A Convenient Preparation of 3,3,3-Trifluoro-1-propynylamines and Their Lewis Acid Catalyzed Reaction with Carbonyl Compounds Leading to (*Z*)-α-(Trifluoromethyl)-α,*β*-unsaturated Amides[1]

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Received December 18, 2000

N,*N*-Dialkyl(3,3,3-trifluoro-1-propynyl)amines were readily prepared by a three-step procedure starting from commercially available 2,2,3,3,3-pentafluoropropanol. These fluorinated alkynylamines reacted smoothly with a variety of aldehydes or ketones in the presence of a catalytic amount of Lewis acid and molecular sieves 4Å at ambient temperature to produce the corresponding α-(trifluoromethyl)-α,*β*-unsaturated amides in good to excellent yields with high *Z*-stereoselectivity.

Introduction

α,*β*-Unsaturated carbonyl compounds have widely been utilized as potent synthetic blocks in organic synthesis, particularly as Michael acceptors for conjugate addition reactions[2] or dienophiles and dipolarophiles for cycloaddition reactions.[3−5] The counterparts carrying the trifluoromethyl substituent at the α position are likewise of great synthetic value as synthons for the construction of a variety of selectively trifluoromethylated compounds, which attract much attention in biological or material chemistry.[6] To our knowledge, only three kinds of methods appear in the literature for the preparation of α-(trifluoromethyl)-α,*β*-unsaturated carbonyl compounds; the pyrolysis of the *O*-acetate of trifluoroacetone cyanohydrin or α-hydroxy-α-(trifluoromethyl)propanoate,[7] the direct or Pd(II)-catalyzed carbonylation of 3,3,3-trifluoro-1-propen-2-yllithium derived from 2-bromo-3,3,3-trifluoro-1-propene,[8,9] and the Reformatsky reaction of 2,2-dichloro-3,3,3-trifluoropropanoate with aldehydes followed by reductive elimination.[10] These methods, however, suffer from serious drawbacks, such as an extremely limited scope of the reaction, lack of stereoselectivity, and/or difficulty in the availability of the starting propanoate. Therefore, there is a great need to develop a more convenient and effective means for the synthesis of such α-trifluoromethylated compounds.

In close connection with our continuing studies on the preparations and applications of polyfluoroalkyl- or alkenylamines,[11,12] we recently directed our attention to fluorinated 1-alkynylamines, which should be expected to serve as useful building blocks for preparing fluorinated organic compounds, since ordinary 1-alkynylamines or ynamines are recognized to have unique and versatile reactivities and thereby to undergo various types of organic reactions,[13−17] for example, the hetero

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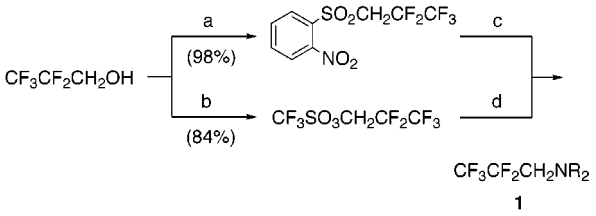
10.1021/jo001760v CCC: $20.00
Published on Web 04/21/2001

Scheme 1[a]



[a] Key: (a) 2-nitrobenzenesulfonyl chloride, NaOH/H_2O, 60 °C, 2 h. (b) $(CF_3SO_2)_2O$, neat, reflux, 3 h. (c) Method A; R_2NH or $BnNMe_2$, neat, 140−160 °C. (d) Method B; R_2NH, neat.

Table 1. Preparation of *N*,*N*-Dialkyl(2,2,3,3,3-pentafluoropropyl)amines 1

entry	amine	method[a]	temp (°C)	time (h)	yield[b] of **1** (%)
1	Bu_2NH	A	150−160	6	**1A**, 48
2	Bu_2NH	B	60	1	**1A**, 93
3	$BnNMe_2$	A	150−160	4	**1B**, 86
4	piperidine	A	140−150	6	**1C**, tr
5	piperidine	B	rt	1	**1C**, 79
6	*i*-Pr_2NH	B	reflux	24	**1D**, 45
7	Bn_2NH	B	reflux	24	**1E**, 49

[a] See the keys (c) and (d) in Scheme 1 as well as the Experimental Section. [b] Isolated yields based on the sulfonates.

Diels−Alder reaction with α,*β*-unsaturated ketones affording *γ*-pyrane derivatives[14a−d] or the reaction with allylic alcohols leading to *γ*,*δ*-unsaturated amines.[17a,b] Despite such attractive utility, there are few reports dealing with the preparation and reactions of fluorine-containing ynamines.[18] In this paper we disclose the first expedient preparation of trifluoromethylated ynamines, *N*,*N*-dialkyl(3,3,3-trifluoro-1-propynyl)amines (**2**) and their Lewis acid catalyzed reactions with carbonyl compounds, demonstrating that these reactions provide us with a highly efficient and general method for the stereoselective synthesis of α-(trifluoromethyl)-α,*β*-unsaturated amides **3**.

Results and Discussion

Preparation of Trifluoromethylated Ynamines 2. As the precursors of trifluoromethylated ynamines, *N*,*N*-dialkyl(2,2,3,3,3-pentafluoropropyl)amines (**1**) were prepared from commercially available 2,2,3,3,3-pentafluoropropanol, which was converted into the corresponding sulfonate esters either by the reaction with *o*-nitrobenzenesulfonyl chloride and sodium hydroxide in water at 60 °C for 2 h[11a] or by the reaction with trifluoromethanesulfonic anhydride at reflux temperature for 3 h.[19] The obtained *o*-nitrobenzenesulfonate and trifluoromethanesulfonate (triflate) were subjected to a Hofmann-like degradation with *N*,*N*-dimethylbenzylamine[11c] or polyfluoroalkylation of a secondary amine, as shown in Scheme 1. The results of the reactions conducted under various conditions are summarized in Table 1. The reaction of *o*-nitrobenzenesulfonate with dibutylamine gave *N*,*N*-dibutyl(2,2,3,3,3-pentafluoropropyl)amine (**1A**) in appreciably lower yield than the reaction using trifluoromethanesulfonate (entries 1 and 2). A similar trend was observed in the preparation of *N*-(2,2,3,3,3-pentafluoropropyl)piperidine (**1C**) through the reactions using *o*-nitrobenzenesulfonate (entry 4) and trifluoromethanesulfonate (entry 5). These trends in the yields of **1** can be considered to result primarily from the difference in reactivity between the two sulfonates. Triflate has a far superior leaving ability. It should be noted that the Hofmann-like degradation between *o*-nitrobenzenesulfonate and an excess amount (3 equiv) of *N*,*N*-dimethylbenzylamine at high temperatures was strongly recommended for preparing *N*,*N*-dimethyl(2,2,3,3,3-pentafluoropropyl)amine (**1B**) (entry 3).[11c] *N*,*N*-diisopropyl- (**1D**) and *N*,*N*-dibenzyl(2,2,3,3,3-pentafluoropropyl)amine (**1E**) were also obtained in moderate yields by the reaction using trifluoromethanesulfonate (entries 6 and 7).

Scheme 2

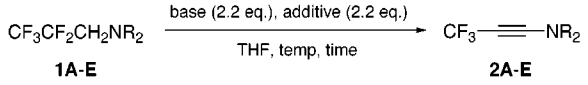


Table 2. Preparation of Ynamines 2 from Tertiary Amines 1

entry	**1**	base	additive	temp (°C)	time (h)	yield[a] of **2** (%)	recovery of **1** (%)
1	**1A**	LDA	none	0	2	**2A,** 14	75
2	**1A**	LDA	none	rt	2	**2A,** 47	41
3	**1A**	LDA	none	rt	24	**2A,** 66	24
4	**1A**	LDA	DMPU	0	2	**2A,** 84	9
5	**1A**	LDA	DMPU	rt	2	**2A,** 94(75)	tr
6	**1A**	BuLi	none	rt	2	**2A,** 5	43
7	**1A**	*t*-BuOK	none	rt	24	**2A,** 23[b]	44
8	**1B**	LDA	DMPU	0	2	**2B,** 92	tr
9	**1C**	LDA	DMPU	rt	2	**2C,** 97	tr
10	**1D**	LDA	DMPU	rt	24	**2D,** 66	21
11	**1E**	LDA	DMPU	rt	24	**2E,** 0	100

[a] Determined by ^{19}F NMR. Value in parentheses is of isolated yield. [b] *N*,*N*-Dibutyl(2,3,3,3-tetrafluoro-1-propenyl)amine was also formed in 33% yield.

