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Studies on the radical addition reaction of perfluoroalkyl iodides with 2,3-allenols and the Pd-catalyzed kinetic resolution via Sonogashira coupling reaction

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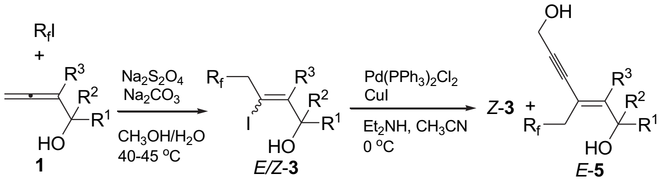
ABSTRACT

A radical addition reaction promoted by $Na_2S_2O_4$ of perfluoroalkyl iodides with 2,3-allenols affording *E*/*Z* mixtures of 3-iodo-4-perfluoroalkyl-substituted allylic alcohols has been studied. Kinetic resolution with Sonogashira coupling reaction was applied to afford the *Z* isomer of 3-iodo-4-perfluoroalkyl-substituted allylic alcohol (*Z*-**3**) and the *E* isomer of conjugated enynic diols (*E*-**5**) in 39–52% and 22–40% yields, respectively.

1. Introduction

In the last couple of years, allenes have become a very important class of compounds in organic chemistry. More and more selective synthetic methodologies have been developed based on the high reactivity of the allene derivatives.[1,2] Compared with the transition metal-catalyzed[1,2b–d,f,g,i–l] or electrophilic reactions,[3,4] the radical addition reactions of allenes have not been well-established.[5,6] Recently, we reported the $Na_2S_2O_4$-promoted radical addition reaction of simple allenes with perfluoroalkyl iodides affording perfluoroalkyl group substituted vinyl iodides. In addition, we also developed a simple kinetic resolution by applying the palladium-catalyzed Sonogashira coupling to afford 2-iodo-1-perfluoroalkyl-2(*Z*)-alkenes and 4-perfluoroalkylmethyl-4(*E*)-en-2-ynols, stereoselectively.[7a,b] However, this reaction could not be extended to allenes with functional groups. In this paper we wish to report the radical addition reaction of 2,3-allenols[4u,8,9] with perfluoroalkyl iodides in aqueous MeOH and the related kinetic resolution (Scheme 1).



Scheme 1.

2. Results and discussion

Based on the previous results of the radical addition reaction of perfluoroalkyl iodide to the simple allenes,[7a,b] we studied the addition reaction of 2,3-allenol **1a** and n-C_4F_9I **2a** using $Na_2S_2O_4$/$NaHCO_3$ as the initiator in 1,4-dioxane/H_2O, affording the expected product[10] **3a** in 34% yield only (entry 1, Table 1). We then started to optimize the reaction conditions by studying the base effect. Organic base, such as (i-Pr)$_2$NH or Et_3N, afforded **3a** in 17% or 28% yield only with 12% of **1a** being recovered (entries 2 and 3, Table 1), respectively, and Cy_2NH led to a complicated reaction (entry 11, Table 1). Then some of the inorganic bases were screened: With Na_2CO_3, K_2CO_3, or NaOH, the reaction afforded the product **3a** in higher yields (entries 5, 6, and 9, Table 1). The reaction in benzene, toluene, hexane or ethyl acetate failed to afford the radical addition product **3a** (entries 1–4, Table 2). When DMSO was used, a mixture of **3a**, **1a**, and some unknown products were obtained after flash chromatography on silica gel (entry 5, Table 2). DMF and DMA gave low yields of **3a** (entries 6 and 7, Table 2). The reaction in CH_3CN, pyridine, or acetone is encouraging giving **3a** in 30–36% yields (entries 8–10, Table 2). Further study led to the observation that EtOH can be used as the solvent (entry 11, Table 2), then some of alcohols were screened (entries 11–14, Table 2): MeOH gave the best result with 1.4% of **1a** being recovered (entry 14, Table 2). After raising the concentration of the reaction mixture to 0.4 M, all of the starting material was converted completely and **3a** was afforded in 44% yield (entry 15, Table 2). Further adjusting on the ratio of organic solvents and water could not improve the yield (entries 17 and 18, Table 2). After raising the reaction temperature to 40–45 °C, the yield of **3a** was improved to 48% (entry

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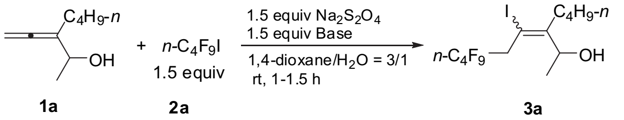
Table 1
The base effect of the radical addition reaction of **1a** with **2a** promoted by $Na_2S_2O_4$



Entry	Base	Isolated yield of **3a** (%)	*E*/*Z* ratio of **3a**
1[a]	$NaHCO_3$	34	80/20
2[b]	$(i\text{-Pr})_2NH$	17	81/19
3[b]	Et_3N	28[c]	75/25
4	Li_2CO_3	29	80/20
5	$\mathbf{Na_2CO_3}$	**39**	**80/20**
6	K_2CO_3	39	77/23
7	Cs_2CO_3	32	80/20
8	Na_3PO_4	35	80/20
9	NaOH	39	79/21
10	KOH	28	76/24
11	Cy_2NH	—[c,d]	—

The significance of the bold values is that Na_2CO_3 gives the best effect.

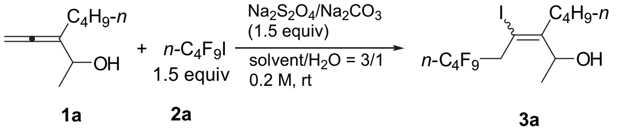
[a] Compound **1a** (0.3 mmol), **2a** (0.2 mmol), $Na_2S_2O_4$ (0.2 mmol), and $NaHCO_3$ (0.2 mmol) were used.

[b] Compound **1a** (12%) was recovered.

[c] The NMR yield was given.

[d] The yield was not able to determine.

Table 2
The solvent effect of the radical addition reaction of **1a** with **2a** promoted by $Na_2S_2O_4$



Entry	Solvent	Isolated yield of **3a** (%)	The *E*/*Z* ratio of **3a**
1	Benzene	NR	—
2	Toluene	NR	—
3	Hexane	NR	—
4	Ethyl acetate	NR	—
5	DMSO	—[a]	—
6	DMF	20	82/18
7	DMA	16	84/16
8	CH_3CN	30	79/21
9	Py	36	80/20
10	Acetone	34	82/18
11	EtOH	32	79/21
12	Glycol	Trace	—
13	*i*-Butanol	NR	—
14[b]	MeOH	46	80/20
15[c]	MeOH	44	78/22
16[d]	MeOH	27	79/21
17	MeOH[e]	35[b]	81/19
18	MeOH[f]	42[g]	78/22
19	**MeOH**[h]	**48**	**75/25**
20	*i*-PrOH[h]	5[i,j]	—

[a] A mixture of **3a**, **1a**, and some unknown products was obtained after flash chromatography.

[b] Compound **1a** (1.4%) was recovered.

[c] The concentration of the substrate was 0.4 M.

[d] The concentration of the substrate was 0.1 M, and 3% of **1a** was recovered.

[e] The ratio of $MeOH/H_2O$ was 2/1.

[f] The ratio of $MeOH/H_2O$ was 4/1.

[g] Compound **1a** (2.5%) was recovered.

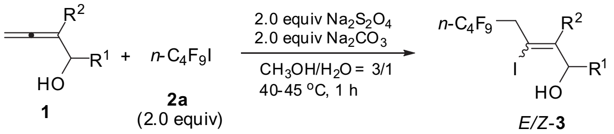
[h] The reaction temperature was 40–45 °C, 2.0 equiv of **2a** were used.

[i] Compound **1a** (45%) was recovered.

[j] NMR yield.

19, Table 2). Thus, this condition was defined as the standard for further study.

Table 3
The radical addition reaction of perfluoroalkyl iodide with 2-substituted 2,3-allenols **1a**–**c** and **1m**

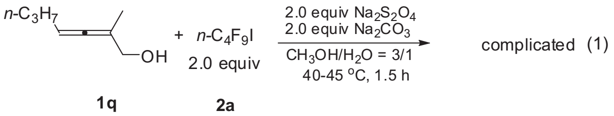


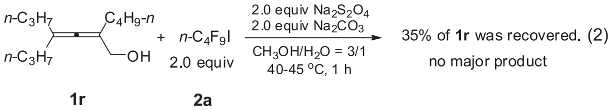
Entry	**1**		Isolated yield of **3** (%)	Ratio of *E*/*Z* isomer
	R^1	R^2		
1	CH_3	$n\text{-}C_4H_9$ (**1a**)	48 (**3a**)	75/25
2	$n\text{-}C_6H_{13}$	$n\text{-}C_4H_9$ (**1b**)	40 (**3b**)	68/32
3	Ph	$n\text{-}C_4H_9$ (**1c**)	43 (**3c**)	75/25
4	H	$n\text{-}C_4H_9$ (**1m**)	34 (**3p**)	76/24

Some of the allenols with substituents on the α and β positions **1a**, **1b**, **1c**, and **1m** were then examined (Table 3). The reaction afforded the corresponding products in 34–48% yields with the *E*/*Z* ratio ranging from 68/32 to 76/24. The reaction of allenol **1m** with R^1 being H afforded the product in 34% yield with the *E*/*Z* ratio being 76/24. The *E* and *Z* isomers could not be separated from each other by flash chromatography on silica gel.

The yields are not ideal, thus, we reasoned that the substituent group (R^2) may affect the radical addition. Thus, the reaction of 1-phenyl-2,3-butadienol **1d** was studied (Table 4). Under the standard reaction conditions, we were happy to observe that *E*-**3d** and *Z*-**3d** were afforded in 31% and 35% yields, respectively. It should be noted that the *E* and *Z* isomers of **3d** may be separated by careful flash chromatography on silica gel. The configuration of the two isomers was determined by NOESY analysis (Fig. 1).

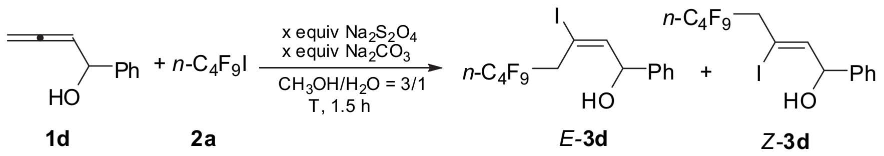
We then studied the scope of the radical addition reaction of perfluoroalkyl iodides with 2-unsubstituted 2,3-allenols (Table 5). The reaction is very general: When R^2 group is H (entries 1–12, Table 5), R^1 group may be phenyl (entry 1, Table 5), substituted phenyl (entries 2 and 3, Table 5), alkyl (entries 4–6, 8–12, Table 5), and benzyl group (entry 7, Table 5); R_f group can be $n\text{-}C_4F_9$ (entries 1–9, Table 5) or $n\text{-}C_6F_{13}$ group (entries 10–12, Table 5). The yields of the reaction are between 60–83%, and the ratio of *E*/*Z* isomers ranged from 36/64 to 46/54. When R^1 is an alkyl group, the stereoselectivity is slightly higher than that of the substituent with an aryl group. When tertiary 2,3-allenol **1k** or **1l** was used, the products can also be afforded in 62% and 65% yields, respectively. It is interesting to observe that the stereoselectivity increases with the ratio of *E*/*Z* being 91/9 and 90/10 (entries 13 and 15, Table 5). In these cases, the two stereoisomers can be easily separated by flash chromatography because of the remarkable difference of their polarity. The configurations of *E*-**3o** and *Z*-**3o** were also established by the NOESY analysis (Fig. 1). When the allenol **1p** was used, the corresponding product *E*-**3s** can be afforded in 49% isolated yield, but *Z*-**3s** could not be isolated in pure form (entry 14, Table 5). The higher selectivity observed in the reaction of tertiary 2,3-allenol could be explained by the steric hindrance effect.





Regretfully, the tri- or tetra-substituted allenols **1q** or **1r** failed to afford the corresponding products (Eqs. 1 and 2).

