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Novel and efficient approach to (*Z*)-4-trifluoroethylidene-1,3-dioxolane derivatives via (trifluoromethyl)ethynylation of ketones and aldehydes

Sung Lan Jeon [a], Ji Hoon Choi [a], Jung Ah Cho [a], Bum Tae Kim [b], In Howa Jeong [a,*]

[a] *Department of Chemistry, Yonsei University, Wonju, Republic of Korea*
[b] *Korea Research Institute of Chemical Technology, Daejeon, Republic of Korea*

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ABSTRACT

Perfluoroalkylated 4-trifluoroethylidene-1,3-dioxolanes **2a–p** were prepared in quantitative yields from the reaction of new stable (trifluoromethyl)ethynylation reagent **1a** with TBAF at −15 °C for 10 min, followed by treatment with phenyl perfluoroalkylated ketones at room temperature. The use of aldehydes under the same reaction condition afforded 1,3-dioxolanes **2q–r** in good yields. The reaction of **1a** with TBAF, followed by treatment with aldehydes or ketones at −15 °C for 10 min and then with trifluoroacetophenone at room temperature provided 1,3-dioxolane derivatives **2s–t** in good yields. Tetrabutylammonium trifluoropropynylide [II] was treated with benzaldehyde derivatives at −15 °C for 10 min, followed by treatment with trifluoroacetophenone, to give the corresponding 1,3-dioxolanes **2u–z** and 1,3-dioxines **3u–z** with different reaction condition.

1. Introduction

Fluorinated 1,3-dioxolane compounds have attracted much attention in recent years because of their unique nonlinear optical, electrical and chemical properties, which are very important factors in the development of new optical material. 4-Trifluoroethylidene-1,3-dioxolane derivatives are outstanding compounds having nonlinear optical properties [1]. Amorphous polymers, new Teflon-AF fluorocopolymer, formed from either polymerization of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole monomer [2] or perfluoro(5-methylene-2,2-dimethyl-1,3-dioxolane) monomer [3] showed better thermal and chemical stability. Fluorinated dioxolane exocyclic olefins are also a quite useful intermediate to give the corresponding epoxides, which furnish as lubricants, curing materials, adhesives and coatings [4]. Several examples have been reported for the synthesis of fluorinated 1,3-dioxolane, but the methodology for its preparations is quite limited. Fluorination of 4- or 5-chlorinated 1,3-dioxolane has been known as a general method for the synthesis of 4- or 5-fluorinated 1,3-dioxolanes [5]. Radical addition reaction of 1,3-dioxolane with perfluoro-1-alkenes in the presence of BPO also gave 4-fluoroalkylated 1,3-dioxolane in excellent yields [6]. 2,2-Bis(trifluoromethyl)-4-methylidene as an exocyclic olefin was synthesized via dehydrobromination of 2,2-bis(trifluoromethyl)-4-bromomethyl-1,3-dioxolane which can be prepared from the reaction of epibromohydrin with hexafluoroacetone [4]. Reaction of trifluoropropyne with enol silyl ether generated from aldehyde in the presence of tetrabutylammoniun fluoride, provided the corresponding 2,5-disubstituted 4-trifluoroethylidene-1,3-dioxolanes as trifluoromethylated exocyclic olefin [7]. 2-Bromotrifluoropropene was reacted with ketones having α-hydrogen from carbonyl group in the presence of sodium methoxide to give the corresponding 2,2,5,5-tetrasubstituted 4-trifluoroethylidene-1,3-dioxolanes in high yields [1]. Although the reaction mechanisms of these two reactions are not clear, it seems that the generation of enolate as an intermediate is a key step to proceed these reactions. Therefore, aldehydes or ketones having α-hydrogen carbonyl group is the key factor for the synthesis of 4-trifluoroethylidene-1,3-dioxolanes.

Herein, we wish to report a novel and efficient method for the synthesis of 4-trifluoroethylidene-1,3-dioxolane derivatives via new stable (trifluoromethyl)ethynylation reagent [8–12] and mechanistic rationalization for the formation of these compounds.

2. Results and discussion

From previous report that described literature report shows the reaction of an ethereal solution of trifluoropropynyl lithium with

* Corresponding author. Tel.: +82 33 760 2240; fax: +82 33 763 4323.
E-mail address: jeongih@yonsei.ac.kr (I.H. Jeong).

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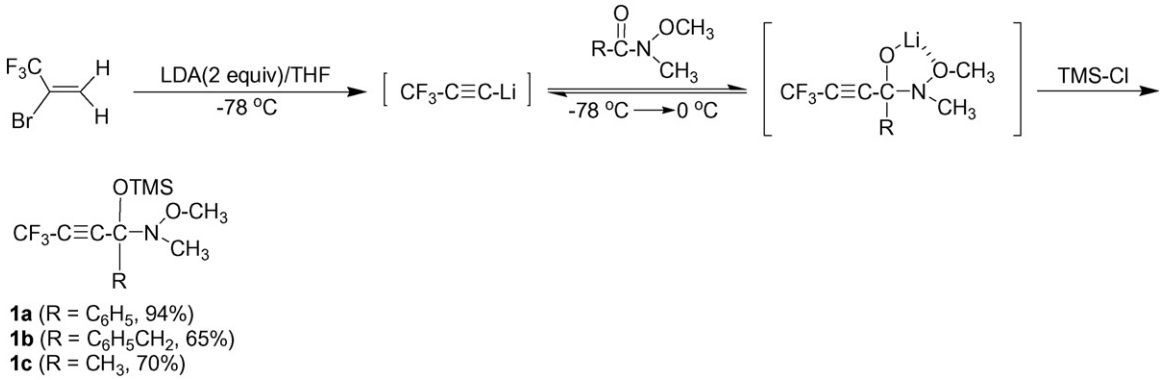


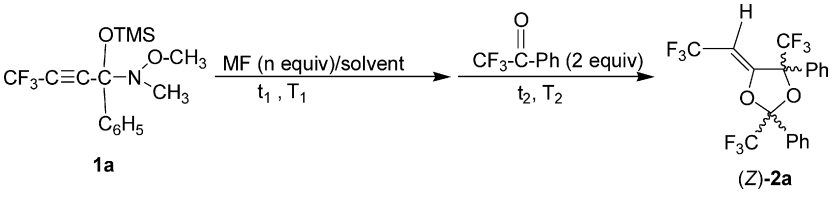
Scheme 1.

Weinreb amide (*N*-methoxy-*N*-methylbenzamide), resulted in the tar formation [13]. By carefully monitoring, it is observed that the intermediate formed from the reaction of trifluoropropynyl lithium with Weinreb amide was stable at 0 °C, in which *N*-methoxy group in Weinreb benzamide plays an important role in the formation of lithium complex. Therefore, the trapping reaction of intermediate with trimethylsilyl chloride at 0 °C, followed by warming to room temperature afforded trifluoromethylated propargyl trimethylsilyl ether derivatives **1a–c** as new stable (trifluoromethyl)ethynylation reagents in 70–94% yields (Scheme 1), in which trifluoropropynyl lithium was generated from the reaction of 2-bromotrifluoropropene with LDA at −78 °C [14–17]. The reaction of 2-bromotrifluoropropene with LDA results in the formation of trifluoropropynyl lithium in higher yields with respect to reactions trifluoropropyne with *n*-BuLi [18].

In order to examine the ability of **1a–c** as (trifluoromethyl)ethynylation reagent we carried out the reaction of **1a–c** with reagents as a fluoride source such as tetrabutylammonium fluoride (TBAF), cesium fluoride, and potassium fluoride in various solvents at different reaction temperatures, followed by treatment with 2,2,2-trifluoroacetophenone (2 equiv.) to give 4-trifluoroethylidene-1,3-dioxolane derivative **2a** (Table 1). It has been found that the reaction of **1a** (1.3 equiv.) with TBAF (1.3 equiv.) in acetonitrile at −15 °C for 10 min, followed by reaction with 2,2,2-trifluoroacetophenone at room temperature for 1 h, afforded only (*Z*)-**2a** (1:1 diastereomer ratio) in 99% yield, while **1b** and **1c** provided (*Z*)-**2a** under the same reaction conditions in 90% and 85% yields, respectively. The use of acetonitrile resulted in better yields as compared to ether and THF. The use of 1.0 equiv. of **1a** in this reaction also provided the low yield of (*Z*)-**2a**. When the reaction of **1a** with TBAF was performed at −35 °C for 10 min, followed by reaction with 2,2,2-trifluoroacetophenone at room temperature for 1 h, however, (*Z*)-**2a** was obtained in 80% yield.

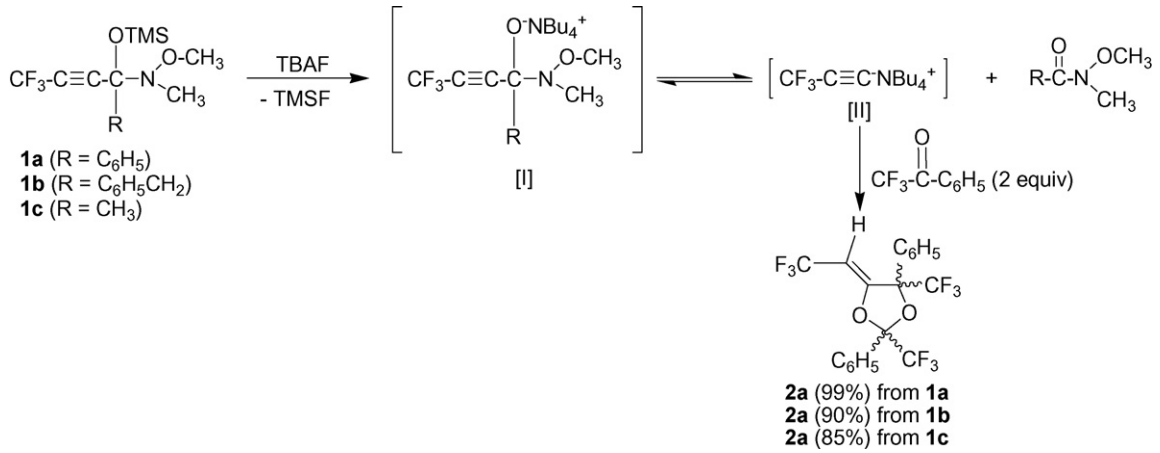
Intermediate [I] generated from the reaction of **1a** with TBAF [11], was suggested to be an equilibrium with *N*-methoxy-*N*-methylbenzamide and tetrabutylammonium trifluoropropynyl anion [II] (Scheme 2) which acts as a (trifluoromethyl)ethynylation reagent to react with 2,2,2-trifluoroacetophenone. *N*-Methoxy-*N*-methylbenzamide, which is a key reagent for the formation of **1** and relatively expensive, was always recovered in quantitative yield at the end of reaction. In order to compare reactivity between [II] and trifluoropropynyl lithium against 2,2,2-trifluoroacetophenone, we also carried out the direct reaction of 2,2,2-trifluoroacetophenone (2 equiv.) with trifluoropropynyl lithium, either generated from the reaction of 2-bromotrifluoropropene with LDA at −78 °C or from the reaction of trifluoropropyne with *n*-BuLi at −78 °C, but desired product (*Z*)-**2a** was obtained in only 35% yield. Thus, tetrabutylammonium, the counter cation of trifluoropropy-

