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Stereoselective generation of *cis*-2-lithio-3-CF_3-oxirane via CF_3-substituted β-oxido carbenoids. Highly stereoselective synthesis of CF_3-substituted tri- and tetrasubstituted oxiranes and tetrasubstituted alkenes

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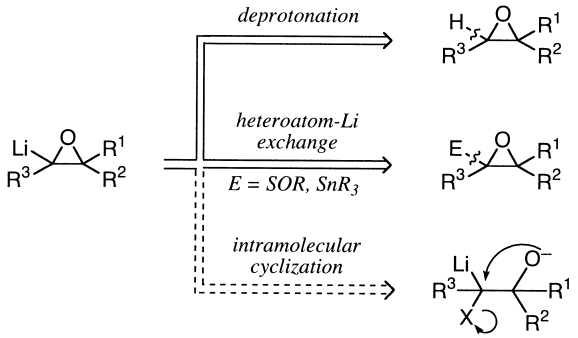
Abstract—Treatment of 2-substituted 3,3-dichloro-1,1,1-trifluoropropan-2-ols with organolithium reagents R^2Li in THF at −98°C stereoselectively produces 2,3-disubstituted 2-lithio-3-trifluoromethyloxiranes with Li and CF_3 *cis*. The reagents react with electrophiles El-X or organoboranes R^3BR_2 to give CF_3-containing tri- and tetrasubstituted oxiranes or tetrasubstituted alkenes, respectively, with high diastereoselectivities.

1. Introduction

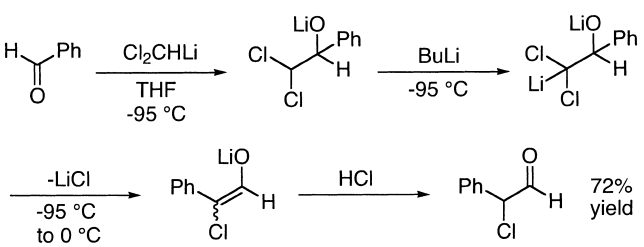
Oxiranyllithiums have been emerging as highly versatile reagents for the stereocontrolled synthesis of functionalized oxiranes as well as alkenes.[1] Strategies for generation of oxiranyllithiums recorded so far are divided into two categories: one involves deprotonation of an oxirane with a base, and the other is exchange of heteroatoms such as sulfur and tin with lithium (Scheme 1). Both methods are synthetically valuable and widely utilized, while stereodefined oxiranes, whose preparations often require robust efforts, are essential as precursors for stereoselective generation of oxiranyllithiums.

On the other hand, intramolecular cyclization of β-oxido lithium carbenoids can, in principle, be the third strategy that is quite unique since acyclic precursors are employed in place of cyclic ones (Scheme 1). β-Oxido carbenoids generated from dihalohydrins (R^3=halogen) with a base, however, reportedly undergo 1,2-rearrangement of a substituent attached at the carbinol carbon, giving rise to carbonyl compounds.[2] For instance, treatment of benzaldehyde with dichloromethyllithium in THF at −95°C followed by the addition of BuLi at −95°C generated phenyl-substituted β-oxide carbenoid in which, upon warming to 0°C, a phenyl group migrated in 1,2-fashion



Scheme 1. Generation of oxiranyllithiums.

without cyclization to produce the corresponding lithium enolate whose hydrolysis gave a homologated aldehyde in a good yield (Scheme 2).[2e,h] Thus, intramolecular cyclization of dihalohydrins leading to oxiranyllithiums is still to be explored.[3]



Scheme 2. Rearrangement of β-oxido carbenoid.

Keywords: carbenoids; fluorine; lithium; oxirane; trifluoromethyl.
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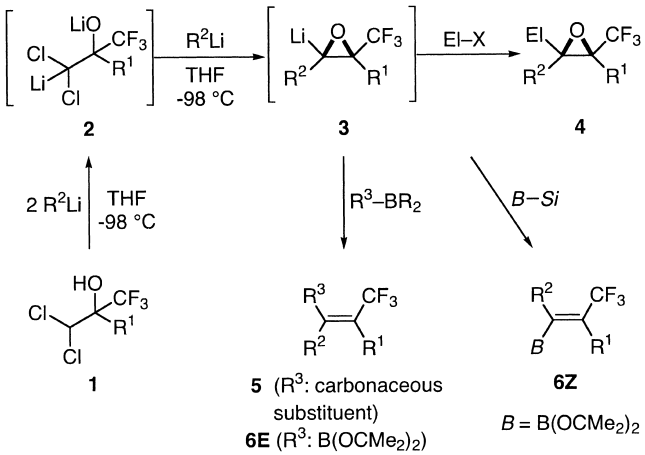
In the course of our study on the novel synthesis of organofluorine compounds utilizing fluorine-containing carbenoid reagents,[4] we focused our attention on novel CF_3-substituted β-oxido carbenoids and have found that the carbenoids are capable of the realization of the third strategy (Scheme 1).[5] We describe herein novel generation of oxiranyllithiums **3** from acyclic dichlorohydrins **1** and their reactions with an electrophile, providing convenient and versatile synthetic methods of preparing CF_3-containing tri- and tetrasubstituted oxiranes **4** and tetrasubstituted alkenes **5** and **6** (Scheme 3).[6]

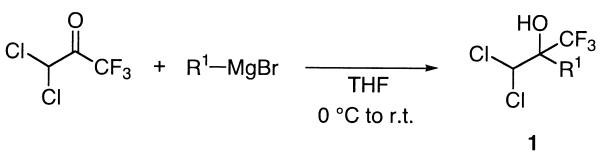


Scheme 3. Novel and stereoselective generation and reactions of CF_3-substituted oxiranyllithiums **3**.

2. Results and discussion

2.1. Preparation of CF_3-containing dichlorohydrins 1

Dichlorohydrins **1** were readily prepared by treatment of freshly distilled 3,3-dichloro-1,1,1-trifluoropropan-2-one with Grignard reagents R^1MgBr in THF at 0°C (Eq. (1)). The results are summarized in Table 1. Various kinds of substituent R^1 were easily introduced in moderate to good yields. In contrast, use of the corresponding organolithium reagents (R^1Li) resulted in the low yields of **1** probably because deprotonation of the ketone by R^1Li competed with the carbonyl addition.



(1)

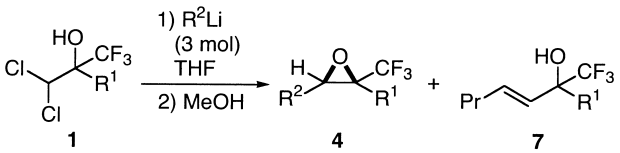
Table 1. Preparation of dichlorohydrins **1**[a]

R^1	1	Yield (%)[b]
$Ph(CH_2)_2$	**1a**	59
(*E*)-PhCH=CH	**1b**	88
PhC≡C	**1c**	86
Ph	**1d**	80

[a] To a 1.0 M THF solution of R^1MgBr (30 mmol) was added freshly distilled 3,3-dichloro-1,1,1-trifluoropropan-2-one (3.2 mL, 28 mmol) at 0°C. The mixture was stirred for 10–30 min at 0°C and stirred at room temperature overnight.
[b] Isolated yields based on the ketone.

2.2. Synthesis of tri- and tetrasubstituted oxiranes 4

Whereas the rearrangement of β-oxido carbenoids generated from dihalohydrins is applicable to homologation of not only aldehydes and ketones but esters (via β-oxido alkylidene-type carbenoids), no precedent is available for CF_3-substituted ketones. Hence, we became interested in a reaction of β-oxido carbenoids **2** to develop a novel method for synthesis of CF_3-containing target compounds. Thus, we first treated **1a** with 3 molar amounts of BuLi in THF at −78°C and then warmed the reaction mixture to room temperature before quenching with MeOH in a manner similar to the reported procedure[2e,h] (Eq. (2), R^2=Bu). Unexpectedly, (*E*)-allylic alcohol **7** was obtained as the sole product in 58% yield (Table 2, entry 1). No products derived from the expected CF_3 or $Ph(CH_2)_2$ rearrangement were detected. When the same reaction was effected and quenched at −78°C, oxirane **4a** was isolated in 33% yield along with **7** (58% yield, entry 2). Moreover, lowering the reaction temperature to −98°C gave **4a** solely in 85% yield as a single diastereomer (entry 3).



(2)

Table 2. Reaction of **1a** with BuLi (R^2=Bu)[a]

Entry	R^1	Temperature (°C)	Isolated yield	
			4a (%)	**7** (%)
1	$Ph(CH_2)_2$	−78 to rt	0	58
2	$Ph(CH_2)_2$	−78	33	58
3	$Ph(CH_2)_2$	−98	85	–

[a] To a solution of **1** (1.0 mmol) in THF (5 mL) was added R^2Li (3.0 mmol) at the temperature indicated. The solution was allowed to warm to room temperature (entry 1) or stirred at the temperature for 15 min before quenching with methanol (entries 2 and 3).

Under the same conditions, formation of oxirane of type **4** was general irrespective of substituents R^1 and R^2 (Eq. (2) and Table 3). Thus, the reaction of dichlorohydrins **1b–d** afforded the corresponding oxiranes **4b–d** in good yields with good to high diastereoselectivity. In addition to BuLi,

Table 3. Synthesis of trisubstituted oxiranes **4**[a]

Run	1	R^1	R^2	4	Yield (%)[b]	Isomer ratio[c]
1	**1b**	(*E*)-PhCH=CH	Bu	**4b**	74	83:17
2	**1c**	PhC≡C	Bu	**4c**	84	>95:<5
3	**1d**	Ph	Bu	**4d**	83	89:11
4	**1a**	$Ph(CH_2)_2$	Ph	**4e**	93	>95:<5
5	**1b**	(*E*)-PhCH=CH	Ph	**4f**	87	>95:<5
6	**1c**	PhC≡C	Ph	**4g**	95	>95:<5
7	**1c**	PhC≡C	Me	**4h**	85	>95:<5
8	**1c**	PhC≡C	C_2H_3	**4i**	67	>95:<5

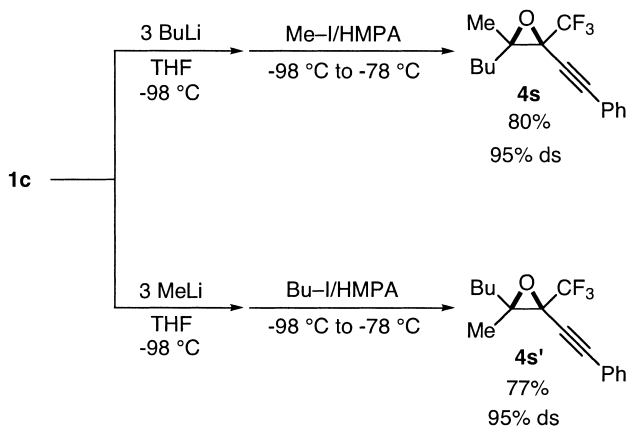
[a] To a solution of **1** (1.0 mmol) in THF (5 mL) was added R^2Li (3.0 mmol) at −98°C. The solution was stirred at −98°C for 15 min before quenching with methanol at −98°C. For entries 4–6, the reaction mixture was allowed to warm to −78°C before quenching with methanol at −78°C.
[b] Isolated yields.
[c] Determined by ^1H and ^{19}F NMR analysis.

phenyllithium, methyllithium, and vinyllithium also reacted with **1a**–**c** to give **4e**–**i** stereoselectively. No reaction took place with phenylethynyllithium, while complex mixture resulted when *s*-BuLi or *t*-BuLi was employed with **1**. In all cases, no product derived from the rearrangement was observed. A solvent mixture of THF/Et_2O/pentane (4:1:1) was also effective for the production of **4**, whereas use of such solvent(s) as Et_2O, Et_2O/TMEDA, hexane, and hexane/TMEDA resulted in the low conversion of **1** and/or the low yield of **4**. In addition, when 2 molar amounts of R^2Li were employed, **4** was produced in moderate yields with recovery of **1**.

