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Facile syntheses of various per- or polyfluoroalkylated internal acetylene derivatives

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Abstract—Treatment of per- or polyfluoroalkylated vinyl iodides **5** with 2 equiv. of *n*-BuLi in THF produced the corresponding lithium acetylides in situ, which were transformed into zinc acetylides by the addition of $ZnCl_2$·TMEDA complex into the reaction mixture. The in situ generated zinc acetylides were exposed to the cross-coupling conditions such as ArI/cat. $Pd(PPh_3)_4$, reflux, 6–12 h, giving rise to the desired per- or polyfluoroalkylated acetylenes in high yields. In the case of trifluoromethylated acetylene, commercially available 2-bromo-3,3,3-trifluoropropene **6** could also be used instead of **5** as the starting material. In the acetylenes having a fluoroalkyl group and an aliphatic side chain, vinyl iodides **7**, prepared by radical addition of perfluoroalkyl iodide to terminal acetylenes, were treated with *t*-BuOK at room temperature or at the reflux temperature of benzene, affording the desired compounds in good yields.

1. Introduction

In view of rapidly growing role of fluorine-containing substances particularly in materials and pharmaceutical science, the synthesis of fluorine-containing substances is becoming more and more important.[1] As one of the most valuable synthetic intermediates for preparation of such substances, fluoroalkylated acetylenes **1**–**4** (Fig. 1) have recently been attracting much attention from organometallic chemists,[2] and synthetic chemists,[3] polymer chemists,[4] pharmaceutical scientists,[5] etc. due to their potentially high synthetic value.[6] There have been several reports on the preparation of fluoroalkylated acetylenes so far. For example, the synthesis of trifluoromethylated acetylenes **1** has been achieved through the use of respective trifluoropropynyl lithium,[7] Grignard[8] or zinc reagents.[9] However, reliance upon trifluoropropyne as a precursor incurs experimental difficulties, associated with the handling of a gaseous reagent (bp −47°C), and has significant cost implications. In addition to limited studies on the preparation of **1**,[10] little attention has been paid on the synthesis of per- or polyfluoroalkylated acetylenes **2**.[11] To the best of our knowledge, no report has been appeared on the preparation of acetylenes **3** and **4** which possess both per- or polyfluoroalkyl group and an *aliphatic* chain R.[12]

In this article we wish to describe three types of synthetic methods (path A–C), all of which would provide us with easy access to a variety of fluoroalkylated acetylenes **1**–**4** (Scheme 1).

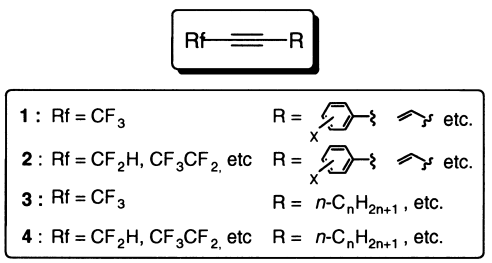

Figure 1.

The path A is via the palladium-catalyzed coupling reaction using various aryl iodides and zinc acetylide derived from vinyl iodide **5** which was easily prepared from commercially available per- or polyfluoroalkylcarbinol. The path B is similar to the path A, in which the acetylenes are synthesized from commercially available 2-bromo-3,3,3-trifluoropropene **6** in a one-pot. The path C is for the synthesis of fluoroalkylated acetylenes bearing an aliphatic substituent via dehydroiodination of vinyl iodides **7**.

2. Results and discussion

2.1. The palladium-catalyzed coupling reaction of zinc acetylide with various aryl iodides (path A)

The starting vinyl iodides **5a**–**c** could readily be prepared

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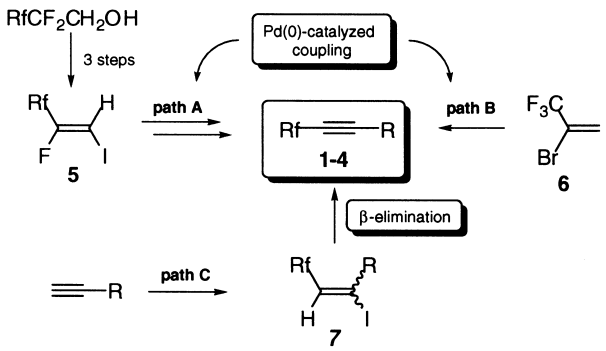
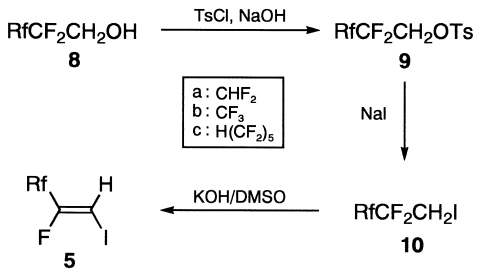


Scheme 1.

from the corresponding polyfluoroalcohols **8** in three steps (Scheme 2).[13] Thus, commercially available **8** was treated with *p*-toluenesulfonyl chloride (1.2 equiv.) and NaOH (1.2 equiv.) at room temperature to give the corresponding tosylate **9** in quantitative yield. The tosylate was subjected to NaI/diethyleneglycol at room temperature, followed by direct distillation, affording polyfluoroalkyl iodide **10**. The iodide was dissolved in DMSO, and to this solution was added a 4N KOH solution. The whole was stirred at room temperature overnight, giving rise to the desired *Z*-vinyl iodide **5** in up to 56% yield for three steps.



Scheme 2.

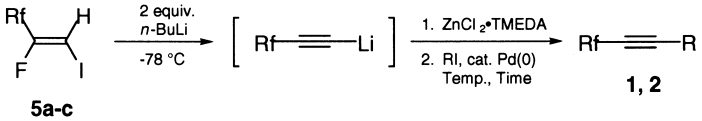
The treatment of **5** with 2 equiv. of *n*-BuLi at −78°C for 1 h produced the corresponding lithium acetylide in situ, which was transmetallated into zinc acetylide by addition of $ZnCl_2$·TMEDA complex into the reaction mixture. In this case, $ZnCl_2$·TMEDA was better than anhydrous $ZnCl_2$ because it was less hydroscopic. After stirring of the reaction mixture for 15 min, the mixture was allowed to warm to room temperature and then stirred for 1 h. To this reaction mixture was added 1 equiv. of aryl iodide and 5 mol% of tetrakis(triphenylphophine)palladium(0) ($Pd(PPh_3)_4$) in this order. The whole mixture was heated at 50–60°C for 4–12 h, resulting in the formation of fluoroalkylated acetylene derivative **1** or **2** in good to high yields. The results are summarized in Table 1.

As shown in entries 1–6, various aryl iodides as well as alkenyl iodides could participate nicely in the present coupling reaction to give the corresponding fluoroalkylated alkynes in high yields. Trifluoromethylated- and decafluoropentylated alkynes were also synthesized in the same procedure (entries 7–12). However, the coupling reaction of fluoroalkylated acetylide with alkyl iodide in the presence of palladium catalyst did not proceed at all, giving the complete recovery of the zinc acetylide. In this way, it was found that the palladium-catalyzed coupling reaction of zinc acetylide with various iodides was very effective for the preparation of fluoroalkylated acetylenes bearing aromatic substituents, not aliphatic ones.

2.2. The one-pot reaction for the preparation of trifluoromethylated acetylenes (path B)

In seeking for more convenient methods for preparing fluorine-containing acetylenes, we examined the one-pot synthesis of trifluoromethylated acetylenes from commercially available, easy-handling 2-bromo-3,3,3-trifluoropropene **6** (bp 34–35°C). Thus, **6** was treated with 2 equiv. of LDA at −78°C,[14] resulting in the formation of trifluoromethylated lithium acetylide in situ. To this reaction mixture was added $ZnCl_2$·TMEDA, $Pd(PPh_3)_4$ and ArI, followed by refluxing the mixture, leading to the formation of the desired alkynes **1**. The results are summarized in Table 2. Generally, the coupling reaction of zinc acetylide with aryl iodides gave the corresponding acetylene derivatives in excellent yields. As shown in entries 3–5, aryl triflate as well as aryl bromide did not give the desired

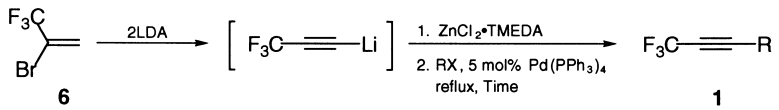
Table 1. Palladium-catalyzed coupling reaction of zinc acetylide with various aryl iodides



Entry	Rf	R	Temp. (°C)	Time (h)	Product	Yield[a] (%)
1	CHF_2	Ph	60	4	**2a**	62
2	CHF_2	*o*-$MeOC_6H_4$	60	12	**2b**	74
3	CHF_2	*m*-$NO_2C_6H_4$	60	12	**2c**	80
4	CHF_2	*p*-$EtO_2COC_6H_4$	60	4	**2d**	76
5	CHF_2	*p*-ClC_6H_4	60	4	**2e**	70
5	CHF_2	(*E*)-PhCH=CH	60	4	**2f**	85
6	CHF_2	(*E*)-*n*-C_6H_{13}CH=CH	60	4	**2g**	74
7	CF_3	*o*-$MeOC_6H_4$	60	12	**1a**	78
8	CF_3	*m*-$NO_2C_6H_4$	60	12	**1b**	76
9	CF_3	*p*-$EtO_2COC_6H_4$	50	4	**1c**	73
10	CF_3	(*E*)-PhCH=CH	50	4	**1d**	75
11	CF_3	(*E*)-*n*-C_6H_{13}CH=CH	50	4	**1e**	81
12	$H(CF_2)_5$	*m*-$NO_2C_6H_4$	50	4	**2h**	77

[a] Isolated yields.

