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Preparation of α- or β-trifluoromethylated vinylstannanes and their cross-coupling reactions

In Howa Jeong*, Young Sam Park, Myong Sang Kim, Yong Sup Song

Department of Chemistry, Yonsei University, Wonju 220-710, South Korea

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Abstract

α- or β-Trifluoromethylated vinylstannanes **1**, **2a**, **3** and **4** were prepared form 1,1-bis(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (**5**) via several steps. The cross-coupling arylation reactions of **1**–**4** with aryl iodides bearing a bromo, methoxy, methyl, nitro or trifluoromethyl group on para- or meta-position of benzene ring afforded the corresponding coupling products in good yields. Compounds **1**, **2a** and **4** underwent the acylation reaction with various types of acyl chlorides to give the corresponding trifluoromethylated enone derivatives in good yields. Reduction of trifluoromethylated enone derivatives with $LiAlH_4$, followed by Fridel-Craft's type of cyclization with $AlCl_3$ provided trifluoromethylated indene derivatives in good yields.

Keywords: Trifluoromethylated vinylstannane; Cross-coupling reaction; Arylation reaction; Acylation reaction

1. Introduction

The considerable efforts have been paid to the development of trifluoromethylated building blocks because of their potential to give new synthetic routes to a variety of trifluoromethylated compounds, some of which exhibit unique biological properties in the areas of agrochemicals, pharmaceuticals and material science [1,2]. In the course of our synthetic studies on trifluoromethylated building blocks, we are interested in the synthesis of α- or β-trifluoromethylated vinylstannanes and utilization of these compounds to prepare trifluoromethylated compounds via cross-coupling reactions. Especially, this methodology can be utilized to synthesize potential mammary tumor inhibitors, such as trifluoromethylated triphenylethene [3,4], diphenylethene [5,6] and indene derivatives [7]. Although a variety of types of trifluoromethylated vinylmetal reagents, such as cadmium [8], copper [9,10], lithium [11–14], mercury [15] and zinc [16–22] has been synthesized and utilized previously, the preparation and synthetic utility of trifluoromethylated vinylstannane reagent have been quite limited. Only several papers described about chemistry of trifluoromethylated vinylstannane reagent. The α-(trifluoromethyl)vinylstannane reagent bearing only hydrogens at β-position has been synthesized from the reaction of 2-bromotrifluoroisopropene with lithium tributylstannate in the presence of CuI and utilized for the cross-coupling reactions with acyl chlorides in the presence of catalytic amount of $Pd(PPh_3)_2(Bn)Cl$ in HMPA at 65 °C to give α-(trifluoromethyl)vinyl ketone derivatives [23]. Ichikawa also carried out the reaction of α-(trifluoromethyl)vinylstannane reagent with α,β-unsaturated acyl chlorides in the presence of catalytic amount of $Pd(PPh_3)_2Cl_2$ and CuCN in toluene at 55–75 °C to give the desired NaZarov substrates [24]. We also reported about the preparation of a novel α-(trifluoromethyl)vinylstannane reagent bearing two phenyl groups at β-position and the cross-coupling reactions of it with aryl iodides to give trifluoromethylated triphenylethene derivatives [25]. Recently, Shen prepared α-fluoro-β-trifluoromethylvinylstannanes stereospecifically from the reaction of corresponding vinylsulfone with tributyltin hydride [26].

In the present paper, we would like to describe the preparation of α-trifluoromethyl-β,β-diphenylvinylstannane **1**, (*E*)-α-trifluoromethyl-β-methyl-β-phenylvinylstannane **2a**, β-fluoro-β-trifluoromethyl-α-phenylvinylstannane **3**, and β-trifluoromethyl-α,β-diphenylvinylstannane **4** reagents, and examine the palladium-promoted cross-coupling reactions of these reagents with aryl iodides and acyl chlorides.

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

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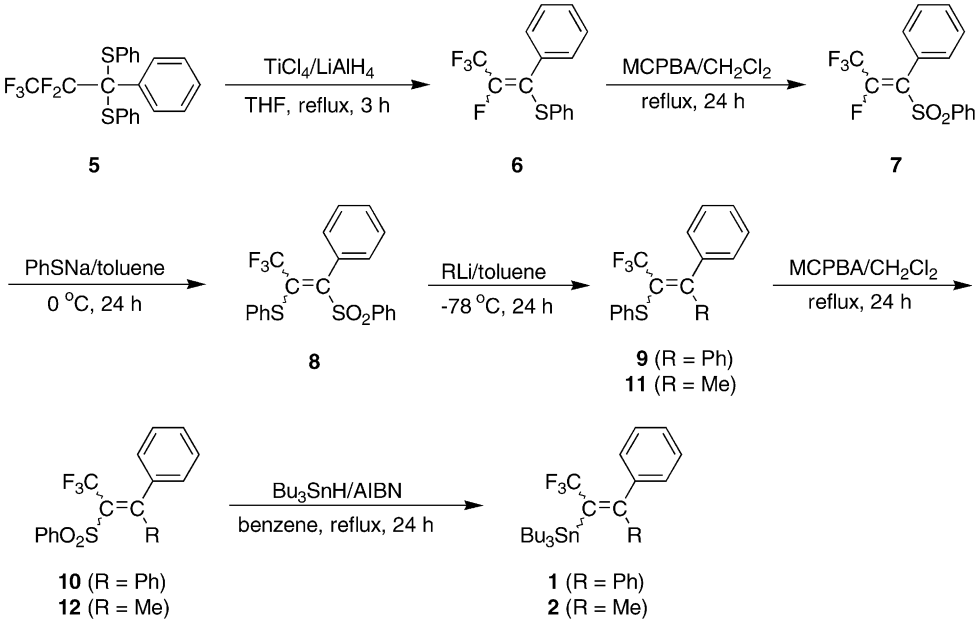
2. Results and discussion

