Tetrahedron 64 (2008) 6500–6509

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Stereoselective synthesis of 2-iodo-1-perfluoroalkyl-2(*Z*)-alkenes and *E* or *Z*-4-perfluoroalkylmethyl-4-en-2-ynol via $Na_2S_2O_4$-promoted radical addition reaction of perfluoroalkyl iodides with allenes and the palladium-catalyzed kinetic resolution with Sonogashira coupling reaction

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ARTICLE INFO

Article history:
Received 11 February 2008
Received in revised form 13 April 2008
Accepted 15 April 2008
Available online 18 April 2008

Keywords:
Radical addition
Allenes
Perfluoroalkyl iodides
Kinetic resolution
Sonogashira coupling

ABSTRACT

A $Na_2S_2O_4$-promoted radical addition reaction of perfluoroalkyl iodides with allenes has been studied in which a *Z*/*E* mixture of 2-iodo-1-perfluoroalkyl-2-alkenes **3** were afforded in 52–69% yields. A kinetic resolution using Sonogashira coupling reaction in MeCN using Et_2NH as the base was developed to synthesize the 2-iodo-1-perfluoroalkyl-2(*Z*)-alkenes (*Z*-**3**) and *E*-4-perfluoroalkylmethylalk-4-en-2-ynols (*E*-**5**) stereoselectively. A complete Sonogashira coupling procedure in Et_2NH at 40 °C was also developed affording a mixture of *E* and *Z*-4-perfluoroalkylmethyl-4-en-2-ynols (*E*-**5** and *Z*-**5**), which may be easily separated by chromatography on silica gel.

1. Introduction

Organofluorine compounds have been receiving significant attention in medicinal chemistry, agrochemistry, and material science.[1] Because of the small size and strong electronegativity, when the fluorine atom is introduced to the molecules, the physicochemical properties and biological activities would change dramatically.[1a,b,2] Consequently, many efforts have been directed toward the development of methodologies for the preparation of organofluorine compounds. One of the most practical and convenient routes for the introduction of F-containing group to organic skeleton is the radical addition reaction of perfluoroalkyl iodides to unsaturated carbon–carbon multiple bonds. Although the addition reactions of perfluoroalkyl halides to alkenes and alkynes have been well explored,[3–5] the radical addition of perfluoroalkyl iodides of allenes using radical addition conditions has not been well established.[6] In addition, the known protocols lack the stereoselectivity usually required by modern synthetic organic chemistry. For instance, Ogawa and co-workers had developed a procedure of radical perfluoroalkylation of allenes initiated by light, in which the *E*/*Z* ratio of addition products was ranged from 63:37 to 20:80.[6a,b] In our group, we had developed a $Na_2S_2O_4$-promoted radical addition reaction, which gave the radical addition products in the *E*/*Z* ratio of 36:64–27:73.[7] Very recently, Liu and his co-workers also reported a $Na_2S_2O_4$-promoted radical iodoperfluoroalkylation reaction of 1,2-propadienyl diphenyl phosphine oxide, 1,2-propadienyl diethyl phosphonate, and ethyl 2,3-butadienoate.[6c] To find a method for the stereoselective synthesis of 2-iodo-1-perfluoroalkylalkene, the sequential $Na_2S_2O_4$-promoted radical addition reaction and the subsequent palladium-catalyzed Sonogashira coupling reaction have been investigated in our group. In this paper, we wish to report the details of these studies.

2. Results and discussion

After optimizing the conditions, we used a combination of $Na_2S_2O_4$ and $NaHCO_3$ as the radical initiator and 1,4-dioxane/H_2O (3:1) as the solvent to study the scope of the radical addition reactions between perfluoroalkyl iodides and various allenes.[7] The results were summarized in Table 1. It can be concluded that allenes containing *n*-C_4F_9I, *n*-$C_6F_{13}I$, *c*-C_6H_{11} group can readily react with either *n*-C_4F_9, *n*-C_6F_{13}, or $Cl(CF_2)_4I$ to smoothly generate the radical addition products, i.e., 2-iodo-1-perfluoroalkyl-2-alkenes **3** in 52–69% yields with *E*/*Z* ratios ranging from 27:63 to 36:64. The formation of the regioisomers **3′** is ≤3%.

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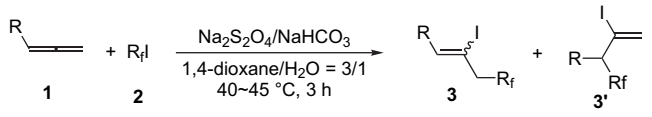
doi:10.1016/j.tet.2008.04.057

Table 1
$Na_2S_2O_4$/$NaHCO_3$-initiated radical addition of perfluoroalkyl iodides with different allenes[a]



Entry	R	R_f	Yield of **3**[b] (%)	*E*/*Z* ratio of **3**[c]	Yield of **3′**[b] (%)
1	Bn (**1a**)	*n*-C_4F_9 (**2a**)	64 (**3a**)	36:64	1 (**3a′**)
2	Bn (**1a**)	*n*-C_6F_{13} (**2b**)	55 (**3b**)	37:63	1 (**3b′**)
3	*n*-C_4H_9 (**1b**)	*n*-C_4F_9 (**2a**)	52 (**3c**)	33:67	2 (**3c′**)
4	*n*-C_5H_{11} (**1c**)	*n*-C_4F_9 (**2a**)	50 (**3d**)	30:70	2 (**3d′**)
5	*n*-C_5H_{11} (**1c**)	*n*-C_6F_{13}(**2b**)	55 (**3e**)	30:70	2 (**3e′**)
6	*n*-C_7H_{15} (**1d**)	$Cl(CF_2)_4$ (**2c**)	60 (**3f**)	27:73	3 (**3f′**)
7	*n*-C_7H_{15} (**1d**)	*n*-C_4F_9 (**2a**)	66 (**3g**)	30:70	3 (**3g′**)
8	*n*-C_7H_{15} (**1d**)	*n*-C_6F_{13} (**2b**)	61 (**3h**)	28:72	3 (**3h′**)
9	*n*-C_8H_{17} (**1e**)	*n*-C_4F_9 (**2a**)	52 (**3i**)	28:72	2 (**3i′**)
10	*c*-C_6H_{11} (**1f**)	*n*-C_4F_9 (**2a**)	61 (**3j**)	31:69	1 (**3j′**)
11	*c*-C_6H_{11} (**1f**)	*n*-C_6F_{13} (**2b**)	63 (**3k**)	30:70	1 (**3k′**)

[a] **1**/**2**/$Na_2S_2O_4$/$NaHCO_3$=1:1.5:1.5:1.5 (molar ratio).
[b] Isolated yield. The *E* and *Z* isomers could not be separated by chromatography on silica gel.
[c] Determined by ^{1}H NMR (400 MHz) analysis.

Because of the difficulty in separating the *E* and *Z* isomers, we tried to conduct a kinetic resolution via the Sonogashira coupling reaction[8] of the *Z*/*E* mixture with propargyl alcohol. In fact, it was found that the *E*-isomer is more reactive to afford the corresponding coupling product *E*-**5** while the *Z*-**3** remained. Due to the big difference of polarity of these two classes of compounds, they can be easily separated via chromatography on silica gel.

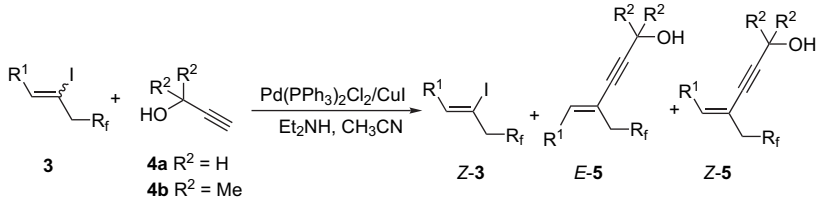
After some optimization, we defined the standard reaction conditions as conducting the reaction with a molar ratio of **3**/**4**/Et_2NH/$Pd(PPh_3)_2Cl_2$/CuI=1:0.6:0.6:0.035:0.035 in CH_3CN. A number of 2-iodo-1-perfluoroalkyl-2-alkenes were examined with monitoring by GC or NMR. These results were summarized in Table 2. Pure iodides *Z*-**3** were formed and isolated in good yields. From this table, it should be noted that the coupling products *E*-**5** may be produced smoothly while the isolated yield of *Z*-**5** was less than 4% (entries 1–5, 7–11, and 13, Table 2). When R_f contains a chlorine atom, i.e., $Cl(CF_2)_4$, the ratio of *E*-**5** and *Z*-**5** was not very good (entry 6, Table 2). When R^1=Bn, the reaction should be carried out at a higher temperature (entries 1 and 12, Table 2); When R_f is *n*-C_6F_{13}, 0.7 equiv of propargyl alcohol was used to achieve the resolution (entries 2, 5, 8, and 11, Table 2). In addition, 2-methyl-3-butyn-2-ol may also be used for this kinetic resolution procedure (entries 12 and 13, Table 2).

Subsequently, we tried to synthesize both *Z*-**5** and *E*-**5** from the radical addition products **3**. Based on the previous study of Sonogashira coupling reaction of **3** with propargyl alcohol, we further optimized the reaction conditions. Using 1.2 equiv of K_2CO_3 or Et_2NH the reaction in CH_3CN only gave a poor combined yield of the coupling product **5ga** (entries 1–3, Table 3). The reaction in Et_3N only afforded *E*-**5** and *Z*-**5** in 38% combined yield (entry 4, Table 3). However, it's fortunate to observe that when secondary amines such as (*i*-Pr)$_2$NH, piperidine, or Et_2NH is used as the solvent, the reaction is much more effective (entries 5–7, Table 3). After studying the effect of the amounts of the catalysts and the reaction temperature, finally we defined 3 mol % $Pd(PPh_3)_2Cl_2$/CuI in Et_2NH at 40 °C as the standard conditions (entry 10, Table 3). By column chromatography on silica gel, *Z*-**5** and *E*-**5** can be easily separated, thus the *Z*-**5** may also be prepared through this Sonogashira coupling reaction.

Some such typical results were summarized in Table 4. All the reactions underwent smoothly to afford the products in good yields: even with R^1=Bn, the reaction of **3a** and **3b** afforded the products *Z*/*E*-**5aa** and *Z*/*E*-**5ba** in 64% and 61% combined yields (entries 1 and 2, Table 4). In addition, when 2-methyl-3-butyn-2-ol was used in this procedure, the reaction also produced the coupling products *Z*- or *E*-**5ab**, **5gb**, **5ib**, and **5jb** smoothly in good yields (entries 11–14, Table 4).