Table 2. The one-pot synthesis of trifluoromethylated acetylenes



6 1

Entry	**5** (equiv.)	RX	Time (h)	Product	Yield[a] (%)
1	1.5	PhI	6	**1f**	99 (83)
2	1.5	*p*-$MeOC_6H_4I$	6	**1g**	99 (99)
3	1.5	*p*-$MeOC_6H_4OTf$	6	–	tr
4	1.5	*p*-$MeOC_6H_4OTf$	6	–	tr[b]
5	1.5	*p*-$MeOC_6H_4Br$	6	–	tr
6	1.5	*p*-$MeOC_6H_4I$	6	–	18[c]
7	1.5	*p*-MeC_6H_4I	6	**1h**	99 (99)
8	1.5	*p*-ClC_6H_4I	6	**1i**	81 (81)
9	1.5	*p*-$EtO_2CC_6H_4I$	6	**1c**	94 (72)
10	1.5	*p*-$O_2NC_6H_4I$	6	**1j**	51
11	1.5	*m*-$MeOC_6H_4I$	6	**1k**	99 (95)
12	1.5	*o*-$MeOC_6H_4I$	12	–	60
13	2.0	*o*-$MeOC_6H_4I$	6	–	85
14	2.0	*o*-$MeOC_6H_4I$	12	**1a**	99 (82)
15	1.5	*o*-ClC_6H_4I	6	–	27
16	2.0	*o*-ClC_6H_4I	24	–	77
17	2.0	*o*-ClC_6H_4I	24	–	83[d]
18	2.0	*o*-ClC_6H_4I	24	**1l**	96 (79)[e]

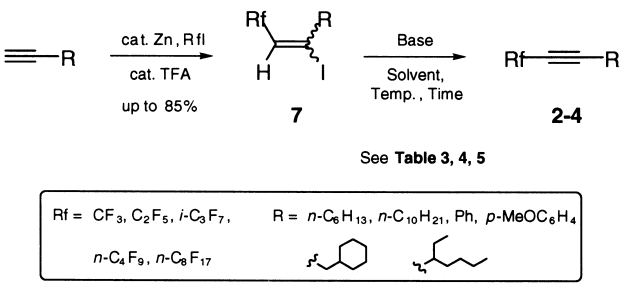
[a] Determined by ^{19}F NMR. Values in parentheses were of isolated yields.
[b] NaI was used.
[c] *n*-Bu_3SnCl was used instead of $ZnCl_2$·TMEDA.
[d] 10 mol% of $Pd(PPh_3)_4$ was used.
[e] 15 mol% of $Pd(PPh_3)_4$ was used.

coupling products at all. Furthermore, Stille coupling using alkynylstannane instead of zinc acetylide afforded the desired product in very low yield (entry 6). *p*-Methyliodobenzene, *p*-chloro-iodobenzene, and ethyl *p*-iodobenzoate were found to be good substrates, while the reaction with *p*-nitroiodobenzene proceeded very sluggishly, giving the desired compound in only 51% yield together with unidentified compounds and unreacted substrate after 6 h. It was also found that the position of substituent on the benzene ring influenced largely on the reaction. *Meta*-substituted substrate gave the desired product in excellent yield (entry 11), however, *ortho*-substituted one did not afford the product in good yields (entries 12 and 16). After several attempts, we found that the prolonged reaction time and increase of the amount of catalyst improved the yields (entries 14 and 18).

2.3. The synthesis of perfluoroalkylated acetylenes bearing an alkyl side chain (path C)

In the preceding sections, we demonstrated two convenient synthetic methods which enabled us to synthesize various types of fluoroalkylated acetylenes bearing aromatic substituents. However, the palladium-catalyzed coupling reaction of zinc acetylide with alkyl iodides failed, the starting materials being recovered quantitatively. To the best of our knowledge, the general synthetic methods for the fluoroalkylated acetylenes **3** and **4** (Fig. 1) which have an aliphatic side chain, have not been reported so far. This prompted us to develop the convenient access to such fluoroalkylated acetylenes.

Our attempt was made to the synthesis of such acetylenes via dehydroiodination from vinyl iodides **7** which were prepared from the radical addition of perfluoroalkyl iodide to terminal acetylenes in the presence of a catalytic amount of Zn/TFA according to the literature (Scheme 3).[15]



Scheme 3.

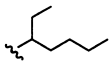
In an initial experiment, vinyl iodide **7b** (R_f=*n*-C_4F_9, R=*n*-C_6H_{13}) was treated with 1.5 equiv. of *n*-BuLi at −78°C in THF or Et_2O, resulting in the recovery of the starting material (see Table 3, entries 1 and 2). Use of LDA or *t*-BuLi instead of *n*-BuLi gave no dramatic improvement (entries 3–6). On the other hand, **7b** was subjected to the reaction conditions such as *t*-BuOK/THF at room temperature to produce the desired acetylene in 30% yield. When the reaction was carried out in Et_2O by using 3 equiv. of *t*-BuOK, the yield was improved to 61%, while no starting material was detected at all. No change was observed even when the reaction was performed at 0°C (entries 10 and 11). As shown in entries 13–17, on the other hand, the reflux conditions gave the satisfactory results. Eventually, we found that the best yield was given when the reaction was carried out in benzene at the reflux temperature for 2 h by using 3 equiv. of *t*-BuOK (78% NMR yield, entry 17). The optimized reaction conditions were applied for various types of vinyl iodides **7**. The results are summarized in Table 4.

Table 3. The synthesis of fluoroalkylated acetylenes bearing an aliphatic substituent (Rf=*n*-C_4F_9, R=*n*-C_6H_{13})

Entry	Base	Equiv. of base	Solvent	Temp. (°C)	Time (h)	Yield [a] (%) of **4b**	Recovery[a] (%) of **7b**
1	*n*-BuLi	1.5	THF	−78	2	tr	91
2	*n*-BuLi	1.5	Et_2O	−78	2	0	30
3	LDA	1.5	THF	−78	2	20	74
4	LDA	1.5	Et_2O	−78	2	0	50
5	*t*-BuLi	1.5	THF	−78	2	0	99
6	*t*-BuLi	1.5	Et_2O	−78	2	0	99
7	*t*-BuOK	1.5	THF	r.t.	2	30	63
8	*t*-BuOK	1.5	Et_2O	r.t.	2	46	45
9	*t*-BuOK	3.0	Et_2O	r.t.	2	61	0
10	*t*-BuOK	1.5	Et_2O	0	2	68	26
11	*t*-BuOK	3.0	Et_2O	0	2	58	0
12	*t*-BuOK	3.0	THF	r.t.	2	24	54
13	*t*-BuOK	1.5	THF	Reflux	2	38	60
14	*t*-BuOK	3.0	THF	Reflux	2	37	52
15	*t*-BuOK	3.0	THF	Reflux	4	51	41
16	*t*-BuOK	1.5	PhH	Reflux	2	64	13
17	*t*-BuOK	3.0	PhH	Reflux	2	78	0

[a] Determined by ^{19}F NMR.

Table 4.

Entry	Rf	R	Substrate	Product	Yield[a] (%) of **2**–**4**
1	*n*-C_8F_{17}	*n*-C_6H_{13}	**7a**	**4a**	74 (49)
2	*n*-C_4F_9	*n*-C_6H_{13}	**7b**	**4b**	78 (44)
3	*n*-C_4F_9	*n*-$C_{10}H_{21}$	**7c**	**4c**	73
4	*n*-C_4F_9		**7d**	**4d**	81
5	*n*-C_4F_9	Ph	**7e**	**2i**	74
6	*n*-C_4F_9	*p*-MeC_6H_4	**7f**	**2j**	77
7	*n*-C_3F_7	*n*-C_6H_{13}	**7g**	**4g**	74 (40)
8	C_5F_5	*n*-C_6H_{13}	**7h**	**4h**	65 (55)
9	CF_3	*n*-C_6H_{13}	**7i**	**3i**	24

[a] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.

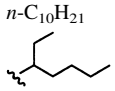
As seen in entries 1, 2, 7 and 8, the substrates bearing various fluoroalkyl groups could participate well in the reaction to give the corresponding acetylenes in good yields, while the isolated yields were moderate owing to their volatility. Additionally, various side chains R such as aliphatic as well as aromatic groups did not influence on the reaction. Interestingly, trifluoromethylated vinyl iodide **7i**, shown in entry 9, was subjected to the same reaction conditions, affording the desired product in only 24% yield with no recovery of the starting vinyl iodide. Therefore, the reaction conditions for the dehydroiodination reaction of **7i** was re-examined in detail. The results are collected in Table 5.