Table 4
The condition optimization of radical addition reaction of **1d** with n-C_4F_9I



Entry	x	n-C_4F_9I (equiv)	T (°C)	Conc	Isolated yield (%)	
					E-**3d**	E-**3d**
1[a]	1.5	1.5	rt	0.2 M	23	27
2[b]	2.0	2.0	rt	0.4 M	33	31
3	2.0	2.0	40–45	0.4 M	31	35
4	2.5	2.5	40–45	0.4 M	29	31

[a] Compound **1d** (11%) was recovered.
[b] Compound **1d** (1.4%) was recovered.

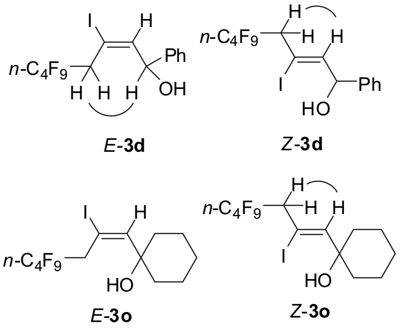
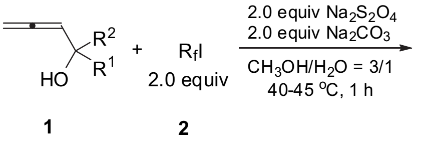


Fig. 1. The NOESY spectrum analysis of E/Z-**3d** and E/Z-**3o**.

Table 5
The radical addition reaction of perfluoroalkyl iodide with the 2-unsubstituted 2,3-allenols



Entry	**1**		**2**	Isolated yield of E/Z-**3** (%)	Ratio of E/Z isomer
	R^1	R^2	R_f		
1[a]	Ph	H (**1d**)	n-C_4F_9 (**2a**)	69 (**3d**)	46/54
2	4-$CH_3C_6H_4$	H (**1e**)	n-C_4F_9 (**2a**)	61 (**3e**)	41/59
3	4-FC_6H_4	H (**1f**)	n-C_4F_9 (**2a**)	69 (**3f**)	44/56
4	n-C_4H_9	H (**1g**)	n-C_4F_9 (**2a**)	77 (**3g**)	38/62
5	n-C_5H_{11}	H (**1h**)	n-C_4F_9 (**2a**)	68 (**3h**)	39/61
6	n-C_6H_{13}	H (**1i**)	n-C_4F_9 (**2a**)	60 (**3i**)	37/63
7	Bn	H (**1j**)	n-C_4F_9 (**2a**)	60 (**3j**)	43/57
8	i-C_3H_7	H (**1n**)	n-C_4F_9 (**2a**)	67 (**3q**)	40/60
9	t-C_4H_9	H (**1o**)	n-C_4F_9 (**2a**)	83 (**3r**)	37/63
10	n-C_4H_9	H (**1g**)	n-C_6F_{13} (**2b**)	73 (**3k**)	38/62
11	n-C_5H_{11}	H (**1h**)	n-C_6F_{13} (**2b**)	61 (**3l**)	37/63
12	n-C_6H_{13}	H (**1i**)	n-C_6F_{13} (**2b**)	83 (**3m**)	36/64
13	Ph	CH_3 (**1k**)	n-C_4F_9 (**2a**)	56 (E); 6 (Z) (**3n**)	91/9
14	n-C_4H_9	n-C_4H_9 (**1p**)	n-C_4F_9 (**2a**)	49 (E) (**3s**)[b]	87/13[c]
15	$-(CH_2)_5-$ (**1l**)		n-C_4F_9 (**2a**)	59 (E); 6 (Z) (**3o**)	90/10

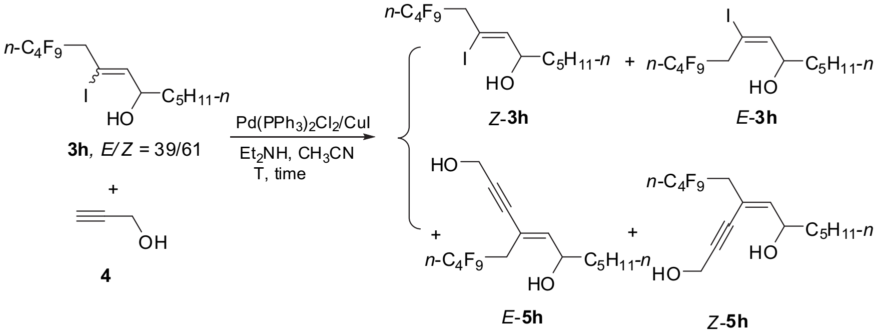
[a] The time was 50 min.
[b] The Z-**3s** could not be isolated in pure form.
[c] The E/Z ratio was determined by ^1H NMR of the crude product.

Due to the difficulty of separating most of E-**3** and Z-**3**, the kinetic resolution developed previously in our group was applied for these addition products.[7] The 10,10,11,11,12,12,13,13,13-nonafluoro-8-iodo-7-tridecen-6-ol **3h** was used as the model substrate to optimize the conditions (Table 6). Under the catalysis of $Pd(PPh_3)_2Cl_2$ and CuI with Et_2NH as the base, E-**3h** can undergo Sonogashira coupling reaction with propargyl alcohol **4** smoothly while Z-**3h** was mostly unreacted[11]. So we adjusted the reaction temperature, the amounts of **4** and the catalyst to control the end of the resolution: finally, it was observed that the reaction with 0.7 equiv of **4** under the catalysis of 5 mol % of $Pd(PPh_3)_2Cl_2$ and CuI at 0 °C is the best conditions for this kinetic resolution, affording Z-**3h** and E-**5h** in 46% and 25% isolated yields, respectively. NMR yields of both E-**3h** and Z-**5h** were less than 3% (entry 4, Table 6).

We then demonstrated the scope of this protocol with some of the typical results being summarized in Table 7. Many different radical addition products, 3-perfluoroalkylmethyl-3-iodo allylic alcohol E/Z-**3**, were submitted to the optimized conditions. It should be noted that the R group may be aryl (entries 1 and 2, Table 7), alkyl (entries 3 and 5–7, Table 7), or Bn group (entry 4, Table 7), and the R_f group may be n-C_4F_9 (entries 1–4, Table 7) or n-C_6F_{13} group (entries 5–7, Table 7) to have a clean and efficient kinetic resolution to afford Z-**3** in 39–52%

Table 6

The condition optimization for kinetic resolution of the 10,10,11,11,12,12,13,13,13-nonafluoro-8-iodo-7-tridecen-6-ol **3h** with propargyl alcohol **4** via palladium-catalyzed Sonogashira coupling reaction

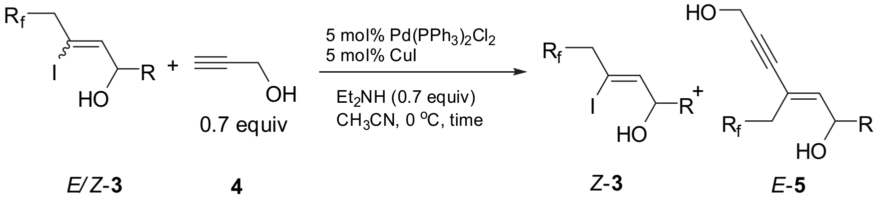


Entry	Catalyst (mol %)	T (°C)	**4** or Et_2NH (equiv)	Time (min)	NMR yield (%)[a]			
					Z-**3h**	*E*-**3h**	*E*-**5h**	*Z*-**5h**
1	2	31	0.6	960	45	6	20	5
2	2	32	0.7	60	40	—	29	13
3	3	0	0.7	140	(55)	(10)	(22)	—
4	5	0	0.7	70	49 (46)	1	28 (25)	3

[a] The numbers in the parenthesis are isolated yields.

Table 7

The kinetic resolution of *E*/*Z*-**3** via the palladium-catalyzed Sonogashira coupling reaction



Entry	R	R_f	Time (min)	Isolated yield of *Z*-**3**	Isolated yield of *E*-**5**
1[a]	Ph	n-C_4F_9 (**3d**)	55	48 (*Z*-**3d**)	40 (*E*-**5d**)
2[a]	p-MeC_6H_4	n-C_4F_9 (**3e**)	45	45 (*Z*-**3e**)	30 (*E*-**5e**)
3	n-C_4H_9	n-C_4F_9 (**3g**)	50	45 (*Z*-**3g**)	29 (*E*-**5g**)
4	Bn	n-C_4F_9 (**3j**)	70	39 (*Z*-**3j**)	39 (*E*-**5j**)
5	n-C_4H_9	n-C_6F_{13} (**3k**)	75	49 (*Z*-**3k**)	27 (*E*-**5k**)
6	n-C_5H_{11}	n-C_6F_{13} (**3l**)	55	49 (*Z*-**3l**)	23 (*E*-**5l**)
7	n-C_6H_{13}	n-C_6F_{13} (**3m**)	45	52 (*Z*-**3m**)	22 (*E*-**5m**)

[a] Compound **4** (0.9 equiv) and Et_2NH were used.

recoveries and *E*-**5** in 22–40% yields. The yields of *E*-**3** and *Z*-**5** are less than 3%.

3. Conclusions

In summary, we have developed a mild radical addition reaction of perfluoroalkyl iodide with 2,3-allenols and the subsequent kinetic resolution to afford *Z* isomer of perfluoroalkyl-substituted allylic alcohols and *E* isomer of perfluoroalkylmethyl-substituted conjugated enynic diols stereoselectively. Further studies in this area are being conducted in our laboratory.

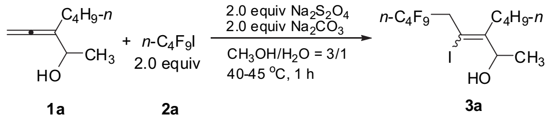
4. Experimental

4.1. General

Chemicals and solvents were all purchased from commercial suppliers and used without further purification. All the radical addition reactions were carried out under an air atmosphere while all the kinetical resolution reactions were carried out under the nitrogen atmosphere in dried glassware. ^1H NMR spectra were recorded on a Bruker-300 or 400 MHz spectrometer, ^{13}C NMR spectra were recorded at 75 or 100 MHz. Chemical shifts (δ) are given in parts per million (ppm) downfield relative to $CDCl_3$. Coupling constants are given in hertz (Hz). Unless otherwise, stated deuterochloroform was used as solvent. In assignment of the ^1H NMR spectra, multiplicities and abbreviations used are as follows: d=doublet, dd=doublet of doublets, m=multiplet, q=quartet, s=singlet, t=triplet.

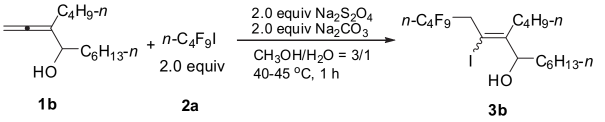
4.2. The $Na_2S_2O_4$-promoted radical addition reaction of R_fI with 2,3-allenols and the corresponding kinetic resolution

*4.2.1. Synthesis of 3-(n-butyl)-6,6,7,7,8,8,9,9,9-nonafluoro-4-iodo-3-nonen-2-ol (**3a**).*



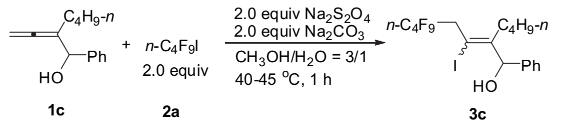
4.2.1.1. Typical procedure 1. To a mixture of $Na_2S_2O_4$ (0.2801 g, 1.61 mmol), Na_2CO_3 (0.1708 g, 1.61 mmol), and 1.0 mL of CH_3OH were added 3-(*n*-butyl)-3,4-butadien-2-ol **1a** (0.1115 g, 0.80 mmol), 0.5 mL of CH_3OH, *n*-C_4F_9I **2a** (0.5551 g, 1.60 mmol), and 0.5 mL of H_2O with stirring sequentially. The mixture was stirred at 40–45 °C for 1 h as monitored by TLC, quenched with 10 mL of brine, extracted with diethyl ether (25 mL×3), and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=20/1) afforded a *E*/*Z* mixture of **3a** (0.1876 g, 48%, *E*/*Z*=75/25): ^1H NMR (300 MHz, $CDCl_3$): δ 4.88–4.72 (m, 1H), 3.90–3.38 (m, 2H), 2.45–2.10 (m, 2H), 1.94 (br s, 1H), 1.70–1.34 (m, 4H), 1.34–1.20 (m, 3H), 1.02–0.85 (m, 3H); IR (neat, cm^{-1}): 3377, 2961, 2936, 2875, 1615, 1461, 1344, 1236, 1135, 1089, 1061, 1019; MS (EI, 70 eV) *m*/*z* (%): 486 (M^+, 1.61), 303 (M^+–I–C_4H_8, 100); Anal. calcd for $C_{13}H_{16}F_9IO$: C 32.12, H 3.32; found: C 32.23, H 3.40.