On reaction with base, these fluorinated tertiary amines **1** underwent dehydrofluorination to the desired ynamines **2** (Scheme 2). As summarized in Table 2, treatment of **1A** with 2.2 equiv of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at 0 °C for 2 h provided the ynamine **2A** in only 14% yield, while 75% of the starting amine **1A** was recovered (entry 1). The reaction at room temperature and/or for a prolonged reaction time led to an increase in the yields of **2A** (entries 2 and 3). The use of 2.2 equiv of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) as an additive was found to allow the reaction to proceed quite efficiently (entries 4 and 5). Thus, the reaction of **1A** with LDA (2.2 equiv) in THF containing DMPU (2.2 equiv) at room temperature for 2 h afforded the ynamine **2A** in 94% yield. Bases other than LDA, such as butyllithium and potassium *tert*-butoxide, were not as effective for the reaction (entries 6 and 7). Similarly, *N*,*N*-dialkyl(3,3,3-trifluoropropynyl)amines **2B**−**D** were prepared through the reactions of **1B**−**D** with LDA in THF and DMPU at 0 °C or room temperature, as shown in entries 8−10. However, no ynamine **2E** could be obtained. The reaction of **1E** with LDA resulted in a quantitative recovery of the starting amine (entry 11).

Reaction of Trifluoromethylated Ynamines 2 with Carbonyl Compounds. First, the reactions of **2A** with benzaldehyde (Scheme 3) were examined under various conditions, as shown in Table 3. Thus, **2A** and benzaldehyde in CH_2Cl_2 in the presence of molecular sieves 4Å (MS 4Å) showed little evidence of reaction. Acidic workup

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Scheme 3

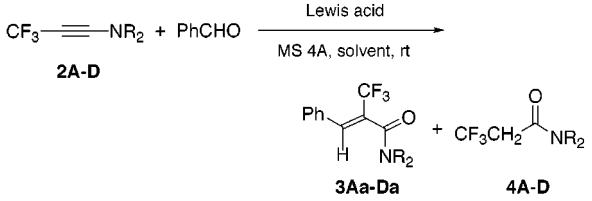


Table 3. Screening of Reaction Conditions for the Reaction of Ynamines 2 with Benzaldehyde

entry	**2**	Lewis acid[a]	solvent	time (h)	yield[b] of **3** (%)	yield[b] of **4** (%)
1	**2A**	none	CH_2Cl_2	24	**3Aa,** 3	79
2	**2A**	BF_3·OEt_2	CH_2Cl_2	1	**3Aa,** 92	tr
3[c]	**2A**	BF_3·OEt_2	CH_2Cl_2	1	**3Aa,** 28	66
4[c]	**2A**	$La(OTf)_3$[d]	CH_2Cl_2	24	**3Aa,** 71	8
5	**2A**	$ZnBr_2$	CH_2Cl_2	1	**3Aa,** 90	5
6	**2A**	$TiCl_4$	CH_2Cl_2	1	**3Aa,** 80	12
7	**2A**	$SnCl_4$	CH_2Cl_2	1	**3Aa,** 81	5
8	**2A**	BF_3·OEt_2	$PhCH_3$	1	**3Aa,** 84	3
9	**2A**	BF_3·OEt_2	Et_2O	1	**3Aa,** 82	6
10	**2A**	BF_3·OEt_2	THF	1	**3Aa,** 82	7
11[c]	**2B**	$La(OTf)_3$[d]	CH_2Cl_2	24	**3Ba,** 65	20
12[c]	**2C**	$La(OTf)_3$[d]	CH_2Cl_2	24	**3Ca,** 73	18
13	**2D**	BF_3·OEt_2	CH_2Cl_2	1	**3Da,** 40	43

[a] 10 mol % of Lewis acid was used, unless otherwise noted. [b] Isolated yields. [c] Without MS 4Å. [d] Employed 30 mol % of $La(OTf)_3$.

of this mixture gave *N*,*N*-dibutyl-3,3,3-trifluoropropanamide (**4A**) in 79% yield, together with 3% of α-(trifluoromethyl)-α,*β*-unsaturated amide **3Aa** (entry 1). When 10 mol % of boron trifluoride etherate (BF_3·OEt_2) was employed as a Lewis acid, the reaction was markedly facilitated to give the desired amide **3Aa** in high yield (entry 2). This amide **3Aa** was an isomeric mixture with *Z*:*E* of >97:<3. The presence of MS 4Å was requisite to suppress the formation of **4A**, which may result from the acidic hydration with a slight amount of water contaminating the starting ynamine **2A**. In fact, ^{19}F NMR analysis for the reaction conducted in the absence of MS 4Å clearly indicated the in situ formation of **4A** as well as **3Aa**, which were obtained in 66% and 28% yield, respectively, after a usual workup (entry 3). The reaction using lanthanum(III) triflate, known to be resistant to hydrolysis,[20] gave a satisfactory result even in the absence of MS 4Å, though the reaction time had to be extended to 24 h (entry 4). Other Lewis acids, such as zinc bromide, titanium(IV) chloride, and tin(IV) chloride, were also effective for the reaction (entries 5−7). Toluene, diethyl ether, and THF could be utilized as solvents comparable to CH_2Cl_2 (entries 8−10). The reactions between **2B** or **2C** and benzaldehyde in the presence of $La(OTf)_3$ (30 mol %) provided the corresponding α,*β*-unsaturated amides **3Ba** and **3Ca** in good yields with high *Z*-stereoselectivity (entries 11 and 12). On the other hand, the ynamine **2D** reacted reluctantly with benzaldehyde in the presence of BF_3·OEt_2, leading to the amide **3Da** in 40% yield (entry 13). Probably, bulky isopropyl groups on the amine nitrogen are responsible in part for such low efficiency of the reaction.

On the basis of these examinations, the reactions of **2A** with other aldehydes or ketones were undertaken by employing BF_3·OEt_2 and CH_2Cl_2 solvent (Scheme 4). The

Scheme 4

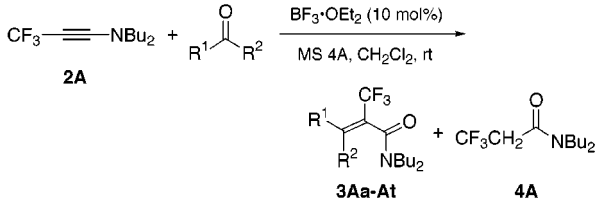


Table 4. Synthesis of α,*β*-Unsaturated Amides 3A by the Reaction of Ynamines 2A with Carbonyl Compounds

entry	R^1	R^2	time (h)	yield[a] of **3A** (%)	isomer ratio[b] of **3A** (*Z*:*E*)	yield[a] of **4A** (%)
1	Ph	H	1	**3Aa**, 92	>97:<3	tr
2	*p*-MeC_6H_4	H	1	**3Ab**, 95	>97:<3	2
3	*p*-$MeOC_6H_4$	H	1	**3Ac**, 81	>97:<3	6
4	*p*-ClC_6H_4	H	1	**3Ad**, 92	>97:<3	4
5	1-naphthyl	H	1	**3Ae**, 87	>97:<3	8
6	2-thienyl	H	1	**3Af**, 97	96:4	tr
7	2-furyl	H	1	**3Ag**, 94	>97:<3	tr
8	(*E*)-PhCH=CH	H	1	**3Ah**, 82	>97:<3	tr
9	(*Z*)-PhCH=CF	H	1	**3Ai**, 97	>97:<3	tr
10	(*E*)-MeCH=CH	H	1	**3Aj**, 95	96:4	3
11	CH_2=C(Me)	H	1	**3Ak**, 88	>97:<3	tr
12	*n*-Pr	H	1	**3Al**, 83	>97:<3	5
13	*n*-Hex	H	1	**3Am**, 75	>97:<3	20
14	*i*-Pr	H	1	**3An**, 89	96:4	3
15	*c*-Hex	H	1	**3Ao**, 82	>97:<3	11
16[c]	*t*-Bu	H	2	**3Ap**, 68	56:44	23
17	Me	Me	2	**3Aq**, 85		6
18	Et	Et	2	**3Ar**, 77		11
19	-$(CH_2)_5$-		2	**3As**, 77		8
20	Ph	Me	2	**3At**, 72	71:29	9