It was found that the amount of base was crucial for obtaining the desired acetylenes in good yields. When the reaction was carried out at room temperature by using 3.0 equiv. of *t*-BuOK, the product was given in only 30% (entry 2). Use of 1.5 equiv. of base improved the yield from 30 to 66%. Eventually, the best yield was obtained when a slight excess of base (1.2 equiv.) was employed at room temperature. This reaction conditions were applied for various types of trifluoromethylated vinyl iodides, as shown in entries 5–7. Various vinyl iodides **7** having a branched side chain as well as a straight side chain could also be applied for the present reaction nicely.

3. Summary

In conclusion, we have demonstrated three types of synthetic methods (path A–C). First, the palladium-catalyzed coupling reaction by using various aryl iodides and zinc acetylide which was readily prepared from the corresponding polyfluoroalcohol, was found to be effective for the preparation of acetylenes substituted by fluoroalkyl group and an aromatic moiety. Secondly, we also achieved the one-pot synthesis of trifluoromethylated internal alkynes from commercially available 2-bromo-3,3,3-trifluoropropene, leading to the development of easy access to **1**. Thirdly, we developed the first synthesis of perfluoroalkylated acetylenes having an

Table 5. (Rf=CF_3)

Entry[a]	Eq of base	R	Substrate	Recovery[b] (%) of **7**	Product	Yield[b] (%) of **3**
1[c]	3	*n*-C_6H_{13}	**7i**	0	**3i**	24
2	3	*n*-C_6H_{13}	**7i**	0	**3i**	30
3	1.5	*n*-C_6H_{13}	**7i**	0	**3i**	66
4	1.2	*n*-C_6H_{13}	**7i**	1	**3i**	73 (48)
5	1.2	*n*-$C_{10}H_{21}$	**7j**	0	**3j**	84 (67)
6	1.2		**7k**	0	**3k**	86
7	1.2		**7l**	0	**3l**	74

[a] All reaction was performed at the room temperature.
[b] Determined by ^{19}F NMR. Values in parentheses are of isolated yields.
[c] Carried out at the reflux temperature of benzene.

aliphatic side chain, which could not be synthesized by the palladium-catalyzed coupling reaction. As a result, these methods enabled us to synthesize a wide variety of fluorine-containing acetylenes in moderate to excellent yields.

4. Experimental

4.1. General methods

Infrared spectra (IR) were taken on a Shimadzu FTIR-8200(PC) spectrometer as film on a NaCl plate. ^{1}H NMR spectra were measured with a 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 with a Bruker DRX-500 (125.75 MHz) NMR spectrometer in a $CDCl_3$ solution with Me_4Si 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. High-resolution mass spectra (HRMS) were taken on a Hitachi M-80B mass spectrometer by electron impact (EI), chemical ionization (CI), and fast atom bombardment (FAB) method. Thin-layer chromatography (TLC) was done on aluminium sheets coated with silica gel (Merck 60 F_{254}), and column chromatography was carried out using silica gel (Wacogel C-200) as absorbent.

4.1.1. Typical procedure for the preparation of vinyl iodide 5b. Polyfluoroalcohol (1.0 mol) and *p*-toluenesulfonyl chloride (1.2 mol) was dissolved in water (350 mL), and then the whole was heated at 50°C. To this solution was dropwise added a NaOH solution (150 mL, 1.2 mol). After stirring of the reaction mixture for 3 h, the reaction mixture was cooled to room temperature, followed by extraction with ether three times. The combined organic layers were washed with NH_3 aq. (twice), then water (three times), and dried over anhydrous Na_2SO_4. After evaporation of the organic materials, the residue and NaI (180 g, 1.2 mol) was dissolved in diethyleneglycol (350 mL). The solution was heated (bath temperature ca. 170°C/760 mmHg) to distill the desired iodide, which was washed with water six times. The crude materials were dissolved in DMSO (250 mL), and to this reaction mixture was added a KOH solution (100 mL, 0.9 mol) at 0–10°C. After stirring of the reaction mixture for 24 h, the reaction mixture was heated at 80–100°C to obtain the light-red oil, which was washed with water, dried over anhydrous Na_2SO_4, then filtered to afford **5b**.

4.1.2. (*Z*)-2,3,3-Trifluoro-1-iodoprop-1-ene (5a). Yield 48%; ^{1}H NMR ($CDCl_3$) δ 6.08 (1H, td, J=53.50, 4.00 Hz), 6.28 (1H, d, J=32.00 Hz); ^{13}C NMR ($CDCl_3$) δ 61.25 (dt, J=20.8, 6.9 Hz), 107.70 (td, J=242.1, 40.8 Hz), 156.84 (dt, J=262.5, 25.4 Hz); ^{19}F NMR ($CDCl_3$) δ −105.6 (1F, dtd, J=33.0, 18.8, 3.3 Hz), −123.2 (2F, dd, J=52.8, 19.8 Hz); IR (neat) 3101, 1670, 1388 cm^{-1}; HRMS (CI) calcd for $C_3H_2F_3I$ 221.9153, found 221.9149.

4.1.3. (*Z*)-2,3,3,3-Tetrafluoro-1-iodoprop-1-ene (5b). Yield 56%; ^{1}H NMR ($CDCl_3$) δ 6.59 (1H, d, J=35.00 Hz); ^{13}C NMR ($CDCl_3$) δ 63.27 (d, J=21.9 Hz), 116.86 (qd, J=272.3, 42.2 Hz), 152.24 (dq, J=262.8, 39.8 Hz); ^{19}F NMR ($CDCl_3$) δ −72.4 (3F, d, J=13.2 Hz), −108.44 (1F, m); IR (neat) 3105, 1674, 1346, 1157 cm^{-1}; HRMS (CI) calcd for C_3HF_4I 239.9059, found 239.9060.

4.1.4. (*Z*)-2,3,3,4,4,5,5,6,6,7,7-Decafluoro-1-iodoprop-1-ene (5c). Yield 52%; ^{1}H NMR ($CDCl_3$) δ 6.03 (1H, tt, J=52.01, 5.00 Hz), 6.64 (1H, d, J=31.00 Hz); ^{13}C NMR ($CDCl_3$) δ 65.33 (d, J=21.4 Hz), 107.58 (tt, J=255.3, 32.1 Hz), 151.24 (dt, J=264.0, 30.5 Hz); ^{19}F NMR ($CDCl_3$) δ −102.89 to −103.34 (1F, m), −116.45 to −116.92 (2F, m), −123.56 to −124.27 (4F, m), −130.13 to −130.18 (2F, m), −137.17 to −138.11 (2F, m); IR (neat) 3109, 1662, 1326, 1195 cm^{-1}; HRMS (CI) calcd for $C_7H_2F_{11}I$ 421.9026, found 421.9032.

4.2. Typical procedure for the synthesis of difluoromethylated acetylene (path A)

To a THF solution of **5a** (0.33 g, 1.5 mmol) was dropwise added a 1.6 M hexane solution of *n*-BuLi (1.88 mL, 3.0 mmol) at −78°C. The reaction mixture was stirred at that temperature for 30 min, followed by addition of $ZnCl_2$·TMEDA complex (0.30 g, 1.2 mmol). After stirring of the reaction mixture for 15 min at −78°C and for 30 min at room temperature, iodobenzene (0.20 g, 1.0 mmol) and tetrakis(triphenylphosphine)palladium (58 mg, 5 mol%) was added to a reaction mixture in this order, then heated at 50–60°C for 4–12 h. The reaction was quenched with sat. NH_4Cl aq. and the whole was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and then evaporated in vacuo. The residue was purified by flash column chromatography to give the corresponding acetylene **2a** (94 mg, 0.62 mmol) in 62% yield.

4.2.1. 1-Phenyl-3,3-difluoropropyne (2a). Yield 62%; ^{1}H NMR ($CDCl_3$) δ 6.41 (1H, t, J=55.01 Hz), 7.32–7.45 (3H, m), 7.50–7.53 (2H, m); ^{13}C NMR ($CDCl_3$) δ 79.75 (t, J=34.0 Hz), 88.40 (t, J=7.6 Hz), 104.20 (t, J=233.8 Hz), 119.87 (t, J=3.4 Hz), 128.51, 130.11, 132.16; ^{19}F NMR ($CDCl_3$) δ −105.8 (2F, d, J=55.0 Hz); IR (neat) 2253, 2222, 1493, 1373 cm^{-1}; HRMS (EI) calcd for $C_9H_6F_2$ *m/z* 152.0438, found 152.0443.

4.2.2. 1-(2-Methoxyphenyl)-3,3-difluoropropyne (2b). Yield 74%; ^{1}H NMR ($CDCl_3$) δ 3.89 (3H, s), 6.46 (1H, t, J=55.51 Hz), 6.90 (1H, d, J=8.50 Hz), 6.93 (1H, t, J=7.50 Hz), 7.38 (1H, dt, J=1.50, 8.00 Hz), 7.46 (1H, dt, J=1.00, 7.50 Hz); ^{13}C NMR ($CDCl_3$) δ 55.76, 83.56 (t, J=33.1 Hz), 85.26 (t, J=7.4 Hz), 104.36 (t, J=230.8 Hz), 109.07, 110.76, 120.48, 131.69, 134.15, 160.80; ^{19}F NMR ($CDCl_3$) δ −105.4 (2F, d, J=55.1 Hz); IR (neat) 2245, 1736, 1596, 1492 cm^{-1}; HRMS (EI) calcd for $C_{10}H_8F_2O$ 182.0543, found 182.0545.