*4.2.2. Synthesis of 8-(n-butyl)-11,11,12,12,13,13,14,14,14-nonafluoro-9-iodo-8-tetra-decen-7-ol (**3b**).*



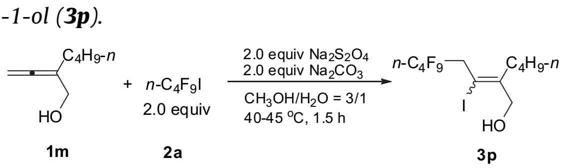
Following typical procedure 1, the reaction of **1b** (79.7 mg, 0.38 mmol), *n*-C_4F_9I **2a** (280.3 mg, 0.81 mmol), $Na_2S_2O_4$ (140.1 mg, 0.81 mmol), and Na_2CO_3 (85.2 mg, 0.80 mmol) in 0.75 mL of CH_3OH and 0.25 mL of H_2O at 40–45 °C for 1 h afforded **3b** (84.5 mg, 40%, *E*/*Z*=68/32) (eluent: petroleum ether/ethyl acetate=60/1): ^1H NMR (400 MHz, $CDCl_3$): δ [4.67–4.61 (*Z*-isomer, m, 0.32H), 4.56–4.49 (*E*-isomer, m, 0.67H)], 3.80–3.38 (m, 2H), 2.39–2.10 (m, 2H), 1.74–1.51 (m, 3H), 1.51–1.38 (m, 4H), 1.38–1.18 (m, 8H), 0.99–0.84 (m, 6H); IR (neat, cm^{-1}): 3426, 2960, 2932, 2861, 1612, 1467, 1380, 1343, 1235, 1198, 1134, 1109, 1019; GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 499 (M^+–C_4H_9, 17.10), 471 (M^+–C_6H_{13}, 23.18), 429 (M^+–I, 100)], [*Z*-isomer, 499 (M^+–C_4H_9, 15.55), 471 (M^+–C_6H_{13}, 21.55), 429 (M^+–I, 100)]; Anal. calcd for $C_{18}H_{26}F_9IO$: C 38.86, H 4.71; found: C 39.07, H 4.93.

*4.2.3. Synthesis of 2-(n-butyl)-5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-phenyl-2-octen-1-ol (**3c**).*



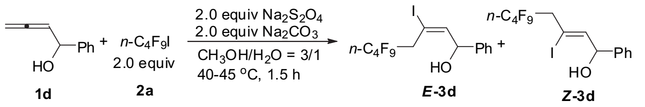
Following typical procedure 1, the reaction of **1c** (83.0 mg, 0.41 mmol), *n*-C_4F_9I **2a** (280.1 mg, 0.81 mmol), $Na_2S_2O_4$ (139.3 mg, 0.80 mmol), and Na_2CO_3 (84.4 mg, 0.80 mmol) in 0.75 mL of CH_3OH and 0.25 mL of H_2O at 40–45 °C for 1 h afforded **3c** (95.9 mg, 43%, *E*/*Z*=75/25) (eluent: petroleum ether/ethyl acetate=40/1): ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.27 (m, 5H), [6.00 (*Z*-isomer, s, 0.25H), 5.75 (*E*-isomer, s, 0.75H)], 4.00–3.47 (m, 2H), 2.28–2.00 (m, 2H), 1.58 (br s, 1H), 1.50–1.31 (m, 1H), 1.31–1.10 (m, 2H), 1.07–0.91 (m, 1H), 0.83–0.75 (m, 3H); IR (neat, cm^{-1}): 3424, 3065, 3031, 2960, 2935, 2874, 1605, 1495, 1452, 1344, 1236, 1134, 1018; GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 548 (M^+, 0.45), 491 (M^+–C_4H_9, 14.06), 421 (M^+–I, 100)], [*Z*-isomer, 548 (M^+, 0.93), 491 (M^+–C_4H_9, 14.11), 421 (M^+–I, 100)]; Anal. calcd for $C_{18}H_{18}F_9IO$: C 39.44, H 3.31; found: C 39.56, H 3.54.

*4.2.4. Synthesis of 2-(n-butyl)-5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-2-octen-1-ol (**3p**).*



Following typical procedure 1, the reaction of **1m** (62.0 mg, 0.49 mmol), *n*-C_4F_9I **2a** (0.17 mL, *d*=2.01, 341.7 mg, 0.99 mmol), $Na_2S_2O_4$ (175.0 mg, 1.0 mmol), and Na_2CO_3 (105.9 mg, 1.0 mmol) in 1.5 mL of CH_3OH and 0.5 mL of H_2O at 40–45 °C for 1.5 h afforded **3p** (79.5 mg, 34%, *E*/*Z*=76/24) (eluent: petroleum ether/ethyl acetate=40/1 to 10/1): ^1H NMR (300 MHz, $CDCl_3$): δ [4.32 (*Z*-isomer, s, 0.48H), 4.19 (*E*-isomer, s, 1.52H)], 3.80–3.52 (m, 2H), 2.52–2.26 (m, 2H), 1.68 (br s, 1H), 1.54–1.30 (m, 4H), 1.00–0.84 (m, 3H); IR (neat, cm^{-1}): 3347, 2961, 2933, 2875, 1714, 1622, 1468, 1429, 1344, 1235, 1135, 1020; GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 472 (M^+, 0.45), 289 (100)], [*Z*-isomer, 472 (M^+, 10.5), 289 (100)]; HRMS calcd for $C_{12}H_{14}OF_9I$ (M^+): 471.9946. found: 471.9943.

*4.2.5. Synthesis of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-phenyl-2-octen-1-ol (E-**3d**) and 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-phenyl-2-octen-1-ol (Z-**3d**).*



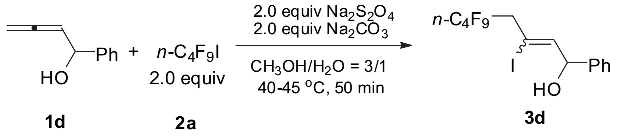
Following typical procedure 1, the reaction of **1d** (57.1 mg, 0.39 mmol), *n*-C_4F_9I **2a** (276.0 mg, 0.80 mmol), $Na_2S_2O_4$ (140.5 mg, 0.81 mmol), and Na_2CO_3 (85.2 mg, 0.80 mmol) in 0.75 mL of CH_3OH and 0.25 mL of H_2O at 40–45 °C for 1.5 h afforded *E*-**3d** (59.7 mg, 31%) and *Z*-**3d** (68.0 mg, 35%) (eluent: petroleum ether/ethyl acetate=12/1).

*4.2.5.1. 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-phenyl-2(E)-octen-1-ol (E-**3d**).* Oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 6.88 (d, *J*=8.8 Hz, 1H), 5.27 (d, *J*=8.4 Hz, 1H), 3.81–3.38 (m, 2H), 2.21 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 140.8, 128.9, 128.4, 126.1, 82.8, 72.2, 39.8 (t, J_{C-F}=21.8 Hz); IR (neat, cm^{-1}): 3346, 3066, 3034, 2925, 1629, 1494, 1455, 1430, 1345, 1233, 1133, 1030; MS (EI, 70 eV) *m*/*z* (%): 492 (M^+, 0.20), 105 (100); Anal. calcd for $C_{14}H_{10}F_9IO$: C 34.17, H 2.05; found: C 34.52, H 2.06.

*4.2.5.2. 5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodo-1-phenyl-2(Z)-octen-1-ol (Z-**3d**).* Oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.44 (m, 2H), 7.43–7.29 (m, 3H), 6.15 (d, *J*=8.0 Hz, 1H), 5.43 (d, *J*=7.6 Hz, 1H), 3.44 (t, *J*=17.6 Hz, 2H), 2.36 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 141.0, 128.8, 128.2, 126.1, 87.1, 78.3, 45.3 (t, J_{C-F}=21.0 Hz); IR (neat, cm^{-1}): 3356, 3065, 3032, 2927, 1636, 1603, 1494, 1453, 1425, 1346, 1235, 1134, 1089, 1019; MS (EI, 70 eV) *m*/*z* (%): 492 (M^+, 0.96), 365 (100); Anal. calcd for $C_{14}H_{10}F_9IO$: C 34.17, H 2.05; found: 34.39, H 1.98.

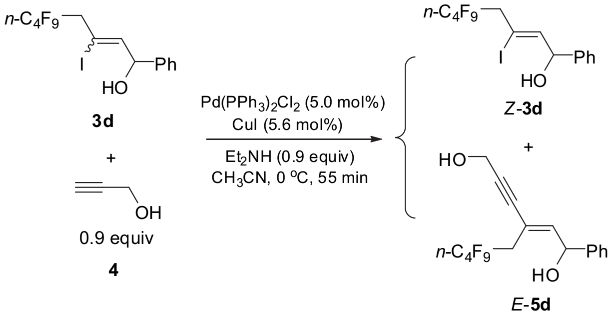
*4.2.6. Synthesis of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-phenyl-2-octen-1-ol (**3d**), 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-phenyl-2(Z)-octen-1-ol (Z-**3d**), and 3-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-1-phenylhex-5-yn-2(E)-en-1,6-diol (E-**5d**).*

*4.2.6.1. Radical addition reaction of **1d** with **2a**.*



Following typical procedure 1, the reaction of **1d** (0.3514 g, 2.41 mmol), *n*-C_4F_9I **2a** (1.6698 g, 4.83 mmol), $Na_2S_2O_4$ (0.8356 g, 4.80 mmol), and Na_2CO_3 (0.5087 g, 4.80 mmol) in 4.5 mL of CH_3OH and 1.5 mL of H_2O at 40–45 °C for 50 min afforded **3d** (0.8135 g, 69%, *E*/*Z*=46/54) (eluent: petroleum ether/ethyl acetate=10/1): ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.49–7.29 (m, 5H), [6.89 (*E*-isomer, d, *J*=8.4 Hz, 0.46H), 6.17 (*Z*-isomer, d, *J*=8.1 Hz, 0.54H)], [5.44 (*Z*-isomer, d, *J*=7.8 Hz, 0.52H), 5.29 (*E*-isomer, d, *J*=8.7 Hz, 0.48H)], 3.80–3.36 (m, 2H), [2.20 (*Z*-isomer, br s, 0.54H), 2.07 (*E*-isomer, br s, 0.46H)]. The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.6.2. Kinetical resolution with Sonogashira coupling reaction.



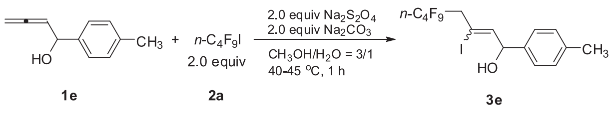
4.2.6.3. Typical procedure 2. To a Schlenk tube containing a mixture of Pd(PPh$_3$)$_2$Cl$_2$ (8.8 mg, 1.3×10^{-2} mmol, 5.0 mol %) and CuI (2.4 mg, 1.4×10^{-2} mol, 5.6 mol %) at 0 °C was added **3d** (123.5 mg, 0.251 mmol, *E*/*Z*=46/54) under a nitrogen atmosphere. Then a solution of Et$_2$NH (16.5 mg, 0.226 mmol) and propargyl alcohol **4** (12.7 mg, 0.227 mmol) in 0.5 mL of CH$_3$CN was added. The resulting mixture was stirred at 0 °C for 55 min monitored by GC, quenched with 10 mL of brine, extracted with diethyl ether (25 mL×3), and dried over anhydrous Na$_2$SO$_4$. Filtration, evaporation, and column chromatography on silica gel afforded *Z*-**3d** (59.1 mg, 48%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5d** (42.0 mg, 40%) (eluent: petroleum ether/ethyl acetate=3/1).

*4.2.6.4. 5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodo-1-phenyl-2(Z)-octen-1-ol (Z-**3d**).* For the analytical data, see the experiment (4) in this Supplementary data.

