the hydrolysis of **4a** to provide the corresponding trifluoromethyl ketone **7a** as (*Z*)-isomer only in 88% yield. As shown in Table 5, various allyl alcohols **4**, derived from aromatic aldehydes (Entries 1–3) and cinnamaldehyde (Entry 4), participated successfully in the hydrolysis to afford the corresponding trifluoromethyl ketones **7** in excellent yields.

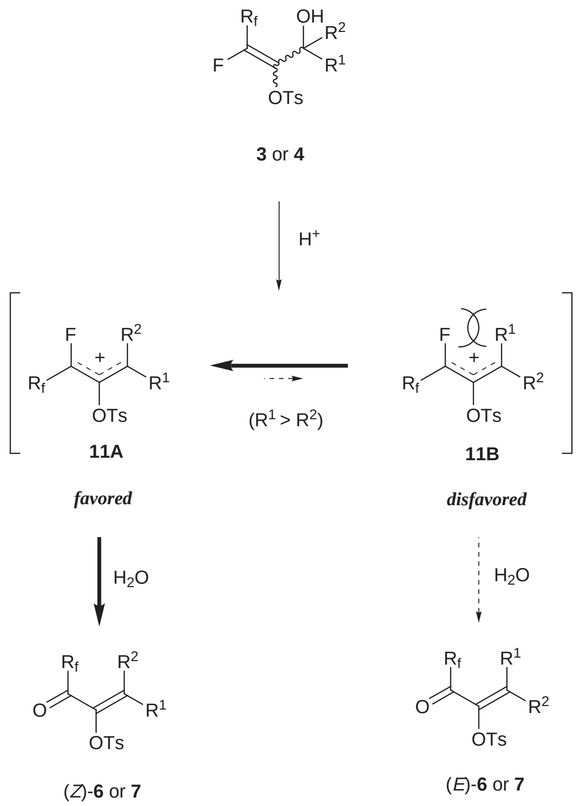
The hydrolysis of alcohol **4e** derived from butanal was very reluctant even by the use of an excess amount (20 equiv.) of conc. H_2SO_4, and the corresponding trifluoromethyl ketone **7e** was obtained in only 17% yield, together with fluorinated diene **9e** in 20% yield (Entry 5).

The stereochemical assignments of **6a** and **7e** were made on the basis of the fact that a long-range coupling between the vinylic hydrogen and the fluorine atoms of the di- or trifluoromethyl group appeared in the ^{1}H NMR spectra (Fig. 1).

Table 5 Synthesis of (*Z*)-1,1,1-trifluoro-3-(tosyloxy)alk-3-en-2-one **7**[a]

Entry	**4** (*Z*:*E*)[b]	Product **7**		Yield[c] (%) of **7** (*Z*:*E*)[b]
1	**4a** (>98:<2)		**7a**	88 (>99:<1)
2	**4b** (>98:<2)		**7b**	83 (>99:<1)
3	**4c** (>98:<2)		**7c**	83 (>99:<1)
4	**4d** (>98:<2)		**7d**	82 (>99:<1)
5[d]	**4e** (>98:<2)		**7e**	17[e] (>99:<1)

[a] Unless otherwise noted, the reaction was carried out at 70 °C for 1 h in THF. [b] Determined by ^{19}F NMR. [c] Isolated yields. [d] Conc. H_2SO_4 (20 equiv.) was used. [e] Fluorinated diene **9e** was obtained in 20% yield.



Scheme 6

Of significance is that allyl alcohols **3** or **4** were hydrolyzed to the corresponding (*Z*)-di- or tri-fluoromethyl ketones **6** or **7** regardless of the configuration of the starting alcohols.

It seems that the hydrolysis occurs *via* a mechanism involving an allyl cation **11**, which may be generated by an acid-assisted elimination of the hydroxy group. The preferential formation of the *Z*-isomer of **6** and **7** would be attributed to the relative stabilities of the cation intermediates **11A** and **11B**. These allyl cations may experience a 1,3-allylic strain between fluorine (or difluoro- or trifluoro-methyl) substituent and the R^1 or R^2 group (R^1 > R^2); the allyl cation **11B** may involve more repulsive strain than **11A** (R^1 > R^2). Thus, the intermediate cation **11A** is more stable than **11B**, leading to the *Z*-isomer of the products (Scheme 6).[12a,b,14]

In conclusion, we have demonstrated that fluorinated prop-1-enyllithiums **5** having the tosyloxy group, react readily with various electrophiles to give the corresponding fluorinated vinyl toluene-*p*-sulfonates in good yields and that the acidic hydrolysis of allyl alcohols **3** and **4**, obtained from vinyllithiums **5** and carbonyl compounds, affords predominantly (*Z*)-di- or tri-fluoromethyl ketones **6** or **7** in high yields. This method can serve as a stereoselective route to functionalized (*Z*)-di- and tri-fluoromethyl ketones, which are difficult to obtain by other methods.

Experimental

General

Melting points were obtained on a Shimadzu MM-2 micro point determination apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Shimadzu IR-400 spectrometer. ^{1}H NMR spectra were measured with Hitachi R-24B (60 MHz), Varian Gemini-200 (200 MHz) and/or General Electric QE-300 (300 MHz) FT-NMR spectrometers in deuteriochloroform ($CDCl_3$) solutions with tetramethylsilane (Me_4Si) as an internal standard. ^{19}F NMR spectra were recorded on a Hitachi R-24F (56.466 MHz) spectrometer in $CDCl_3$ solutions using trifluoroacetic acid as an external standard and converted to $CFCl_3$ standard by the calculation of $\delta(CFCl_3) = -[77.0 - \delta(TFA)]$. Mass spectra (MS) were taken on a Hitachi-80B spectrometer operating at an ionization potential of 70 eV. Elemental analyses were made on a Yanaco MT-5 CHN recorder. The isolation of pure products was carried out with column chromatography using silica gel (Wakogel C-200, 100–200 mesh, Wako Pure Chemical Ind. Ltd.).

Materials

Tetrahydrofuran (THF) was freshly distilled from lithium aluminium hydride or sodium diphenylketyl. Butyllithium (Bu^nLi) (a 1.6 M hexane solution) was commercially available from Aldrich Chemical Co. Inc. or Kanto Chemical Co. Inc. 2,2,3,3-Tetrafluoropropan-1-ol and 2,2,3,3,3-pentafluoropropan-1-ol were purchased from Daikin Kogyo Co. Ltd. 1,3-Dimethylperhydropyrimidin-2-one (DMPU) and 1,3-dimethylimidazolidin-2-one (DMI) were distilled over calcium hydride under vacuum. Aldehydes and ketones were distilled (or vacuum distilled) over calcium hydride or recrystallized from hexane, and stored under argon. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use.

Typical procedure for the preparation of polyfluoropropyl toluene-*p*-sulfonates 1a and 1b

Method A. A solution of NaOH (1.50 g, 36.0 mmol) in water (4.5 ml) was gradually added to a suspension of 2,2,3,3-tetrafluoropropan-1-ol (3.961 g, 30.0 mmol), toluene-*p*-sulfonyl chloride (6.863 g, 36.0 mmol) and water (10.5 ml) below 40 °C. Then the mixture was stirred for 1 h at 50 °C. After being cooled to room temperature, the mixture was extracted with diethyl ether (15 ml × 3) and the ethereal extracts were washed with 25% aqueous ammonia (30 ml × 3) and brine (30 ml × 3), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Column chromatography of the residue on silica gel eluting with benzene provided 2,2,3,3-tetrafluoropropyl toluene-*p*-sulfonate (**1a**) (7.844 g) in 91 % yield.

Method B. Triethylamine (3.643 g, 36.0 mmol) was added dropwise to a solution of 2,2,3,3-tetrafluoropropan-1-ol (3.961 g, 30.0 mmol) and toluene-*p*-sulfonyl chloride (6.863 g, 36.0 mmol) in dichloromethane (20 ml) at 0 °C, and the resultant mixture was stirred for 3 h at room temperature. The reaction mixture was quenched with brine (50 ml), and extracted with diethyl ether (50 ml × 3). The combined organic layers were washed with 25% aqueous ammonia (30 ml × 3) and brine (30 ml × 3) and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure to leave the residual oil, which was subjected to column chromatography (benzene) to give **1a** (8.323 g) in 97% yield.

2,2,3,3-Tetrafluoropropyl toluene-*p*-sulfonate 1a. ν_{max}(film)/cm^{-1} 1379, 1179; δ_H(60 MHz) 2.39 (3H, s, CH_3), 4.22 (2H, tt, *J* 12.0, 1.3, CH_2), 5.69 (1H, tt, *J* 52.0, 4.1, CHF_2), 7.18 and 7.59 (4H, AB quartet, *J* 8.0, aryl H); δ_F −122.6 (2F, dt, *J* 12.0, 4.1, CF_2), −136.5 (2F, dt, *J* 52.0, 1.3, CHF_2); *m*/*z* (EI) 286.0281 (M^+, 29%, $C_{10}H_{10}F_4O_3S$ requires 286.0287), 91 (100), 78 (19), 65 (23).