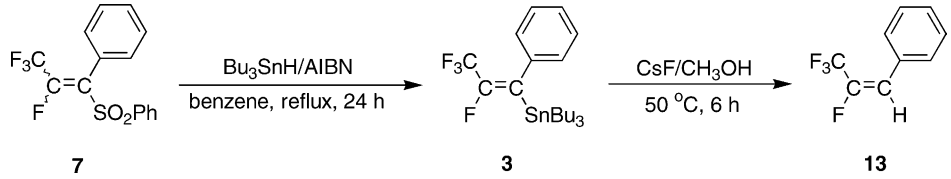
2.1. Preparation of α- or β-trifluoromethylated vinylstannanes *1–4*

All trifluoromethylated vinylstannanes **1**, **2a**, **3** and **4** can be prepared from 1,1-bis(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (**5**) [27] via several steps. The reaction of **5** with a mixture of $TiCl_4$ (2 eq.) and $LiAlH_4$ (4 eq.) in THF at reflux temperature for 3 h provided an isomeric mixture of 2,3,3,3-tetrafluoro-1-phenyl-1-phenylthiopropene (**6**) in 92% yield [28]. Oxidation of **6** with MCPBA (2.5 eq.) in CH_2Cl_2 at reflux temperature for 24 h gave an isomeric mixture (16:84) of 2,3,3,3-tetrafluoro-1-phenyl-1-phenylsulfonylpropene (**7**) in 92% yield. Treatment of **7** with sodium thiophenoxide (4 eq.) in toluene at 0 °C for 24 h resulted in the formation of 3,3,3-trifluoro-1-phenyl-1-phenylsulfonyl-2-phenylthiopropene (**8**) in 81% yield. The choice of solvent and reaction temperature were quite important to give **8** in this reaction. The use of solvent, such as THF, CH_3CN or DMF, or elevated reaction temperature caused to form a significant amount of 1,2-bis(phenylthio)-3,3,3-trifluoro-1-phenylpropene. The reaction of **8** with phenyllithium (1.5 eq.) in toluene at −78 °C for 24 h afforded 3,3,3-trifluoro-1,1-diphenyl-2-phenylthiopropene (**9**) in 82% yield. Oxidation of **9** with MCPBA (2.5 eq.) in CH_2Cl_2 at reflux temperature for 24 h resulted in the formation of 3,3,3-trifluoro-1,1-diphenyl-2-phenylsulfonylpropene (**10**) in 94% yield. Finally, reaction of **10** with Bu_3SnH (1.5 eq.)/AIBN (10 mol%) in benzene at reflux temperature for 24 h yielded α-trifluoromethyl-β,β-diphenylvinylstannane **1** in 84% yield (Scheme 1). When **8** was reacted with methyllithium (1.5 eq.) in toluene at −78 °C for 24 h, an isomeric mixture of 1,1,1-trifluoro-3-phenyl-2-phenylthio-2-butene (**11**) in 68% yield. Oxidation of **11** with MCPBA (2.5 eq.) in CH_2Cl_2 at reflux temperature for 24 h resulted in the formation of an isomeric mixture of 1,1,1-trifluoro-3-phenyl-2-phenylsulfonyl-2-butene (**12**) in 92% yield. The reaction of **12** with Bu_3SnH (1.5 eq.)/AIBN (10 mol%) in benzene at reflux temperature for 24 h yielded an isomeric mixture of α-trifluoromethyl-β-methyl-β-phenylvinylstannane **2** (*E*:*Z* = 81:19) in 67% yield (Scheme 1). The *E* and *Z* isomers were separated by column chromatography. The assignment of stereoisomer of **2** was based on the chemical shift of OCH_3 group in ^1H NMR spectrum after cross-coupling reaction of **2** with *p*-iodoanisole in the presence of $Pd(PPh_3)_4$ and CuI. Generally, the *p*-OCH_3 protons attached to benzene ring which are arranged to the same side with benzene ring are more shielded than those arranged to the other side [29]. Therefore, the chemical shift of *p*-OCH_3 protons attached to benzene ring which are arranged to the same side with benzene ring is 3.64 ppm, whereas the chemical shift of those protons arranged to the other side is 3.78 ppm. Another useful diagnosis for analysis of *E* and *Z* isomers of **2** is to use H–F homoallylic coupling constant. The H–F *cis* coupling constant (J = 2.7 Hz) is bigger than trans H–F coupling constant (J = 2.2 Hz).

Treatment of **7** with Bu_3SnH (3.0 eq.)/AIBN (10 mol%) in benzene at reflux temperature for 24 h resulted in the formation of β-fluoro-β-trifluoromethyl-α-phenylvinylstannane **3** (only *Z* isomer) in 75% yield (Scheme 2). Only one stereoisomer was observed in the GC–MS spectroscopy and the reducing product, (*E*)-2,3,3,3-tetrafluoro-1-phenylpropene, was not observed. The use of less than 3.0 eq. of tributyltin hydride caused to recover some amount of **7**. The assignment of stereoisomer **3** was made by the comparison



Scheme 1.



7 3 13

Scheme 2.

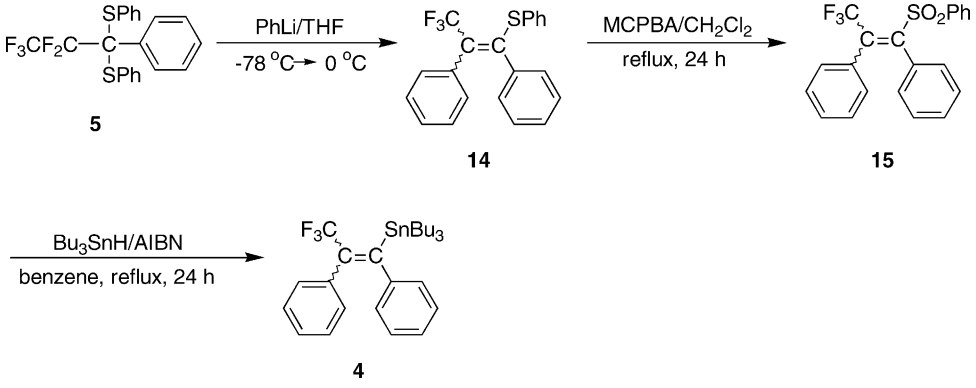
with ^{1}H and ^{19}F NMR spectrum of authentic sample [30] after the conversion to reducing product **13** which can be obtained from the reaction of **3** with CsF (5 eq.) in methanol at 50 °C for 6 h. It was found that this reducing process from the vinylstannane reagents was stereospecific reaction and the reaction was proceeded with the retention of configuration [31]. ^{19}F NMR spectrum of **13** exhibited a characteristic doublet of quartet ($J_{H,F} = 20.4$ Hz, $J_{F,CF_3} = 9.9$ Hz) at −125.62 ppm and ^{1}H NMR spectrum showed a doublet ($J_{H,F} = 21.0$ Hz) at 6.77 ppm. It is postulated that the appearance of doublet in ^{1}H and ^{19}F NMR spectra is due to the *cis* H–F coupling. The stereospecifical result of stannylation of **7** can be rationalized by previous similar mechanism suggestion [32].