*4.2.6.5. 3-(2′,2′,3′,3′,4′,4′,5′,5′,5′-Nonafluoropentyl)-1-phenylhex-5-yn-2(E)-en-1,6-diol (E-**5d**).* Oil; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.41–7.27 (m, 5H), 6.40 (d, *J*=8.7 Hz, 1H), 5.34 (d, *J*=8.7 Hz, 1H), 4.32 (s, 2H), 3.26–2.94 (m, 2H), 2.63 (br s, 1H), 2.28 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 145.4, 141.3, 128.8, 128.3, 126.1, 112.1, 87.4, 85.6, 70.4, 51.1, 32.4 (t, $J_{\text{C-F}}$=21.7 Hz); IR (neat, cm^{-1}): 3334, 2926, 2868, 2224, 1632, 1495, 1455, 1436, 1348, 1220, 1134, 1099, 1023; MS (EI, 70 eV) *m*/*z* (%): 402 (M$^+$−H$_2$O, 11.87), 105 (100); Anal. calcd for C$_{17}$H$_{13}$F$_9$O$_2$: C 48.58, H 3.12; found: C 48.65, H 3.48.

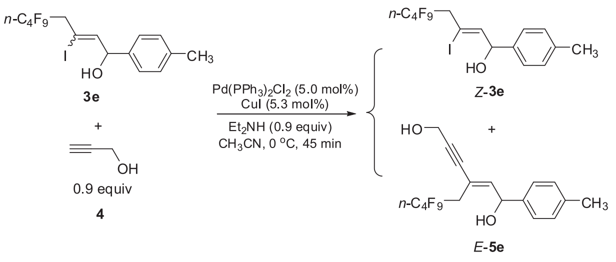
*4.2.7. Synthesis of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-(4′-methylphenyl)-2-octen-1-ol (**3e**), 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-(4′-methylphenyl)-2(Z)-octen-1-ol (Z-**3e**), and 3-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-1-(4′-methyl-phenyl)hex-5-yn-2(E)-en-1,6-diol (E-**5e**).*

*4.2.7.1. Radical addition reaction of **1e** with **2a**.*



Following typical procedure 1, the reaction of **1e** (0.3841 g, 2.40 mmol), *n*-C$_4$F$_9$I **2a** (1.6924 g, 4.89 mmol), Na$_2$S$_2$O$_4$ (0.8352 g, 4.80 mmol), and Na$_2$CO$_3$ (0.5090 g, 4.80 mmol) in 4.5 mL of CH$_3$OH and 1.5 mL of H$_2$O at 40–45 °C for 1 h afforded **3e** (0.7459 g, 61%, *E*/*Z*=41/59) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.26 (d, *J*=7.8 Hz, 1H), 7.19–7.05 (m, 3H), [6.80 (*E*-isomer, *J*=8.4 Hz, 0.41H), 6.08 (*Z*-isomer, *J*=7.5 Hz, 0.58H)], [5.31 (*Z*-isomer, *J*=7.8 Hz, 0.55H), 5.17 (*E*-isomer, *J*=8.7 Hz, 0.42H)], 3.70–3.26 (m, 2H), 2.27 (s, 3H), 1.96 (br s, 1H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.7.2. Kinetical resolution with Sonogashira coupling reaction.

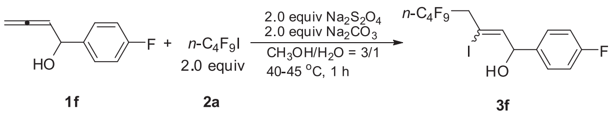


Following typical procedure 2, the reaction of the *E*/*Z* mixture of **3e** (101.2 mg, 0.200 mmol), propargyl alcohol **4** (10.3 mg, 0.184 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (7.0 mg, 1.0×10^{-2} mmol, 5.0 mol %), CuI (2.0 mg, 1.1×10^{-2} mol, 5.3 mol %), and Et$_2$NH (13.1 mg, 0.179 mmol) in 0.4 mL of CH$_3$CN at 0 °C for 45 min afforded *Z*-**3e** (45.4 mg, 45%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5e** (26.4 mg, 30%) (eluent: dichloromethane/ethyl acetate=10/1).

*4.2.7.3. 5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodo-1-(4′-methylphenyl)-2(Z)-octen-1-ol (Z-**3e**).* Oil; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.33 (d, *J*=8.1 Hz, 2H), 7.18 (d, *J*=7.8 Hz, 2H), 6.15 (d, *J*=7.8 Hz, 1H), 5.38 (d, *J*=7.8 Hz, 1H), 3.42 (t, *J*=17.4 Hz, 2H), 2.35 (s, 3H), 2.32 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 146.3, 138.04, 137.99, 129.4, 126.1, 86.7, 78.2, 45.2 (t, $J_{\text{C-F}}$=21.2 Hz), 21.1; IR (neat, cm^{-1}): 3345, 2955, 2926, 2856, 1512, 1459, 1424, 1346, 1235, 1135, 1082, 1019; MS (EI, 70 eV) *m*/*z* (%): 506 (M$^+$, 0.84), 119 (100); Anal. calcd for C$_{15}$H$_{12}$F$_9$IO: C 35.59, H 2.39; found: C 35.91, H 2.51.

*4.2.7.4. 3-(2′,2′,3′,3′,4′,4′,5′,5′,5′-Nonafluoropentyl)-1-(4′-methylphenyl)hex-5-yn-2(E)-en-1,6-diol (E-**5e**).* Oil; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.22 (d, *J*=8.4 Hz, 2H), 7.16 (d, *J*=8.1 Hz, 2H), 6.40 (d, *J*=9.0 Hz, 1H), 5.31 (d, *J*=10.5 Hz, 1H), 4.33 (d, *J*=5.1 Hz, 2H), 3.25–2.95 (m, 2H), 2.34 (s, 3H), 2.40–2.28 (m, 1H), 2.08–1.96 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 145.6, 138.4, 138.2, 129.5, 126.1, 111.8, 87.2, 85.7, 70.4, 51.2, 32.4, (t, $J_{\text{C-F}}$=22.0 Hz), 21.1; IR (neat, cm^{-1}): 3320, 2927, 2869, 2224, 1635, 1616, 1514, 1437, 1349, 1220, 1134, 1099, 1025; MS (EI, 70 eV) *m*/*z* (%): 416 (M$^+$−H$_2$O, 1.30), 119 (100); Anal. calcd for C$_{18}$H$_{15}$F$_9$O$_2$: C 49.78, H 3.48; found: C 49.33, H 3.57.

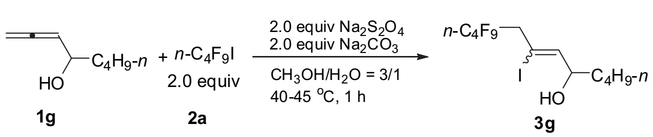
*4.2.8. Synthesis of 5,5,6,6,7,7,8,8,8-nonafluoro-3-iodo-1-(4′-fluorophenyl)-2-octen-1-ol (**3f**).*



Following typical procedure 1, the reaction of **1f** (0.3924 g, 2.39 mmol), n-C_4F_9I **2a** (1.6588 g, 4.79 mmol), $Na_2S_2O_4$ (0.8388 g, 4.82 mmol), and Na_2CO_3 (0.5103 g, 4.81 mmol) in 4.5 mL of CH_3OH and 1.5 mL of H_2O at 40–45 °C for 1 h afforded **3f** (0.8468 g, 69%, *E*/*Z*=44/56) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^1H NMR (300 MHz, $CDCl_3$): δ 7.45–7.36 (m, 1H), 7.36–7.26 (m, 1H), 7.12–6.98 (m, 2H), [6.83 (*E*-isomer, *J*=8.4 Hz, 0.44H), 6.12 (*Z*-isomer, *J*=7.8 Hz, 0.55H)], [5.40 (d, *J*=7.8 Hz, 0.53H), 5.25 (d, *J*=8.7 Hz, 0.46H)], 3.79–3.34 (m, 2H), [2.54 (*Z*-isomer, br s, 0.55H), 2.39 (*E*-isomer, br s, 0.45H)]. GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 383 (M^+–I, 99.23), 123 (100)], [*Z*-isomer, 383 (M^+–I, 32.45), 123 (100)], Anal. calcd for $C_{14}H_9F_{10}OI$: C 32.96, H 1.78; found: C 33.24, H 1.76.

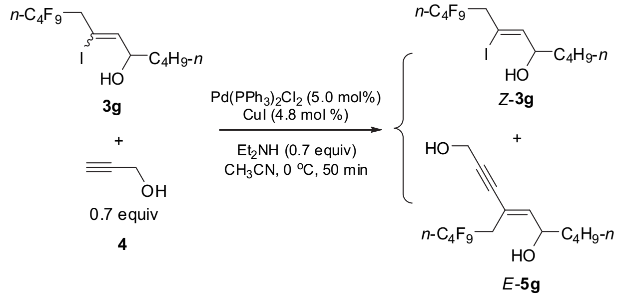
*4.2.9. Synthesis of 9,9,10,10,11,11,12,12,12-nonafluoro-7-iodo-6-dodecen-5-ol (**3g**), 9,9,10,10,11,11,12,12,12-nonafluoro-7-iodo-6(Z)-dodecen-5-ol (Z-**3g**), and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-dec-2-yn-4(E)-1,6-diol (E-**5g**).*

*4.2.9.1. Radical addition reaction of **1g** with **2a**.*



Following typical procedure 1, the reaction of **1g** (0.3045 g, 2.42 mmol), n-C_4F_9I **2a** (1.6716 g, 4.83 mmol), $Na_2S_2O_4$ (0.8376 g, 4.81 mmol), and Na_2CO_3 (0.5054 g, 4.77 mmol) in 4.5 mL of CH_3OH and 1.5 mL of H_2O at 40–45 °C for 1 h afforded **3g** (0.8800 g, 77%, *E*/*Z*=38/62) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^1H NMR (300 MHz, $CDCl_3$): δ [6.67 (*E*-isomer, d, *J*=9.0 Hz, 0.38H), 5.91 (*Z*-isomer, d, *J*=7.8 Hz, 0.62H)], [4.36–4.25 (*Z*-isomer, m, 0.64H), 4.24–4.14 (*E*-isomer, m, 0.39H)], 3.70–3.26 (m, 2H), 2.09 (br s, 1H), 1.70–1.45 (m, 2H), 1.45–1.20 (m, 4H), 0.98–0.82 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.9.2. Kinetical resolution with Sonogashira coupling reaction.



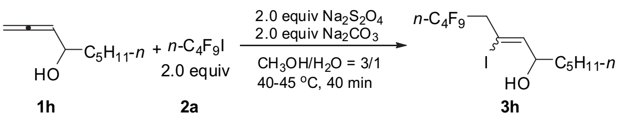
Following typical procedure 2, the reaction of the *E*/*Z* mixture of **3g** (118.0 mg, 0.250 mmol), propargyl alcohol **4** (9.8 mg, 0.175 mmol), $Pd(PPh_3)_2Cl_2$ (8.8 mg, 1.3×10^{-2} mmol, 5.0 mol %), CuI (2.3 mg, 1.2×10^{-2} mol, 4.8 mol %), and Et_2NH (13.0 mg, 0.179 mmol) in 0.5 mL of CH_3CN at 0 °C for 50 min afforded *Z*-**3g** (53.6 mg, 45%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5g** (29.3 mg, 29%) (eluent: petroleum ether/ethyl acetate=3/1).

*4.2.9.3. 9,9,10,10,11,11,12,12,12-Nonafluoro-7-iodo-6(Z)-dodecen-5-ol (Z-**3g**).* Oil; ^1H NMR (400 MHz, $CDCl_3$): δ 5.92 (d, *J*=7.2 Hz, 1H), 4.36–4.28 (m, 1H), 3.53–3.30 (m, 2H), 1.76 (br s, 1H), 1.70–1.51 (m, 2H), 1.47–1.28 (m, 4H), 0.92 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 86.1, 76.5, 45.3 (t, J_{C-F}=21.2 Hz), 35.5, 27.0, 22.6, 13.9; IR (neat, cm^{-1}): 3356, 2960, 2930, 2862, 1639, 1580, 1460, 1426, 1378, 1344, 1235, 1135, 1101, 1020; MS (EI, 70 eV) *m*/*z* (%): 472 (M^+, 0.05), 415 (M^+–C_4H_9, 100); Anal. calcd for $C_{12}H_{14}F_9IO$: C 30.53, H 2.99; found: C 30.72, H 3.03.