Table 1
Optimization of reaction condition for the preparation of 4-trifluoroethylidene-1,3-dioxolane derivatives **2a**

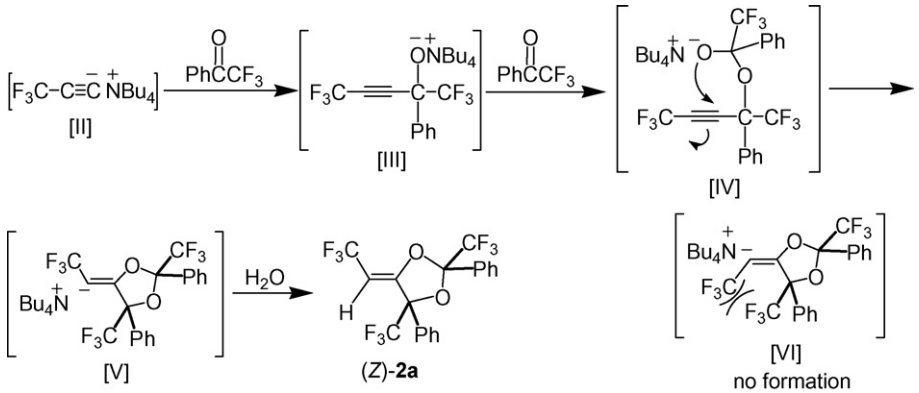


Entry	MF	*n*	Solvent	t_1 (°C)	T_1 (min)	t_2 (°C)	T_2 (h)	Yield (%)[a]
1	TBAF	1.0	Ether	−78	60	−78	1	0
2	TBAF	1.0	Ether	−35	60	−35	1	0
3	TBAF	1.0	Ether	−15	60	−15	1	0
4	TBAF	1.0	Ether	−15	60	−15	1	0
5	TBAF	1.0	Ether	−15	10	−15	1	0
6	TBAF	1.0	Ether	−15	10	−15 → rt	1	30
7	TBAF	1.0	Ether	−15	10	rt	1	79
8	TBAF	1.3	Ether	−15	10	rt	1	96
9	TBAF	1.3	THF	−15	10	rt	1	80
10	TBAF	1.3	CH_3CN	−15	10	rt	1	99
11	TBAF	1.3	CH_3CN	−35	10	rt	1	80
12	KF	1.3	DMF	−15	10	rt	1	25

[a] Isolated yield.



Scheme 2.



Scheme 3.

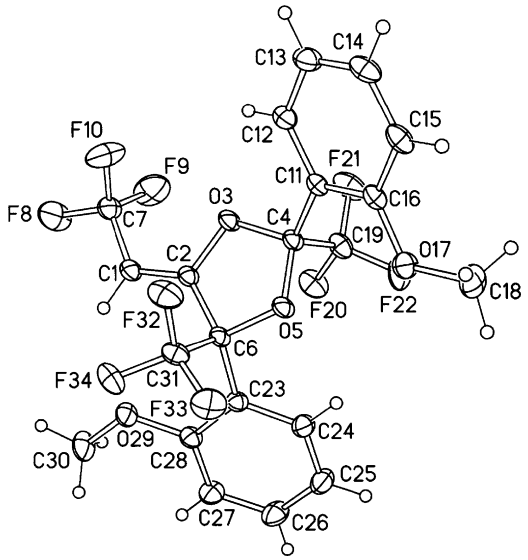


Fig. 1. ORTEP representation of *anti*-(*Z*)-**2e** at the 50% probability level. Selected bond lengths (Å) and angles (°): C1–C2 1.318(2), C1–C7 1.479(3), C1–H1A 0.9300, C2–O3 1.3606(19), C2–C6 1.523(2), O3–C4 1.4172(19), C4–O5 1.405(2), C4–C11 1.515(2), C4–C19 1.548(3), O5–C6 1.4317(18), C6–C23 1.542(2), C6–C31 1.544(3); C2–C1–C7 123.38(17), C2–C1–H1A 118.3, C7–C1–H1A 118.3, C1–C2–O3 119.99(16), C1–C2–C6 131.65(16), O3–C2–C6 108.20(13), C2–O3–C4 109.93(13), O5–C4–O3 106.29(12), O5–C4–C11 112.67(14), O3–C4–C11 109.90(14), O5–C4–C19 109.88(15), O3–C4–C19 105.15(15), C11–C4–C19 112.50(14), C4–O5–C6 110.91(12), O5–C6–C2 102.38(12), O5–C6–C23 108.76(13), C2–C6–C23 119.47(14), O5–C6–C31 103.27(13), C23–C6–C31 111.66(14), C2–C6–C31 109.67(15).

nyl anion, plays an important role for the formation of **2a** in quantitative yield. However, the addition of tetrabutylammonium chloride in this direct reaction did not provide improved yield of (*Z*)-**2a**.

It seems likely that the reaction mechanism in the formation of (*Z*)-**2a** involves the addition of intermediate [II] toward 2,2,2-trifluoroacetophenone to give an intermediate [III], which further reacts with another equivalence of 2,2,2-trifluoroacetophenone to afford an intermediate [IV] that undergoes diagonal exocyclization to give vinyl carbanion intermediate [V]. Protonation of intermediate [V] provided two diastereomers (syn:anti = 1:1). (*Z*)-Stereospecificity of **2a** can be rationalized by the less steric hindrance between vinylic trifluoromethyl group and groups on the allylic position in the formation of intermediate [V]. The plausible mechanism was described in Scheme 3.

The assignment of *syn* and *anti* diastereomers of (*Z*)-**2a** was confirmed by the comparison of X-ray diffraction of **2e**, whose both diastereomers can be crystallized, with ^{19}F NMR spectrum. The X-ray data [19] of two diastereomers of **2e** (Figs. 1 and 2) showed that the vinylic trifluoromethyl group is arranged to O-3 position of 1,3-dioxolane ring system and two phenyl rings are arranged on the same side in the *syn* isomer and on the opposite side in the *anti* isomer. It has been found that ^{19}F NMR signal (−58.62 ppm) in the *syn* isomer of (*Z*)-**2e** is more shielded than *anti* (−58.46 ppm).

The reactions of **1a** with 2,2,2-trifluoroacetophenone or pentafluoroethyl phenyl ketone derivatives having proton, chloro, fluoro, methoxy, trifluoromethyl, vinyl, and phenoxy substitution on the benzene rings afforded (*Z*)-**2a–o** in 97–99% yields. However, the longer reaction time was required in reaction of

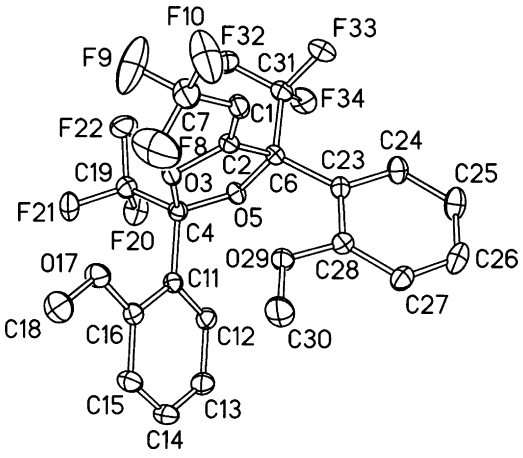


Fig. 2. ORTEP representation of *syn*-(*Z*)-**2e** at the 50% probability level. Selected bond lengths (Å) and angles (°): C1–C2 1.313(6), C1–C7 1.459(6), C1–H1A 0.9300, C2–O3 1.363(5), C2–C6 1.521(5), O3–C4 1.413(4), C4–O5 1.420(4), C4–C11 1.516(5), C4–C19 1.539(6), O5–C6 1.445(5), C6–C23 1.520(5), C6–C31 1.544(5); C2–C1–C7 123.8(4), C2–C1–H1A 118.1, C7–C1–H1A 118.1, C1–C2–O3 122.7(3), C1–C2–C6 128.5(4), O3–C2–C6 108.7(3), C2–O3–C4 110.5(3), O5–C4–O3 106.6(3), O5–C4–C11 114.4(3), O3–C4–C11 114.7(3), O5–C4–C19 106.6(3), O3–C4–C19 106.6(3), C11–C4–C19 110.3(3), C4–O5–C6 110.6(3), O5–C6–C2 102.4(3), O5–C6–C23 111.2(3), C2–C6–C23 116.5(3), O5–C6–C31 104.7(3), C23–C6–C31 113.4(3), C2–C6–C31 107.4(3).