The reaction of **5** with 2.1 eq. of phenyllithium at −78 °C, followed by warming to 0 °C provided an isomeric mixture of 3,3,3-trifluoro-1,2-diphenyl-1-phenylthiopropene (**14**) in 87% yield. Oxidation of **14** with MCPBA resulted in the formation of 3,3,3-trifluoro-1,2-diphenyl-1-phenylsulfonylpropene (**15**) in 87% yield. Treatment of **15** with Bu_3SnH (4.0 eq.)/AIBN (10 mol%) in benzene at reflux temperature for 24 h yielded an isomeric mixture of α-trifluoromethyl-α,β-diphenylvinylstannane **4** (*E*:*Z* = 12:88) in 38% yield (Scheme 3). The assignment of stereoisomer **4** was made by the comparison with ^{1}H and ^{19}F NMR spectra of authentic sample [3] after cross-coupling reaction of **4** with *p*-iodoanisole in the presence of $Pd(PPh_3)_4$ and CuI.

2.2. Arylation of vinylstannanes 1–4 with iodobenzene derivatives

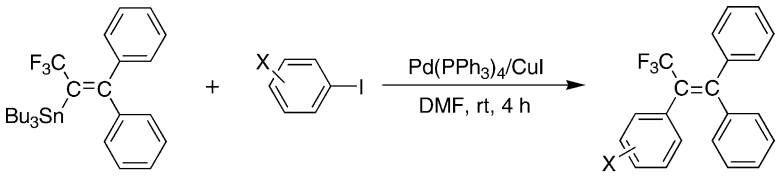
Since vinylstannane group is an excellent functionality for the carbon–carbon bond formation with electrophiles in the presence of palladium catalyst [33], we examined the reaction of **1** with aryl iodides bearing a substituent on benzene ring in the presence of several palladium catalyst. The use of Pd catalyst, such as $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ in THF, DMF, toluene or HMPA did not provide any cross-coupling product. However, the cross-coupling reaction was well proceeded by using a catalytic system of 10 mol% $Pd(PPh_3)_4$ and 10 mol% CuI in DMF. The reaction was completed in 4 h at room temperature. Aryl bromides did not provide a cross-coupling adduct even at 80 °C. Therefore, aryl iodides bearing a bromo, methoxy, methyl, nitro or trifluoromethyl on para- or meta-position of benzene ring underwent the cross-coupling reaction with **1** in the presence of 10 mol% $Pd(PPh_3)_4$ and 10 mol% CuI in DMF at room temperature for 4 h, and the corresponding coupling products **16** were obtained in high yields. Unfortunately, the coupling product, formed from the reaction of **1** with aryl iodides bearing a methoxy or methyl on ortho-position of benzene ring, was obtained in less than 5% yield under the same reaction conditions, whereas a reducing product and homocoupling product (butadiene) were formed as major products. The heating of the reaction mixture at 80 °C resulted in the formation of a messy reaction mixture. The results of these reactions are summarized in Scheme 4 and Table 1. Although role of CuI in the coupling reaction is obscure, it was suggested that copper iodide facilitates the transmetallation step in the cross-coupling mechanism cycle [34].

Similarly, the reactions of (*E*)-β-methyl-β-phenyl-α-(trifluoromethyl)vinylstannane (**2a**) with aryl iodides in the presence of several palladium catalyst were also examined to give the corresponding coupling products **17**. The cross-coupling reaction was well proceeded by using a catalytic



5 14 15 4

Scheme 3.



1 **16**

Scheme 4.

Table 1
The cross-coupling reactions of **1** with aryl iodide

Compound	X	Yield (%)[a]
16a	H	93
16b	*p*-Br	86
16c	*p*-OCH_3	89
16d	*p*-CH_3	88
16e	*p*-NO_2	93
16f	*p*-CF_3	90
16g	*m*-Br	88
16h	*m*-OCH_3	80
16i	*m*-CH_3	81
16j	*m*-NO_2	82
16k	*m*-CF_3	85

[a] Isolated yields.

Table 2
The cross-coupling reactions of **2a** with aryl iodides

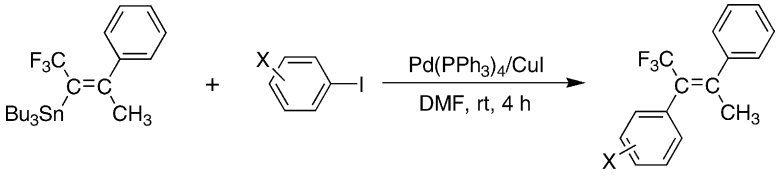
Compound	X	Yield (%)[a]
17a	H	80
17b	*p*-Br	74
17c	*p*-OCH_3	85
17d	*p*-CH_3	84
17e	*p*-NO_2	78
17f	*m*-OCH_3	79
17g	*m*-CH_3	86

[a] Isolated yields.

system of 10 mol% $Pd(PPh_3)_4$ and 10 mol% CuI in DMF. The reaction was completed in 4 h at room temperature. The adopted reaction condition tolerated substituents, such as bromo, methoxy, methyl or nitro group on para- or meta-position of benzene ring. However, the coupling reaction with aryl iodides bearing a methoxy or methyl on ortho-position of benzene ring, was unsuccessful under the same reaction conditions. The results of the coupling reactions of **2a** with aryl iodides are summarized in Scheme 5 and Table 2. It has been well known that diphenylethene derivatives, such as diethylstibestrol and dienestrol are useful mammary tumor inhibitors [5,6]. Replacement of alkyl or vinyl group in those compounds by trifluoromethyl substituent resulted in the enhancement of binding affinity as well as estrogenic activity [6]. However, the previous method for the preparation of trifluoromethylated diphenylethene derivatives has one drawback, such as synthesis of only symmetrical bis(trifluoromethyl) diphenylethene derivatives [6].