*4.2.9.4. 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-Nonafluoropentyl)-dec-2-yn-4(E)-1,6-diol (E-**5g**).* Oil, ^1H NMR (300 MHz, $CDCl_3$): δ 6.19 (d, *J*=9.0 Hz, 1H), 4.37 (s, 2H), 4.33–4.22 (m, 1H), 3.20–2.87 (m, 2H), 2.66 (br s, 1H), 2.31 (br s, 1H), 1.70–1.56 (m, 1H), 1.56–1.42 (m, 1H), 1.42–1.20 (m, 4H), 0.90 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 111.9, 86.9, 85.7, 68.2, 51.2, 36.5, 32.4 (t, J_{C-F}=22.2 Hz), 27.1, 22.5, 13.8; IR (neat, cm^{-1}): 3346, 2957, 2926, 2856, 2225, 1460, 1377, 1348, 1235, 1221, 1135, 1098, 1024; MS (EI, 70 eV) *m*/*z* (%): 382 (M^+–H_2O, 5.27), 85 (100); Anal. calcd for $C_{15}H_{17}F_9O_2$: C 45.01, H 4.28; found: C 45.20, H 4.23.

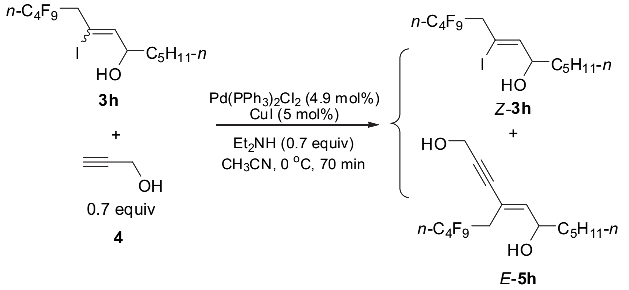
*4.2.10. Synthesis of 10,10,11,11,12,12,13,13,13-nonafluoro-8-iodo-7-tridecen-6-ol (**3h**), 10,10,11,11,12,12,13,13,13-nonafluoro-8-iodo-7(Z)-tridecen-6-ol (Z-**3h**), and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-undec-2-yn-4(E)-1,6-diol (E-**5h**).*

*4.2.10.1. Radical addition reaction of **1h** with **2a**.*



Following typical procedure 1, the reaction of **1h** (0.2764 g, 1.97 mmol), n-C_4F_9I **2a** (1.3984 g, 4.04 mmol), $Na_2S_2O_4$ (0.6991 g, 4.02 mmol), and Na_2CO_3 (0.4270 g, 4.03 mmol) in 6 mL of CH_3OH and 2 mL of H_2O at 40–45 °C for 40 min afforded **3h** (0.6508 mg, 68%, *E*/*Z*=39/61) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^1H NMR (400 MHz, $CDCl_3$): δ [6.67 (*E*-isomer, d, *J*=8.4 Hz, 0.38H), 5.92 (*Z*-isomer, d, *J*=7.2 Hz, 0.60H)], [4.36–4.27 (*Z*-isomer, m, 0.63H), 4.25–4.16 (*E*-isomer, m, 0.42H)], 3.66–3.30 (m, 2H), 1.70–1.47 (m, 3H), 1.47–1.27 (m, 6H), 0.92–0.87 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.10.2. Kinetical resolution with Sonogashira coupling reaction.

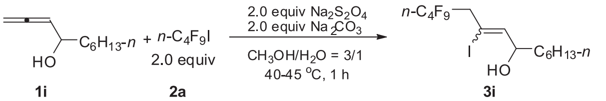


Following typical procedure 2, the reaction of the *E*/*Z* mixture of **3h** (121.9 mg, 0.251 mmol), propargyl alcohol **4** (9.8 mg, 0.175 mmol), $Pd(PPh_3)_2Cl_2$ (8.7 mg, 1.2×10^{-2} mmol, 4.9 mol %), CuI (2.4 mg, 1.3×10^{-2} mol, 5.0 mol %), and Et_2NH (12.9 mg, 0.177 mmol) in 0.5 mL of CH_3CN at 0 °C for 70 min afforded *Z*-**3h** (56.3 mg, 46%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5h** (25.6 mg, 25%) (eluent: petroleum ether/ethyl acetate=3/1).

*4.2.10.3. 10,10,11,11,12,12,13,13,13-Nonafluoro-8-iodo-7(Z)-tridecen-6-ol (Z-**3h**).* Oil, ^1H NMR (400 MHz, $CDCl_3$): δ 5.91 (d, *J*=8.0 Hz, 1H), 4.35–4.27 (m, 1H), 3.52–3.30 (m, 2H), 1.88 (br s, 1H), 1.68–1.50 (m, 2H), 1.50–1.23 (m, 6H), 0.89 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 86.1, 76.5, 45.3 (t, J_{C-F}=21.3 Hz), 35.8, 31.7, 24.6, 22.5, 13.9; IR (neat, cm^{-1}): 3346, 2961, 2935, 2863, 1639, 1468, 1426, 1344, 1235, 1135, 1101, 1020; MS (EI, 70 eV) *m*/*z* (%): 486 (M^+, 0.03), 415 [$(M-C_5H_{11})^+$, 100]; Anal. calcd for $C_{13}H_{16}F_9IO$: C 32.12, H 3.32; found: C 32.45, H 3.38.

*4.2.10.4. 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-Nonafluoropentyl)-undec-2-yn-4(E)-1,6-diol (E-**5h**).* Oil; ^1H NMR (400 MHz, $CDCl_3$): δ 6.17 (d, *J*=8.8 Hz, 1H), 4.37 (s, 2H), 4.32–4.23 (m, 1H), 3.16–2.91 (m, 2H), 1.87 (br s, 2H), 1.66–1.53 (m, 1H), 1.53–1.43 (m, 1H), 1.43–1.20 (m, 6H), 0.88 (t, *J*=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 146.6, 112.0 (t, J_{C-F}=3.0 Hz), 86.9, 85.8, 68.2, 51.3, 36.8, 32.5 (t, J_{C-F}=21.3 Hz), 31.6, 24.7, 22.5, 13.9; IR (neat, cm^{-1}): 3334, 2960, 2934, 2863, 2225, 1438, 1348, 1235, 1134, 1099, 1024; MS (EI, 70 eV) *m*/*z* (%): 414 (M^+, 0.01), 396 (M^+-H_2O, 4.27), 99 (100); Anal. calcd for $C_{16}H_{19}F_9O_2$: C 46.38, H 4.62; found: C 46.35, H 4.72.

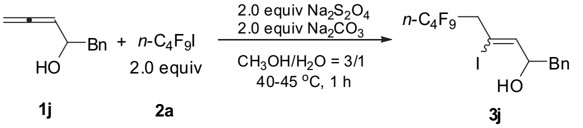
*4.2.11. Synthesis of 11,11,12,12,13,13,14,14,14-nonafluoro-9-iodo-8-tetradecen-7-ol (**3i**).*



Following typical procedure 1, the reaction of **1i** (0.3687 g, 2.39 mmol), *n*-C_4F_9I **2a** (1.6645 g, 4.81 mmol), $Na_2S_2O_4$ (0.8334 g, 4.79 mmol), and Na_2CO_3 (0.5082 g, 4.79 mmol) in 4.5 mL of CH_3OH and 1.5 mL of H_2O at 40–45 °C for 1 h afforded **3i** (0.7124 g, 60%, *E*/*Z*=37/63) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* [6.67 (*E*-isomer, d, *J*=8.7 Hz, 0.37H), 5.92 (*Z*-isomer, d, *J*=7.5 Hz, 0.63H)], [4.37–4.28 (*Z*-isomer, m, 0.66H), 4.26–4.15 (*E*-isomer, m, 0.39H)], 3.68–3.20 (m, 2H), 1.84–1.47 (m, 3H), 1.47–1.20 (m, 8H), 0.92–0.80 (m, 3H); GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 415 ($M^+-C_6H_{13}$, 98.40), 113 (100)], [*Z*-isomer, 415 ($M^+-C_6H_{13}$, 15.06), 113 (100)], Anal. calcd for $C_{14}H_{18}F_9OI$: C 33.62, H 3.63; found: C 33.83, H 3.70.

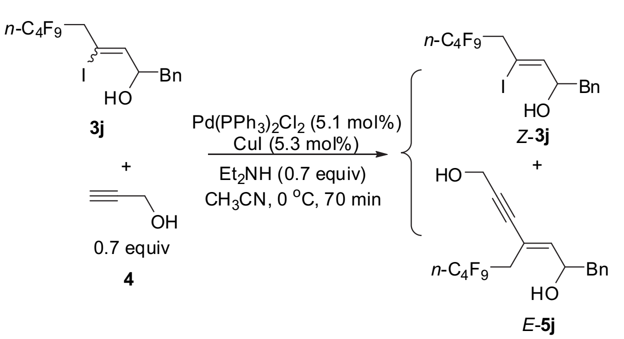
*4.2.12. Synthesis of 6,6,7,7,8,8,9,9,9-nonafluoro-4-iodo-1-phenyl-3-nonen-2-ol (**3j**), 6,6,7,7,8,8,9,9,9-nonafluoro-4-iodo-1-phenyl-3(Z)-nonen-2-ol (Z-**3j**), and 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-nonafluoropentyl)-7-phenylhept-2-yn-4(E)-1,6-diol (E-**5j**).*

*4.2.12.1. Radical addition reaction of **1j** with **2a**.*



Following typical procedure 1, the reaction of **1j** (0.3215 g, 2.01 mmol), *n*-C_4F_9I **2a** (1.3986 g, 4.04 mmol), $Na_2S_2O_4$ (0.6971 g, 4.01 mmol), and Na_2CO_3 (0.4257 g, 4.02 mmol) in 3.75 mL of CH_3OH and 1.25 mL of H_2O at 40–45 °C for 1 h afforded **3j** (0.6101 g, 60%, *E*/*Z*=43/57) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.37–7.30 (m, 2H), 7.30–7.23 (m, 2H), 7.21–7.16 (m, 1H), [6.70 (*E*-isomer, d, *J*=8.4 Hz, 0.43H), 6.00 (*Z*-isomer, d, *J*=7.2 Hz, 0.57H)], [4.55–4.47 (*Z*-isomer, m, 0.57H), 4.45–4.34 (*E*-isomer, m, 0.51H)], 3.54–3.16 (m, 2H), 3.00–2.72 (m, 2H), 1.73 (br s, 1H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.12.2. Kinetical resolution with Sonogashira coupling reaction.

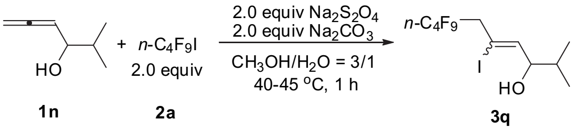


Following typical procedure 2, The reaction of the *E*/*Z* mixture of **3j** (126.5 mg, 0.250 mmol) prepared above, propargyl alcohol **4** (9.7 mg, 0.173 mmol), $Pd(PPh_3)_2Cl_2$ (8.9 mg, 1.3×10^{-2} mmol, 5.1 mol %), CuI (2.5 mg, 1.3×10^{-2} mol, 5.3 mol %), and Et_2NH (12.8 mg, 0.175 mmol) in 0.5 mL of CH_3CN at 0 °C for 70 min afforded *Z*-**3j** (49.9 mg, 39%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5j** (42.3 mg, 39%) (eluent: petroleum ether/ethyl acetate=2/1).

*4.2.12.3. 6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-1-phenyl-3(Z)-nonen-2-ol (Z-**3j**).* Solid; mp: 56–57 °C (*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.36–7.29 (m, 2H), 7.29–7.22 (m, 3H), 5.98 (d, *J*=7.2 Hz, 1H), 4.55–4.45 (m, 1H), 3.53–3.28 (m, 2H), 2.94 (dd, J_1=14.0 Hz and J_2=4.4 Hz, 1H), 2.78 (dd, J_1=13.6 Hz and J_2=8.0 Hz, 1H), 1.94 (d, *J*=3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 146.3, 136.6, 129.6, 128.6, 126.9, 86.3, 77.5, 45.2 (t, J_{C-F}=20.9 Hz), 41.9; IR (neat, cm^{-1}): 3406, 1638, 1494, 1455, 1421, 1347, 1232, 1212, 1132, 1089, 1056; MS (EI, 70 eV) *m*/*z* (%): 506 (M^+, 0.01), 415 [$(M-C_6H_5CH_2)^+$, 61.11], 92 (100); Anal. calcd for $C_{15}H_{12}F_9IO$: C 35.59, H 2.39; found: C 35.64, H 2.48.

