

"Syn Effect" in Nucleophilic Addition of Amines to 1,3-Dienyl Sulfone and Ethyl (*E*)-2,4-Pentadienoate

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The stereochemistry of nucleophilic addition of amines to (*E*)-1-tosyl-1,3-butadiene was investigated. The Z/E ratios of the resulting allylic sulfones varied with amines, solvents, temperature, and concentration. When diethylamine was reacted in low concentration at high temperature, the corresponding sterically unfavorable (*Z*)-4-amino-2-butenyl sulfone was preferentially obtained. The stereochemistry of nucleophilic addition of amines to ethyl (*E*)-2,4-pentadienoate, which possesses an ester group as a conjugated electron-withdrawing group instead of a *p*-toluenesulfonyl (Ts) group, was also found to realize similar high Z selectivity. The predominant formation of Z isomers in both cases was rationalized by a "syn effect," which might be mainly due to n/$\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity.

Allylic sulfones are versatile synthetic intermediates in organic synthesis.[1] During the course of studies on the preparation of allylic sulfones,[2] we investigated the stereochemistry of isomerization of α-unsubstituted (*E*)-vinylic sulfones to the corresponding allylic sulfones in the presence of a base and found that the sterically unfavorable (*Z*)-allylic sulfones were predominantly formed.[3] This result was rationalized by a "syn effect,"[4] which is primarily caused by $\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity (Figure 1).[5] In studies related to allylic sulfones, the predominant formation of (*Z*)-olefins, which could also be ascribed to the "syn effect," was found in the desulfonylation reaction of α,α-dialkylated (*E*)-allylic sulfones,[5a] the isomerization of (*E*)-α-fluorovinylic sulfones to the corresponding allylic sulfones under basic conditions,[5b] and the desilylation reaction of γ-silylated allylic and vinylic sulfones.[5d] Furthermore, we revealed that the "syn effect" works also in the conversion of (*E*)-α,β-unsaturated esters and aldehydes into the corresponding β,γ-unsaturated esters and silyl enol ethers,[5c,5e] respectively, the elimination reaction of (*E*)-allylic acetates catalyzed by palladium under specific conditions utilizing a base,[5f] and the 1,4-eliminative ring-opening reaction of (*E*)-1-propenyloxirane derivatives by treatment with metal amides.[5g]

For the preparation of allylic sulfones, nucleophilic addition to dienyl sulfones is a useful method. A couple of reactions of conjugate addition to dienyl sulfones have been reported.[6,7] A nucleophilic addition of aniline derivatives to (*E*)-1-tosyl-1,3-butadiene (**1**) in the presence of K_2CO_3 afforded the corresponding (*E*)-allylic sulfones with good to complete stereoselectivity.[6a] Asymmetric conjugate addition of a β-ketoester to (*E*)-1-(benzenesulfonyl)-1,3-butadiene in the presence of K_2HPO_4 also gave the corresponding adduct with complete E selectivity.[6b] Interestingly, it has been reported that addition of a transition-metal reagent, lithium dibutylcuprate, to (*E*)-1-(allylsulfonyl)-1,3-butadiene gave a 65/35 mixture of (*Z*)- and (*E*)-allylic sulfones. Furthermore, the addition of the same lithium dibutylcuprate to **1** was reported to give only (*Z*)-1-tosyl-2-octene in 21% yield.[6c] However, both isomers were obtained in 96% total yield with Z preference (Z/E = 65/35) in our reexamination. This inconsistent result prompted us to investigate the stereochemistry of the nucleophilic addition of various nucleophiles. Among non-metallic compounds, amines showed various stereoselectivities depending on the kinds of amines and reaction conditions. Herein, we describe the results of the stereochemistry of the nucleophilic addition of amines to (*E*)-1-tosyl-1,3-butadiene (**1**)[8] and to ethyl (*E*)-2,4-pentadienoate (**4**).

Results and Discussion

First, the nucleophilic addition of various amines **2a**–**2k** to

Figure 1. Proposed origin of the "syn effect" in the isomerization of α-unsubstituted (*E*)-vinylic sulfones to the corresponding allylic sulfones.

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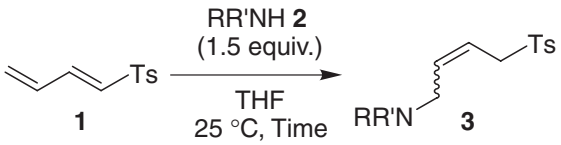
(*E*)-1-tosyl-1,3-butadiene (**1**) was carried out in THF at 25 °C and the results are summarized in Table 1. The Z/E ratios of the resulting allylic sulfones **3a**–**3k** varied depending on the kinds of amines. Primary amines such as propylamine and butylamine gave the corresponding (*E*)-allylic amines mainly (Entries 1 and 2). To the contrary, acyclic secondary amines preferentially formed (*Z*)-allylic amines (Entries 3–5 and 7–9) as opposed to E isomers. Especially, *n*-Pr_2NH and *n*-Bu_2NH showed relatively high Z preference although the reaction was sluggish (Entries 5 and 7). Addition of cyclic secondary amines gave almost equal amounts of (*Z*)- and (*E*)-allylic amines (Entries 10 and 11).

Next, the stereochemistry of the nucleophilic addition of Et_2NH (**2d**) to (*E*)-1-tosyl-1,3-butadiene (**1**) was examined in detail, paying attention to the effect of solvents, temperature, and concentration; the results are summarized in Tables 2 and 3. Ethereal solvents generally afforded the (*Z*)-allylic amine preferentially, but less polar benzene and highly polar CH_3CN and DMSO gave the E isomer mainly as shown in Table 2. It was found that polar and less bulky ethers, such as DME and THF, showed high Z selectivity (Entries 2 and 5). The time-course of the addition reaction checked by ^{1}H NMR in THF-d_8 revealed that the Z/E ratio was almost constant as the reaction proceeded.[9] It is noteworthy that the Z selectivity was enhanced when the reaction was carried

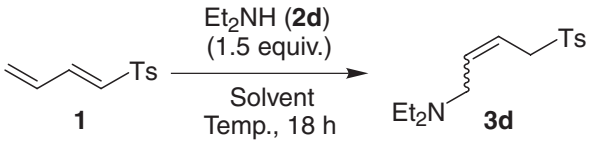
Table 1. Stereochemistry of Nucleophilic Addition of Various Amines **2a**–**2k** to (*E*)-1-Tosyl-1,3-butadiene (**1**)[a]



Entry	RR′NH **2**		Time/h	**1**/**3**[b]	Yield/%[c]	Z/E[d]
1[e]	*n*-$PrNH_2$	**a**	72	11/89	70	21/79
2[e]	*n*-$BuNH_2$	**b**	72	11/89	71	23/77
3	Me_2NH[f]	**c**	24	0/100	91	60/40
4	Et_2NH	**d**	72	19/81	75	74/26
5	*n*-Pr_2NH	**e**	72	52/48	43	85/15
6	*i*-Pr_2NH	**f**	72	100/0	—	—
7	*n*-Bu_2NH	**g**	72	48/52	46	87/13
8	*n*-Bu(Me)NH	**h**	72	0/100	85	72/28
9	*i*-Pr(Me)NH	**i**	72	38/62	58	80/20
10	Pyrrolidine	**j**	6	0/100	83	44/56
11	Piperidine	**k**	12	0/100	85	55/45

a) Concentration of amines **2** was 150 mM (mmol dm^{-3}) in all cases. b) The ratios were determined based on the isolated yields. c) Isolated total yield of **3**. d) The ratios were determined by 400 MHz ^{1}H NMR spectra. e) Formation of $(TsCH_2CH{=}CHCH_2)_2NR$ (R = *n*-Pr, 5%; *n*-Bu, 7%) was observed. f) A commercially available 2.0 M (mol dm^{-3}) solution of Me_2NH in THF was used.

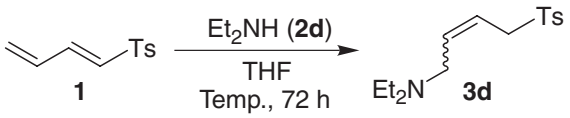
Table 2. Stereochemistry of Nucleophilic Addition of Et_2NH (**2d**) to (*E*)-1-Tosyl-1,3-butadiene (**1**) in Various Solvents[a]



Entry	Solvent	Temp/°C	**1**/**3d**[b]	Yield/%[c]	Z/E[d]
1	DME	0	84/16	16	67/33
2		25	58/42	40	82/18
3		60	33/67	61	88/12
4	THF	0	65/35	28	52/48
5		25	59/41	38	78/22
6		60	27/73	64	86/14
7	1,4-Dioxane	25	32/68	61	64/36
8	THP	25	41/59	48	61/39
9	Et_2O	25	61/39	35	31/69
10	*t*-BuOMe	25	52/48	47	28/72
11	Pyridine	25	3/97	73	71/29
12	*N*-Methylmorpholine	25	71/29	26	63/37
13	*N*-Methylpyrrolidine	25	81/19	15	53/47
14	$CHCl_3$	25	44/56	56	44/56
15	Tetrahydrothiophene	25	0/100	90	41/59
16	Benzene	25	27/73	70	30/70
17	MeCN	25	0/100	98	37/63
18	DMSO	25	0/100	77	27/73

a) Concentration of **2d** was 150 mM in all cases. b) The ratios were determined based on the isolated yields. c) Isolated total yield of **3d**. d) The ratios were determined by 400 MHz ^{1}H NMR spectra.

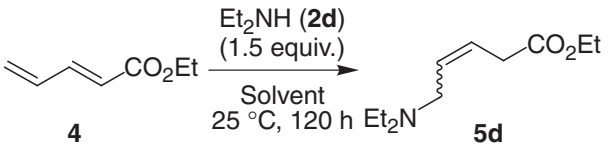
Table 3. Effect of Concentration on Nucleophilic Addition of Et_2NH (**2d**) to (*E*)-1-Tosyl-1,3-butadiene (**1**)



Entry	Concentrations		**2d**/**1**	Temp/°C	**1**/**3d**[a]	Yield/%[b]	Z/E[c]
	1/mM	**2d**/mM					
1	100	150	1.5	25	19/81	75	74/26
2	50	75	1.5	25	51/49	48	93/7
3	25	37.5	1.5	25	64/36	33	96/4
4	25	37.5	1.5	60	38/62	50	96/4
5	3.1	37.5	12.0	60	28/72	72	98/2
6	10	15	1.5	25	86/14	12	94/6

a) The ratios were determined based on the isolated yields. b) Isolated total yield of **3d**. c) The ratios were determined by 400 MHz ^{1}H NMR spectra.

Table 4. Stereochemistry of Nucleophilic Addition of Et_2NH (**2d**) to Ethyl (*E*)-2,4-Pentadienoate (**4**) in Various Solvents[a)]



4 **5d**

Entry	Solvent	**4**/**5d**[b)]	Yield/%[c)]	Z/E[d)]
1	DME	87/13	9	85/15
2	THF	88/12	10	86/14
3	1,4-Dioxane	92/8	6	69/31
4	THP	93/7	5	69/31
5	Et_2O	94/6	4	42/58
6	Pyridine	58/42	30	23/77[e)]
7	$CHCl_3$	91/9	7	34/66
8	Benzene	90/10	7	49/51
9	MeCN	65/35	34	17/83[e)]
10	EtOH	79/21	18	9/91

a) Concentration of Et_2NH (**2d**) was 150 mM in all cases. b) The ratios were determined based on the isolated yields. c) Isolated total yield of **5d** based on **4**. d) The ratios were determined by 400 MHz ^{1}H NMR spectra.[11] e) Isomerization of Z isomer to E isomer was observed during the reaction.

out at higher temperature (Entries 1–6).

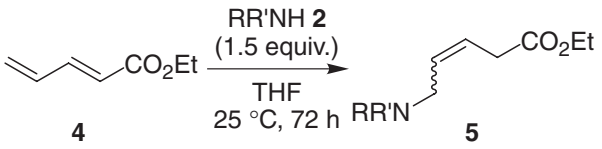
The effect of concentration is shown in Table 3. The lower concentration of Et_2NH remarkably increased the Z selectivity of **3d** (Entries 1–3 and 6), though the reaction became sluggish. Finally, using excess Et_2NH at 60 °C, (*Z*)-allylic sulfone **3d** was obtained in 72% yield with the highest Z selectivity (Entry 5).

As we described above, unprecedented Z selectivity in the conjugate addition of amines to (*E*)-1-tosyl-1,3-butadiene (**1**) was discovered. This phenomenon was suspected to be specific to sulfonyl compounds. Therefore, nucleophilic addition of amines to ethyl (*E*)-2,4-pentadienoate (**4**), which possesses an ester group as a conjugated electron-withdrawing group instead of a *p*-toluenesulfonyl (Ts) group, was next carried out.