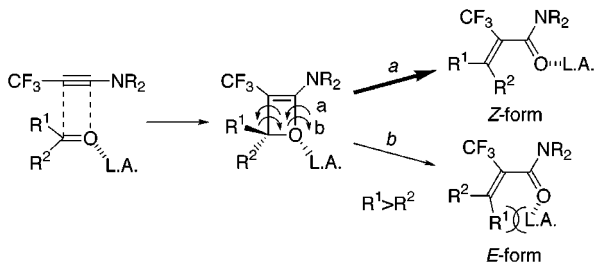
[a] Isolated yields. [b] Measured by ^{19}F NMR before isolation. [c] Carried out by using 20 mol % of BF_3·OEt_2.

results are summarized in Table 4. Thus, when various types of aldehydes, such as aromatic, heteroaromatic, α,*β*-unsaturated, and aliphatic aldehydes, were allowed to react with **2A** under the influence of 10 mol % of BF_3·OEt_2 and MS 4Å in CH_2Cl_2 at ambient temperature for 1 h, the corresponding α-(trifluoromethyl)-α,*β*-unsaturated amides **3A** were provided in good to excellent yields. More significantly, these reactions of aldehydes, except 2,2-dimethylpropanal, took place with very high levels of stereoselectivity to produce the (*Z*)-isomers predominantly (entries 1−15). The reaction of 2,2-dimethylpropanal needed 20 mol % of BF_3·OEt_2 and a prolonged reaction period and gave rise to 68% yield of the amide **3Ap** consisting of the two geometrical isomers in a *Z*:*E* ratio of 56:44 (entry 16). A variety of ketones, such as acetone, 3-pentanone, cyclohexanone, and acetophenone, were also found to participate nicely in the reaction with **2A**, leading to the corresponding α,*β*-unsaturated amides **3Aq**−**3At** in good yields, as shown in entries 17−20. All of the reactions using ketones required a longer reaction time of 2 h for satisfactory results. The reaction of acetophenone occurred in an appreciably low stereoselective manner to result with the formation of **3At** as an isomeric mixture of *Z*:*E* = 71:29 (entry 20)

The geometry of α,*β*-unsaturated amides **3A** was determined as follows. The ^{19}F NMR spectrum of the crude amide **3Ba** (isomer ratio, 97:3) showed two resonance peaks due to the trifluoromethyl group at −57.74 and −64.81 ppm for the major and minor isomers, respectively. Since crystallographic analysis of the major isomer of **3Ba**[21] permitted the straightforward assignment of its *Z*-geometry, the former peak (at lower field)

(20) For a review on lanthanide triflates, see: Kobayashi, S.; Hachiya, I. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 370.

Scheme 5



corresponding to the major isomer could be distinctly assigned to the (*Z*)-isomer and the latter (at higher field) to the (*E*)-isomer. These results served to assign the stereochemistry of other amides **3A**. In ^{19}F NMR spectra of the crude amides **3Aa**−**3Ap**, their major isomers exhibited the resonance peaks around −54 to −60 ppm, whereas the minor isomers showed the peaks at consistently higher fields of 5−8 ppm than the major ones. Such a tendency for the resonances of the two isomers enabled us to make their geometrical assignments; the isomer having a lower fluorine chemical shift was determined as the (*Z*)-isomer and the isomer possessing a higher chemical shift as *E*.

The reactions leading to the amides **3** are presumed to occur via the mechanism depicted in Scheme 5, essentially similar to that proposed recently for the reaction between alkynolates and carbonyl compounds.[22a,c] Thus, the ynamine **2** may attack a carbonyl compound activated by a Lewis acid[23] to form an oxetene intermediate. This intermediate would be subject to conrotatory ring opening in such a way, designated with the arrow *a* in Scheme 5, that the Lewis acid part (L.A.) and the substituent R^1 or R^2 ($R^1 > R^2$) exert their mutual repulsive interaction minimally, resulting in the preferential formation of the (*Z*)-isomers of the products **3**.

In conclusion, we have demonstrated that trifluoromethylated ynamines **2**, prepared in three steps from readily available 2,2,3,3,3-pentafluoropropanol, efficiently undergo Lewis acid catalyzed reactions with a variety of carbonyl compounds to give predominantly the (*Z*)-isomers of the corresponding α-(trifluoromethyl)-α,*β*-unsaturated amides **3** in high yields. This reaction will serve as a convenient and efficient means for the stereoselective synthesis of such compounds **3** that are otherwise difficult to prepare.

Experimental Section

General Methods. Melting points were obtained on a Shimadzu MM-2 micro melting point determination apparatus and are uncorrected. Infrared spectra (IR) were taken on a Shimadzu IR-400 and/or FTIR-8200(PC) spectrophotometer as film on a NaCl plate or as KBr pellet. ^1H NMR spectra were measured with a Varian Gemini-200, General Electric QE-300, and/or Bruker DRX-500 NMR spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane (Me_4Si) as an internal reference. ^{13}C NMR spectra were recorded on a General Electric QE-300 (75.61 MHz) and/or Bruker DRX-500 (125.75 MHz) NMR spectrometer in a $CDCl_3$ solution with Me_4-Si as an internal standard. A JEOL JNM-EX90A (84.21 MHz) FT-NMR spectrometer was used for determining ^{19}F NMR spectra in a $CDCl_3$ solution with the internal standard of trichlorofluoromethane. Mass (MS) and high-resolution mass spectra (HRMS) were taken on a Hitachi M-80B or JEOL JMS-700 mass spectrometer by electron impact (EI) or chemical ionization (CI) method. Elemental analyses were conducted with a Yanaco CHN corder MT-5 instrument. Thin-layer chromatography (TLC) was done on glass plates coated with silica gel (Merck 60 F_{254}), and column chromatography was carried out using silica gel (Wakogel C-200) as absorbent.

Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium/benzophenone ketyl under argon. Other solvents were dried according to the conventional methods before use. Butyllithium (a 1.6 M hexane solution) was commercially available from Aldrich or Kanto Chemical Co. Aldehydes and ketones were distilled (or vacuum distilled) over calcium hydride or recrystallized from appropriate solvents and were stored under argon. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. 2,2,3,3,3-Pentafluoropropyl *o*-nitrobenzenesulfonate and trifluoromethanesulfonate were prepared according to the literature method[11a] or slightly modified procedure.[19]

Typical Procedure for the Preparation of Tertiary Amines 1. Method A.[11c] A mixture of *o*-nitrobenzenesulfonate (50.27 g, 150 mmol) and *N*,*N*-dimethylbenzylamine (60.84 g, 450 mmol) was heated with stirring at such temperatures (140−160 °C) that tertiary amine **1B** formed in situ was constantly distilled. The collected distillate was subjected to fractional distillation giving the desired amine **1B** (86%). **Method B.** A mixture of trifluoromethanesulfonate (42.32 g, 150 mmol) and dibutylamine (58.16 g, 450 mmol) was stirred without solvent at 60 °C for 1 h. After cooling to room temperature, the mixture was filtered to remove dibutylammonium salt, which was washed with ether (ca. 50 mL). The filtrate was washed successively with 5% HCl (100 mL × 2) and with water (50 mL), followed by drying over anhydrous Na_2SO_4, filtration, and concentration. The resultant oil was distilled to yield **1A** (93%).

***N*,*N*-Dibutyl(2,2,3,3,3-pentafluoropropyl)amine (1A):** bp 75.0−76.0 °C/20 Torr; IR (film) 2960, 1190, 1110 cm^{-1}; ^1H NMR (200 MHz) δ 0.91 (t, J = 7.1 Hz, 6H), 1.22−1.49 (m, 8H), 2.57 (t, J = 7.1 Hz, 4H), 3.03 (tq, J = 15.8, 1.1 Hz, 2H); ^{13}C NMR (125.75 MHz) δ 13.91, 20.23, 29.38, 53.63 (t, J = 21.8 Hz), 55.16, 115.03 (tq, J = 253.9, 35.6 Hz), 119.23 (tq, J = 35.6, 286.7 Hz); ^{19}F NMR (84.21 MHz) δ −117.83 (t, J = 15.8 Hz, 2F), −82.17 (t, J = 1.1 Hz, 3F); MS (EI) *m*/*z* (rel intensity) 261 (M^+, 6), 218 (100); HRMS (EI) calcd for $C_{11}H_{20}F_5N$ (M^+) 261.1516, found 261.1515. Anal. Calcd for $C_{11}H_{20}F_5N$: C, 50.57; H, 7.72; N, 5.36. Found: C, 49.94; H, 7.62; N, 5.41.