Since product distribution of **4a** and **7** was dependent on the reaction temperature as shown in Table 2, we considered that oxiranyllithiums **3** should be produced as an intermediate at −98°C (for discussion of the mechanism, see Section 2.3). Accordingly, we treated **1** with BuLi or PhLi in THF at −98°C and then with an electrophile at −98°C. The resulting mixture was allowed to warm to −78°C and quenched with MeOH at −78°C. We found that silylation with chlorotrimethylsilane, borylation with (isopropoxy)-(pinacolato)borane, aldehyde addition, ketone addition, and allylation with allyl bromide proceeded smoothly to give the corresponding tetrasubstituted oxiranes **4j**–**r** in good yields with excellent diastereoselectivity (Table 4). These results clearly demonstrate the generation of **3** from acyclic **1** and the realization of the third strategy in Scheme 1.

In the case of alkylation, both diastereomers of tetrasubstituted oxiranes **4** can be prepared by proper choice of R^2Li and El-X. For example, treatment of **1c** with BuLi and then iodomethane in HMPA afforded **4s**, while another diastereomer **4s′** was obtained by methyllithium-induced generation of **3** followed by trapping with iodobutane in HMPA as illustrated in Scheme 4.[7]

Stereochemistry of **4** was determined by X-ray crystallographic analysis of benzophenone adducts **4o** and **4q** in which a CF_3 group and $Ph_2C(OH)$ were *cis* (Fig. 1).[8] These results clearly indicate that oxiranyllithiums **3** were stereoselectively generated as intermediates with CF_3 and Li being *cis* in all cases.[9]

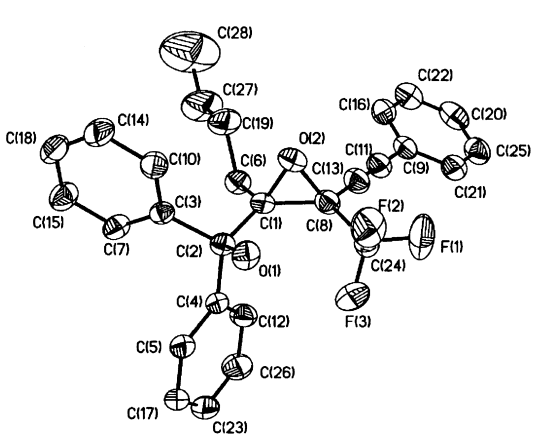


Scheme 4. Stereodivergent synthesis of tetrasubstituted oxiranes **4**.

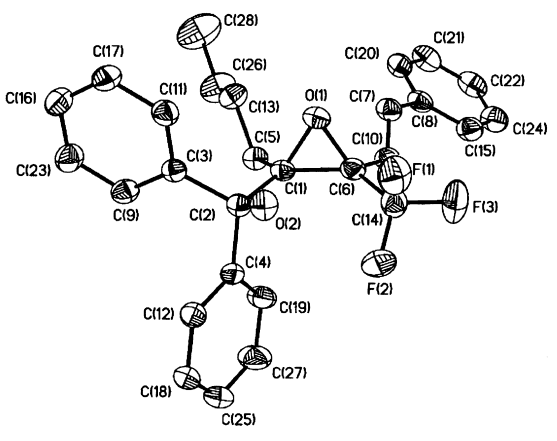
Table 4. Synthesis of tetrasubstituted oxiranes **4**[a]

Run	R^1	R^2	El[b]	**4**	Yield (%)[c]	Isomer ratio[d]
1	PhC≡C	Bu	Me_3Si	**4j**	79	>95:<5
2	PhC≡C	Bu	$B(OCMe_2)_2$	**4k**	62	>95:<5
3	PhC≡C	Ph	$B(OCMe_2)_2$	**4l**	76	>95:<5
4	PhC≡C	Bu	PhCH(OH)	**4m**	82	–[e]
5	PhC≡C	Bu	$Et_2C(OH)$	**4n**	71	>95:<5
6	PhC≡C	Bu	$Ph_2C(OH)$	**4o**	68	>95:<5
7	$Ph(CH_2)_2$	Bu	$Ph_2C(OH)$	**4p**	57	>95:<5
8	(*E*)-PhCH=CH	Bu	$Ph_2C(OH)$	**4q**	55	89:11
9	PhC≡C	Bu	C_3H_5	**4r**	70	>95:<5

[a] To a solution of **1** (1.0 mmol) in THF (5 mL) was added R^2Li (3 mmol) at −98°C and the mixture was stirred at −98°C for 15 min before adding El-X (1.5 mmol). The resulting solution was gradually warmed to −78°C and quenched with MeOH at −78°C.
[b] El-X employed were as follows: entry 1, Me_3SiCl; entries 2 and 3, $(i\text{-PrO})B(OCMe_2)_2$; entry 4, PhCHO; entry 5, Et_2CO; entries 6–8, Ph_2CO; entry 9, allyl bromide.
[c] Isolated yield.
[d] Determined by ^1H and ^{19}F NMR analysis.
[e] Two of four possible diastereomers were obtained in a ratio of 60:40.



4o

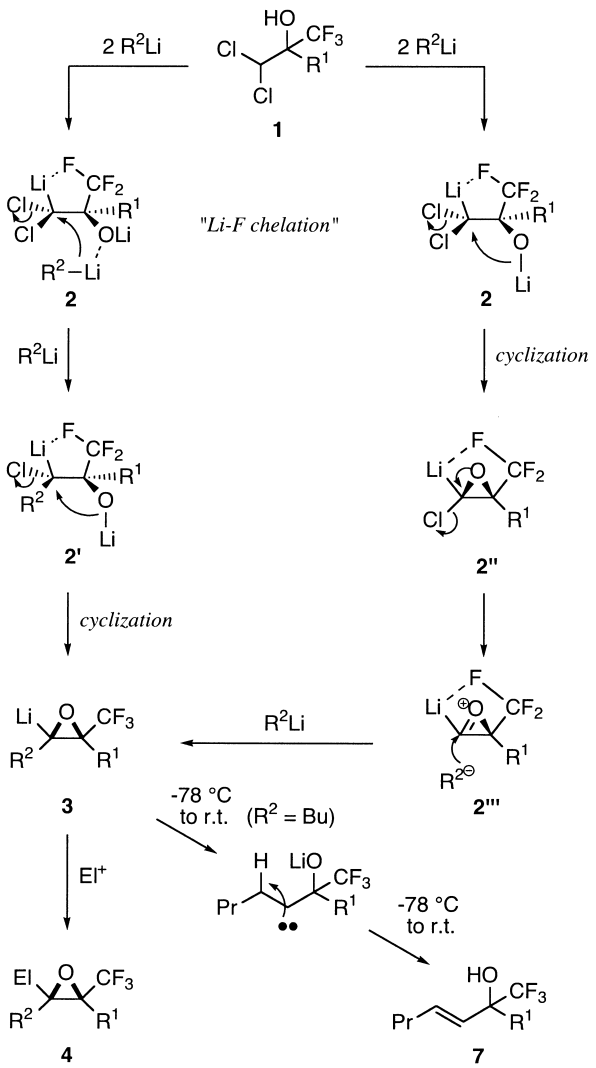


4q

Figure 1. ORTEP drawings of **4o** and **4q**.

2.3. Mechanism for the generation of 3

The mechanism for the stereoselective generation of **3** from **1** is proposed in Scheme 5. At first, **1** would react with 2 molar amounts of R^2Li to produce β-oxido carbenoid **2**. We assume that **2** favors a conformation in which a CF_3 group and a lithium atom connecting a carbenoid carbon are positioned *synclinal* due to lithium–fluorine chelation.[10] Starting from the Li–F chelated conformer **2**, there are two plausible pathways. Substitution of chlorine in **2** with the third R^2Li from the OLi side would produce **2′** which would undergo intramolecular cyclization to generate **3** that was stable at −98°C and reacted with an electrophile producing **4**. Alternatively, cyclization of **2** would take place at first to generate chlorolithiooxirane **2″** which might form oxonium ion **2‴** by participation of a lone pair of electrons in oxygen. Subsequently, the third R^2Li would add to the carbon substituted by a lithium atom to afford **3** with retention of configuration of **2″**.[11] The fact that **3** was generated at some extent with remaining **1** by use of 2 molar amounts of R^2Li indicated that deprotonation by the third R^2Li was a rate-determining step. At temperatures above −78°C, **3** would cause ring-opening via α-elimination of lithium and oxygen to generate a carbene which would undergo adjacent C–H bond insertion with R^2=Bu, giving rise to **7**.



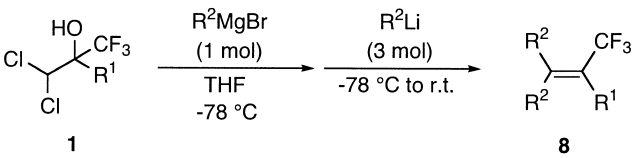
Scheme 5. Proposed mechanism for the stereoselective generation and reactions of oxiranyllithiums **3**.

2.4. Reaction of β-MgO carbenoids leading to CF_3-containing tetrasubstituted alkenes 8

So far, we have demonstrated that β-LiO carbenoids react with an organolithium reagent to generate oxiranyllithiums **3** via intramolecular cyclization. We expected that changing lithium to magnesium might suppress the intramolecular cyclization and perform rearrangement reaction of β-oxido carbenoids. Thus, we treated **1a** with MeMgBr in THF at −78°C to prepare the corresponding magnesium alkoxide. To the solution, we added 3 molar amount of MeLi at −78°C and warmed the mixture to room temperature (Scheme 6). No rearranged product, however, formed but tetrasubstituted alkene **8a** was obtained in 60% yield (Table 5, entry 1). The alkene formation was applicable to **1b–d** and BuLi as R^2Li as shown in Table 5 although the yields of **8b** and **8c** were low.

2.5. Stereoselective synthesis of CF_3-containing tetrasubstituted alkenes 5 and 6

Regio- and stereoselective synthesis of tetrasubstituted alkenes is a challenging issue in organic synthesis.[12] Oxiranyllithiums are reported to react with such organometallic reagents as RLi, R_3Al, R_2Zn, and R_4CeLi to give alkylated alkenes.[13] We envisioned that CF_3-containing tetrasubstituted alkenes should be synthesized stereoselectively if such transformation would be applicable to **3**. Then, we examined a reaction of **3** with various kinds of organometallic reagents. Treatment of **1c** with more than 3 molar amounts of BuLi followed by warming to room



Scheme 6. Reaction of CF_3-substituted β-MgO lithium carbenoids.