Conjugate 1,6-addition reactions to (*E*)-2,4-pentadienoate were reported to generally furnish the corresponding (*E*)-3-pentenoate.[10] For example, addition of nitroalkanes in the presence of Amberlyst A 27 or a lithium salt of a bislactim ether afforded the exclusively E adducts.[10a,10b] Asymmetric conjugate addition of β-ketoesters to (*E*)-2,4-pentadienoate using an inorganic base in the presence of cinchona alkaloids also gave the corresponding adduct with complete E selectivity.[6b] Nickel-catalyzed addition of morpholine has been reported to give an (*E*)-allylic amine.[10c] Addition of organocopper reagents afforded (*E*)-β,γ-unsaturated esters.[10d] Only the transition-metal-catalyzed addition reactions gave (*Z*)-β,γ-unsaturated esters.[10e] Thus, generally 1,6-conjugate addition to 2,4-pentadienoate has been believed to give the (*E*)-β,γ-unsaturated esters at least in the absence of transition-metal catalyst.

First, the stereochemistry of the nucleophilic addition of Et_2NH to **4** was investigated in various solvents as listed in Table 4. Although the reactions were rather sluggish compared with the reaction of (*E*)-1-tosyl-1,3-butadiene (**1**), similar high Z selectivity was realized in polar and less bulky ethers, such as THF and DME, to give the corresponding (*Z*)-5-amino-3-pentenoate **5d** selectively (Table 4, Entries 1 and 2).

Table 5. Stereochemistry of Nucleophilic Addition of Various Amines **2** to **4**[a)]



4 **5**

Entry	RR′NH **2**		**4**/**5**[b)]	Yield/%[c)]	Z/E[d)]
1[e)]	*n*-$PrNH_2$	**a**	86/14	10	7/93
2[e)]	*n*-$BuNH_2$	**b**	89/11	8	11/89
3	Me_2NH[f)]	**c**	52/48	32	76/24
4	Et_2NH	**d**	89/11	9	87/13
5	*n*-Pr_2NH	**e**	96/4	4	90/10
6	*n*-Bu_2NH	**g**	94/6	5	94/6
7	*n*-Bu(Me)NH	**h**	66/34	25	74/26
8	*i*-Pr(Me)NH	**i**	85/15	15	82/18
9	Pyrrolidine	**j**	6/94	90	59/41
10	Piperidine	**k**	39/61	58	68/32

a) Concentration of amines **2** was 150 mM in all cases. b) The ratios were determined based on the isolated yields. c) Isolated total yield of **5** based on **4**. d) The ratios were determined by 400 MHz ^{1}H NMR spectra.[11] e) Formation of 1-alkyl-1,6-dihydropyridin-2(3*H*)-one (alkyl = *n*-Pr, 5%; *n*-Bu, 6%) was observed. f) A commercially available 2.0 M solution of Me_2NH in THF was used.

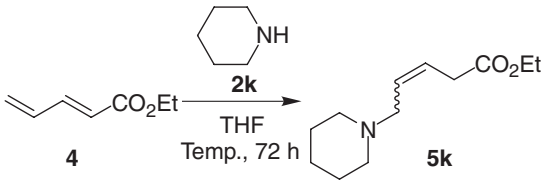
In order to promote the addition reaction, several kinds of proton sources were added to activate the ester carbonyl group and/or to protonate to the anion developing at the α-position. The reaction rate was remarkably accelerated by using proton sources with lower pK_a, however, Z selectivity of **5d** was decreased in contrast.[12]

Although the addition reaction of Et_2NH (**2d**) proceeded with higher stereoselectivity, the chemical yield was poor. Next, we investigated the nucleophilic addition of various amines **2** to **4** in THF at 25 °C. The results are summarized in Table 5. Similar tendency toward Z selectivity in the case of (*E*)-1-tosyl-1,3-butadiene (**1**) was observed: Acyclic secondary amines, especially *n*-Pr_2NH (**2e**) and *n*-Bu_2NH (**2g**), showed relatively high Z selectivity although the chemical yields were poorer (Entries 5 and 6). Pyrrolidine (**2j**), a cyclic secondary amine, showed high chemical yield, but Z selectivity was not particularly good (Entry 9). The reaction rate of nucleophilic addition of piperidine (**2k**) was moderate to afford relatively good Z selectivity (Entry 10).

Thus, the reaction of piperidine (**2k**) to **4** was examined in detail paying attention to the effect of temperature and concentration, and the results are summarized in Table 6. It is noteworthy that the Z selectivity of **5k** was again enhanced when the reaction was carried out at higher temperature (Entries 2–4, 7 and 8) and at lower concentration of piperidine (Entries 1 and 3, 5 and 6) up to 89/11 in 50% yield. On the other hand, the concentration of **4** little affected the Z/E ratio of **5k** (Entries 3 and 5, 6 and 7, and 8 and 9, respectively).

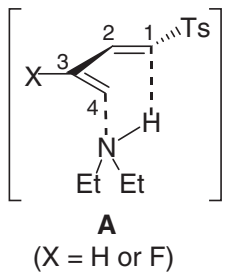
As described above, nucleophilic addition of secondary amines to electron-deficient dienes **1** and **4** realized unprecedented high Z selectivity to give the corresponding sterically

Table 6. Effect of Temperature and Concentration on Nucleophilic Addition of Piperidine (**2k**) to **4**



Entry	Concentrations		**2k**/**4**	Temp/°C	**4**/**5k**[a]	Yield/%[b]	Z/E[c]
	4/mM	**2k**/mM					
1	100	600	6.0	25	0/100	99	34/66
2	100	150	1.5	0	47/53	38	29/71
3	100	150	1.5	25	39/61	58	68/32
4	100	150	1.5	60	14/86	74	72/28
5	25	150	6.0	25	18/82	67	65/35
6	25	37.5	1.5	25	72/28	21	83/17
7	6.25	37.5	6.0	25	72/28	25	81/19
8	6.25	37.5	6.0	60	44/56	50	89/11
9	3.125	37.5	12.0	60	35/65	55	87/13

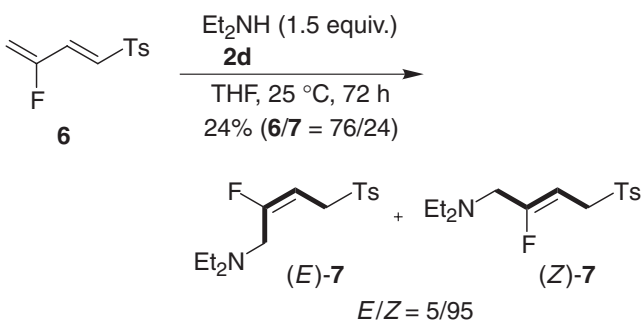
a) The ratios were determined based on the isolated yields. b) Isolated total yield of **5k** based on **4**. c) The ratios were determined by 400 MHz ^{1}H NMR spectra.



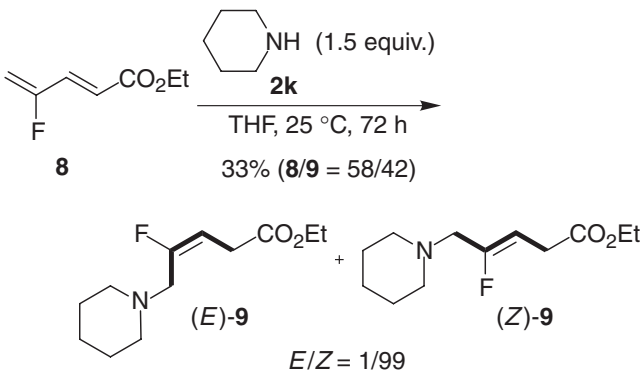
A
(X = H or F)

Figure 2. Another possible origin of the "syn effect:" 1,4-addition.

unfavorable (*Z*)-allylic compounds **3d** and **5k**. The mechanism for predominant formation of (*Z*)-olefins is not yet clear.[13] To confirm the possibility of a concerted 1,4-addition mechanism (Figure 2, **A**), nucleophilic addition of Et_2NH (**2d**) (150 mM) to (*E*)-3-fluoro-1-tosyl-1,3-butadiene (**6**) was investigated (eq 1). Selective formation of (*Z*)-3-fluoro-2-butenyl sulfone derivative (*Z*)-**7** was observed. In addition, nucleophilic addition of piperidine (**2k**) (150 mM) to ethyl (*E*)-4-fluoro-2,4-pentadienoate (**8**) (100 mM) also gave the corresponding Z adduct, (*Z*)-**9**, selectively (eq 2). Selective formations of (*Z*)-olefins, (*Z*)-**7** and (*Z*)-**9**, could exclude the 1,4-addition mechanism **A**.



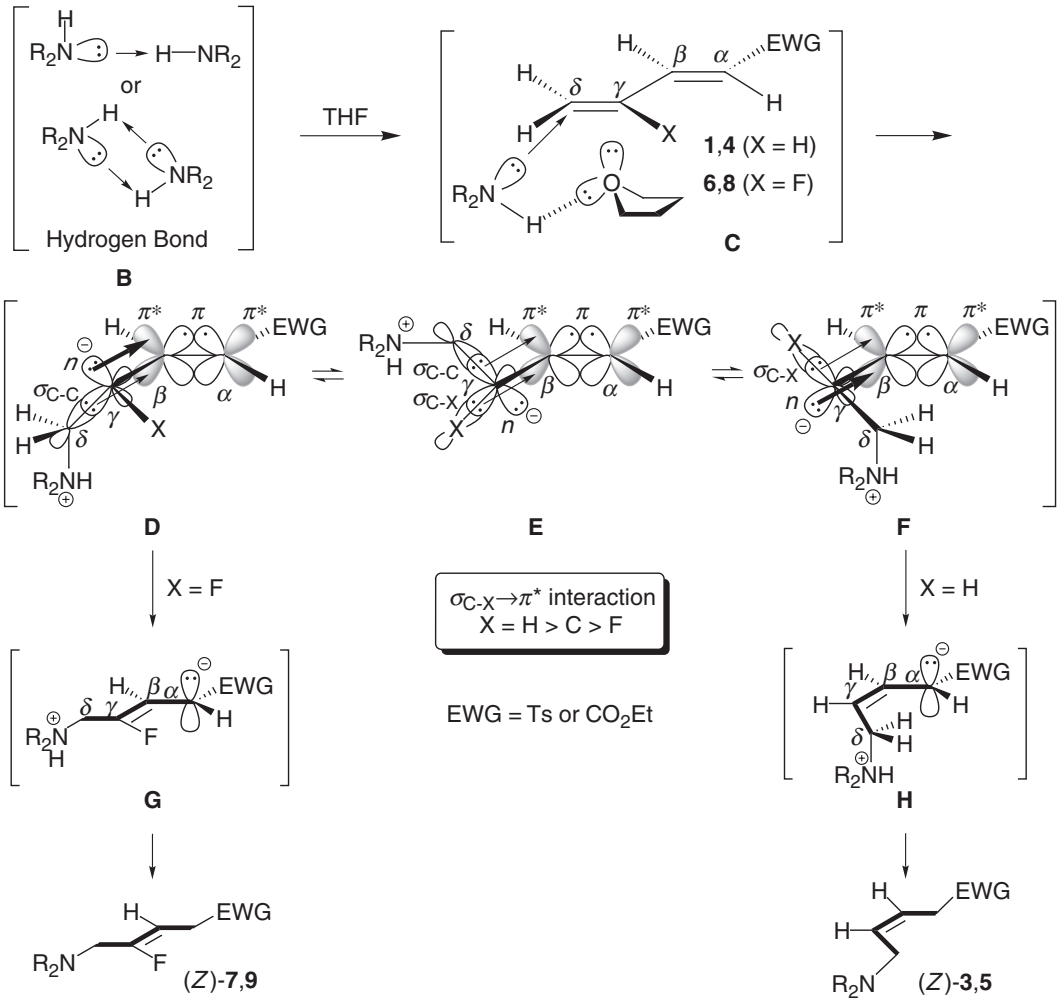
(1)



(2)

The elucidation of selective formation of (*Z*)-allylic sulfone (*Z*)-**3d** and (*Z*)-3-pentenoate (*Z*)-**5k** and variation of Z/E ratios by kinds of amines, solvents, temperature, and concentration are quite difficult. The most favorable conformation of (*E*)-dienyl sulfone **1** and (*E*)-2,4-pentadienoate **4** might be s-trans conformation.[14] If the present addition reaction were kinetically controlled reflecting the initial conformation shown in **C** (Scheme 1), it would be impossible to explain the Z selectivity. We try to rationalize the origin of the present "syn effect" in two ways, $n/\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity in the following,[15] taking into account the effects of kinds of amines, solvents, temperature, and concentration.