2,2,3,3,3-Pentafluoropropyl toluene-*p*-sulfonate 1b. Mp 51.5–51.8 °C; ν_{max}(KBr)/cm^{-1} 1367, 1173; δ_H(200 MHz) 2.46 (3H, s, CH_3), 4.42 (2H, qt, *J* 12.3, 0.9, CH_2), 7.39 and 7.81 (4H, AB quartet, *J* 8.2, aryl H); δ_F −82.5 (3F, s, CF_3), −121.8 (2F, t, *J* 12.3, CF_2); *m*/*z* (EI) 304.0188 (M^+, 20%, $C_{10}H_9F_5O_3S$ requires 304.0190), 241 (3), 213 (3), 201 (3).

Preparation of 2,3,3-trifluoroprop-1-enyl toluene-*p*-sulfonate 2a

To a solution of **1a** (858 mg, 3.0 mmol) in THF (12 ml) was added dropwise Bu^{n}Li (4.1 ml of a 1.6 M hexane solution, 6.6 mmol) at −78 °C over 20 min under argon. After 10 min at −78 °C, the reaction was quenched with a cold 10% HCl solution. The resulting mixture was extracted with diethyl ether (30 ml × 3) and the extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. After the isomer distribution in the product was determined by ^{19}F NMR, the residue was purified by silica gel column chromatography to give 2,3,3-trifluoroprop-1-enyl toluene-*p*-sulfonate (**2a**) (*Z*:*E* = 86:16) (559 mg) in 70% yield. The *E*- and *Z*-isomers were easily separated by silica gel column chromatography eluting with hexane-benzene (1:1). *Z*-Isomer: mp 75.0–76.0 °C; ν_{max}(KBr)/cm^{-1} 1720, 1350, 1172; δ_H(60 MHz) 2.46 (3H, s, CH_3), 5.96 (1H, dt, *J* 52.6, 7.0, CHF_2), 6.63 (1H, dt, *J* 18.0, 2.0, vinyl H), 7.30 and 7.74 (4H, AB quartet, *J* 8.8, aryl H); δ_F −122.4 (2F, ddd, *J* 52.6, 17.6, 2.0, CHF_2), −145.3 (1F, ddt, *J* 18.0, 17.6, 7.0, vinyl F); *m*/*z* (CI) 267.0246 (M^+ + 1, 32%, $C_{10}H_{10}F_3O_3S$ requires 267.0303), 91 (100), 65 (35). *E*-Isomer: mp 24.1–25.5 °C; ν_{max}(KBr)/cm^{-1} 1720, 1379, 1172; δ_H(60 MHz) 2.44 (3H, s, CH_3), 6.16 (1H, dt, *J* 51.2, 15.8, CHF_2), 6.85 (1H, d, *J* 4.4, vinyl H), 7.30 and 7.71 (4H, AB quartet, *J* 8.2, aryl H); δ_F −125.3 (2F, dd, *J* 51.2, 16.9, CHF_2), −164.0 (1F, ddt, *J* 16.9, 15.8, 4.4, vinyl F); *m*/*z* (CI) 267.0278 (M^+ + 1, 20%, $C_{10}H_{10}F_3O_3S$ requires 267.0303), 91 (100), 65 (54) (Found: C, 44.86; H, 3.37. $C_{10}H_9F_3O_3S$ requires C, 45.11; H, 3.41%).

Preparation of 2,3,3,3-tetrafluoroprop-1-enyl toluene-*p*-sulfonate 2b

To a solution of **1b** (1.824 g, 6.0 mmol) and DMPU (1.692 g, 13.2 mmol) in THF (24 ml) was added dropwise Bu^{n}Li (8.4 ml of 1.57 M hexane solution, 13.2 mmol) at −78 °C over 20 min under argon. After 10 min at the same temperature, the resultant mixture was quenched with a cold 10% HCl solution, followed by extraction with diethyl ether (30 ml × 3). The extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. After the determination of the isomer distribution in the product by ^{19}F NMR, the residue was purified by silica gel column chromatography to give analytically pure sulfonate **2b** (*Z*:*E* = >98:<2) (1.139 g) in 67% yield. Mp 36.0–36.5 °C (*Z*:*E* = >98:<2); ν_{max}(KBr)/cm^{-1} 1713, 1375, 1192; δ_H(200 MHz) 2.46 (3H, s, CH_3), 7.00 (1H, dq, *J* 16.9, 1.1, vinyl H) for *Z*-isomer, 7.18 (1H, d, *J* 6.3, vinyl H) for *E*-isomer, 7.41 and 7.84 (4H, AB quartet, *J* 8.0, aryl H); δ_F −70.5 (3F, dd, *J* 11.3, 1.1, CF_3) for *Z*-isomer, −67.2 (3F, d, *J* 9.0, CF_3) for *E*-isomer, −147.3 (1F, dq, *J* 16.9, 11.3, vinyl F) for *Z*-isomer, −161.1 (1F, dq, *J* 9.0, 6.3, vinyl F) for *E*-isomer; *m*/*z* (CI) 285.0201 (M^+ + 1, 100%, $C_{10}H_9F_4O_3S$ requires 285.0209), 237 (4), 227 (6), 213 (5), 177 (5), 139 (8), 127 (7), 101 (24), 73 (24), 63 (10) (Found: C, 41.95; H, 2.81. $C_{10}H_8F_4O_3S$ requires C, 42.26; H, 2.84%).

Typical procedure for the deuteration of vinyllithium intermediates 5

A hexane solution of Bu^{n}Li (4.17 ml of 1.6 M hexane solution, 6.67 mmol) was added dropwise to a solution of 2,2,3,3-tetrafluoropropyl toluene-*p*-sulfonate (**1a**) (867 mg, 3.0 mmol) in THF (11 ml) at −78 °C under argon. To this mixture, after 10 min, was slowly added a THF (1 ml) solution of D_2O (300 mg, 15.2 mmol) at −78 °C. After being warmed up to 10 °C, the reaction mixture was poured into dilute HCl. The resultant mixture was extracted with diethyl ether (30 ml × 3). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. After the ratio of two geometrical isomers was determined by ^{19}F NMR, the residue was purified by silica gel column chromatography to give 1-deuterio-2,3,3-trifluoroprop-1-enyl toluene-*p*-sulfonate ([^{2}H]**2a**) (525 mg, 65%). The *E*- and *Z*-isomers were easily separated by silica gel column chromatography eluting with hexane–benzene (1:1). The results are summarized in Table 2.

1-Deuterio-2,3,3-trifluoroprop-1-enyl toluene-*p*-sulfonate [^{2}H]2a. *Z*-Isomer: mp 64.2–65.5 °C; ν_{max}(KBr)/cm^{-1} 1705, 1384, 1168; δ_H(60 MHz) 2.42 (3H, s, CH_3), 6.90 (1H, dt, *J* 51.5, 7.8, CHF_2), 7.23 and 7.67 (4H, AB quartet, *J* 8.8, aryl H); δ_F −122.6 (2F, dd, *J* 51.5, 17.2, CHF_2), −146.2 (1F, ddt, *J* 17.2, 7.8, 2.2, vinyl F); *m*/*z* (CI) 268.0358 (M^+ + 1, 75%, $C_{10}H_9DF_3O_3S$ requires 268.0287), 91 (100). *E*-Isomer: mp 22.5–23.1 °C; ν_{max}(KBr)/cm^{-1} 1792, 1384, 1180; δ_H(60 MHz) 2.45 (3H, s, CH_3), 6.16 (1H, dt, *J* 51.2, 15.8, CHF_2), 7.32 and 7.73 (4H, AB quartet, *J* 8.2, aryl H); δ_F −125.4 (2F, dd, *J* 51.2, 16.7, CHF_2), −164.3 (1F, dt, *J* 16.7, 15.8, vinyl F); *m*/*z* (CI) 268.0364 (M^+ + 1, 24%, $C_{10}H_9DF_3O_3S$ requires 268.0287), 51 (100) (Found: C, 44.83; H, 3.22; F, 21.36. $C_{10}H_8DF_3O_3S$ requires C, 44.94; H, 3.02; F, 21.33%).

1-Deuterio-2,3,3,3-tetrafluoroprop-1-enyl toluene-*p*-sulfonate [^{2}H]2b. Mp 35.7–36.3 °C (*Z*:*E* = >98:<2); ν_{max}(KBr)/cm^{-1} 1692, 1392, 1175; δ_H(200 MHz) 2.48 (3H, s, CH_3), 7.42 and 7.84 (4H, AB quartet, *J* 8.1, aryl H); δ_F −70.2 (3F, d, *J* 11.7, CF_3) for *Z*-isomer, −67.7 (3F, d, *J* 9.0, CF_3) for *E*-isomer, −147.3 (1F, dt, *J* 11.7, 2.2, vinyl F) for *Z*-isomer, −162.3 (1F, q, *J* 9.0, vinyl F) for *E*-isomer; *m*/*z* (CI) 286.0263 (M^+ + 1, 100%, $C_{10}H_7DF_4O_3S$ requires 286.0269), 225 (4), 156 (44), 139 (7).