4.2.3. 1-(3-Nitrophenyl)-3,3-difluoropropyne (2c). Yield 80%; ^{1}H NMR ($CDCl_3$) δ 6.45 (1H, t, J=54.01 Hz), 7.61 (1H, t, J=7.50 Hz), 7.86 (1H, d, J=8.00 Hz), 8.29–8.32 (1H, m), 8.49 (1H, s); ^{13}C NMR ($CDCl_3$) δ 81.82 (t, J=34.7 Hz), 85.42 (t, J=7.2 Hz), 103.75 (t, J=233.5 Hz), 121.64 (t, J=2.5 Hz), 124.85, 127.06 (t, J=2.2 Hz), 129.77, 137.70, 148.10; ^{19}F NMR ($CDCl_3$) δ −107.15 (2F, d, J=55.0 Hz); IR (neat) 2257, 2233, 1535, 1373, 1353 cm^{-1};

HRMS (FAB) calcd for $C_9H_5F_2NO_2$ 197.0288, found 197.0291.

4.2.4. 1-(4-Ethoxycarbonyl)-3,3-difluoropropyne (2d). Yield 76%; ^{1}H NMR ($CDCl_3$) δ 1.40 (3H, t, J=7.25 Hz), 4.39 (2H, q, J=7.25 Hz), 6.43 (1H, t, J=54.51 Hz), 7.58 (2H, d, J=8.25 Hz), 8.04 (2H, d, J=8.25 Hz); ^{13}C NMR ($CDCl_3$) δ 14.23, 61.38, 81.92 (t, J=34.5 Hz), 87.28 (t, J=7.3 Hz), 103.97 (t, J=232.7 Hz), 124.13, 129.54, 131.71, 132.06, 165.60; ^{19}F NMR ($CDCl_3$) δ −106.5 (2F, d, J=55.1 Hz); IR (neat) 2253, 2226, 1720, 1608, 1373, 1273 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{11}F_2O_2$ (M+H) 225.0727, found 225.0734.

4.2.5. 1-(4-Chlorophenyl)-3,3-difluoropropyne (2e). Yield 70%; ^{1}H NMR ($CDCl_3$) δ 6.40 (1H, t, J=50.51 Hz), 7.35 (2H, d, J=8.50 Hz), 7.44 (2H, d, J=8.50 Hz); ^{13}C NMR ($CDCl_3$) δ 80.60 (t, J=34.0 Hz), 87.19 (t, J=7.2 Hz), 104.05 (t, J=232.7 Hz), 118.30, 128.96, 133.37, 136.45; ^{19}F NMR ($CDCl_3$) δ −110.7 (2F, d, J=50.5 Hz); IR (neat) 2253, 2226, 1489, 1373 cm^{-1}; HRMS (EI) calcd for $C_9H_5^{35}ClF_2$ 186.0048, found 186.0034.

4.2.6. 1-Phenyl-5,5-difluoro-1-penten-3-yne (2f). Yield 85%; ^{1}H NMR ($CDCl_3$) δ 6.17 (1H, dt, J=16.25, 4.00 Hz), 6.36 (1H, t, J=55.01 Hz), 7.15 (1H, d, J=16.25 Hz), 7.33–7.45 (5H, m); ^{13}C NMR ($CDCl_3$) δ 81.32 (t, J=33.3 Hz), 87.81 (t, J=7.4 Hz), 104.18 (t, J=233.0 Hz), 104.74 (t, J=3.7 Hz), 126.69, 128.86, 129.68, 135.13, 145.58; ^{19}F NMR ($CDCl_3$) δ −105.32 (2F, dd, J=4.4, 55.0 Hz); IR (neat) 2218, 1450, 1373 cm^{-1}; HRMS (EI) calcd for $C_{11}H_8F_2$ 178.0594, found 178.0593.

4.2.7. 1,1-Difluoro-4-dodecen-2-yne (2g). Yield 74%; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, J=7.00 Hz), 1.22–1.33 (6H, m), 1.35–1.43 (2H, m), 2.15 (2H, q, J=7.00 Hz), 5.47–5.85 (1H, m), 6.28 (1H, t, J=55.01 Hz), 6.38 (1H, dt, J=15.00, 7.50 Hz); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.55, 28.25, 28.72, 31.58, 33.24, 78.28 (t, J=33.5 Hz), 87.59 (t, J=7.4 Hz), 104.22 (t, J=231.0 Hz), 106.81 (t, J=4.0 Hz), 150.15 (t, J=3.7 Hz); ^{19}F NMR ($CDCl_3$) δ −105.0 (2F, d, J=4.4, 55.0 Hz); IR (neat) 2932, 2858, 2226, 1373 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{15}F_2$ (M−H) 185.1142, found 185.1145.

4.2.8. 1-(2-Methoxyphenyl)-3,3,3-trifluoropropyne (1a). Yield 78%; ^{1}H NMR ($CDCl_3$) δ 3.90 (3H, s), 6.92 (1H, d, J=8.50 Hz), 6.96 (1H, t, J=7.80 Hz), 7.43 (1H, dt, J=1.30, 7.90 Hz), 7.49 (1H, dd, J=1.30, 7.80 Hz); ^{13}C NMR ($CDCl_3$) δ 55.75, 79.29 (q, J=52.1 Hz), 83.76 (q, J=6.1 Hz), 107.74, 110.86, 115.03 (q, J=256.4 Hz), 120.50, 132.49, 134.32, 161.29; ^{19}F NMR ($CDCl_3$) δ −49.95 (3F, s); IR (neat) 2253, 1597, 1497, 1466, 1323 cm^{-1}; HRMS calcd for $C_{10}H_7F_3O$ m/z 200.0449, found 200.0427.

4.2.9. 1-(3-Nitrophenyl)-3,3,3-trifluoropropyne (1b). Yield 76%; ^{1}H NMR ($CDCl_3$) δ 7.63 (1H, t, J=8.20 Hz), 7.88 (1H, d, J=7.50 Hz), 8.34 (1H, d, J=10.00 Hz), 8.43 (1H, s); ^{13}C NMR ($CDCl_3$) δ 76.74–77.4 (overlap), 83.39 (q, J=6.2 Hz), 114.36 (q, J=259.0 Hz), 113.30, 120.20, 125.60, 127.30, 129.90, 137.90; ^{19}F NMR ($CDCl_3$) δ −51.0 (3F, s); IR (neat) 3089, 2858, 2268, 2237, 1535, 1477 cm^{-1}; MS (FAB) m/z (rel intensity) 215 (100, M) calcd for $C_9H_4F_3NO_2$ 215.0194, found 215.0189.

4.2.10. Ethyl 4-(3,3,3-trifluoropropynyl)benzoate (1c). Yield 73%; ^{1}H NMR ($CDCl_3$) δ 1.41 (3H, t, J=7.30 Hz), 4.40 (2H, q, J=7.20 Hz), 7.63 (2H, d, J=8.00 Hz), 8.07 (2H, d, J=8.00 Hz); ^{13}C NMR ($CDCl_3$) δ 14.15, 61.43, 77.57 (q, J=53.2 Hz), 85.23 (q, J=6.4 Hz), 114.55 (q, J=257.3 Hz), 122.61, 128.24, 129.57, 132.30, 165.35; ^{19}F NMR ($CDCl_3$) δ −50.68 (3F, s); IR (neat) 2986, 2257, 1724, 1404, 1369, 1315 cm^{-1}; HRMS calcd for $C_{12}H_9F_3O_2$ m/z 242.0555, found 242.0533.

4.2.12. 1,1,1-Trifluoro-5-phenylpent-4-en-2-yne (1d). Yield 75%; ^{1}H NMR ($CDCl_3$) δ 6.14 (1H, dq, J=16.50, 3.00 Hz), 7.24 (1H, d, J=5.50 Hz), 7.36–7.42 (5H, m); ^{13}C NMR ($CDCl_3$) δ 75.67 (q, J=52.5 Hz), 86.07 (q, J=6.2 Hz), 103.41, 114.83 (q, J=256.5 Hz), 126.88, 128.03, 128.95, 130.12, 147.35; ^{19}F NMR ($CDCl_3$) δ −50.1 (3F, s); IR (neat) 3031, 2931, 2233, 1573, 1492, 1450, 1261 cm^{-1}; HRMS (EI) calcd for $C_{11}H_7F_3$ 196.0500, found 196.0500.