The former is as follows (Scheme 1): When a pair of electrons on the amine nitrogen interacts with a π^* orbital of $C_\gamma{=}C_\delta$ at the δ-position of **1** and **4** via s-trans conformation as shown in **C**, an anion would develop on the γ-carbon which might acquire sp^3 character altering from sp^2 character. The nonbonding electron pair (n) of the γ-carbanion can more effectively interact with the π^* orbital of $C_\alpha{=}C_\beta$ in the eclipsed conformations **D** and **F**, in both of which the n-orbital is aligned with the π^* orbital ($n \rightarrow \pi^*$ interaction), and conformation **E** can be neglected.[16] Further, the contribution of $\sigma \rightarrow \pi^*$ interaction might determine the preference of **D** or **F**,

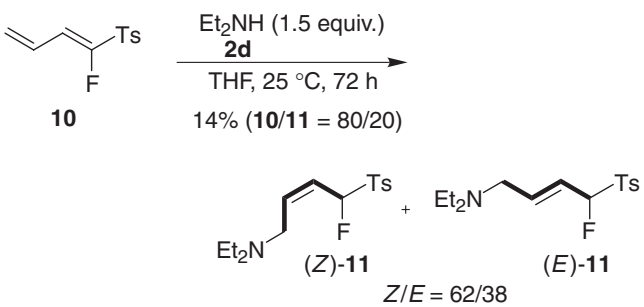


Scheme 1.

because $\sigma \rightarrow \pi^*$ interactions decrease in the order of $\sigma_{C-H} \rightarrow \pi^* > \sigma_{C-C} \rightarrow \pi^* > \sigma_{C-F} \rightarrow \pi^*$.[17] Thus, (*Z*)-**3** and (*Z*)-**5** were predominantly obtained in the case of **1** and **4** via conformation **F** (X = H), whereas (*Z*)-**7** and (*Z*)-**9** were formed in the case of **6** and **8** via **D** (X = F). Higher temperature and lower concentration in coordinating solvent like THF might dissociate the aggregation of bulkier dialkylamine (**B**) via hydrogen bonding[18] to generate the more nucleophilic monomeric amine shown in **C**.[19]

In addition, 6π-electron homoaromaticity seems to also contribute to the "syn effect" (Figure 3). When a monomeric dialkylamine reacts with an electron deficient diene, the syn intermediate **J** might be stabilized by 6π-electron homoaromaticity, followed by protonation to afford the corresponding (*Z*)-**3** and (*Z*)-**5**. In the case of γ-fluorinated dienes **6** and **8**, the participation of a lone pair of electrons on γ-fluorine atom to 6π-electron homoaromaticity, as depicted in **L**, may be much more effective than that of methylene in **K**. As a result, (*Z*)-**7** and (*Z*)-**9** were selectively obtained.

Furthermore, the reaction of Et_2NH (**2d**) (150 mM) with (*E*)-1-fluoro-1-tosyl-1,3-butadiene (**10**) was examined, and (*Z*)-allylic sulfone **11** was mainly obtained (eq 3). Addition of piperidine (150 mM) to octyl (*Z*)-2-fluoro-2,4-pentadienoate (**12**) mainly gave (*E*)-2-fluoro-5-amino-3-pentenoate **13** (Table 7, Entry 1), whereas Z selectivity was enhanced under dilute conditions at higher temperature as shown in Table 7.[20] Their syn intermediate forms 8π-electron system **N**, which has no advantage compared with anti intermediate **M** leading to (*E*)-allylic products. The fact that a considerable amount of Z isomers were still produced might suggest the contribution of n/$\sigma \rightarrow \pi^*$ interaction discussed above, or that of a hydrogen bond between the α-fluorine atom and a proton of ammonium ion as depicted in **O**.



(3)

In conclusion, unprecedented Z selective conjugate addition of amines to (*E*)-1-tosyl-1,3-butadiene (**1**) and ethyl (*E*)-2,4-pentadienoate (**4**) was discovered. Especially, higher Z selec-

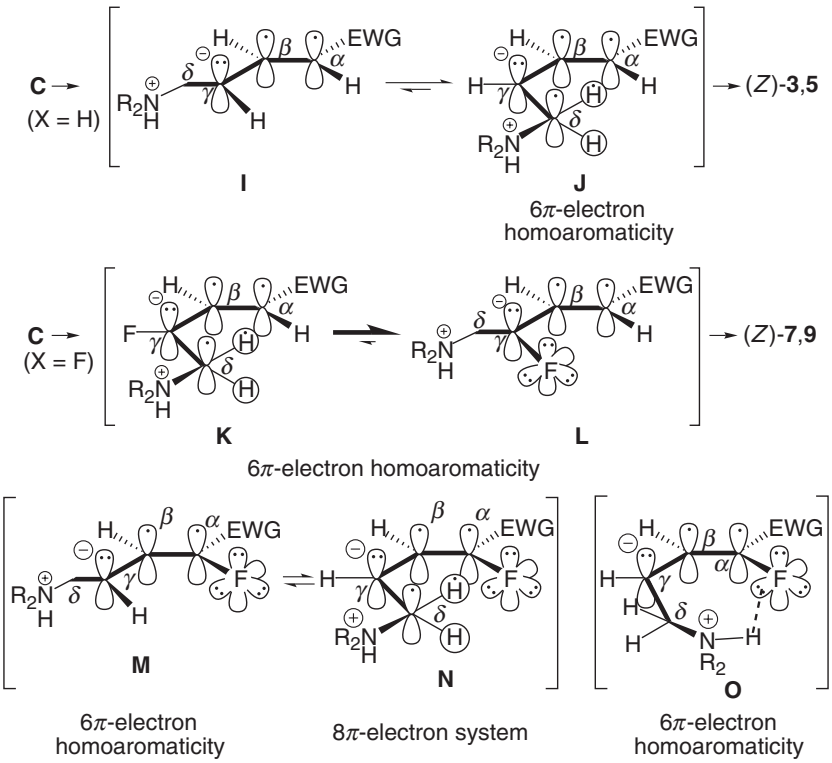
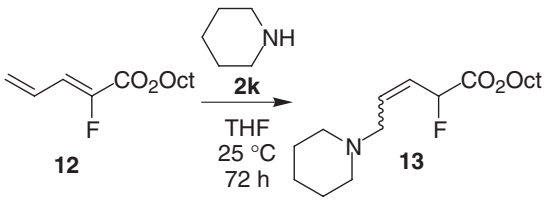


Figure 3. "Syn effect" based on 6π-electron homoaromaticity.

Table 7. Effect of Temperature and Concentration on Nucleophilic Addition of Piperidine (**2k**) to **12**



Entry	Concentrations		**2k**/**12**	Temp/°C	**12**/**13**[a)]	Yield/%[b)]	Z/E[c)]
	12/mM	**2k**/mM					
1	100	150	1.5	25	66/34	33	18/82
2	100	150	1.5	60	26/74	73	20/80
3	25	37.5	1.5	25	97/3	3	32/68
4	6.25	37.5	6.0	25	96/4	4	35/65
5	6.25	37.5	6.0	60	88/12	12	50/50

a) The ratios were determined based on the isolated yields. b) Isolated total yield of **13** based on **12**. c) The ratios were determined by 400 MHz ^{1}H NMR spectra.

tivity could be realized when the reaction was carried out in lower concentration of secondary amines at higher temperature in polar ethereal solvent. The "syn effect" observed in the present addition reaction was rationalized by n/$\sigma \rightarrow \pi^*$ interaction and/or 6π-electron homoaromaticity.

Experimental

^{1}H and ^{19}F NMR spectra were recorded on a JEOL Lambda 400 NMR spectrometer (400 MHz for ^{1}H and 376 MHz for ^{19}F). Chemical shifts were determined in the δ-scale relative to Si(CH_3)$_4$ (δ 0) and C_6F_6 (δ −162.90) as internal standards, respectively. IR spectra were measured on a JASCO FT/IR-230 spectrometer. MS spectra were recorded with a JEOL SX-102A mass spectrometer. THF and Et_2O were freshly distilled from sodium diphenylketyl. All other solvents were distilled and stored over drying agents. Thin-layer chromatography (TLC), flash column chromatography, and recycle HPLC were performed by using Merck silica gel 60 PF_{254} (Art. 7749), Cica silica gel 60 (No. 37571), and JAIGL-SIL (s-043-15), respectively.

(*E*)-1-Tosyl-1,3-butadiene (1).[21] To a solution of (*E*)-1-iodo-4-tosyl-2-butene[5a] (758 mg, 2.25 mmol) in THF (7.0 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.370 mL, 2.48 mmol) under a nitrogen atmosphere. After 5 min, the reaction mixture was treated with a saturated aqueous solution of NH_4Cl, and the solvent was evaporated. The organic substances were extracted with EtOAc, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue

was purified by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v) to give **1** in 99% yield (465 mg) as an oil. IR (neat) 3050, 2923, 2850, 1596, 1493, 1449, 1425, 1410, 1303, 1182, 1147, 1087, 1020, 969, 890, 821, 728, 669 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.44 (3H, s), 5.59 (1H, d, J = 10.25 Hz), 5.71 (1H, d, J = 16.83 Hz), 6.37 (1H, ddd, J = 16.83, 11.22, 10.25 Hz), 6.38 (1H, d, J = 14.88 Hz), 7.23 (1H, dd, J = 14.88, 11.22 Hz), 7.34 (2H, d, J = 8.24 Hz), 7.78 (2H, d, J = 8.24 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 209.06386. Calcd for $C_{11}H_{13}O_2S$: 209.06363.

Representative Procedure for the Nucleophilic Addition Reaction of Diethylamine (2d) to (*E*)-1-Tosyl-1,3-butadiene (1) (Table 1, Entry 4). To a solution of (*E*)-1-tosyl-1,3-butadiene (**1**) (94 mg, 0.45 mmol) in THF (4.5 mL) was added diethylamine (**2d**) (0.070 mL, 0.68 mmol) at 25 °C under a nitrogen atmosphere. After stirring for 72 h, the reaction mixture was quenched by adding silica gel (3.00 g), and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v, EtOAc, then EtOAc/MeOH = 3/1, v/v) to give a mixture of (*Z*)- and (*E*)-**3d** (95 mg, 75%, Z/E = 74/26) and to recover unreacted **1** (17 mg, 18%).

In a similar way, addition reaction of amines **2a**–**2c** and **2e**–**2k** was carried out to give the corresponding allylic amines **3a**–**3c** and **3e**–**3k**. The physical and spectral data of **3a**–**3e** and **3g**–**3k** and by-products are given in the following. Z/E ratios were determined by 400 MHz ^1H NMR spectra.

***N*-Propyl-4-tosyl-2-butenylamine (3a):** An oil (Z/E = 21/79). IR (neat) 3321, 2958, 2929, 2874, 2810, 1597, 1495, 1455, 1403, 1381, 1317, 1303, 1238, 1145, 1088, 1018, 973, 816, 730, 665 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 0.87 (3H, t, J = 7.32 Hz), 1.41 (2H, sext, J = 7.32 Hz), 1.56 (1H, brs), 2.40 (2H, t, J = 7.32 Hz), 2.44 (3H, s), 3.00 (2H, dd, J = 6.83, 1.46 Hz), 3.90 (2H, d, J = 8.05 Hz), 5.49 (1H, dtt, J = 10.73, 8.05, 1.46 Hz), 5.88 (1H, dt, J = 10.73, 6.83 Hz), 7.34 (2H, d, J = 7.81 Hz), 7.75 (2H, d, J = 7.81 Hz). E isomer; ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, J = 7.32 Hz), 1.45 (2H, sext, J = 7.32 Hz), 1.56 (1H, brs), 2.44 (3H, s), 2.46 (2H, t, J = 7.32 Hz), 3.19 (2H, d, J = 4.64 Hz), 3.77 (2H, d, J = 6.10 Hz), 5.58 (1H, dt, J = 15.37, 6.10 Hz), 5.63 (1H, dt, J = 15.37, 4.64 Hz), 7.33 (2H, d, J = 7.81 Hz), 7.73 (2H, d, J = 7.81 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 268.13820. Calcd for $C_{14}H_{22}NO_2S$: 268.13712.