Typical procedure for the reactions of fluorinated vinyllithiums 5 with electrophiles

A hexane solution of Bu^{n}Li (1.38 ml of 1.6 M hexane solution, 2.2 mmol) was added dropwise to a solution of **2a** (532 mg, 2.0 mmol, *Z*:*E* = 84:16) in THF (8 ml) at −78 °C under argon. To this mixture, after 10 min, was slowly added a THF (1 ml) solution of benzaldehyde (318 mg, 3.0 mmol) at −78 °C. After being stirred for 30 min at the same temperature, the reaction mixture was poured into saturated aqueous NH_4Cl (50 ml). The resultant mixture was extracted with diethyl ether (30 ml × 3). The combined extracts were washed with saturated aqueous $NaHCO_3$ (20 ml × 2) and brine (20 ml × 2), followed by drying over anhydrous Na_2SO_4, filtration, and concentration under reduced pressure. After the isomer ratio of the product was measured by ^{19}F NMR, the residue was purified by silica gel column chromatography (hexane–diethyl ether = 3:1) to give 3,4,4-trifluoro-1-phenyl-2-(tosyloxy)but-2-en-1-ol (**3a**) (601 mg, 81%). The *E*- and *Z*-isomers were easily separated by silica gel column chromatography eluting with benzene. The results are summarized in Table 3.

3,4,4-Trifluoro-1-phenyl-2-(tosyloxy)but-2-en-1-ol 3a. *Z*-Isomer: mp 59.1–60.9 °C; ν_{max}(KBr)/cm^{-1} 3510, 1708, 1360, 1152; δ_H(60 MHz) 2.37 (3H, s, CH_3), 3.31 (1H, d, *J* 4.2, OH), 5.52 (1H, br s, C*H*OH), 6.72 (1H, dt, *J* 51.8, 15.6, CHF_2), 7.11 and 7.64 (4H, AB quartet, *J* 10.6, aryl H), 7.20 (5H, s, aryl H); δ_F −121.3 (2F, ddd, *J* 51.8, 17.3, 1.5, CHF_2), −138.7 (1F, ddt, *J* 17.3, 15.6, 4.2, vinyl F); *m/z* (CI) 355.0596 ($M^+ + 1 - H_2O$, 40%, $C_{17}H_{16}F_3O_4S - H_2O$ requires 355.0616), 271 (9), 236 (6), 200 (25). *E*-Isomer: mp 80.9–82.0 °C; ν_{max}(KBr)/cm^{-1} 3525, 1598, 1344, 1180; δ_H(60 MHz) 2.41 (3H, s, CH_3), 3.08 (1H, s, OH), 5.75 (1H, d, *J* 3.2, C*H*OH), 6.25 (1H, dt, *J* 51.0, 17.8, CHF_2), 7.22 and 7.64 (4H, AB quartet, *J* 8.4, aryl H), 7.21 (5H, s, aryl H); δ_F −123.6 (2F, ddd, *J* 51.0, 21.4, 18.4, CHF_2), −150.2 (1F, ddt, *J* 18.4, 17.8, 3.2, vinyl F); *m/z* (CI) 355.0603 ($M^+ + 1 - H_2O$, 43%, $C_{17}H_{16}F_3O_4S - H_2O$ requires 355.0616), 271 (6), 200 (33).

3,4,4-Trifluoro-1-(4-methylphenyl)-2-(tosyloxy)but-2-en-1-ol 3b. Mp 84.0–85.2 °C; ν_{max}(KBr)/cm^{-1} 3525, 1710, 1360, 1158; δ_H(60 MHz) 2.30 (3H, s, CH_3), 2.39 (3H, s, CH_3), 3.11 (1H, s, OH), 5.51 (1H, m, C*H*OH) for *Z*-isomer, 5.70 (1H, m, aryl H) for *E*-isomer, 6.27 (1H, dt, *J* 50.8, 17.6, CHF_2) for *E*-isomer, 6.77 (1H, dt, *J* 52.2, 15.7, CHF_2) for *Z*-isomer, 7.12 (4H, s, aryl H), 7.23 and 7.70 (4H, AB quartet, *J* 9.4, aryl H); δ_F −121.5 (2F, dd, *J* 52.2, 17.0, CHF_2), −139.3 (1F, dt, *J* 17.0, 15.7, vinyl F) for *Z*-isomer, −123.4 (2F, ddd, *J* 50.8, 17.7, 17.7, CHF_2), −150.5 (1F, dt, *J* 17.7, 17.6, vinyl F) for *E*-isomer; *m/z* (CI) 369.0766 ($M^+ + 1 - H_2O$, 88%, $C_{18}H_{18}F_3O_4S - H_2O$ requires 369.0773), 285 (27), 257 (19), 213 (93).

3,4,4-Trifluoro-1-(4-methoxyphenyl)-2-(tosyloxy)but-2-en-1-ol 3c. ν_{max}(film)/cm^{-1} 3550, 1702, 1368, 1167; δ_H(200 MHz) 2.44 (3H, s, CH_3) for *Z*-isomer, 2.47 (3H, s, CH_3) for *E*-isomer, 3.33 (1H, br s, OH), 3.77 (3H, s, OCH_3) for *E*-isomer, 3.78 (3H, s, OCH_3) for *Z*-isomer, 5.57 (1H, br s, C*H*OH) for *Z*-isomer, 5.77 (1H, br s, C*H*OH) for *E*-isomer, 6.32 (1H, dt, *J* 51.3, 17.3, CHF_2) for *E*-isomer, 6.80 and 7.24 (4H, AB quartet, *J* 8.9, aryl H), 6.90 (1H, dt, *J* 52.0, 15.9, CHF_2) for *Z*-isomer, 7.31 and 7.77 (4H, AB quartet, *J* 8.1, aryl H); δ_F −121.6 (2F, ddd, *J* 52.0, 17.4, 1.7, CHF_2), −140.5 (1F, dt, *J* 17.4, 15.9, vinyl F) for *Z*-isomer, −121.6 (2F, ddd, *J* 51.3, 17.9, 12.7, CHF_2), −151.4 (1F, dt, *J* 17.9, 17.3, vinyl F) for *E*-isomer; *m/z* (EI) 384.0684 ($M^+ - H_2O$, 1%, $C_{18}H_{17}F_3O_5S - H_2O$ requires 384.0644), 382 (5), 227 (60), 199 (100), 171 (40), 148 (67).

1-(4-Chlorophenyl)-3,4,4-trifluoro-2-(tosyloxy)but-2-en-1-ol 3d. Mp 64.5–65.4 °C; ν_{max}(KBr)/cm^{-1} 3530, 1708, 1360, 1155; δ_H(200 MHz) 2.45 (3H, s, CH_3) for *Z*-isomer, 2.48 (3H, s, CH_3) for *E*-isomer, 3.11 (1H, br s, OH), 5.65 (1H, d, *J* 1.9, C*H*OH) for *Z*-isomer, 5.83 (1H, d, *J* 3.5, C*H*OH) for *E*-isomer, 6.46 (1H, dt, *J* 50.8, 17.2, CHF_2) for *E*-isomer, 6.82 (1H, dt, *J* 51.9, 14.8, CHF_2) for *Z*-isomer, 7.18–7.36 (4H, m, aryl H), 7.33 and 7.76 (4H, AB quartet, *J* 8.2, aryl H); δ_F −121.2 (2F, dd, *J* 51.9, 16.1, CHF_2), −138.3 (1F, dt, *J* 16.1, 14.8, vinyl F) for *Z*-isomer, −123.7 (2F, ddd, *J* 50.8, 17.7, 12.6, CHF_2), −150.1 (1F, dt, *J* 17.7, 17.2, vinyl F) for *E*-isomer; *m/z* (CI) 391.0192 ($M^+ + 2 + 1 - H_2O$, 12%, $C_{17}H_{15}{}^{37}ClF_3O_4S - H_2O$ requires 391.0302), 389.0231 ($M^+ + 1 - H_2O$, 32%, $C_{17}H_{15}{}^{35}ClF_3O_4S - H_2O$ requires 389.0332), 316 (7), 235 (7), 213 (6).

3,4,4-Trifluoro-1-(1-naphthyl)-2-(tosyloxy)but-2-en-1-ol 3e. ν_{max}(film)/cm^{-1} 3520, 1703, 1380, 1174; δ_H(60 MHz) 2.28 (3H, s, CH_3) for *Z*-isomer, 2.32 (3H, s, CH_3) for *E*-isomer, 3.56 (1H, d, *J* 4.2, OH), 6.17 (1H, m, C*H*OH), 6.25 (1H, dt, *J* 51.3, 16.6, CHF_2) for *E*-isomer, 6.78 (1H, dt, *J* 51.9, 16.3, CHF_2) for *Z*-isomer, 6.9–8.1 (11H, m, aryl H); δ_F −122.5 (2F, ddd, *J* 51.3, 17.5, 1.7, CHF_2), −138.2 (1F, dt, *J* 17.5, 16.3, vinyl F) for *Z*-isomer, −123.5 (2F, ddd, *J* 51.9, 19.0, 19.0, CHF_2), −148.1 (1F, dt, *J* 19.0, 16.6, vinyl F) for *E*-isomer; *m/z* (CI) 422.0791 ($M^+ + 1$, 9%, $C_{21}H_{17}F_3O_4S$ requires 422.0800), 266 (3), 250 (26), 222 (41), 199 (36).