***N*,*N*-Dimethyl(2,2,3,3,3-pentafluoropropyl)amine (1B):** bp 58.0 °C; IR (film) 2960, 1200, 1105 cm^{-1}; ^1H NMR (200 MHz) δ 2.41 (s, 6H), 2.93 (tq, J = 15.6, 1.1 Hz, 2H); ^{13}C NMR (125.75 MHz) δ 46.46, 57.76 (t, J = 22.3 Hz), 114.96 (tq, J = 254.1, 35.8 Hz), 119.12 (tq, J = 35.8, 285.6 Hz); ^{19}F NMR (84.21 MHz) δ −117.30 (t, J = 15.6 Hz, 2F), −82.23 (t, J = 1.1 Hz 3F); MS (EI) *m*/*z* (rel intensity) 177 (M^+, 100); HRMS (EI) calcd for $C_5H_8F_5N$ (M^+) 177.0577, found 177.0573.

***N*-(2,2,3,3,3-Pentafluoropropyl)piperidine (1C):** bp 122.0−123.0 °C; IR (film) 2941, 1198, 1134 cm^{-1}; ^1H NMR (300 MHz) δ 1.38−1.46 (m, 2H), 1.55−1.463 (m, 4H), 2.58 (t, J = 5.3 Hz, 4H), 2.91 (tq, J = 15.6, 1.2 Hz, 2H); ^{13}C NMR (125.75 MHz) δ 23.70, 25.97, 55.66, 57.44 (t, J = 22.0 Hz), 114.92 (tq, J = 290.1, 35.6 Hz), 119.06 (tq, J = 35.6, 286.2 Hz); ^{19}F NMR (84.21 MHz) δ −119.51 (t, J = 15.6 Hz, 2F), −84.54 (t, J = 1.2 Hz, 3F); MS (EI) *m*/*z* (rel intensity) 217 (M^+, 19), 98 (100); HRMS (EI) calcd for $C_8H_{12}F_5N$ (M^+) 217.0870, found 217.0894.

***N*,*N*-Diisopropyl(2,2,3,3,3-pentafluoropropyl)amine (1D):** bp 136.0−136.5 °C; IR (film) 2972, 1194, 1153 cm^{-1}; ^1H NMR (300 MHz) δ 1.02 (d, J = 6.5 Hz, 12H), 2.99−3.11 (m,

(21) For details regarding the X-ray crystal structure of **3Ba**, see the Supporting Information.

(22) Shindo et al. have recently proposed the mechanism for the [2 + 2] cycloaddition reactions of alkynolates with carbonyl and related compounds; see: (a) Shindo, M.; Sato, Y.; Shishido, K. *Tetrahedron Lett*. **1998**, *39*, 4857. (b) Shindo, M.; Sato, Y.; Shishido, K. *J. Am. Chem. Soc*. **1999**, *121*, 6507. (c) Shindo, M.; Sato, Y.; Shishido, K. *J. Org. Chem*. **2000**, *65*, 5443. (d) Shindo, M.; Oya, S.; Murakami, R.; Sato, Y.; Shishido, K. *Tetrahedron Lett*. **2000**, *41*, 5947.

(23) Taking into account the highly electronegative nature of the trifluoromethyl goup, one can assume that as basicity of the ynamine **2** is reduced definitely by its electronic effect, the carbonyl compound may participate effectively in coordination with Lewis acid.

4H); ^{13}C NMR (125.75 MHz) δ 20.80, 45.44 (t, J = 22.3 Hz), 49.50, 114.73 (tq, J = 252.1, 35.5 Hz), 119.55 (tq, J = 35.5, 286.5 Hz); ^{19}F NMR (84.21 MHz) δ −120.35 (t, J = 15.6 Hz, 2F), −84.43 (s, 3F); MS (EI) m/z (rel intensity) 233 (M^+, 2), 176 (100); HRMS (EI) calcd for $C_9H_{16}F_5N$ (M^+) 233.2102, found 233.1207.

***N,N*-Dibenzyl(2,2,3,3,3-pentafluoropropyl)amine (1E):** bp 149.0 °C/3 Torr; IR (film) 3030, 1196, 1130 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.11 (tq, J = 15.6, 0.9 Hz, 2H), 3.76 (s, 4H), 7.20−7.35 (m, 10H); ^{19}F NMR (84.21 MHz) δ −118.57 (t, J = 15.6 Hz, 2F), −84.61 (s, 3F); MS (EI) m/z (rel intensity) 329 (M^+, 5), 210 (100); HRMS (EI) calcd for $C_{17}H_{16}F_5N$ (M^+) 329.1203, found 329.1204.

Typical Procedure for the Preparation of Ynamines 2. To a solution of LDA (2.2 mmol) in THF (3.0 mL) was gradually added a solution of **1A** (0.262 g, 1.0 mmol) in THF (1.0 mL) and DMPU (0.282 g, 2.2 mmol) at 0 °C under argon. The mixture was stirred at room temperature for 2 h. After being quenched with water, the resulting mixture was extracted with ether (20 mL × 3). The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to leave crude **2A**, of which the yield was determined by ^{19}F NMR using α,α,α-trifluorotoluene as the reference. The ynamine **2A** thus obtained was subjected to the following reactions without any purification.

***N,N*-Dibutyl(3,3,3-trifluoro-1-propynyl)amine (2A):** bp 36 °C/15 Torr; IR (film) 2361 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.94 (t, J = 7.2 Hz, 6H), 1.31−1.43 (m, 4H), 1.55−1.65 (m, 4H), 2.98 (t, J = 7.2 Hz, 4H); ^{13}C NMR (125.75 MHz) δ 13.48, 19.71, 29.70, 52.56, 55.76 (q, J = 52.08 Hz), 100.51 (q, J = 7.12 Hz), 118.32 (q, J = 255.01 Hz);^{19}F NMR (84.21 MHz) δ −46.15 (s, 3F); MS (EI) m/z (rel intensity) 221 (M^+, 19), 128 (100); HRMS (EI) calcd for $C_{11}H_{18}F_3N$ (M^+) 221.1391, found 221.1378.

***N,N*-Dimethyl(3,3,3-trifluoro-1-propynyl)amine (2B):** IR (THF soln) 2218 cm^{-1}; ^{19}F NMR (84.21 MHz, THF) δ −46.21 (s, 3F). Other spectral data could not be obtained because of contamination with the solvent.

***N*-(3,3,3-Trifluoro-1-propynyl)piperidine (2C):** IR (film) 2222 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.48−1.60 (m, 6H), 3.10 (t, J = 5.5 Hz, 4H); ^{13}C NMR (125.75 MHz) δ 23.02, 24.62, 51.52, 52.96 (q, J = 52.4 Hz), 98.83 (q, J = 6.8 Hz), 117.77 (q, J = 254.4 Hz); ^{19}F NMR (84.21 MHz) δ −46.34 (s, 3F).

***N,N*-Diisopropyl(3,3,3-trifluoro-1-propynyl)amine (2D):** IR (film) 2203 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.22 (d, J = 6.5 Hz 12H), 3.19 (sept, J = 6.5 Hz, 4H); ^{13}C NMR (125.75 MHz) δ 21.23, 52.34, 60.73 (q, J = 51.7 Hz), 98.71 (q, J = 5.5 Hz), 118.65 (q, J = 255.1 Hz);^{19}F NMR (84.21 MHz) δ −44.77 (s, 3F).

General Procedure for the Reaction of 2 with Various Carbonyl Compounds Leading to α,β-Unsaturated Amides 3. To a solution of **2** (1.0 mmol) in CH_2Cl_2 (3.0 mL) containing MS 4Å (1.0 g) were dropwise added successively aldehyde (1.1 mmol) and BF_3·OEt_2 (0.1 mmol) at 0 °C under an argon atmosphere. After stirring at room temperature for 1 h, the mixture was filtered to remove MS 4Å. The filtrate was poured into 3% HCl (10 mL), and the resulting mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to leave a residual oil, which was submitted to ^{19}F NMR analysis. The residue was chromatographed on a silica gel column with benzene to provide analytically pure product **3**, together with a small amount of **4** in some cases.