4.2.13. 1,1,1-Trifluoroundec-4-en-2-yne (1e). Yield 81%; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, J=6.75 Hz), 1.24–1.33 (6H, m), 1.41 (2H, sex, J=7.12 Hz), 2.17 (2H, q, J=7.33 Hz), 5.5 (1H, m), 6.48 (1H, dt, J=16.00, 7.00 Hz); ^{13}C NMR ($CDCl_3$) δ 14.00, 22.53, 28.10, 28.71, 31.56, 33.33, 74.21 (q, J=51.8 Hz), 85.78 (q, J=6.5 Hz), 105.78, 114.84 (q, J=256.0 Hz), 152.24; ^{19}F NMR ($CDCl_3$) δ −50.7 (3F, s); IR (neat) 2931, 2858, 2237, 1631, 1465 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{15}F_3$ (M+H) 205.1204, found 205.1208.

4.2.14. 1-(3-Nitrophenyl)-3,3,4,4,5,5,6,6,7,7-decafluoro-1-heptyne (2h). Yield 77%; ^{1}H NMR ($CDCl_3$) δ 6.08 (1H, tt, J=10.00, 52.76 Hz) 7.64 (1H, t, J=8.00 Hz), 7.89 (1H, d, J=8.00 Hz), 8.36 (1H, d, J=8.00 Hz), 8.43 (1H, s); ^{13}C NMR ($CDCl_3$) δ 76.46–77.25 (overlap), 88.87 (t, J=6.28 Hz), 103–111 (5C, m), 120.26, 125.76, 127.37, 130.01, 137.97, 148.13; ^{19}F NMR ($CDCl_3$) δ −137.8 (2F, d, J=27.0 Hz), −130.32 (2F, s), −123.44 (4F, s), −99.1 (2F, s); IR (neat) 2256, 1539, 1477 cm^{-1}; MS (FAB) m/z (rel intensity) 397 (55) calcd for $C_{13}H_5F_{10}NO_2$ 397.0161, found 397.0160.

4.3. Typical procedure for the synthesis of trifluoromethylated acetylene derivatives. To a solution of diisopropylamine (0.46 mL, 3.3 mmol) in THF (3.0 mL) was added 2.06 mL (3.3 mmol) of n-BuLi (1.6 M hexane solution) at −78°C and the whole was stirred for 15 min. To this solution was added dropwise 2-bromo-3,3,3-trifluoropropene (0.15 mL, 1.5 mmol), followed by addition of zinc chloride tetramethylethylenediamine complex ($ZnCl_2$·TMEDA) (0.417 g, 1.65 mmol) in one portion. The reaction was stirred for 30 min at −78°C, then allowed to warm to room temperature and stirred for 30 min. After the mixture was stirred for 30 min at room temperature, iodobenzene (0.204 g, 1.0 mmol) and tetrakis(triphenyl–phosphine)palladium(0) ($Pd(PPh_3)_4$) (0.058 g, 0.05 mmol) were added and the whole was stirred for 6 h at the reflux temperature of THF. The reaction mixture was quenched with NH_4Cl aq. and extracted with EtOAc three times. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The

residue was chromatographed on silica gel (hexane only) to afford 1-phenyl-3,3,3-trifluoropropyne (0.142 g, 0.83 mmol).

4.3.1. 1-Phenyl-3,3,3-trifluoropropyne (1f). Yield 83%; ^{1}H NMR ($CDCl_3$) δ 7.40 (2H, t, J=7.50 Hz), 7.49 (1H, t, J=7.50 Hz), 7.57 (2H, d, J=7.50 Hz); ^{13}C NMR ($CDCl_3$) δ 75.67 (q, J=52.5 Hz), 86.50 (q, J=6.2 Hz), 114.86 (q, J=256.8 Hz), 118.51, 128.64, 130.87, 132.43; ^{19}F NMR ($CDCl_3$) δ −50.3 (3F, s); IR (neat) 2928, 2855, 2257, 1493, 1447 cm^{-1}; HRMS (EI) calcd for $C_9H_5F_3$ 170.0343, found 170.0347.

4.3.2. 1-(4-Methoxyphenyl)-3,3,3-trifluoropropyne (1g). Yield 99%; ^{1}H NMR ($CDCl_3$) δ 3.84 (3H, s), 6.90 (2H, d, J=8.50 Hz), 7.49 (2H, d, J=8.50 Hz); ^{13}C NMR ($CDCl_3$) δ 55.37, 74.78 (q, J=52.1 Hz), 87.05 (q, J=6.8 Hz), 110.30, 114.30, 115.05 (q, J=256.3 Hz), 134.15, 161.53; ^{19}F NMR ($CDCl_3$) δ −49.9 (3F, s); IR (neat) 2253, 1609, 1512, 1323 cm^{-1}; HRMS calcd for $C_{10}H_7F_3O$ m/z 200.0449, found 200.0434.

4.3.3. 1-(4-Methylphenyl)-3,3,3-trifluoropropyne (1h). Yield 99%; ^{1}H NMR ($CDCl_3$) δ 2.39 (3H, s), 7.20 (2H, d, J=8.00 Hz), 7.45 (2H, d, J=8.00 Hz); ^{13}C NMR ($CDCl_3$) δ 21.37, 75.20 (q, J=52.0 Hz), 86.92 (q, J=6.8 Hz), 114.92 (q, J=256.6 Hz), 115.40, 129.39, 132.34, 141.45; ^{19}F NMR ($CDCl_3$) δ −50.1 (3F, s); IR (neat) 2253, 1512, 1315 cm^{-1}; HRMS calcd for $C_{10}H_7F_3$ m/z 184.0500, found 184.0490.

4.3.4. 1-(4-Chlorophenyl)-3,3,3-trifluoropropyne (1i). Yield 81%; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, d, J=8.50 Hz), 7.49 (2H, d, J=8.00 Hz); ^{13}C NMR ($CDCl_3$) δ 76.53 (q, J=53.3 Hz), 85.30 (q, J=6.2 Hz), 115.30 (q, J=256.9 Hz), 116.93, 129.14, 133.65, 137.36; ^{19}F NMR ($CDCl_3$) δ −49.9 (3F, s); IR (neat) 2257, 1593, 1493, 1400, 1312 cm^{-1}; HRMS calcd for $C_9H_4^{35}ClF_3$ 203.9954, found 203.9929.

4.3.5. 1-(4-Nitrophenyl)-3,3,3-trifluoropropyne (1j). Yield 51%; ^{1}H NMR ($CDCl_3$) δ 7.75 (2H, d, J=9.00 Hz), 8.28 (2H, d, J=9.00 Hz); ^{13}C NMR ($CDCl_3$) δ 79.32 (q, J=53.4 Hz), 83.64 (q, J=6.3 Hz), 114.35 (q, J=258.0 Hz), 123.82, 124.88, 133.47, 148.81; ^{19}F NMR ($CDCl_3$) δ −51.2 (3F, s); IR (neat) 2260, 1535, 1353 cm^{-1}; HRMS calcd for $C_9H_4F_3NO_2$ 215.0194, found 215.0203.

4.3.6. 1-(3-Methoxyphenyl)-3,3,3-trifluoropropyne (1k). Yield 95%; ^{1}H NMR ($CDCl_3$) δ 3.82 (3H, s), 7.02 (1H, dd, J=2.50, 8.50 Hz), 7.06 (1H, s), 7.15 (1H, d, J=7.50 Hz), 7.30 (1H, t, J=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 55.35, 75.35 (q, J=52.6 Hz), 86.43 (q, J=6.2 Hz), 114.82 (q, J=256.8 Hz), 117.01, 117.57, 119.38, 124.89, 129.79, 159.41; ^{19}F NMR ($CDCl_3$) δ −50.3 (3F, s); IR (neat) 2264, 2241, 1597, 1489 cm^{-1}; HRMS calcd for $C_{10}H_7F_3O$ m/z 200.0449, found 200.0434.

4.3.7. 1-(2-Chlorophenyl)-3,3,3-trifluoropropyne (1l). Yield 79%; ^{1}H NMR ($CDCl_3$) δ 7.30 (1H, t, J=7.50 Hz), 7.41 (1H, t, J=7.80 Hz), 7.46 (1H, d, J=8.50 Hz), 7.58 (1H, d, J=7.50 Hz); ^{13}C NMR ($CDCl_3$) δ 80.03 (q, J=52.9 Hz), 83.03 (q, J=6.4 Hz), 114.73 (q, J=257.3 Hz), 118.82, 126.72, 129.69, 131.94, 134.21, 137.08; ^{19}F NMR ($CDCl_3$) δ −50.6 (3F, s); IR (neat) 2260, 1475, 1436 cm^{-1}; HRMS calcd for $C_9H_4^{35}ClF_3$ 203.9954, found 203.9952.

4.4. Typical procedure for the preparation of vinyl iodide 5 via radical addition of perfluoroalkyl iodide to terminal acetylene

Zinc (powder, 10 mol%, 65 mg, 1.0 mmol) was placed in a 10 mL round-bottom flask followed by 2 mL of CH_2Cl_2 and terminal alkyne (10.0 mmol). To this mixture were added perfluoroalkyl iodide (10 mmol) and 20 mol% of TFA slowly (228 mg, 2.0 mmol). The mixture was allowed to stir overnight at room temperature, diluted with 10 mL of CH_2Cl_2, and filtered to remove zinc. The solvent was removed in vacuo to provide the crude materials which were purified by column chromatography to give the corresponding fluoroalkylated vinyl iodide with preferential E selectivity (up to 95% selectivity). Only physical data of E-vinyl iodides is described below.