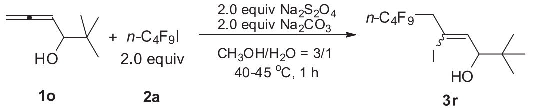
*4.2.12.4. 4-(2′,2′,3′,3′,4′,4′,5′,5′,5′-Nonafluoropentyl)-7-phenylhept-2-yn-4(E)-1,6-diol (E-**5j**).* Solid; mp 62–63 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.38–7.23 (m, 3H), 7.20 (d, *J*=6.9 Hz, 2H), 6.23 (d, *J*=8.7 Hz, 1H), 4.49 (q, *J*=6.3 Hz, 1H), 4.38 (d, *J*=5.1 Hz, 2H), 3.01–2.73 (m, 4H), 1.85–1.80 (m, 1H), 1.76 (t, *J*=5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.2, 136.5, 129.5, 128.8, 127.0, 112.4, 87.0, 85.7, 69.5, 51.4, 43.2, 32.4 (t, J_{C-F}=22.0 Hz); IR (neat, cm^{-1}): 3299, 3036, 2932, 2863, 2223, 1636, 1604, 1496, 1455, 1347, 1216, 1136, 1099, 1046, 1009; MS (EI, 70 eV) *m*/*z* (%): 416 (M^+-H_2O, 2.06), 325 (100); Anal. calcd for $C_{18}H_{15}F_9O_2$: C 49.78, H 3.48; found: C 49.67, H 3.65.

*4.2.13. Synthesis of 7,7,8,8,9,9,10,10,10-nonafluoro-5-iodo-2-methyl-4-decen-3-ol **3q**.*



Following typical procedure 1, the reaction of **1n** (67.1 mg, 0.60 mmol), *n*-C_4F_9I **2a** (0.21 mL, *d*=2.01, 0.4221 g, 1.22 mmol), $Na_2S_2O_4$ (0.2098 g, 1.21 mmol), and Na_2CO_3 (0.1277 g, 1.20 mmol) in 1.5 mL of CH_3OH and 0.5 mL of H_2O at 40–45 °C for 1 h afforded **3q** (185.2 mg, 67%, *E*/*Z*=40/60) (eluent: petroleum ether/diethyl ether=20/1 to 10/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* [6.69 (*E*-isomer, d, *J*=9.0 Hz), 5.91 (*Z*-isomer, d, *J*=7.8 Hz), 1H], [4.11–4.04 (*Z*-isomer, m), 3.96–3.87 (*E*-isomer, m), 1H], 3.71–3.29 (m, 2H), 1.98–1.58 (m, 2H), 1.03–0.89 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *δ* 150.7, 145.9, 87.3, 83.2, 81.1, 75.1, 45.6 (t, J_{C-F}=21.3 Hz), 39.7 (t, J_{C-F}=20.9 Hz), 33.8, 33.6, 18.04, 18.01, 17.74, 17.72, 17.7, 17.6; IR (neat, cm^{-1}): 3363, 2966, 1633, 1470, 1427, 1345, 1236, 1135, 1019; GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 415 ($M^+-C_3H_7$, 100)]; [*Z*-isomer: 415 ($M^+-C_3H_7$, 100)]; Anal. calcd for $C_{11}H_{12}F_9OI$: C 28.84, H 2.64; found: C 29.27, H 2.70.

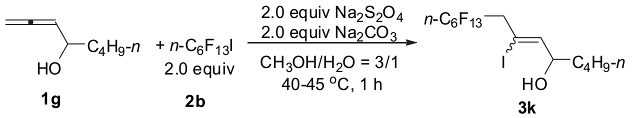
*4.2.14. Synthesis of 7,7,8,8,9,9,10,10,10-nonafluoro-5-iodo-2,2-dimethyl-4-decen-3-ol **3q**.*



Following typical procedure 1, the reaction of **1o** (76.6 mg, 0.61 mmol), *n*-C_4F_9I **2a** (0.21 mL, *d*=2.01, 0.4221 g, 1.22 mmol), $Na_2S_2O_4$ (208.9 mg, 1.20 mmol), and Na_2CO_3 (128.8 mg, 1.22 mmol) in 1.5 mL of CH_3OH and 0.5 mL of H_2O at 40–45 °C for 1 h afforded **3r** (237.8 mg, 83%, *E*/*Z*=37/63) (eluent: 30–60 °C petroleum ether/diethyl ether=20/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* [6.76 (*E*-isomer, d, *J*=9.0 Hz, 0.37H), 5.89 (*Z*-isomer, d, *J*=8.4 Hz, 0.63H)], [4.00 (*Z*-isomer, d, *J*=8.7 Hz), 3.84 (*E*-isomer, d, *J*=9.0 Hz), 1H], 3.63–3.30 (m, 2H), 1.72 (br s, 1H), [0.97 (s), 0.93 (s), 6H]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.2, 144.5, 88.5, 83.9, 83.5, 77.4, 45.8 (t, J_{C-F}=21.0 Hz), 39.6 (t, J_{C-F}=21.0 Hz), 35.7, 35.0, 25.6, 25.2; IR (neat, cm^{-1}): 3424, 2963, 2874, 1719, 1629, 1479, 1467, 1366, 1344, 1236, 1135, 1089, 1035; GC–MS (EI, 70 eV) *m*/*z* (%): [*E*-isomer, 415 ($M^+-C_4H_9$, 7.6), 57 (100)]; [*Z*-isomer, 415 ($M^+-C_4H_9$, 0.5), 57 (100)]; Anal. calcd for $C_{12}H_{14}F_9OI$: C 30.53, H 2.99; found: C 31.29, H 3.15. HRMS calcd for $C_{12}H_{14}F_9OI$ (M^+): 471.9946. found: 471.9962.

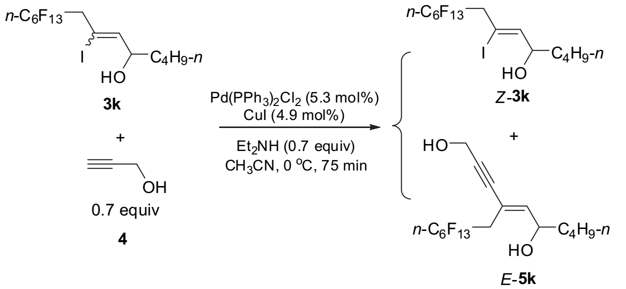
*4.2.15. Synthesis of 9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-7-iodo-6-tetradecen-5-ol (**3k**), 9,9,10,10,11,11,12,12,13,13,14,14,14-tridecafluoro-7-iodo-6(Z)-tetradecen-5-ol (Z-**3k**), and 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoro-heptyl)-dec-2-yn-4(E)-1,6-diol (E-**5k**).*

*4.2.15.1. Radical addition reaction of **1g** with **2b**.*



Following typical procedure 1, the reaction of **1g** (0.2517 g, 2.00 mmol), *n*-$C_6F_{13}I$ **2b** (1.7856 g, 4.00 mmol), $Na_2S_2O_4$ (0.6954 g, 4.00 mmol), and Na_2CO_3 (0.4240 g, 4.00 mmol) in 3.75 mL of CH_3OH and 1.25 mL of H_2O at 40–45 °C for 1 h afforded **3k** (0.8304 g, 73%, *E*/*Z*=38/62) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.67 (*E*-isomer, d, *J*=8.8 Hz, 0.38H), 5.92 (*Z*-isomer, d, *J*=7.6 Hz, 0.61H)], [4.36–4.27 (*Z*-isomer, m, 0.64H), 4.25–4.17 (*E*-isomer, m, 0.39H)], 3.70–3.30 (m, 2H), 1.67 (br s, 1H), 1.64–1.47 (m, 2H), 1.47–1.24 (m, 4H), 0.96–0.87 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.15.2. Kinetical resolution with Sonogashira coupling reaction.



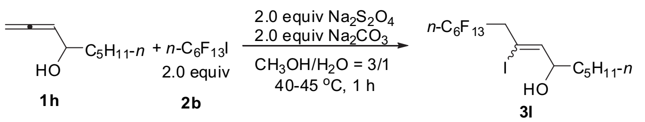
Following typical procedure 2, the reaction of the *E*/*Z* mixture of **3k** (129.6 mg, 0.227 mmol) prepared above, propargyl alcohol **4** (8.8 mg, 0.157 mmol), $Pd(PPh_3)_2Cl_2$ (8.4 mg, 1.2×10^{-2} mmol, 5.3 mol %), CuI (2.0 mg, 1.1×10^{-2} mol, 4.9 mol %), and Et_2NH (12.0 mg, 0.164 mmol) in 0.46 mL of CH_3CN at 0 °C for 75 min afforded *Z*-**3k** (64.1 mg, 49%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5k** (30.8 mg, 27%) (eluent: petroleum ether/ethyl acetate=3/1).

*4.2.15.3. 9,9,10,10,11,11,12,12,13,13,14,14,14-Tridecafluoro-7-iodo-6(Z)-tetradecen-5-ol (Z-**3k**).* Oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (d, *J*=8.0 Hz, 1H), 4.36–4.28 (m, 1H), 3.54–3.30 (m, 2H), 1.84 (br s, 1H), 1.71–1.51 (m, 2H), 1.47–1.28 (m, 4H), 0.92 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 86.1, 76.5, 45.4 (t, J_{C-F}=21.4 Hz), 35.5, 27.0, 22.6, 13.9; IR (neat, cm^{-1}): 3357, 3962, 2935, 2863, 1467, 1426, 1349, 1239, 1206, 1145, 1122, 1102, 1030; MS (EI, 70 eV) *m*/*z* (%): 572 (M^+, 0.07), 515 [$(M-C_4H_9)^+$, 100]; Anal. calcd for $C_{14}H_{14}F_{13}IO$: C 29.39, H 2.47; found: C 29.70, H 2.37.

*4.2.15.4. 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-Tridecafluoro-heptyl)-dec-2-yn-4(E)-1,6-diol (E-**5k**).* Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.19 (d, *J*=9.0 Hz, 1H), 4.38 (d, *J*=3.3 Hz, 2H), 4.28 (q, *J*=7.3 Hz, 1H), 3.20–2.88 (m, 2H), 2.44 (br s, 1H), 2.14 (br s, 1H), 1.70–1.56 (m, 1H), 1.56–1.42 (m, 1H), 1.42–1.20 (m, 4H), 0.90 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 111.9, 86.8, 85.7, 68.2, 51.2, 36.4, 32.4 (t, J_{C-F}=21.9 Hz), 27.1, 22.5, 13.8; IR (neat, cm^{-1}): 3320, 2967, 2936, 2865, 2222, 1635, 1437, 1357, 1238, 1206, 1145, 1122, 1099, 1067, 1023; MS (EI, 70 eV) *m*/*z* (%): 482 (M^+-H_2O, 11.03), 425 ($M^+-H_2O-C_4H_9$, 79.46), 85 (100); Anal. calcd for $C_{17}H_{17}F_{13}O_2$: C 40.81, H 3.42; found: C 41.02, H 3.59.