***N,N*-Dibutyl-(*Z*)-3-phenyl-2-(trifluoromethyl)-2-propenamide (3Aa):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.94 (t, J = 7.1 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H), 1.23−1.46 (m, 4H), 1.53−1.68 (m, 4H), 3.39 (t, J = 7.9 Hz, 2H), 3.44 (t, J = 7.6 Hz, 2H), 6.94 (s, 1H), 7.35−7.44 (m, 5H); ^{13}C NMR (125.75 MHz) δ 13.68, 13.79, 19.89, 20.10, 29.19, 30.48, 44.44, 48.49, 121.77 (q, J = 274.7 Hz), 127.49 (q, J = 32.6 Hz), 128.43, 128.90 (q, J = 2.0 Hz), 129.44, 132.53, 137.9 (q, J = 4.1 Hz), 165.5 (q, J = 2.1 Hz); ^{19}F NMR (84.21 MHz) δ −54.70 (s, 3F); MS (EI) m/z (rel intensity) 327 (M^+, 7), 199 (100); HRMS (EI) calcd for $C_{18}H_{24}F_3NO$ (M^+) 327.1810, found 327.1807. Anal. Calcd for $C_{18}H_{24}F_3NO$: C, 66.04; H, 7.39; N, 4.28. Found: C, 66.48; H, 7.45; N, 4.07.

***N,N*-Dimethyl-(*Z*)-3-phenyl-2-(trifluoromethyl)-2-propenamide (3Ba):** mp 71−72 °C; IR (KBr) 1628 cm^{-1}; ^{1}H NMR (300 MHz) δ 3.05 (s, 3H), 3.12 (s, 3H), 6.98 (s, 1H), 7.36−7.45 (m, 5H); ^{13}C NMR (125.75 MHz) δ 34.92, 38.59, 121.70 (q, J = 274.7 Hz), 126.81 (q, J = 32.7 Hz), 128.40, 128.96, 129.56, 132.34, 138.83 (q, J = 4.0 Hz), 165.55 (q, J = 2.3 Hz); ^{19}F NMR (84.21 MHz) δ −57.74 (s, 3F); MS (EI) m/z (rel intensity) 243 (M^+, 31), 199 (100); HRMS (EI) calcd for $C_{12}H_{12}F_3NO$ (M^+) 243.0871, found 243.0871. Anal. Calcd for $C_{12}H_{12}F_3NO$: C, 59.26; H, 4.97; N, 5.76. Found: C, 59.54; H, 5.03; N, 5.34.

***N,N*-Pentamethylene-(*Z*)-3-phenyl-2-(trifluoromethyl)-2-propenamide (3Ca):** IR (film) 1639 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.57−1.66 (m, 6H), 3.53−3.63 (m, 4H), 6.94 (s, 1H), 7.31−7.44 (m, 5H); ^{13}C NMR (125.75 MHz) δ 24.22, 25.23, 26.00, 42.80, 48.19, 121.67 (q, J = 274.9 Hz), 126.70 (q, J = 32.6 Hz), 128.29, 128.89, 128.90, 129.40, 132.33, 137.98 (q, J = 3.2 Hz), 163.83 (q, J = 2.4 Hz); ^{19}F NMR (84.21 MHz) δ −57.74 (s, 3F); MS (EI) m/z (rel intensity) 283 (M^+, 24), 199 (100); HRMS (EI) calcd for $C_{15}H_{16}F_3NO$ (M^+) 283.1184, found 283.1176.

***N,N*-Diisopropyl-(*Z*)-3-phenyl-2-(trifluoromethyl)-2-propenamide (3Da):** IR (film) 1639 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.24 (d, J = 6.4 Hz, 6H), 1.50 (d, J = 6.2 Hz, 6H), 3.41−3.60 (m, 1H), 4.11−4.30 (m, 1H), 6.86 (s, 1H), 7.35−7.46 (m, 5H); ^{13}C NMR (125.75 MHz) δ 20.03, 20.15, 45.89, 51.14, 121.87 (q, J = 274.8 Hz), 128.27, 128.61 (q, J = 31.8 Hz), 128.87 (q, J = 1.9 Hz), 129.23, 132.50, 136.15 (q, J = 3.4 Hz), 164.40 (q, J = 2.2 Hz); ^{19}F NMR (84.21 MHz) δ −57.67 (s, 3F); MS (EI) m/z (rel intensity) 299 (M^+, 11), 199 (100); HRMS (EI) calcd for $C_{16}H_{20}F_3NO$ (M^+) 299.1498, found 299.1500.

***N,N*-Dibutyl-(*Z*)-3-(4-methylphenyl)-2-(trifluoromethyl)-2-propenamide (3Ab):** IR (film) 1630 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92 (t, J = 6.7 Hz, 3H), 0.96 (t, J = 6.9 Hz, 3H), 1.22−1.45 (m, 4H), 1.53−1.67 (m, 4H), 2.37 (s, 3H), 3.38 (t, J = 7.6 Hz, 2H), 3.43 (t, J = 7.6 Hz, 2H), 6.88 (s, 1H), 7.20 and 7.34 (AB quartet, J = 8.2 Hz, 4H); ^{13}C NMR (125.75 MHz) δ 13.57, 13.70, 19.79, 20.03, 21.18, 29.14, 30.40, 44.37, 48.43, 121.87 (q, J = 274.5 Hz), 126.30 (q, J = 32.3 Hz), 129.03, 129.05, 129.13, 129.52, 137.92 (q, J = 4.0 Hz), 165.50 (q, J = 2.1 Hz); ^{19}F NMR (84.21 MHz) δ −55.02 (s, 3F); MS (EI) m/z (rel intensity) 341 (M^+, 5), 213 (100); HRMS (EI) calcd for $C_{19}H_{26}F_3NO$ (M^+) 341.1966, found 341.1964. Anal. Calcd for $C_{19}H_{26}F_3NO$: C, 66.84; H, 7.68; N, 4.10. Found: C, 66.57; H, 7.57; N, 3.79.

***N,N*-Dibutyl-(*Z*)-3-(4-methoxyphenyl)-2-(trifluoromethyl)-2-propenamide (3Ac):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H), 1.21−1.45 (m, 4H), 1.51−1.73 (m, 4H), 3.38 (t, J = 7.8 Hz, 2H), 3.43 (t, J = 7.6 Hz, 2H), 3.84 (s, 3H), 6.82 (s, 1H), 6.91 and 7.41 (AB quartet, J = 8.9 Hz, 4H); ^{13}C NMR (125.75 MHz) δ 13.59, 13.71, 19.79, 20.05, 29.15, 30.40, 44.36, 48.43, 55.16,122.04 (q, J = 274.3 Hz), 124.69, 124.75 (q, J = 39.6 Hz), 131.05, 137.62 (q, J = 3.9 Hz), 160.66, 165.73 (q, J = 2.2 Hz); ^{19}F NMR (84.21 MHz) δ −55.03 (s, 3F); MS (EI) m/z (rel intensity) 357 (M^+, 16), 229 (100); HRMS (EI) calcd for $C_{19}H_{26}F_3NO_2$ (M^+) 357.1917, found 357.1910. Anal. Calcd for $C_{19}H_{26}F_3NO_2$: C, 63.85; H, 7.33; N, 3.92. Found: C, 64.04; H, 7.13; N, 3.84.

***N,N*-Dibutyl-(*Z*)-3-(4-chlorophenyl)-2-(trifluoromethyl)-2-propenamide (3Ad):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.96 (t, J = 7.0 Hz, 3H), 0.99 (t, J = 7.0 Hz, 3H), 1.29−1.44 (m, 4H), 1.55−1.70 (m, 4H), 3.40 (t, J = 7.1 Hz, 2H), 3.47 (t, J = 7.4 Hz, 2H), 6.90 (s, 1H), 7.39 (s, 4H); ^{13}C NMR (125.75 MHz) δ 13.52, 13.64, 19.75, 19.97, 29.07, 30.35, 44.35, 48.46, 121.58 (q, J = 275.0 Hz), 128.03 (q, J = 32.2 Hz), 128.63, 130.15 (q, J = 2.0 Hz), 130.85, 136.39 (q, J = 3.7 Hz), 164.85 (q, J = 2.1 Hz); ^{19}F NMR (84.21 MHz) δ −55.03 (s, 3F); MS (EI) m/z (rel intensity) 361 (M^+, 6), 233 (100); HRMS (EI) calcd for $C_{18}H_{23}ClF_3NO$ (M^+) 361.1420, found 361.1413. Anal. Calcd for $C_{18}H_{23}ClF_3NO$: C, 59.75; H, 6.41; N, 3.87. Found: C, 60.00; H, 6.51; N, 3.76.