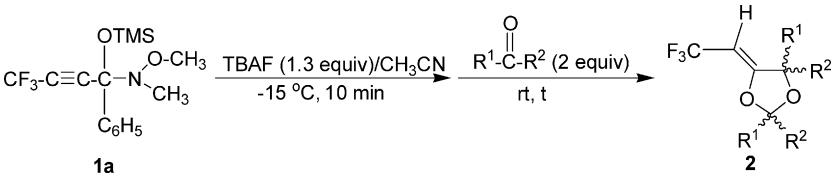
1a with ketone derivatives having chloro, fluoro, 2-methoxy and trifluoromethyl substitution on the benzene ring. Although we did not carry out the reaction with the longer perfluroalkylated ketone than pentafluoroethylated one, the similar results could be obtained because the steric effect does not affect on the addition reaction of tetrabutylammonium trifluoropropynylide [II] toward perfluoroalkylated ketone. Trifluoromethylated ketones having heterocyclic moieties such as a thiophene also reacted with tetrabutylammonium trifluoropropynylide [II] to give the corresponding dioxolane (*Z*)-**2p** in 98% yield. When **1a** was reacted with TBAF, followed by reaction with 1,1,1-trifluoroacetone under the same reaction condition, however, several products were obtained which could not be identified. The treatment of tetrabutylammonium trifluoropropynylide [II] with 2 equiv. aldehydes such as butanal, 2-methylbutanal and cyclohexancarbaldehyde resulted in the formation of the corresponding 4-trifluoroethylidene-1,3-dioxolane derivatives (*Z*)-**2q–r** in 72–74% yields, while the reaction with 2 equiv. of ketones did not provide any desired products. The experimental results of these reactions are summarized in Table 2.

Treatment of tetrabutylammonium trifluoropropynylide [II] with 1 equiv. of butanal or cyclohexanone, followed by 1 equiv. of trifluoroacetophenone, resulted in the formation of the corresponding 4-trifluoroethylidene-1,3-dioxolane derivatives **2s** and **2t** in 72% and 82% yields, respectively (Scheme 4).

However, tetrabutylammonium trifluoropropynylide [II] was treated with 1 equiv. of benzaldehyde derivatives at −15 °C for 10 min, followed by 1 equiv. of trifluoroacetophenone, to give the corresponding 1,3-dioxolane derivatives **2u–z** and 1,3-dioxine derivatives **3u–z** depending on the reaction conditions. Generally, the high temperature and prolong reaction time resulted in the formation of **3** as a single product. The experimental results of these reactions are summarized in Table 3.

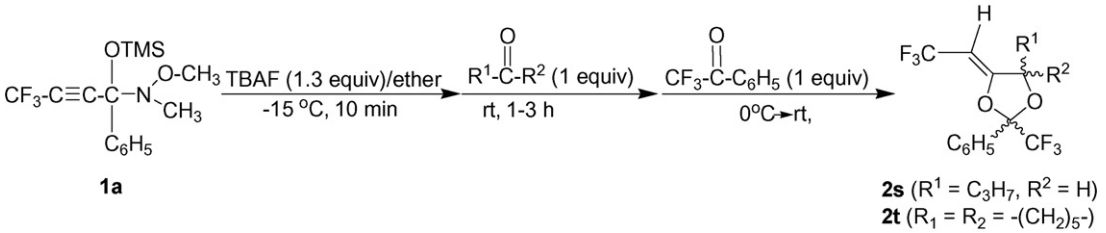
Formation of **3** can be rationalized by the rearrangement of the carbanion intermediate [V] to [VI] which undergoes endo-diagonal cyclization to produce the six-membered ring intermediate. 1,3-H shift, followed by protonation afforded the dioxine derivatives **3**. The driving force to produce the intermediate [VI] is due to the resonance stabilization of the carbanion by phenyl group and relatively high stability of 1,3-dioxine system as compare to ethylidene-1,3-dioxolane system. Comparison of entries 8, 10, 12

Table 2
Preparation of 4-trifluoroethylidene-1,3-dioxolane derivatives **2**



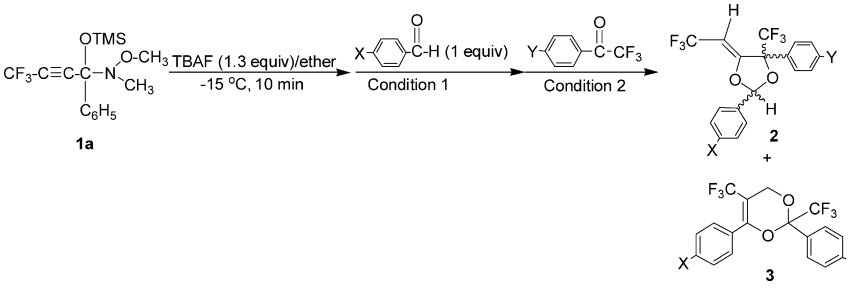
Compound	R^1	R^2	t (h)	Yield (%)[a,b]
2a	CF_3	C_6H_5	1	99
2b	CF_3	4-F–C_6H_4	2	98
2c	CF_3	4-Cl–C_6H_4	2	97
2d	CF_3	4-CH_3O–C_6H_4	1	99
2e	CF_3	2-CH_3O–C_6H_4	3	99
2f	CF_3	4-CF_3–C_6H_4	5	98
2g	CF_3	3-CF_3–C6H4	5	98
2h	CF_3	4-CH_2=CH–C_6H_4	1	97
2i	CF_3	4-C_6H_5O–C_6H_4	1	99
2j	C_2F_5	C_6H_5	1	99
2k	C_2F_5	4-CH_3O–C_6H_4	1	99
2l	C_2F_5	4-CF_3–C_6H_4	12	97
2m	C_2F_5	4-Cl–C_6H_4	2	98
2n	C_2F_5	4-CH_2=CH–C_6H_4	1	97
2o	C_2F_5	4-C_6H_5O–C_6H_4	1	98
2p	CF_3	2-Thienyl	1	98
2q	C_3H_7	H	1	72[c]
2r	*c*-Hex	H	2	74[c]

[a] Isolated yield.
[b] All products were obtained as a 1:1 diastereomer mixture.
[c] Reaction of 2nd step was performed at −20 °C, followed by warming to room temperature.



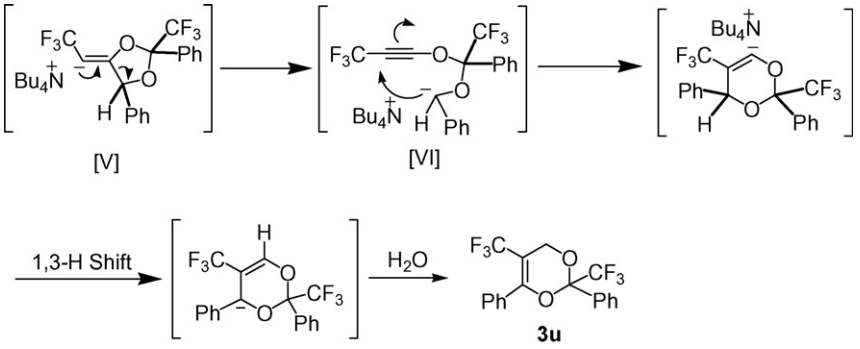
Scheme 4.

Table 3
Preparation of 2,5-bis(trifluoromethyl)-1,3-dioxine derivatives **3**



Entry	X	Y	Condition 1	Condition 2	Compound	Yield (%)[a]	
						2	3
1	H	H	−15 °C, 10 min	−15 °C, 10 min	**2u**, **3u**	42	18
2	H	H	−15 °C, 10 min	−15 °C → rt, 30 min	**2u**, **3u**	0	65
3	H	OCH_3	−15 °C, 10 min	−15 °C, 10 min	**2v**, **3v**	43	20
4	H	OCH_3	−15 °C, 10 min	−15 °C → rt, 30 min	**2v**, **3v**	0	65
5	H	CF_3	−15 °C, 10 min	−15 °C, 10 min	**2w**, **3w**	51	12
6	H	CF_3	−15 °C, 10 min	−15 °C → rt, 30 min	**2w**, **3w**	0	67
7	OCH_3	H	−15 °C, 10 min	−15 °C → rt, 30 min	**2x**, **3x**	29	0
8	OCH_3	H	−15 °C, 10 min	−15 °C → rt, 12 h	**2x**, **3x**	0	28
9	F	H	−15 °C, 10 min	−15 °C → 0 °C, 30 min	**2y**, **3y**	51	0
10	F	H	−15 °C, 10 min	−15 °C → rt, 3 h	**2y**, **3y**	0	51
11	CF_3	H	−15 °C, 10 min	−15 °C, 10 min	**2z**, **3z**	32	24
12	CF_3	H	−15 °C, 10 min	−15 °C → rt, 30 min	**2z**, **3z**	0	55

[a] Isolated yield.



Scheme 5.

in Table 3 would support the mechanistic consideration as shown in Scheme 5. Thus, the final 1,3-H shift should be facilitated by the electron-withdrawing substituent on the aromatic ring and the electron-releasing group should work in an opposite manner.

3. Conclusions

In this paper, we have explored the (trifluoromethyl)ethynylation to perfluoroalkylated phenyl ketones and aldehydes with a wide range of substituents to produce the corresponding 4-trifluoroethylidene-1,3-dioxolane derivatives in good to excellent yields. Several stable and isolable (trifluoromethyl)ethynylation reagents were successfully prepared from the reaction of Weinreb amides with trifluoropropynyl lithium formed from 2-bromotrifluoropropene. Tetrabutylammonium trifluoropropynylide [II], from the reaction of (trifluoromethyl)ethynylation reagents with TBAF, was reacted with 1 equiv. of benzaldehyde derivatives at −15 °C for 10 min, followed by treatment with 1 equiv. of trifluoroacetophenone, to give the corresponding 1,3-dioxolane and 1,3-dioxine derivatives depending on the reaction condition.

Generally, the prolong reaction time at relatively high temperature afforded the corresponding 1,3-dioxine derivatives.

4. Experimental

^{1}H NMR spectra were recorded on a 200-MHz Gemini-200 NMR spectrometer and ^{19}F NMR spectra were recorded on a 100-MHz Bruker AC-100F NMR spectrometer with tetramethylsilane (TMS) and $CFCl_3$ as an internal standard, respectively and the upfield as negative. All chemical shifts (δ) are expressed in parts per million and coupling constant (J) are given in Hertz. Infrared spectra were determined on a Mattson Genesis series FT High Resolution Spectrophotometer. Mass spectra were obtained by using GC/MS-Qp1000-Shimadzu (EI, 70 eV). Melting points were determined in open capillary tubes and are uncorrected.