***N*-Propyl-4-tosyl-*N*-(4-tosyl-2-butenyl)-2-butenylamine:** An oil (a mixture of at least 3 isomers based on ^1H NMR). IR (neat) 2960, 2929, 2872, 1597, 1495, 1455, 1403, 1316, 1235, 1142, 1087, 1018, 976, 881, 815, 728, 666 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.76–0.81 (2H, m), 0.79 (3H, t, J = 7.32 Hz), [0.80 (3H, t, J = 7.32 Hz), minor isomers], 2.09–2.19 (2H, m), 2.44 (6H, s), [2.46 (6H, s), minor isomers], 2.86 (2H, d, J = 3.90 Hz), 2.91 (2H, d, J = 3.42 Hz), [2.69–2.76 (4H, m), minor isomers], 3.74–3.78 (4H, m), [3.83–3.87 (4H, m), minor isomers], 5.48–5.79 (4H, m), 7.32–7.36 (4H, m), 7.70–7.68 (4H, m). HRMS (FAB^+) $(M+H)^+$, Found: m/z 476.19165. Calcd for $C_{25}H_{34}NO_4S_2$: 476.19293.

***N*-Butyl-4-tosyl-2-butenylamine (3b):** An oil (Z/E = 23/77). IR (neat) 3323, 3030, 2956, 2927, 2871, 2810, 1597, 1493, 1457, 1402, 1377, 1318, 1303, 1240, 1146, 1088, 1045, 1018, 972, 917, 875, 816, 731, 695, 664 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, J = 7.07 Hz), 1.31 (2H, sext, J = 7.07 Hz), 1.43 (2H, quint, J = 7.07 Hz), 1.73 (1H, brs), 2.44 (3H, s), 2.51 (2H, t, J = 7.07 Hz), 3.01 (2H, dd, J = 6.83, 1.46 Hz), 3.89 (2H, d, J = 7.81 Hz), 5.49 (1H, dtt, J = 10.98, 7.81, 1.46 Hz), 5.88 (1H, dt, J = 10.98, 6.83 Hz), 7.34 (2H, d, J = 7.81 Hz), 7.75 (2H, d, J = 7.81 Hz). E isomer; ^1H NMR ($CDCl_3$) δ 0.91 (3H, t, J = 7.07 Hz), 1.31 (2H, sext, J = 7.07 Hz), 1.43 (2H, quint, J = 7.07 Hz), 1.73 (1H, brs), 2.44 (3H, s), 2.51 (2H, t, J = 7.07 Hz), 3.21 (2H, d, J = 4.64 Hz), 3.77 (2H, d, J = 6.34 Hz), 5.59 (1H, dt, J = 15.61, 6.34 Hz), 5.64 (1H, dt, J = 15.61, 4.64 Hz), 7.34 (2H, d, J = 7.81 Hz), 7.74 (2H, d, J = 7.81 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 282.15262. Calcd for $C_{15}H_{24}NO_2S$: 282.15277.

***N*-Butyl-4-tosyl-*N*-(4-tosyl-2-butenyl)-2-butenylamine:** An oil (a mixture of at least 3 isomers based on ^1H NMR). IR (neat) 3030, 2955, 2927, 2871, 2813, 1597, 1494, 1455, 1403, 1316, 1303, 1237, 1142, 1087, 1018, 975, 882, 816, 728, 690, 664 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.85 (3H, t, J = 7.08 Hz), [0.86 (3H, t, J = 7.08 Hz), minor isomers], 1.14–1.34 (4H, m), 2.15–2.23 (2H, m), 2.44 (6H, s), [2.46 (6H, s), minor isomers], 2.86 (2H, d, J = 3.39 Hz), 2.91 (2H, d, J = 3.17 Hz), [2.69–2.76 (4H, m), minor isomers], 3.72–3.79 (4H, m), [3.82–3.88 (4H, m), minor isomers], 5.45–5.79 (4H, m), 7.32–7.36 (4H, m), 7.70–7.76 (4H, m). HRMS (FAB^+) $(M+H)^+$, Found: m/z 490.20833. Calcd for $C_{26}H_{36}NO_4S_2$: 490.20858.

***N*,*N*-Dimethyl-4-tosyl-2-butenylamine (3c):** An oil (Z/E = 60/40). IR (neat) 3031, 2943, 2860, 2818, 2773, 1597, 1494, 1458, 1402, 1317, 1239, 1148, 1088, 1019, 977, 891, 852, 816, 713, 689, 663 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 2.07 (6H, s), 2.44 (3H, s), 2.67 (2H, dd, J = 6.58, 1.46 Hz), 3.90 (2H, d, J = 8.05 Hz), 5.54 (1H, dtt, J = 10.98, 8.05, 1.46 Hz), 5.82 (1H, dt, J = 10.98, 6.58 Hz), 7.34 (2H, d, J = 8.29 Hz), 7.76 (2H, d, J = 8.29 Hz). E isomer; ^1H NMR ($CDCl_3$) δ 2.12 (6H, s), 2.44 (3H, s), 2.87 (2H, d, J = 3.90 Hz), 3.79 (2H, d, J = 6.10 Hz), 5.52–5.60 (1H, m), 5.60 (1H, dt, J = 15.34, 6.10 Hz), 7.33 (2H, d, J = 8.29 Hz), 7.73 (2H, d, J = 8.29 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 254.12169. Calcd for $C_{13}H_{20}NO_2S$: 254.12147.

***N*,*N*-Diethyl-4-tosyl-2-butenylamine (3d):** An oil (Z/E = 74/26). IR (neat) 3030, 2970, 2932, 2873, 2807, 1597, 1494, 1452, 1384, 1317, 1303, 1239, 1200, 1141, 1088, 1019, 976, 880, 816, 769, 712, 688 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 0.91 (6H, t, J = 7.32 Hz), 2.31 (4H, q, J = 7.32 Hz), 2.44 (3H, s), 2.76 (2H, d, J = 6.59 Hz), 3.89 (2H, d, J = 7.81 Hz), 5.53 (1H, dt, J = 10.00, 7.81 Hz), 5.83 (1H, dt, J = 10.00, 6.59 Hz), 7.34 (2H, d, J = 8.05 Hz), 7.76 (2H, d, J = 8.05 Hz). ^1H NMR (C_6D_6) δ 0.79 (6H, t, J = 7.08 Hz), 1.86 (3H, s), 2.12 (4H, q, J = 7.08 Hz), 2.58 (2H, d, J = 6.34 Hz), 3.64 (2H, d, J = 7.81 Hz), 5.42 (1H, dt, J = 10.98, 7.81 Hz), 5.65 (1H, dt, J = 10.98, 6.34 Hz), 6.74 (2H, d, J = 8.05 Hz), 7.70 (2H, d, J = 8.05 Hz). E isomer; ^1H NMR ($CDCl_3$) δ 0.95 (6H, t, J = 7.32 Hz), 2.37 (4H, q, J = 7.32 Hz), 2.44 (3H, s), 3.02 (2H, d, J = 3.66 Hz), 3.79 (2H, d, J = 5.12 Hz), 5.50–5.64 (2H, m), 7.34 (2H, d, J = 8.05 Hz), 7.72 (2H, d, J = 8.05 Hz). ^1H NMR (C_6D_6) δ 0.83 (6H, t, J = 7.08 Hz), 1.87 (3H, s), 2.21 (4H, q, J = 7.08 Hz), 2.75 (2H, d, J = 5.86 Hz), 3.41 (2H, d, J = 7.32 Hz), 5.33 (1H, dt, J = 15.61, 5.86 Hz), 5.48 (1H, dt, J = 15.61, 7.32 Hz), 6.76 (2H, d, J = 7.81 Hz), 7.69 (2H, d, J = 7.81 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 282.15198. Calcd for $C_{15}H_{24}NO_2S$: 282.15277.

***N*,*N*-Dipropyl-4-tosyl-2-butenylamine (3e):** An oil (Z/E = 85/15). IR (neat) 3030, 2958, 2932, 2871, 2804, 1597, 1458, 1404, 1381, 1318, 1303, 1239, 1185, 1141, 1088, 1020, 976, 889, 816, 712, 688 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 0.81 (6H, t, J = 7.32 Hz), 1.33 (4H, sext, J = 7.32 Hz), 2.18 (4H, t, J = 7.32 Hz), 2.44 (3H, s), 2.74 (2H, dd, J = 6.34, 1.71 Hz),

3.89 (2H, d, $J = 8.05$ Hz), 5.52 (1H, dtt, $J = 10.98$, 8.05, 1.71 Hz), 5.83 (1H, dt, $J = 10.98$, 6.34 Hz), 7.34 (2H, d, $J = 8.05$ Hz), 7.75 (2H, d, $J = 8.05$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.83 (6H, t, $J = 7.32$ Hz), 1.39 (4H, sext, $J = 7.32$ Hz), 2.27 (4H, t, $J = 7.32$ Hz), 2.44 (3H, s), 3.02 (2H, d, $J = 4.88$ Hz), 3.78 (2H, d, $J = 6.10$ Hz), 5.53–5.60 (1H, m), 5.61 (1H, dt, $J = 15.37$, 4.88 Hz), 7.33 (2H, d, $J = 8.05$ Hz), 7.73 (2H, d, $J = 8.05$ Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 310.18535. Calcd for $C_{17}H_{28}NO_2S$: 310.18407.

***N*,*N*-Dibutyl-4-tosyl-2-butenylamine (3g):** An oil (Z/E = 87/13). IR (neat) 3030, 2955, 2930, 2871, 2803, 1598, 1495, 1457, 1404, 1378, 1318, 1303, 1234, 1140, 1088, 1019, 974, 887, 815, 712, 687 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, $J = 7.31$ Hz), 1.20–1.40 (8H, m), 2.20 (4H, t, $J = 7.81$ Hz), 2.44 (3H, s), 2.72 (2H, dd, $J = 6.34$, 1.71 Hz), 3.89 (2H, d, $J = 7.81$ Hz), 5.52 (1H, dtt, $J = 10.98$, 7.81, 1.71 Hz), 5.82 (1H, dt, $J = 10.98$, 6.34 Hz), 7.33 (2H, d, $J = 8.05$ Hz), 7.76 (2H, d, $J = 8.05$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.89 (6H, t, $J = 7.07$ Hz), 1.20–1.40 (8H, m), 2.29 (4H, t, $J = 7.56$ Hz), 2.44 (3H, s), 3.01 (2H, d, $J = 4.64$ Hz), 3.78 (2H, d, $J = 6.10$ Hz), 5.48–5.56 (1H, m), 5.61 (1H, dt, $J = 15.37$, 4.64 Hz), 7.32 (2H, d, $J = 8.42$ Hz), 7.73 (2H, d, $J = 8.42$ Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 338.21518. Calcd for $C_{19}H_{32}NO_2S$: 338.21537.

***N*-Butyl-*N*-methyl-4-tosyl-2-butenylamine (3h):** An oil (Z/E = 72/28). IR (neat) 3030, 2956, 2931, 2871, 2789, 1597, 1494, 1458, 1403, 1376, 1318, 1303, 1240, 1206, 1144, 1088, 1040, 1019, 976, 886, 859, 816, 782, 713, 688, 664 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, $J = 7.32$ Hz), 1.22–1.44 (4H, m), 2.02 (3H, s), 2.16 (2H, t, $J = 7.81$ Hz), 2.44 (3H, s), 2.70 (2H, dd, $J = 6.34$, 1.46 Hz), 3.90 (2H, d, $J = 7.81$ Hz), 5.54 (1H, dtt, $J = 10.98$, 7.81, 1.46 Hz), 5.83 (1H, dt, $J = 10.98$, 6.34 Hz), 7.34 (2H, d, $J = 8.05$ Hz), 7.75 (2H, d, $J = 8.05$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, $J = 7.32$ Hz), 1.22–1.44 (4H, m), 2.08 (3H, s), 2.24 (2H, t, $J = 7.81$ Hz), 2.44 (3H, s), 2.94 (2H, d, $J = 4.64$ Hz), 3.79 (2H, d, $J = 5.37$ Hz), 5.52–5.62 (1H, m), 5.61 (1H, dt, $J = 15.38$, 5.37 Hz), 7.33 (2H, d, $J = 7.81$ Hz), 7.73 (2H, d, $J = 7.81$ Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 296.16882. Calcd for $C_{16}H_{26}NO_2S$: 296.16842.