***N,N*-Dibutyl-(*Z*)-3-(1-naphthyl)-2-(trifluoromethyl)-2-propenamide (3Ae):** mp 58.0−59.0 °C; IR (KBr) 1640 cm^{-1};

^{1}H NMR (200 MHz) δ 0.98 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H), 1.30−1.50 (m, 4H), 1.58−1.79 (m, 4H), 3.50 (t, J = 7.4 Hz, 2H), 3.54 (t, J = 6.5 Hz, 2H), 7.34 (s, 1H), 7.43−7.92 (m, 7H); ^{13}C NMR (125.75 MHz) δ 13.74, 13.77, 20.04, 20.10, 29.23, 30.79, 44.52, 48.78, 121.75 (q, J = 275.5 Hz), 124.02, 125.17, 126.21, 126.29 (q, J = 2.5 Hz), 126.57, 128.66, 129.43, 130.24, 130.50 (q, J = 31.4 Hz), 130.87, 133.12, 136.46 (q, J = 4.0 Hz), 164.96 (q, J = 2.0 Hz); ^{19}F NMR (84.21 MHz) δ −55.07 (s, 3F); MS (EI) m/z (rel intensity) 377 (M^+, 9), 229 (100); HRMS (EI) calcd for $C_{22}H_{26}F_3NO$ (M^+) 377.1966, found 377.1961. Anal. Calcd for $C_{22}H_{26}F_3NO$: C, 70.01; H, 6.94; N, 3.71. Found: C, 70.26 H, 7.03, N, 3.33.

***N,N*-Dibutyl-(*Z*)-3-(2-thienyl)-2-(trifluoromethyl)-2-propenamide (3Af):** mp 38.0−38.5 °C; IR (KBr) 1610 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.90 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H), 1.23−1.60 (m, 8H), 3.35 (t, J = 8.1 Hz, 2H), 3.42 (t, J = 7.2 Hz, 2H), 6.90 (s, 1H), 7.07 (dd, J = 3.7, 5.0 Hz, 1H), 7.36 (d, J = 3.7 Hz, 1H), 7.51 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125.75 MHz) δ 13.60, 13.76, 19.76, 20.09, 29.18, 30.42, 44.43, 48.45, 121.94 (q, J = 273.9 Hz), 123.22 (q, J = 33.4 Hz), 127.85, 129.74 (q, J = 4.1 Hz), 130.52, 132.46 (q, J = 2.4 Hz), 134.42, 165.24 (q, J = 2.4 Hz); ^{19}F NMR (84.21 MHz) δ −57.01 (s, 3F); MS (EI) m/z (rel intensity) 333 (M^+, 46), 264 (100); HRMS (EI) calcd for $C_{16}H_{22}F_3NOS$ (M^+) 333.1374, found 333.1372. Anal. Calcd for $C_{16}H_{22}F_3NOS$: C, 57.64; H, 6.65; N, 4.20. Found: C, 57.97; H, 6.59; N, 4.12.

***N,N*-Dibutyl-(*Z*)-3-(2-furyl)-2-(trifluoromethyl)-2-propenamide (3Ag):** IR (film) 1643 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.90 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.22−1.63 (m, 8H), 3.33 (t, J = 7.5 Hz, 2H), 3.41 (t, J = 7.5 Hz, 2H), 6.50 (dd, J = 1.5, 3.6 Hz, 1H), 6.62 (s, 1H), 6.81 (d, J = 3.6 Hz, 1H), 7.55 (d, J = 1.5 Hz, 1H); ^{13}C NMR (125.75 MHz) δ 13.58, 13.75, 19.74, 20.07, 29.16, 30.38, 44.38, 48.43, 112.40, 116.44 (q, J = 2.2 Hz), 121.85 (q, J = 273.7 Hz), 122.26 (q, J = 34.4 Hz), 124.25 (q, J = 3.5 Hz), 145.33, 147.41, 165.19 (q, J = 2.3 Hz); ^{19}F NMR (84.21 MHz) δ -60.22 (s, 3F); MS (EI) m/z (rel intensity) 317 (M^+, 23), 189 (100); HRMS (EI) calcd for $C_{20}H_{26}F_3NO$ (M^+) 317.1602, found 317.1610. Anal. Calcd for $C_{16}H_{22}F_3NO_2$: C, 60.56; H, 6.99; N, 4.41. Found: C, 60.53; H, 6.94; N, 3.95.

***N,N*-Dibutyl-(2*Z*,4*E*)-5-phenyl-2-(trifluoromethyl)-2,4-pentadienamide (3Ah):** mp 52.5−53.0 °C; IR (KBr) 1640 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.91 (t, J = 7.0 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.20−1.58 (m, 8H), 3.32 (t, J = 7.8 Hz, 2H), 3.41 (t, J = 7.2 Hz, 2H), 6.58 (d, J = 11.5 Hz, 1H), 6.83 (d, J = 15.4 Hz, 1H), 7.13 (ddq, J = 11.5, 15.4, 2.0 Hz, 1H), 7.27−7.50 (m, 5H);^{13}C NMR (125.75 MHz) δ 13.66, 13.81, 19.77, 20.11, 29.23, 30.47, 44.44, 48.52, 121.45, 122.32 (q, J = 274.7 Hz), 125.40 (q, J = 31.9 Hz), 127.36, 128.75, 129.37, 135.45, 137.24 (q, J = 3.5 Hz), 141.87, 165.11 (q, J = 2.3 Hz); ^{19}F NMR (84.21 MHz) δ −54.83 (br s, 3F); MS (EI) m/z (rel intensity) 353 (M^+, 18), 225 (100); HRMS (EI) calcd for $C_{20}H_{26}F_3NO$ (M^+) 353.1966, found 353.1966. Anal. Calcd for $C_{20}H_{26}F_3NO$: C, 67.97; H, 7.42; N, 3.96. Found: C, 68.27; H, 7.46; N, 3.72.

***N,N*-Dibutyl-(2*Z*,4*E*)-4-fluoro-5-phenyl-2-(trifluoromethyl)-2,4-pentadienamide (3Ai):** IR (film) 1640 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.92 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.26−1.38 (m, 4H), 1.53−1.61 (m, 4H), 3.29−3.50 (m, 4H), 6.05 (d, J = 34.1, Hz, 1H), 6.24 (d, J = 30.0 Hz, 1H), 7.31−7.61 (m, 5H); ^{13}C NMR (125.75 MHz) δ 13.60, 13.76, 19.75, 20.07, 29.12, 30.32, 44.40, 48.31, 119.68 (q, J = 9.1 Hz), 121.27 (q, J = 273.1 Hz), 126.87 (dq, J = 35.6, 4.40 Hz), 128.71, 128.90, 129.20, 129.68 (d, J = 8.1 Hz), 132.12 (d, J = 3.7 Hz), 152.67 (d, J = 265.0 Hz), 164.65 (q, J = 2.3 Hz); ^{19}F NMR (84.21 MHz) δ −56.91 (d, J = 30.9 Hz, 3F), −113.30 (ddq, J = 30.0, 30.9, 34.1 Hz, 1F); MS (EI) m/z (rel intensity) 371 (M^+, 24), 86 (100); HRMS (EI) calcd for $C_{20}H_{25}F_4ON$ (M^+) 371.1872, found 371.1864.

***N,N*-Dibutyl-(2*Z*,4*E*)-2-(trifluoromethyl)-2,4-hexadienamide (3Aj):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92−0.96 (m, 6H), 1.26−1.56 (m, 8H), 1.89 (d, J = 6.8 Hz, 3H), 3.28 (t, J = 7.6 Hz, 2H), 3.38 (t, J = 7.4 Hz, 2H), 6.10 (dq, J = 13.6, 6.8 Hz, 1H), 6.34−6.48 (m, 2H); ^{13}C NMR (125.75 MHz) δ 13.44, 13.59, 18.48, 19.59, 19.94, 29.10, 30.33, 44.17, 48.29, 122.17 (q, J = 274.6 Hz), 123.34 (q, J = 31.8 Hz), 125.20, 137.49 (q, J = 3.3 Hz), 141.02, 165.21; ^{19}F NMR (84.21 MHz) δ −57.72 (s, 3F); MS (EI) m/z (rel intensity) 291 (M^+, 4), 163 (100); HRMS (EI) calcd for $C_{15}H_{24}F_3NO$ (M^+) 291.1811, found 291.1800.