Table 5. Synthesis of tetrasubstituted alkenes **8**[a]

Entry	1	R^1	R^2	8	Yield (%)[b]
1	**1a**	$Ph(CH_2)_2$	Me	**8a**	60
2	**1b**	(*E*)-PhCH=CH	Me	**8b**	15
3	**1b**	(*E*)-PhCH=CH	Bu	**8c**	26
4	**1c**	PhC≡C	Me	**8d**	55
5	**1c**	PhC≡C	Bu[c]	**8e**	71
6	**1d**	Ph	Me	**8f**	69
7	**1d**	Ph	Bu	**8g**	60

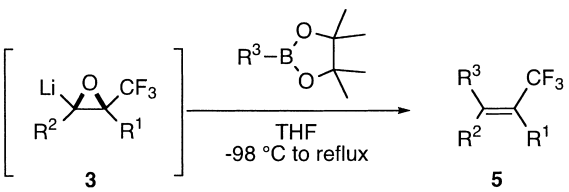
[a] To a THF (3 mL) solution of **1** (1.0 mmol) was added R^2MgBr (1.0 mmol) at −78°C. After stirred at −78°C for 1 h, the solution was added R^2Li (3.0 mmol) at −78°C and was allowed to warm to room temperature before quenching with saturated aqueous NH_4Cl solution.
[b] Isolated yields.
[c] BuMgCl was used instead of BuMgBr.

Table 6. Stereoselective synthesis of tetrasubstituted alkenes **5** (R^1=PhC≡C)[a]

Entry	R^2	R^3	5	Yield (%)[b]	Isomer ratio
1	Bu	PhC≡C	**5c**	74	>95: <5
2	Bu	(*E*)-BuCH=CH	**5d**	56	>95: <5
3	Bu	Ph	**5e**	66	97: 3
4	Ph	Bu	**5e**′	84	96: 4

[a] To a solution of **1c** (1.0 mmol) in THF (5 mL) was added BuLi (1.50 M, 2.0 mL, 3.0 mmol) at −98°C. The solution was stirred at −98°C for 15 min and then was added $R^3B(OCMe_2)_2$ (2.0 mmol) at −98°C. The resulting solution was gradually warmed to room temperature and then refluxed for 4h before quenching with aqueous saturated NH_4Cl solution.
[b] Isolated yield.

temperature and quenching with MeOH produced only **7**, indicating that no reaction of **3** (R^2=Bu) occurred.[14] When **3** (R^2=Bu) was treated with Me_3Al or Et_2Zn, methylated or ethylated alkene **5a** or **5b** was obtained in low yields, respectively. On the other hand, triethylborane reacted with **3** (R^2=Bu) to afford **5b** in 45% yield with excellent stereoselectivity (>95%).[15] Furthermore, (pinacolato)borane exhibited better reactivity (Eq. (3)). Thus, alkynyl, alkenyl, aryl, and alkyl groups were applicable to this stereospecific formation of **5** as a R^3 substituent (Table 6). Noteworthy is that appropriate combination of R^2 and R^3 allows us to prepare either stereoisomer of **5** at will as demonstrated in entries 3 and 4.



(3)

Since a CF_3 and a phenyl groups in **5e** were shown to be *cis* by X-ray analysis (Fig. 2),[8] stereochemistry of **5** was assumed to be similar: CF_3 group and R^3 substituent are always *cis*.

Finally, reaction of **3** with bis(pinacolato)diboron and (dimethylphenylsilyl)(pinacolato)borane were studied to prepare β-CF_3-substituted alkenylboronates (Scheme 7).[16] Thus, treatment of a THF solution of **3** (R^2=Bu or Ph) with

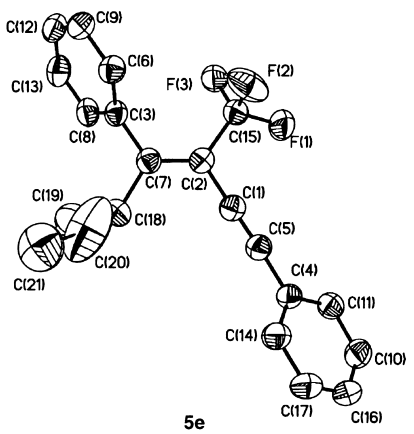
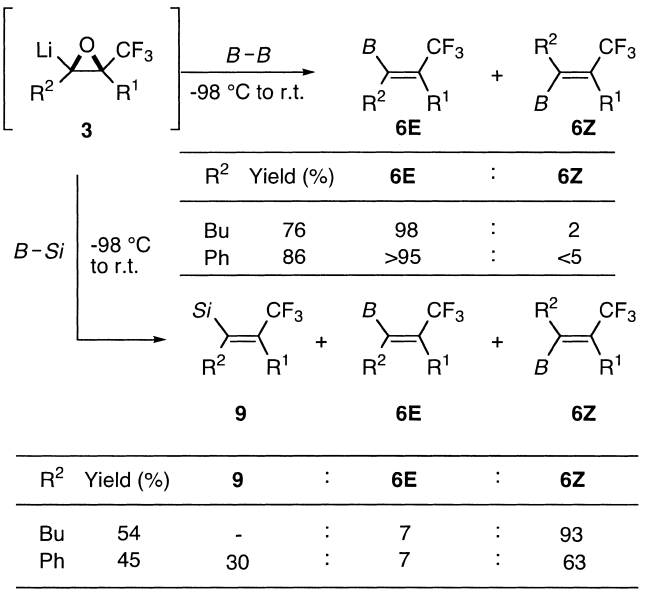


Figure 2. ORTEP drawing of **5e**.



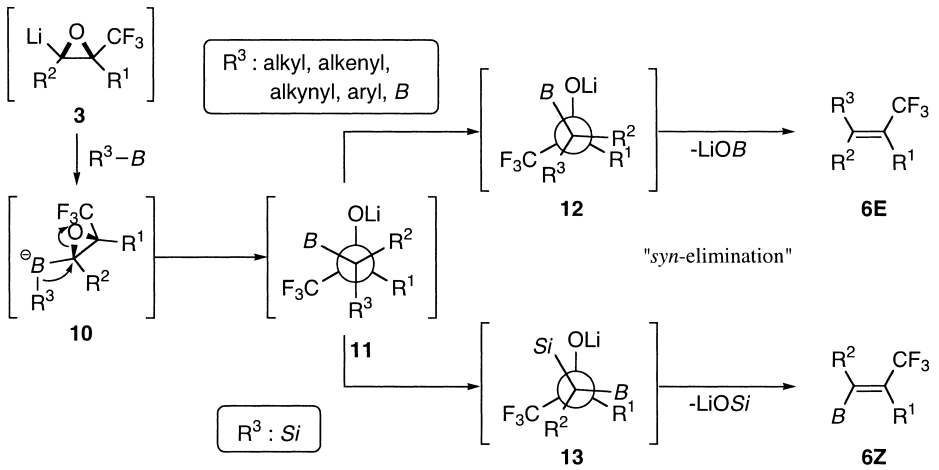
Scheme 7. Stereodivergent synthesis of β-CF_3-substituted alkenylboronates **6** (R^1=PhC≡C, *B*=$B(OCMe_2)_2$, *Si*=$SiMe_2Ph$).

the diboron at −98°C followed by warming the solution to room temperature gave stereoselectively **6E** in which CF_3 and boryl group were arranged *cis*, respectively. On the other hand, alkenylboronates **6Z** was stereoselectively produced in favor of **6E** or β-CF_3-substituted alkenylsilane **9** when the silylborane was employed.

Stereoselective formation of **6E** or **6Z** can be explained by assuming a *syn*-elimination of LiO*B* or LiO*Si* at the last step as illustrated in Scheme 8. First, **3** should react with borane reagent R^3-B to give borate **10** in which 1,2-migration of substituent R^3 would take place and cause the ring-opening to generate lithium alkoxide **11**. In cases of alkyl, alkenyl, alkynyl, aryl, and boryl groups for R^3, minimum rotation for eclipsing carbon–boron and carbon–oxygen bonds would lead to **12** from which **6E** was produced by *syn*-elimination of LiO*B*.[17] When the silylborane was employed (i.e. R^3 in **11** was the silyl group), the carbon–boron bond should turn by 180° for LiOSi to eliminate in *cis* fashion, giving rise to **6Z**.[18]

3. Conclusion

We have demonstrated that CF_3-substituted oxiranyllithiums can be generated from readily available acyclic CF_3-containing dichlorohydrins and organolithium reagents via novel reaction of β-oxido carbenoids. Noteworthy is that the generation proceeds with high stereoselectivity that involves CF_3 and Li being *cis*. The oxiranyllithiums react stereospecifically not only with various kinds of electrophiles to give tri- and tetrasubstituted oxiranes but also with organoborane reagents to afford tetrasubstituted alkenes, which serve as highly versatile intermediates for stereocontrolled synthesis of CF_3-containing complex organic molecules which are receiving much attention in pharmaceutical and material sciences.[19]



Scheme 8. Proposed mechanism for stereodivergent formation of tetrasubstituted alkenes **6** (B=B(OCMe$_2$)$_2$, Si=SiMe$_2$Ph).

4. Experimental

4.1. General remarks

Melting points were determined using a Yanagimoto Micro Melting Point Apparatus. ^{1}H NMR spectra were measured on a Varian Mercury 200 (200 MHz) spectrometer. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ=0 ppm) or chloroform (δ=7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. ^{13}C NMR spectra were measured on a Varian Mercury 200 (50 MHz) spectrometer with tetramethylsilane as an internal standard (δ=0 ppm) or chloroform-*d* (δ=77.0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 200 (188 MHz) spectrometer with $CFCl_3$ as an internal standard (δ=0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. Tetrahydrofuran was distilled from benzophenone and sodium before use under a nitrogen atmosphere. All reactions were carried out under an argon atmosphere.

4.2. Materials

Anhydrous tetrahydrofuran was purchased from Kanto Chemicals. Butyllithium in hexane, methyllithium in diethyl ether, phenyllithium in cyclohexane/diethyl ether were purchased from Aldrich or Kanto Chemicals, and titrated according to the literature method prior to use. 3,3-Dichloro-1,1,1-trifluoropropan-2-one was generously provided by Central Glass Co. Ltd.

4.3. General procedure for the preparation of dichlorohydrin 1

To a THF solution of R^{1}MgBr (30 mmol, 1.0 M) was added freshly distilled 3,3-dichloro-1,1,1-trifluoropropan-2-one (3.2 mL, 28 mmol) at 0°C. The mixture was stirred for 10–30 min at 0°C and stirred at room temperature overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give the crude compound, which was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) giving rise to **1**.

4.3.1. 1,1-Dichloro-2-trifluoromethyl-4-phenylbutan-2-ol (1a). Yield: 59%. Colorless oil. R_f 0.22 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 2.30–2.41 (m, 2H), 2.80 (t, J=8.6 Hz, 2H), 2.95 (brs, 1H), 5.99 (s, 1H), 7.21–7.37 (m, 5H). ^{13}C NMR δ 28.6, 33.3, 72.9, 78.6 (q, J=26.8 Hz), 124.3 (q, J=287.0 Hz), 126.5, 128.3, 128.7, 140.2. ^{19}F NMR (188 MHz, $CDCl_3$, δ −73.5. IR (neat): 3540, 3034, 1951, 1805, 1601, 1503, 1461, 1329, 1184, 1122, 911, 810, 782, 740, 671 cm^{-1}. MS *m/z* 290 (2, M$^+$+4), 288 (9, M$^+$+2), 287 (2, M$^+$+1), 286 (14, M$^+$), 91 (100). Anal. calcd for $C_{11}H_9Cl_2F_3O$: C, 46.02; H, 3.86. Found: C, 46.15; H, 3.80.