Commercially available reagents were purchased from Aldrich, Lancaster, Tokyo Kasei and Fluorochem. All solvents were dried by general purification method. Flash chromatography was performed on 40–60 μm silica gel (230–400 mesh).

4.1. General procedure for the preparation of (trifluoromethyl)ethynylation reagents 1

A 100-mL three-neck round bottom flask equipped with a magnetic stirrer bar, a septum and condenser connected to an argon source was charged with 50 mL of THF and 2-bromo-3,3,3-trifluoropropene (6.25 mmol) and then cooled to −78 °C. After LDA (12.5 mmol) was added and stirred at −78 °C for 0.5 h, Weinreb amide (3.125 mmol) was added and then the reaction mixture was allowed to warm to 0 °C, followed by quench with TMSCl (3.2 mmol). The reaction mixture was allowed to warm to room temperature, extracted with ether twice, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of hexane and ether (19:1) provided (trifluoromethyl)ethynylation reagents **1a–c**.

4.1.1. 4,4,4-Trifluoro-1-(N-methoxy-N-methylamino)-1-phenyl-1-(trimethylsiloxyl)-2-butyne (1a)

1a was prepared in 94% yield (0.972 g) according to the general procedure (*N*-methoxy-*N*-methylbenzamide was used as a Weinreb amide). **1a**: oil; ^{1}H NMR ($CDCl_3$) δ 7.65–7.60 (m, 2H), 7.38–7.35 (m, 3H), 3.46 (s, 3H), 2.40 (s, 3H), 0.20 (s, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −51.20 (s, 3F); MS, *m*/*z* (relative intensity) 331 (M^+, 5), 271 (100), 242 (36), 208 (12), 179 (11), 151 (23), 105 (27), 77 (10), 73 (47); IR (neat) 3067, 2960, 2262,1273, 1147, 1087 cm^{-1}. Anal. Calcd. for $C_{15}H_{20}F_3NO_2Si$: C, 54.36; H, 6.08. Found: C, 54.08; H, 6.01.

4.1.2. 4,4,4-Trifluoro-1-(N-methoxy-N-methylamino)-1-benzyl-1-(trimethylsiloxyl)-2-butyne (1b)

1b was prepared in 65% yield (0.701 g) according to the general procedure (*N*-methoxy-*N*-methylphenylacetamide was used as a Weinreb amide). **1b**: oil; ^{1}H NMR ($CDCl_3$) δ 7.36–7.32 (m, 5H), 3.66 (s, 3H), 3.12 (s, 2H), 2.41 (s, 3H), 0.21 (s, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −51.47 (s, 3F); MS, *m*/*z* (relative intensity) 345 (M^+, 3), 285 (11), 254 (21), 151 (18), 134 (16), 91 (44), 77 (11), 73 (100), 65 (16), 45 (51); IR (neat) 3050, 2960, 2271,1275, 1147, 1099 cm^{-1}. Anal. Calcd. for $C_{16}H_{22}F_3NO_2Si$: C, 55.63; H, 6.42. Found: C, 55.39; H, 6.31.

4.1.3. 4,4,4-Trifluoro-1-(N-methoxy-N-methylamino)-1-methyl-1-(trimethylsiloxyl)-2-butyne (1c)

1c was prepared in 70% yield (0.588 g) according to the general procedure (*N*-methoxy-*N*-methylacetamide was used as a Weinreb amide). **1c**: oil; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 3H), 2.60 (s, 3H), 1.64 (s, 3H), 0.23 (s, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −51.19 (s, 3F); MS, *m*/*z* (relative intensity) 269 (M^+, 3), 176 (10), 89 (7), 83 (39), 70 (37), 69 (48), 43 (100); IR (neat) 2960, 2275,1281, 1150, 1040 cm^{-1}. Anal. Calcd. for $C_{10}H_{18}F_3NO_2Si$: C, 44.59; H, 6.74. Found: C, 44.45; H, 6.77.

4.2. General procedure for the preparation of 4-trifluoroethylidene-1,3-dioxolanes 2

A 25-mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and condenser connected to an argon source was charged with 5 mL of CH_3CN and **1a** (0.430 g, 1.3 mmol) and then cooled to −15 °C. After TBAF (1.3 mmol, 1.0 M in THF) was added and stirred at −15 °C for 10 min, perfluoroalkylated ketone (2.0 mmol) was added and then the reaction mixture was allowed to warm to room temperature. The reaction mixture was extracted with ether twice, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of hexane and ether (9:1) provided 4-trifluoroethylidene-1,3-dioxolanes **2**.

4.2.1. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-diphenyl-1,3-dioxolane (2a)

2a (anti:syn = 1:1) was prepared in 99% yield (0.438 g) according to the general procedure (trifluoroacetophenone was used as a perfluoroalkylated ketone). **2a** (syn): mp 64–65 °C; ^{1}H NMR ($CDCl_3$) δ 7.70–7.66 (m, 4H), 7.52–7.48 (m, 6H), 5.40 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.64 (d, J = 7.1 Hz, 3F), −77.17 (s, 3F), −82.51 (s, 3F); MS, *m*/*z* (relative intensity) 442 (M^+, 1), 373 (32), 199 (13), 171 (10), 151 (29), 105 (100), 77 (12); IR (KBr) 3136, 3078, 2937, 1709, 1500, 1454, 1279, 1207, 1132, 1063, 731, 698 cm^{-1}. Anal. Calcd. for $C_{19}H_{11}F_9O_2$: C, 51.60; H, 2.51. Found: C, 51.44; H, 2.47%. **2a** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.52–7.17 (m, 10H), 5.43 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.53 (d, J = 7.1 Hz, 3F), −76.84 (s, 3F), −83.18 (s, 3F). Anal. Calcd. for $C_{19}H_{11}F_9O_2$: C, 51.60; H, 2.51. Found: C, 51.48; H, 2.49%.

4.2.2. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(p-fluorophenyl)-1,3-dioxolane (2b)

2b (anti:syn = 1:1) was prepared in 98% yield (0.468 g) according to the general procedure (trifluoromethyl *p*-fluorophenyl ketone was used as a perfluoroalkylated ketone). **2a** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.72–7.63 (m, 4H), 7.25–7.02 (m, 4H), 5.38 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.69 (d, J = 6.9 Hz, 3F), −77.30 (s, 3F), −82.68 (s, 3F), −109.67 (s, 1F), −110.48 (s, 1F); MS, *m*/*z* (relative intensity) 478 (M^+, 1), 409 (30), 258 (33), 217 (22), 189 (25), 169 (17), 123 (100), 95 (20), 75 (8); IR (neat) 3118, 2924, 1715, 1611, 1372, 1290, 1206, 1083, 842 cm^{-1}. Anal. Calcd. for $C_{19}H_9F_{11}O_2$: C, 47.72; H, 1.90. Found: C, 47.65; H, 1.85%. **2a** (anti): mp 54–55 °C; ^{1}H NMR ($CDCl_3$) δ 7.49–7.40 (m, 4H), 7.04–6.90 (m, 4H), 5.43 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.63 (d, J = 7.1 Hz, 3F), −77.00 (s, 3F), −83.37 (s, 3F), −109.37 (s, 1F), −110.05 (s, 1F). Anal. Calcd. for $C_{19}H_9F_{11}O_2$: C, 47.72; H, 1.90. Found: C, 47.59; H, 1.84%.

4.2.3. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(p-chlorophenyl)-2,4-bis(trifluoromethyl)-1,3-dioxolane (2c)

2c (anti:syn = 1:1) was prepared in 97% yield (0.496 g) according to the general procedure (*p*-chlorophenyl trifluoromethyl ketone was used as a perfluoroalkylated ketone). **2c** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.65–7.22 (m, 8H), 5.45 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.66 (d, J = 6.9 Hz, 3F), −76.93 (s, 3F), −83.26 (s, 3F); MS, *m*/*z* (relative intensity) 512 (M^++2, 2), 510 (M^+, 4), 441 (24), 274 (28), 205 (12), 139 (100), 111

(25), 75 (14), 69 (4); IR (neat) 3124, 2929, 1711, 1600, 1369, 1281, 1137, 1096, 839 cm^{-1}. Anal. Calcd. for $C_{19}H_9Cl_2F_9O_2$: C, 44.64; H, 1.77. Found: C, 44.32; H, 1.83%. **2c** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.65–7.22 (m, 8H), 5.38 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.63 (d, J = 6.9 Hz, 3F), −77.25 (s, 3F), −82.59 (s, 3F). Anal. Calcd. for $C_{19}H_9Cl_2F_9O_2$: C, 44.64; H, 1.77. Found: C, 44.37; H, 1.82%.

4.2.4. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(p-methoxyphenyl)-1,3-dioxolane (2d)

2d (anti:syn = 1:1) was prepared in 99% yield (0.497 g) according to the general procedure (trifluoromethyl *p*-methoxyphenyl ketone was used as a perfluoroalkylated ketone). **2d** (syn): mp 69–70 °C; ^1H NMR ($CDCl_3$) δ 7.64–7.57 (m, 4H), 7.04–6.95 (m, 4H), 5.33 (q, J = 7.1 Hz, 1H), 3.85 (s, 6H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.56 (d, J = 7.1 Hz, 3F), −77.17 (s, 3F), −82.70 (s, 3F); MS, m/z (relative intensity) 502 (M^+, 15), 433 (13), 270 (64), 201 (23), 135 (100), 84 (18), 77 (19); IR (KBr) 3124, 2964, 1710, 1614, 1370, 1260, 1177, 1079, 837 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_9O_4$: C, 50.21; H, 3.01. Found: C, 49.85; H, 2.94%. **2d** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.40–7.33 (m, 4H), 6.80–6.71 (m, 4H), 5.36 (q, J = 7.1 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.48 (d, J = 7.1 Hz, 3F), −77.05 (s, 3F), −83.42 (s, 3F). Anal. Calcd. for $C_{21}H_{15}F_9O_4$: C, 50.21; H, 3.01. Found: C, 49.91; H, 2.97%.