***N*-Isopropyl-*N*-methyl-4-tosyl-2-butenylamine (3i):** An oil (Z/E = 80/20). IR (neat) 3030, 2966, 2792, 1597, 1453, 1402, 1383, 1362, 1317, 1304, 1236, 1143, 1088, 1018, 975, 876, 816, 769, 712, 688, 664 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.92 (6H, d, $J = 6.58$ Hz), 1.99 (3H, s), 2.44 (3H, s), 2.68 (1H, sept, $J = 6.58$ Hz), 2.73 (2H, dd, $J = 6.34$, 1.22 Hz), 3.91 (2H, d, $J = 8.05$ Hz), 5.52 (1H, dtt, $J = 10.98$, 8.05, 1.22 Hz), 5.83 (1H, dt, $J = 10.98$, 6.34 Hz), 7.35 (2H, d, $J = 8.05$ Hz), 7.76 (2H, d, $J = 8.05$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.93 (6H, d, $J = 6.58$ Hz), 2.04 (3H, s), 2.44 (3H, s), 2.68 (1H, sept, $J = 6.57$ Hz), 2.98 (2H, d, $J = 4.15$ Hz), 3.78 (2H, d, $J = 5.86$ Hz), 5.56–5.62 (1H, m), 5.60 (1H, dt, $J = 15.14$, 5.86 Hz), 7.32 (2H, d, $J = 8.05$ Hz), 7.73 (2H, d, $J = 8.05$ Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 282.15318. Calcd for $C_{15}H_{24}NO_2S$: 282.15277.

1-(4-Tosyl-2-butenyl)pyrrolidine (3j): An oil (Z/E = 44/56). IR (neat) 3030, 2963, 2875, 2789, 1597, 1494, 1459, 1402, 1347, 1317, 1304, 1291, 1236, 1142, 1088, 1018, 969, 929, 878, 816, 715, 669 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 1.65–1.78 (4H, m), 2.28–2.40 (4H, m), 2.44 (3H, s), 2.88 (2H, d, $J = 6.59$ Hz), 3.91 (2H, d, $J = 7.81$ Hz), 5.51 (1H, dt, $J = 10.98$, 7.81 Hz), 5.84 (1H, dt, $J = 10.98$, 6.59 Hz), 7.34 (2H, d, $J = 8.29$ Hz), 7.76 (2H, d, $J = 8.29$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.65–1.80 (4H, m), 2.28–2.40 (4H, m), 2.44 (3H, s), 3.05 (2H, d, $J = 4.88$ Hz), 3.78 (2H, d, $J = 5.86$ Hz), 5.60 (1H, dt, $J = 15.34$, 5.86 Hz), 5.64 (1H, dt, $J = 15.34$, 4.88 Hz), 7.33 (2H, d, $J = 8.29$ Hz), 7.73 (2H, d, $J = 8.29$ Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 280.13644. Calcd for $C_{15}H_{22}NO_2S$: 280.13712.

1-(4-Tosyl-2-butenyl)piperidine (3k): An oil (Z/E = 55/45). IR (neat) 3030, 2933, 2853, 2795, 2754, 1597, 1494, 1467, 1453, 1402, 1372, 1318, 1303, 1242, 1141, 1118, 1088, 1041, 1019, 991, 901, 861, 816, 778, 734, 713, 690, 664 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 1.30–1.45 (2H, m), 1.45–1.55 (4H, m), 2.10–2.30 (4H, m), 2.44 (3H, s), 2.98 (2H, dd, $J = 6.59$, 1.71 Hz), 3.90 (2H, d, $J = 7.81$ Hz), 5.54 (1H, dtt, $J = 10.98$, 7.81, 1.71 Hz), 5.84 (1H, dt, $J = 10.98$, 6.59 Hz), 7.33 (2H, d, $J = 8.29$ Hz), 7.72 (2H, d, $J = 8.29$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.30–1.45 (2H, m), 1.40–1.55 (4H, m), 2.10–2.30 (4H, m), 2.44 (3H, s), 2.88 (2H, d, $J = 4.64$ Hz), 3.79 (2H, d, $J = 5.37$ Hz), 5.50–5.60 (1H, m), 5.58 (1H, dt, $J = 15.59$, 5.37 Hz), 7.34 (2H, d, $J = 8.29$ Hz), 7.76 (2H, d, $J = 8.29$ Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 294.15420. Calcd for $C_{16}H_{24}NO_2S$: 294.15277.

Nucleophilic Addition Reaction of Diethylamine (2d) to (*E*)-1-Tosyl-1,3-butadiene (1) under Dilute Conditions at 60 °C (Table 3, Entry 5). To a solution of (*E*)-1-tosyl-1,3-butadiene (**1**) (129 mg, 0.62 mmol) in THF (198 mL) was added diethylamine (**2d**) (0.77 mL, 7.43 mmol) at 60 °C under a nitrogen atmosphere. After stirring for 72 h, the reaction mixture was quenched by adding silica gel (3.34 g), and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v, EtOAc, then EtOAc/MeOH = 3/1, v/v) to give a mixture of (*Z*)- and (*E*)-**3d** (125 mg, 72%, Z/E = 98/2) and to recover unreacted **1** (36 mg, 28%).

A Representative Procedure for the Nucleophilic Addition Reaction of Piperidine (2k) to Ethyl (*E*)-2,4-Pentadienoate (4) (Table 5, Entry 10). To a solution of ethyl (*E*)-2,4-pentadienoate (**4**)[22] (67 mg, 0.53 mmol) in THF (5.3 mL) was added piperidine (**2k**) (0.079 mL, 0.80 mmol) at 25 °C under a nitrogen atmosphere. After stirring for 72 h, the reaction mixture was quenched by adding silica gel (2.80 g), and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v, EtOAc, then EtOAc/MeOH = 3/1, v/v) to give a mixture of (*Z*)- and (*E*)-**5k** (65 mg, 58%, Z/E = 68/32) and to recover unreacted **4** (25 mg, 37%).

In a similar way, reactions of amines **2a**–**2e** and **2g**–**2j** with ethyl (*E*)-2,4-pentadienoate (**4**) were carried out to give the corresponding addition products **5a**–**5e** and **5g**–**5j**. The physical and spectral data of **5a**–**5e** and **5g**–**5k** and by-products are given in the following. Z/E ratios were determined by 400 MHz ^{1}H NMR spectra. In the cases of Me_2NH, Et_2NH, *n*-Pr_2NH, *n*-Bu_2NH, *n*-Bu(Me)NH, *i*-Pr(Me)NH, and pyrrolidine, the Z/E ratios were measured in $CDCl_3$ containing CF_3CO_2D in order to separate ^{1}H NMR peaks, and no isomerization was observed for 24 h. Only specific chemical shifts, which were measured in $CDCl_3$ containing CF_3CO_2D and used for determination of Z/E ratios, are shown.

Ethyl 5-(Propylamino)-3-pentenoate (5a): An oil (Z/E = 7/93). IR (neat) 3317, 2960, 2933, 2874, 2816, 1738, 1652, 1462, 1408, 1369, 1330, 1301, 1256, 1175, 1096, 1029, 972, 937, 856, 808, 786, 751 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.52 (2H, sext, $J = 7.32$ Hz), 2.10–2.25 (1H, m), 2.59 (2H, t, $J = 7.32$ Hz), 3.12 (2H, d, $J = 5.12$ Hz), 3.30 (2H, d, $J = 4.64$ Hz),

4.15 (2H, q, $J = 7.07$ Hz), 5.72–5.78 (2H, m). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.52 (2H, sext, $J = 7.32$ Hz), 2.10–2.25 (1H, m), 2.59 (2H, t, $J = 7.32$ Hz), 3.06 (2H, d, $J = 5.85$ Hz), 3.26 (2H, d, $J = 5.37$ Hz), 4.14 (2H, q, $J = 7.07$ Hz), 5.67 (1H, dt, $J = 15.61$, 5.37 Hz), 5.74 (1H, dt, $J = 15.61$, 5.85 Hz). HRMS (FAB^+) $(M + H)^+$, Found: m/z 186.14923. Calcd for $C_{10}H_{20}NO_2$: 186.14940.

1-Propyl-3,6-dihydro-1*H*-pyridin-2-one: An oil. IR (neat) 2964, 2931, 2872, 1637, 1497, 1458, 1411, 1267, 1164, 979, 900, 675 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, $J = 7.32$ Hz), 1.61 (2H, sext, $J = 7.32$ Hz), 2.90–2.98 (2H, m), 3.39 (2H, t, $J = 7.32$ Hz), 3.88–3.93 (2H, m), 5.66–5.80 (2H, m). HRMS (FAB^+) $(M + H)^+$, Found: m/z 140.10772. Calcd for $C_8H_{14}NO$: 140.10754.

Ethyl 5-(Butylamino)-3-pentenoate (5b): An oil (Z/E = 11/89). IR (neat) 3391, 2959, 2931, 2872, 2821, 1736, 1652, 1540, 1465, 1409, 1370, 1303, 1254, 1174, 1096, 1029, 973, 940, 856, 810, 736 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.34 (2H, sext, $J = 7.32$ Hz), 1.48 (2H, quint, $J = 7.32$ Hz), 1.90–2.02 (1H, m), 2.62 (2H, t, $J = 7.32$ Hz), 3.12 (2H, d, $J = 5.37$ Hz), 3.30 (2H, d, $J = 4.88$ Hz), 4.15 (2H, q, $J = 7.07$ Hz), 5.66–5.77 (2H, m). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.34 (2H, sext, $J = 7.32$ Hz), 1.48 (2H, quint, $J = 7.32$ Hz), 1.90–2.02 (1H, m), 2.61 (2H, t, $J = 7.32$ Hz), 3.06 (2H, d, $J = 5.61$ Hz), 3.25 (2H, d, $J = 5.12$ Hz), 4.14 (2H, q, $J = 7.07$ Hz), 5.67 (1H, dt, $J = 15.61$, 5.12 Hz), 5.73 (1H, dt, $J = 15.61$, 5.61 Hz). HRMS (FAB^+) $(M + H)^+$, Found: m/z 200.16450. Calcd for $C_{11}H_{22}NO_2$: 200.16505.

1-Butyl-3,6-dihydro-1*H*-pyridin-2-one: An oil. IR (neat) 3047, 2958, 2931, 2871, 1634, 1496, 1456, 1411, 1375, 1326, 1298, 1251, 1197, 1165, 1131, 1112, 1083, 984, 854, 734, 677 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.94 (3H, t, $J = 7.56$ Hz), 1.34 (2H, sext, $J = 7.56$ Hz), 1.56 (2H, quint, $J = 7.56$ Hz), 2.93–2.97 (2H, m), 3.42 (2H, t, $J = 7.56$ Hz), 3.88–3.94 (2H, m), 5.69–5.80 (2H, m). HRMS (FAB^+) $(M + H)^+$, Found: m/z 154.12298. Calcd for $C_9H_{16}NO$: 154.12319.

Ethyl 5-(Dimethylamino)-3-pentenoate (5c): An oil (Z/E = 76/24). IR (neat) 2979, 2941, 2857, 2817, 2772, 1737, 1652, 1457, 1367, 1320, 1259, 1175, 1096, 1031, 975, 853 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, $J = 7.07$ Hz), 2.24 (6H, s), 2.96 (2H, d, $J = 6.34$ Hz), 3.13 (2H, d, $J = 6.42$ Hz), 4.15 (2H, q, $J = 7.07$ Hz), 5.67 (1H, dt, $J = 10.98$, 6.34 Hz), 5.75 (1H, dt, $J = 10.98$, 6.42 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.74–3.82 (2H, m). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, $J = 7.07$ Hz), 2.23 (6H, s), 2.92 (2H, d, $J = 6.34$ Hz), 3.07 (2H, d, $J = 6.59$ Hz), 4.14 (2H, q, $J = 7.07$ Hz), 5.61 (1H, dt, $J = 15.37$, 6.34 Hz), 5.72 (1H, dt, $J = 15.37$, 6.59 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.63–3.71 (2H, m). HRMS (FAB^+) $(M + H)^+$, Found: m/z 172.13432. Calcd for $C_9H_{18}NO_2$: 172.13375.