In conclusion, we have developed a mild, good-yielding, and stereoselective method for the synthesis of *Z*-1-perfluoroalkyl-2-iodo-2-alkenes and *E*/*Z*-4-perfluoroalkylmethylalk-4-en-2-ynols. From the readily available allenes[9] and perfluoroalkyl iodides,

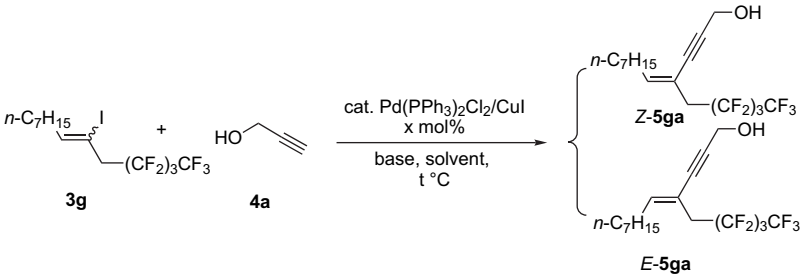
Table 2
Kinetic resolution of different 2-iodo-1-perfluoroalkyl-2-alkenes by the Pd(0)-catalyzed Sonogashira coupling reaction with propargylic alcohols[a]



Entry	R^1	R_f	R^2	Temp (°C)/time (min)	Yield of *Z*-**3**[b] (%)	Yield of *E*-**5**[b] (%)	Yield of *Z*-**5**[b] (%)
1	Bn	*n*-C_4F_9 (**3a**)	H	13/30	43 (*Z*-**3a**)	34 (*E*-**5aa**)	4 (*Z*-**5aa**)
2	Bn	*n*-C_6F_{13} (**3b**)	H[c]	0/100	42 (*Z*-**3b**)	26 (*E*-**5ba**)	2 (*Z*-**5ba**)
3	*n*-C_4H_9	*n*-C_4F_9 (**3c**)	H	0/75	49 (*Z*-**3c**)	26 (*E*-**5ca**)	3 (*Z*-**5ca**)
4	*n*-C_5H_{11}	*n*-C_4F_9 (**3d**)	H	0/60	48 (*Z*-**3d**)	23 (*E*-**5da**)	1 (*Z*-**5da**)
5	*n*-C_5H_{11}	*n*-C_6F_{13} (**3e**)	H[c]	0/120	57 (*Z*-**3e**)	29 (*E*-**5ea**)	2 (*Z*-**5ea**)
6	*n*-C_7H_{15}	$Cl(CF_2)_4$ (**3f**)	H	0/60	68 (*Z*-**3f**)	23 (*E*-**5fa**)	7 (*Z*-**5fa**)
7	*n*-C_7H_{15}	*n*-C_4F_9 (**3g**)	H	0/60	58 (*Z*-**3g**)	22 (*E*-**5ga**)	1 (*Z*-**5ga**)
8[d]	*n*-C_7H_{15}	*n*-C_6F_{13} (**3h**)	H[c]	0/150	73 (*Z*-**3h**)	19 (*E*-**5ha**)	—(*Z*-**5ha**)
9	*n*-C_8H_{17}	*n*-C_4F_9 (**3i**)	H	0/120	61 (*Z*-**3i**)	23 (*E*-**5ia**)	2 (*Z*-**5ia**)
10	*c*-C_6H_{11}	*n*-C_4F_9 (**3j**)	H	0/60	61 (*Z*-**3j**)	24 (*E*-**5ja**)	2 (*Z*-**5ja**)
11	*c*-C_6H_{11}	*n*-C_6F_{13} (**3k**)	H[c]	0/150	53 (*Z*-**3k**)	25 (*E*-**5ka**)	3 (*Z*-**5ka**)
12	Bn	*n*-C_4F_9 (**3a**)	Me[c]	10/120	35 (*Z*-**3a**)	33 (*E*-**5ab**)	7 (*Z*-**5ab**)
13	*n*-C_7H_{15}	*n*-C_4F_9 (**3g**)	Me[c]	11/80	30 (*Z*-**3g**)	29 (*E*-**5gb**)	4 (*Z*-**5gb**)

[a] **3**/**4**/Et_2NH/$Pd(PPh_3)_2Cl_2$/CuI=1:0.6:0.6:0.035:0.035 (molar ratio).
[b] Isolated yield.
[c] **3**/**4**/Et_2NH/$Pd(PPh_3)_2Cl_2$/CuI=1:0.7:0.7:0.035:0.035 (molar ratio).
[d] *Z*/*E*=97:3, which was determined by ^{1}H NMR (400 MHz) analysis.

Table 3
Optimization of the reaction conditions for the complete Sonogashira coupling reaction of 2-iodo-1-perfluoroalkyl-2-alkenes with propargyl alcohol



Entry	Base	Solvent	**4a** (equiv)	Temp (°C)	Time (h)	Cat. (*x* mol %)	Isolated yield	
							Z-**5ga** (%)	*E*-**5ga** (%)
1	K_2CO_3[a]	CH_3CN	1.2	60	24	3	12	4
2	Et_2NH[a]	CH_3CN	1.2	60	47.5	3	26	13
3	Et_2NH[b]	CH_3CN	2	60	11	3	29	14
4	Et_3N		1.2	60	28	3	23	15
5	Hexahydropyridine		1.2	60	9.5	3	48	16
6	$(i\text{-Pr})_2NH$		1.2	60	10	3	48	20
7	Et_2NH		1.2	60	10	5	49	19
8	Et_2NH		1.2	60	10.5	3	51	18
9	Et_2NH		1.2	60	22	1	46	19
10	*Et_2NH*		*1.2*	*40*	*11.5*	*3*	*53*	*21*
11	Et_2NH		1.2	40	17.5	1	46	23
12	Et_2NH		1.2	20	10	3	45	16

[a] 1.2 equiv of the base was used.
[b] 2 equiv of the base was used.

a mixture of *E* and *Z* isomers of 1-perfluoroalkyl-2-iodo-2-alkenes was formed by radical addition reaction, which may be kinetically resolved to afford *Z*-1-perfluoroalkyl-2-iodo-2-alkenes and *E*-4-perfluoroalkylmethylalk-4-en-2-ynols via the Sonogashira coupling in MeCN using Et_2NH as the base. In addition, a complete Sonogashira coupling in Et_2NH at 40 °C was realized to produce both *E*- and *Z*-4-perfluoroalkylmethylalk-4-en-2-ynols, which can be separated by chromatography on silica gel. Further studies in this area are being conducted in our laboratory.

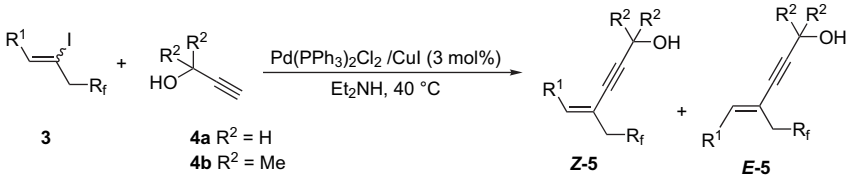
3. Experimental section

3.1. The $Na_2S_2O_4$-promoted radical addition reaction of R_fI with allenes[1]

*3.1.1. 3-Iodo-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenyl-2-octene (**3a**)*

Typical procedure. To a mixture of $Na_2S_2O_4$ (523.6 mg, 3.01 mmol), $NaHCO_3$ (253.4 mg, 3.02 mmol), and 10 mL of 1,4-dioxane were added 4-phenyl-1,2-butadiene **1a** (258.8 mg,

Table 4
Synthesis of various 4-perfluoroalkylmethyl-4-en-2-ynols by Sonogashira coupling reaction of 2-iodo-1-perfluoroalkyl-2-alkenes with propargylic alcohols[a]



Entry	R^1	R_f	R^2	Isolated yields	
				Z-**5** (%)	*E*-**5** (%)
1	Bn	$n\text{-}C_4F_9$ (**3a**)	H	44 (*Z*-**5aa**)	20 (*E*-**5aa**)
2	Bn	$n\text{-}C_6F_{13}$ (**3b**)	H	40 (*Z*-**5ba**)	21 (*E*-**5ba**)
3	$n\text{-}C_4H_9$	$n\text{-}C_4F_9$ (**3c**)	H	57 (*Z*-**5ca**)	24 (*E*-**5ca**)
4	$n\text{-}C_5H_{11}$	$n\text{-}C_4F_9$ (**3d**)	H	58 (*Z*-**5da**)	24 (*E*-**5da**)
5	$n\text{-}C_5H_{11}$	$n\text{-}C_6F_{13}$ (**3e**)	H	55 (*Z*-**5ea**)	24 (*E*-**5ea**)
6	$n\text{-}C_7H_{15}$	$n\text{-}C_4F_9$ (**3g**)	H	53 (*Z*-**5ga**)	21 (*E*-**5ga**)
7	$n\text{-}C_7H_{15}$	$n\text{-}C_6F_{13}$ (**3h**)	H	51 (*Z*-**5ha**)	34 (*E*-**5ha**)
8	$n\text{-}C_8H_{17}$	$n\text{-}C_4F_9$ (**3i**)	H	54 (*Z*-**5ia**)	24 (*E*-**5ia**)
9	$c\text{-}C_6H_{11}$	$n\text{-}C_4F_9$ (**3j**)	H	68 (*Z*-**5ja**)	25 (*E*-**5ja**)
10	$c\text{-}C_6H_{11}$	$n\text{-}C_6F_{13}$ (**3k**)	H	60 (*Z*-**5ka**)	26 (*E*-**5ka**)
11	Bn	$n\text{-}C_4F_9$ (**3a**)	Me	53 (*Z*-**5ab**)	27 (*E*-**5ab**)
12	$n\text{-}C_7H_{15}$	$n\text{-}C_4F_9$ (**3g**)	Me	58 (*Z*-**5gb**)	24 (*E*-**5gb**)
13	$n\text{-}C_8H_{17}$	$n\text{-}C_4F_9$ (**3i**)	Me	58 (*Z*-**5ib**)	19 (*E*-**5ib**)
14[b]	$c\text{-}C_6H_{11}$	$n\text{-}C_4F_9$ (**3j**)	Me	59 (*Z*-**5jb**)	28 (*E*-**5jb**)

[a] **3**/**4**=1:1.2 (molar ratio). Unless otherwise stated, the reaction was carried out at 40 °C.
[b] The reaction was carried out at 60 °C.

1.99 mmol), **2a** (1.0482 g, 3.03 mmol), 2 mL of 1,4-dioxane, and 4 mL of H_2O sequentially. The mixture was stirred at 40–45 °C for 9 h as monitored by TLC, quenched with 10 mL of brine, extracted with diethyl ether (40 mL×3), and dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel (eluent: petroleum ether) afforded a *Z*/*E* mixture of **3a** (612.7 mg, 65%, *Z*/*E*=36:64). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.28 (m, 2H), 7.28–7.20 (m, 2H), 7.20–7.14 (m, 1H), [6.84 (*E*-isomer, t, *J*=7.6 Hz, 0.36H); 6.04 (*Z*-isomer, t, *J*=6.6 Hz, 0.64H)], 3.61–3.37 (m, 4H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.2. 3-Iodo-1-phenyl-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-2-decene (**3b**)

The reaction of **1a** (262.0 mg, 2.02 mmol), **2b** (1.3529 g, 3.03 mmol), $Na_2S_2O_4$ (525.0 mg, 3.02 mmol), and $NaHCO_3$ (255.2 mg, 3.04 mmol) in 16 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 4 h afforded **3b** (651.4 mg, 56%, *E*/*Z*=37:63). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.28 (m, 2H), 7.28–7.18 (m, 2H), 7.18–7.13 (m, 1H), [6.83 (*E*-isomer, t, *J*=7.6 Hz, 0.37H); 6.03 (*Z*-isomer, t, *J*=6.8 Hz, 0.63H)], 3.60–3.36 (m, 4H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.3. 6-Iodo-8,8,9,9,10,10,11,11,11-nonafluoro-5-undecene (**3c**)

The reaction of **1b** (95.4 mg, 0.99 mmol), **2a** (515.4 mg, 1.49 mmol), $Na_2S_2O_4$ (261.4 mg, 1.50 mmol), and $NaHCO_3$ (126.0 mg, 1.50 mmol) in 8 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3c** (238.2 mg, 54%, *E*/*Z*=33:67). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.65 (*E*-isomer, t, *J*=7.8 Hz, 0.33H), 5.82 (*Z*-isomer, t, *J*=6.8 Hz, 0.67H)], 3.39 (t, J_{H-F}=17.2 Hz, 2H), [2.18 (*Z*-isomer, q, *J*=7.2 Hz, 1.34H), 2.04 (*E*-isomer, q, *J*=7.2 Hz, 0.66H)], 1.48–1.28 (m, 4H), 0.95–0.84 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.4. 6-Iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6-dodecene (**3d**)

The reaction of **1c** (111.0 mg, 1.01 mmol), **2a** (525.3 mg, 1.52 mmol), $Na_2S_2O_4$ (261.6 mg, 1.50 mmol), and $NaHCO_3$ (124.9 mg, 1.49 mmol) in 8 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3d** (237.4 mg, 52%, *E*/*Z*=30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.66 (*E*-isomer, t, *J*=7.6 Hz, 0.30H), 5.84 (*Z*-isomer, t, *J*=6.6 Hz, 0.70H)], 3.40 (t, J_{H-F}=17.6 Hz, 2H), [2.18 (*Z*-isomer, q, *J*=7.1 Hz, 1.40H), 2.05 (*E*-isomer, q, *J*=7.2 Hz, 0.60H)], 1.50–1.37 (m, 2H), 1.37–1.23 (m, 4H), 0.97–0.83 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.5. 7-Iodo-9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-7-tetradecene (**3e**)