4.4.1. (*E*)-9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluoro-7-iodo-7-hexadecene (7a). Yield 62%; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, J=6.70 Hz), 1.31–1.36 (6H, m), 1.55–1.59 (2H, m), 2.63 (2H, t, J=7.50 Hz), 6.32 (1H, t, J=15.00 Hz); ^{13}C NMR ($CDCl_3$) δ 13.89, 22.48, 28.13, 30.06, 31.48, 41.17, 108.12–121.88 (m), 123.04 (t, J=6.5 Hz), 126.52 (t, J=23.8 Hz); ^{19}F NMR ($CDCl_3$) δ−81.6 (3F, t, J=8.8 Hz), −105.7 (2F, m), −122.3 to −124 (10F, m), −126.7 (2F, m); IR (neat) 2935, 2862, 1635, 1465 cm^{-1}; MS (CI) calcd for $C_{16}H_{14}F_{17}I$ 655.9869, found 655.9860.

4.4.2. (*E*)-1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodo-5-dodecene (7b). Yield 81%; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, J=6.70 Hz), 1.31–1.36 (6H, m), 1.55–1.59 (2H, m), 2.63 (2H, t, J=7.50 Hz), 6.32 (1H, t, J=14.50 Hz); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.47, 28.1, 30.02, 31.46, 41.16, 108.04–121.52 (m), 123.14 (t, J=7.5 Hz), 126.35 (t, J=23.8 Hz); ^{19}F NMR ($CDCl_3$) δ −80.3 (3F, m), −104.3 to −104.6 (2F, m), −123.1 to −123.2 (2F, m), −124.7 to −125.0 (2F, m); IR (neat) 2935, 2862, 1635 cm^{-1}; MS (CI) calcd for $C_{12}H_{14}F_9I$ 455.9997, found 456.0000.

4.4.3. (*E*)-1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodo-5-hexadecene (7c). Yield 81%; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J=6.70 Hz), 1.27–1.30 (14H, m), 1.55–1.59 (2H, m), 2.63 (2H, t, J=7.50 Hz), 6.32 (1H, t, J=14.30 Hz); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.68, 28.43, 29.28, 29.31, 29.44, 29.55, 30.05, 31.90, 41.15, 108.22–121.51 (m), 123.15 (t, J=6.0 Hz), 126.33 (t, J=23.7 Hz); ^{19}F NMR ($CDCl_3$) δ −80.8 (3F, t, m), −105.1 (2F, m), −123.8 (2F, m), −125.3 (2F, m); IR (neat) 2927, 2858, 1635, 1465 cm^{-1}; MS (CI) calcd for $C_{16}H_{22}F_9I$ 512.0622, found 512.0622.

4.4.4. (*E*)-1,1,1,2,2,3,3,4,4-Nonafluoro-7-ethyl-6-iodo-5-undecene (7d). Yield 55%; ^{1}H NMR ($CDCl_3$) δ 0.84 (3H, t, J=7.50 Hz), 0.90 (3H, t, J=7.20 Hz), 1.16–1.46 (8H, m), 1.91 (1H, m), 6.49 (1H, t, J=14.75 Hz); ^{13}C NMR ($CDCl_3$) δ 11.13, 13.83, 22.73, 28.86, 29.24, 36.02, 47.27, 112.3–121.83 (m), 127.32 (t, J=22.0 Hz), 135.14 (t, J=6.3 Hz); ^{19}F NMR ($CDCl_3$) δ −81.8 (3F, t, J=10.1 Hz), −103.1 to −104.6 (2F, m), −124.4 to −124.5 (2F, m), −126.1 to −126.3 (2F, m); IR (neat) 2935, 2862, 1624, 1458,

1353 cm^{-1}; MS (CI) calcd for $C_{13}H_{16}F_9I$ 470.0153, found 470.0155.

4.4.5. (*E*)-1-Phenyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-iodo-1-hexene (7e). Yield 62%; ^1H NMR ($CDCl_3$) δ 6.59 (1H, t, J=13.75 Hz), 7.28–7.33 (5H, m); ^{13}C NMR ($CDCl_3$) δ 112.77 (t, J=6.3 Hz), 113.64–116.41 (m), 126.83, 126.89 (t, J=21.9 Hz), 127.89, 129.28, 141.30; ^{19}F NMR ($CDCl_3$) δ −81.6 (3F, t, J=9.9 Hz), −106.1 (2F, q, J=12.1 Hz), −124.2 to −124.5 (2F, m), −126.2 to −126.7 (2F, m); IR (neat) 1639, 1488, 1353, 1234 cm^{-1}; HRMS (CI) calcd for $C_{12}H_6F_9I$ 447.9370, found 447.9362.

4.4.6. (*E*)-1-(4-Methylphenyl)-3,3,4,4,5,5,6,6,6-nonafluoro-1-hexyne (7f). Yield 65%; ^1H NMR ($CDCl_3$) δ 2.34 (3H, s), 6.56 (1H, t, J=13.50 Hz), 7.13 (2H, d, J=8.00 Hz), 7.19 (2H, d, J=8.00 Hz); ^{13}C NMR ($CDCl_3$) δ 21.32, 113.38 (t, J=6.2 Hz), 113.4–116 (m), 126.53 (t, J=22.6 Hz), 126.89, 128.66, 138.50, 139.51; ^{19}F NMR ($CDCl_3$) δ −81.6 (3F, t, J=9.9 Hz), −105.9 (2F, q, J=13.2 Hz), −124.2 to −124.5 (2F, m), −126.3 to −126.7 (2F, m); IR (neat) 1635, 1508, 1353 cm^{-1}; HRMS (CI) calcd for $C_{13}H_8F_9I$ 461.9527, found 461.9517.

4.4.7. (*E*)-1-Perfluoroisopropyl-2-iodo-1-octene (7g). Yield 84%; ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, J=6.70 Hz), 1.30–1.35 (6H, m), 1.54–1.58 (2H, m), 2.64 (2H, t, J=7.50 Hz), 6.15 (1H, d, J=2.50 Hz); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.48, 28.10, 29.99, 31.45, 41.32, 92–94 (m), 119.77 (dd, J=27.9, 287.2 Hz), 121.95 (d, J=13.8 Hz); ^{19}F NMR ($CDCl_3$) δ −76.5 (6F, d, J=8.4 Hz), −182.5 (1F, m); IR (neat) 2931, 2862, 1635, 1458, 1303 cm^{-1}; MS (CI) calcd for $C_{11}H_{14}F_7I$ 406.0028, found 406.0029.

4.4.8. (*E*)-1,1,1,2,2-Pentafluoro-4-iodo-3-decene (7h). Yield 85%; ^1H NMR ($CDCl_3$) δ 0.90 (3H, t, J=6.70 Hz), 1.27–1.36 (6H, m), 1.53–1.60 (2H, m), 2.63 (2H, t, J=7.50 Hz), 6.29 (1H, t, J=14.30 Hz); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.46, 28.07, 29.94, 31.45, 41.08, 109.68–121.91 (m), 123.06 (t, J=6.0 Hz), 126.19 (t, J=23.4 Hz); ^{19}F NMR ($CDCl_3$) δ −84.7 (3F, t, J=17.5 Hz), −108.5 (2F, d, J=13.2 Hz); IR (neat) 2931, 2862, 1635, 1458, 1334 cm^{-1}; MS (CI) calcd for $C_{10}H_{14}F_5I$ 356.0060, found 356.0059.

4.4.9. (*E*)-1,1,1-Trifluoro-3-iodo-2-nonene (7i). Yield 78%; ^1H NMR ($CDCl_3$) δ 0.90 (3H, t, J=6.7 Hz), 1.32–1.36 (6H, m), 1.51–1.58 (2H, m), 2.60 (2H, t, J=7.50 Hz), 6.38 (1H, q, J=7.83 Hz); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.48, 27.99, 29.59, 31.46, 40.72, 121.00 (q, J=6.3 Hz), 121.92 (q, J=274.1 Hz), 128.95 (q, J=34.1 Hz); ^{19}F NMR ($CDCl_3$) δ −57.2 (d, J=8.8 Hz); IR (neat) 2931, 2858, 1639, 1465 cm^{-1}; MS (CI) calcd for $C_9H_{14}F_3I$ 306.0092, found 306.0085.

4.4.10. (*E*)-1,1,1-Trifluoro-3-iodo-2-tridecene (7j). Yield 45%; ^1H NMR ($CDCl_3$) δ 0.88 (3H, t, J=7.00 Hz), 1.27–1.30 (14H, m), 1.52–1.57 (2H, m), 2.6 (2H, t, J=7.50 Hz), 6.38 (1H, q, J=7.60 Hz); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.68, 28.32, 29.26, 29.30, 29.43, 29.54, 29.62, 31.89, 40.71, 121.05 (q, J=6.9 Hz), 121.92 (q, J=274.1 Hz), 128.92 (q, J=34.4 Hz); ^{19}F NMR ($CDCl_3$) δ −57.8 (3F, d, J=8.4 Hz); IR (neat) 2927, 2854, 1639, 1465 cm^{-1}; MS (CI) calcd for $C_{13}H_{22}F_3I$ 362.0718, found 362.0717.