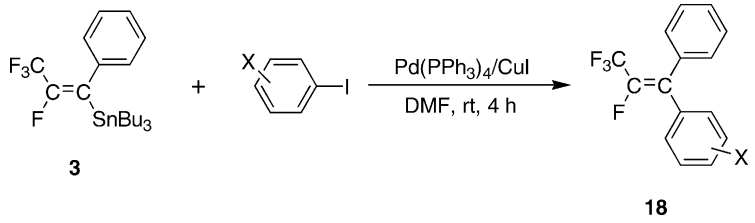
We introduced this process to the reaction of **3** with aryl iodides bearing a substituent on benzene ring in the presence of palladium catalysts. When **3** was reacted with iodobenzene in the presence of a mixture of 10 mol% $Pd(PPh_3)_4$ and 10 mol% CuI in DMF at room temperature for 5 h, the cross-coupling product **18a** was obtained in 70% yield. The use of bromobenzene instead of iodobenzene in the same reaction provided a trace amount of **18a** along with several unidentified adducts. Aryl iodides bearing a bromo, chloro, fluoro, methoxy, methyl, or nitro group on para- or meta-position of benzene ring underwent the cross-coupling reaction with **3** under the same reaction condition, and the corresponding coupling products were obtained in 61–82% yields. The reaction of **3** with 2-iodotoluene under the same reaction condition also afforded the coupling product **18j** in 71% yield, but the same reaction of **3** with *o*-iodoanisole and *o*-iodobenzotrifluoride provided the only trace amount of corresponding products. All of these coupling reactions proceeded with retention of configuration at the double bond except for the reaction with *para*-iodonitrobenzene in which an *E* and *Z* isomeric mixture (75/25) of coupling product was obtained. The results of these reaction are summarized in Scheme 6 and Table 3.

The reactions of **3** with iodo substituted heterocyclic compounds were also examined. Therefore, when **3** was



2a **17**

Scheme 5.



Scheme 6.

Table 3
The cross-coupling reactions of **3** with aryl iodides

Compound	X	Yield (%)[a]
18a	H	70
18b	*p*-Br	68
18c	*p*-Cl	67
18d	*p*-F	61
18e	*p*-OCH_3	82
18f	*p*-CH_3	71
18g	*p*-NO_2	77[b]
18h	*m*-OCH_3	79
18i	*m*-CH_3	68
18j	*o*-CH_3	71

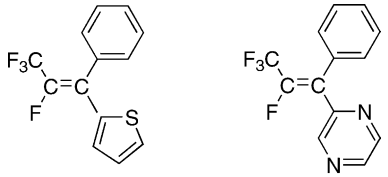
[a] Isolated yields.
[b] An isomeric mixture of product (75/25) was obtained.

Table 4
The cross-coupling reactions of **4** with aryl iodides

Compound	X	Yield (%)[a,b]
21a	H	56
21b	*p*-F	50
21c	*p*-Cl	45
21d	*p*-Br	50
21e	*p*-OCH_3	58
21f	*p*-CF_3	63
21g	*p*-NO_2	64
21h	*m*-CH_3	51
21i	*m*-OCH_3	65
21j	*m*-CF_3	53

[a] Isolated yields.
[b] An isomeric mixture of product (*E*:*Z* = 12:88) was obtained.

reacted with 2-iodothiophene and 2-iodopyrazine under the same reaction condition, the corresponding coupling products **19** and **20** were obtained in 63 and 65% yields, respectively (Scheme 7).

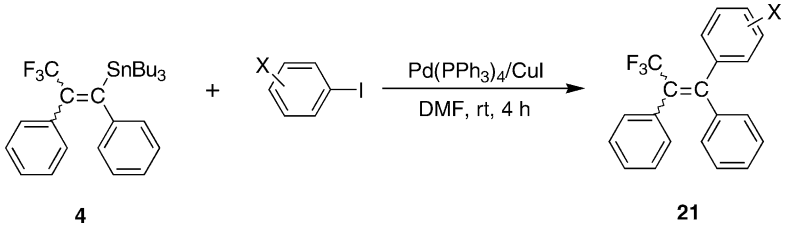


Scheme 7.

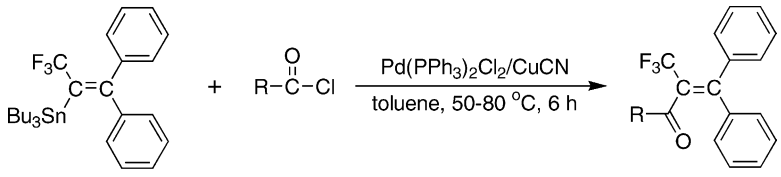
Finally, coupling reactions of **4** with aryl iodides bearing a substituent on benzene ring in the presence of palladium catalysts were also performed under the employed condition. Treatment of **4** with iodobenzene in the presence of a mixture of 10 mol% $Pd(PPh_3)_4$ and 10 mol% CuI in DMF at room temperature for 4 h, the cross-coupling product **21a** was obtained in 56% yield. Aryl iodides bearing a bromo, chloro, fluoro, methoxy, methyl, nitro or trifluoromethyl group on para- or meta-position of benzene ring underwent the cross-coupling reaction with **4** under the same reaction condition, and the corresponding coupling products were obtained in 45–65% yields. The results of these reaction are summarized in Scheme 8 and Table 4.