4.3.2. (*E*)-1,1-Dichloro-2-trifluoromethyl-4-phenyl-but-3-en-2-ol (1b). Addition reaction of styrylmagnesium bromide, prepared from a *E*/*Z* mixture of β-bromostyrene (Aldrich), to 3,3-dichloro-1,1,1-trifluoropropan-2-one gave a *E*/*Z* mixture of the corresponding adducts which was separated by silica gel column chromatography. Yield: 88%. Pale yellow oil. R_f 0.26 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 3.07 (brs, 1H), 6.01 (s, 1H), 6.38 (d, J=15.9 Hz, 1H), 7.10 (d, J=15.9 Hz, 1H), 7.34–7.55 (m, 5H). ^{13}C NMR δ 72.9, 79.0 (q, J=28.1 Hz), 119.0, 123.4 (q, J=286.1 Hz), 127.1, 128.8, 129.1, 134.9, 136.8. ^{19}F NMR δ −75.3. IR (neat): 3540, 1646, 1489, 1450, 1182, 965, 744, 685 cm^{-1}. MS *m/z* 288 (0.6, M$^+$+4), 286 (3, M$^+$+2), 285 (0.7, M$^+$+1), 284 (5, M$^+$), 201 (100). Anal. calcd for $C_{11}H_9Cl_2F_3O$: C, 46.34; H, 3.18. Found: C, 46.51; H, 3.05.

4.3.3. 1,1-Dichloro-2-trifluoromethyl-4-phenylbut-3-yn-2-ol (1c). Yield: 86%. Pale yellow oil. R_f 0.13 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 3.53 (s, 1H), 5.96 (s, 1H), 7.37–7.43 (m, 3H), 7.52–7.57 (m, 2H). ^{13}C NMR δ 71.8, 76.1 (q, J=31.1 Hz), 79.0, 89.9, 120.1, 122.2 (q, J=285.7 Hz), 128.5, 130.0, 132.3. ^{19}F NMR δ −75.6. IR (neat): 3554, 2241, 1601, 1487, 1436, 1355, 1201, 1105, 982, 803, 753, 710, 685 cm^{-1}. MS m/z 286 (0.4, M$^+$+4), 284 (3, M$^+$+2), 283 (0.5, M$^+$+1), 282 (4, M$^+$), 199 (100). Anal. calcd for $C_{11}H_7Cl_2F_3O$: C, 46.67; H, 2.49. Found: C, 46.69; H, 2.69.

4.3.4. 1,1-Dichloro-3,3,3-trifluoro-2-phenylpropan-2-ol (1d). Yield: 80%. Colorless oil. R_f 0.25 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 3.50 (brs, 1H), 6.35 (s, 1H), 7.43–7.47 (m, 3H), 7.57–7.62 (m, 2H). ^{13}C NMR δ 74.0, 80.3 (q, J=285.0 Hz), 123.7 (q, J=125.7 Hz), 125.7, 128.7, 129.6, 134.0. ^{19}F NMR δ −73.1. IR (neat): 3550, 1456, 1310, 1163, 1075, 1004, 930, 789, 702, 645 cm^{-1}. MS m/z 262 (0.1, M$^+$+4), 260 (0.5, M$^+$+2), 259 (0.1, M$^+$+1), 258 (1, M$^+$), 175 (100). Anal. calcd for $C_9H_7Cl_2F_3O$: C, 41.73; H, 2.72. Found: C, 42.02; H, 2.90.

4.4. General procedure for the preparation of trisubstituted oxiranes 4

To a solution of **1** (1.0 mmol) in THF (5 mL) was added R^2Li (3.0 mmol) at −98°C. The solution was stirred at −98°C for 15 min before quenching with methanol. To the reaction mixture was added saturated aqueous NH_4Cl solution, and the aqueous layer was extracted with diethyl ether three times. Combined organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give a crude product. Purification by column chromatography on silica gel (hexane/diethyl ether 10:1) gave **4**.

4.4.1. (3*R,4*S**)-3,4-Epoxy-1-phenyl-3-trifluoromethyloctane (4a).** Yield: 85%. Colorless oil. R_f 0.54 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.94 (t, J=6.8 Hz, 3H), 1.25–1.72 (m, 6H), 2.07 (t, J=8.6 Hz, 2H), 2.86 (t, J=8.6 Hz, 1H), 3.26 (t, J=6.0 Hz, 1H), 7.21–7.38 (m, 5H). ^{13}C NMR δ 13.8, 22.4, 27.3, 28.2, 28.3, 30.7, 59.6 (q, J=34.0 Hz), 59.7, 124.4 (q, J=278.3 Hz), 126.3, 128.2, 128.6, 140.9. ^{19}F NMR δ −75.4. IR (neat): 2951, 1767, 1601, 1446, 1332, 1259, 1148, 1021, 943, 905, 804, 741, 691 cm^{-1}. MS m/z 274 (0.1, M$^+$+2), 273 (1, M$^+$+1), 272 (8, M$^+$), 104 (100). Anal. calcd for $C_{15}H_{19}F_3O$: C, 66.16; H, 7.03. Found: C, 66.29; H, 6.96.

4.4.2. 1-Phenyl-3-trifluoromethyloct-4-en-3-ol (7). Yield: 58%. Colorless oil. R_f 0.28 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.94 (t, J=7.4 Hz, 3H), 1.26–1.60 (m, 2H), 1.92–2.22 (m, 5H), 2.70 (t, J=13.4 Hz, 2H), 5.57 (d, J=15.6 Hz, 1H), 6.01 (dt, J=15.6, 6.6 Hz, 1H), 7.19–7.38 (m, 5H). ^{13}C NMR δ 15.1, 22.1, 28.6, 34.2, 35.6, 75.8 (q, J=27.2 Hz), 125.7, 126.1, 128.3, 128.4, 128.5, 132.6 (q, J=298.0 Hz), 141.4. ^{19}F NMR δ −82.1. IR (neat): 3470, 2950, 1600, 1500, 1450, 1260, 1170, 980, 750, 700 cm^{-1}. MS m/z 274 (0.3, M$^+$+2), 273 (3, M$^+$+1), 272 (19, M$^+$), 91 (100). Anal. calcd for $C_{15}H_{19}F_3O$: C, 66.16; H, 7.03. Found: C, 66.39; H, 6.97.

4.4.3. (3*R,4*S**)-3,4-Epoxy-1-phenyl-3-trifluoromethyl-(*E*)-oct-1-ene (4b).** Yield: 74% of a mixture of both diastereomers (83:17). Colorless oil. R_f 0.61 (hexane/ethyl acetate 10:1). Major (3*R**,4*S**)-diastereomer: ^{1}H NMR δ 0.90 (t, J=7.0 Hz, 3H), 1.35–1.62 (m, 6H), 3.46 (t, J=5.6 Hz, 1H), 6.32 (d, J=16.0 Hz, 1H), 6.81 (d, J=16.0 Hz, 1H), 7.32–7.54 (m, 5H). ^{13}C NMR δ 13.8, 22.2, 26.1, 27.9, 61.1 (q, J=35.5 Hz), 62.0, 115.4, 123.5 (q, J=277.6 Hz), 126.7, 128.67, 128.71, 133.0, 136.8. ^{19}F NMR δ −75.9. IR (neat): 2949, 2848, 1652, 1491, 1441, 1322, 1263, 1151, 972, 935, 741, 984 cm^{-1}. MS m/z 272 (0.6, M$^+$+2), 271 (8, M$^+$+1), 270 (41, M$^+$), 213 (100, M$^+$−CF$_3$). Anal. calcd for $C_{15}H_{17}F_3O$: C, 66.72; H, 6.32. Found: C, 66.65; H, 6.34. Minor (3*R**,4*R**)-diastereomer (assignable peaks only are shown): ^{1}H NMR δ 2.96 (t, J=5.4 Hz, 1H), 6.38 (d, J=16.0 Hz, 1H), 6.76 (d, J=16.0 Hz, 1H). ^{19}F NMR δ −68.9.

4.4.4. (3*R,4*S**)-3,4-Epoxy-1-phenyl-3-trifluoromethyloct-1-yne (4c).** Yield: 84%. Colorless oil. R_f 0.59 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.95 (t, J=7.2 Hz, 3H), 1.37–1.63 (m, 4H), 1.79–1.90 (m, 2H), 3.44 (t, J=6.0 Hz, 1H), 7.34–7.42 (m, 3H), 7.49–7.54 (m, 2H). ^{13}C NMR δ 13.9, 22.3, 27.7, 28.6, 61.5, 54.0 (q, J=40.4 Hz), 78.1, 88.1, 120.8, 122.0 (q, J=276.2 Hz), 128.4, 129.6, 132.2. ^{19}F NMR δ −75.8. IR (neat): 2951, 2861, 2242, 1487, 1458, 1346, 1315, 1211, 1193, 1162, 1100, 1002, 924, 754, 721, 690 cm^{-1}. MS m/z 270 (0.3, M$^+$+2), 269 (2, M$^+$+1), 268 (11, M$^+$), 199 (4, M$^+$−CF$_3$), 182 (100). Anal. calcd for $C_{15}H_{15}F_3O$: C, 67.16; H, 5.64. Found: C, 66.98; H, 5.71.

4.4.5. (1*R,2*S**)-1,2-Epoxy-1-phenyl-1-trifluoromethylhexane (4d).** Yield: 83% of a mixture of both diastereomers (89:11). Colorless oil. R_f 0.59 (hexane/ethyl acetate 10:1). Major (1*R**,2*S**)-diastereomer: ^{1}H NMR δ 0.82 (t, J=7.0 Hz, 3H), 1.02–1.63 (m, 6H), 3.51 (t, J=7.0 Hz, 1H), 7.39–7.46 (m, 5H). ^{13}C NMR δ 13.7, 22.2, 27.7, 27.9, 60.7, 62.0 (q, J=35.5 Hz), 123.6 (q, J=277.3 Hz), 126.7, 128.4, 129.0, 129.7. ^{19}F NMR δ −75.0. IR (neat): 2951, 2925, 2860, 1756, 1678, 1451, 1179, 1068, 903, 762, 721, 701 cm^{-1}. MS m/z 246 (1, M$^+$+2), 245 (13, M$^+$+1), 244 (100, M$^+$), 187 (59, M$^+$−Bu), 175 (55, M$^+$−CF$_3$). Anal. calcd for $C_{13}H_{15}F_3O$: C, 63.93; H, 6.19. Found: C, 63.82; H, 6.09. Minor (1*R**,2*R**)-diastereomer (only assignable peaks are shown): ^{1}H NMR δ 2.94–3.01 (m, 1H). ^{19}F NMR δ −66.7.