The reaction of **1c** (223.2 mg, 2.03 mmol), **2b** (1.3711 g, 3.07 mmol), $Na_2S_2O_4$ (520.5 mg, 2.99 mmol), and $NaHCO_3$ (253.0 mg, 3.01 mmol) in 8 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3e** (643.3 mg, 57%, *E*/*Z*=30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.66 (*E*-isomer, t, *J*=7.4 Hz, 0.30H), 5.83 (*Z*-isomer, t, *J*=6.8 Hz, 0.70H)], 3.40 (t, J_{H-F}=17.4 Hz, 2H), [2.17 (*Z*-isomer, q, *J*=7.2 Hz, 1.40H), 2.04 (*E*-isomer, q, *J*=7.6 Hz, 0.60H)], 1.50–1.37 (m, 2H), 1.37–1.22 (m, 4H), 0.96–0.82 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.6. 1-Chloro-6-iodo-1,1,2,2,3,3,4,4-octafluoro-6-tetradecene (**3f**)

The reaction of **1d** (68.7 mg, 0.50 mmol), **2c** (280.0 mg, 0.77 mmol), $Na_2S_2O_4$ (130.4 mg, 0.75 mmol), and $NaHCO_3$ (64.4 mg, 0.77 mmol) in 4 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3f** (156.3 mg, 63%, *E*/*Z*=27:73). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.65 (*E*-isomer, t, *J*=7.8 Hz, 0.27H), 5.83 (*Z*-isomer, t, *J*=6.8 Hz, 0.73H)], 3.39 (t, J_{H-F}=17.6 Hz, 2H), [2.17 (*Z*-isomer, q, *J*=7.1 Hz, 1.47H), 2.04 (*E*-isomer, q, *J*=7.2 Hz, 0.53H)], 1.49–1.36 (m, 2H), 1.36–1.19 (m 8H), 0.94–0.79 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.7. 6-Iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6-tetradecene (**3g**)

The reaction of **1d** (70.0 mg, 0.51 mmol), **2a** (265.9 mg, 0.77 mmol), $Na_2S_2O_4$ (131.1 mg, 0.75 mmol), and $NaHCO_3$ (63.0 mg, 0.75 mmol) in 4 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3g** (169.8 mg, 69%, *E*/*Z*=30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.65 (*E*-isomer, t, *J*=7.6 Hz, 0.30H), 5.83 (*Z*-isomer, t, *J*=6.8 Hz, 0.70H), 3.40 (t, J_{H-F}=17.6 Hz, 2H), [2.17 (*Z*-isomer, q, *J*=7.2 Hz, 1.40H), 2.04 (*E*-isomer, q, *J*=7.3 Hz, 0.60H)], 1.49–1.36 (m, 2H), 1.36–1.20 (m, 8H), 0.94–0.82 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.8. 8-Iodo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-hexadecene (**3h**)

The reaction of **1d** (415.6 mg, 3.01 mmol), **2b** (2.0754 g, 4.65 mmol), $Na_2S_2O_4$ (786.7 mg, 4.52 mmol), and $NaHCO_3$ (376.8 mg, 4.49 mmol) in 12 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 2.5 h afforded **3h** (1.1276 g, 64%, *E*/*Z*=28:72). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.65 (*E*-isomer, t, *J*=7.8 Hz, 0.28H), 5.83 (*Z*-isomer, t, *J*=6.8 Hz, 0.72H)], 3.39 (t, J_{H-F}=17.4 Hz, 2H), [2.17 (*Z*-isomer, q, *J*=7.6 Hz, 1.45H), 2.04 (*E*-isomer, q, *J*=7.2 Hz, 0.55H)], 1.49–1.36 (m, 2H), 1.36–1.18 (m 8H), 0.93–0.82 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.9. 6-Iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6-pentadecene (**3i**)

The reaction of **1e** (152.8 mg, 1.01 mmol), **2a** (519.0 mg, 1.50 mmol), $Na_2S_2O_4$ (262.6 mg, 1.51 mmol), and $NaHCO_3$ (125.7 mg, 1.50 mmol) in 8 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3i** (269.2 mg, 54%, *E*/*Z*=28:72). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.65 (*E*-isomer, t, *J*=7.6 Hz, 0.28H), 5.82 (*Z*-isomer, t, *J*=6.8 Hz, 0.72H), 3.39 (t, J_{H-F}=17.6 Hz, 2H), [2.17 (*Z*-isomer, q, *J*=7.6 Hz, 1.44H), 2.03 (*E*-isomer, q, *J*=7.6 Hz, 0.56H)], 1.48–1.36 (m, 2H), 1.36–1.20 (m, 10H), 0.88 (t, *J*=6.8 Hz, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.1.10. 1-Cyclohexyl-2-iodo-4,4,5,5,6,6,7,7,7-nonafluoro-1-heptene (**3j**)

The reaction of **1f** (120.1 mg, 0.98 mmol), **2a** (522.2 mg, 1.51 mmol), $Na_2S_2O_4$ (262.2 mg, 1.51 mmol), and $NaHCO_3$ (128.1 mg, 1.53 mmol) in 8 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3j** (287.0 mg, 62%, *E*/*Z*=31:69). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.49 (*E*-isomer, d, *J*=10.0 Hz, 0.31H), 5.63 (*Z*-isomer, d, *J*=8.4 Hz, 0.69H)], [3.41 (*E*-isomer, t, *J*=17.8 Hz), 3.36 (*Z*-isomer, t, *J*=17.6 Hz), 2H], [2.32–2.20 (*Z*-isomer, m, 0.69H), 2.16–2.03 (*E*-isomer, m, 0.31H)], 1.80–1.58 (m, 5H), 1.40–1.03 (m, 5H). The *E*/*Z* mixture was submitted to the next step without further characterization.

3.1.11. 1-Cyclohexyl-2-iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-1-nonene (**3k**)

The reaction of **1f** (121.0 mg, 0.99 mmol), **2b** (665.4 mg, 1.49 mmol), $Na_2S_2O_4$ (260.6 mg, 1.50 mmol), and $NaHCO_3$ (128.1 mg, 1.53 mmol) in 8 mL of mixed solvent of 1,4-dioxane and H_2O (3:1 v/v) for 3 h afforded **3k** (360.1 mg, 64%, *E*/*Z*=30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.49 (*E*-isomer, d, *J*=10.0 Hz, 0.28H), 5.63 (*Z*-isomer, d, *J*=8.4 Hz, 0.72H)], [3.39 (*E*-isomer, t, *J*=17.8 Hz), 3.36 (*Z*-isomer, t, *J*=17.4 Hz), 2H], [2.30–2.19 (*Z*-isomer, m, 0.69H), 2.17–2.04 (*E*-isomer, m, 0.30H)], 1.82–1.59 (m, 5H), 1.40–1.04 (m, 5H).

The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

3.2. The kinetic resolution of 3 via Sonogashira coupling reaction

*3.2.1. Synthesis of 3-iodo-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenyl-2(Z)-octene (Z-**3a**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-6-phenylhex-4(E) or (Z)-en-2-ynol (**5aa**)*

Typical procedure. To a Schlenk tube containing a mixture of $Pd(PPh_3)_2Cl_2$ (6.2 mg, 8.84×10^{-3} mmol, 3.5 mol %) and CuI (1.7 mg, 9.47×10^{-3} mmol. 3.8 mol %) was added **3a** (118.7 mg, 0.25 mmol, *E*/*Z*=36:64) under a nitrogen atmosphere. Then a solution of Et_2NH (11.1 mg, 0.15 mmol) and **4a** (8.5 mg, 0.15 mmol) in 0.5 mL of CH_3CN was added. The resulting mixture was stirred at room temperature for 30 min as monitored by GC, quenched with 10 mL of brine, extracted with diethyl ether (25 mL×3), and dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel afforded *Z*-**3a** (eluent: petroleum ether, 50.9 mg, 43%), *Z*-**5aa** (eluent: petroleum ether/ethyl acetate=10:1, 4.0 mg, 4%), and *E*-**5aa** (eluent: petroleum ether/ethyl acetate=10:1, 33.9 mg, 34%).

*Compound Z-**3a***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J*=7.8 Hz, 2H), 7.28–7.17 (m, 3H), 6.04 (t, *J*=6.6 Hz, 1H), 3.56 (d, *J*=6.4 Hz, 2H), 3.46 (t, J_{H-F}=17.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 137.9, 128.7, 128.4, 126.7, 87.4, 45.2 (t, J_{C-F}=21.7 Hz), 43.4; MS (EI, 70 eV) *m*/*z* (%): 476 (M^+, 4.37), 91 (100); IR (neat, cm^{-1}): 1603, 1234, 1133; EA calcd for $C_{14}H_{10}F_9I$: C, 35.32; H, 2.12. Found: C, 35.13; H, 2.11.

Compound *Z*-**5aa** was fully characterized using the sample prepared in Section 3.3.1.

*Compound E-**5aa***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J*=7.4 Hz, 2H), 7.25 (t, *J*=7.8 Hz, 1H), 7.17 (d, *J*=7.2 Hz, 2H), 6.43 (t, *J*=7.2 Hz, 1H), 4.39 (s, 2H), 3.50 (d, *J*=7.6 Hz, 2H), 3.08 (t, J_{H-F}=18.4 Hz, 2H), 1.65 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 138.3, 128.8, 128.4, 126.6, 111.0, 86.3, 85.6, 51.5, 34.9, 32.3 (t, J_{C-F}=22.2 Hz); MS (EI, 70 eV) *m*/*z* (%): 404 (M^+, 1.68), 153 (100); IR (neat, cm^{-1}): 3333, 2222, 1234, 1133, 741; EA calcd for $C_{17}H_{13}F_9O$: C, 50.51; H, 3.24. Found: C, 50.20; H, 3.26.

*3.2.2. Synthesis of 3-iodo-1-phenyl-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-2(Z)-decene (Z-**3b**) and 6-phenyl-4-(2′,2′,3′,3′,4′,4′,5′,5′, 6′,6′,7′,7′,7′-tridecafluoro-heptyl)hex-4(E) or (Z)-en-2-ynol (**5ba**)*

The reaction of **3b** (173.6 mg, 0.30 mmol, *E*/*Z*=37:63), **4a** (11.9 mg, 0.21 mmol), $Pd(PPh_3)_2Cl_2$ (7.3 mg, 1.04×10^{-2} mmol, 3.5 mol %), CuI (2.0 mg, 1.05×10^{-2} mmol, 3.5 mol %), and Et_2NH (15.3 mg, 0.21 mmol) in 0.6 mL of CH_3CN for 100 min afforded *Z*-**3b** (73.3 mg, 42%), *Z*-**5ba** (3.6 mg, 2%), and *E*-**5ba** (39.7 mg, 26%).

*Compound Z-**3b***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J*=7.2 Hz, 2H), 7.27–7.14 (m, 3H), 6.02 (t, *J*=6.8 Hz, 1H), 3.54 (d, *J*=7.2 Hz, 2H), 3.44 (t, J_{H-F}=17.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 137.9, 128.7, 128.4, 126.6, 87.4, 45.2 (t, J_{C-F}=20.7 Hz), 43.4; MS (EI, 70 eV) *m*/*z* (%): 576 (M^+, 15.24), 449 (100); IR (neat, cm^{-1}): 3030, 2923, 1637, 1603, 1496, 1454, 1425, 1351, 1240, 1207, 1145, 1117, 1076, 1029; HRMS calcd for $C_{16}H_{10}F_{13}I$ (M^+): 575.9620, found: 575.9615.

Compound *Z*-**5ba** was fully characterized using the sample prepared in Section 3.3.2.