4.2.5. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(o-methoxyphenyl)-1,3-dioxolane (2e)

2e (anti:syn = 1:1) was prepared in 99% yield (0.497 g) according to the general procedure (trifluoromethyl *o*-methoxyphenyl ketone was used as a perfluoroalkylated ketone). **2e** (syn): mp 112–113 °C; ^1H NMR ($CDCl_3$) δ 7.85–7.81 (m, 1H), 7.66–7.62 (m, 1H), 7.49–7.41 (m, 2H), 7.12–6.99 (m, 4H), 5.80 (q, J = 7.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.62 (d, J = 7.5 Hz, 3F), −75.29 (s, 3F), −81.14 (s, 3F); MS, m/z (relative intensity) 502 (M^+, 8), 433 (22), 270 (9), 201 (5), 135 (100), 84 (7), 77 (19); IR (KBr) 3014, 2948, 1708, 1603, 1360, 1261, 1128, 1068, 756 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_9O_4$: C, 50.21; H, 3.01. Found: C, 49.98; H, 2.98%. **2e** (anti): mp 110–111 °C; ^1H NMR ($CDCl_3$) δ 7.68–7.64 (m, 1H), 7.41–7.24 (m, 3H), 6.96–6.72 (m, 4H), 5.31 (q, J = 7.5 Hz, 1H), 3.88 (s, 3H), 3.39 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.56 (d, J = 7.5 Hz, 3F), −74.35 (s, 3F), −81.61 (s, 3F). Anal. Calcd. for $C_{21}H_{15}F_9O_4$: C, 50.21; H, 3.01. Found: C, 49.94; H, 2.96%.

4.2.6. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(p-trifluoromethylphenyl)-1,3-dioxolane (2f)

2f (anti:syn = 1:1) was prepared in 98% yield (0.566 g) according to the general procedure (trifluoromethyl *p*-trifluoromethylphenyl ketone was used as a perfluoroalkylated ketone). **2f** (syn): oil; ^1H NMR ($CDCl_3$) δ 7.88–7.76 (m, 8H), 5.47 (q, J = 6.0 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.77 (d, J = 6.9 Hz, 3F), −63.45 (s, 3F), −63.55 (s, 3F), −77.14 (s, 3F), −82.42 (s, 3F); MS, m/z (relative intensity) 578 (M^+, 2), 509 (23), 308 (12), 267 (21), 219 (17), 173 (100), 145 (11); IR (neat) 3078, 2952, 1713, 1624, 1328, 1208, 1136, 1089, 837 cm^{-1}. Anal. Calcd. for $C_{21}H_9F_{15}O_2$: C, 43.62; H, 1.57. Found: C, 43.39; H, 1.61%. **2f** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.68–7.53 (m, 8H), 5.55 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.77 (d, J = 6.9 Hz, 3F), −63.78 (s, 3F), −63.80 (s, 3F), −76.61 (s, 3F), −82.97 (s, 3F). Anal. Calcd. for $C_{21}H_9F_{15}O_2$: C, 43.62; H, 1.57. Found: C, 43.24; H, 1.52%.

4.2.7. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(m-trifluoromethylphenyl)-1,3-dioxolane (2g)

2g (anti:syn = 1:1) was prepared in 98% yield (0.566 g) according to the general procedure (trifluoromethyl *m*-trifluoromethylphenyl ketone was used as a perfluoroalkylated ketone). **2g** (syn): oil; ^1H NMR ($CDCl_3$) δ 7.97–7.39 (m, 8H), 5.53 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.73 (d, J = 7.1 Hz, 3F), −63.66 (s, 3F), 63.78 (s, 3F), −76.76 (s, 3F), −83.09 (s, 3F); MS, m/z (relative intensity) 578 (M^+, 1), 461 (8), 308 (10), 267 (18), 239 (24), 219 (45), 173 (100), 145 (95), 126 (36), 95 (21), 75 (23); IR (neat) 3084, 2964, 1713, 1621, 1369, 1267, 1136, 1094, 1076, 875, 775, 690 cm^{-1}. Anal. Calcd. for $C_{21}H_9F_{15}O_2$: C, 43.62; H, 1.57. Found: C, 43.35; H, 1.53%. **2g** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.65–7.22 (m, 8H), 5.46 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.73 (d, J = 7.1 Hz, 3F), −63.45 (s, 6F), −77.19 (s, 3F), −82.49 (s, 3F). Anal. Calcd. for $C_{21}H_9F_{15}O_2$: C, 43.62; H, 1.57. Found: C, 43.41; H, 1.56%.

4.2.8. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(p-vinylphenyl)-1,3-dioxolane (2h)

2h (anti:syn = 1:1) was prepared in 97% yield (0.479 g) according to the general procedure (trifluoromethyl *p*-vinylphenyl ketone was used as a perfluoroalkylated ketone). **2h** (syn): oil; ^1H NMR ($CDCl_3$) δ 7.68–7.43 (m, 8H), 6.75 (dd, J = 17.7, 11.0 Hz, 2H), 5.85 (d, J = 17.7 Hz, 2H), 5.44–5.26 (m, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.63 (d, J = 6.5 Hz, 3F), −77.09 (s, 3F), −82.48 (s, 3F); MS, m/z (relative intensity) 494 (M^+, 11), 425 (18), 266 (37), 197 (12), 177 (18), 131 (100), 103 (31), 77 (25); IR (neat) 3074, 2988, 1707, 1611, 1369, 1202, 1125, 1094, 839 cm^{-1}. Anal. Calcd. for $C_{23}H_{15}F_9O_2$: C, 55.88; H, 3.06. Found: C, 55.45; H, 3.00%. **2h** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.49–7.24 (m, 8H), 6.70–6.53 (m, 2H), 5.73 (dd, J = 17.5, 5.3 Hz, 2H), 5.42 (d, J = 7.1 Hz, 1H), 5.31 (dd, J = 13.6, 2.8 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.57 (d, J = 7.1 Hz, 3F), −76.81 (s, 3F), −83.14 (s, 3F). Anal. Calcd. for $C_{23}H_{15}F_9O_2$: C, 55.88; H, 3.06. Found: C, 55.53; H, 3.01%.

4.2.9. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(p-phenoxyphenyl)-1,3-dioxolane (2i)

2i (anti:syn = 1:1) was prepared in 99% yield (0.620 g) according to the general procedure (trifluoromethyl *p*-phenoxyphenyl ketone was used as a perfluoroalkylated ketone). **2i** (syn): oil; ^1H NMR ($CDCl_3$) δ 7.65–6.80 (m, 18H), 5.38 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.57 (d, J = 7.1 Hz, 3F), −76.88 (s, 3F), −83.23 (s, 3F); MS, m/z (relative intensity) 626 (M^+, 17), 557 (4), 239 (8), 197 (100), 169 (10), 141 (18), 115 (15), 77 (30); IR (neat) 3067, 2927, 1710, 1613, 1371, 1247, 1133, 1087, 842 cm^{-1}. Anal. Calcd. for $C_{31}H_{19}F_9O_4$: C, 59.43; H, 3.06. Found: C, 59.11; H, 3.01%. **2i** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.65–6.80 (m, 18H), 5.38 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.50 (d, J = 7.1 Hz, 3F), −77.09 (s, 3F), −82.55 (s, 3F). Anal. Calcd. for $C_{31}H_{19}F_9O_4$: C, 59.43; H, 3.06. Found: C, 59.04; H, 2.99%.

4.2.10. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(pentafluoroethyl)-2,4-diphenyl-1,3-dioxolane (2j)

2j (anti:syn = 2:1) was prepared in 99% yield (0.537 g) according to the general procedure (pentafluoroethyl phenyl ketone was used as a perfluoroalkylated ketone). **2j** (syn): oil; ^1H NMR ($CDCl_3$) δ 7.68–7.62 (m, 4H), 7.56–7.40 (m, 6H), 5.55 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.78 (d, J = 6.9 Hz, 3F), −78.25 (s, 3F), −79.79 (s, 3F), −118.21 (d, J = 279.6 Hz, 1F), −120.17 (d, J = 279.6 Hz, 1F), −126.02 (s, 1F), −126.16 (s, 1F); MS, m/z (relative intensity) 542 (M^+, 1), 423 (19), 299 (3), 199 (3), 151 (10), 105 (100), 77 (27); IR (neat) 3079, 1708, 1455, 1275, 1199, 1052, 755, 698 cm^{-1}. Anal. Calcd. for $C_{21}H_{11}F_{13}O_2$: C, 46.51; H, 2.04. Found: C, 46.24; H, 2.08%. **2j** (anti): oil; ^1H NMR ($CDCl_3$) δ 7.50–7.09 (m, 10H), 5.57 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.74 (d, J = 7.1 Hz, 3F), −78.44 (s, 3F), −79.88 (s, 3F), −119.11 to −120.02

(m, 2F), −126.57 to −126.66 (m, 2F). Anal. Calcd. for $C_{21}H_{11}F_{13}O_2$: C, 46.51; H, 2.04. Found: C, 46.19; H, 2.09%.

*4.2.11. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(pentafluoroethyl)-2,4-bis(p-methoxyphenyl)-1,3-dioxolane (**2k**)*

2k (anti:syn = 1:1) was prepared in 99% yield (0.596 g) according to the general procedure (pentafluoroethyl *p*-methoxyphenyl ketone was used as a perfluoroalkylated ketone). **2k** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.62–7.52 (m, 4H), 7.03–6.93 (m, 4H), 5.48 (q, J = 7.1 Hz, 1H), 3.85 (s, 6H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.70 (d, J = 7.1 Hz, 3F), −78.19 (s, 3F), −79.77 (s, 3F), −117.03 (d, J = 279.3 Hz, 1F), −122.16 (d, J = 279.3 Hz, 1F), −125.98 (s, 1F), −126.16 (s, 1F); MS, *m*/*z* (relative intensity) 602 (M^+, 1), 483 (6), 320 (3), 229 (3), 201 (11), 181 (7), 135 (100), 92 (16), 77 (16); IR (neat) 3010, 2963, 1707, 1613, 1342, 1260, 1179, 1083, 839 cm^{-1}. Anal. Calcd. for $C_{23}H_{15}F_{13}O_4$: C, 45.86; H, 2.52. Found: C, 45.61; H, 2.47%. **2k** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.41–7.27 (m, 4H), 6.81–6.64 (m, 4H), 5.50 (q, J = 7.1 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.58 (d, J = 7.1 Hz, 3F), −78.41 (s, 3F), −79.87 (s, 3F), −119.34 to −119.59 (m, 1F), −119.98 (s, 1F), −126.60 (s, 2F). Anal. Calcd. for $C_{23}H_{15}F_{13}O_4$: C, 45.86; H, 2.52. Found: C, 45.52; H, 2.45%.