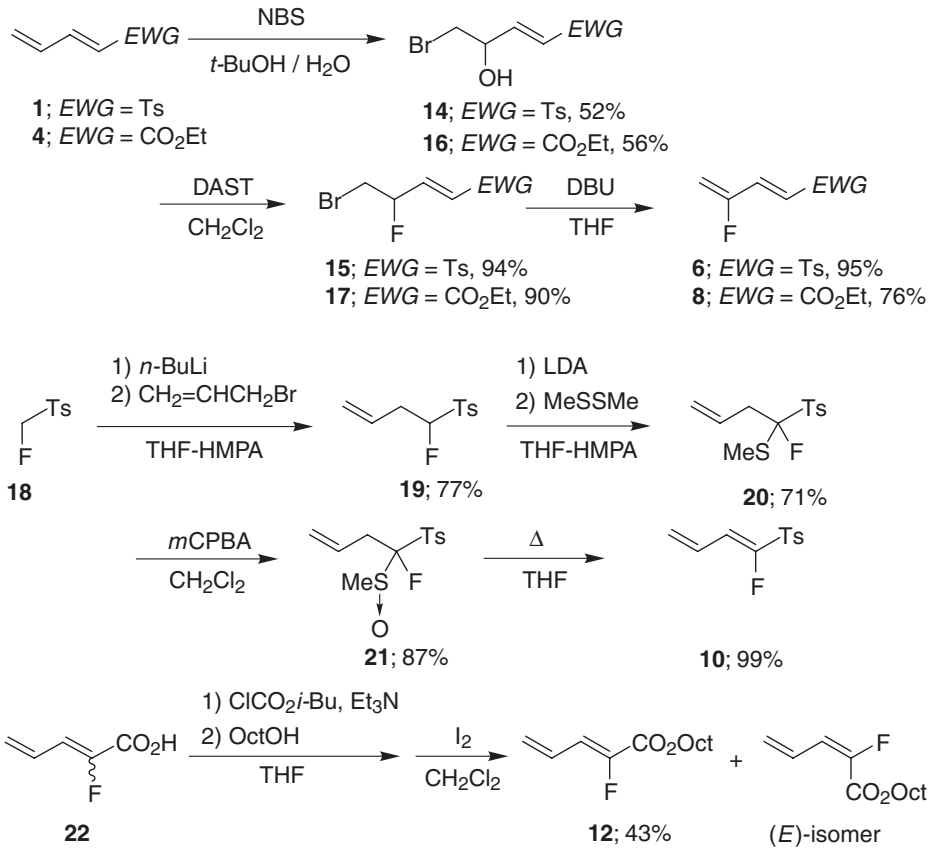
Ethyl 5-(Diethylamino)-3-pentenoate (5d): An oil (Z/E = 87/13). IR (neat) 2960, 2923, 2853, 1732, 1457, 1367, 1280, 1260, 1181, 1033, 850, 705, 670 cm^{-1}. Z isomer; ^{1}H NMR (C_6D_6) δ 0.90 (6H, t, $J = 7.08$ Hz), 0.93 (3H, t, $J = 7.07$ Hz), 2.35 (4H, q, $J = 7.08$ Hz), 2.95–2.98 (4H, m), 3.92 (2H, q, $J = 7.07$ Hz), 5.66 (1H, dtt, $J = 10.98$, 6.59, 1.46 Hz), 5.78 (1H, dtt, $J = 10.98$, 7.32, 1.46 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 2.97 (2H, d, $J = 6.59$ Hz). E isomer; ^{1}H NMR (C_6D_6) δ 0.94 (9H, t, $J = 7.08$ Hz), 2.39 (4H, q, $J = 7.08$ Hz), 2.87 (2H, dd, $J = 6.83$, 1.22 Hz), 2.94 (2H, dd, $J = 6.34$, 1.22 Hz), 3.92 (2H, q, $J = 7.08$ Hz), 5.56 (1H, dtt, $J = 15.37$, 6.34, 1.22 Hz), 5.73 (1H, dtt, $J = 15.37$, 6.83, 1.22 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 2.83 (2H, d, $J = 7.07$ Hz). HRMS (FAB^+) $(M + H)^+$, Found: m/z 200.16450. Calcd for $C_{11}H_{22}NO_2$: 200.16505.

Ethyl 5-(Dipropylamino)-3-pentenoate (5e): An oil (Z/E = 90/10). IR (neat) 3030, 2959, 2934, 2873, 2800, 1740, 1458, 1367, 1319, 1254, 1163, 1095, 1075, 1033, 973, 848, 748, 676 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.87 (6H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.32$ Hz), 1.47 (4H, sext, $J = 7.32$ Hz), 2.39 (4H, t, $J = 7.32$ Hz), 3.12 (2H, d, $J = 5.61$ Hz), 3.13 (2H, d, $J = 4.64$ Hz), 4.15 (2H, q, $J = 7.32$ Hz), 5.68 (1H, dt, $J = 10.98$, 4.64 Hz), 5.73 (1H, dt, $J = 10.98$, 5.61 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.84 (2H, d, $J = 4.64$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.87 (6H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.32$ Hz), 1.47 (4H, sext, $J = 7.32$ Hz), 2.42 (4H, t, $J = 7.32$ Hz), 3.07 (4H, d, $J = 6.34$ Hz), 4.14 (2H, q, $J = 7.32$ Hz), 5.63 (1H, dt, $J = 15.61$, 6.34 Hz), 5.66 (1H, dt, $J = 15.61$, 6.34 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.75 (2H, d, $J = 6.34$ Hz). HRMS (FAB^+) $(M + H)^+$, Found: m/z 228.19671. Calcd for $C_{13}H_{26}NO_2$: 228.19635.

Ethyl 5-(Dibutylamino)-3-pentenoate (5g): An oil (Z/E = 94/6). IR (neat) 3030, 2957, 2932, 2871, 2798, 1740, 1652, 1456, 1367, 1318, 1252, 1162, 1096, 1034, 973, 937, 852, 735, 668 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.90 (6H, t, $J = 7.07$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.29 (4H, sext, $J = 7.07$ Hz), 1.43 (4H, tt, $J = 7.56$, 7.07 Hz), 2.41 (4H, t, $J = 7.56$ Hz), 3.09 (2H, d, $J = 5.86$ Hz), 3.12 (2H, d, $J = 5.61$ Hz), 4.15 (2H, q, $J = 7.07$ Hz), 5.68 (1H, dt, $J = 10.73$, 5.86 Hz), 5.72 (1H, dt, $J = 10.73$, 5.61 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.85 (2H, d, $J = 5.61$ Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.90 (6H, t, $J = 7.07$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.27 (4H, sext, $J = 7.07$ Hz), 1.43 (4H, tt, $J = 7.32$, 7.07 Hz), 2.40 (4H, t, $J = 7.32$ Hz), 3.06 (4H, d, $J = 5.61$ Hz), 4.13 (2H, q, $J = 7.07$ Hz), 5.62 (1H, dt, $J = 15.61$, 5.61 Hz), 5.68 (1H, dt, $J = 15.61$, 5.61 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.76 (2H, d, $J = 5.61$ Hz). HRMS (FAB^+) $(M + H)^+$, Found: m/z 256.22696. Calcd for $C_{15}H_{30}NO_2$: 256.22765.

Ethyl 5-(Butylmethylamino)-3-pentenoate (5h): An oil, (Z/E = 74/26). IR (neat) 3028, 2957, 2933, 2872, 2840, 2787, 1739, 1652, 1462, 1367, 1319, 1255, 1164, 1096, 1063, 1033, 973, 858, 736 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.31 (2H, sext, $J = 7.32$ Hz), 1.46 (2H, quint, $J = 7.32$ Hz), 2.21 (3H, s), 2.33 (2H, t, $J = 7.32$ Hz), 3.02 (2H, d, $J = 5.86$ Hz), 3.12 (2H, d, $J = 6.34$ Hz), 4.15 (2H, q, $J = 7.07$ Hz), 5.68 (1H, dt, $J = 10.73$, 6.34 Hz), 5.74 (1H, dt, $J = 10.73$, 5.86 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.10–3.25 (4H, m). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, $J = 7.32$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 1.31 (2H, sext, $J = 7.32$ Hz), 1.45 (2H, quint, $J = 7.32$ Hz), 2.21 (3H, s), 2.34 (2H, t, $J = 7.32$ Hz), 2.99 (2H, d, $J = 6.59$ Hz), 3.07 (2H, d, $J = 6.34$ Hz), 4.14 (2H, q, $J = 7.07$ Hz), 5.63 (1H, dt, $J = 15.86$, 6.34 Hz), 5.71 (1H, dt, $J = 15.86$, 6.59 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 2.95–3.05 (4H, m). HRMS (FAB^+) $(M + H)^+$, Found: m/z 214.18101. Calcd for $C_{12}H_{24}NO_2$: 214.18070.

Ethyl 5-(Isopropylmethylamino)-3-pentenoate (5i): An oil (Z/E = 82/18). IR (neat) 3030, 2966, 2930, 2880, 2840, 2789, 1739, 1652, 1456, 1366, 1320, 1258, 1176, 1094, 1034, 974, 874, 796, 688 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 1.05 (6H, d, $J = 6.59$ Hz), 1.26 (3H, t, $J = 7.07$ Hz), 2.21 (3H, s), 2.90 (1H, sept, $J = 6.59$ Hz), 3.10 (2H, d, $J = 6.10$ Hz), 3.13 (2H, d, $J = 5.85$ Hz), 4.15 (2H, q, $J = 7.07$ Hz), 5.70 (1H, dt, $J = 10.98$, 6.10 Hz), 5.74 (1H, dt, $J = 10.98$, 5.85 Hz). ^{1}H NMR ($CDCl_3$ with



Scheme 2.

CF_3CO_2D) δ 2.75 (3H, s). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.06 (6H, d, J = 6.59 Hz), 1.26 (3H, t, J = 7.07 Hz), 2.23 (3H, s), 2.91 (1H, sept, J = 6.59 Hz), 3.08 (2H, d, J = 6.83 Hz), 3.10 (2H, d, J = 6.10 Hz), 4.14 (2H, q, J = 7.07 Hz), 5.67 (1H, dt, J = 15.37, 6.83 Hz), 5.71 (1H, dt, J = 15.37, 6.10 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 2.72 (3H, s). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 200.16542. Calcd for $C_{11}H_{22}NO_2$: 200.16505.

Ethyl 5-(Pyrrolidin-1-yl)-3-pentenoate (5j): An oil (Z/E = 59/41). IR (neat) 3029, 2967, 2908, 2875, 2787, 1739, 1655, 1461, 1445, 1407, 1368, 1345, 1320, 1256, 1173, 1096, 1033, 940, 902, 879, 858 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, J = 7.07 Hz), 1.72–1.82 (4H, m), 2.50–2.57 (4H, m), 3.14 (2H, d, J = 6.34 Hz), 3.15 (2H, d, J = 5.86 Hz), 4.15 (2H, q, J = 7.07 Hz), 5.70 (1H, dt, J = 10.98, 6.34 Hz), 5.73 (1H, dt, J = 10.98, 5.86 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.73 (2H, d, J = 5.86 Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, J = 7.07 Hz), 1.72–1.82 (4H, m), 2.50–2.57 (4H, m), 3.06 (2H, d, J = 5.61 Hz), 3.10 (2H, d, J = 5.37 Hz), 4.15 (2H, q, J = 7.07 Hz), 5.69 (1H, dt, J = 15.39, 5.61 Hz), 5.75 (1H, dt, J = 15.39, 5.37 Hz). ^{1}H NMR ($CDCl_3$ with CF_3CO_2D) δ 3.66 (2H, d, J = 5.37 Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 198.14951. Calcd for $C_{11}H_{20}NO_2$: 198.14940.

Ethyl 5-(Piperidin-1-yl)-3-pentenoate (5k): An oil (Z/E = 68/32). IR (neat) 3030, 2935, 2854, 2790, 1739, 1651, 1455, 1367, 1319, 1254, 1160, 1115, 1037, 999, 861, 792 cm^{-1}. Z isomre; ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, J = 7.08 Hz), 1.38–1.50 (2H, m), 1.59 (4H, quint, J = 5.61 Hz), 2.31–2.44 (4H, m), 2.98 (2H, d, J = 5.12 Hz), 3.12 (2H, d, J = 5.37 Hz), 4.14 (2H, q, J = 7.08 Hz), 5.70 (1H, dt, J = 10.25, 5.37 Hz), 5.72 (1H, dt, J = 10.25, 5.12 Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.26 (3H, t, J = 7.08 Hz), 1.38–1.50 (2H, m), 1.59 (4H, quint, J = 5.61 Hz), 2.31–2.44 (4H, m), 2.95 (2H, d, J = 5.37 Hz), 3.07 (2H, d, J = 5.61 Hz), 4.13 (2H, q, J = 7.08 Hz), 5.65 (1H, dt, J = 15.39, 5.61 Hz), 5.68 (1H, dt, J = 15.39, 5.37 Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 212.16534. Calcd for $C_{12}H_{22}NO_2$: 212.16505.

Nucleophilic Addition Reaction of Piperidine (2k) to Ethyl (*E*)-2,4-Pentadienoate (4) under Dilute Conditions at 60 °C (Table 6, Entry 8). To a solution of ethyl (*E*)-2,4-pentadienoate (**4**) (65 mg, 0.52 mmol) in THF (83 mL) was added piperidine (**2k**) (0.306 mL, 3.09 mmol) at 60 °C under a nitrogen atmosphere. After stirring for 72 h, the reaction mixture was quenched by adding silica gel (3.02 g), and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v, EtOAc, then EtOAc/MeOH = 3/1, v/v) to give a mixture of (*Z*)- and (*E*)-**5k** (54 mg, 50%, Z/E = 89/11) and to recover unreacted **4** (26 mg, 40%).

Fluorine-substituted dienes **6**, **8**, **10**, and **12** were prepared as shown in Scheme 2.