3,4,4-Trifluoro-1-(2-thienyl)-2-(tosyloxy)but-2-en-1-ol 3f. ν_{max}(film)/cm^{-1} 3520, 1708, 1379, 1175; δ_H(60 MHz) 2.37 (3H, s, CH_3), 3.83 (1H, s, OH), 5.79 (1H, br s, C*H*OH) for *Z*-isomer, 5.90 (1H, br s, C*H*OH) for *E*-isomer, 6.35 (1H, dt, *J* 51.6, 16.7, CHF_2) for *E*-isomer, 6.7–7.4 (3H, m, aryl H), 6.77 (1H, dt, *J* 51.8, 15.8, CHF_2) for *Z*-isomer, 7.12 (4H, s, aryl H), 7.22 and 7.73 (4H, AB quartet, *J* 8.7, aryl H); δ_F −121.9 (2F, dd, *J* 51.8, 17.2, CHF_2), −138.8 (1F, ddt, *J* 17.2, 15.8, 2.7, vinyl F) for *Z*-isomer, −123.6 (2F, ddd, *J* 51.6, 17.8, 14.8, CHF_2), −149.2 (1F, ddt, *J* 17.8, 16.7, 2.8, vinyl F) for *E*-isomer; *m/z* (CI) 361.0171 ($M^+ + 1 - H_2O$, 100%, $C_{15}H_{14}F_3O_4S_2 - H_2O$ requires 361.0181), 295 (8), 277 (12), 241 (10), 227 (10), 177 (10).

(5*E*)-1,1,2-Trifluoro-3-(tosyloxy)hepta-2,5-dien-4-ol 3g. ν_{max}(film)/cm^{-1} 3525, 1705, 1667, 1375, 1175; δ_H(200 MHz) 1.69 (3H, d, *J* 6.4, CH_3), 2.44 (3H, s, CH_3) for *Z*-isomer, 2.46 (3H, s, CH_3) for *E*-isomer, 3.0–3.6 (1H, br s, OH), 4.96 (1H, m, C*H*OH) for *Z*-isomer, 5.09 (1H, m, C*H*OH) for *E*-isomer, 5.50 (1H, ddd, *J* 15.3, 6.6, 1.4, vinyl H), 5.79 (1H, dq, *J* 15.3, 6.4, vinyl H), 6.28 (1H, dt, *J* 51.4, 17.1, CHF_2) for *E*-isomer, 6.80 (1H, dt, *J* 51.8, 16.2, CHF_2) for *Z*-isomer, 7.36 and 7.85 (4H, AB quartet, *J* 8.3, aryl H); δ_F −122.6 (2F, dd, *J* 51.8, 17.8, CHF_2), −140.9 (1F, dt, *J* 17.8, 16.2, vinyl F) for *Z*-isomer, −123.9 (2F, ddd, *J* 51.4, 18.1, 7.7, CHF_2), −151.3 (1F, dd, *J* 18.1, 17.1, vinyl F) for *E*-isomer; *m/z* (CI) 319.0614 ($M^+ + 1 - H_2O$, 7%, $C_{14}H_{16}F_3O_4S - H_2O$ requires 319.0616), 277 (3), 227 (3), 216 (9), 207 (3), 195 (4), 182 (4), 164 (100).

(5*E*)-1,1,2-Trifluoro-6-phenyl-3-(tosyloxy)hexa-2,5-dien-4-ol 3h. ν_{max}(film)/cm^{-1} 3540, 1708, 1654, 1380, 1178; δ_H(200 MHz) 2.39 (3H, s, CH_3), 3.68 (1H, br s, OH), 5.17 (1H, br s, C*H*OH) for *Z*-isomer, 5.32 (1H, br s, C*H*OH) for *E*-isomer, 6.13 (1H, dd, *J* 15.9, 5.9, vinyl H) for *E*-isomer, 6.16 (1H, dd, *J* 15.8, 6.3, vinyl H) for *Z*-isomer, 6.32 (1H, dt, *J* 51.4, 17.1, CHF_2) for *E*-isomer, 6.61 (1H, dd, *J* 15.9, 1.4, vinyl H) for *E*-isomer, 6.63 (1H, dd, *J* 15.8, 1.1, vinyl H) for *Z*-isomer, 6.83 (1H, dt, *J* 51.8, 16.0, CHF_2) for *Z*-isomer, 7.15–7.38 (m, 5H, aryl H), 7.29 and 7.83 (4H, AB quartet, *J* 8.3, aryl H); δ_F −122.1 (2F, dd, *J* 51.8, 17.0, CHF_2), −139.4 (1F, ddt, *J* 17.0, 16.0, 2.9, vinyl F) for *Z*-isomer, −123.7 (2F, ddd, *J* 51.4, 18.3, 7.7, CHF_2), −150.2 (1F, ddt, *J* 18.3, 17.1, 2.9, vinyl F) for *E*-isomer; *m/z* (CI) 381.0749 ($M^+ + 1 - H_2O$, 85%, $C_{19}H_{18}F_3O_4S - H_2O$ requires 381.0773), 367 (22), 279 (16), 265 (10), 223 (82), 209 (100).

1,1,2-Trifluoro-3-(tosyloxy)hept-2-en-4-ol 3i. *Z*-isomer: ν_{max}(film)/cm^{-1} 3540, 1708, 1374, 1174; δ_H(60 MHz) 0.5–2.0 (7H, m, $CH_2CH_2CH_3$), 2.41 (3H, s, CH_3), 3.06 (1H, d, *J* 6.0, OH), 4.47 (1H, d, *J* 6.0, C*H*OH), 6.64 (1H, dt, *J* 51.4, 15.3, CHF_2), 7.31 and 7.85 (4H, AB quartet, *J* 10.8, aryl H); δ_F −121.5 (2F, ddd, *J* 51.4, 16.9, 6.0, CHF_2), −139.7 (1F, dt, *J* 16.9, 15.3, vinyl F). *E*-Isomer: ν_{max}(film)/cm^{-1} 3540, 1705, 1380, 1176; δ_H(60 MHz) 0.5–2.1 (7H, $CH_2CH_2CH_3$), 2.47 (3H, s, CH_3), 3.10 (1H, s, OH), 4.60 (1H, br s, C*H*OH), 6.15 (1H, dt, *J* 51.0, 16.8, CHF_2), 7.38 and 7.82 (4H, AB quartet, *J* 8.8, aryl H); δ_F −123.8 (2F, ddd, *J* 51.0, 26.1, 16.9, CHF_2), −152.9 (1F, ddt, *J* 16.9, 16.8, 3.2, vinyl F); *m/z* (CI) 321.0780 ($M^+ + 1 - H_2O$, 15%, $C_{14}H_{18}F_3O_4S - H_2O$ requires 321.0773), 301 (19), 155 (100).

1,1,2-Trifluoro-5,5-dimethyl-3-(tosyloxy)hex-2-en-4-ol 3j. ν_{max}(film)/cm^{-1} 3550, 1700, 1374, 1178; δ_H(200 MHz) 0.95 [9H, s, $C(CH_3)_3$], 2.45 (3H, s, CH_3), 3.26 (1H, d, *J* 4.9, OH), 4.27 (1H, s, C*H*OH), 6.77 (1H, ddt, *J* 51.7, 17.2, 2.0, CHF_2), 7.36 and 7.88 (4H, AB quartet, *J* 8.3, aryl H) for *Z*-isomer, 0.90 [9H, s, $C(CH_3)_3$], 2.49 (3H, s, CH_3), 2.61 (1H, br s, OH), 4.38 (1H, br s, C*H*OH), 6.47 (1H, ddt, *J* 51.3, 17.3, 1.3, CHF_2), 7.41 and 7.91 (4H, AB quartet, *J* 7.9, aryl H) for *E*-isomer; δ_F −123.8 (2F, ddd, *J* 51.7, 17.5, 17.4, CHF_2), −141.4 (ddt, *J* 17.4, 17.2, 3.1, 1F, vinyl F) for *Z*-isomer, −124.3 (2F, ddd, *J* 51.3, 46.4, 18.9, CHF_2), −150.3 (1F, ddt, *J* 18.9, 17.3, 2.9, vinyl F) for *E*-isomer; *m/z* (CI) 335.0932 ($M^+ + 1 - H_2O$, 3%, $C_{15}H_{20}F_3O_4S - H_2O$ requires 335.0929), 296 (1), 276 (2), 163 (100).

4-Ethyl-1,1,2-trifluoro-3-(tosyloxy)hex-2-en-1-ol 3k. ν_{max}(film)/cm^{-1} 3540, 1680, 1370, 1172; δ_H(60 MHz) 0.92 [6H, t, *J* 7.0, $C(CH_2CH_3)_2$], 1.2–2.2 [5H, m, $C(CH_2CH_3)_2$ and OH], 2.43 (3H, s, CH_3), 7.09 (1H, dt, *J* 52.5, 17.6, CHF_2) 7.28 and 7.80 (4H, AB quartet, *J* 10.4, aryl H) for *Z*-isomer, 0.92 [6H, t, *J* 7.0, $C(CH_2CH_3)_2$], 1.4–2.4 [4H, m, $C(CH_2CH_3)_2$], 2.45 (3H, s, CH_3), 2.68 (1H, s, OH), 6.29 (1H, dt, *J* 51.2, 16.8, CHF_2), 7.1–8.1 (4H, m, aryl H) for *E*-isomer; δ_F −122.1 (2F, dd, *J* 52.5, 17.9, CHF_2), −137.1 (1F, dd, *J* 17.9, 17.6, vinyl F) for *Z*-isomer, −122.7 (2F, dd, *J* 51.2, 18.6, CHF_2), −148.4 (1F, dt, *J* 18.6, 16.8, vinyl F) for *E*-isomer; *m/z* (CI) 335.0920 ($M^+ + 1 - H_2O$, 32%, $C_{15}H_{20}F_3O_4S - H_2O$ requires 335.0930), 295 (12), 241 (5), 227 (7), 213 (7), 180 (31), 163 (100).