*4.2.12. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(pentafluoroethyl)-2,4-bis(p-trifluoromethylphenyl)-1,3-dioxolane (**2l**)*

2l (anti:syn = 1:1) was prepared in 97% yield (0.658 g) according to the general procedure (pentafluoroethyl *p*-trifluoromethylphenyl ketone was used as a perfluoroalkylated ketone). **2l** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.87–7.73 (m, 8H), 5.60 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.92 (d, J = 6.9 Hz, 3F), −63.94 (s, 3F), −78.33 (s, 3F), −79.76 (s, 3F), −118.52 (d, J = 281.1 Hz, 1F), −119.56 (d, J = 281.1 Hz, 1F), −126.95 (s, 1F), 127.03 (s, 3F); MS, *m*/*z* (relative intensity) 678 (M^+, 1), 659 (1), 560 (1), 371 (9), 219 (32), 173 (90), 145 (100), 126 (35), 69 (35); IR (neat) 3137, 2959, 1710, 1624, 1326, 1226, 1138, 1072, 839 cm^{-1}. Anal. Calcd. for $C_{23}H_9F_{19}O_2$: C, 40.73; H, 1.34. Found: C, 40.29; H, 1.30%. **2l** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.85–7.36 (m, 8H), 5.65 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.81 (d, J = 6.9 Hz, 3F), −63.94 (s, 6F), −78.33 (s, 3F), −79.76 (s, 3F), −119.07 to −119.93 (m, 2F), −126.40 (s, 2F). Anal. Calcd. for $C_{23}H_9F_{19}O_2$: C, 40.73; H, 1.34. Found: C, 40.34; H, 1.29%.

*4.2.13. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(p-chlorophenyl)-2,4-bis(pentafluoroethyl)-1,3-dioxolane (**2m**)*

2m (anti:syn = 1:1) was prepared in 98% yield (0.600 g) according to the general procedure (pentafluoroethyl *p*-chlorophenyl ketone was used as a perfluoroalkylated ketone). **2m** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.64–7.42 (m, 8H), 5.52 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.86 (d, J = 6.9 Hz, 3F), −78.12 (s, 3F), −79.66 (s, 3F), −118.38 (d, J = 280.5 Hz, 1F), −120.76 (d, J = 280.5 Hz, 1F), −126.97 to −127.08 (m, 2F); MS, *m*/*z* (relative intensity) 611 (M^+, 1), 491 (22), 333 (4), 187 (4), 158 (7), 141 (26), 139 (100), 111 (5); IR (neat) 3077, 1708, 1602, 1281, 1197, 1083, 841 cm^{-1}. Anal. Calcd. for $C_{21}H_9Cl_2F_{13}O_2$: C, 41.22; H, 1.48. Found: C, 40.93; H, 1.44%. **2m** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.63–7.15 (m, 8H), 5.56 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.75 (d, J = 6.9 Hz, 3F), −78.38 (s, 3F), −79.79 (s, 3F), −119.17 to −120.70 (m, 2F), −126.60 to −126.70 (m, 2F). Anal. Calcd. for $C_{21}H_9Cl_2F_{13}O_2$: C, 41.22; H, 1.48. Found: C, 40.88; H, 1.42%.

4.2.14. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-bis(p-vinylphenyl)-1,3-

dioxolane (**2n**)

2n (anti:syn = 1:1) was prepared in 97% yield (0.576 g) according to the general procedure (pentafluoroethyl *p*-vinylphenyl ketone was used as a perfluoroalkylated ketone). **2n** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.66–7.47 (m, 8H), 6.75 (dd, J = 17.6, 11.0 Hz, 2H), 5.85 (d, J = 17.6 Hz, 2H), 5.53 (q, J = 6.9 Hz, 1H), 5.37 (d, J = 11.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.77 (d, J = 6.9 Hz, 3F), −78.17 (s, 3F), −79.71 (s, 3F), −118.24 (d, J = 279.5 Hz, 1F), −120.79 (d, J = 279.5 Hz, 1F), −125.91 to −126.06 (m, 2F); MS, *m*/*z* (relative intensity) 594 (M^+, 3), 475 (15), 337 (2), 177 (6), 131 (100), 103 (15), 77 (10); IR (neat) 3094, 2987, 1708, 1613, 1282, 1195, 1085, 837 cm^{-1}. Anal. Calcd. for $C_{25}H_{15}F_{13}O_2$: C, 50.52; H, 2.54. Found: C, 50.27; H, 2.49%. **2n** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.60–7.16 (m, 8H), 6.70–6.50 (m, 2H), 5.79–5.64 (m, 2H), 5.56 (q, J = 6.9 Hz, 1H), 5.23–5.33 (m, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.64 (d, J = 6.9 Hz, 3F), −78.44 (s, 3F), −79.82 (s, 3F), −119.23 to −119.88 (m, 2F), −126.53 to 126.66 (m, 2F). Anal. Calcd. for $C_{25}H_{15}F_{13}O_2$: C, 50.52; H, 2.54. Found: C, 50.21; H, 2.48%.

*4.2.15. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(pentafluoroethyl)-2,4-bis(p-phenoxyphenyl)-1,3-dioxolane (**2o**)*

2o (anti:syn = 1:1) was prepared in 98% yield (0.711 g) according to the general procedure (pentafluoroethyl *p*-phenoxyphenyl ketone was used as a perfluoroalkylated ketone). **2o** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.63–6.75 (m, 18H), 5.56–5.45 (m, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.60 to −58.76 (m, 3F), −78.11 to −78.28 (m, 3F), −79.68 to −79.79 (m, 3F), −116.07 to −123.02 (m, 2F), −125.91 to −126.38 (m, 2F); MS, *m*/*z* (relative intensity) 726 (M^+, 12), 607 (8), 469 (1), 382 (3), 304 (2), 244 (3), 197 (100), 141 (5), 77 (5); IR (neat) 3064, 2969, 1707, 1612, 1366, 1223, 1134, 1084, 840 cm^{-1}. Anal. Calcd. for $C_{33}H_{19}F_{13}O_4$: C, 54.56; H, 2.64. Found: C, 54.20; H, 2.57%. **2o** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.63–6.75 (m, 18H), 5.56–5.45 (m, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.60 to −58.76 (m, 3F), −78.11 to −78.28 (m, 3F), −79.68 to −79.79 (m, 3F), −116.07 to −123.02 (m, 2F), −125.91 to −126.38 (m, 2F). Anal. Calcd. for $C_{33}H_{19}F_{13}O_4$: C, 54.56; H, 2.64. Found: C, 54.24; H, 2.58%.

*4.2.16. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-bis(trifluoromethyl)-2,4-dithiophen-2-yl-1,3-dioxolane (**2p**)*

2p (anti:syn = 1:1) was prepared in 98% yield (0.445 g) according to the general procedure (trifluoromethyl 2-thiophenyl ketone was used as a perfluoroalkylated ketone). **2p** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.54–7.49 (m, 2H), 7.44–7.40 (m, 2H), 7.14–7.09 (m, 2H), 5.37 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.88 (d, J = 7.1 Hz, 3F), −77.78 (s, 3F), −82.70 (s, 3F); MS, *m*/*z* (relative intensity) 454 (M^+, 8), 274 (36), 255 (9), 246 (100), 205 (16), 177 (53), 132 (12), 111 (63), 83 (28), 69 (11); IR (neat) 3119, 2962, 1714, 1372, 1275, 1137, 1069 cm^{-1}. Anal. Calcd. for $C_{15}H_7F_9O_2S_2$: C, 39.66; H, 1.55. Found: C, 39.39; H, 1.52%. **2p** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.36–7.33 (m, 2H), 7.20–7.16 (m, 2H), 6.95–6.89 (m, 2H), 5.38 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.78 (d, J = 7.1 Hz, 3F), −77.63 (s, 3F), −83.13 (s, 3F). Anal. Calcd. for $C_{15}H_7F_9O_2S_2$: C, 39.66; H, 1.55. Found: C, 39.35; H, 1.51%.

*4.2.17. (Z)-5-(2,2,2-Trifluoroethylidene)-2,4-dipropyl-1,3-dioxolane (**2q**)*

2q (anti:syn = 1:1) was prepared in 72% yield (0.171 g) according to the general procedure (butanal was used as a carbonyl compound). **2q** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 5.30 (t, J = 4.7 Hz, 1H), 4.57–4.44 (m, 1H), 4.48 (q, J = 7.7 Hz, 1H), 1.85–1.43 (m, 4H), 0.97 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.28 (d, J = 7.7 Hz, 3F); MS, *m*/*z* (relative intensity) 238 (M^+, 1), 210 (7), 195 (35), 149 (37), 127 (33), 109 (34), 91 (40), 55 (100); IR (neat) 2965, 1703, 1395, 1252, 1110 cm^{-1}. Anal. Calcd. for $C_{11}H_{17}F_3O_2$: C, 55.45; H, 7.19. Found: C, 55.03; H, 7.03%. **2q** (anti):

oil; ^{1}H NMR ($CDCl_3$) δ 5.52 (t, J = 4.7 Hz, 1H), 4.69–4.66 (m, 1H), 4.51 (q, J = 7.5 Hz, 1H), 1.85–1.43 (m, 4H), 0.97 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.27 (d, J = 7.5 Hz, 3F). Anal. Calcd. for $C_{11}H_{17}F_3O_2$: C, 55.45; H, 7.19. Found: C, 55.09; H, 7.07%.