(*E*)-1-Bromo-4-tosylbut-3-en-2-ol (14): To a solution of **1** (198 mg, 0.951 mmol) in *t*-BuOH (10 mL) and H_2O (12 mL) was added NBS (254 mg, 1.43 mmol). After 48 h, the reaction mixture was quenched with a saturated solution of $NaHSO_3$, and the solvent was evaporated. The organic substances were extracted with Et_2O, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was separated by preparative TLC (SiO_2, hexane/EtOAc = 5/1, v/v) to give **14** in 52% yield (152 mg). Mp 119.5–120.0 °C (from hexane/EtOAc). IR (KBr) 3481, 3054, 2980, 2940, 2870, 1630, 1596,

1494, 1399, 1375, 1316, 1303, 1145, 1086, 1044, 1018, 971, 915, 813, 733, 706, 662 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.43 (3H, s), 3.25 (1H, d, $J = 5.37$ Hz), 3.43 (1H, dd, $J = 10.49$, 6.10 Hz), 3.53 (1H, dd, $J = 10.49$, 4.39 Hz), 4.58–4.63 (1H, m), 6.71 (1H, dd, $J = 15.37$, 2.44 Hz), 6.92 (1H, dd, $J = 15.37$, 3.66 Hz), 7.33 (2H, d, $J = 7.81$ Hz), 7.75 (2H, d, $J = 7.81$ Hz). Found: C, 43.34; H, 4.24%. Calcd for $C_{11}H_{13}O_3SBr$: C, 43.29; H, 4.29%.

(*E*)-4-Bromo-3-fluoro-1-tosyl-1-butene (15): To a solution of **14** (92 mg, 0.301 mmol) in CH_2Cl_2 (4 mL) was added DAST (0.060 mL, 0.452 mmol) at 0 °C under a nitrogen atmosphere. After 4 h, the reaction mixture was quenched with cool water, and the solvent was evaporated. The organic substances were extracted with EtOAc, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by preparative TLC (SiO_2, hexane/EtOAc = 3/1, v/v) to give **15** in 94% yield (87 mg). Mp 94.5–95.0 °C (from hexane/EtOAc). IR (KBr) 3075, 3030, 2970, 2920, 1596, 1422, 1315, 1304, 1280, 1210, 1149, 1086, 1019, 964, 934, 841, 812, 795, 708, 696, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.45 (3H, s), 3.55 (1H, ddd, $J = 20.91$, 11.37, 5.50 Hz), 3.58 (1H, ddd, $J = 17.79$, 11.37, 4.95 Hz), 5.37 (1H, ddddd, $J = 46.95$, 5.50, 4.95, 3.30, 1.83 Hz), 6.69 (1H, dd, $J = 15.04$, 1.83 Hz), 6.92 (1H, ddd, $J = 20.72$, 15.04, 3.30 Hz), 7.36 (2H, d, $J = 7.89$ Hz), 7.78 (2H, d, $J = 7.89$ Hz). ^{19}F NMR ($CDCl_3$) δ −182.2 (1F, ddt, $J =$ 46.95, 17.79, 20.91 Hz). Found: C, 42.81; H, 3.90%. Calcd for $C_{11}H_{12}O_2SFBr$: C, 43.01; H, 3.94%.

(*E*)-3-Fluoro-1-tosyl-1,3-butadiene (6): To a solution of **15** (129 mg, 0.420 mmol) in THF (4.0 mL) was added DBU (0.069 mL, 0.462 mmol) under a nitrogen atmosphere. After 5 min, the reaction mixture was quenched with a saturated solution of NH_4Cl, and the solvent was evaporated. The organic substances were extracted with EtOAc, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v) to give **6** in 95% yield (90 mg). Mp 90.3–90.5 °C (from hexane/EtOAc). IR (KBr) 3060, 1649, 1593, 1312, 1291, 1269, 1205, 1146, 1086, 1018, 971, 950, 885, 844, 831, 816, 705, 670 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.45 (3H, s), 4.96 (1H, dd, $J = 45.86$, 3.17 Hz), 5.13 (1H, dd, $J = 14.39$, 3.17 Hz), 6.66 (1H, d, $J = 14.88$ Hz), 7.05 (1H, dd, $J = 25.13$, 14.88 Hz), 7.35 (2H, d, $J = 8.05$ Hz), 7.78 (2H, d, $J = 8.05$ Hz). ^{19}F NMR ($CDCl_3$) δ −111.8 (1F, ddd, $J = 45.86$, 25.13, 14.39 Hz). Found: C, 58.68; H, 5.00%. Calcd for $C_{11}H_{11}FO_2S$: C, 58.39; H, 4.90%.

Ethyl (*E*)-5-Bromo-4-hydroxy-2-pentenoate (16): To a solution of **4** (252 mg, 2.00 mmol) in *t*-BuOH (5.0 mL) and H_2O (6.0 mL) was added NBS (534 g, 3.00 mmol). After 20 h, the reaction mixture was quenched with a saturated solution of $NaHSO_3$, and the solvent was evaporated. The organic substances were extracted with Et_2O, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by preparative TLC (SiO_2, hexane/EtOAc = 3/1, v/v) to give **16** in 56% yield (252 mg) as an oil. IR (neat) 3443, 2982, 2939, 2904, 2874, 1716, 1659, 1467, 1445, 1420, 1393, 1370, 1307, 1276, 1220, 1182, 1096, 1040, 982, 900, 877, 858, 722, 655 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.30 (3H, t, $J = 7.08$ Hz), 3.15 (1H, brs), 3.44 (1H, dd, $J = 10.49$, 6.59 Hz), 3.56 (1H, dd, $J = 10.49$, 4.15 Hz), 4.21 (2H, q, $J = 7.08$ Hz), 4.52–4.60 (1H, m), 6.16 (1H, dd, $J = 15.61$, 1.71 Hz), 6.90 (1H, dd, $J = 15.61$, 4.65 Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 222.99672, 224.99452. Calcd for $C_7H_{12}O_3{}^{79}Br$: 222.99698, Calcd for $C_7H_{12}O_3{}^{81}Br$: 224.99494.

Ethyl (*E*)-5-Bromo-4-fluoro-2-pentenoate (17): To a solution of **16** (125 mg, 0.560 mmol) in CH_2Cl_2 (4.0 mL) was added DAST (0.111 mL, 0.841 mmol) at 0 °C under a nitrogen atmosphere. After 70 min, the reaction mixture was quenched with cool water, and the solvent was evaporated. The organic substances were extracted with EtOAc, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by preparative TLC (SiO_2, hexane/EtOAc = 5/1, v/v) to give **17** in 90% yield (114 mg) as an oil. IR (neat) 2983, 2940, 2906, 2875, 1722, 1665, 1467, 1446, 1420, 1392, 1370, 1347, 1308, 1274, 1183, 1095, 1065, 1044, 979, 902, 876, 857, 825, 720, 687 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.31 (3H, t, $J = 7.07$ Hz), 3.51 (1H, ddd, $J = 24.15$, 9.27, 5.86 Hz), 3.54 (1H, ddd, $J = 24.15$, 9.27, 5.86 Hz), 4.23 (2H, q, $J = 7.07$ Hz), 5.29 (1H, dddt, $J = 47.08$, 4.39, 1.71, 5.86 Hz), 6.17 (1H, dt, $J = 15.61$, 1.71 Hz), 6.88 (1H, ddd, $J = 19.27$, 15.61, 4.39 Hz). ^{19}F NMR ($CDCl_3$) δ −181.1 (1F, ddt, $J = 47.08$, 19.27, 24.15 Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 224.99253, 226.99238. Calcd for $C_7H_{11}O_2F^{79}Br$: 224.99264. Calcd for $C_7H_{11}O_2FB^{81}Br$: 226.99060.

Ethyl (*E*)-4-Fluoro-2,4-pentadienoate (8): To a solution of **17** (76 mg, 0.338 mmol) in THF (3.0 mL) was added DBU (0.056 mL, 0.371 mmol) under a nitrogen atmosphere. After 5 min, the reaction mixture was quenched with a saturated solution of NH_4Cl, and the solvent was evaporated. The organic substances were extracted with EtOAc, followed by washing with H_2O, brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was separated by column chromatography (SiO_2, hexane/EtOAc = 5/1, v/v) to give **8** in 76% yield (37 mg) as an oil. IR (neat) 3050, 2984, 2940, 2906, 1719, 1653, 1618, 1467, 1447, 1395, 1367, 1307, 1258, 1230, 1177, 1096, 1036, 973, 953, 891, 866, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.31 (3H, t, $J = 7.08$ Hz), 4.23 (2H, q, $J = 7.08$ Hz), 4.84 (1H, dd, $J = 46.35$, 2.93 Hz), 5.04 (1H, dd, $J = 14.64$, 2.93 Hz), 6.20 (1H, d, $J = 15.61$ Hz), 7.05 (1H, dd, $J = 26.10$, 15.61 Hz). ^{19}F NMR ($CDCl_3$) δ −112.99 (1F, ddd, $J = 46.35$, 26.10, 14.64 Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 145.06616. Calcd for $C_7H_{10}O_2F$: 145.06648.

4-Fluoro-4-tosyl-1-butene (19): To a mixed solution of **18**[5b] (300 mg, 1.59 mmol) and HMPA (0.415 mL, 2.39 mmol) in THF (15.9 mL) was added a solution of *n*-BuLi in hexane (1.14 mL, 1.75 mmol, 1.54 M) at −72 °C under a nitrogen atmosphere, followed by addition of allyl bromide (0.165 mL, 1.91 mmol) after 30 min. The reaction mixture was stirred for 10 min at −72 °C and for 3 h at room temperature, and then quenched by addition of a saturated NH_4Cl solution. After removing the solvent under reduced pressure, the organic substances were extracted with EtOAc, followed by washing with H_2O, brine, and drying over Na_2SO_4. After evaporating the solvent, the residue was separated by preparative TLC (SiO_2, hexane/EtOAc = 5/1, v/v) to give **19** in 77% yield (278 mg) as an oil. IR (neat) 3084, 2983, 2925, 1644, 1597, 1494, 1431, 1375, 1330, 1305, 1245, 1221, 1185, 1155, 1090, 1078, 1044, 1018, 989, 928, 867, 816, 737, 705, 663 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.47 (3H, s), 2.63 (1H, ddddt, $J =$ 20.00, 15.37, 9.76, 6.83, 1.22 Hz), 2.88 (1H, ddddt, $J = 36.10$, 15.37, 6.83, 2.93, 1.22 Hz), 5.10 (1H, ddd, $J = 48.30$, 9.76, 2.93 Hz), 5.22 (1H, dd, $J = 10.02$, 1.22 Hz), 5.24 (1H, dd, $J =$ 17.08, 1.22 Hz), 5.80 (1H, ddt, $J = 17.08$, 10.02, 6.83 Hz), 7.39 (2H, d, $J = 8.29$ Hz), 7.82 (2H, d, $J = 8.29$ Hz). ^{19}F NMR ($CDCl_3$) δ −179.7 (1F, ddd, $J = 48.30$, 36.10, 20.00 Hz). HRMS (FAB$^+$) $(M + H)^+$, Found: m/z 229.06941. Calcd for $C_{11}H_{14}O_2FS$: 229.06985.

(*E*)-4-Fluoro-4-methylsulfanyl-4-tosyl-1-butene (20): In a

dry flask, *n*-BuLi in hexane (0.740 mL, 1.14 mmol, 1.54 M) was added to a solution of *i*-Pr_2NH (115 mL, 1.14 mmol) in THF (9.4 mL) at −72 °C and the mixture was stirred for 30 min, followed by dropwise addition of a solution of **19** (220 mg, 0.964 mmol) in THF (2.0 mL). After stirring for 30 min at −72 °C, MeSSMe (0.154 mL, 1.71 mmol) was added to the reaction mixture and the mixture was stirred for 90 min at room temperature. Then, the reaction mixture was quenched with phosphate-buffer (pH 7.2). After evaporating the organic solvent, the product was extracted with EtOAc, followed by washing with H_2O, brine, and drying over Na_2SO_4. After evaporating the solvent, the residue was separated by preparative TLC (hexane/EtOAc = 9/1, v/v) to afford **20** in 71% yield (188 mg) as an oil. IR (neat) 3083, 3027, 2983, 2935, 1642, 1597, 1493, 1428, 1333, 1306, 1292, 1244, 1212, 1185, 1155, 1087, 1040, 1018, 984, 970, 928, 873, 815, 762, 706 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.34 (3H, d, J = 1.46 Hz), 2.48 (3H, s), 2.73–2.81 (2H, m), 5.14 (1H, dd, J = 17.08, 1.46 Hz), 5.21 (1H, dd, J = 10.00, 1.46 Hz), 5.79 (1H, ddt, J = 17.08, 10.00, 6.83 Hz), 7.39 (2H, d, J = 8.05 Hz), 7.85 (2H, d, J = 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −141.3 (1F, dd, J = 20.65, 18.36 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 275.05846. Calcd for $C_{12}H_{16}O_2FS_2$: 275.05758.