***N,N*-Dibutyl-(*Z*)-4-methyl-2-(trifluoromethyl)-2,4-pentadienamide (3Ak):** IR (film) 1643, 1646 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.90 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H), 1.179−1.346 (m, 4H), 1.462−1.630 (m, 4H), 1.910 (s, 3H), 3.27 (t, J = 7.8 Hz, 2H), 3.36 (t, J = 7.5 Hz, 2H), 5.14 (s, 1H), 5.19 (s, 1H), 6.35 (s, 1H); ^{19}F NMR (84.21 MHz) δ -55.94 (s, 3F); MS (EI) m/z (rel intensity) 291 (M^+, 14), 163 (100); HRMS (EI) calcd for $C_{15}H_{24}F_3NO$ (M^+) 291.1809, found 291.1815.

***N,N*-Dibutyl-(*Z*)-2-(trifluoromethyl)-2-hexenamide (3Al):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.90−1.00 (m, 9H), 1.22−1.60 (m, 10H), 2.33 (dtq, J = 7.9, 7.5, 2.1 Hz, 2H), 3.26 (t, J = 7.7 Hz, 2H), 3.37 (t, J = 7.4 Hz, 2H), 6.00 (tq, J = 7.9, 0.8 Hz, 1H); ^{13}C NMR (125.75 MHz) δ 13.58, 13.73, 19.79, 20.04, 21.81, 29.19, 30.28, 30.46, 44.33, 48.40, 122.10 (q, J = 275.1 Hz), 128.78 (q, J = 31.2 Hz), 141.43 (q, J = 3.5 Hz), 165.24 (q, J = 2.1 Hz); ^{19}F NMR (84.21 MHz) δ −55.67 (br s, 3F); MS (EI) m/z (rel intensity) 293 (M^+, 4), 165 (100); HRMS (EI) calcd for $C_{15}H_{26}F_3NO$ (M^+) 293.1968, found 293.1964.

***N,N*-Dibutyl-(*Z*)-2-(trifluoromethyl)-2-nonenamide (3Am):** IR (film) 1641 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.87−0.96 (m, 9H), 1.24−1.58 (m, 16H), 2.34 (dtq, J = 7.8, 7.5, 2.1 Hz, 2H), 3.26 (t, J = 7.5 Hz, 2H), 3.37 (t, J = 7.5 Hz, 2H), 6.00 (t, J = 7.8 Hz, 1H); ^{19}F NMR (84.21 MHz) δ −58.32 (s, 3F); MS (EI) m/z (rel intensity) 335 (M^+, 19), 250 (100); HRMS (EI) calcd for $C_{20}H_{26}F_3NO$ (M^+) 335.2436, found 335.2438. Anal. Calcd for $C_{18}H_{32}F_3NO$: C, 64.45; H, 9.62; N, 4.18. Found: C, 64.42; H, 9.49; N, 4.01.

***N,N*-Dibutyl-(*Z*)-4-methyl-2-(trifluoromethyl)-2-pentenamide (3An):** IR (film) 1650 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.07 (d, J = 6.4 Hz, 6H), 1.20−1.63 (m, 8H), 2.79−2.99 (m, 1H), 3.26 (t, J = 7.8 Hz, 2H), 3.37 (t, J = 7.4 Hz, 2H), 5.78 (d, J = 11.0 Hz, 1H); ^{13}C NMR (125.75 MHz) δ 13.31, 13.44, 19.62, 19.81, 21.62, 28.00, 29.03, 30.25, 44.21, 48.27, 122.02 (q, J = 275.0 Hz), 126.00 (q, J = 31.5 Hz), 147.19 (q, J = 3.4 Hz), 164.88 (q, J = 2.1 Hz); ^{19}F NMR (84.21 MHz) δ −55.67 (br s, 3F); MS (EI) m/z (rel intensity) 293 (M^+, 5), 165 (100); HRMS (EI) calcd for $C_{15}H_{26}F_3NO$ (M^+) 293.1968, found 293.1970.

***N,N*-Dibutyl-(*Z*)-3-cyclohexyl-2-(trifluoromethyl)propenamide (3Ao):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.1 Hz, 3H), 1.02−1.77 (m, 18H), 2.45−2.69 (m, 1H), 3.25 (t, J = 7.1 Hz, 2H), 3.37 (t, J = 7.5 Hz, 2H), 5.80 (dq, J = 10.8, 0.8 Hz, 1H); ^{13}C NMR (125.75 MHz) δ 13.42, 13.51, 19.68, 19.87, 24.90, 25.36, 29.08, 29.36, 31.75, 37.66, 44.25, 48.34, 122.09 (q, J = 275.2 Hz), 126.24 (q, J = 31.4 Hz), 145.83, 165.07; ^{19}F NMR (84.21 MHz) δ −55.67 (br s, 3F); MS (EI) m/z (rel intensity) 333 (M^+, 18), 250 (100); HRMS (EI) calcd for $C_{18}H_{30}F_3NO$ (M^+) 333.2279, found 333.2273.

***N,N*-Dibutyl-(*E*)-4,4-dimethyl-2-(trifluoromethyl)-2-pentenamide ((*E*)-3Ap):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.94 (t, J = 7.2 Hz, 6H), 1.12 (s, 9H), 1.21−1.67 (m, 8H), 3.05−3.52 (m, 4H), 6.14 (q, J = 1.5 Hz, 1H); ^{19}F NMR (84.21 MHz) δ −61.42 (br s, 3F); MS (EI) m/z (rel intensity) 307 (M^+, 3), 250 (100); HRMS (EI) calcd for $C_{16}H_{28}F_3NO$ (M^+) 307.2123, found 307.2118.

***N,N*-Dibutyl-(*Z*)-4,4-dimethyl-2-(trifluoromethyl)-2-pentenamide ((*Z*)-3Ap):** IR (film) 1645 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.93 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.7 Hz, 3H), 1.21 (s, 9H), 1.27−1.76 (m, 8H), 3.21−3.36 (m, 4H), 5.93 (s, 1H); ^{13}C NMR (125.75 MHz) δ 13.68, 13.74, 20.16, 20.35, 28.48, 28.72, 29.81, 34.12, 44.10, 49.09, 122.64 (q, J = 274.5 Hz), 124.44 (q, J = 29.9 Hz), 146.08 (q, J = 15.1 Hz), 163.57; ^{19}F NMR (84.21 MHz) δ −53.25 (s, 3F); MS (EI) m/z (rel intensity) 307 (M^+, 3), 250 (100); HRMS (EI) calcd for $C_{16}H_{28}F_3NO$ (M^+) 307.2123, found 307.2125. Anal. Calcd for $C_{16}H_{28}F_3NO$: C, 62.52; H, 9.18; N, 4.56. Found: C, 62.60; H, 9.20; N, 4.43.

***N,N*-Dibutyl-3-methyl-2-(trifluoromethyl)-2-butenamide (3Aq):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.19−1.65 (m,

8H), 1.81 (q, J = 2.2 Hz, 3H), 1.96 (q, J = 2.0 Hz, 3H), 3.22 (dd, J = 6.8, 9.1 Hz, 2H), 3.35 (dt, J = 13.5, 7.6 Hz, 1H), 3.45 (dt, J = 13.5, 7.7 Hz, 1H); ^{19}F NMR (84.21 MHz) δ −54.53 (br s, 3F); MS (EI) m/z (rel intensity) 279 (M^+, 4), 151 (100); HRMS (EI) calcd for $C_{14}H_{24}F_3NO$ (M^+) 279.1811, found 279.1809. Anal. Calcd for $C_{14}H_{24}F_3NO$: C, 60.20; H, 8.66; N, 5.01. Found: C, 60.16; H, 8.68; N, 4.82.

***N,N*-Dibutyl-3-ethyl-2-(trifluoromethyl)-2-pentenamide (3Ar):** IR (film) 1635 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.91 (t, J = 6.6 Hz, 3H), 0.95 (t, J = 6.4 Hz, 3H), 1.07 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H), 1.18−1.64 (m, 8H), 2.00−2.50 (m, 4H), 3.18−3.51 (m, 4H); ^{13}C NMR (125.75 MHz) δ 11.69, 12.14, 19.70, 19.92, 23.23, 25.80, 28.76, 29.96, 43.80, 47.98, 122.30 (q, J = 274.9 Hz), 123.46 (q, J = 30.7 Hz), 154.64 (q, J = 3.6 Hz), 164.48 (q, J = 2.1 Hz); ^{19}F NMR (84.21 MHz) δ −54.11 (br s, 3F); MS (EI) m/z (rel intensity) 307 (M^+, 7), 179 (100); HRMS (EI) calcd for $C_{16}H_{28}F_3NO$ (M^+) 307.2124, found 307.2123.