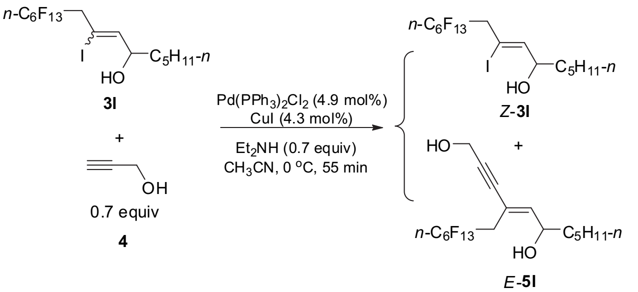
*4.2.16. Synthesis 10,10,11,11,12,12,13,13,14,14,15,15,15-tridecafluoro-8-iodo-7-pentadecen-6-ol (**3l**), 10,10,11,11,12,12,13,13,14,14,15,15,15-tridecafluoro-8-iodo-7(Z)-pentadecen-6-ol (Z-**3l**), and 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoro-heptyl)-undec-2-yn-4(E)-1,6-diol (E-**5l**).*

*4.2.16.1. Radical addition reaction of **1h** with **2b**.*



Following typical procedure 1, the reaction of **1h** (0.3369 g, 2.41 mmol), *n*-$C_6F_{13}I$ **2b** (2.1682 g, 4.86 mmol), $Na_2S_2O_4$ (0.8363 g, 4.81 mmol), and Na_2CO_3 (0.5075 g, 4.79 mmol) in 4.5 mL of CH_3OH and 1.5 mL of H_2O at 40–45 °C for 1 h afforded **3l** (0.8759 g, 61%, *E*/*Z*=37/63) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ [6.67 (*E*-isomer, d, *J*=9.0 Hz, 0.37H), 5.92 (*Z*-isomer, d, *J*=7.5 Hz, 0.63H)], [4.37–4.27 (*Z*-isomer, m, 0.65H), 4.26–4.16 (*E*-isomer, m, 0.39H)], 3.68–3.28 (m, 2H), 1.80–1.47 (m, 3H), 1.47–1.20 (m, 6H), 0.95–0.84 (m, 3H). The *E*/*Z* mixture was submitted to the kinetic resolution step without further characterization.

4.2.16.2. Kinetical resolution with Sonogashira coupling reaction.



Following typical procedure 2, the reaction of the *E*/*Z* mixture of **3l** (235.2 mg, 0.401 mmol) prepared above, propargyl alcohol **4** (15.6 mg, 0.279 mmol), $Pd(PPh_3)_2Cl_2$ (13.9 mg, 2.0×10^{-2} mmol, 4.9 mol %), CuI (3.3 mg, 1.7×10^{-2} mol, 4.3 mol %), and Et_2NH (20.5 mg, 0.281 mmol) in 0.8 mL of CH_3CN at 0 °C for 55 min afforded *Z*-**3l** (115.9 mg, 49%) (eluent: petroleum ether/ethyl acetate=10/1) and *E*-**5l** (46.6 mg, 23%) (eluent: petroleum ether/ethyl acetate=3/1).

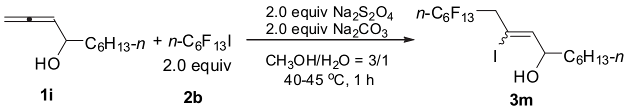
*4.2.16.3. 10,10,11,11,12,12,13,13,14,14,15,15,15-Tridecafluoro-8-iodo-7(Z)-pentadecen-6-ol (Z-**3l**).* Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.92 (d, *J*=7.8 Hz, 1H), 4.37–4.27 (m, 1H), 3.56–3.27 (m, 2H), 1.88 (br s, 1H), 1.72–1.49 (m, 2H), 1.49–1.27 (m, 6H), 0.90 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 86.0, 76.5, 45.3 (t, J_{C-F}=21.5 Hz), 35.7, 31.7, 24.6, 22.5, 13.9; IR (neat, cm^{-1}): 3334, 2958, 2934, 2861, 1639, 1468, 1426, 1350, 1240, 1204, 1146, 1122, 1066, 1027; MS (EI, 70 eV) *m*/*z* (%): 586 (M^+, 0.30), 515 (100); Anal. calcd for $C_{15}H_{16}F_{13}IO$: C 30.74, H 2.75; found: C 31.08, H 3.07.

*4.2.16.4. 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-Tridecafluoro-heptyl)-undec-2-yn-4(E)-1,6-diol (E-**5l**).* Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.19 (d, *J*=9.3 Hz, 1H), 4.39 (d, *J*=5.1 Hz, 2H), 4.35–4.23 (m, 1H), 3.20–2.90 (m, 2H), 1.94–1.88 (m, 1H), 1.86–1.67 (m, 1H), 1.67–1.52

(m, 1H), 1.52–1.44 (m, 1H), 1.44–1.20 (m, 6H), 0.89 (t, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 112.0, 86.8, 85.8, 68.2, 51.3, 36.7, 32.5 (t, J_{C-F}=21.8 Hz), 31.6, 24.7, 22.5, 13.9; IR (neat, cm^{-1}): 3333, 2960, 2935, 2863, 2222, 1632, 1462, 1437, 1357, 1238, 1206, 1145, 1122, 1099, 1066, 1024; MS (EI, 70 eV) m/z (%): 514 (M^+, 0.11), 496 (M^+-H_2O, 6.63), 425 ($M^+-H_2O-C_5H_{11}$, 28.84), 99 (100); Anal. calcd for $C_{18}H_{19}F_{13}O_2$: C 42.03, H 3.72; found: C 42.45, H 4.08.

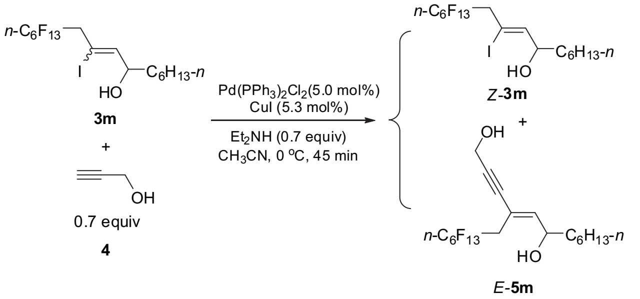
*4.2.17. Synthesis of 11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-9-iodo-8-hexadecen-7-ol (**3m**), 11,11,12,12,13,13,14,14,15,15,16,16,16-tridecafluoro-9-iodo-8(Z)-hexadecen-7-ol (Z-**3m**), and 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-tridecafluoro-heptyl)-dodec-2-yn-4(E)-1,6-diol (E-**5m**).*

*4.2.17.1. Radical addition reaction of **1i** with **2b**.*



Following typical procedure 1, the reaction of **1i** (0.3073 g, 2.00 mmol), n-$C_6F_{13}I$ **2b** (1.7996 g, 4.03 mmol), $Na_2S_2O_4$ (0.6964 g, 4.00 mmol), and Na_2CO_3 (0.4228 g, 3.99 mmol) in 3.75 mL of CH_3OH and 1.25 mL of H_2O at 40–45 °C for 1 h afforded **3m** (0.9901 g, 83%, E/Z=36/64) (eluent: petroleum ether/ethyl acetate=10/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ [6.66 (E-isomer, d, J=8.4 Hz, 0.36H), 5.91 (Z-isomer, d, J=8.0 Hz, 0.64H)], [4.36–4.27 (Z-isomer, m, 0.68H), 4.25–4.17 (E-isomer, m, 0.39H)], 3.70–3.30 (m, 2H), 1.65 (br s, 1H), 1.64–1.48 (m, 2H), 1.48–1.21 (m, 8H), 0.92–0.84 (m, 3H). The E/Z mixture was submitted to the kinetic resolution step without further characterization.

4.2.17.2. Kinetical resolution with Sonogashira coupling reaction.

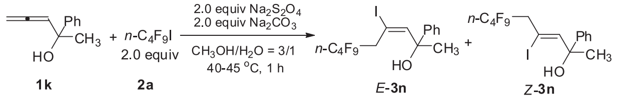


Following typical procedure 2, the reaction of the E/Z mixture of **3m** (149.4 mg, 0.249 mmol) prepared above, propargyl alcohol **4** (9.8 mg, 0.175 mmol), $Pd(PPh_3)_2Cl_2$ (8.7 mg, 1.2×10^{-2} mmol, 5.0 mol %), CuI (2.5 mg, 1.3×10^{-2} mol, 5.3 mol %), and Et_2NH (12.6 mg, 0.173 mmol) in 0.5 mL of CH_3CN at 0 °C for 45 min afforded Z-**3m** (77.9 mg, 52%) (eluent: petroleum ether/ethyl acetate=10/1) and E-**5m** (29.1 mg, 22%) (eluent: petroleum ether/ethyl acetate=3/1).

*4.2.17.3. 11,11,12,12,13,13,14,14,15,15,16,16,16-Tridecafluoro-9-iodo-8(Z)-hexadecen-7-ol (Z-**3m**).* Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (d, J=8.0 Hz, 1H), 4.32 (q, J=6.8 Hz, 1H), 3.54–3.29 (m, 2H), 2.04 (br s, 1H), 1.69–1.50 (m, 2H), 1.48–1.21 (m, 8H), 0.88 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 86.1, 76.5, 45.4 (t, J_{C-F}=20.7 Hz), 35.8, 31.7, 29.2, 24.8, 22.5, 14.0; IR (neat, cm^{-1}): 3346, 2932, 2860, 1637, 1460, 1426, 1349, 1239, 1207, 1145, 1122, 1065; MS (EI, 70 eV) m/z (%): 600 (M^+, 0.04), 515 ($M^+-C_6H_{13}$, 100); Anal. calcd for $C_{16}H_{18}F_{13}IO$: C 32.02, H 3.02; found: C 32.36, H 3.31.

*4.2.17.4. 4-(2′,2′,3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,7′-Tridecafluoro-heptyl)-dodec-2-yn-4(E)-1,6-diol (E-**5m**).* Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.19 (d, J=9.0 Hz, 1H), 4.38 (s, 2H), 4.33–4.23 (m, 1H), 3.20–2.88 (m, 2H), 2.09 (br s, 1H), 1.87 (br s, 1H), 1.70–1.55 (m, 1H), 1.55–1.42 (m, 1H), 1.42–1.18 (m, 8H), 0.88 (t, J=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.6, 111.9, 86.8, 85.7, 68.2, 51.3, 36.7, 32.5 (t, J_{C-F}=21.3 Hz), 31.7, 29.1, 25.0, 22.5, 14.0; IR (neat, cm^{-1}): 3318, 2961, 2933, 2861, 2226, 1635, 1459, 1437, 1357, 1238, 1207, 1145, 1122, 1100, 1066, 1024; MS (EI, 70 eV) m/z (%): 510 (M^+-H_2O, 16.14), 425 (100); Anal. calcd for $C_{19}H_{21}F_{13}O_2$: C 43.19, H 4.01; found: C 43.45, H 4.20.

*4.2.18. Synthesis of 6,6,7,7,8,8,9,9,9-nonafluoro-4-iodo-2-phenyl-3(E)-nonen-2-ol (E-**3n**) and 6,6,7,7,8,8,9,9,9-nonafluoro-4-iodo-2-phenyl-3(Z)-nonen-2-ol (Z-**3n**).*

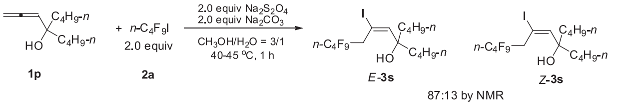


Following typical procedure 1, the reaction of **1k** (0.1314 g, 0.82 mmol), n-C_4F_9I **2a** (0.5661 g, 1.64 mmol), $Na_2S_2O_4$ (0.2802 g, 1.61 mmol), and Na_2CO_3 (0.1694 g, 1.60 mmol) in 1.5 mL of CH_3OH and 0.5 mL of H_2O at 40–45 °C for 1 h afforded E-**3n** (0.2337 g, 56%) (eluent: petroleum ether/diethyl ether=60/1) and Z-**3n** (0.0246 g, 6%) (eluent: petroleum ether/diethyl ether=20/1).

*4.2.18.1. 6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-2-phenyl-3(E)-nonen-2-ol (E-**3n**).* Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.39 (m, 2H), 7.39–7.31 (m, 2H), 7.31–7.23 (m, 1H), 6.91 (s, 1H), 4.18–3.94 (m, 1H), 3.78–3.56 (m, 1H), 2.09 (br s, 1H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 145.5, 128.7, 127.6, 124.8, 82.7, 78.2, 39.5 (t, J_{C-F}=20.3 Hz), 31.2; IR (neat, cm^{-1}): 3567, 3463, 3062, 3029, 2981, 1677, 1616, 1494, 1448, 1421, 1348, 1236, 1198, 1134, 1093, 1062, 1035, 1002; MS (EI, 70 eV) m/z (%): 491 (M^+-CH_3, 1.89), 379 (M^+-I, 100); Anal. calcd for $C_{15}H_{12}F_9IO$: C 35.59, H 2.39; found: C 35.62; H 2.60.