*Compound E-**5ba***. Solid, mp: 42–43 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J*=7.6 Hz, 2H), 7.24 (t, *J*=7.4 Hz, 1H), 7.17 (d, *J*=7.6 Hz, 2H), 6.42 (t, *J*=7.6 Hz, 1H), 4.38 (s, 2H), 3.49 (d, *J*=7.2 Hz, 2H), 3.07 (t, J_{H-F}=18.4 Hz, 2H), 1.65 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 138.3, 128.7, 128.3, 126.6, 111.0, 86.3, 85.6, 51.4, 34.9, 32.3 (t, J_{C-F}=20.9 Hz); MS (EI, 70 eV) *m*/*z* (%): 504 (M^+, 5.89), 153 (100); IR (KBr, cm^{-1}): 3432, 3034, 2925, 2223, 1636, 1498, 1438, 1358, 1318, 1237, 1208, 1183, 1138, 1101, 1067, 1015; EA calcd for $C_{19}H_{13}F_{13}O$: C, 45.25; H, 2.60. Found: C, 45.22; H, 2.68.

*3.2.3. Synthesis of 6-iodo-8,8,9,9,10,10,11,11,11-nonafluoro-5(Z)-undecene (Z-**3c**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-non-4(E) or (Z)-en-2-ynol (**5ca**)*

The reaction of **3c** (132.8 mg, 0.30 mmol, *E*/*Z*=33:67), **4a** (10.2 mg, 0.18 mmol), $Pd(PPh_3)_2Cl_2$ (7.4 mg, 1.06×10^{-2} mmol, 3.5 mol %), CuI (2.0 mg, 1.05×10^{-2} mmol, 3.5 mol %), and Et_2NH (13.1 mg, 0.18 mmol) in 0.6 mL of CH_3CN for 75 min afforded *Z*-**3c** (65.6 mg, 49%), *Z*-**5ca** (3.3 mg, 3%), and *E*-**5ca** (29.2 mg, 26%).

*Compound Z-**3c***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (t, *J*=6.8 Hz, 1H), 3.39 (t, J_{H-F}=17.6 Hz, 2H), 2.18 (q, *J*=6.8 Hz, 2H), 1.48–1.29 (m, 4H), 0.92 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 86.0, 45.1 (t, J_{C-F}=20.8 Hz), 36.8, 30.0, 22.2, 13.9; MS (EI, 70 eV) *m*/*z* (%): 442 (M^+, 91.59), 55 (100); IR (neat, cm^{-1}): 2962, 2934, 2863, 1638, 1467, 1425, 1346, 1236, 1135, 1098, 1023; HRMS calcd for $C_{11}H_{12}F_9I$ (M^+): 441.9840, found: 441.9836.

Compound *Z*-**5ca** was fully characterized using the sample prepared in Section 3.3.3.

*Compound E-**5ca***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.25 (t, *J*=7.6 Hz, 1H), 4.37 (s, *J*=4.8 Hz, 2H), 2.94 (t, J_{H-F}=18.0 Hz, 2H), 2.11 (q, *J*=7.2 Hz, 2H), 1.80 (br s, 1H), 1.44–1.27 (m, 4H), 0.90 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 110.0 (t, J_{C-F}=3.1 Hz), 86.7, 84.8, 51.5, 32.1 (t, J_{C-F}=22.1 Hz), 30.8, 28.6, 22.2, 13.8; MS (EI, 70 eV) *m*/*z* (%): 370 (M^+, 83.81), 313 (100); IR (neat, cm^{-1}): 3333, 2962, 2932, 2864, 2223, 1628, 1461, 1350, 1236, 1135, 1098, 1024; HRMS calcd for $C_{14}H_{15}F_9ONa$ ($M+Na^+$): 393.0871, found: 393.0873.

*3.2.4. Synthesis of 6-iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6(Z)-dodecene (Z-**3d**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-dec-4(E) or (Z)-en-2-ynol (**5da**)*

The reaction of **3d** (114.5 mg, 0.25 mmol, *E*/*Z*=30:70), **4a** (8.3 mg, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (6.2 mg, 8.84×10^{-3} mmol, 3.5 mol %), CuI (1.8 mg, 9.47×10^{-3} mmol, 3.8 mol %), and Et_2NH (11.1 mg, 0.15 mmol) in 0.5 mL of CH_3CN for 60 min afforded *Z*-**3d** (54.8 mg, 48%), *Z*-**5da** (0.5 mg, 2%), and *E*-**5da** (21.7 mg, 23%).

*Compound Z-**3d***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (t, *J*=7.0 Hz, 1H), 3.40 (t, J_{H-F}=17.6 Hz, 2H), 2.18 (q, *J*=7.1 Hz, 2H), 1.52–1.40 (m, 2H), 1.40–1.21 (m, 4H), 0.91 (t, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 86.0, 45.1 (t, J_{C-F}=21.2 Hz), 37.0, 31.2, 27.5, 22.5, 13.9; IR (neat, cm^{-1}): 2931, 1638, 1235, 1134; MS (EI, 70 eV) *m*/*z* (%): 456 (M^+, 53.66), 287 (100); HRMS calcd for $C_{12}H_{14}F_9INa$ ($M+Na^+$): 478.9889, found: 478.9881.

Compound *Z*-**5da** was fully characterized using the sample prepared in Section 3.3.4.

*Compound E-**5da***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26 (t, *J*=7.6 Hz, 1H), 4.38 (s, 2H), 2.95 (t, J_{H-F}=18.4 Hz, 2H), 2.12 (q, *J*=7.5 Hz, 2H), 1.65 (br s, 1H), 1.49–1.36 (m, 2H), 1.36–1.24 (m, 4H), 0.90 (t, *J*=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.6, 110.0, 86.7, 84.8, 51.5, 32.2 (t, J_{C-F}=22.2 Hz), 31.3, 28.9, 28.3, 22.4, 13.9; IR (neat, cm^{-1}): 3333, 2932, 2222, 1236, 1134, 1025; MS (EI, 70 eV) *m*/*z* (%): 384 (M^+, 19.21), 43 (100); EA calcd for $C_{15}H_{17}F_9O$: C, 46.88; H, 4.46. Found: C, 47.15; H, 4.58.

*3.2.5. Synthesis of 7-iodo-9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-6(Z)-tetradecene (Z-**3e**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′, 6′,6′,7′,7′,7′-tridecafluoroheptyl)-dec-4(E) or (Z)-en-2-ynol (**5ea**)*

The reaction of **3e** (139.7 mg, 0.25 mmol, *E*/*Z*=30:70), **4a** (9.7 mg, 0.173 mmol), $Pd(PPh_3)_2Cl_2$ (6.2 mg, 8.84×10^{-3} mmol, 3.5 mol %), CuI (1.8 mg, 9.47×10^{-3} mmol, 3.8 mol %), and Et_2NH (12.7 mg, 0.174 mmol) in 0.5 mL of CH_3CN for 120 min afforded *Z*-**3e** (79.5 mg, 57%), *Z*-**5ea** (2.3 mg, 2%), and *E*-**5ea** (35.3 mg, 29%).

Compound ***Z*-3e**. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 (t, *J*=6.6 Hz, 1H), 3.39 (t, J_{H-F}=17.4 Hz, 2H), 2.17 (q, *J*=7.6 Hz, 2H), 1.51–1.39 (m, 2H), 1.39–1.24 (m, 4H), 0.90 (t, *J*=6.8 Hz, 3H); ^{13}C NMR

($CDCl_3$, 100 MHz): δ 145.6, 86.1, 45.2 (t, J_{C-F}=21.7 Hz), 37.0, 31.2, 27.5, 22.5, 13.9; MS (EI, 70 eV) *m*/*z* (%): 556 (M^+, 36.75), 55 (100); IR (neat, cm^{-1}): 2961, 2932, 2861, 1639, 1469, 1426, 1350, 1239, 1207, 1145, 1122, 1099, 703; HRMS calcd for $C_{14}H_{14}F_{13}I$ (M^+): 555.9933, found: 555.9943.

Compound *Z*-**5ea** was fully characterized using the sample prepared in Section 3.3.5.

*Compound E-**5ea***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.25 (t, *J*=7.6 Hz, 1H), 4.37 (s, 2H), 2.94 (t, J_{H-F}=18.4 Hz, 2H), 2.10 (q, *J*=7.6 Hz, 2H), 1.89 (br s, 1H), 1.46–1.35 (m, 2H), 1.35–1.22 (m, 4H), 0.88 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 110.0, 86.6, 84.8, 51.4, 32.2 (t, J_{C-F}=21.9 Hz), 31.3, 28.9, 28.3, 22.4, 13.9; MS (EI, 70 eV) *m*/*z* (%): 484 (M^+, 39.17), 41 (100); IR (neat, cm^{-1}): 3316, 2962, 2933, 2863, 2223, 1459, 1358, 1240, 1205, 1145, 1121, 1099, 1024; HRMS calcd for $C_{17}H_{17}F_{13}O$ (M^+): 484.1072, found: 484.1070.

3.2.6. Synthesis of 1-chloro-6-iodo-1,1,2,2,3,3,4,4-octafluoro-6(*Z*)-tetradecene (*Z*-**3f**) and 4-(5′-chloro-2′,2′,3′,3′,4′,4′,5′,5′-octafluoropentyl)dodec-4(*E*) or (*Z*)-en-2-ynol (**5fa**)

The reaction of **3f** (207.0 mg, 0.41 mmol, *E*/*Z*=27:73), **4a** (14.0 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (10.1 mg, 1.44×10^{-2} mmol, 3.5 mol %), CuI (2.8 mg, 1.47×10^{-2} mmol, 3.6 mol %), and Et_2NH (18.1 mg, 0.25 mmol) in 0.8 mL of CH_3CN for 60 min afforded *Z*-**3f** (140.5 mg, 68%), *Z*-**5fa** (11.5 mg, 7%), and *E*-**5fa** (41.3 mg, 23%).

*Compound Z-**3f***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (t, *J*=7.0 Hz, 1H), 3.39 (t, J_{H-F}=17.6 Hz, 2H), 2.17 (q, *J*=7.1 Hz, 2H), 1.49–1.39 (m, 2H), 1.39–1.20 (m, 8H), 0.89 (t, *J*=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 86.2, 45.2 (t, J_{C-F}=21.2 Hz), 37.1, 31.8, 29.1, 29.0, 27.9, 22.6, 14.1; IR (neat, cm^{-1}): 2928, 1638, 1189, 1134; MS (EI, 70 eV) *m*/*z* (%): 502 (M^+ (^{37}Cl), 9.15), 500 (M^+ (^{35}Cl), 27.69), 43 (100); HRMS calcd for $C_{14}H_{18}^{35}ClF_8IK$ (M^++K): 538.9646, found 538.9647.

*Compound E-**5fa***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.26 (t, *J*=7.4 Hz, 1H), 4.38 (s, 2H), 2.94 (t, J_{H-F}=18.4 Hz, 2H), 2.11 (q, *J*=7.3 Hz, 2H), 1.69 (br s, 1H), 1.45–1.35 (m, 2H), 1.35–1.19 (m, 8H), 0.89 (t, *J*=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 110.0, 86.7, 84.8, 51.5, 32.2 (t, J_{C-F}=21.9 Hz), 31.7, 29.1, 29.0, 28.9, 28.7, 22.6, 14.0; IR (neat, cm^{-1}): 3331, 2929, 2222, 1190, 1133; MS (EI, 70 eV) *m*/*z* (%): 430 (M^+ (^{37}Cl), 3.77), 428 (M^+ (^{35}Cl), 11.43), 43 (100); EA calcd for $C_{17}H_{21}ClF_8O$: C, 47.62; H, 4.94. Found: C, 47.95; H, 5.13.

3.2.7. Synthesis of 6-iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6(*Z*)-tetradecene (*Z*-**3g**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)dodec-4(*E*) or (*Z*)-en-2-ynol (**5ga**)

The reaction of **3g** (125.4 mg, 0.26 mmol, *E*/*Z*=30:70), **4a** (8.7 mg, 0.16 mmol), $Pd(PPh_3)_2Cl_2$ (6.4 mg, 9.13×10^{-3} mmol, 3.5 mol %), CuI (1.7 mg, 8.95×10^{-3} mmol, 3.4 mol %), and Et_2NH (11.6 mg, 0.16 mmol) in 0.5 mL of CH_3CN for 60 min afforded *Z*-**3g** (73.0 mg, 58%), *Z*-**5ga** (1.0 mg, 1%), and *E*-**5ga** (23.5 mg, 22%).