(*E*)-1-Fluoro-1-tosyl-1,3-butadiene (10): Compound **20** (156 mg, 0.569 mmol) was treated with *m*CPBA (ca. 65%, 151 mg, 0.569 mmol) in the presence of $NaHCO_3$ (96 mg, 1.14 mmol) in CH_2Cl_2 (6.0 mL) for 30 min at room temperature. Then, the reaction mixture was quenched with a saturated aqueous solution of $NaHSO_3$. After evaporating the organic solvent, the product was extracted with EtOAc, followed by washing with a saturated solution of $NaHCO_3$, H_2O, brine, and drying over Na_2SO_4. After removal of solvent, the residue was purified by preparative TLC (hexane/EtOAc = 5/1, v/v) to afford **21** in 87% yield (144 mg). A THF (4.0 mL) solution of the obtained sulfoxide **21** (65 mg, 0.224 mmol) was refluxed for 2 h. The reaction mixture was condensed in vacuo to afford **10** in 99% yield (50 mg) as an oil. The obtained **10** was used for the reaction with diethylamine without further purification. IR (neat) 3050, 2925, 2854, 1812, 1724, 1651, 1596, 1492, 1457, 1333, 1305, 1212, 1154, 1087, 984, 930, 815, 706, 666 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 5.51 (1H, d, J = 10.25 Hz), 5.65 (1H, d, J = 17.08 Hz), 6.49 (1H, ddd, J = 17.08, 10.98, 10.25 Hz), 6.70 (1H, dd, J = 30.74, 10.98 Hz), 7.38 (2H, d, J = 8.05 Hz), 7.83 (2H, d, J = 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −126.9 (1F, d, J = 30.74 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 227.05495. Calcd for $C_{11}H_{12}O_2FS$: 227.05420.

Octyl (*Z*)-2-Fluoro-2,4-pentadienoate (12): To a mixed solution of (*Z*)- and (*E*)-2-fluoro-2,4-pentadienoic acid (**22**)[23] (252 mg, 2.17 mmol) in THF (5.0 mL) was added triethylamine (0.303 mL, 2.17 mmol) and isobutyl chloroformate (0.282 mL, 2.17 mmol) at −15 °C under a nitrogen atmosphere, followed by addition of octanol (0.684 mL, 4.34 mmol) after 30 min. The reaction mixture was stirred at room temperature overnight, and then quenched by adding a saturated NH_4Cl solution, and the solvent was evaporated. The organic substances were extracted with EtOAc, followed by washing with brine, and dried over Na_2SO_4. After evaporating the solvent, the residue was purified by preparative TLC (SiO_2, hexane/EtOAc = 30/1, v/v) to give a mixture of (*Z*)-ester **12** and the corresponding E isomer. Then, the mixture of esters (291 mg, 1.27 mmol) was treated with iodide (49 mg, 0.191 mmol) in CH_2Cl_2 (5.0 mL) at room temperature overnight to isomerize (*E*)-ester to (*Z*)-ester **12**. To the reaction mixture was added H_2O and the product was extracted with EtOAc, followed by washing with a saturated solution of $NaHSO_3$, brine, and drying over Na_2SO_4. The solvent was evaporated and the resulting residue was purified by recycle HPLC (SiO_2, hexane/EtOAc = 40/1, v/v) to give (*Z*)-ester **12** in 43% yield (214 mg) as an oil. IR (neat) 3094, 2957, 2927, 2857, 1824, 1729, 1646, 1598, 1468, 1421, 1391, 1380, 1338, 1288, 1227, 1189, 1140, 1100, 1000, 923, 774, 723, 658 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, J = 7.08 Hz), 1.30–1.40 (10H, m), 1.70 (2H, quint, J = 6.83 Hz), 4.23 (2H, t, J = 6.83 Hz), 5.44 (1H, d, J = 10.25 Hz), 5.58 (1H, d, J = 16.59 Hz), 6.58 (1H, dd, J = 29.76, 10.98 Hz), 6.68 (1H, ddd, J = 16.59, 10.98, 10.25 Hz). ^{19}F NMR ($CDCl_3$) δ −128.48 (1F, d, J = 29.78 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 229.15848. Calcd for $C_{13}H_{22}O_2F$: 229.16038.

The addition reaction of amines **2d** and **2k** to the synthesized fluorine-substituted dienes **6**, **8**, **10**, and **12** was carried out in a similar manner described for the addition to **1** and **4**. The physical and spectral data of the corresponding allylic products are given in the following.

***N*,*N*-Diethyl-2-fluoro-4-tosyl-2-butenylamine (7):** An oil (Z/E = 95/5). IR (neat) 2970, 2927, 2873, 1705, 1597, 1455, 1385, 1318, 1303, 1147, 1087, 920, 817, 753, 669 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 0.96 (6H, t, J = 7.08 Hz), 2.44 (3H, s), 2.44 (4H, q, J = 7.08 Hz), 3.08 (2H, d, J = 14.88 Hz), 3.89 (2H, d, J = 7.81 Hz), 4.95 (1H, dt, J = 33.42, 7.81 Hz), 7.33 (2H, d, J = 8.05 Hz), 7.76 (2H, d, J = 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −104.9 (1F, dt, J = 33.42, 14.88 Hz). E isomer; ^1H NMR ($CDCl_3$) δ 0.96 (6H, t, J = 7.08 Hz), 2.44 (3H, s), 2.44 (4H, q, J = 7.08 Hz), 2.98 (2H, d, J = 17.81 Hz), 3.92 (2H, d, J = 8.78 Hz), 5.22 (1H, dt, J = 18.78, 8.78 Hz), 7.33 (2H, d, J = 8.05 Hz), 7.76 (2H, d, J = 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −92.0 (1F, dt, J = 18.78, 17.81 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 300.14305. Calcd for $C_{15}H_{23}NO_2SF$: 300.14335. The stereochemistry of (*Z*)- and (*E*)-**7** was assigned based on J_{H-F} through the double bond.[24] Furthermore, NOE analysis between methylene protons and a vinylic proton in (*Z*)-**7** supported the assignment (Figure 4).

Ethyl 4-Fluoro-5-(piperidin-1-yl)-3-pentenoate (9): An oil (Z/E = 99/1). IR (neat) 2970, 2937, 2856, 2807, 1739, 1371, 1343, 1308, 1248, 1183, 1029, 993, 949, 864, 669 cm^{-1}. Z isomer; ^1H NMR ($CDCl_3$) δ 1.26 (3H, t, J = 7.07 Hz), 1.40–1.48 (2H, m), 1.60 (4H, quint, J = 5.61 Hz), 2.40–2.48 (4H, m), 3.05 (2H, d, J = 18.54 Hz), 3.16 (2H, dd, J = 7.31, 0.98 Hz), 4.15 (2H, q, J = 7.07 Hz), 4.97 (1H, dt, J = 35.62, 7.32 Hz). E isomer; ^1H NMR ($CDCl_3$) δ 1.26 (3H, t, J = 7.07 Hz), 1.40–1.48 (2H, m), 1.60 (4H, quint, J = 5.61 Hz), 2.40–2.48 (4H, m), 2.88 (2H, d, J = 18.05 Hz), 3.32 (2H, d, J = 8.05 Hz), 4.15 (2H, q, J = 7.07 Hz), 5.44 (1H, dt, J = 20.25, 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −100.2 (1F, dt, J = 20.25, 18.05 Hz). HRMS (FAB^+) $(M+H)^+$, Found: m/z 230.15619. Calcd for $C_{12}H_{21}NO_2F$: 230.15563. The stereochemistry of (*Z*)- and (*E*)-**9** was assigned based on J_{H-F} through the double bond.[24]

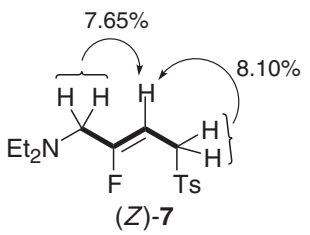


Figure 4.

***N*,*N*-Diethyl-4-fluoro-4-tosyl-2-butenylamine (11):** An oil (Z/E = 62/38). IR (neat) 2970, 2933, 2808, 1596, 1492, 1458, 1384, 1330, 1305, 1200, 1153, 1088, 1045, 816, 712, 669 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 1.02 (6H, t, J = 7.08 Hz), 2.48 (3H, s), 2.50 (4H, q, J = 7.08 Hz), 3.19–3.23 (2H, m), 5.48 (1H, ddd, J = 13.91, 11.47, 8.54 Hz), 6.05 (1H, dd, J = 47.33, 8.54 Hz), 6.18 (1H, dt, J = 11.47, 5.61 Hz), 7.39 (2H, d, J = 8.05 Hz), 7.81 (2H, d, J = 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −171.3 (1F, dd, J = 47.33, 13.91 Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 1.00 (6H, t, J = 7.08 Hz), 2.47 (3H, s), 2.47 (4H, q, J = 7.08 Hz), 3.11–3.21 (2H, m), 5.50 (1H, dd, J = 47.08, 6.34 Hz), 5.77 (1H, ddd, J = 15.37, 15.12, 6.34 Hz), 6.10 (1H, dt, J = 15.12, 6.10 Hz), 7.37 (2H, d, J = 8.05 Hz), 7.79 (2H, d, J = 8.05 Hz). ^{19}F NMR ($CDCl_3$) δ −174.7 (1F, dd, J = 47.08, 15.37 Hz). HRMS (FAB$^+$) $(M+H)^+$, Found: m/z 300.14327. Calcd for $C_{15}H_{23}NO_2SF$: 300.14335.

Octyl 2-Fluoro-5-(piperidin-1-yl)-3-pentenoate (13): An oil (Z/E = 50/50). IR (neat) 2931, 2856, 2799, 2760, 1764, 1742, 1467, 1278, 1197, 1156, 1119, 1039, 991, 862 cm^{-1}. Z isomer; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.83 Hz), 1.20–1.40 (10H, m), 1.40–1.50 (2H, m), 1.58 (4H, quint, J = 5.61 Hz), 1.64 (2H, quint, J = 6.83 Hz), 2.30–2.50 (4H, m), 3.10–3.25 (2H, m), 4.19 (2H, dt, J = 6.83, 1.46 Hz), 5.62 (1H, ddd, J = 46.59, 9.27, 1.78 Hz), 5.68 (1H, dtt, J = 10.98, 9.27, 1.46 Hz), 5.91 (1H, dt, J = 10.98, 6.83 Hz). ^{19}F NMR ($CDCl_3$) δ −182.9 (1F, dd, J = 46.59, 9.27 Hz). E isomer; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 6.83 Hz), 1.20–1.40 (10H, m), 1.40–1.50 (2H, m), 1.58 (4H, quint, J = 5.61 Hz), 1.64 (2H, quint, J = 6.83 Hz), 2.30–2.50 (4H, m), 2.98–3.03 (2H, m), 4.19 (2H, dt, J = 1.22, 6.83 Hz), 5.26 (1H, ddd, J = 48.81, 6.34, 1.78 Hz), 5.77 (1H, dtt, J = 6.34, 15.37, 1.46 Hz), 6.08 (1H, dddt, J = 15.37, 3.42, 1.22, 6.59 Hz). ^{19}F NMR ($CDCl_3$) δ −184.8 (1F, dd, J = 48.81, 15.37 Hz). HRMS (FAB$^+$) $(M+H)^+$, Found: m/z 314.24791. Calcd for $C_{18}H_{33}NO_2F$: 314.24953.

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4 The "syn effect" is herein defined as an effect which stabilizes the syn conformation against the steric hindrance at the transition state.

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12 Reaction conditions: **4** (100 mM), Et_2NH (300 mM), proton source (150 mM), THF, 25 °C, 24 h. Without proton source (4% yield; Z/E = 83/17), CF_3CO_2H (pK_a = 0;[25a] 42%; 7/93), HCO_2H (3.7;[25a] 14%; 12/88), 2,4,6-tri(*t*-butyl)phenol (12.19;[25c] 10%; 66/34), EtOH (17;[25a] 6%; 73/27), *i*-PrOH (18;[25b] 5%; 82/18), *t*-BuOH (19;[25a] 5%; 83/17).

13 Radical mechanism could be ruled out because the presence of TEMPO, *N*-hydroxyphthalimide, or galvinoxyl free radical did not affect the Z/E ratios.

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