4.2.18. (Z)-5-(2,2,2-trifluoroethylidene)-2,4-dicyclohexyl-1,3-dioxolane (2r)

2r (anti:syn = 1:1) was prepared in 74% yield (0.235 g) according to the general procedure (cyclohexylcarbaldehyde was used as a carbonyl compound). **2r** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 5.27 (d, J = 4.5 Hz, 1H), 4.50 (q, J = 7.7 Hz, 1H), 4.44–4.42 (m, 1H), 1.76–1.05 (m, 22H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.18 (d, J = 7.7 Hz, 3F); MS, m/z (relative intensity) 318 (M^+, 1), 235 (60), 207 (27), 189 (100), 147 (16), 111 (9), 95 (43), 81 (31), 67 (12); IR (neat) 2930, 1701, 1322, 1284, 1110 cm^{-1}. Anal. Calcd. for $C_{17}H_{25}F_3O_2$: C, 64.13; H, 7.91. Found: C, 63.88; H, 7.79%. **2r** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 5.03 (d, J = 4.1 Hz, 1H), 4.49 (q, J = 7.7 Hz, 1H), 4.38–4.37 (m, 1H), 1.76–1.05 (m, 22H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.09 (d, J = 7.7 Hz, 3F). Anal. Calcd. for $C_{17}H_{25}F_3O_2$: C, 64.13; H, 7.91. Found: C, 63.85; H, 7.80%.

4.2.19. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-2-phenyl-4-propyl-1,3-dioxolane (2s)

2s (anti:syn = 1:1) was prepared in 72% yield (0.245 g) according to the general procedure (butanal and trifluoroacetophenone were used as a carbonyl compound). **2s** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.65–7.58 (m, 2H), 7.54–7.38 (m, 3H), 5.10 (s, 1H), 4.71 (q, J = 7.5 Hz, 1H), 1.86–1.42 (m, 4H), 0.93 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.92 (d, J = 7.5 Hz, 3F), −82.82 (s, 3F); MS, m/z (relative intensity) 340 (M^+, 1), 271 (31), 229 (7), 149 (9), 123 (10), 105 (100), 91 (20), 77 (33); IR (neat) 3069, 2967, 1716, 1291, 1218, 1119, 1088, 1048, 755, 698 cm^{-1}. Anal. Calcd. for $C_{15}H_{14}F_6O_2$: C, 52.95; H, 4.15. Found: C, 52.51; H, 4.07%. **2s** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.65–7.58 (m, 2H), 7.54–7.38 (m, 3H), 4.77–4.61 (m, 2H), 1.85–1.42 (m, 4H), 1.01 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.90 (d, J = 7.5 Hz, 3F), −83.30 (s, 3F). Anal. Calcd. for $C_{15}H_{14}F_6O_2$: C, 52.95; H, 4.15. Found: C, 52.48; H, 4.06%.

4.2.20. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-2-phenyl-1,3-dioxaspiro[4,5]decane (2t)

2t (anti:syn = 1:1) was prepared in 82% yield (0.300 g) according to the general procedure (cyclohexanone and trifluoroacetophenone were used as a carbonyl compound). **2t** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.69–7.64 (m, 2H), 7.44–7.40 (m, 3H), 4.65 (q, J = 7.5 Hz, 1H), 2.13–2.07 (m, 1H), 1.86–1.23 (m, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.69 (d, J = 7.5 Hz, 3F), −84.08 (s, 3F); MS, m/z (relative intensity) 366 (M^+, 3), 297 (56), 192 (14), 175 (20), 123 (21), 105 (100), 91 (17), 81 (64), 67 (27); IR (neat) 3067, 2944, 1708, 1374, 1257, 1194, 1084, 751, 696 cm^{-1}. Anal. Calcd. for $C_{17}H_{16}F_6O_2$: C, 55.74; H, 4.40. Found: C, 55.32; H, 4.28%. **2t** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.69–7.64 (m, 2H), 7.44–7.40 (m, 3H), 4.60 (q, J = 7.5, 1H), 2.15–2.09 (m, 1H), 1.88–1.25 (m, 9H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −57.64 (d, J = 7.5 Hz, 3F), −84.48 (s, 3F). Anal. Calcd. for $C_{17}H_{16}F_6O_2$: C, 55.74; H, 4.40. Found: C, 55.41; H, 4.30%.

4.2.21. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-2,4-diphenyl-1,3-dioxolane (2u)

2u (anti:syn = 1:1) was prepared in 42% yield (0.157 g) according to the general procedure (benzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C for 10 min). **2u** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.72–7.42 (m, 10H), 5.48–5.47(m, 1H), 4.41 (q, J = 6.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.24 (d, J = 6.9 Hz, 3F), −82.84 (s, 3F); MS, m/z (relative intensity) 374 (M^+, 6), 305 (28), 100 (35), 172 (100), 131 (37), 105 (60), 77 (74), 51 (36); IR (neat) 3079, 2915, 1714, 1500, 1454, 1266, 1197, 1136, 1081, 755, 698 cm^{-1}. Anal. Calcd. for $C_{18}H_{12}F_6O_2$: C, 57.76; H, 3.23. Found: C, 57.41; H, 3.16%. **2u** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.72–7.39 (m, 10H), 5.99 (s, 1H), 4.48 (q, J = 7.1 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.21 (d, J = 7.1 Hz, 3F), −82.37 (s, 3F). Anal. Calcd. for $C_{18}H_{12}F_6O_2$: C, 57.76; H, 3.23. Found: C, 57.38; H, 3.14%.

4.2.22. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-2-(p-methoxyphenyl)-4-phenyl-1,3-dioxolane (2v)

2v (anti:syn = 1:1) was prepared in 43% yield (0.174 g) according to the general procedure (benzaldehyde and trifluoromethyl p-methoxyphenyl ketone were used as carbonyl compounds and condition 2 is −15 °C for 10 min). **2v** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.92–6.90 (m, 9H), 5.49–5.45(m, 1H), 4.49 (q, J = 7.5 Hz, 1H), 3.84 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.19 (d, J = 7.5 Hz, 3F), −83.03 (s, 3F); MS, m/z (relative intensity) 404 (M^+, 12), 335 (54), 172 (83), 135 (100), 107 (12), 77 (34); IR (neat) 3014, 2941, 1708, 1602, 1310, 1268, 1170, 1077, 835, 755, 698 cm^{-1}. Anal. Calcd. for $C_{19}H_{14}F_6O_3$: C, 56.44; H, 3.49. Found: C, 56.23; H, 3.46%. **2v** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.67–6.92 (m, 9H), 5.97 (s, 1H), 4.46 (q, J = 7.3 Hz, 1H), 3.85 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.17 (d, J = 7.3 Hz, 3F), −82.54 (s, 3F). Anal. Calcd. for $C_{19}H_{14}F_6O_3$: C, 56.44; H, 3.49. Found: C, 56.19; H, 3.44%.

4.2.23. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-2-(p-trifluoromethylphenyl)-4-phenyl-1,3-dioxolane (2w)

2w (anti:syn = 1:1) was prepared in 51% yield (0.225 g) according to the general procedure (benzaldehyde and trifluoromethyl p-trifluoromethylphenyl ketone were used as carbonyl compounds and condition 2 is −15 °C for 10 min). **2w** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.87–7.18 (m, 9H), 6.02 (s, 1H), 4.53 (q, J = 7.5 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.34 (d, J = 7.5 Hz, 3F), −63.54 (s, 3F), −82.36 (s, 3F); MS, m/z (relative intensity) 442 (M^+, 5), 373 (17), 200 (42), 181 (9), 172 (100), 145 (31), 131 (36), 103 (17), 77 (18); IR (neat) 3071, 2930, 1716, 1264, 1132, 1072, 837, 753, 695 cm^{-1}. Anal. Calcd. for $C_{19}H_{11}F_9O_3$: C, 51.60; H, 2.51. Found: C, 51.32; H, 2.42%. **2w** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.87–7.18 (m, 9H), 5.50–5.47 (m, 1H), 4.46 (q, J = 7.5 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.30 (d, J = 7.5 Hz, 3F), −63.54 (s, 3F), −82.75 (s, 3F). Anal. Calcd. for $C_{19}H_{11}F_9O_3$: C, 51.60; H, 2.51. Found: C, 51.37; H, 2.44%.

4.2.24. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-4-(p-methoxyphenyl)-2-phenyl-1,3-dioxolane (2x)

2x (anti:syn = 1:1) was prepared in 29% yield (0.117 g) according to the general procedure (p-methoxybenzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C to room temperature). **2x** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.76–7.66 (m, 2H), 7.50–7.42 (m, 3H), 7.38–7.29 (m, 2H), 7.00–6.95 (m, 2H), 5.45–5.42 (m, 1H), 4.40 (q, J = 7.5 Hz, 1H), 3.85 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.18 (d, J = 7.5 Hz, 3F), −82.94 (s, 3F); MS, m/z (relative intensity) 404 (M^+, 27), 335 (1), 230 (7), 202 (100), 187 (13), 133 (8), 105 (22), 77 (17); IR (neat) 3069, 2961, 1714, 1614, 1353, 1256, 1178, 1075, 839, 754, 696 cm^{-1}. Anal. Calcd. for $C_{19}H_{14}F_6O_3$: C, 56.44; H, 3.49. Found: C, 56.15; H, 3.38%. **2x** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.71–7.69 (m, 2H), 7.60–7.41 (m, 3H), 7.19–7.11 (m, 2H), 5.96 (s, 1H), 4.47 (q, J = 7.5 Hz, 1H), 3.80 (s, 3H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.15 (d, J = 7.5 Hz, 3F), −82.31 (s, 3F). Anal. Calcd. for $C_{19}H_{14}F_6O_3$: C, 56.44; H, 3.49. Found: C, 56.11; H, 3.41%.