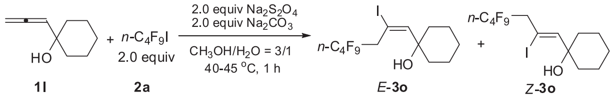
*4.2.18.2. 6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-2-phenyl-3(Z)-nonen-2-ol (Z-**3n**).* Oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48–7.41 (m, 2H), 7.40–7.24 (m, 3H), 6.83 (s, 1H), 3.63–3.35 (m, 2H), 2.99 (br s, 1H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.5, 145.6, 128.4, 127.3, 125.8, 84.8, 75.2, 46.7 (t, J=21.3 Hz), 31.7; IR (neat, cm^{-1}): 3432, 2925, 2853, 1628, 1493, 1448, 1427, 1344, 1235, 1134, 1074, 1029, 1018; MS (EI, 70 eV) m/z (%): 491 (M^+-CH_3, 5.91), 379 (M^+-I, 100); HRMS calcd for $C_{14}H_9F_9IO$ (M^+-CH_3): 490.9554. found: 490.9556.

*4.2.19. Synthesis of 9,9,10,10,11,11,12,12,12-nonafluoro-7-iodo-5-butyl-6(E)-dodecen-5-ol E-**3s**.*



Following typical procedure 1, the reaction of **1p** (54.6 mg, 0.30 mmol), n-C_4F_9I **2a** (0.10 mL, d=2.01, 0.201 g, 0.58 mmol), $Na_2S_2O_4$ (105.3 mg, 0.61 mmol), and Na_2CO_3 (63.8 mg, 0.60 mmol) in 1.5 mL of CH_3OH and 0.5 mL of H_2O at 40–45 °C for 1 h afforded E-**3s** (77.2 mg, 49%) and Z-**3s** (not pure) (eluent: petroleum ether/diethyl ether=80/1 to 20/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 1H), 3.98 (t, J=18.0 Hz, 2H), 1.56–1.42 (m, 5H), 1.42–1.20 (m, 8H), 0.97–0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.4, 81.4, 80.5, 41.7, 39.5 (t, J_{C-F}=20.1 Hz), 25.6, 23.0, 14.0; IR (neat, cm^{-1}): 3479, 2960, 2936, 2864, 1631, 1468, 1349, 1236, 1134, 1113, 1038; GC–MS (EI, 70 eV) m/z (%): [528 (M^+, 0.02), 471 ($M^+-C_4H_9$, 100)]; HRMS calcd for $C_{16}H_{21}F_9OI$ ($[M-1]^+$): 527.0493. found: 527.0483.

*4.2.20. Synthesis of 1-(4′,4′,5′,5′,6′,6′,7′,7′,7′-nonafluoro-2′-iodo-1′(E)-heptyl)-cyclohexanol (E-**3o**) and 1-(4′,4′,5′,5′,6′,6′,7′,7′,7′-nonafluoro-2′-iodo-1′(Z)-heptyl)-cyclohexanol (Z-**3o**).*



Following typical procedure 1, the reaction of **1l** (0.1117 g, 0.81 mmol), *n*-C_4F_9I **2a** (0.5379 g, 1.55 mmol), $Na_2S_2O_4$ (0.2800 g, 1.61 mmol), and Na_2CO_3 (0.1687 g, 1.59 mmol) in 1.5 mL of CH_3OH and 0.5 mL of H_2O at 40–45 °C for 1 h afforded *E*-**3o** (0.2307 g, 59%) (eluent: petroleum ether/diethyl ether=40/1) and *Z*-**3o** (0.0216 g, 6%) (eluent: petroleum ether/diethyl ether=20/1).

*4.2.20.1. 1-(4′,4′,5′,5′,6′,6′,7′,7′,7′-Nonafluoro-2′-iodo-1′(E)-heptyl)-cyclohexanol (E-**3o**).* Oil; ^1H NMR (300 MHz, $CDCl_3$): δ 6.68 (s, 1H), 4.01 (t, J=18.0 Hz, 2H), 1.70–1.42 (m, 10H), 1.38–1.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 81.8, 76.3, 39.5 (t, J_{C-F}=20.1 Hz), 38.2, 24.9, 21.4; IR (neat, cm^{-1}): 3609, 3480, 2937, 2861, 1624, 1452, 1423, 1348, 1235, 1134, 1115, 1057, 1035, 1003; MS (EI, 70 eV) m/z (%): 484 (M^+, 0.86), 441 ($M^+-C_3H_7$, 10.20), 357 (M^+-I, 100); Anal. calcd for $C_{13}H_{14}F_9IO$: C 32.25, H 2.91; found: C 32.46, H 2.84.

*4.2.20.2. 1-(4′,4′,5′,5′,6′,6′,7′,7′,7′-Nonafluoro-2′-iodo-1′(Z)-heptyl)-cyclohexanol (Z-**3o**).* Oil; ^1H NMR (300 MHz, $CDCl_3$): δ 6.35 (s, 1H), 3.45 (t, J=17.4 Hz, 2H), 2.36 (br s, 1H), 1.79–1.61 (m, 6H), 1.56–1.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 80.2, 72.1, 47.2 (t, J_{C-F}=20.6 Hz), 37.3, 25.1, 21.7; IR (neat, cm^{-1}): 3442, 2934, 2859, 1627, 1451, 1345, 1235, 1134, 1110, 1018; MS (EI, 70 eV) m/z (%): 484 (M^+, 1.15), 441 ($M^+-C_3H_7$, 14.16), 357 (M^+-I, 100); HRMS calcd for $C_{13}H_{14}F_9IO$: 483.9946; found: 483.9961.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.044.

References and notes

1. (a) Patai, S. *The Chemistry of Ketenes, Allenes, and Related Compounds*; John Wiley: New York, NY, 1980, Part 1; (b) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley: New York, NY, 1984; (c) Landor, S. R. *The Chemistry of Allenes*; Academic Press: New York, NY, 1982; Vols. 1–3; (d) Ma, S. Carbopalladation of allenes In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley: New York, NY, 2002; p 1491; (e) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH: Weinheim, Germany, 2004; Vols. 1–2; (f) Ma, S. Pd-Catalyzed two- or three component cyclization of functionalized allenes In *Topics in Organometallic Chemistry*; Tsuji, J., Ed.; Springer: Heidelberg, 2005; p 183.
2. For reviews on the chemistry of allenes, see: (a) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207; (b) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067; (c) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590; (d) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535; (e) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12; (f) Tius, M. A. *Acc. Chem. Res.* **2003**, *36*, 284; (g) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701; (h) Wei, L.-L.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773; (i) Ma, S. *Chem. Rev.* **2005**, *105*, 2829; (j) Ma, S. *Aldrichimica Acta* **2007**, *40*, 91.
3. For the reviews, see Ref. 2j, and Ma, S. Ionic addition to allenes In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004.
4. (a) Ma, S.; Shi, Z.; Yu, Z. *Tetrahedron Lett.* **1999**, *40*, 2393; (b) Ma, S.; Shi, Z.; Yu, Z. *Tetrahedron* **1999**, *55*, 12137; (c) Ma, S.; Wei, Q.; Wang, H. *Org. Lett.* **2000**, *2*, 3893; (d) Ma, S.; Ren, H.; Wei, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4817; (e) Ma, S.; Hao, X.; Huang, X. *Org. Lett.* **2003**, *5*, 1217; (f) Ma, S.; Hao, X.; Huang, X. *Chem. Commun.* **2003**, 1082; (g) Ma, S.; Hao, X.; Meng, X.; Huang, X. *J. Org. Chem.* **2004**, *69*, 5720; (h) Fu, C.; Huang, X.; Ma, S. *Tetrahedron Lett.* **2004**, *45*, 6063; (i) Ma, S.; Pan, F.; Hao, X.; Huang, X. *Synlett* **2004**, 85; (j) Fu, C.; Li, J.; Ma, S. *Chem. Commun.* **2005**, 4119; (k) Fu, C.; Chen, G.; Liu, X.; Ma, S. *Tetrahedron* **2005**, *61*, 7768; (l) Fu, C.; Ma, S. *Eur. J. Org. Chem.* **2005**, 3942; (m) Chen, G.; Fu, C.; Ma, S. *Tetrahedron* **2006**, *62*, 4444; (n) Chen, G.; Fu, C.; Ma, S. *J. Org. Chem.* **2006**, *71*, 9877; (o) Gu, Z.; Deng, Y.; Shu, W.; Ma, S. *Adv. Synth. Catal.* **2007**, *349*, 1653; (p) Zhou, C.; Fu, C.; Ma, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4379; (q) Zhou, C.; Fu, C.; Ma, S. *Tetrahedron* **2007**, *63*, 7612; (r) He, G.; Zhou, C.; Fu, C.; Ma, S. *Tetrahedron* **2007**, *63*, 3800; (s) Zhou, C.; Ma, Z.; Gu, Z.; Fu, C.; Ma, S. *J. Org. Chem.* **2008**, *73*, 772; (t) Zhou, C.; Li, J.; Lü, B.; Fu, C.; Ma, S. *Org. Lett.* **2008**, *10*, 581; (u) Li, J.; Fu, C.; Chai, G.; Ma, S. *Adv. Synth. Catal.* **2008**, *350*, 1376.
5. For the reviews of radical reactions of allenes, see: (a) Pan, F.; Fu, C.; Ma, S. *Chin. J. Org. Chem.* **2004**, *24*, 1168; (b) Hartung, J.; Kopf, T. In *Fundamentals and Application of Free Radical Addition to Allenes*; Krause, N., Hashmi, A. S. K. , Eds.; Modern Allene Chemistry; Wiley-VCH: Weinheim, Germany, 2004; Vols. 1–2.
6. Recent reports for radical reaction of allenes, see: (a) Shen, L.; Hsung, R. P. *Org. Lett.* **2005**, *7*, 775; (b) Dai, W.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2005**, *70*, 6647; (c) Wu, Z.; Huang, X. *Synthesis* **2007**, 45; (d) Alcaide, B.; Almendros, P.; Aragoncillo, C.; Redondo, M. C. *J. Org. Chem.* **2007**, *72*, 1604; (e) Hayashi, N.; Hirokawa, Y.; Shibata, I.; Yasuda, M.; Baba, A. *Org. Biomol. Chem.* **2008**, *6*, 1949; (f) Yang, D.; Cwynar, V.; Donahue, M. G.; Hart, D. J.; Mbogo, G. *J. Org. Chem.* **2009**, *74*, 8726; (g) Curry, L.; Hallside, M. S.; Powell, L. H.; Sprague, S. J.; Burton, J. W. *Tetrahedron* **2009**, *65*, 10882; (h) Kawaguchi, S.; Shirai, T.; Ohe, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. *J. Org. Chem.* **2009**, *74*, 1751; (i) Bucher, G.; Mahajan, A. A.; Schmittel, M. *J. Org. Chem.* **2009**, *74*, 5850; (j) Mei, Y.; Liu, J.; Liu, Z. *Synthesis* **2007**, 739.
7. (a) Ma, S.; Ma, Z. *Synlett* **2006**, 1263; (b) Ma, Z.; Ma, S. *Tetrahedron* **2008**, *64*, 6500; (c) Lü, B.; Jiang, X.; Fu, C.; Ma, S. *J. Org. Chem.* **2009**, *74*, 438; (d) and the corrigendum: Jiang, X.; Fu, C.; Ma, S. *Chem.—Eur. J.* **2008**, *14*, 9656; *Chem.—Eur. J.* **2009**, *15*, 1295.
8. For a review of the reaction of 2,3-allenols and their derivatives, see: Deng, Y.; Gu, Z.; Ma, S. *Chin. J. Org. Chem.* **2006**, *26*, 1468.
9. (a) Deng, Y.; Yu, Y.; Ma, S. *J. Org. Chem.* **2008**, *73*, 585; (b) Deng, Y.; Li, J.; Ma, S. *Chem.—Eur. J.* **2008**, *14*, 4263.
10. (a) Huang, W.; Wang, W.; Huang, B. *Acta Chim. Sinica* **1985**, *43*, 663; (b) Huang, W.; Wang, W.; Huang, B. *Acta Chim. Sinica* **1986**, *44*, 488; (c) Huang, W.; Lü, L.; Zhang, Y. *Chin. J. Chem.* **1990**, *8*, 350.
11. Ma, S.; Ren, H.; Wei, Q. *J. Am. Chem. Soc.* **2003**, *125*, 4817.