2,3,3-Trifluoro-1-(trimethylsilyl)prop-1-enyl toluene-*p*-sulfonate 3l. *Z*-Isomer: mp 71.0–72.2 °C; ν_{max}(KBr)/cm^{-1} 1652, 1365, 1174; δ_H(60 MHz) 0.31 [9H, s, Si(CH$_3$)$_3$], 2.42 (3H, s, CH$_3$), 5.96 (1H, dt, *J* 51.0, 17.6, CHF$_2$), 7.29 and 7.70 (4H, AB quartet, *J* 8.2, aryl H); δ_F −124.8 (2F, dd, *J* 51.0, 18.8, CHF$_2$), −143.5 (1F, dt, *J* 18.8, 17.6, vinyl F); *m*/*z* (CI) 338.0683 (M$^+$ + 1, 3%, $C_{13}H_{18}F_3O_3SSi$ requires 339.0620), 323 (83), 266 (7), 229 (8). *E*-Isomer: mp 78.5–79.0 °C; ν_{max}(KBr)/cm^{-1} 1646, 1363, 1170; δ_H(200 MHz) 0.36 [9H, s, Si(CH$_3$)$_3$], 2.45 (3H, s, CH$_3$), 6.12 (1H, ddd, *J* 51.8, 50.5, 15.1, CHF$_2$), 7.34 and 7.81 (4H, AB quartet, *J* 8.4, aryl H); δ_F −120.3–(−121.8) (2F + 1F, m, CHF$_2$ and vinyl F); *m*/*z* (CI) 339.0698 (M$^+$ + 1, 4%, $C_{13}H_{18}F_3O_3SSi$ requires 339.0620), 323 (37), 212 (5), 165 (6).

2,3,3-Trifluoro-1-(tributylstannyl)prop-1-enyl toluene-*p*-sulfonate 3m. *Z*-Isomer: ν_{max}(film)/cm^{-1} 1729, 1382, 1179; δ_H(60 MHz) 0.7–1.9 (27H, m, 3 × C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 2.41 (3H, s, CH$_3$), 5.84 (1H, dt, *J* 51.5, 17.6, CHF$_2$), 7.21 and 7.62 (4H, AB quartet, *J* 8.2, aryl H); δ_F −124.5 (2F, dd, *J* 51.5, 20.3, CHF$_2$), −147.3 (1F, dt, *J* 20.3, 17.6, vinyl F); *m*/*z* (EI) no parent to 556, 499 (M$^+$ − Bu^n, 42), 155 (78), 91 (100). *E*-Isomer: ν_{max}(film)/cm^{-1} 1658, 1375, 1175; δ_H(60 MHz) 0.6–1.7 (27H, 3 × C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 2.36 (3H, s, CH$_3$), 5.74 (1H, dt, *J* 51.0, 12.0, CHF$_2$), 7.12 and 7.59 (4H, AB quartet, *J* 8.0, aryl H); δ_F −119.8 (2F, m, CHF$_2$), −147.6 (1F, dt, *J* 20.7, 12.0, vinyl F); *m*/*z* (EI) no parent to 556, 541 (M$^+$ − Me, 43), 499 (M$^+$ − Bu^n, 17), 325 (10), 155 (78), 91 (100).

2,3,3-Trifluoro-1-methylprop-1-enyl toluene-*p*-sulfonate 3n. *Z*-Isomer: mp 56.0–57.0 °C; ν_{max}(KBr)/cm^{-1} 1725, 1375, 1175; δ_H(60 MHz) 2.04 (3H, dt, *J* 4.4, 3.0, CH$_3$), 2.48 (3H, s, CH$_3$), 6.16 (1H, dt, *J* 51.0, 12.4, CHF$_2$), 7.22 and 7.77 (4H, AB quartet, *J* 9.6, aryl H); δ_F −120.1 (2F, ddq, *J* 51.0, 16.6, 3.0, CHF$_2$), −142.2 (1F, dqt, *J* 16.6, 12.4, 4.4, vinyl F); *m*/*z* (CI) 281 (M$^+$ + 1, 41), 155 (100), 139 (3), 91 (63). *E*-Isomer: mp 31.0–31.5 °C; ν_{max}(KBr)/cm^{-1} 1720, 1371, 1155; δ_H(200 MHz) 2.01 (3H, dt, *J* 5.5, 3.7, CH$_3$), 2.48 (3H, s, CH$_3$), 6.18 (1H, dt, *J* 51.4, 17.8, CHF$_2$), 7.41 and 7.83 (4H, AB quartet, *J* 8.5, aryl H); δ_F −123.0 (2F, ddq, *J* 51.4, 17.3, 3.7, CHF$_2$), −156.0 (1F, dqt, *J* 17.8, 17.3, 5.5, vinyl F); *m*/*z* (CI) 281 (M$^+$ + 1, 0.1), 261 (9), 155 (100), 139 (3), 91 (72).

3,4,4,4-Tetrafluoro-1-phenyl-2-(tosyloxy)but-2-en-1-ol 4a. ν_{max}(film)/cm^{-1} 3533, 1700, 1382, 1171; δ_H(200 MHz) 2.42 (3H, s, CH$_3$), 3.20 (1H, br s, OH), 5.76 (1H, m, C*H*OH), 7.29 (5H, s, aryl H), 7.30 and 7.76 (4H, AB quartet, *J* 8.24, aryl H): δ_F −63.1 (3F, d, *J* 8.5, CF$_3$), −130.4 (1F, dq, *J* 8.5, 1.5, vinyl F); *m*/*z* (CI) 373.0528 (M$^+$ + 1 − H$_2$O, 90%, $C_{17}H_{15}F_4O_4S - H_2O$ requires 373.0522), 261 (70), 235 (11).

1-(4-Chlorophenyl)-3,4,4,4-tetrafluoro-2-(tosyloxy)but-2-en-1-ol 4b. ν_{max}(film)/cm^{-1} 3530, 1700, 1379, 1150; δ_H(200 MHz) 2.44 (3H, s, CH$_3$), 3.59 (1H, br s, OH), 5.73 (1H, br s, C*H*OH), 7.17 and 7.25 (4H, AB quartet, *J* 9.0, aryl H), 7.31 and 7.74 (4H, AB quartet, *J* 8.4, aryl H); δ_F −63.0 (3F, d, *J* 8.5, CF$_3$), −131.5 (1F, q, *J* 8.5, vinyl H); *m*/*z* (CI) 409.0091 (M$^+$ + 2 + 1 − H$_2$O, 10%, $C_{17}H_{14}{}^{37}ClF_4O_4S - H_2O$ requires 409.0103), 407.0123 (M$^+$ + 1 − H$_2$O, 34%, $C_{17}H_{14}{}^{35}ClF_4O_4S - H_2O$ requires 407.0132), 323 (4), 295 (5), 277 (9), 227 (9).

3,4,4,4-Tetrafluoro-1-thienyl-2-(tosyloxy)but-2-en-1-ol 4c. Mp 74.8–75.8 C; ν_{max}(KBr)/cm^{-1} 3508, 1692, 1367, 1185; δ_H(200 MHz) 2.46 (3H, s, CH$_3$), 3.26 (1H, br s, OH), 5.97 (1H, br s, C*H*OH), 6.94–7.31(3H, m, aryl H), 7.35 and 7.85 (4H, AB quartet, *J* 8.4, aryl H): δ_F −63.5 (3F, d, *J* 8.5, CF$_3$), −132.5 (1F, dq, *J* 8.5, 1.5, vinyl F); *m*/*z* (CI) 379.0092 (M$^+$ + 1 − H$_2$O, 93%, $C_{15}H_{13}F_4O_4S_2 - H_2O$ requires 379.0086), 317 (14), 291 (12), 267 (17).

(5*E*)-1,1,1,2-Tetrafluoro-6-phenyl-3-(tosyloxy)hexa-2,5-dien-4-ol 4d. ν_{max}(film)/cm^{-1} 3530, 1700, 1650, 1377, 1171; δ_H(200 MHz) 2.39 (3H, s, CH$_3$), 3.20 (1H, br s, OH), 5.29 (1H, d, *J* 6.0, C*H*OH), 6.16 (1H, dd, *J* 15.9, 6.0, vinyl H), 6.63 (1H, dd, *J* 15.9, 1.1, vinyl H), 7.24–7.33 (5H, m, aryl H), 7.28 and 7.85 (4H, AB quartet, *J* 8.3, aryl H); δ_F −63.5 (3F, d, *J* 8.5, CF$_3$), −132.9 (1F, q, *J* 8.5, vinyl F); *m*/*z* (CI) 399.0683 (M$^+$ + 1 − H$_2$O, 74%, $C_{19}H_{17}F_4O_4S - H_2O$ requires 399.0679), 335 (15), 244 (88), 227 (100).

1,1,1,2-Tetrafluoro-3-(tosyloxy)hept-2-en-4-ol 4e. ν_{max}(film)/cm^{-1} 3542, 1700, 1375, 1173; δ_H(200 MHz) 0.92 (3H, t, *J* 7.2, CH$_2$CH$_2$C*H*$_3$), 1.2–1.8 (4H, m, C*H*$_2$C*H*$_2$CH$_3$), 2.47 (3H, s, CH$_3$), 2.75 (1H, d, *J* 6.3, OH), 4.58 (1H, dt, *J* 6.3, 6.2, C*H*OH), 7.38 and 7.91 (4H, AB quartet, *J* 8.5, aryl H): δ_F −63.6 (3F, d, *J* 9.0, CF$_3$), −133.3 (1F, dq, *J* 9.0, 0.9, vinyl F); *m*/*z* (CI) 339.0683 (M$^+$ + 1 − H$_2$O, 86%, $C_{14}H_{17}F_4O_4S - H_2O$ requires 339.0679), 257 (5), 239 (5), 227 (90), 209 (17), 184 (14).