*4.2.25. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-4-(fluorophenyl)-2-phenyl-1,3-dioxolane (**2y**)*

2y (anti:syn = 1:1) was prepared in 51% yield (0.200 g) according to the general procedure (fluorobenzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 to 0 °C). **2y** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.69–7.65 (m, 2H), 7.57–7.38 (m, 3H), 7.29–7.01 (m, 4H), 5.98 (s, 1H), 4.47 (q, J = 7.3 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.23 (d, J = 7.3 Hz, 3F), −82.45 (s, 3F), −110.75 to −11.37 (m, 1F); MS, m/z (relative intensity) 392 (M^+, 10), 323 (31), 218 (32), 190 (100), 149 (12), 105 (35), 77 (20); IR (neat) 3071, 2926, 1714, 1608, 1373, 1264, 1123, 1053, 840, 753, 695 cm^{-1}. Anal. Calcd. for $C_{18}H_{11}F_7O_2$: C, 55.11; H, 2.83. Found: C, 54.83; H, 2.77%. **2y** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.69–7.65 (m, 2H), 7.56–7.38 (m, 3H), 7.29–7.01 (m, 4H), 5.48–5.45 (m, 1H), 4.39 (q, J = 7.3 Hz, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.20 (d, J = 7.3 Hz, 3F), −82.90 (s, 3F), −110.75 to −111.37 (m, 1F). Anal. Calcd. for $C_{18}H_{11}F_7O_2$: C, 55.11; H, 2.83. Found: C, 54.87; H, 2.78%.

*4.2.26. (Z)-5-(2,2,2-Trifluoroethylidene)-2-trifluoromethyl-4-(p-trifluoromethylphenyl)-2-phenyl-1,3-dioxolane (**2z**)*

2z (anti:syn = 1:1) was prepared in 32% yield (0.141 g) according to the general procedure (trifluoromethylbenzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C for 10 min. **2z** (syn): oil; ^{1}H NMR ($CDCl_3$) δ 7.82–7.39 (m, 9H), 7.16 (s, 1H), 4.62–4.40 (m, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.35 (d, J = 7.3 Hz, 3F), −63.38 (s, 3F), −82.50 to −82.20 (m, 3F); MS, m/z (relative intensity) 442 (M^+, 10), 373 (26), 240 (55), 199 (31), 173 (92), 145 (100), 127 (39), 105 (77), 77 (86); IR (neat) 3067, 2929, 1713, 1620, 1327, 1266, 1171, 1071, 842, 755, 692 cm^{-1}. Anal. Calcd. for $C_{19}H_{11}F_9O_2$: C, 51.60; H, 2.51. Found: C, 51.27; H, 2.45%. **2z** (anti): oil; ^{1}H NMR ($CDCl_3$) δ 7.82–7.39 (m, 9H), 5.55–5.53 (m, 1H), 4.62–4.40 (m, 1H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −58.31 (d, J = 7.5 Hz, 3F), −63.35 (s, 3F), −82.44 to −82.01 (m, 3F). Anal. Calcd. for $C_{19}H_{11}F_9O_2$: C, 51.60; H, 2.51. Found: C, 51.31; H, 2.46%.

*4.3. General procedure for the preparation of 4-trifluoroethylidene-4H-1,3-dioxines **3***

A 25-mL two-neck round bottom flask equipped with a magnetic stirrer bar, a septum and condenser connected to an argon source was charged with 5 mL of CH_3CN and **1a** (0.430 g, 1.3 mmol) and then cooled to −15 °C. After TBAF (1.3 mmol, 1.0 M in THF) was added and stirred at −15 °C for 10 min, perfluoroalkylated ketone (2.0 mmol) was added and then the reaction mixture was allowed to warm to room temperature. The reaction mixture was extracted with ether twice, dried over anhydrous $MgSO_4$ and chromatographed on SiO_2 column. Elution with a mixture of hexane and ether (9:1) provided 4-trifluoroethylidene-4*H*-1,3-dioxines **3**.

*4.3.1. 2,5-Bis(trifluoromethyl)-2,6-diphenyl-4H-1,3-dioxine (**3u**)*

3u was prepared in 65% yield (0.243 g) according to the general procedure (benzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C to room temperature). **3u**: oil; ^{1}H NMR ($CDCl_3$) δ 7.72–7.69 (m, 2H), 7.51–7.34 (m, 8H), 3.33 (dq, J = 9.6, 4.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −64.92 (t, J = 9.6 Hz, 3F), −84.97 (s, 3F); MS, m/z (relative intensity) 374 (M^+, 53), 305 (100), 221 (7), 165 (9), 105 (18), 77 (42); IR (neat) 3067, 2939, 1711, 1603, 1375, 1227, 1137, 1032, 754, 698 cm^{-1}. Anal. Calcd. for $C_{18}H_{12}F_6O_2$: C, 57.76; H, 3.23. Found: C, 57.38; H, 3.15%.

*4.3.2. 2,5-Bis(trifluoromethyl)-2-(p-methoxyphenyl)-6-phenyl-4H-1,3-dioxine (**3v**)*

3v was prepared in 65% yield (0.263 g) according to the general procedure (benzaldehyde and trifluoromethyl *p*-methoxyphenyl ketone were used as carbonyl compounds and condition 2 is −15 °C to room temperature). **3v**: oil; ^{1}H NMR ($CDCl_3$) δ 7.65–6.89 (m, 9H), 3.83 (s, 3H), 3.32 (q, J = 9.6 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −65.02 (t, J = 9.6 Hz, 3F), −85.07 (s, 3F); MS, m/z (relative intensity) 404 (M^+, 11), 335 (83), 270 (14), 201 (9), 172 (27), 135 (100), 107 (22), 92 (20), 77 (52); IR (neat) 3064, 2963, 1711, 1613, 1373, 1260, 1136, 1083, 840, 755, 697 cm^{-1}. Anal. Calcd. for $C_{19}H_{14}F_6O_3$: C, 56.44; H, 3.49. Found: C, 56.03; H, 3.41%.

*4.3.3. 2,5-Bis(trifluoromethyl)-2-(p-trifluoromethylphenyl)-6-phenyl-4H-1,3-dioxine (**3w**)*

3w was prepared in 67% yield (0.296 g) according to the general procedure (benzaldehyde and trifluoromethyl *p*-trifluoromethylphenyl ketone were used as carbonyl compounds and condition 2 is −15 °C to room temperature). **3w**: oil; ^{1}H NMR ($CDCl_3$) δ 7.87–7.83 (m, 2H), 7.77–7.70 (m, 2H), 7.52–7.35 (m, 5H), 3.34 (q, J = 9.6 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −63.51 (s, 3F), −64.94 (q, J = 9.6 Hz, 3F), −84.81 (s, 3F); MS, m/z (relative intensity) 442 (M^+, 22), 423 (8), 373 (85), 289 (8), 173 (100), 145 (51), 108 (29), 77 (43); IR (neat) 3066, 2941, 1714, 1499, 1326, 1266, 1197, 1137, 1089, 843, 755, 695 cm^{-1}. Anal. Calcd. for $C_{19}H_{11}F_9O_2$: C, 51.60; H, 2.51. Found: C, 51.37; H, 2.44%.

*4.3.4. 2,5-Bis(trifluoromethyl)-6-(p-methoxyphenyl)-2-phenyl-4H-1,3-dioxine (**3x**)*

3x was prepared in 28% yield (0.113 g) according to the general procedure (*p*-methoxybenzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C to room temperature for 12 h). **3x**: oil; ^{1}H NMR ($CDCl_3$) δ 7.73–6.83 (m, 9H), 3.83 (s, 3H), 3.29 (dq, J = 9.8, 2.0 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −65.05 (t, J = 9.8 Hz, 3F), −84.95 (s, 3F); MS, m/z (relative intensity) 404 (M^+, 60), 373 (23), 335 (54), 240 (13), 202 (100), 167 (11), 105 (81), 77 (28); IR (neat) 3067, 2939, 1712, 1373, 1256, 1137, 1087, 841, 749, 696 cm^{-1}. Anal. Calcd. for $C_{19}H_{14}F_6O_3$: C, 56.44; H, 3.49. Found: C, 56.23; H, 3.46%.

*4.3.5. 2,5-Bis(trifluoromethyl)-6-(p-fluorophenyl)-2-phenyl-4H-1,3-dioxine (**3y**)*

3y was prepared in 51% yield (0.200 g) according to the general procedure (*p*-fluorobenzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C to room temperature for 3 h). **3y**: oil; ^{1}H NMR ($CDCl_3$) δ 7.86–7.67 (m, 2H), 7.56–7.42 (m, 3H), 7.38–7.01 (m, 4H), 3.29 (dq, J = 9.7, 2.4 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −64.97 (t, J = 9.7 Hz, 3F), −85.01 (s, 3F), −111.18 to −111.37 (m, 1F); MS, m/z (relative intensity) 392 (M^+, 20), 373 (30), 323 (64), 240 (16), 190 (88), 105 (100), 77 (37); IR (neat) 3068, 2931, 1712, 1372, 1266, 1137, 1087, 843, 752, 694 cm^{-1}. Anal. Calcd. for $C_{18}H_{11}F_7O_2$: C, 55.11; H, 2.83. Found: C, 54.83; H, 2.77%.

*4.3.6. 2,5-Bis(trifluoromethyl)-6-(p-trifluoromethylphenyl)-2-phenyl-4H-1,3-dioxine (**3z**)*

3z was prepared in 55% yield (0.200 g) according to the general procedure (*p*-trifluoromethylbenzaldehyde and trifluoroacetophenone were used as carbonyl compounds and condition 2 is −15 °C to room temperature). **3z**: oil; ^{1}H NMR ($CDCl_3$) δ 7.77–7.18 (m, 9H), 3.37 (dq, J = 9.6, 2.2 Hz, 2H); ^{19}F NMR ($CDCl_3$, internal standard $CFCl_3$) δ −63.70 (s, 3F), −64.68 (t, J = 9.6 Hz, 3F), −85.00 (s, 3F); MS, m/z (relative intensity) 442 (M^+, 12), 373 (31), 240 (5), 173 (22), 145 (28), 105 (100), 91 (17), 77 (60); IR (neat) 3069, 2942, 1709,

1374, 1266, 1194, 1085, 841, 754, 697 cm^{-1}. Anal. Calcd. for $C_{19}H_{11}F_9O_2$: C, 51.60; H, 2.51. Found: C, 51.32; H, 2.45%.

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