*Compound Z-**3g***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.84 (t, *J*=6.8 Hz, 1H), 3.40 (t, J_{H-F}=17.4 Hz, 2H), 2.18 (q, *J*=7.2 Hz, 2H), 1.52–1.40 (m, 2H), 1.40–1.22 (m, 8H), 0.90 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 86.0, 45.1 (t, J_{C-F}=21.9 Hz), 37.0, 31.8, 29.1, 29.0, 27.8, 22.6, 14.1; IR (neat, cm^{-1}): 2928, 1628, 1235; MS (EI, 70 eV) *m*/*z* (%): 484 (M^+, 33.55), 43 (100); HRMS calcd for $C_{14}H_{18}F_9INa$ (M+Na^+): 507.0189, found: 507.0202.

Compound *Z*-**5ga** was fully characterized using the sample prepared in Section 3.3.6.

*Compound E-**5ga***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.26 (t, *J*=7.8 Hz, 1H), 4.38 (s, 2H), 2.95 (t, J_{H-F}=18.6 Hz, 2H), 2.11 (q, *J*=7.5 Hz, 2H), 1.59 (br s, 1H), 1.45–1.34 (m, 2H), 1.34–1.18 (m, 8H), 0.88, (t, *J*=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.6, 109.9, 86.7, 84.8, 51.5, 32.1 (t, J_{C-F}=22.2 Hz), 31.7, 29.1, 29.0, 28.9, 28.7, 22.6, 14.0; IR (neat, cm^{-1}): 3334, 2929, 2222, 1235, 1134; MS (EI, 70 eV) *m*/*z* (%): 412 (M^+, 22.13), 43 (100); EA calcd for $C_{17}H_{21}F_9O$: C, 49.52; H, 5.13. Found: C, 49.40; H, 5.11.

3.2.8. Synthesis of 8-iodo-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8(*Z*)-hexadecene (*Z*-**3h**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)dodec-4(*E*) or (*Z*)-en-2-ynol (**5ha**)

The reaction of **3h** (146.4 mg, 0.25 mmol, *E*/*Z*=28:72), **4a** (10.0 mg, 0.179 mmol), $Pd(PPh_3)_2Cl_2$ (6.2 mg, 8.84×10^{-3} mmol, 3.5 mol %), CuI (1.8 mg, 9.47×10^{-3} mmol, 3.8 mol %), and Et_2NH (13.0 mg, 0.178 mmol) in 0.5 mL of CH_3CN for 150 min afforded *Z*-**3h** (106.6 mg 73%, *Z*/*E*=97:3), and *E*-**5ha** (24.1 mg, 19%).

*Compound Z-**3h***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.83 (t, *J*=6.8 Hz, 1H), 3.39 (t, J_{H-F}=17.6 Hz, 2H), 2.17 (q, *J*=7.6 Hz, 2H), 1.51–1.39 (m, 2H), 1.39–1.20 (m, 8H), 0.89 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 86.1, 45.2 (t, J_{C-F}=20.6 Hz), 37.1, 31.8, 29.1, 29.0, 27.9, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 584 (M^+, 35.27), 401 (100); IR (neat, cm^{-1}): 2959, 2929, 2858, 1638, 1467, 1426, 1351, 1239, 1206, 1145, 1122; HRMS calcd for $C_{16}H_{18}F_{13}I$ (M^+): 584.0240, found: 584.0220.

*Compound E-**5ha***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.25 (t, *J*=7.6 Hz, 1H), 4.37 (s, 2H), 2.94 (t, J_{H-F}=18.4 Hz, 2H), 2.11 (q, *J*=7.6 Hz, 2H), 1.63 (br s, 1H), 1.48–1.35 (m, 2H), 1.35–1.17 (m, 8H), 0.88 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.6, 110.0, 86.7, 84.8, 51.5, 32.2 (t, J_{C-F}=21.8 Hz), 31.7, 29.1, 29.0, 28.9, 28.7, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 512 (M^+, 11.67), 441 (100); IR (neat, cm^{-1}): 3333, 2955, 2930, 2859, 2223, 1460, 1358, 1239, 1206, 1145, 1121, 1099, 1066, 1023; HRMS calcd for $C_{19}H_{21}F_{13}O$ (M^+): 512.1379, found: 512.1404.

3.2.9. Synthesis of 6-iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6(*Z*)-pentadecene (*Z*-**3i**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tridec-4(*E*) or (*Z*)-en-2-ynol (**5ia**)

The reaction of **3i** (149.9 mg, 0.30 mmol, *E*/*Z*=28:72), **4a** (10.0 mg, 0.179 mmol), $Pd(PPh_3)_2Cl_2$ (7.5 mg, 1.07×10^{-2} mmol, 3.6 mol %), CuI (2.1 mg, 1.11×10^{-2} mmol, 3.7 mol %), and Et_2NH (13.1 mg, 0.179 mmol) in 0.6 mL of CH_3CN for 120 min afforded *Z*-**3i** (90.8 mg, 61%), *Z*-**5ia** (2.3 mg, 2%), and *E*-**5ia** (29.5 mg, 23%).

*Compound Z-**3i***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.83 (t, *J*=6.8 Hz, 1H), 3.39 (t, J_{H-F}=17.6 Hz, 2H), 2.17 (q, *J*=7.2 Hz, 2H), 1.50–1.39 (m, 2H), 1.39–1.19 (m, 10H), 0.89 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.5, 86.0, 45.2 (t, J_{C-F}=21.4 Hz), 37.1, 31.9, 29.4, 29.2, 29.1, 27.9, 22.7, 14.1; MS (EI, 70 eV) *m*/*z* (%): 498 (M^+, 47.07), 315 (100); IR (neat, cm^{-1}): 2958, 2928, 2857, 1638, 1466, 1425, 1345, 1236, 1135, 1103, 1022; HRMS calcd for $C_{15}H_{20}F_9I$ (M^+): 498.0460, found: 498.0476.

Compound *Z*-**5ia** was fully characterized using the sample prepared in Section 3.3.8.

*Compound E-**5ia***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.25 (t, *J*=7.6 Hz, 1H), 4.37 (d, *J*=5.6 Hz, 2H), 2.94 (t, J_{H-F}=18.8 Hz, 2H), 2.11 (q, *J*=7.2 Hz, 2H), 1.67 (t, *J*=5.6 Hz, 1H), 1.46–1.35 (m, 2H), 1.35–1.18 (m, 10H), 0.88 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 110.0, 86.7, 84.9, 51.5, 32.2 (t, J_{C-F}=22.3 Hz), 31.8, 29.3, 29.19, 29.16, 28.9, 28.7, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 426 (M^+, 9.47), 341 (100); IR (neat, cm^{-1}): 3331, 2929, 2858, 2223, 1631, 1467, 1350, 1236, 1135, 1100, 1025; HRMS calcd for $C_{18}H_{23}F_9ONa$ (M+Na^+) 449.1497, found: 449.1505.

3.2.10. Synthesis of 1-cyclohexyl-2-iodo-4,4,5,5,6,6,7,7,7-nonafluoro-1(*Z*)-heptene (*Z*-**3j**) and 5-cyclohexyl-4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl) pent-4(*E*) or (*Z*)-en-2-ynol (**5ja**)

The reaction of **3j** (111.5 mg, 0.24 mmol, *E*/*Z*=31:69), **4a** (8.2 mg, 0.146 mmol), $Pd(PPh_3)_2Cl_2$ (5.9 mg, 8.42×10^{-3} mmol, 3.5 mol %), CuI (1.5 mg, 7.89×10^{-3} mmol, 3.3 mol %), and Et_2NH (10.6 mg, 0.145 mmol) in 0.5 mL of CH_3CN for 60 min afforded *Z*-**3j** (68.4 mg, 61%), *Z*-**5ja** (1.4 mg, 2%), and *E*-**5ja** (22.2 mg, 24%).

*Compound Z-**3j***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.64 (d, *J*=8.8 Hz, 1H), 3.37 (t, *J*=17.4 Hz, 2H), 2.33–2.21 (m, 1H), 1.82–1.63 (m, 5H), 1.41–1.09 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 83.4, 46.0, 45.2 (t, J_{C-F}=20.7 Hz), 31.1, 25.8, 25.4; IR (neat, cm^{-1}): 2929,

2854, 1636, 1450, 1233, 1133; MS (EI, 70 eV) *m*/*z* (%): 468 (M^+, 27.28), 82 (100); HRMS calcd for $C_{13}H_{14}F_9I$ (M^+): 467.9997, found: 467.9993.

Compound *Z*-**5ja** was fully characterized using the sample prepared in Section 3.3.9.

*Compound E-**5ja***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.09 (d, J=10.4 Hz, 1H), 4.37 (s, 2H), 2.95 (t, J=18.4 Hz, 2H), 2.22–2.09 (m, 1H), 1.81–1.56 (m, 6H), 1.35–1.03 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4, 108.0, 86.7, 84.8, 51.4, 38.2, 32.2 (t, J_{C-F}=21.8 Hz), 32.1, 25.7, 25.4; IR (neat, cm^{-1}): 3345, 2929, 2855, 2218, 1629, 1234, 1133, 1025; MS (ESI) *m*/*z*: 418.8 (M+Na^+); EA calcd for $C_{16}H_{17}F_9O$: C, 48.49; H, 4.32. Found: C, 48.64; H, 4.59.

3.2.11. Synthesis of 1-cyclohexyl-2-iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-1(Z)-nonene (Z-**3k**) and 5-cyclohexyl-4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)pent-4(E) or (Z)-en-2-ynol (**5ka**)

The reaction of **3k** (170.3 mg, 0.30 mmol, *E*/*Z*=30:70), **4a** (11.9 mg, 0.21 mmol), $Pd(PPh_3)_2Cl_2$ (7.5 mg, 1.07×10^{-2} mmol, 3.6 mol %), CuI (2.1 mg, 1.11×10^{-2} mmol, 3.7 mol %), and Et_2NH (15.2 mg, 0.21 mmol) in 0.6 mL of CH_3CN for 150 min afforded *Z*-**3k** (90.6 mg, 53%), *Z*-**5ka** (3.8 mg, 3%), and *E*-**5ka** (37.6 mg, 25%).

*Compound Z-**3k***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.63 (d, J=8.4 Hz, 1H), 3.36 (t, J_{H-F}=17.2 Hz, 2H), 2.36–2.19 (m, 1H), 1.85–1.58 (m, 5H), 1.42–1.03 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 83.5, 46.1, 45.3 (t, J_{C-F}=20.4 Hz), 31.1, 25.8, 25.5; MS (EI, 70 eV) *m*/*z* (%): 568 (M^+, 5.96), 82 (100); IR (neat, cm^{-1}): 2929, 2855, 1636, 1451, 1426, 1351, 1239, 1145, 1121, 1096, 1068, 703; HRMS calcd for $C_{15}H_{14}F_{13}I$ (M^+): 567.9933, found: 567.9936.

Compound *Z*-**5ka** was fully characterized using the sample prepared in Section 3.3.10.

*Compound E-**5ka***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.08 (d, J=10.8 Hz, 1H), 4.36 (s, 2H), 2.94 (t, J_{H-F}=18.8 Hz, 2H), 2.22–2.08 (m, 1H), 1.85–1.50 (m, 6H), 1.36–1.01 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.5, 107.9, 86.7, 84.8, 51.4, 38.3, 32.3 (t, J_{C-F}=21.7 Hz), 32.1, 25.6, 25.4; MS (EI, 70 eV) *m*/*z* (%): 496 (M^+, 19.63), 67 (100); IR (neat, cm^{-1}): 3322, 2930, 2856, 2222, 1629, 1451, 1358, 1240, 1207, 1145, 1122, 1024; HRMS calcd for $C_{18}H_{17}F_{13}O$ (M^+): 496.1072, found: 496.1073.