4.4.11. (*E*)-1,1,1-Trifluoro-4-ethyl-3-iodo-2-octene (7k). Yield 66%; ^1H NMR ($CDCl_3$) δ 0.82 (3H, t, J=7.20 Hz), 0.89 (3H, t, J=7.20 Hz), 1.12–1.45 (8H, m), 1.84 (1H, quint, J=5 Hz), 6.54 (1H, q, J=7.80 Hz); ^{13}C NMR ($CDCl_3$) δ 11.14, 13.88, 22.67, 28.84, 28.93, 35.73, 47.25, 122.09 (q, J=274.1 Hz), 130.08 (q, J=34.0 Hz), 132.64 (q, J=6.2 Hz); ^{19}F NMR ($CDCl_3$) δ −55.6 (3F, d, J=8.7 Hz); IR (neat) 2962, 2931, 2862, 1631, 1461, 1315 cm^{-1}; MS (EI) 320 (M^+, 3.1), 264 (100), 193 (1.9), 174 (9.9), 137 (32.1), 59 (61.3); HRMS was not obtained due to the instability of the corresponding molecular ion.

4.4.12. (*E*)-1,1,1-Trifluoro-4-cyclohexyl-3-iodo-2-octene (7l). Yield 62%; ^1H NMR ($CDCl_3$) δ 0.89–0.99 (2H, m), 1.1–1.3 (3H, m), 1.6–1.7 (6H, m), 2.4 (2H, d, J=5.50 Hz), 6.44 (1H, q, J=7.80 Hz); ^{13}C NMR ($CDCl_3$) δ 26.17, 32.07, 38.19, 47.24, 120.23 (q, J=6.3 Hz), 121.87 (q, J=274.8 Hz), 129.77 (q, J=34.1 Hz); ^{19}F NMR ($CDCl_3$) δ −56.6 (3F, d, J=8.8 Hz); IR (neat) 2927, 2854, 1639, 1450 cm^{-1}; MS (EI) calcd for $C_{10}H_{14}F_3I$ 318.0092, found 318.0085.

4.5. Typical procedure for path C

Potassium *t*-butoxide (3.0 mmol, 336 mg) was suspended in 5 mL of benzene, and the reaction mixture was cooled to 0°C. To this solution was added the mixture of fluoroalkylated vinyl iodide (1.0 mmol) in benzene (2 mL) at that temperature, then stirred for 10 min. The reaction mixture was allowed to warm gradually to the reflux temperature, and stirred for 2 h. The mixture was cooled to room temperature, and poured into sat. NH_4Cl aq. The whole was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The obtained crude materials were purified by silica gel column chromatography to afford the corresponding fluoroalkylated alkyne.

4.5.1. 9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluoro-7-hexadecyne (4a). Yield 49%; ^1H NMR ($CDCl_3$) δ 0.82 (3H, t, J=7.00 Hz), 1.19–1.36 (6H, m), 1.51 (2H, quint, J=7.40 Hz), 2.28 (2H, quint, J=6.40 Hz); ^{13}C NMR ($CDCl_3$) δ 13.85, 18.46, 22.38, 27.15, 28.25, 31.08, 67.38 (t, J=36.6 Hz), 95.42 (t, J=6.3 Hz); ^{19}F NMR ($CDCl_3$) δ −81.6 (3F, t, J=8.8 Hz), −95.5 (2F, m), −122.3 to −126.7 (10F, m), −163.3 to −164.2 (2F, m); IR (neat) 2935, 2866, 2260, 1211 cm^{-1}; MS (CI) calcd for $C_{16}H_{12}F_{17}$ (M−H) 527.0668, found 527.0663.

4.5.2. 1,1,1,2,2,3,3,4,4-Nonafluoro-5-dodecyne (4b). Yield 44%; ^1H NMR ($CDCl_3$) δ 0.90 (3H, t, J=7.00 Hz), 1.26–1.43 (6H, m), 1.59 (2H, quint, J=7.40 Hz), 2.35 (2H, quint, J=6.40 Hz); ^{13}C NMR ($CDCl_3$) δ 13.89, 18.46, 22.4, 27.15, 28.26, 31.08, 67.25 (t, J=35.8 Hz), 95.46 (t, J=6.3 Hz); ^{19}F NMR ($CDCl_3$) δ −81.76 (3F, t, J=9.9 Hz), −96.4 (2F, m), −123.89 to −124.4 (2F, m), −125.75 to −126.14 (2F, m); IR (neat) 2935, 2862, 2260, 1353, 1238 (s), 1137 cm^{-1}; MS (CI) calcd for $C_{12}H_{14}F_9$ (M+H) 329.0952, found 329.0954.

4.5.3. 1,1,1,2,2,3,3,4,4-Nonafluoro-5-hexadecyne (4c). Yield 70%; ^1H NMR ($CDCl_3$) δ 0.81 (3H, t, J=7.00 Hz),

1.20–1.34 (14H, m), 1.51 (2H, quint, J=7.40 Hz), 2.28 (2H, quint, J=6.40 Hz); ^{13}C NMR ($CDCl_3$) δ 14.06, 18.47, 22.66, 27.20, 28.60, 28.91, 29.28, 29.37, 29.48, 31.88, 67.29 (t, J=36.5 Hz), 95.48 (t, J=6.4 Hz); ^{19}F NMR ($CDCl_3$) δ −80.8 (3F, m), −95.9 (2F, m), −123.2 (2F, m), −125.1 (2F, m); IR (neat) 2927, 2858, 2256, 1465, 1353 cm^{-1}; MS (CI) calcd for $C_{16}H_{21}F_9$ 384.1500, found 384.1505.

4.5.4. 1,1,1,2,2,3,3,4,4-Nonafluoro-7-ethyl-5-undecyne (4d). Yield 81%; ^{1}H NMR ($CDCl_3$) δ 0.91 (3H, t, J=7.25 Hz), 1.01 (3H, t, J=7.50 Hz), 1.26–1.6 (8H, m), 2.42 (1H, quint, J=6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 11.38, 13.82, 22.36, 26.96, 29.23, 33.15, 33.34, 68.42 (t, J=35.8 Hz), 98.68 (t, J=6.9 Hz), 105–120 (m); ^{19}F NMR ($CDCl_3$) δ −80.8 (3F, t, J=8.8 Hz), −96.1 (2F, m), −123.4 (2F, m), −125.3 (2F, m); IR (neat) 2935, 2866, 2252, 1647, 1461 cm^{-1}; MS (CI) calcd for $C_{13}H_{16}F_9$ (M+H) 343.1108, found 343.1125.

4.5.5. 3,3,4,4,5,5,6,6,6-Nonafluoro-1-phenyl-2-hexyne (2i). Yield 74%; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, t, J=7.80 Hz), 7.48 (1H, t, J=7.50 Hz), 7.56 (2H, d, J=7.00 Hz); ^{13}C NMR ($CDCl_3$) δ 74.63 (t, J=36.5 Hz), 92.34 (t, J=6.3 Hz), 107–118 (m), 128.67, 131.09, 132.48; ^{19}F NMR ($CDCl_3$) δ −81.6 (3F, t, J=9.9 Hz), −97.8 to −98.0 (2F, m), −123.8 to −124.2 (2F, m), −125.8 to −126.1 (2F, m); IR (neat) 2248, 1728, 1492 cm^{-1}; HRMS (CI) calcd for $C_{12}H_5F_9$ 320.0248, found 320.0241.

4.5.6. 3,3,4,4,5,5,6,6,6-Nonafluoro-1-(4-methylphenyl)-2-hexyne (2j). Yield 77%; ^{1}H NMR ($CDCl_3$) δ 2.39 (3H, s), 7.19 (2H, d, J=8.00 Hz), 7.44 (2H, d, J=8.00 Hz); ^{13}C NMR ($CDCl_3$) δ 21.67, 74.15 (t, J=35.8 Hz), 92.81 (t, J=6.3 Hz), 107.28–125.09 (m), 129.43, 132.41, 141.76; ^{19}F NMR ($CDCl_3$) δ −81.5 (3F, t, J=9.9 Hz), −97.2 to −97.8 (2F, m), −123.8 to −124.0 (2F, m), −125.7 to −126.0 (2F, m); IR (neat) 2245, 1512, 1353 cm^{-1}; HRMS (CI) calcd for $C_{13}H_7F_9$ 334.0404, found 334.0402.

4.5.7. 1-Heptafluoroisopropyl-1-octyne (4g). Yield 40%; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, J=7.00 Hz), 1.26–1.43 (6H, m), 1.58 (2H, quint, J=7.25 Hz), 2.34 (2H, q, J=7.20 Hz); ^{13}C NMR ($CDCl_3$) δ 13.85, 18.64, 22.39, 27.24, 28.19, 31.05, 65.43 (d, J=26.4 Hz), 96.52 (d, J=8.8 Hz), 111.62–125.41 (m); ^{19}F NMR ($CDCl_3$) δ −75.5 (6F, d, J=11.0 Hz), −163.6 (1F, m); IR (neat) 2935, 2866, 2256, 1647 cm^{-1}; MS (CI) calcd for $C_{11}H_{14}F_7$ (M+H) 279.0984, found 279.0984.