2.3. Acylation of vinylstannanes *1–4* with acyl chloride derivatives

We examined palladium-promoted acylation of this reagent with acyl chlorides to give β,β-diphenyl-α-trifluoromethylated enone derivatives which are useful intermediates for the formation of novel 1,3-disubstituted 2-(trifluoromethyl)indene derivatives via Friedel-Craft's type of the cyclization. Since nonfluorinated 1,3-disubstituted indene derivative, such as Indenestrol A exhibited mammary tumor inhibiting antiestrogen activity, it is expected that 1,3-disubstituted 2-(trifluoromethyl)indene derivatives also have



Scheme 8.



1 22

Scheme 9.

a potential similar activity. First of all, the acylation reaction of **1** with acetyl chloride was carried out in the presence of several palladium catalyst. The use of Pd catalyst, such as $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ in THF, DMF, toluene or HMPA did not provide any acylated product. However, acylation reaction to give acylated product **22** was successfully accomplished by using a mixture of 10 mol% $Pd(PPh_3)_2Cl_2$ and 10 mol% CuCN in toluene at 50 °C for 6 h. The higher temperature (80 °C) was needed for the completion of acylation of **1** with types of benzoyl chlorides bearing a bromo, methoxy, methyl, or nitro on the benzene ring. Furthermore, starting material **1** also underwent the acylation reaction with various types of acyl chlorides, such as ethyl chloroformate, furoyl chloride, naphthoyl chloride to give the corresponding trifluoromethylated enone derivatives **22** at 80 °C for 6 h. The experimental results of the acylation reactions are summarized in Scheme 9 and Table 5.

Reduction of **22a** with $LiAlH_4$ (1.5 eq.) in ether at reflux temperature for 3 h afforded the corresponding allylic alcohols **23a** in 71% yield. The use of $NaBH_4$ did not provide the desired product, whereas the starting material was always recovered. The Fridel-Craft's type of cyclization of **23a** was successfully accomplished to give 2-trifluoromethyl-3-methyl-1-phenylindene (**24a**) by using $AlCl_3$ (1.2 eq.) in methylene chloride at −78 °C, followed by the slowly warming to room temperature. The use of dilute H_2SO_4 instead of $AlCl_3$ at reflux temperature caused not only to decrease the yield of indene derivatives **24a**, but also to extend the reaction time. The more excess of $AlCl_3$ (2.0 eq.) was necessary to carry out the cyclization of **23d** because of possible coordination of oxygen of methoxy group with $AlCl_3$. Reduction of other types of enone derivatives **22**, followed by treatment with $AlCl_3$ under the same reaction condition also provided the corresponding 1,3-disubstituted 2-(trifluoromethyl)indene derivatives **24** in good yields. The experimental results of reduction and cyclization reactions are summarized in Scheme 10 and Table 6.

Table 5
The acylation reactions of **1** with acyl chlorides

Compound	T (°C)	R	Yield (%)[a]
22a	50	CH_3	68
22b	80	C_6H_5	80
22c	80	(o-CH_3)-C_6H_4	78
22d	80	(p-CH_3)-C_6H_4	88
22e	80	(p-OCH_3)-C_6H_4	85
22f	80	(m-NO_2)-C_6H_4	72
22g	80	(m-CH_3)-C_6H_4	81
22h	80	(m-Br)-C_6H_4	77
22i	80	C_2H_5O	62
22j	80	2-Furanyl	75
22k	80	2-Naphthyl	86

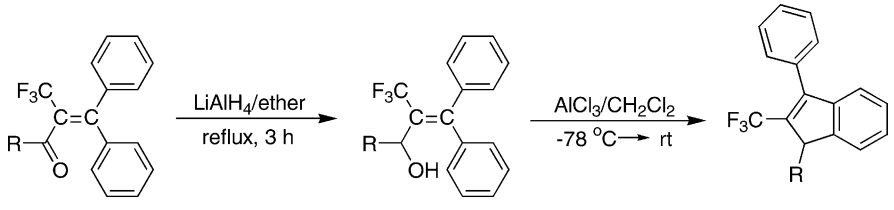
[a] Isolated yields.

Table 6
The synthesis of 1,3-disubstituted 2-trifluoromethylated indene derivatives **24**

Compound	R	Yield of **23** (%)[a]	Yield of **24** (%)[a]
23a, **24a**	CH_3	71	76
23b, **24b**	C_6H_5	74	78
23c, **24c**	(p-CH_3)-C_6H_4	69	71
23d, **24d**	(p-OCH_3)-C_6H_4	73	68
23e, **24e**	2-Naphthyl	71	74

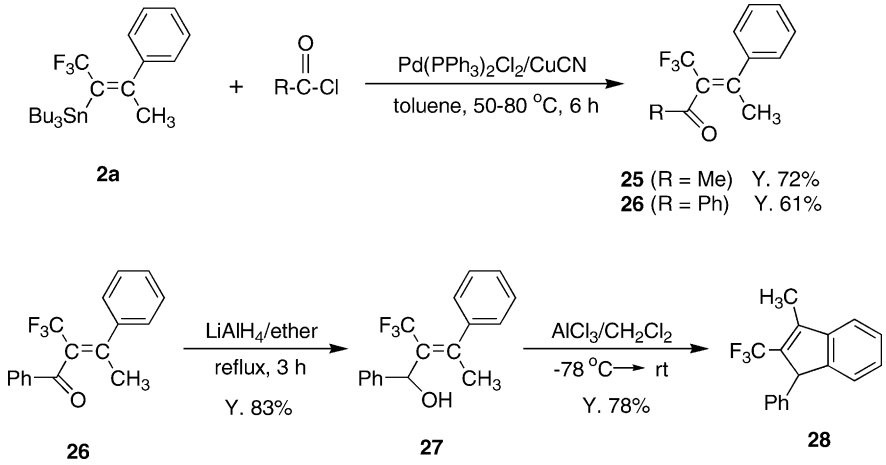
[a] Isolated yields.

The cross-coupling reaction of **2a** with acyl chlorides were also examined in a similar manner. When **2a** was reacted with acetyl chloride or benzoyl chloride in the presence of 10 mol% $Pd(PPh_3)_2Cl_2$ and 10 mol% CuCN in toluene at 50–80 °C for 6 h, the corresponding acylated



22 23 24

Scheme 10.