3.2.12. Synthesis of 3-iodo-5,5,6,6,7,7,8,8,8-nonafluoro-1-phenyl-2(Z)-octene (Z-**3a**) and 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-7-phenylhept-5(E) or (Z)-en-3-yn-2-ol (**5ab**)

The reaction of **3a** (119.5 mg, 0.25 mmol, *E*/*Z*=36:64), **4b** (14.9 mg, 0.177 mmol), $Pd(PPh_3)_2Cl_2$ (6.0 mg, 8.56×10^{-3} mmol, 3.4 mol %), CuI (1.7 mg, 8.95×10^{-3} mmol, 3.6 mol %), and Et_2NH (12.8 mg, 0.175 mmol) in 0.5 mL of CH_3CN for 120 min afforded *Z*-**3a** (42.0 mg 35%), *Z*-**5ab** (8.0 mg, 7%), and *E*-**5ab** (36.2 mg, 33%).

Compound *Z*-**5ab** was fully characterized using the sample prepared in Section 3.3.11.

*Compound E-**5ab***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J=7.2 Hz, 2H), 7.24 (t, J=7.4 Hz, 1H), 7.16 (d, J=7.6 Hz, 2H), 6.36 (t, J=7.6 Hz, 1H), 3.47 (d, J=7.2 Hz, 2H), 3.05 (t, J_{H-F}=18.4 Hz, 2H), 2.00 (br s, 1H), 1.53 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 138.4, 128.7, 128.4, 126.6, 111.0, 92.2, 82.7, 65.4, 34.9, 32.5 (t, J_{C-F}=21.9 Hz), 31.2; MS (EI, 70 eV) *m*/*z* (%): 432 (M^+, 2.66), 399 (100); IR (neat, cm^{-1}): 3381, 3031, 2984, 2934, 2222, 1604, 1496, 1455, 1349, 1236, 1133, 1098, 1028; HRMS calcd for $C_{19}H_{17}F_9ONa$ (M+Na^+): 455.1028, found: 455.1016.

3.2.13. Synthesis of 6-iodo-1,1,1,2,2,3,3,4,4-nonafluoro-6(Z)-tetradecene (Z-**3g**) and 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tridec-5(E) or (Z)-en-3-yn-2-ol (**5gb**)

The reaction of **3g** (120.9 mg, 0.25 mmol, *E*/*Z*=30:70), **4b** (14.8 mg, 0.176 mmol), $Pd(PPh_3)_2Cl_2$ (6.1 mg, 8.70×10^{-3} mmol, 3.5 mol %), CuI (1.7 mg, 8.95×10^{-3} mmol, 3.6 mol %), and Et_2NH (12.8 mg, 0.175 mmol) in 0.5 mL of CH_3CN for 80 min afforded *Z*-**3g** (36.0 mg, 30%), *Z*-**5gb** (4.2 mg, 4%), and *E*-**5gb** (32.1 mg, 29%).

Compound *Z*-**5gb** was fully characterized using the sample prepared in Section 3.3.12.

*Compound E-**5gb***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 6.19 (t, J=7.6 Hz, 1H), 2.93 (t, J_{H-F}=18.0 Hz, 2H), 2.09 (q, J=7.2 Hz, 2H), 1.98 (br s, 1H), 1.52 (s, 6H), 1.44–1.34 (m, 2H), 1.34–1.18 (m, 8H), 0.88 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 110.0, 91.5, 83.1, 65.5, 32.3 (t, J_{C-F}=21.8 Hz), 31.7, 31.3, 29.2, 29.0, 28.9, 28.7, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 440 (M^+, 4.01), 425 (100); IR (neat, cm^{-1}): 3357, 2930, 2859, 2222, 1460, 1349, 1236, 1167, 1134, 1089, 1026, 880, 741; HRMS calcd for $C_{19}H_{25}F_9ONa$ (M+Na^+): 463.1654, found: 463.1662.

3.3. Synthesis of various 4-perfluoroalkylmethyl-4-en-2-ynols by Sonogashira coupling reaction of 2-iodo-1-perfluoroalkyl-2-alkenes

3.3.1. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-6-phenylhex-4(Z)-en-2-ynol (Z-**5aa**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-6-phenylhex-4(E)-en-2-ynol (E-**5aa**)

Typical Procedure. Under nitrogen atmosphere, to a Schlenk tube containing a mixture of $Pd(PPh_3)_2Cl_2$ (6.5 mg, 9.27×10^{-3} mmol, 3.1 mol %) and CuI (1.7 mg, 8.95×10^{-3} mmol, 3.0 mol %) were added **3a** (144.1 mg, 0.30 mmol, *E*/*Z*=36:64), **4a** (21.0 mg, 0.375 mmol), and 1.2 mL of Et_2NH sequentially. This mixture was degassed using freeze–pump–thaw cycles and then was heated at 40 °C under nitrogen. After 7 h, the reaction was complete as monitored by TLC, the mixture was quenched with 10 mL of brine, diluted with 80 mL diethyl ether, washed by brine (10 mL×3), and the organic layer was dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=10:1) afforded *E*-**5aa** (53.7 mg, 44%) and *Z*-**5aa** (25.0 mg, 20%).

*Compound Z-**5aa***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J=7.4 Hz, 2H), 7.28–7.17 (m, 3H), 6.12 (t, J=7.4 Hz, 1H), 4.46 (s, 2H), 3.70 (d, J=7.2 Hz, 2H), 2.94 (t, J_{H-F}=18.4 Hz, 2H), 1.85 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.3, 138.9, 128.6, 128.4, 126.4, 111.3, 92.2, 82.8, 51.5, 37.9 (t, J_{C-F}=22.3 Hz), 37.0; MS (EI, 70 eV) *m*/*z* (%): 404 (M^+, 4.27), 153 (100); IR (neat, cm^{-1}): 3363, 3031, 2924, 2181, 1668, 1599, 1496, 1455, 1345, 1233, 1133, 1105, 1030; HRMS calcd for $C_{17}H_{13}F_9ONa$ (M+Na^+): 427.0715, found: 427.0707.

3.3.2. Synthesis of 6-phenyl-4-(2′,2′,3′,3′,4′,4′,5′,5′, 6′,6′,7′,7′,7′-tridecafluoro-heptyl)hex-4(Z)-en-2-ynol (Z-**5ba**) and 6-phenyl-4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)hex-4(E)-en-2-ynol (E-**5ba**)

The reaction of **3b** (175.1 mg, 0.30 mmol, *E*/*Z*=37:63), **4a** (20.5 mg, 0.37 mmol), $Pd(PPh_3)_2Cl_2$ (6.2 mg, 8.84×10^{-3} mmol, 2.9 mol %), and CuI (2.0 mg, 1.05×10^{-2} mmol, 3.5 mol %) in 1.2 mL of Et_2NH for 9.5 h afforded *Z*-**5ba** (61.7 mg, 40%) and *E*-**5ba** (32.3 mg, 21%).

*Compound Z-**5ba***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J=7.2 Hz, 2H), 7.27–7.17 (m, 3H), 6.11 (t, J=7.6 Hz, 1H), 4.44 (s, 2H), 3.70 (d, J=7.6 Hz, 2H), 2.94 (t, J_{H-F}=18.4 Hz, 2H), 2.30 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.2, 138.9, 128.6, 128.4, 126.4, 111.4, 92.3, 82.7, 51.3, 38.0 (t, J_{C-F}=21.7 Hz), 37.0; MS (EI, 70 eV) *m*/*z* (%): 504 (M^+, 2.52), 153 (100); IR (neat, cm^{-1}): 3329, 3031, 2924, 2222, 1603, 1496, 1453, 1430, 1351, 1238, 1205, 1145, 1036; HRMS calcd for $C_{19}H_{13}F_{13}O$ (M^+): 504.0759, found: 504.0761.

3.3.3. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)non-4(Z)-en-2-ynol (Z-**5ca**) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)non-4(E)-en-2-ynol (E-**5ca**)

The reaction of **3c** (175.1 mg, 0.40 mmol, *E*/*Z*=33:67), **4a** (27.2 mg, 0.49 mmol), $Pd(PPh_3)_2Cl_2$ (8.7 mg, 1.24×10^{-2} mmol,

3.1 mol %), and CuI (2.2 mg, 1.16×10^{-2} mmol, 2.9 mol %) in 1.6 mL of Et_2NH for 9 h afforded *Z*-**5ca** (83.9 mg, 57%) and *E*-**5ca** (35.6 mg, 24%).

*Compound Z-**5ca***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.94 (t, J=7.2 Hz, 1H), 4.42 (s, 2H), 2.86 (t, J_{H-F}=18.4 Hz, 2H), 2.33 (q, J=7.2 Hz, 2H), 2.01 (br s, 1H), 1.45–1.27 (m, 4H), 0.90 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 110.1, 91.7, 83.1, 51.5, 37.9 (t, J_{C-F}=21.9 Hz), 30.7, 30.5, 22.2, 13.8; MS (EI, 70 eV) *m*/*z* (%): 370 (M^+, 41.68), 341 (100); IR (neat, cm^{-1}): 3330, 2962, 2934, 2863, 2223, 1624, 1431, 1344, 1301, 1235, 1134, 1099, 1024; HRMS calcd for $C_{14}H_{15}F_9ONa$ ($M+Na^+$): 393.0871, found: 393.0873.

3.3.4. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)dec-4(Z)-en-2-ynol (Z-5da) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)dec-4(E)-en-2-ynol (E-5da)

The reaction of **3d** (137.3 mg, 0.30 mmol, *E*/*Z*=30:70), **4a** (20.5 mg, 0.37 mmol), $Pd(PPh_3)_2Cl_2$ (6.4 mg, 9.13×10^{-3} mmol, 3.0 mol %), and CuI (1.8 mg, 9.41×10^{-3} mmol, 3.2 mol %) in 1.2 mL of Et_2NH for 7 h afforded *Z*-**5da** (67.0 mg, 58%) and *E*-**5da** (28.0 mg, 24%).

*Compound Z-**5da***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.95 (t, J=7.2 Hz, 1H), 4.42 (s, 2H), 2.86 (t, J_{H-F}=18.0 Hz, 2H), 2.32 (q, J=6.8 Hz, 2H), 1.90 (br s, 1H), 1.48–1.36 (m, 2H), 1.36–1.20 (m, 4H), 0.89 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.8, 110.1, 91.8, 83.0, 51.5, 38.0 (t, J_{C-F}=21.4 Hz), 31.3, 30.8, 28.2, 22.4, 13.9; MS (EI, 70 eV) *m*/*z* (%): 384 (M^+, 10.25), 41 (100); IR (neat, cm^{-1}): 3319, 2961, 2932, 2861, 2224, 1460, 1432, 1344, 1235, 1134, 1100, 1025, 879, 742; HRMS calcd for $C_{15}H_{17}F_9O$ (M^+): 384.1136, found: 384.1129.

3.3.5. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)-dec-4(Z)-en-2-ynol (Z-5ea) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)-dec-4(E)-en-2-ynol (E-5ea)

The reaction of **3e** (141.5 mg, 0.25 mmol, *E*/*Z*=30:70), **4a** (16.9 mg, 0.30 mmol), $Pd(PPh_3)_2Cl_2$ (5.3 mg, 7.56×10^{-3} mmol, 3.0 mol %), and CuI (1.4 mg, 7.37×10^{-3} mmol, 2.9 mol %) in 0.5 mL of Et_2NH for 9.5 h afforded *Z*-**5ea** (67.9 mg, 55%) and *E*-**5ea** (29.5 mg, 24%).