4.4.6. (1*R,2*S**)-1,2-Epoxy-1,4-diphenyl-2-trifluoromethylbutane (4e).** Yield: 93%. Colorless oil. R_f 0.58 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 1.84 (t, J=8.6 Hz, 2H), 2.69 (m, 2H), 4.41 (s, 1H), 6.88 (m, 2H), 7.12–7.25 (m, 3H), 7.30–7.42 (m, 5H). ^{13}C NMR δ 27.4, 30.5, 59.7, 61.7 (q, J=34.3 Hz), 123.0 (q, J=279.2 Hz), 126.1, 126.4, 128.1, 128.4, 128.5, 128.7, 132.6, 140.7. ^{19}F NMR δ −75.1. IR (neat): 3064, 3028, 2939, 2871, 1604, 1496, 1456, 1344, 1168, 1147, 1037, 941, 918, 871, 698 cm^{-1}. MS m/z 293 (0.8, M$^+$+1), 292 (5, M$^+$), 201 (100). Anal. calcd for $C_{17}H_{15}F_3O$: C, 69.85; H, 5.17. Found: C, 69.85; H, 5.25.

4.4.7. (*E*)-(3*R,4*S**)-3,4-Epoxy-1,4-phenyl-3-trifluoromethylbut-1-ene (4f).** Yield: 87% as a colorless solid, mp 51–52°C. R_f 0.58 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 4.57 (s, 1H), 5.99 (d, J=16.4 Hz, 1H), 6.87 (d, J=16.4 Hz, 1H), 7.25–7.32 (m, 5H). ^{13}C NMR δ 61.5, 62.7 (q,

J=35.3 Hz), 114.5, 122.0 (q, J=278.1 Hz), 126.8, 127.0, 128.2, 128.58, 128.62, 128.7, 135.2, 138.4. ^{19}F NMR δ −75.3. MS m/z 291 (6, M^++1), 290 (33, M^+), 289 (3, M^+−1), 105 (100). Anal. calcd for $C_{17}H_{13}F_3O$: C, 70.34; H, 4.51. Found: C, 70.26; H, 4.46.

4.4.8. (3*R,4*S**)-3,4-Epoxy-1,4-diphenyl-3-trifluoromethylbut-1-yne (4g).** Yield: 95%. Colorless oil. R_f 0.50 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 4.51 (s, 1H), 7.27–7.36 (m, 4H), 7.37–7.52 (m, 6H). ^{13}C NMR (CD_3COCD_3) δ 57.4 (q, J=40.2 Hz), 62.8, 78.5, 89.9, 121.2, 123.0 (q, J=276.2 Hz), 128.5, 129.2, 129.7, 130.5, 131.0, 132.6, 132.9. ^{19}F NMR δ −75.6. IR (neat): 3067, 3038, 2233, 1491, 1458, 1406, 1356, 1327, 1213, 1184, 1128, 1013, 916, 889, 756, 721, 696 cm^{-1}. MS m/z 288 (0.1, M^++2), 289 (3, M^++1), 288 (18, M^+), 219 (11, M^+-CF_3), 182 (100). Anal. calcd for $C_{17}H_{11}F_3O$: C, 70.83; H, 3.85. Found: C, 71.12; H, 3.96.

4.4.9. (3*R,4*S**)-3,4-Epoxy-1-phenyl-3-trifluoromethylpent-1-yne (4h).** Yield: 85%. Colorless oil. R_f 0.49 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 1.57 (d, J=5.2 Hz, 3H), 3.57 (q, J=5.2 Hz, 1H), 7.27–7.37 (m, 3H), 7.41–7.55 (m, 2H). ^{13}C NMR δ 14.4, 54.3 (q, J=40.2 Hz), 57.6, 77.9, 88.3, 120.7, 121.9 (q, J=276.3 Hz), 128.4, 129.6, 132.2. ^{19}F NMR δ −75.8. IR (neat): 3152, 3002, 2925, 2225, 1606, 1491, 1442, 1409, 1355, 1305, 1209, 1178, 1056, 911, 755, 695 cm^{-1}. MS m/z 227 (2, M^++1), 226 (14, M^+), 182 (100). Anal. calcd for $C_{12}H_9F_3O$; C, 63.72; H, 4.01. Found: C, 64.00; H, 4.26.

4.4.10. (3*R,4*S**)-3,4-Epoxy-1-phenyl-3-trifluoromethylhex-5-en-1-yne (4i).** Yield: 67%. Colorless oil. R_f 0.50 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 3.89 (d, J=7.0 Hz, 1H), 5.59–5.95 (m, 3H), 7.29–7.46 (m, 3H), 7.49–7.59 (m, 2H). ^{13}C NMR δ 55.2 (q, J=40.6 Hz), 61.2, 78.7, 88.7, 120.6, 121.6 (q, J=276.8 Hz), 124.8, 128.4, 129.7, 130.1, 132.1. ^{19}F NMR δ −75.9. IR (neat): 3061, 2928, 2241, 1491, 1445, 1356, 1298, 1221, 1182, 1153, 1130, 1009, 982, 957, 908, 756, 729, 689 cm^{-1}. MS m/z 240 (0.3, M^++2), 239 (4, M^++1), 238 (31, M^+), 169 (48, M^+-CF_3), 141 (100). Anal. calcd for $C_{13}H_9F_3O$: C, 65.55; H, 3.81. Found: C, 65.50; H, 4.09.

4.4.11. (3*R,4*R**)-3,4-Epoxy-1-phenyl-3-trifluoromethyl-4-(trimethylsilyl)oct-1-yne (4j).** Purified by silica gel column chromatography (hexane/diethyl ether 10:1) followed by GPC. Yield: 79%. Colorless oil. R_f 0.63 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.24 (s, 9H), 0.94 (t, J=7.1 Hz, 3H), 1.31–1.71 (m, 5H), 2.05–2.17 (m, 1H), 7.29–7.40 (m, 3H), 7.44–7.51 (m, 2H). ^{13}C NMR δ 1.22 (q, J=2.7 Hz), 13.9, 23.0, 27.4, 36.2, 58.5 (q, J=42.9 Hz), 65.3, 81.0, 86.7, 120.2, 123.0 (q, J=276.6 Hz), 128.4, 129.3, 132.0. ^{19}F NMR δ −70.7. IR (neat): 3049, 2951, 2860, 2224, 1598, 1488, 1335, 1250, 1181, 1069, 1020, 908, 842, 755, 686 cm^{-1}. MS m/z 342 (0.3, M^++2), 341 (1, M^++1), 340 (5.0, M^+), 271 (100, M^+-CF_3). Anal. calcd for $C_{18}H_{23}F_3OSi$: C, 63.50; H, 6.81. Found: C, 63.43; H, 6.76.

4.4.12. (3*R,4*S**)-3,4-Epoxy-1-phenyl-3-trifluoromethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-oct-1-yne (4k).** Yield: 62%. Pale yellow oil. R_f 0.38 (hexane/ethyl acetate 10:1). ^{1}H NMR (500 MHz) δ 0.93 (t, J=7.3 Hz, 3H), 1.30 (s, 12H), 1.17–1.60 (m, 4H), 1.81 (m, 1H), 1.98 (m, 1H), 7.31–7.37 (m, 3H), 7.46–7.48 (m, 2H). ^{13}C NMR (125 MHz) δ 13.8, 22.6, 24.5, 24.6, 27.8, 32.9, 57.2 (q, J=40.2 Hz), 60.6, 79.2, 84.9, 88.1, 120.9, 121.2 (q, J=276.2 Hz), 128.3, 129.4, 132.0. ^{19}F NMR δ −73.2. IR (neat): 3060, 2979, 2873, 2235, 1444, 1340, 1188, 1134, 1033, 850, 758 cm^{-1}. MS m/z 394 (4, M^+), 393 (16, M^+−1), 310 (100). Anal. calcd for $C_{21}H_{26}BF_3O_3$: C, 63.98; H, 6.65. Found: C, 64.07; H, 6.42.

4.4.13. (3*R,4*S**)-3,4-Epoxy-1,4-diphenyl-3-trifluoromethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-yne (4l).** Yield: 76% as an off-white solid, mp 82°C (dec). R_f 0.35 (hexane/ethyl acetate 10:1). ^{1}H NMR (500 MHz) δ 1.25 (s, 6H), 1.26 (s, 6H), 7.02–7.04 (m, 2H), 7.14–7.18 (m, 2H), 7.22–7.26 (m, 1H), 7.30–7.38 (m, 3H), 7.54–7.57 (m, 2H). ^{13}C NMR (125 MHz) δ 24.3, 24.6, 59.1 (q, J=40.2 Hz), 61.6, 78.8, 85.2, 88.3, 120.6, 121.0 (q, J=276.2 Hz), 126.5, 127.9, 128.1 (2C), 129.3, 131.9, 134.8. ^{19}F NMR δ −73.2. MS m/z 415 (4, M^++1), 414 (16, M^+), 413 (16, M^+−1), 331 (100). Anal. calcd for $C_{23}H_{22}BF_3O_3$: C, 66.69; H, 5.35. Found: C, 66.65; H, 5.54.

4.4.14. (3*R,4*R**)-3,4-Epoxy-4-(hydroxyphenyl)methyl-1-phenyl-3-trifluoromethyloct-1-yne (4m).** Purified by silica gel column chromatography (hexane/diethyl ether 10:1) followed by GPC. Yield: 82% of a 60:40 diastereomeric mixture. Pale yellow oil. R_f 0.35 (hexane/ethyl acetate 10:1). Major (3*R**,4*R**)-diastereomer: ^{1}H NMR δ 0.77 (t, J=7.2 Hz, 3H), 0.92–1.28 (m, 3H), 1.39–1.55 (m, 1H), 1.65–1.88 (m, 1H), 1.93–2.08 (m, 1H), 2.40 (brs, 1H), 5.14 (s, 1H), 7.30–7.52 (m, 10H). ^{13}C NMR δ 13.7, 23.0, 27.4, 29.0, 58.8 (q, J=40.2 Hz), 72.2 (q, J=4.2 Hz), 73.2, 79.3, 89.0, 120.7, 122.6 (q, J=277.9 Hz), 125.6, 127.9, 128.3, 128.5, 129.6, 132.0, 138.3. ^{19}F NMR δ −66.5. IR (neat): 3449, 3065, 2961, 2934, 2874, 2235, 1603, 1493, 1452, 1381, 1325, 1246, 1182, 1055, 937, 841, 756, 731, 689 cm^{-1}. MS m/z 375 (0.1, M^++1), 374 (0.4, M^+), 176 (90), 183 (45), 133 (100). Anal. calcd for $C_{22}H_{21}F_3O_2$: C, 70.58; H, 5.65. Found: C, 70.46; H, 5.62. Minor (3*R**,4*S**)-diastereomer (only assignable peaks are shown): ^{1}H NMR δ 0.72 (t, J=7.8 Hz, 3H), 2.41 (brs, 1H), 5.04 (s, 1H). ^{13}C NMR δ 13.6, 22.8, 26.4, 29.0, 60.4 (q, J=40.0 Hz), 72.7 (q, J=3.4 Hz), 71.4, 79.7, 88.7, 120.9, 122.7 (q, J=278.0 Hz), 125.6, 128.0, 128.4, 128.5, 129.5, 132.0, 139.6. ^{19}F NMR δ −65.8.