Scheme 11.

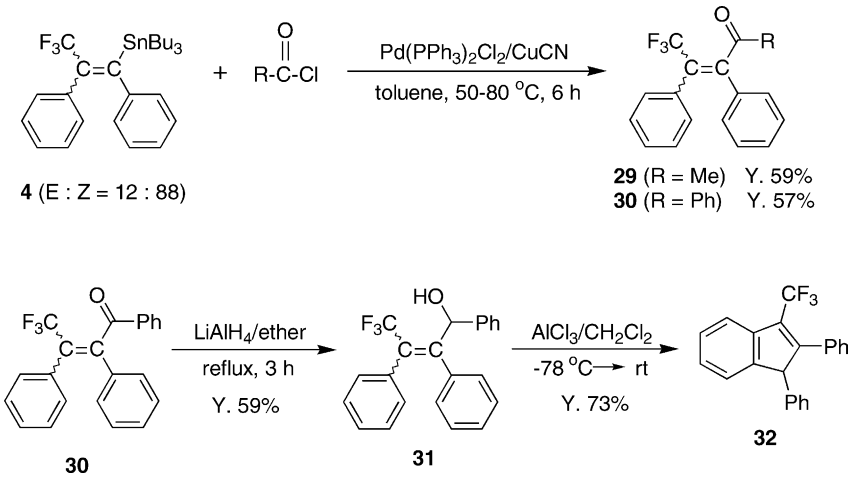
products **25** and **26** were obtained in 72 and 61% yields, respectively. Reduction of **26** with $LiAlH_4$ (1.5 eq.) in ether at reflux temperature for 3 h afforded the corresponding allylic alcohol, 2-trifluoromethyl-1,3-diphenyl-2-buten-1-ol (**27**) in 83% yield. Cyclization of **27** was successfully accomplished to give indene derivative **28** in 78% yield by using $AlCl_3$ (1.2 eq.) in methylene chloride at −78 °C, followed by the slowly warming to room temperature (Scheme 11).

Unfortunately, the acylation reaction of **3** with benzoyl chloride under the same reaction condition provided the acylated product in less than 10% yield, whereas homocoupling product, butadiene, was obtained as a major product. It seems likely that slow transmetallation between **3** and oxidative palladium addition intermediate to benzoyl chloride leads to the formation of homocoupling product. We employed several Pd catalyst conditions, such as $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ in THF, DMF, toluene or HMPA, but it was failed to have the desired acylated product.

The acylation reaction of **4** with acyl chlorides was also performed under the same reaction condition. Therefore, when **4** was reacted with acetyl chloride or benzoyl chloride in the presence of a mixture of 10 mol% $Pd(PPh_3)_2Cl_2$ and 10 mol% CuCN in toluene at 80 °C for 6 h, the acylated products **29** (*E*:*Z* = 12:88) and **30** (*E*:*Z* = 12:88) were formed in 59 and 57% yields, respectively. Reduction of **30** with $LiAlH_4$ (1.5 eq.) in ether at reflux temperature for 3 h afforded the corresponding allylic alcohols **31** in 59% yield. Cyclization of **31** in the presence of $AlCl_3$ (1.2 eq.) in methylene chloride at −78 °C, followed by the slowly warming to room temperature resulted in the formation of indene derivative **32** in 73% yield (Scheme 12).

3. Experimental

^1H NMR 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



Scheme 12.

Mattson Genesis series FT High Resolution Spectrophotometer. Mass spectra were obtained by using Hewlett-Packard 5890 GC/5970B MSD (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 solvent were dried by general purification method.

3.1. 2-Tributylstannanyl-3,3,3-trifluoro-1,1-diphenylpropene ***1***

3.1.1. 2,3,3,3-Tetrafluoro-1-phenyl-1-phenylthiopropene ***6***

A mixture of titanium tetrachloride (5.50 ml, 50 mmol) and lithium aluminum hydride (3.80 g, 0.1 mol) in dry THF (200 ml) was stirred at room temperature for 1 h under nitrogen atmosphere and then heated to boiling. 1,1-bis-(phenylthio)-2,2,3,3,3-pentafluoropropylbenzene (10.65 g, 25 mmol) in THF was added under reflux and the reaction mixture was kept boiling for further 3 h. After cooling, the reaction mixture was poured on ice water, neutralized with conc. HCl and extracted with ether. The ether solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane provided **6** in 92% yield. **6**: oil; ^{1}H NMR ($CDCl_3$) δ 7.50–7.16 (m, 10H); ^{19}F NMR ($CDCl_3$) δ −63.87 (d, $J = 8.6$ Hz, 3F, one isomer), −64.84 (d, $J = 11.1$ Hz, 3F, the other isomer), −115.13 (q, $J = 8.6$ Hz, 1F, one isomer), −119.00 (q, $J = 11.1$ Hz, 1F, the other isomer); MS, *m/z* (relative intensity) 298 (, 31), 229 (61), 196 (91), 121 (100), 77 (8); IR (neat) 3061, 2958, 1664, 1581, 1476, 1443, 1328, 1201, 1137, 748, 691 cm^{-1}. Anal. Calcd. for $C_{15}H_{10}F_4S$: C, 62.27; H, 3.38. Found: C, 62.01; H, 3.30.