*Compound Z-**5ea***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.94 (t, J=7.6 Hz, 1H), 4.42 (s, 2H), 2.86 (t, J_{H-F}=18.2 Hz, 2H), 2.32 (q, J=7.2 Hz, 2H), 2.01 (br s, 1H), 1.47–1.36 (m, 2H), 1.36–1.23 (m, 4H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 110.1, 91.7, 83.0, 51.4, 38.0 (t, J_{C-F}=22.1 Hz), 31.3, 30.7, 28.2, 22.4, 13.9; MS (EI, 70 eV) *m*/*z* (%): 484 (M^+, 27.00), 441 (100); IR (neat, cm^{-1}): 3320, 2961, 2933, 2862, 2224, 1632, 1461, 1432, 1350, 1316, 1240, 1206, 1145, 1121, 1100, 1067, 1032, 997; HRMS calcd for $C_{17}H_{17}F_{13}O$ (M^+): 484.1072, found: 484.1065.

3.3.6. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-dodec-4(Z)-en-2-ynol (Z-5ga) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)dodec-4(E)-en-2-ynol (E-5ga)

The reaction of **3g** (121.9 mg, 0.25 mmol, *E*/*Z*=30:70), **4a** (16.9 mg, 0.30 mmol), $Pd(PPh_3)_2Cl_2$ (5.3 mg, 7.56×10^{-3} mmol, 3.0 mol %), and CuI (1.4 mg, 7.37×10^{-3} mmol, 2.9 mol %) in 0.5 mL of Et_2NH for 7.5 h afforded *Z*-**5ga** (55.1 mg, 53%) and *E*-**5ga** (21.9 mg 21%).

*Compound Z-**5ga***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.94 (t, J=7.2 Hz, 1H), 4.42 (s, 2H), 2.86 (t, J_{H-F}=18.4 Hz, 2H), 2.32 (q, J=7.2 Hz, 2H), 1.89 (br s, 1H), 1.46–1.35 (m, 2H), 1.35–1.18 (m, 8H), 0.87 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 110.1 (t, J_{C-F}=2.8 Hz), 91.7, 83.0, 51.5, 37.9 (t, J_{C-F}=21.9 Hz), 31.7, 30.8, 29.1, 29.0, 28.6, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 412 (M^+, 2.09), 341 (100); IR (neat, cm^{-1}): 3319, 2964, 2929, 2859, 2223, 1628, 1461, 1431, 1344, 1236, 1134, 1101, 1023; HRMS calcd for $C_{17}H_{21}F_9ONa$ ($M+Na^+$): 435.1341, found: 435.1334.

3.3.7. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)dodec-4(Z)-en-2-ynol (Z-5ha) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)dodec-4(E)-en-2-ynol (E-5ha)

The reaction of **3h** (177.0 mg, 0.30 mmol, *E*/*Z*=28:72), **4a** (20.7 mg, 0.37 mmol), $Pd(PPh_3)_2Cl_2$ (6.1 mg, 8.70×10^{-3} mmol, 2.9 mol %), and CuI (1.8 mg, 9.47×10^{-3} mmol, 3.2 mol %) in 1.2 mL of Et_2NH for 11 h afforded *Z*-**5ha** (78.4 mg, 51%) and *E*-**5ha** (52.8 mg, 34%).

*Compound Z-**5ha***. Liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (t, J=7.6 Hz, 1H), 4.42 (d, J=5.6 Hz, 2H), 2.87 (t, J_{H-F}=18.4 Hz, 2H), 2.32 (q, J=7.2 Hz, 2H), 1.85 (t, J=5.6 Hz, 1H), 1.48–1.35 (m, 2H), 1.35–1.19 (m, 8H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 110.1, 91.7, 83.1, 51.5, 38.1 (t, J_{C-F}=21.4 Hz), 31.8, 30.8, 29.1, 29.0, 28.6, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 512 (M^+, 3.24), 441 (100); IR (neat, cm^{-1}): 3330, 2959, 2929, 2859, 2224, 1461, 1432, 1350, 1315, 1239, 1206, 1145, 1121, 1101, 1024; HRMS calcd for $C_{19}H_{21}F_{13}O$ (M^+): 512.1379, found: 512.1402.

3.3.8. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-tridec-4(Z)-en-2-ynol (Z-5ia) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tridec-4(E)-en-2-ynol (E-5ia)

The reaction of **3i** (149.9 mg, 0.30 mmol, *E*/*Z*=28:72), **4a** (19.9 mg, 0.36 mmol), $Pd(PPh_3)_2Cl_2$ (6.3 mg, 8.99×10^{-3} mmol, 3.0 mol %), and CuI (1.6 mg, 8.42×10^{-3} mmol, 2.8 mol %) in 1.2 mL of Et_2NH for 7.5 h afforded *Z*-**5ia** (69.4 mg, 54%) and *E*-**5ia** (30.3 mg, 24%).

*Compound Z-**5ia***. Liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 5.94 (t, J=7.6 Hz, 1H), 4.42 (s, 2H), 2.86 (t, J_{H-F}=18.0 Hz, 2H), 2.32 (q, J=7.6 Hz, 2H), 1.84 (br s, 1H), 1.47–1.35 (m, 2H), 1.35–1.17 (m, 10H), 0.87 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.9, 110.0 (t, J_{C-F}=2.7 Hz), 91.7, 83.1, 51.6, 38.0 (t, J_{C-F}=21.7 Hz), 31.8, 30.8, 29.4, 29.2, 29.1, 28.6, 22.7, 14.1; MS (EI, 70 eV) *m*/*z* (%): 426 (M^+, 0.97), 341 (100); IR (neat, cm^{-1}): 3320, 2958, 2928, 2858, 2224, 1631, 1460, 1431, 1380, 1344, 1301, 1235, 1134, 1102, 1023; HRMS calcd for $C_{18}H_{23}F_9ONa$ ($M+Na^+$) 449.1497, found: 449.1505.

3.3.9. Synthesis of 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-5-cyclohexylpent-4(Z)-en-2-ynol (Z-5ja) and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-5-cyclohexylpent-4(E)-en-2-ynol (E-5ja)

The reaction of **3j** (232.3 mg, 0.50 mmol, *E*/*Z*=31:69), **4a** (34.5 mg, 0.62 mmol), $Pd(PPh_3)_2Cl_2$ (10.8 mg, 1.54×10^{-2} mmol, 3.1 mol %), and CuI (3.0 mg, 1.58×10^{-3} mmol, 3.2 mol %) in 2 mL of Et_2NH for 6 h afforded *Z*-**5ja** (133.4 mg, 68%) and *E*-**5ja** (49.7 mg, 25%).

*Compound Z-**5ja***. Solid, mp: 36–37 °C (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 5.76 (d, J=9.6 Hz, 1H), 4.42 (s, 2H), 2.83 (t, J_{H-F}=18.0 Hz, 2H), 2.63–2.48 (m, 1H), 2.13 (br s, 1H), 1.80–1.56 (m, 5H), 1.40–1.00 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.1, 108.1 (t, J_{C-F}=2.8 Hz), 91.3, 83.0, 51.6, 39.8, 38.0 (t, J_{C-F}=22.2 Hz), 31.9, 25.8, 25.5; MS (EI, 70 eV) *m*/*z* (%): 396 (M^+, 28.85), 67 (100); IR (neat, cm^{-1}): 3317, 2929, 2854, 2222, 1450, 1344, 1301, 1234, 1133, 1091, 1032, 879, 742; EA calcd for $C_{16}H_{17}F_9O$: C, 48.49; H, 4.32. Found: C, 48.62; H, 4.48.

3.3.10. Synthesis of 5-cyclohexyl-4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)pent-4(Z)-en-2-ynol (Z-5ka) and 5-cyclohexyl-4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoroheptyl)pent-4(E)-en-2-ynol (E-5ka)

The reaction of **3k** (224.6 mg, 0.40 mmol, *E*/*Z*=30:70), **4a** (27.6 mg, 0.49 mmol), $Pd(PPh_3)_2Cl_2$ (8.6 mg, 1.23×10^{-2} mmol, 3.1 mol %), and CuI (2.4 mg, 1.26×10^{-2} mmol, 3.2 mol %) in 1.6 mL of Et_2NH for 11.5 h afforded *Z*-**5ka** (117.3 mg, 60%) and of *E*-**5ka** (50.9 mg, 26%).

*Compound Z-**5ka***. Solid, mp: 52–53 °C (hexane); ^1H NMR (400 MHz, $CDCl_3$): δ 5.76 (d, J=9.2 Hz, 1H), 4.42 (s, 2H), 2.84 (t, J_{H-F}=17.8 Hz, 2H), 2.63–2.48 (m, 1H), 2.07 (br s, 1H), 1.80–1.57 (m, 5H),

1.39–0.98 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.0, 108.2, 91.4, 83.0, 51.5, 39.8, 38.2 (t, J_{C-F}=22.4 Hz), 32.0, 25.8, 25.5; MS (EI, 70 eV) *m*/*z* (%): 496 (M^+, 90.71), 67 (100); IR (KBr, cm^{-1}): 3231, 2927, 2857, 2222, 1451, 1352, 1242, 1185, 1138, 1090, 1066, 1035; EA calcd for $C_{18}H_{17}F_{13}O$: C, 43.56; H, 3.45. Found: C, 43.75; H, 3.58.

*3.3.11. Synthesis of 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-7-phenyl-hept-5(Z)-en-3-yn-2-ol (Z-**5ab**) and 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-7-phenylhept-5(E)-en-3-yn-2-ol (E-**5ab**)*

The reaction of **3a** (189.2 mg, 0.40 mmol, *E*/*Z*=36:64), **4b** (40.3 mg, 0.48 mmol), $Pd(PPh_3)_2Cl_2$ (8.4 mg, 1.20×10^{-2} mmol, 3.0 mol %), and CuI (2.3 mg, 1.21×10^{-2} mmol, 3.0 mol %) in 1.6 mL of Et_2NH for 8 h afforded *Z*-**5ab** (90.6 mg, 53%) and *E*-**5ab** (45.6 mg, 27%).

*Compound Z-**5ab***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, *J*=7.4 Hz, 2H), 7.26–7.16 (m, 3H), 6.07 (t, *J*=7.6 Hz, 1H), 3.67 (d, *J*=7.2 Hz, 2H), 2.91 (t, J_{H-F}=17.6 Hz, 2H), 2.25 (s, 1H), 1.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5, 139.0, 128.6, 128.4, 126.4, 111.5, 99.0, 79.3, 65.6, 38.1 (t, J_{C-F}=22.2 Hz), 37.0, 31.3; MS (EI, 70 eV) *m*/*z* (%): 432 (M^+, 0.52), 399 (100); IR (neat, cm^{-1}): 3379, 3031, 2984, 2934, 2222, 1603, 1495, 1454, 1344, 1235, 1133, 1103, 1027; HRMS calcd for $C_{19}H_{17}F_9ONa$ ($M+Na^+$): 455.1028, found: 455.1024.

*3.3.12. Synthesis of 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tridec-5(Z)-en-3-yn-2-ol (Z-**5gb**) and 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tridec-5(E)-en-3-yn-2-ol (E-**5gb**)*

The reaction of **3g** (194.2 mg, 0.40 mmol, *E*/*Z*=30:70), **4b** (40.7 mg, 0.48 mmol), $Pd(PPh_3)_2Cl_2$ (8.6 mg, 1.23×10^{-2} mmol, 3.1 mol %), and CuI (2.1 mg, 1.11×10^{-2} mmol, 2.8 mol %) in 1.6 mL of Et_2NH for 7 h afforded *Z*-**5gb** (103.2 mg, 58%) and *E*-**5gb** (41.6 mg, 24%).

*Compound Z-**5gb***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (t, *J*=7.2 Hz, 1H), 2.84 (t, J_{H-F}=18.0 Hz, 2H), 2.29 (q, *J*=7.2 Hz, 2H), 2.15 (s, 1H), 1.54 (s, 6H), 1.46–1.35 (m, 2H), 1.35–1.18 (m, 8H), 0.87 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.0, 110.4, 98.5, 79.5, 65.6, 38.2 (t, J_{C-F}=20.5 Hz), 31.8, 31.3, 30.7, 29.0, 28.5, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 440 (M^+, 2.71), 341 (100); IR (neat, cm^{-1}): 3363, 2955, 2930, 2859, 2222, 1629, 1459, 1344, 1302, 1236, 1134, 1101, 1025; HRMS calcd for $C_{19}H_{25}F_9ONa$ ($M+Na^+$): 463.1654, found: 463.1659.