2,3,3,3-Tetrafluoro-1-(trimethylsilyl)prop-1-enyl toluene-*p*-sulfonate 4g. Mp 45.2–46.0 °C; ν_{max}(KBr)/cm^{-1} 1642, 1342, 1179; δ_H(200 MHz) 0.35 [9H, s, Si(CH$_3$)$_3$], 2.45 (3H, s, CH$_3$), 7.35 and 7.81 (4H, AB quartet, *J* 8.4, aryl H); δ_F −66.0 (3F, d, *J* 10.4, CF$_3$), −117.4 (1F, q, *J* 10.4, vinyl F); *m*/*z* (CI) 357.0593 (M$^+$ + 1, 7%, $C_{13}H_{17}F_4O_3SSi$ requires 357.0599).

Typical procedure for the synthesis of (*Z*)-1,1-difluoro-3-(tosyloxy)alk-3-en-2-one 6

To a solution of **3a** (601 mg, 1.62 mmol, *Z*:*E* = 83:17) in THF (1.6 ml) was added concentrated H$_2$SO$_4$ (1.632 g, 16.2 mmol) at such a rate that the temperature should not rise above 0 °C. This mixture was stirred at room temperature for 30 min, followed by quenching with crushed ice and water (50 ml). The resulting mixture was extracted with diethyl ether (50 ml × 3). The extracts were washed with saturated aqueous NaHCO$_3$ (30 ml × 2) and brine (30 ml × 3), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated. The residue was chromatographed on a column of silica gel eluting with benzene to afford (*Z*)-1,1-difluoro-4-phenyl-3-(tosyloxy)but-3-en-2-one (**6a**) (467 mg, 82%, *Z*:*E* = >97:<3). The results are summarized in Table 4.

(*Z*)-1,1-Difluoro-4-phenyl-3-(tosyloxy)but-3-en-2-one 6a. Mp 77.8–78.1 °C; ν_{max}(KBr)/cm^{-1} 1688, 1618, 1590, 1370, 1165; δ_H(200 MHz) 2.32 (3H, s, CH$_3$), 6.39 (1H, dt, *J* 53.4, 0.8, CHF$_2$), 7.12 and 7.69 (4H, AB quartet, *J* 8.1, aryl H), 7.17–7.42 (5H, m, aryl H), 7.32 (1H, s, vinyl H); δ_F −122.8 (2F, d, *J* 53.4); *m*/*z* (EI) 352.0581 (M$^+$, 3%, $C_{17}H_{14}F_2O_4S$ requires 352.0581), 245 (9).

(*Z*)-1,1-Difluoro-4-(4-methylphenyl)-3-(tosyloxy)but-3-en-2-one 6b. Mp 50.5–50.7 °C; ν_{max}(KBr)/cm^{-1} 1680, 1595, 1373, 1168; δ_H(200 MHz) 2.33 (3H, s, CH$_3$), 2.35 (3H, s, CH$_3$), 6.34 (1H, t, *J* 53.4, CHF$_2$), 7.07 and 7.47 (4H, AB quartet, *J* 8.5, aryl H), 7.16 and 7.73 (4H, AB quartet, *J* 8.5, aryl H), 7.31 (s, 1H, vinyl H); δ_F −122.0 (2F, d, *J* 53.4, CHF$_2$); *m*/*z* (EI) 366.0737 (M$^+$, 13%, $C_{18}H_{16}F_2O_4S$ requires 366.0738), 259 (18), 211 (21), 195 (3), 183 (100), 163 (6), 132 (46), 104 (39).

1,1-Difluoro-4-(4-methoxyphenyl)-3-(tosyloxy)but-3-en-2-one 6c. Mp 79.5–79.9 °C; ν_{max}(KBr)/cm^{-1} 1688, 1588, 1374, 1168; δ_H(200 MHz) 2.36 (3H, s, CH$_3$), for *Z*-isomer, 2.45 (3H, s, CH$_3$), for *E*-isomer, 3.81 (3H, s, OCH$_3$), 6.29 (1H, t, *J* 53.5, CHF$_2$) for *E*-isomer, 6.32 (1H, t, *J* 53.5, CHF$_2$) for *Z*-isomer, 6.64 (1H, s, vinyl H) for *E*-isomer, 6.78 and 7.60 (4H, AB quartet, *J* 9.0, aryl H), 7.20 and 7.77 (4H, AB quartet, *J* 8.6, aryl H), 7.31 (1H, s) for *Z*-isomer; δ_F −126.2 (2F, d, *J* 53.5, CHF$_2$) for *E*-isomer, −121.2 (2F, d, *J* 53.5, CHF$_2$) for *Z*-isomer; *m*/*z* (EI) 382.0683 (M$^+$, 6%, $C_{18}H_{16}F_2O_5S$ requires 382.0687), 227 (82), 199 (100), 171 (43).

(*Z*)-1,1-Difluoro-4-(4-chlorophenyl)-3-(tosyloxy)but-3-en-2-one 6d. Mp 54.8–55.1 °C; ν_{max}(KBr)/cm^{-1} 1692, 1620, 1586, 1370, 1168; δ_H(200 MHz) 2.40 (3H, s, CH$_3$) for *Z*-isomer, 2.50 (3H, s, CH$_3$) for *E*-isomer, 6.28 (1H, dt, *J* 53.3, CHF$_2$) for *E*-isomer, 6.37 (1H, dt, *J* 53.3, 0.7, CHF$_2$) for *Z*-isomer, 6.67 (1H, s, vinyl H) for *E*-isomer, 7.19 (4H, AB quartet, *J* 8.0, aryl H), 7.23 and 7.49 (4H, AB quartet, *J* 8.5, aryl H), 7.31 (1H, s, vinyl H) for *Z*-isomer; δ_F −122.5 (2F, d, *J* 53.3, CHF$_2$); *m*/*z* (EI) 388.0179 (M$^+$ + 2, 3%, $C_{17}H_{13}{}^{37}ClF_2O_4S$ requires 388.0162), 386.0183 (M$^+$, 9%, $C_{17}H_{13}{}^{35}ClF_2O_4S$ requires 386.0190), 215 (3), 175 (36), 156 (17).

(*Z*)-1,1-Difluoro-4-(1-naphthyl)-3-(tosyloxy)but-3-en-2-one 6e. Mp 102.5–103.1 °C; ν_{max}(KBr)/cm^{-1} 1705, 1622, 1592, 1363, 1167; δ_H(200 MHz) 1.85 (3H, s, CH_3), 6.5–6.6 (2H, m, aryl H), 6.57 (1H, t, *J* 53.3, CHF_2), 7.22–7.35 (3H, m, aryl H + vinyl H), 7.42–7.53 (2H, m, aryl H), 7.56–7.68 (2H, m, aryl H), 7.69–7.81 (2H, m, aryl H), 7.97 (1H, s, aryl H); δ_F −123.5 (2F, d, *J* 53.3, CHF_2); *m*/*z* (EI) 402.0734 (M$^+$, 18%, $C_{21}H_{16}F_2O_4S$ requires 402.0738), 247 (75), 219 (67) (Found: C, 62.52; H, 4.03. $C_{21}H_{16}F_2O_4S$ requires C, 62.68; H, 4.01%).

(*Z*)-1,1-Difluoro-4-(2-thienyl)-3-(tosyloxy)but-3-en-2-one 6f. Mp 80.8–81.2 °C; ν_{max}(KBr)/cm^{-1} 1694, 1608, 1373, 1172; δ_H(200 MHz) 2.40 (3H, s, CH_3), 6.27 (1H, t, *J* 53.4, CHF_2), 7.06 (1H, dd, *J* 5.2, 3.8, aryl H), 7.29 and 7.87 (4H, AB quartet, *J* 8.5, aryl H), 7.51 (1H, dm, *J* 3.8, aryl H), 7.60 (1H, dm, *J* 5.2, aryl H), 7.61 (1H, s, vinyl H); δ_F −121.3 (2F, d, *J* 53.4, CHF_2); *m*/*z* (EI) 358.0142 (M$^+$, 13%, $C_{15}H_{12}F_2O_4S_2$ requires 358.0146), 267 (16), 236 (9), 217 (11), 203 (74), 175 (100), 163 (7), 147 (73) (Found: C, 50.07; H, 3.42. $C_{15}H_{12}F_2O_4S_2$ requires C, 50.27; H, 3.37%).

(3*Z*,5*E*)-1,1-Difluoro-3-(tosyloxy)hepta-3,5-dien-2-one 6g. ν_{max}(film)/cm^{-1} 1708, 1630, 1597, 1377, 1174; δ_H(200 MHz) 1.83 (3H, dd, *J* 6.5, 0.7, CH_3), 2.46 (3H, s, CH_3), 6.16 (1H, t, *J* 53.4, CHF_2), 6.25 (1H, ddq, *J* 15.2, 10.4, 0.7, vinyl H), 6.40 (1H, dq, *J* 15.2, 6.5, vinyl H), 7.14 (1H, d, *J* 10.4, vinyl H), 7.37 and 7.88 (4H, AB quartet, *J* 8.2, aryl H); δ_F −121.8 (2F, d, *J* 53.4, CHF_2); *m*/*z* (EI) 316.0572 (M$^+$, 4%, $C_{14}H_{14}F_2O_4S$ requires 316.0581), 237 (5), 225 (6), 161 (11), 149 (3), 139 (19).