4.4.15. (3*R,4*R**)-3,4-Epoxy-4-(diethylhydroxy)methyl-1-phenyl-3-trifluoromethyloct-1-yne (4n).** Purified by silica gel column chromatography (hexane/diethyl ether 10:1) followed by GPC. Yield: 71%. Yellow oil. R_f 0.38 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.93 (t, J=7.0 Hz, 3H), 0.99 (t, J=7.6 Hz, 6H), 1.23–1.57 (m, 5H), 1.64–1.82 (m, 4H), 1.88 (brs, 1H), 2.05–2.28 (m, 1H), 7.24–7.39 (m, 3H), 7.44–7.50 (m, 2H). ^{13}C NMR δ 7.45, 7.78, 13.9, 23.1, 27.3, 29.5, 30.8, 31.6, 58.5 (q, J=42.1 Hz), 74.7, 76.8, 81.3, 89.1, 121.2, 123.1 (q, J=277.4 Hz), 128.4, 129.4, 131.9. ^{19}F NMR δ −60.0. IR (neat): 3601, 2963, 2858, 1485, 1459, 1387, 1305, 1240, 1183, 1150, 1068, 1153, 1070, 1038, 911, 838, 746, 685 cm^{-1}. MS m/z 356 (4, M^++2), 355 (23, M^++1), 354 (100, M^+), 183 (89). Anal. calcd for $C_{20}H_{25}F_3O$: C, 67.78; H, 7.11. Found: C, 68.06; H, 7.00.

4.4.16. (3*R,4*R**)-3,4-Epoxy-4-(hydroxydiphenyl)-methyl-1-phenyl-3-trifluoromethyloct-1-yne (4o).** Purified by silica gel column chromatography (hexane/diethyl ether 10:1) followed by GPC. Yield: 68% as colorless crystals, mp 127°C. R_f 0.32 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.29–0.47 (m, 1H), 0.52 (t, J=7.2 Hz, 3H), 0.79–0.94 (m, 2H), 0.98–1.26 (m, 1H), 1.83 (dt, J=12.6, 4.8 Hz, 1H), 2.26 (dt, J=12.6, 4.8 Hz, 1H), 3.23 (brs, 1H), 7.24–7.52 (m, 15H). ^{13}C NMR δ 13.5, 22.3, 26.0, 33.1, 60.4 (q, J=42.2 Hz), 75.6, 80.1 (q, J=278.3 Hz), 80.7, 90.1, 120.9, 121.8 (q, J=278.3 Hz), 127.8, 127.9, 128.05, 128.09 (2C), 128.2, 128.5, 129.6, 132.0, 140.8, 141.7. ^{19}F NMR δ −60.6. IR (nujol): 3563, 2920, 2850, 2230, 1493, 1310, 1238, 1193, 1180, 960, 760, 698, 660 cm^{-1}. MS m/z 452 (0.1, M$^+$+2), 451 (3, M$^+$+1), 450 (10, M$^+$), 393 (21, M$^+$−Bu), 183 (100), 105 (80). Anal. calcd for $C_{28}H_{25}F_3O$: C, 74.65; H, 5.59. Found: C, 74.85; H, 5.68.

4.4.17. (3*R,4*R**)-3,4-Epoxy-4-(hydroxydiphenyl)-methyl-1-phenyl-3-trifluoromethyloctane (4p).** Purified by silica gel column chromatography (hexane/diethyl ether 10:1) followed by GPC. Yield: 57% as colorless crystals, mp 117°C. R_f 0.30 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.11–0.22 (m, 1H), 0.52 (t, J=7.0 Hz, 3H), 0.66–0.98 (m, 4H), 1.79–1.96 (m, 2H), 2.23–2.38 (m, 1H), 2.96 (t, J=9.6 Hz, 2H), 3.40 (brs, 1H), 7.18–7.45 (m, 15H). ^{13}C NMR δ 13.4, 22.2, 26.5, 30.4, 31.4, 33.3, 66.2 (q, J=39.4 Hz), 73.2, 80.1, 124.1 (q, J=281.5 Hz), 126.5, 127.6 (2C), 127.9, 128.0 (2C), 128.11, 128.13, 128.7, 140.7, 142.1. ^{19}F NMR δ −59.7. IR (nujol): 3568, 2924, 2855, 1493, 1305, 1259, 1173, 1155, 1107, 1043, 883, 772, 706 cm^{-1}. MS m/z 455 (0.1, M$^+$+1), 454 (0.2, M$^+$), 183 (100), 105 (85). Anal. calcd for $C_{28}H_{29}F_3O$: C, 73.99; H, 6.43. Found: C, 74.09; H, 6.59.

4.4.18. (3*R,4*R**)-3,4-Epoxy-4-(hydroxydiphenyl)-methyl-1-phenyl-3-trifluoromethyloct-1-ene (4q).** Purified by silica gel column chromatography (hexane/diethyl ether 10:1) followed by GPC. Yield: 55% of a diastereomeric mixture of 89: 11. Major (3*R**,4*R**)-isomer was separated from the mixture in 46% yield as colorless crystals, mp. 124°C. R_f 0.29 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.09–0.26 (m, 1H), 0.38 (t, J=7.0 Hz, 3H), 0.48–0.88 (m, 3H), 1.69 (dt, J=10.8, 5.4 Hz, 2H), 3.47 (brs, 1H), 6.44 (d, J=16.0 Hz, 1H), 6.84 (d, J=16.0 Hz, 1H), 7.27–7.48 (m, 15H). ^{13}C NMR δ 13.3, 22.2, 26.6, 31.2, 67.6 (q, J=37.2 Hz), 75.5, 79.9, 119.8, 123.3 (q, J=280.0 Hz), 126.8, 127.6, 127.7 (2C), 127.9, 128.1, 128.3, 128.6, 128.8, 134.1, 142.7, 145.5. ^{19}F NMR δ −60.7. IR (nujol): 3574, 2924, 2852, 1493, 1448, 1254, 1190, 1146, 1115, 1086, 1026, 974, 914, 764, 752, 700, 665 cm^{-1}. MS m/z 454 (0.2, M$^+$+2) 453 (4, M$^+$+1), 452 (13, M$^+$), 252 (92), 183 (69), 105 (100). Anal. calcd for $C_{28}H_{27}F_3O$: C, 74.32; H, 6.01. Found: C, 74.08; H, 5.91.

4.4.19. (3*R,4*R**)-3,4-Epoxy-4-(prop-1-en-3-yl)-1-phenyl-3-trifluoromethyloct-1-yne (4r).** To a solution of **1c** (1.0 mmol) in THF (5 mL) was added BuLi (3.0 mmol) at −98°C. The solution was stirred at −98°C for 15 min. Allyl bromide (130 μL, 1.5 mmol) in hexamethylphosphoric triamide (HMPA) (1.0 mL, 6 mmol) was added to the solution at −98°C and the resulting solution was allowed to warm gradually to −78°C over a period of 3 h before quenching with saturated aqueous NH_4Cl solution. Usual workup and silica gel column chromatography (hexane/diethyl ether 10: 1) followed by GPC gave **4r**. Yield: 70%. Pale yellow oil. R_f 0.50 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.93 (t, J=7.1 Hz, 3H), 1.33–1.60 (m, 4H), 1.73–2.07 (m, 2H), 2.48–2.70 (m, 2H), 5.20 (d, J=11.2 Hz, 1H), 5.22 (d, J=15.8 Hz, 1H), 5.73–5.94 (m, 1H), 7.29–7.39 (m, 3H), 7.42–7.49 (m, 2H). ^{13}C NMR δ 13.9, 22.7, 26.7, 34.0 (q, J=3.1 Hz), 58.6 (q, J=34.8 Hz), 69.7, 80.2, 87.9, 119.0, 121.1, 122.6 (q, J=277.5 Hz), 128.4, 129.5, 131.9, 132.1. ^{19}F NMR δ −67.2. IR (neat): 3084, 2961, 2874, 2235, 1643, 1491, 1445, 1406, 1333, 1250, 1184, 1155, 1049, 924, 756, 727, 689 cm^{-1}. MS m/z 309 (0.2, M$^+$+1), 308 (1, M$^+$), 182 (100). Anal. calcd for $C_{18}H_{19}F_3O$: C, 70.12; H, 6.21. Found: C, 70.39; H, 6.22.

4.4.20. (3*R,4*R**)-4-(Dimethylphenyl)silyl-3,4-epoxy-1-phenyl-3-trifluoromethyloct-1-yne (4s).** To a solution of **1c** (280 mg, 1.0 mmol) in THF (5 mL) was added BuLi (1.50 M, 2.0 mL, 3.0 mmol) at −98°C. The solution was stirred at −98°C for 15 min. Iodomethane (93 μL, 1.5 mmol) in HMPA (1.0 mL, 6.0 mmol) were added to the solution at −98°C and the resulting solution was gradually warmed to −78°C over a period of 3 h before quenching with aqueous saturated NH_4Cl solution. Usual workup followed purification on silica gel column chromatography (hexane/diethyl ether 10:1) gave **4s** (180 mg, 64% yield). Colorless oil. R_f 0.58 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.46 (s, 3H), 0.52 (s, 3H), 0.71 (t, J=7.2 Hz, 3H), 0.89–1.62 (m, 5H), 1.90 (dt, J=12.2, 4.5 Hz, 1H), 7.29–7.64 (m, 10H). ^{13}C NMR δ −2.78, −3.29, 13.5, 22.7, 26.8, 36.3, 58.7 (q, J=41.0 Hz), 65.8, 80.9, 86.9, 121.2, 122.9 (q, J=277.0 Hz), 127.7, 128.4, 129.3, 129.5, 132.0, 134.2, 136.5. ^{19}F NMR δ −70.4. IR (neat): 30.61, 2950, 2859, 2221, 1483, 1419, 1332, 1252, 1180, 1162, 1098, 1071, 1118, 903, 810, 753, 693 cm^{-1}. MS m/z 404 (3, M$^+$+2), 403 (11, M$^+$+1), 402 (36, M$^+$), 135 (100). Anal. Calcd for $C_{23}H_{25}F_3OSi$: C, 68.63; H, 6.26. Found: C, 68.49; H, 6.25.

4.4.21. (3*R,4*R**)-3,4-Epoxy-4-methyl-1-phenyl-3-trifluoromethyloct-1-yne (4s′).** Yield: 77%. Colorless oil. R_f 0.58 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.93 (t, J=7.0 Hz, 3H), 1.26–1.52 (m, 4H), 1.62 (s, 3H), 1.75–1.86 (m, 2H), 7.28–7.42 (m, 3H), 7.47–7.53 (m, 2H). ^{13}C NMR δ 13.8, 20.9, 22.7, 32.3 (q, J=3.1 Hz), 58.6 (q, J=39.7 Hz), 68.3, 80.5, 87.8, 121.1, 122.7 (q, J=277.4 Hz), 128.4, 129.4, 132.1. ^{19}F NMR δ −67.7. IR (neat): 3059, 2961, 2936, 2874, 2235, 1491, 1445, 1385, 1331, 1252, 1188, 1155, 1063, 1011, 922, 897, 756, 729, 691 cm^{-1}. MS m/z 284 (0.2, M$^+$+2), 283 (1, M$^+$+1), 282 (7, M$^+$), 267 (1, M$^+$−Me), 182 (100). Anal. calcd for $C_{16}H_{17}F_3O$: C, 68.07; H, 6.07. Found: C, 68.02; H, 6.04.