***N,N*-Dibutyl-2-(cyclohexylidene)-3,3,3-trifluoropropanamide (3As):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.92 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.19−1.75 (m, 14H), 1.92−2.52 (m, 4H), 3.13−3.43 (m, 4H); ^{13}C NMR (125.75 MHz) δ 13.36, 13.49, 19.71, 19.99, 25.53, 27.26, 28.88, 30.16, 30.70, 32.73, 43.87, 47.98, 121.27 (q, J = 30.7 Hz), 122.30 (q, J = 274.9 Hz), 151.75 (q, J = 3.6 Hz), 164.54 (q, J = 1.7 Hz); ^{19}F NMR (84.21 MHz) δ −53.28 (br s, 3F); MS (EI) m/z (rel intensity) 319 (M^+, 11), 191 (100); HRMS (EI) calcd for $C_{17}H_{28}F_3NO$ (M^+) 319.2124, found 319.2120.

***N,N*-Dibutyl-(*E*)-3-phenyl-2-(trifluoromethyl)-2-butenamide ((*E*)-3At):** IR (film) 1635 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.74−1.42 (m, 14H), 2.29 (q, J = 2.1 Hz, 3H), 2.59−2.91 (m, 2H), 3.11−3.52 (m, 2H), 7.33 (s, 5H); ^{13}C NMR (125.75 MHz) δ 13.36, 13.49, 19.71, 19.99, 25.53, 27.26, 28.88, 30.16, 30.70, 32.73, 43.87, 47.98, 121.27 (q, J = 30.7 Hz), 122.30 (q, J = 274.9 Hz), 151.75 (q, J = 3.6 Hz), 163.46; ^{19}F NMR (84.21 MHz) δ −57.72 (q, J = 2.1 Hz, 3F); MS (EI) m/z (rel intensity) 341 (M^+, 5), 213 (100); HRMS (EI) calcd for $C_{19}H_{26}F_3NO$ (M^+) 341.1968, found 341.1973.

***N,N*-Dibutyl-(*Z*)-3-phenyl-2-(trifluoromethyl)-2-butenamide ((*Z*)-3At):** IR (film) 1640 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.97 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.26−1.69 (m, 8H), 2.09 (q, J = 2.0 Hz, 3H), 3.35−3.59 (m, 4H), 7.19−7.43 (m, 5H); ^{13}C NMR (75.61 MHz) δ 13.75, 13.82, 20.22, 20.36, 24.52, 29.28, 30.53, 44.43, 48.41, 121.90 (q, J = 274.7 Hz), 125.72 (q, J = 30.8 Hz), 126.59, 128.11, 128.25, 139.50, 147.26 (q, J = 3.8 Hz), 164.60; ^{19}F NMR (84.21 MHz) δ −55.23 (q, J = 2.1 Hz,3F); MS (EI) m/z (rel intensity) 341 (M^+, 4), 213 (100); HRMS (EI) calcd for $C_{19}H_{26}F_3NO$ (M^+) 341.1968, found 341.1963.

***N,N*-Dibutyl-3,3,3-trifluoropropanamide (4A):** IR (film) 1660 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.93 (t, J = 7.3 Hz,3H), 0.96 (t, J = 7.3 Hz, 3H), 1.22−1.64 (m, 8H), 3.20 (q, J = 10.0 Hz, 2H), 3.24 (t, J = 7.8 Hz, 2H), 3.35 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125.75 MHz) δ 13.50, 13.57, 19.81, 19.95, 29.42, 30.92, 37.61 (q, J = 28.6 Hz), 45.75, 47.98, 124.15 (q, J = 276.5 Hz), 162.46 (q, J = 3.4 Hz); ^{19}F NMR (84.21 MHz) δ −60.50 (t, J = 10.0 Hz, 3F); MS (EI) m/z (rel intensity) 239 (M^+, 3), 86 (100); HRMS (EI) calcd for $C_{11}H_{20}F_3NO$ (M^+) 239.1498, found 239.1493. Anal. Calcd for $C_{11}H_{20}F_3NO$: C, 55.22; H, 8.42; N, 5.85. Found: C, 55.12; H, 8.28; N, 5.79.

***N,N*-Dimethyl-3,3,3-trifluoropropanamide (4B):** mp 43.8−44.7 °C; IR (KBr) 1665 cm^{-1}; ^{1}H NMR (200 MHz) δ 3.01 (s, 3H), 3.08 (s, 3H), 3.26 (q, J = 10.1 Hz, 2H); ^{13}C NMR (125.75 MHz) δ 35.47, 37.64, 37.98 (q, J = 28.5 Hz), 124.13 (q, J = 276.6 Hz), 163.08 (q, J = 2.9 Hz); ^{19}F NMR (84.21 MHz) δ −60.66 (t, J = 10.1 Hz, 3F); MS (EI) m/z (rel intensity) 155 (M^+, 100); HRMS (EI) calcd for $C_5H_8F_3NO$ (M^+) 155.0558, found 155.0558. Anal. Calcd for $C_5H_8F_3NO$: C, 38.71; H, 5.20; N, 9.03. Found: C, 38.67; H, 5.15; N, 9.03.

***N*-(3,3,3-Trifluoropropanoyl)piperidine (4C):** IR (film) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.52−1.73 (m, 6H), 3.24 (q, J = 10.2 Hz, 2H), 3.39−3.62 (m, 4H); ^{13}C NMR (125.75 MHz) δ 24.18, 25.28, 26.25, 38.00 (q, J = 28.9 Hz), 42.94, 47.43, 124.22 (q, J = 276.8 Hz), 161.25 (q, J = 3.0 Hz); ^{19}F NMR (84.21 MHz) δ −60.53 (t, J = 10.2 Hz, 3F); MS (EI) m/z (rel intensity) 195 (M^+, 100); HRMS (EI) calcd for $C_8H_{12}F_3NO$ (M^+) 195.0872, found 195.0860. Anal. Calcd for $C_8H_{12}F_3NO$: C, 49.23; H, 6.20; N, 7.18. Found: C, 49.58; H, 5.84; N, 7.05.

***N,N*-Diisopropyl-3,3,3-trifluoropropanamide (4D):** IR (film) 1655 cm^{-1}; ^{1}H NMR (300 MHz) δ 1.40 (d, J = 6.6 Hz, 6H), 2.47 (d, J = 6.9 Hz, 6H), 3.21 (q, J = 10.2 Hz, 2H), 3.53 (sept, J = 6.9 Hz, 1H), 3.89 (sept, J = 6.6 Hz, 1H); ^{13}C NMR (125.75 MHz) δ 20.20, 20.70, 39.58 (q, J = 28.2 Hz), 46.24, 49.52, 124.30 (q, J = 276.7 Hz), 161.68 (q, J = 2.3 Hz); ^{19}F NMR (84.21 MHz) δ −62.85 (t, J = 10.2 Hz, 3F); MS (EI) m/z (rel intensity) 211 (M^+, 24), 154 (100); HRMS (EI) calcd for $C_9H_{16}F_3NO$ (M^+) 211.1184, found 211.1189. Anal. Calcd for $C_9H_{16}F_3NO$: C, 51.18; H, 7.64; N, 6.63. Found: C, 50.91; H, 7.57; N, 6.54.

X-ray Crystal Structure Determination for 3Ba. A colorless prismatic crystal of approximate dimensions 0.20 × 0.20 × 0.20 mm^3 was mounted on thin glass fiber with epoxy cement. Data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα radiation and a rotating anode generator. The material crystallizes in the monoclinic space group $C2/c$ with a = 25.588 (2) Å, b = 6.724 (2) Å, c = 14.397 (2) Å, β = 107.332 (9)°, V = 2364.5 (7) Å^3, and Z = 8. Data collection, reduction, solution, and refinement were all carried out using teXsan[7] crystallographic software package of Molecular Structure Corporation. All non-H atoms were refined anisotropically; 1679 observations, 203 variables; R_1 = 0.063 for $F_2 > 4\sigma(F_2)$ and wR_2 = 0.074 for all F_2.

Acknowledgment. We are grateful to Central Glass Co., Ltd., Japan and Daikin Industry, Co., Ltd., Japan for their generous gifts of trifluoromethanesulfonic anhydride and pentafluoropropanol, respectively.

Supporting Information Available: X-ray crystallographic data and an ORTEP diagram for compound **3Ba**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO001760V