(2*E*,4*E*)-1,1,2-Trifluoro-3-(tosyloxy)hepta-2,4,6-triene (2*E*,4*E*)-8g. ν_{max}(film)/cm^{-1} 1672, 1597, 1384, 1178; δ_H(60 MHz) 2.43 (3H, s, CH_3), 4.9–5.4 (2H, m, 2 × vinyl H), 6.0–6.3 (3H, m, 3 × vinyl H), 6.23 (1H, dt, *J* 50.8, 17.6, CHF_2), 7.31 and 7.77 (4H, AB quartet, *J* 8.1, aryl H); δ_F −122.6 (2F, dd, *J* 50.8, 18.8, CHF_2), −150.6 (1F, dd, *J* 18.8, 17.6, vinyl F); *m*/*z* (EI) 318.0532 (M$^+$, 3%, $C_{14}H_{13}F_3O_3S$ requires 318.0538), 139 (11), 115 (7), 91 (100), 81 (37), 65 (44).

(2*Z*,4*E*)-1,1,2-Trifluoro-3-(tosyloxy)hepta-2,4,6-triene (2*Z*,4*E*)-8g. ν_{max}(film)/cm^{-1} 1673, 1599, 1384, 1177; δ_H(200 MHz) 2.47 (3H, s, CH_3), 5.29 (1H, m, vinyl H), 5.37 (1H, m, vinyl H), 6.16 (1H, dm, *J* 14.8, vinyl H), 6.27–6.45 (1H, m, vinyl H), 6.41 (1H, dt, *J* 52.0, 12.4, CHF_2), 6.54 (1H, dd, *J* 14.8, 10.7, vinyl H), 7.38 and 7.88 (4H, AB quartet, *J* 7.8, aryl H); δ_F −119.4 (2F, dd, *J* 52.0, 16.9, CHF_2), −136.5 (1F, dd, *J* 16.9, 12.4, vinyl F); *m*/*z* (EI) 318.0548 (M$^+$, 3%, $C_{14}H_{13}F_3O_3S$ requires 318.0538), 139 (11), 115 (7), 91 (100), 81 (37), 65 (44).

(3*Z*,5*E*)-1,1-Difluoro-6-phenyl-3-(tosyloxy)hexa-3,5-dien-2-one 6h. Mp 74.8–75.4 °C; ν_{max}(KBr)/cm^{-1} 1690, 1590, 1368, 1157; δ_H(200 MHz) 2.27 (3H, s, CH_3), 6.25 (1H, t, *J* 53.4, CHF_2), 6.71 (1H, dd, *J* 15.6, 10.9, vinyl H), 6.98 (1H, d, *J* 15.6, vinyl H), 7.23–7.38 (6H, m, aryl H + vinyl H), 7.28 and 7.90 (4H, AB quartet, *J* 8.4, aryl H); δ_F −121.8 (2F, d, *J* 53.4, CHF_2); *m*/*z* (EI) 378.0731 (M$^+$, 13%, $C_{19}H_{16}F_2O_4S$ requires 378.0739), 225 (2), 224 (14), 223 (89), 222 (9), 195 (32) (Found: C, 60.01; H, 4.25. $C_{19}H_{16}F_2O_4S$ requires C, 60.31; H, 4.26%).

Typical procedure for the synthesis of 1,1-difluoro-3-(tosyloxy)-alk-3-en-2-ones (6i and 6k)

To a solution of concentrated H_2SO_4 (1.632 g, 16.16 mmol) and water (92 mg, 5.1 mmol) was added dropwise allyl alcohol **3i** (347 mg, 1.0 mmol, *Z*:*E* = 79:21) at such a rate that the temperature should not rise above 0 °C. This mixture was stirred at room temperature for 30 min, and thereafter was quenched with crushed ice and water (50 ml). The resulting mixture was extracted with diethyl ether (50 ml × 3). The organic extracts were washed with saturated aqueous $NaHCO_3$ (30 ml × 2) and brine (30 ml × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane-benzene (1:1) and then benzene as eluents to afford 1,1,2-trifluoro-3-(tosyloxy)hepta-2,4-diene **9** (78 mg, 24%) and 1,1-difluoro-3-(tosyloxy)hept-3-en-2-one **6i** (152 mg, 47%, *Z*:*E* = >97:<3).

(*Z*)-1,1-Difluoro-3-(tosyloxy)hept-3-en-2-one 6i. ν_{max}(film)/cm^{-1} 1718, 1637, 1594, 1374, 1172; δ_H(60 MHz) 0.89 (3H, t, *J* 7.0, $CH_2CH_2CH_3$), 1.38 (2H, qt, *J* 7.0, 7.0, $CH_2CH_2CH_3$), 2.24 (2H, dt, *J* 7.4, 7.0, $CH_2CH_2CH_3$), 2.42 (3H, s, CH_3), 6.08 (1H, t, *J* 53.0, CHF_2), 6.75 (1H, t, *J* 7.4, vinyl H), 7.29 and 7.81 (4H, AB quartet, *J* 8.2, aryl H); δ_F −121.9 (2F, d, *J* 53.0, CHF_2); *m*/*z* (EI) 319.0818 (M$^+$, 34, $C_{14}H_{17}F_2O_4S$ requires 319.0816), 239 (3), 227 (4), 195 (15), 173 (5), 163 (24), 149 (8), 139 (8), 127 (5).

(2*E*,4*E*)-1,1,2-Trifluoro-3-(tosyloxy)hepta-2,4-diene (2*E*,4*E*)-8i. Mp 31.0–31.5 °C; ν_{max}(KBr)/cm^{-1} 1668, 1632, 1591, 1372, 1168; δ_H(200 MHz) 0.89 (3H, t, *J* 7.5, CH_2CH_3), 2.04 (2H, ddq, *J* 7.5, 5.7, 1.4, CH_2CH_3), 2.48 (3H, s, CH_3), 5.93 (1H, dt, *J* 15.6, 5.7, vinyl H), 6.08 (1H, dt, *J* 15.6, 1.4, vinyl H), 6.35 (1H, dt, *J* 51.3, 18.1, CHF_2), 7.40 and 7.83 (4H, AB quartet, *J* 8.5, aryl H); δ_F −122.6 (2F, dd, *J* 51.3, 20.7, CHF_2), −154.1 (1F, dt, *J* 20.7, 18.1, vinyl F); *m*/*z* (CI) 321 (M$^+$ + 1, 9), 301.0663 (M$^+$ + 1 − HF, 1%, $C_{14}H_{16}F_3O_3S$ − HF requires 301.0711), 300 (4), 139 (3), 91 (100).

(2*Z*,4*E*)-1,1,2-Trifluoro-3-(tosyloxy)hepta-2,4-diene (2*Z*,4*E*)-8i. ν_{max}(film)/cm^{-1} 1680, 1632, 1600, 1380, 1170; δ_H(200 MHz) 0.99 (3H, t, *J* 7.4, CH_2CH_3), 2.15 (2H, ddq, *J* 7.4, 6.3, 1.5, CH_2CH_3), 2.46 (3H, s, CH_3), 5.97 (1H, dt, *J* 15.3, 1.5, vinyl H), 6.20 (1H, dt, *J* 15.3, 6.3, vinyl H), 6.38 (1H, dt, *J* 51.7, 13.7, CHF_2), 7.36 and 7.86 (4H, AB quartet, *J* 8.4, aryl H); δ_F −119.5 (2F, dd, *J* 51.7, 16.9, CHF_2), −140.9 (1F, dt, *J* 16.9, 13.7, vinyl F); *m*/*z* (CI) 321.0764 (M$^+$ + 1, 9%, $C_{14}H_{16}F_3O_3S$ requires 321.0773), 301 (24), 213 (6), 173 (39), 149 (100), 139 (11).

4-Ethyl-1,1-difluoro-3-(tosyloxy)hex-3-en-2-one 6k. Mp 35.5–36.8 °C; ν_{max}(KBr)/cm^{-1} 1716, 1604, 1592, 1360, 1168 cm; δ_H(200 MHz) 0.79 (3H, t, *J* 7.6, CH_2CH_3), 1.04 (3H, t, *J* 7.5, CH_2CH_3), 1.77 (2H, q, *J* 7.6, CH_2CH_3), 2.31 (2H, q, *J* 7.5, CH_2CH_3), 2.48 (3H, s, CH_3), 6.41 (1H, t, *J* 53.7, CHF_2), 7.39 and 7.78 (4H, AB quartet, *J* 8.3, aryl H); δ_F −127.5 (2F, d, *J* 53.7, CHF_2); *m*/*z* (CI) 333.0981 (M$^+$ + 1, 27%, $C_{15}H_{19}F_2O_4S$ requires 333.0984), 313 (18), 227 (12), 213 (7), 177 (25), 161 (53).