4.5.8. 1,1,1,2,2-Pentafluoro-3-decyne (4h). Yield 55%; ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, J=7.00 Hz), 1.25–1.43 (6H, m), 1.55–1.61 (2H, m), 2.31–2.39 (2H, m); ^{13}C NMR ($CDCl_3$) δ 13.85, 18.64, 22.39, 27.25, 28.19, 31.05, 65.43 (d, J=26.9 Hz), 96.52 (d, J=8.4 Hz), 115.22–124.01 (m); ^{19}F NMR ($CDCl_3$) δ −85.4 (3F, t, J=4.4 Hz), −99.9 (2F, m); IR (neat) 2931, 2874, 1666, 1465, 1369, 1207 cm^{-1}; HRMS (CI) calcd for $C_{10}H_{13}F_5$ (M+H) 229.1016, found 229.1021.

For the synthesis of trifluoromethylated alkynes, **3i–l**, the reaction was carried out in a similar manner as described above except for the reaction temperature (2 h) and an amount of *t*-BuOK (1.2 equiv.).

4.5.9. 1,1,1-Trifluoro-2-nonyne (3i). Yield 48%; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, J=7.00 Hz), 1.27–1.43 (6H, m), 1.58 (2H, quint, J=7.37 Hz), 2.27–2.32 (2H, m); ^{13}C NMR ($CDCl_3$) δ 13.92, 18.10, 22.43, 27.22, 28.38, 31.14, 68.35 (q, J=51.6 Hz), 89.31 (q, J=6.3 Hz), 114.19 (q, J=256.1 Hz); ^{19}F NMR ($CDCl_3$) δ −49.2 (t, J=4.7 Hz); IR (neat) 2935, 2862, 2264, 1720, 1465 cm^{-1}; MS (CI) calcd for $C_9H_{12}F_3$ (M−H) 177.0891, found 177.0896.

4.5.10. 1,1,1-Trifluoro-2-tridecyne (3j). Yield 67%; ^{1}H NMR ($CDCl_3$) δ 0.81 (3H, t, J=6.75 Hz), 1.2–1.33 (14H, m), 1.50 (2H, quint, J=8.10 Hz), 2.2–2.25 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.07, 18.01, 22.66, 27.22, 28.69, 28.94, 29.27, 29.38, 29.50, 31.88, 68.33 (q, J=52.8 Hz), 89.34 (q, J=6.3 Hz), 114.17 (q, J=256.5 Hz); ^{19}F NMR ($CDCl_3$) δ −48.8 (t, J=4.7 Hz); IR (neat) 2927, 2858, 2268, 1720, 1465 cm^{-1}; MS (CI) calcd for $C_{13}H_{20}F_3$ (M−H) 233.1517, found 233.1521.

4.5.11. 1,1,1-Trifluoro-4-ethyl-2-octyne (3k). Yield 86%; ^{1}H NMR ($CDCl_3$) δ 0.86–1.02 (6H, m), 1.22–1.61 (8H, m), 2.37–2.44 (1H, m); ^{13}C NMR ($CDCl_3$) δ 11.58, 13.87, 22.39, 26.93, 29.35, 32.93, 33.14, 69.15 (q, J=51.5 Hz), 89.8 (q, J=6.3 Hz), 114.13 (q, J=255.2 Hz); ^{19}F NMR ($CDCl_3$) δ −49.1 (3F, s); IR (neat) 2935, 2866, 2272, 1458 cm^{-1}; HRMS (CI) calcd for $C_{10}H_{14}F_3$ (M−H) 191.1048, found 191.1041.

4.5.12. 1,1,1-Trifluoro-4-cyclohexyl-2-butyne (3l). Yield 74%; ^{1}H NMR ($CDCl_3$) δ 1.01 (2H, q, J=12.00 Hz), 1.1–1.19 (1H, m), 1.26 (2H, q, J=12.50 Hz), 1.65–1.81 (6H, m), 2.18–2.21 (2H, m); ^{13}C NMR ($CDCl_3$) δ 25.78, 25.92, 32.54, 36.36, 69.18 (q, J=51.6 Hz), 88.38 (q, J=6.3 Hz), 114.18 (q, J=255.3 Hz); ^{19}F NMR ($CDCl_3$) δ −47.2 (d, J=4.4 Hz); IR (neat) 2931, 2854, 2260, 1720, 1450 cm^{-1}; MS (EI) calcd for $C_{10}H_{12}F_3$ (M−H) 189.0891, found 189.0894.

References

1. (a) Banks, R. E. *Organofluorine Chemistry: Principals and Commercial Applications*; Plenum: New York, 1994. (b) Banks, R. E. *Fluorine Chemistry at the Millenium: Fascinated by Fluorine*; Elsevier: Amsterdam, 2000; and references therein.
2. (a) Fields, R.; Hazeldine, R. N.; Hubbard, A. F. *J. Chem. Soc. C* **1971**, 3838–3843. (b) Clark, H. C.; Fiess, P. L.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 177–188. (c) Attig, T. G.; Clark, H. C.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 189–198. (d) Clark, H. S.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961–6972.
3. Bumgardner, C. L.; Bunch, J. E.; Whangbo, M.-H. *Tetrahedron Lett.* **1986**, *27*, 1883–1886.
4. Bunch, J. E.; Bumgaradner, C. L. *J. Fluorine Chem.* **1987**, *36*, 313–317.
5. Kobayashi, Y.; Yamashita, T.; Takahashi, K.; Kuroda, H.; Kumadaki, I. *Tetrahedron Lett.* **1982**, *23*, 343–344.
6. For the synthetic applications of nonfluorinated counterparts, see (a) Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257–3282. (b) Sato, F.; Urabe, H.; Okamoto, S.

Chem. Rev. **2000**, *100*, 2835–2886. (c) Yoshida, H.; Shirakawa, E.; Nakano, Y.; Honda, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn* **2001**, *74*, 637–647. (d) Shirakawa, E.; Hiyama, T. *Bull. Chem. Soc. Jpn* **2002**, *75*, 1435–1450. (e) Asao, N.; Yamamoto, Y. *Bull. Chem. Soc. Jpn* **2000**, *73*, 1071–1087.

7. Drakesmith, F. G.; Stewart, O. J.; Tarrant, P. *J. Org. Chem.* **1968**, *33*, 280–285.
8. (a) Henne, A. L.; Nager, M. *J. Am. Chem. Soc.* **1952**, *74*, 650–652. (b) Bruce, M. I.; Harbourne, A. L.; Waugh, F.; Stone, F. G. A. *J. Chem. Soc. (A)* **1968**, 356–359.
9. Yoneda, N.; Matsuoka, S.; Miyaura, N.; Fukuhara, T.; Suzuki, A. *Bull. Chem. Soc. Jpn* **1990**, *63*, 2124–2126.
10. (a) Laurent, A. J.; Le Drean, I. M.; Selmi, A. *Tetrahedron Lett.* **1991**, *32*, 3071–3074. (b) Porta, P. L.; Capuzzi, L.; Bettarini, F. *Synthesis* **1994**, 287–290. (c) Meazza, G.; Capuzzi, L.; Piccardi, P. *Synthesis* **1989**, 331–334. (d) Hiyama, T.; Sato, K.; Fujita, M. *Bull. Chem. Soc. Jpn* **1989**, *62*, 1352–1354. (e) Finnegan, W. G.; Norris, W. P. *J. Am. Chem. Soc.* **1963**, *85*, 1139–1140. (f) Brisdon, A. K.; Crossley, I. R. *Chem. Commun.* **2002**, 2420–2421.
11. Only a few reports have been published on the synthesis of perfluoroalkylated acetylenes in addition to trifluoro-methylated acetylenes. See (a) Hamper, B. C. *J. Org. Chem.* **1988**, *53*, 5558–5562. (b) Hamper, B. C. *Org. Synth.* **1991**, *70*, 246–253. (c) See Ref. 9.
12. We attempted the conventional method for the preparation of internal acetylene derivatives. Thus the reaction of trifluoromethylated lithium acetylide with benzyl bromide at −78°C or 0°C, however, no trace of the desired alkyne was detected. This may be due to less nucleophilisity of the acetylide, which is derived from an electronwithdrawing CF_3 group.
13. Yamanaka, H.; Araki, T.; Kuwabara, M.; Fukunishi, K.; Nomura, M. *Nippon Kagaku Kaishi* **1986**, 1321–1328.
14. (a) Yamazaki, T.; Mizutani, K.; Kitazume, T. *J. Org. Chem.* **1995**, *60*, 6046–6056. (b) Mizutani, K.; Yamazaki, T.; Kitazume, T. *J. Chem. Soc., Chem. Commun.* **1995**, 51–52. (c) Katritzky, A. R.; Qi, M.; Wells, A. P. *J. Fluorine Chem.* **1996**, *80*, 145–147.
15. Jennings, M. P.; Cork, E. A.; Ramachandran, P. V. *J. Org. Chem.* **2000**, *65*, 8763–8766.