3.1.2. 2,3,3,3-Tetrafluoro-1-phenyl-1-phenylsulfonylpropene ***7***

A mixture of **6** (7.45 g, 25 mmol) and MCPBA (21.5 g) in dry CH_2Cl_2 (150 ml) was heated to reflux for 24 h under nitrogen atmosphere. After cooling, the reaction mixture was washed with a mixture of saturated $NaHCO_3$ and 10% $NaHSO_3$ solution and extracted with CH_2Cl_2. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane and ethyl acetate (4:1) provided **7** in 92% yield. **7**: mp 104–106 °C; ^{1}H NMR ($CDCl_3$) δ 7.65–7.01 (m, 10H); ^{19}F NMR ($CDCl_3$) δ −62.49 (d, $J = 4.2$ Hz, 3F, one isomer), −66.25 (d, $J = 4.2$ Hz, 3F, the other isomer), −102.16 (q, $J = 4.2$ Hz, 1F, one isomer), −108.77 (q, $J = 8.2$ Hz, 1F, the other isomer); MS, *m/z* (relative intensity) 330 (M^+, 48), 266 (5), 189 (53), 169 (100), 125 (52), 77 (47), 51(33); IR (KBr) 3065, 1652, 1447, 1347, 1306, 1196, 1156, 1088, 761, 696 cm^{-1}. Anal. Calcd. for $C_{15}H_{10}F_4O_2S$: C, 54.54; H, 3.05. Found: C, 54.17; H, 3.14.

3.1.3. 3,3,3-Trifluoro-1-phenyl-1-phenylsulfonyl-2-phenylthiopropene ***8***

To a dry toluene (100 ml) solution of sodium thiophenoxide formed in situ from NaH (3.60 g, 90 mmol) and thiophenol (9.90 g, 90 mmol) was added **7** (7.43 g, 22.5 mol) in toluene at 0 °C and the reaction mixture was stirred at 0 °C for 24 h. The reaction mixture was washed with water and then extracted with ether twice. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane and ethyl acetate (4:1) provided **8** in 81% yield. **8**: mp 94–96 °C; ^{1}H NMR ($CDCl_3$) δ 7.90–6.85 (m, 15H); ^{19}F NMR ($CDCl_3$) δ −53.58 (s, 3F, one isomer), −54.50 (s, 3F, the other isomer); MS, *m/z* (relative intensity) 420 (M^+, 17), 259 (13), 239 (100), 210 (78), 186 (67), 109 (77), 77 (72), 65 (42), 51 (38); IR (KBr) 3061, 2962, 2924, 1726, 1581, 1476, 1445, 1326, 1260, 1146, 1084, 1024, 811, 753, 727, 689 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3O_2S_2$: C, 59.99; H, 3.60. Found: C, 59.71; H, 3.51.

3.1.4. 3,3,3-Trifluoro-1,1-diphenyl-2-phenylthiopropene ***9***

To a dry toluene (50 ml) solution of **8** (5.10 g, 12 mmol) was added phenyllithium (11.4 ml, 20.6 mmol) in toluene at −78 °C and the reaction mixture was stirred at −78 °C for 24 h. The reaction mixture was washed with water and then extracted with ether twice. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane provided **9** in 82% yield. **9**: mp 68–70 °C; ^{1}H NMR ($CDCl_3$) δ 7.37–7.02 (m, 15H); ^{19}F NMR ($CDCl_3$) δ −56.22 (s, 3F); MS, *m/z* (relative intensity) 356 (M^+, 100), 287 (52), 254 (19), 239 (25), 227 (25), 210 (27), 178 (30), 165 (34), 152 (10), 109 (8), 77 (23); IR (KBr) 3059, 2926, 2854, 1721, 1582, 1491, 1443, 1293, 1253, 1184, 1033, 991, 742, 699 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3S$: C, 70.77; H, 4.24. Found: C, 70.49; H, 4.19.

3.1.5. 3,3,3-Trifluoro-1,1-diphenyl-2-phenylsulfonylpropene ***10***

A mixture of **9** (6.2 g, 16 mmol) and MCPBA (13.8 g) in dry CH_2Cl_2 (150 ml) was heated to reflux for 24 h under nitrogen atmosphere. After cooling, the reaction mixture was washed with a mixture of saturated $NaHCO_3$ and 10% $NaHSO_3$ solution and extracted with CH_2Cl_2. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane and ethyl acetate (4:1) provided **10** in 94% yield. **10**: mp 111–113 °C; ^{1}H NMR ($CDCl_3$) δ 7.60–6.97 (m, 15H); ^{19}F NMR ($CDCl_3$) δ −52.14 (s, 3F); MS, *m/z* (relative intensity) 388 (M^+, 10), 246 (100), 227 (48), 178 (25), 165 (10), 125 (17), 77 (57), 51 (34); IR (KBr) 3062, 3030, 1583, 1490, 1449, 1323, 1294, 1247, 1192, 1154, 1083, 998, 759, 735, 687 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3O_2S$: C, 64.94; H, 3.89. Found: C, 64.69; H, 3.80.

3.1.6. 2-Tributylstannanyl-3,3,3-trifluoro-1,1-diphenylpropene ***1***

To a dry benzene (50 ml) solution of **10** (3.88 g, 10 mmol) was added tributyltin hydride (15 mmol) and AIBN (catalytic amount) and the reaction mixture was heated at 80–90 °C for 24 h. After cooling, the reaction mixture was concentrated and then the residue was chromatographed on SiO_2 column. Elution with *n*-hexane provided **1** in 84% yield. **1**: oil; ^{1}H NMR ($CDCl_3$) δ 7.34–7.12 (m,

10H), 1.53–0.59 (m, 27H); ^{19}F NMR ($CDCl_3$) δ −49.47 (s, 3F); MS, *m/z* (relative intensity) 481 ($M^+ - 56$, 4), 210 (16), 209 (100), 207 (12), 189 (11), 183 (9), 177 (5), 139 (3), 57 (6); IR (neat) 3058, 3025, 2957, 2924, 2854, 2362, 2342, 1491, 1445, 1243, 1170, 1126, 1074, 764, 699 cm^{-1}. Anal. Calcd. for $C_{27}H_{37}F_3Sn$: C, 60.36; H, 6.94. Found: C, 60.54; H, 6.83.