4.5. General procedure for the preparation of tetrasubstituted alkenes 8

To a solution of **1** (1.0 mmol) in THF (3 mL) was added Grignard reagent R^2MgBr (1.0 mmol) at −78°C. After stirred at −78°C for 1 h, the solution was added R^2Li (3.0 mmol) at −78°C and was allowed to warm to room temperature gradually before quenching with saturated aqueous NH_4Cl solution. The aqueous layer was extracted with diethyl ether three times and the combined organic

layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel giving rise to **8**.

4.5.1. 2-Methyl-5-phenyl-3-trifluoromethylpet-2-ene (8a). Yield: 60%. Colorless oil. R_f 0.63 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 1.63 (q, J=2.2 Hz, 3H), 1.88 (q, J=2.6 Hz, 3H), 2.47 (t, J=8.6 Hz, 2H), 2.69 (m, 2H), 7.18–7.36 (m, 5H). ^{13}C NMR δ 21.5, 21.6, 30.6 (q, J=2.7 Hz), 35.3, 123.7 (q, J=27.0 Hz), 125.2 (q, J=274.3 Hz), 126.0, 128.4, 128.5, 141.3, 141.4. ^{19}F NMR δ −57.8. IR (neat): 3030, 2930, 1660, 1600, 1600, 1500, 1450, 1320, 1220, 1180, 1110, 1040, 750, 700 cm^{-1}. MS m/z 230 (0.2, M^++2), 229 (3, M^++1), 228 (18, M^+), 91 (100). HRMS (EI) m/z M^+ calcd for $C_{13}H_{15}F_3$, 228.1126; found, 228.1109. Anal. calcd for $C_{13}H_{15}F_3$: C, 68.41; H, 6.62. Found: C, 68.67; H, 6.90.

4.5.2. 1-Phenyl-4-methyl-3-trifluoromethylpenta-1,3-diene (8b). Yield: 15%. Colorless oil. R_f 0.50 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 2.00–2.07 (m, 6H), 6.59 (d, J=16.8 Hz, 1H), 6.70 (d, J=16.8 Hz, 1H), 7.24–7.48 (m, 5H). ^{19}F NMR δ −56.9. IR (neat): 3020, 2920, 1640, 1600, 1490, 1440, 1340, 1220, 1110, 960, 750, 690 cm^{-1}. MS m/z 228 (0.4, M^++2), 227 (7, M^++1), 226 (50, M^+), 211 (100). HRMS (EI) m/z M^+ calcd for $C_{13}H_{13}F_3$, 228.1126; found, 228.1109.

4.5.3. 4-Butyl-1-phenyl-3-trifluoromethylocta-1,3-diene (8c). Yield: 26%. Colorless oil. R_f 0.65 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.89–0.97 (m, 6H), 1.31–1.50 (m, 8H), 2.20–2.40 (m, 4H), 6.60 (d, J=16.4 Hz, 1H), 6.73 (d, J=16.4 Hz, 1H), 7.26–7.46 (m, 5H). ^{13}C NMR δ 13.89, 13.93, 22.9, 23.1, 30.7, 31.1, 33.5, 34.0, 123.4 (q, J=28.0 Hz), 124.5 (q, J=275.0 Hz), 126.3, 127.8, 128.7, 132.7, 137.3, 152.5. ^{19}F NMR δ −56.2. IR (neat): 2960, 2870, 1590, 1460, 1340, 1230, 1110, 960, 750, 690 cm^{-1}. MS m/z 312 (2, M^++2), 311 (17, M^++1), 310 (78, M^+), 197 (100). Anal. calcd for $C_{19}H_{25}F_3$: C, 73.52; H, 8.12. Found: C, 73.45; H, 8.24.

4.5.4. 4-Methyl-1-phenyl-3-trifluoromethylpent-3-en-1-yne (8d). Yield: 55%. Colorless oil. R_f 0.63 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 2.08 (q, J=2.2 Hz, 3H), 2.18 (q, J=2.2 Hz, 3H), 7.31–7.37 (m, 3H), 7.44–7.51 (m, 2H). ^{19}F NMR δ −58.4. IR (neat): 3050, 2910, 2200, 1620, 1590, 1480, 1440, 1370, 1340, 1250, 1230, 1160, 1120, 1040, 890, 750 cm^{-1}. MS m/z 226 (0.8, M^++2), 225 (13, M^++1), 224 (100, M^+), 155 (54). HRMS (EI) m/z M^+ calcd for $C_{13}H_{11}F_3$, 224.0813; found, 224.0802.

4.5.5. 4-Butyl-1-phenyl-3-trifluoromethyloct-3-en-1-yne (8e). Yield: 71%. Colorless oil. R_f 0.59 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.90–0.99 (m, 6H), 1.32–1.63 (m, 8H), 2.36 (m, 2H), 2.49 (t, J=7.2 Hz, 2H), 7.32–7.37 (m, 3H), 7.42–7.48 (m, 2H). ^{13}C NMR δ 13.77, 13.80, 22.9, 23.0, 30.0, 60.6, 32.5, 35.5, 82.8, 95.3, 11.3 (q, J=33.5 Hz), 122.5 (q, J=273.0 Hz), 123.0, 128.3, 128.4, 131.3, 162.3. ^{19}F NMR δ −57.8. IR (neat): 2960, 2870, 1610, 1590, 1490, 1460, 1350, 1260, 1160, 1120, 1060, 750, 690 cm^{-1}. MS m/z 310 (2, M^++2), 309 (19, M^++1), 308 (94, M^+), 196 (100). Anal. calcd for $C_{19}H_{23}F_3$: C, 74.00; H, 7.52. Found: C, 73.73; H, 7.58.

4.5.6. 1,1,1-Trifluoro-3-methyl-2-phenylbut-2-ene (8f). Yield: 69%. Colorless oil. R_f 0.68 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 1.62 (q, J=2.4 Hz, 3H), 2.07 (q, J=2.4 Hz, 3H), 7.13–7.17 (m, 2H), 7.32–7.42 (m, 3H). ^{19}F NMR δ −56.3 (t, J=2.6 Hz). MS m/z 202 (0.8, M^++2), 201 (12, M^++1), 200 (100, M^+), 185 (41). HRMS (EI) m/z M^+ Calcd for $C_{11}H_{11}F_3$, 200.0813; found, 200.0821.

4.5.7. 3-Butyl-1,1,1-trifluoro-2-phenylhep-2-ene (8g). Yield: 60%. Colorless oil. R_f 0.66 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.73 (t, J=7.2 Hz, 3H), 0.96 (t, J=7.2 Hz, 3H), 1.00–1.53 (m, 8H), 1.88 (t, J=6.8 Hz, 2H), 2.33–2.40 (m, 2H), 7.14–7.18 (m, 2H), 7.34–7.41 (m, 3H). ^{13}C NMR δ 13.7, 13.9, 22.6, 23.0, 30.3, 31.1, 31.6, 33.3, 124.3 (q, J=274.0 Hz), 127.1 (q, J=29.0 Hz), 127.6, 128.2, 130.0, 135.9, 152.0 (q, J=2.7 Hz). ^{19}F NMR δ −56.0. IR (neat): 2960, 2870, 1640, 1460, 1330, 1240, 1150, 1110, 910, 760, 700 cm^{-1}. MS m/z 286 (0.7, M^++2), 285 (9, M^++1), 284 (5, M^+), 172 (100). Anal. calcd for $C_{17}H_{23}F_3$: C, 71.80; H, 8.15. Found: C, 71.98; H, 8.37.

4.5.8. (*E*)-4-Methyl-1-phenyl-3-trifluoromethyloct-3-en-1-yne (5a). R_f 0.60 (hexane/ethyl acetate 10: 1). ^{1}H NMR δ 0.96 (t, J=7.0 Hz, 3H), 1.26–1.62 (m, 4H), 2.05 (q, J=2.2 Hz, 3H), 2.51 (dt, J=7.7, 1.3 Hz, 2H), 7.29–7.34 (m, 3H), 7.39–7.48 (m, 2H). ^{13}C NMR δ 13.9, 19.1 (q, J=1.9 Hz), 22.5, 29.5 (q, J=1.2 Hz), 38.17, 82.53 (q, J=3.7 Hz), 95.09, 111.5 (q, J=33.9 Hz), 122.5 (q, J=272.9 Hz), 123.0, 128.3, 128.4, 131.3, 157.6. ^{19}F NMR δ −58.5. IR (neat): 3050, 2950, 2850, 2200, 1615, 1595, 1485, 1440, 1350, 1255, 1225, 1120, 1080, 1010, 910, 750, 690 cm^{-1}. MS m/z 268 (3, M^++2), 267 (29, M^++1), 266 (100, M^+), 251 (4, M^+−Me), 197 (53, M^+−CF_3). Anal. calcd for $C_{16}H_{17}F_3$: C, 72.16; H, 6.43. Found: C, 72.22; H, 6.51.

4.5.9. (*E*)-4-Methyl-1-phenyl-3-trifluoromethyloct-3-en-1-yne (5b). R_f 0.58 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.95 (t, J=7.0 Hz, 3H), 1.10 (t, J=7.5 Hz, 3H), 1.36–1.62 (m, 4H), 2.38 (ddq, J=7.5, 1.6, 1.6 Hz, 2H), 2.45–2.53 (m, 2H), 7.28–7.35 (m, 3H), 7.38–7.48 (m, 2H). ^{13}C NMR δ 12.9, 13.9, 22.9, 25.8 (q, J=1.9 Hz), 30.0, 35.1, 82.8 (q, J=3.0 Hz), 95.2, 111.1 (q, J=33.8 Hz), 122.5 (q, J=272.9 Hz), 123.0, 128.35, 128.41, 131.3, 163.4 (q, J=2.3 Hz). ^{19}F NMR δ −58.0. IR (neat): 3057, 2959, 2876, 2210, 1612, 1595, 1491, 1458, 1445, 1356, 1275, 1256, 1217, 1165, 1123, 1055, 999, 914, 754, 729, 689 cm^{-1}. MS m/z 282 (3, M^++2), 281 (26, M^++1), 280 (100, M^+), 223 (38, M^+−Bu), 251 (27, M^+−Et), 211 (9, M^+−CF_3). Anal. calcd for $C_{16}H_{17}F_3$: C, 72.84; H, 6.83. Found: C, 72.80; H, 6.90.

4.6. Typical procedure for the preparation of tetrasubstituted alkenes 5

To a solution of **1c** (280 mg, 1.0 mmol) in THF (5 mL) was added BuLi (1.50 M, 2.0 mL, 3.0 mmol) at −98°C. The solution was stirred at −98°C for 15 min and then was added PhC≡CB(OCMe$_2$)$_2$ (460 mg, 2.0 mmol) at −98°C. The resulting solution was gradually warmed to room temperature and then refluxed for 4 h before quenching with aqueous saturated NH_4Cl solution. The aqueous layer was extracted with diethyl ether three times. The combined

organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The subsequent purification by column chromatography on silica gel (hexane only) gave **5c** (260 mg, 74% yield).