4-Ethyl-1,1,2-trifluoro-3-(tosyloxy)hexa-2,4-diene 8k. ν_{max}(film)/cm^{-1} 1700, 1648, 1600, 1498, 1380, 1175; δ_H(200 MHz) 0.89 (3H, t, *J* 7.6, CH_2CH_3) for 2*Z*-isomer, 0.90 (3H, t, *J* 7.0, CH_2CH_3) for 2*E*-isomer, 1.60 (3H, d, *J* 7.1, CH_3) for 2*E*-isomer, 1.72 (3H, d, *J* 7.0, CH_3) for 2*Z*-isomer, 2.01 (2H, q, *J* 7.0, CH_2CH_3) for 2*E*-isomer, 2.08 (2H, q, *J* 7.6, CH_2CH_3) for 2*Z*-isomer, 2.46 (3H, s, CH_3), 5.74 (1H, q, *J* 7.0, vinyl H) for 2*Z*-isomer, 5.80 (1H, q, *J* 7.1, vinyl H) for 2*E*-isomer, 6.03 (1H, ddt, *J* 51.9, 17.1, 0.7, CHF_2) for 2*E*-isomer, 6.14 (1H, ddt, *J* 51.9, 16.3, 0.7, CHF_2) for 2*Z*-isomer, 7.35 and 7.80 (4H, AB quartet, *J* 8.4, aryl H); δ_F −122.8 (2F, dd, *J* 51.9, 18.6, CHF_2), −154.4 (1F, dt, *J* 18.6, 17.1, vinyl F) for 2*E*-isomer, −118.5 (2F, dd, *J* 51.9, 18.2, CHF_2), −143.7 (1F, dt, *J* 51.9, 18.6, vinyl F) for 2*Z*-isomer; *m*/*z* (CI) 335.0922 (M$^+$ + 1, 8%, $C_{15}H_{18}F_3O_3S$ requires 335.0924), 295 (14), 227 (4), 213 (12), 173 (17).

1,1,2-Trifluoro-4,5-dimethyl-3-(tosyloxy)hexa-2,4-diene 10. Mp 46.5–47.6 °C; ν_{max}(KBr)/cm^{-1} 1654, 1600, 1370, 1168; δ_H(200 MHz) 1.55 (3H, s, CH_3), 1.65 (3H, s, CH_3), 1.81 (3H, s, CH_3), 2.45 (3H, s, CH_3), 6.00 (1H, dt, *J* 51.7, 16.9, CHF_2) for 2*Z*-isomer, 6.55 (1H, dt, *J* 51.9, 17.0, CHF_2) for 2*E*-isomer, 7.77 and 7.34 (4H, AB quartet, *J* 8.2, aryl H); δ_F −119.7–(−124.7) (2F, m, CHF_2), −146.9 (1F, dt, *J* 18.4, 15.1, vinyl F) for 2*Z*-isomer, −123.3 (2F, dd, *J* 51.9, 20.0, CHF_2), −74.0 (1F, dt, *J* 20.0, 17.0, vinyl F) for 2*E*-isomer; *m*/*z* (EI) 334.0846 (M$^+$, 9%, $C_{15}H_{17}F_3O_3S$ requires 334.0846), 179 (7), 162 (84).

Typical procedure for the synthesis of (*Z*)-1,1,1-trifluoro-3-(tosyloxy)alk-3-en-2-ones 7

To a THF solution of **4a** (295 mg, 0.76 mmol) was added concentrated H_2SO_4 (756 mg, 7.564 mmol) at 0 °C. The whole mixture was stirred at 70 °C for 1 h, and then was quenched with crushed ice and water (50 ml), followed by extraction with diethyl ether (30 ml × 3). The combined extracts were washed with saturated aqueous $NaHCO_3$ (20 ml × 2) and brine (30 ml × 3), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (benzene : hexane = 2 : 1) to give (*Z*)-1,1,1-trifluoro-4-phenyl-3-(tosyloxy)but-3-ene-2-one (**7a**) (246 mg, 88%, *Z* : *E* = >99 : 1<). The results of the hydrolysis of **4a–e** were summarized in Table 5.

(*Z*)-1,1,1-Trifluoro-4-phenyl-3-(tosyloxy)but-3-en-2-one 7a. ν_{max}(film)/cm^{-1} 1721, 1621, 1598, 1385, 1175; δ_H(200 MHz) 2.37 (3H, s, CH_3), 7.20 and 7.76 (4H, AB quartet, *J* 8.24, aryl H), 7.25–7.73 (5H, m, aryl H), 7.36 (1H, s, vinyl H): δ_F −69.0 (3F, s, CF_3); *m*/*z* (EI) 370.0480 (M$^+$, 4%, $C_{17}H_{13}F_3O_4S$ requires 370.0487), 245 (4), 187 (21).

(*Z*)-4-(4-Chlorophenyl)-1,1,1-trifluoro-3-(tosyloxy)but-3-en-2-one 7b. Mp 51.8–52.5 °C; ν_{max}(KBr)/cm^{-1} 1708, 1617, 1583, 1352, 1173; δ_H(200 MHz) 2.40 (3H, s, CH_3), 7.22 and 7.75 (4H, AB quartet, *J* 8.4, aryl H), 7.29 and 7.58 (4H, AB quartet, *J* 8.6, aryl H), 7.35 (1H, s, vinyl H): δ_F −69.2 (3F, s, CF_3); *m*/*z* (EI) 406.0072 (M$^+$ + 2, 3%, $C_{17}H_{12}{}^{37}ClF_2O_4S$ requires 406.0068), 404.0094 (M$^+$, 6%, $C_{17}H_{12}{}^{35}ClF_3O_4S$ requires 404.0098), 154 (11), 139 (23), 91 (100), 78 (4), 65 (37) (Found: C, 50.26; H, 3.01. $C_{17}H_{12}ClF_3O_4S$ requires C, 50.44; H, 2.99%).

(*Z*)-1,1,1-Trifluoro-4-(2-thienyl)-3-(tosyloxy)but-3-en-2-one 7c. ν_{max}(film)/cm^{-1} 1708, 1607, 1500, 1177; δ_H(200 MHz) 2.42 (3H, s, CH_3), 7.09–7.15 (1H, m, aryl H), 7.32 and 7.90 (4H, AB quartet, *J* 8.4, aryl H), 7.34 (1H, s, vinyl H), 7.61–7.71 (2H, m, aryl H); δ_F −68.9 (3F, s, CF_3); *m*/*z* (EI) 376.0044 (M$^+$, 13%, $C_{15}H_{11}F_3O_4S_2$ requires 376.0051), 329 (4), 317 (5), 267 (7), 236 (4), 221 (56).

(3*Z*,5*E*)-1,1,1-Trifluoro-6-phenyl-3-(tosyloxy)hexa-3,5-dien-2-one 7d. Mp 86.0–87.0 °C; ν_{max}(KBr)/cm^{-1} 1704, 1607, 1583, 1379, 1150; δ_H(200 MHz) 2.37 (3H, s, CH_3), 6.98 (1H, dd, *J* 15.6, 10.3, vinyl H), 7.13 (1H, d, *J* 15.6, vinyl H), 7.28 (1H, d, *J* 10.3, vinyl H), 7.34–7.46 (5H, m, aryl H), 7.35 and 7.94 (4H, AB quartet, *J* 8.4, aryl H); δ_F −69.2 (3F, s, CF_3); *m*/*z* (EI) 396.0641 (M$^+$, 18%, $C_{19}H_{15}F_3O_4S$ requires 396.0644), 241 (100).

(*Z*)-1,1,1-Trifluoro-3-(tosyloxy)hept-3-en-2-one 7e. ν_{max}(film)/cm^{-1} 1729, 1638, 1598, 1383, 1150; δ_H(300 MHz) 0.96 (3H, t, *J* 7.4 Hz, $CH_2CH_2CH_3$), 1.54 (2H, qt, *J* 7.5, 7.4, $CH_2CH_2CH_3$), 2.44 (2H, dt, *J* 7.5, 7.5, $CH_2CH_2CH_3$), 2.47 (3H, s, CH_3), 6.88 (1H, qt, *J* 7.5, 0.9, vinyl H), 7.38 and 7.90 (4H, AB quartet, *J* 8.4, aryl H); δ_F −69.5 (3F, s, CF_3); *m*/*z* (EI) 337.0713 (M$^+$, 65%, $C_{14}H_{16}F_3O_4S$ requires 337.0722), 277 (15), 239 (12), 227 (16), 195 (49), 173 (14), 158 (11), 139 (30).

(2*Z*,4*E*)-1,1,1,2-Tetrafluoro-3-(tosyloxy)hepta-2,4-diene 9e. ν_{max}(film)/cm^{-1} 1675, 1632, 1600, 1385, 1179; δ_H(200 MHz) 0.98 (3H, t, *J* 7.4, CH_2CH_3), 2.16 (2H, dq, *J* 7.4, 6.1, CH_2CH_3), 2.47 (3H, s, CH_3), 6.14 (1H, dq, *J* 15.2, 1.1, vinyl H), 6.29 (1H, dt, *J* 15.2, 6.1, vinyl H), 7.38 and 7.87 (4H, AB quartet, *J* 8.2, aryl H); δ_F −64.0 (3F, d, *J* 9.4, CF_3), −138.25 (1F, q, *J* 9.4, vinyl F); *m*/*z* (EI) 338.0597 (M$^+$, 2%, $C_{14}H_{14}F_4O_3S$ requires 338.0600), 183 (4), 173 (10), 157 (25), 139 (16).

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