*3.3.13. Synthesis of 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tetradec-5(Z)-en-3-yn-2-ol (Z-**5ib**) and 2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)tetradec-5(E)-en-3-yn-2-ol (E-**5ib**)*

The reaction of **3i** (198.5 mg, 0.40 mmol, *E*/*Z*=28:72), **4b** (41.9 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (8.4 mg, 1.20×10^{-2} mmol, 3.0 mol %), and CuI (2.3 mg, 1.21×10^{-2} mmol, 3.0 mol %) in 1.6 mL of Et_2NH for 12 h afforded *Z*-**5ib** (104.7 mg, 58%) and *E*-**5ib** (33.6 mg, 19%).

*Compound Z-**5ib***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (t, *J*=7.6 Hz, 1H), 2.84 (t, J_{H-F}=18.4 Hz, 2H), 2.30 (q, *J*=7.6 Hz, 2H), 2.13 (s, 1H), 1.54 (s, 6H), 1.46–1.35 (m, 2H), 1.35–1.18 (m, 10H), 0.87 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.1, 110.3 (t, J_{C-F}=2.4 Hz), 98.5, 79.6, 65.6, 38.1 (t, J_{C-F}=21.9 Hz), 31.8, 31.3, 30.7, 29.3, 29.2, 29.1, 28.5, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 454 (M^+, 2.19), 341 (100); IR (neat, cm^{-1}): 3355, 2959, 2929, 2858, 2223, 1630, 1459, 1431, 1343, 1302, 1236, 1221, 1167, 1134, 1101, 1025; HRMS calcd for $C_{20}H_{27}F_9ONa$ ($M+Na^+$): 477.1810, found: 477.1825.

*Compound E-**5ib***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (t, *J*=7.6 Hz, 1H), 2.93 (t, J_{H-F}=18.4 Hz, 2H), 2.09 (q, *J*=7.6 Hz, 2H), 1.98 (s, 1H), 1.52 (s, 6H), 1.46–1.34 (m, 2H), 1.34–1.17 (m, 10H), 0.88 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 110.1 (t, J_{C-F}=3.3 Hz), 91.5, 83.1, 65.5, 32.4 (t, J_{C-F}=21.8 Hz), 31.8, 31.3, 29.3, 29.22, 29.17, 28.9, 28.7, 22.6, 14.0; MS (EI, 70 eV) *m*/*z* (%): 454 (M^+, 3.10), 439 (100); IR (neat, cm^{-1}): 3354, 2958, 2929, 2858, 2221, 1629, 1460, 1349, 1236, 1220, 1167, 1134, 1090, 1026, 878, 732; HRMS calcd for $C_{20}H_{27}F_9ONa$ ($M+Na^+$): 477.1810, found: 477.1816.

*3.3.14. Synthesis of 6-cyclohexyl-2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)hex-5(Z)-en-3-yn-2-ol (Z-**5jb**) and 6-cyclohexyl-2-methyl-5-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)hex-5(E)-en-3-yn-2-ol (E-**5jb**)*

The reaction of **3j** (140.8 mg, 0.30 mmol, *E*/*Z*=31:69), **4b** (30.0 mg, 0.36 mmol), $Pd(PPh_3)_2Cl_2$ (6.3 mg, 8.99×10^{-3} mmol, 3.0 mol %), and CuI (1.6 mg, 8.42×10^{-3} mmol, 2.8 mol %) in 0.6 mL of Et_2NH for 10.5 h afforded *Z*-**5jb** (75.1 mg 59%) and *E*-**5jb** (35.4 mg, 28%).

*Compound Z-**5jb***. Solid, mp: 44–45 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 (d, *J*=9.2 Hz, 1H), 2.81 (t, J_{H-F}=18.0 Hz, 2H), 2.58–2.45 (m, 1H), 2.18 (s, 1H), 1.80–1.60 (m, 5H), 1.54 (s, 6H), 1.37–1.00 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.4, 108.5 (t, J_{C-F}=2.6 Hz), 98.1, 79.5, 65.6, 39.8, 38.1 (t, J_{C-F}=21.9 Hz), 31.9, 31.2, 25.8, 25.6; MS (EI, 70 eV) *m*/*z* (%): 424 (M^+, 7.15), 381 (100); IR (neat, cm^{-1}): 3390, 2983, 2931, 2855, 2222, 1633, 1451, 1345, 1236, 1167, 1134, 1089, 1027; HRMS calcd for $C_{18}H_{21}F_9ONa$ ($M+Na^+$): 447.1341, found: 447.1340.

*Compound E-**5jb***. Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (d, *J*=10.8 Hz, 1H), 2.93 (t, J_{H-F}=18.4 Hz, 2H), 2.20–2.08 (m, 1H), 1.96 (s, 1H), 1.80–1.55 (m, 5H), 1.52 (s, 6H), 1.38–1.02 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.5, 108.0 (t, J_{C-F}=3.5 Hz), 91.4, 83.1, 65.5, 38.2, 32.4 (t, J_{C-F}=22.8 Hz), 32.1, 31.2, 25.6, 25.4; MS (EI, 70 eV) *m*/*z* (%): 424 (M^+, 6.28), 43 (100); IR (neat, cm^{-1}): 3353, 2983, 2930, 2855, 2222, 1451, 1350, 1234, 1166, 1135, 1079, 1026, 879, 733; HRMS calcd for $C_{18}H_{21}F_9O$ (M^+): 424.1449, found: 424.1452.

Acknowledgements

Financial support from the National Natural Science Foundation of China (20672094) and Major State Basic Research and Development Program (2006CB806105) is greatly appreciated. S.M. is a Qiu Shi Adjunct Professor at Zhejiang University. We thank Mr. Wangqing Kong in this group for reproducing the results presented in entry 1 of Table 1, entry 1 of Table 2, and entries 12 and 14 of Table 4.

Supplementary data

Copies of ^{1}H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.04.057.

References and notes

1. For books and reviews, see: (a) Kirsch, P. *Modern Fluoroorganic Chemistry*, 1st ed.; Wiley-VCH: Weinheim, Germany, 2004; (b) Wilkinson, J. A. *Chem. Rev.* **1992**, *92*, 505; (c) Ma, J.-A.; Cahard, D. *Chem. Rev.* **2004**, *104*, 6119.
2. (a) Iseki, K. *Tetrahedron* **1998**, *54*, 13887; (b) Resnati, G. *Tetrahedron* **1993**, *49*, 9385; (c) Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 214.
3. For reviews, see: (a) Huang, W.-Y. *J. Fluorine Chem.* **1992**, *58*, 1; (b) Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557; (c) Brace, N. O. *J. Fluorine Chem.* **1999**, *93*, 1; (d) Brace, N. O. *J. Fluorine Chem.* **1999**, *96*, 101; (e) Brace, N. O. *J. Fluorine Chem.* **2001**, *108*, 147.
4. For some selected reports of addition reactions of perfluoroalkyl halides to alkenes, see: (a) Lu, X.; Ma, S.; Zhu, J. *Tetrahedron Lett.* **1988**, *29*, 5129; (b) Napoli, M.; Gambaretto, G. P. *J. Fluorine Chem.* **1997**, *84*, 101; (c) Bravo, A.; Bjørsvik, H.-R.; Fontana, F.; Liguori, L.; Mele, A.; Minisci, F. *J. Org. Chem.* **1997**, *62*, 7128; (d) Guo, X.-C.; Chen, Q.-Y. *J. Fluorine Chem.* **1998**, *88*, 63; (e) Wu, F.-H.; Huang, W.-Y. *J. Fluorine Chem.* **1998**, *92*, 85; (f) Guo, X.-C.; Chen, Q.-Y. *J. Fluorine Chem.* **1999**, *93*, 81; (g) Long, Z.-Y.; Chen, Q.-Y. *J. Org. Chem.* **1999**, *64*, 4775; (h) Yoshida, M.; Ohkoshi, M.; Aoki, N.; Ohnuma, Y.; Iyoda, M. *Tetrahedron Lett.* **1999**, *40*, 5731; (i) Uneyama, K. *J. Organomet. Chem.* **2000**, *611*, 158; (j) Huang, X.-T.; Chen, Q.-Y. *J. Org. Chem.* **2001**, *66*, 4651; (k) Vincent, J.-M.;

Rabion, A.; Yachandra, V. K.; Fish, R. H. *Can. J. Chem.* **2001**, *79*, 888; (l) Zou, X. W.; Wu, F. H. *Chin. Chem. Lett.* **2002**, *13*, 410; (m) Brace, N. O. *J. Fluorine Chem.* **2003**, *123*, 237; (n) Zou, X.; Wu, F.; Shen, Y.; Xu, S.; Huang, W. *Tetrahedron* **2003**, *59*, 2555; (o) Blaauw, R. H.; Ijzendoorn, D. R.; Cremers, J. G. O.; Rutjes, F. P. J. T.; Broxterman, Q. B.; Schoemaker, H. E. *Chimia* **2004**, *58*, 104; (p) Wu, K.; Chen, Q.-Y. *Chin. J. Chem.* **2004**, *22*, 371; (q) Antonietti, F.; Mele, A.; Minisci, F.; Punta, C.; Recupero, F.; Fontana, F. *J. Fluorine Chem.* **2004**, *125*, 205; (r) Yang, Z.-Y. *J. Org. Chem.* **2004**, *69*, 2394; (s) Sun, J.-Y.; Li, J.; Qiu, X.-L.; Qing, F.-L. *J. Fluorine Chem.* **2005**, *126*, 1425; (t) Delon, L.; Laurent, P.; Blancou, H. *J. Fluorine Chem.* **2005**, *126*, 1487; (u) Tsuchii, K.; Ueta, Y.; Kamada, N.; Einaga, Y.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2005**, *46*, 7275; (v) Wu, F.-H.; Gu, S.; Huang, W.-Y. *Chin. J. Org. Chem.* **2006**, *26*, 671; (w) Yajima, T.; Nagano, H. *Org. Lett.* **2007**, *9*, 2513.

5. For some selected reports on radical addition reactions of perfluoroalkyl halides to alkynes, see Refs. 4g, 4i, 4j, and 4u. See also: (a) Ma, S.; Lu, X. *Tetrahedron* **1990**, *29*, 357; (b) Guan, H.-P.; Tang, X.-Q.; Luo, B.-H.; Hu, C.-M. *Synthesis* **1997**, 1489; (c) Jennings, M. P.; Cork, E. A.; Ramachandran, P. V. *J. Org. Chem.* **2000**, *65*, 8763; (d) Motoda, D.; Kinoshita, H.; Shinokubo, H.; Oshima, K. *Adv. Synth. Catal.* **2002**, *344*, 261; (e) Konno, T.; Chae, J.; Kanda, M.; Nagai, G.; Tamura, K.; Ishihara, T.; Yamanaka, H. *Tetrahedron* **2003**, *59*, 7571; (f) Tsuchii, K.; Ogawa, A. *Tetrahedron Lett.* **2003**, *44*, 8777; (g) Tewari, A.; Hein, M.; Zapf, A.; Beller, M. *Tetrahedron Lett.* **2004**, *45*, 7703.
6. (a) Ogawa, A.; Imura, M.; Kamada, N.; Hirao, T. *Tetrahedron Lett.* **2001**, *42*, 2489; (b) Tsuchii, K.; Imura, M.; Kamada, N.; Hirao, T.; Ogawa, A. *J. Org. Chem.* **2004**, *69*, 6658; (c) Mei, Y.-Q.; Liu, J.-T.; Liu, Z.-J. *Synthesis* **2007**, 739.
7. Ma, S.; Ma, Z. *Synlett* **2006**, 1263.
8. (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467; (b) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874; (c) Doucet, H.; Hierso, J.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 834.
9. (a) Serratosa, F. *Tetrahedron Lett.* **1964**, *5*, 895; (b) Brandsma, L.; Arens, J. F. *Recl. Trav. Chim.* **1967**, *86*, 734; (c) Taherirastgar, F.; Brandsma, L. *Synth. Commun.* **1997**, *27*, 4035.