4.6.1. (*Z*)-1-Phenyl-4-phenylethynyl-3-trifluoromethyl-oct-3-en-1-yne (5c). Pale yellow oil. R_f 0.58 (hexane/ethyl acetate 10: 1). ^{1}H NMR δ 0.99 (t, J=7.1 Hz, 3H), 1.42 (tq, J=7.2, 7.1 Hz, 2H), 1.74 (tt, J=7.4, 7.2 Hz, 2H), 2.70 (t, J=7.4 Hz, 2H), 7.32–7.41 (m, 6H). ^{13}C NMR δ 13.9, 22.2, 30.0, 36.2, 82.6, 86.3, 101.7, 104.2, 118.5 (q, J=33.4 Hz), 121.6 (q, J=273.1 Hz), 122.4, 128.4 (2C), 129.1, 131.4 (2C), 131.9, 137.9. ^{19}F NMR δ −61.1. IR (neat): 3063, 2959, 2930, 2862, 2210, 2187, 1597, 1570, 1491, 1443, 1356, 1242, 1192, 1132, 1069, 914, 754, 689, 665 cm^{-1}. MS m/z 354 (4, M$^+$+2), 353 (28, M$^+$+1), 352 (100, M$^+$), 241 (37, M$^+$−PhCC). Anal. calcd for $C_{23}H_{19}F_3$: C, 78.39; H, 5.43. Found: C, 78.63; H, 5.36.

4.6.2. (3*Z*,5*E*)-4-Butyl-1-phenyl-3-trifluoromethyldec-3,5-dien-1-yne (5d). Yield: 56%. Pale yellow oil. R_f 0.60 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.92 (t, J=7.4 Hz, 3H), 0.96 (t, J=7.0 Hz, 3H), 1.27–1.60 (m, 8H), 2.21 (t, J=7.8 Hz, 2H), 2.67 (t, J=7.5 Hz, 2H), 6.17 (dt, J=15.6, 7.8 Hz, 1H), 6.59 (d, J=15.6 Hz, 1H), 7.28–7.34 (m, 3H), 7.39–7.50 (m, 2H). ^{13}C NMR δ 13.9, 14.0, 22.3, 23.0, 31.1, 31.3, 31.8, 33.3, 84.1, 98.3, 110.1 (q, J=33.6 Hz), 122.5 (q, J=273.5 Hz), 123.1, 125.5, 128.4, 128.5, 131.3, 139.5, 154.0. ^{19}F NMR δ −56.0. IR (neat): 3063, 2961, 2934, 2874, 2203, 1784, 1684, 1597, 1491, 1469, 1350, 1242, 1171, 1126, 1069, 908, 756, 733, 689, 665 cm^{-1}. MS m/z 336 (0.2, M$^+$+2), 335 (3, M$^+$+1), 334 (14, M$^+$), 236 (100). HRMS (EI) m/z M$^+$ calcd for $C_{21}H_{25}F_3$, 334.1908; found, 334.1877.

4.6.3. (*Z*)-1,4-Diphenyl-3-trifluoromethyloct-3-en-1-yne (5e). Yield: 66% as colorless crystals, mp 67°C. R_f 0.59 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.89 (t, J=7.0 Hz, 3H), 1.27–1.44 (m, 4H), 2.80 (t, J=6.4 Hz, 2H), 7.10–7.21 (m, 2H), 7.27–7.40 (m, 6H), 7.46–7.53 (m, 2H). ^{13}C NMR δ 13.9, 22.5, 29.2, 39.1, 82.7, 95.9, 112.2 (q, J=32.8 Hz), 121.9 (q, J=273.1 Hz), 122.7, 127.0, 127.9, 128.0, 128.4, 128.8, 131.5, 138.8, 158.9. ^{19}F NMR δ −57.2. IR (nujol): 2926, 2858, 2210, 1589, 1572, 1489, 1445, 1344, 1231, 1182, 1096, 1070, 1011, 920, 779, 756, 706, 691, 646 cm^{-1}. MS m/z 330 (3, M$^+$+2), 329 (22, M$^+$+1), 328 (100, M$^+$), 271 (15, M$^+$−Bu), 251 (15, M$^+$−Ph). HRMS (EI) M$^+$ calcd for $C_{21}H_{19}F_3$, 328.1439; found, 328.1471.

4.6.4. (*E*)-1-4-Diphenyl-3-trifluoromethyloct-3-en-1-yne (5e′). Yield: 84%. Colorless oil. R_f 0.59 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.85 (t, J=6.8 Hz, 3H), 1.21–1.34 (m, 4H), 2.64–2.80 (m, 2H), 7.09–7.58 (m, 10H). ^{13}C NMR δ 13.7, 22.6, 30.4, 34.5, (q, J=1.9 Hz), 93.8, 94.4 112.5 (q, J=33.6 Hz), 122.5 (q, J=273.5 Hz), 122.7, 128.0, 128.2, 128.3, 128.4, 128.7, 131.2, 140.3, 159.7. ^{19}F NMR δ −58.0. IR (neat): 3059, 2961, 2932, 2874, 2212, 1591, 1491, 1442, 1356, 1271, 1248, 1171, 1126, 1069, 914, 756, 691, 665, 646 cm^{-1}. MS m/z 330 (3, M$^+$+2), 329 (25, M$^+$+1), 328 (100, M$^+$), 271 (14, M$^+$−Bu), 251 (14, M$^+$−Ph). HRMS (EI) m/z M$^+$ calcd for $C_{21}H_{19}F_3$, 328.1439; found, 328.1425.

4.6.5. (*E*)-2-(1-Butyl-4-phenyl-2-trifluoromethylbut-1-en-3-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6E, R^2=Bu). Yield: 76%. Pale yellow oil. R_f 0.34 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.94 (t, J=7.0 Hz, 3H), 1.31 (s, 12H), 1.35–1.62 (m, 4H), 2.57 (t, J=6.8 Hz, 2H), 7.24–7.36 (m, 3H), 7.42–7.49 (m, 2H). ^{13}C NMR δ 13.8, 22.6, 24.6, 30.2, 34.1, 81.5, 84.5, 96.9, 119.3 (q, J=33.8 Hz), 122.2 (q, J=271.9 Hz), 122.4, 128.3, 128.8, 131.6, 151.0. ^{19}F NMR δ −62.9. IR (neat): 2961, 2861, 2208, 1612, 1491, 1445, 1346, 1249, 1180, 1134, 1030, 962, 851, 756, 689, 665 cm^{-1}. MS m/z 380 (3, M$^+$+2), 379 (25, M$^+$+1), 378 (100, M$^+$), 377 (23, M$^+$−1). Anal. calcd for $C_{21}H_{26}BF_3O_2$: C, 66.68; H, 6.93. Found: C, 66.44; H, 6.96.

4.6.6. (*E*)-2-(1,4-Diphenyl-2-trifluoromethyl-but-1-en-3-ynyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (6E, R^2=Ph). Yield: 86%. Pale yellow oil. R_f 0.24 (hexane/ethyl acetate 10:1). ^{1}H NMR (500 MHz) δ 1.29 (s, 12H), 7.24–7.40 (m, 8H), 7.58 (m, 2H). ^{13}C NMR (125 MHz) δ 24.6, 82.8, 84.8, 95.8, 119.2 (q, J=33.5 Hz), 122.2, 123.5 (q, J=272.2 Hz), 128.1, 128.3 (2C), 128.6, 128.9, 131.6, 137.5, 147.7. ^{19}F NMR δ −63.1. IR (neat): 3058, 2981, 2931, 2208, 1737, 1602, 1490, 1444, 1373, 1340, 1253, 1217, 1137, 1068, 977, 850 cm^{-1}. MS m/z 400 (1, M$^+$+2), 399 (7, M$^+$+1), 398 (28, M$^+$), 298 (100). Anal. calcd for $C_{23}H_{22}BF_3O_2$: C, 69.37; H, 5.57. Found: C, 69.63; H, 5.83.

4.6.7. (*Z*)-2-(1-Butyl-4-phenyl-2-trifluoromethyl-but-1-en-3-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6Z, R^2=Bu). Yield: 54%. Pale yellow oil. R_f 0.34 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.95 (t, J=6.8 Hz, 3H), 1.32 (s, 12H), 1.17–1.63 (m, 4H), 2.41–2.59 (m, 2H), 7.29–7.34 (m, 2H), 7.43–7.48 (m, 3H). ^{13}C NMR δ 13.8, 22.7,24.7, 31.2, 31.6, (q, J=1.5 Hz), 84.1, 84.4, 93.0, 120.0 (q, J=30.0 Hz), 121.6 (q, J=276.0 Hz), 122.7, 128.3, 128.6, 131.5, 151.4. ^{19}F NMR δ −59.2. IR (neat): 2980, 2931, 2874, 2210, 1599, 1490, 1445, 1381, 1310, 1246, 1178, 1063, 964, 847, 756, 691, 667 cm^{-1}. MS m/z 380 (3, M$^+$+2), 379 (23, M$^+$+1), 378 (100, M$^+$), 377 (23, M$^+$−1). HRMS (EI) m/z M$^+$ calcd for $C_{21}H_{26}BF_3O_2$, 378.1978; found, 378.2009.

4.6.8. (*Z*)-2-(1,4-Diphenyl-2-trifluoromethyl-but-1-en-3-ynyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (6Z, R^2=Ph). Yield: 31%. Pale yellow oil. R_f 0.24 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 1.28 (s, 12H), 7.22–7.55 (m, 10H). ^{13}C NMR δ 24.4, 84.2, 84.8, 94.2, 120.1 (q, J=33.4 Hz), 121.1 (q, J=275.7 Hz), 122.3, 127.1, 127.8, 128.1, 128.4, 129.0, 131.7, 136.9, 150.1. ^{19}F NMR δ −58.5. MS m/z 400 (0.6, M$^+$+2), 399 (4, M$^+$+1), 398 (14, M$^+$), 298 (100). Anal. calcd for $C_{23}H_{22}BF_3O_2$: C, 69.37; H, 5.57. Found: C, 69.20; H, 5.45.

4.6.9. (*Z*)-(1,4-Diphenyl-2-trifluoromethyl-but-1-en-3-ynyl)-dimethyl-phenyl-silane (9). Yield: 14%. Pale yellow oil. R_f 0.46 (hexane/ethyl acetate 10:1). ^{1}H NMR δ 0.33 (s, 3H), 0.34 (s, 3H), 6.96–7.04 (m, 3H), 7.17–7.38 (m, 10H), 7.48–7.56 (m, 2H). ^{13}C NMR δ −0.77, 0.85, 84.0, 98.3, 120.8 (q, J=272.8 Hz), 122.2, 125.7 (q, J=35.3 Hz), 126.5, 126.7, 127.68, 127.73, 128.0, 128.1, 128.8, 129.2, 131.6, 133.0, 133.8, 136.9, 139.8, 143.4. ^{19}F NMR δ −60.1. IR (neat): 3069, 3053, 3022, 2956, 2204, 1596, 1489, 1427, 1338, 1249, 1168, 1132, 1066, 939, 813, 756, 700 cm^{-1}.

MS *m/z* 408 (7, M^++2), 407 (27, M^++1), 406 (78, M^+), 309 (100). HRMS (EI) *m/z* M^+ calcd for $C_{25}H_{21}F_3Si$, 406.1365; found, 406.1362.

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