3.2. 2-Tributylstannanyl-1,1,1-trifluoro-3-phenyl-2-butene **2**

3.2.1. 1,1,1-Trifluoro-3-phenyl-2-phenylthio-2-butene **11**

To a dry toluene (50 ml) solution of **8** (3.38 g, 8.07 mmol) was added methyllithium (8.07 ml, 12.1 mmol) in toluene at −78 °C and the reaction mixture was stirred at −78 °C for 24 h. The reaction mixture was washed with water and then extracted with ether twice. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane provided **11** in 68% yield. **11**: mp 56–57 °C; ^{1}H NMR ($CDCl_3$) δ 7.44–7.09 (m, 10H), 2.42 (q, $J = 2.3$ Hz, 3H, one isomer), 2.22 (q, $J = 2.1$ Hz, 3H, the other isomer); ^{19}F NMR ($CDCl_3$) δ −56.29 (s, 3F, one isomer), −57.58 (s, 3F, the other isomer); MS, *m/z* (relative intensity) 294 (M^+, 100), 279 (6), 253 (2), 225 (53), 197 (17), 165 (27), 147 (91), 133 (13), 115 (43), 91 (10), 77 (38); IR (KBr) 3118, 2988, 1716, 1660, 1541, 1507, 1457, 1340, 1151, 1086, 1059, 742, 699 cm^{-1}. Anal. Calcd. for $C_{16}H_{13}F_3S$: C, 65.29; H, 4.45. Found: C, 65.08; H, 4.60.

3.2.2. 1,1,1-Trifluoro-3-phenyl-2-phenylsulfonyl-2-butene **12**

A mixture of **11** (2.33 g, 7.91 mmol) and MCPBA (3.4 g) in dry CH_2Cl_2 (150 ml) was heated to reflux for 24 h under nitrogen atmosphere. After cooling, the reaction mixture was washed with a mixture of saturated $NaHCO_3$ and 10% $NaHSO_3$ solution and extracted with CH_2Cl_2. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane and ethyl acetate (4:1) provided **12** in 92% yield. **12**: mp 107–109 °C; ^{1}H NMR ($CDCl_3$) δ 8.08–7.98 (m, 2H), 7.66–7.07 (m, 8H), 2.63 (q, $J = 1.5$ Hz, 3H, one isomer), 2.36 (q, $J = 2.3$ Hz, 3H, the other isomer); ^{19}F NMR ($CDCl_3$) δ −51.85 (s, 3F, one isomer), −54.56 (s, 3F, the other isomer); MS, *m/z* (relative intensity) 326 (M^+, 8), 260 (25), 241 (19), 221 (19), 164 (32), 125 (18), 115 (71), 77 (100), 51 (59); IR (KBr) 3063, 2926, 2340, 1736, 1593, 1490, 1446, 1330, 1292, 1227, 1152, 1079, 1030, 764, 695 cm^{-1}. Anal. Calcd. for $C_{16}H_{13}F_3O_2S$: C, 58.89; H, 4.02. Found: C, 58.67; H, 4.11.

3.2.3. 2-Tributylstannanyl-1,1,1-trifluoro-3-phenyl-2-butene **2**

To a dry benzene (50 ml) solution of **12** (2.61 g, 8 mmol) was added tributyltin hydride (12 mmol) and AIBN (catalytic amount) and the reaction mixture was heated at 80–90 °C for 24 h. After cooling, the reaction mixture was concentrated and then the residue was chromatographed on SiO_2 column. Elution with *n*-hexane provided **2a** and **2b** in 67% yield. **2a**: oil; ^{1}H NMR ($CDCl_3$) δ 7.38–6.69 (m, 5H), 2.12 (q, $J = 2.2$ Hz, 3H), 1.67–0.76 (m, 27H); ^{19}F NMR ($CDCl_3$) δ −50.09 (s, 3F); MS, *m/z* (relative intensity) 419 ($M^+ - 56$, 6), 361 (1), 305 (1), 253 (9), 177 (1), 147 (100), 127 (8), 69 (7); IR (neat) 3021, 2956, 2924, 2923, 2853, 1595, 1463, 1376, 1273, 1245, 1134, 1106, 1075, 998, 873, 763, 700 cm^{-1}. Anal. Calcd. for $C_{22}H_{35}F_3Sn$: C, 55.60; H, 7.42. Found: C, 55.81; H, 7.49. **2b**: oil; ^{1}H NMR ($CDCl_3$) δ 7.32–7.06 (m, 5H), 2.26 (q, $J = 2.7$ Hz, 3H), 1.71–0.83 (m, 27H); ^{19}F NMR ($CDCl_3$) δ −51.91 (s, 3F); MS, *m/z* (relative intensity) 419 ($M^+ - 56$, 6), 361 (1), 305 (1), 253 (5), 177 (1), 147 (100), 127 (6), 69 (4); IR (neat) 3021, 2956, 2924, 2923, 2853, 1595, 1463, 1376, 1273, 1245, 1134, 1106, 1075, 998, 873, 763, 700 cm^{-1}. Anal. Calcd. for $C_{22}H_{35}F_3Sn$: C, 55.60; H, 7.42. Found: C, 55.89; H, 7.53.

3.3. 1-Tributylstannanyl-2,3,3,3-tetrafluoro-1-phenylpropene **3**

To a dry benzene (50 ml) solution of **7** (2.64 g, 8 mmol) was added tributyltin hydride (24 mmol) and AIBN (catalytic amount) and the reaction mixture was heated at 80–90 °C for 24 h. After cooling, the reaction mixture was concentrated and then the residue was chromatographed on SiO_2 column. Elution with *n*-hexane provided **3** in 75% yield. **3**: oil; ^{1}H NMR ($CDCl_3$) δ 7.37–6.89 (m, 5H), 1.72–0.71 (m, 27H); ^{19}F NMR ($CDCl_3$) δ −62.40 (d, $J = 10.2$ Hz, 3F), −104.8 (q, $J = 10.4$ Hz, 1F); MS, *m/z* (relative intensity) 423 ($M^+ - 56$, 4), 310 (4), 291 (7), 253 (100), 251 (77), 195 (5), 177 (26), 151 (98), 121 (7), 41 (9), 29 (7); IR (CCl_4) 3078, 3061, 2924, 2958, 2925, 2872, 1671, 1596, 1554, 1490, 1378, 1310, 1196, 1143, 1093, 1001, 961, 893, 866, 698, 670 cm^{-1}. Anal. Calcd. for $C_{21}H_{32}F_4Sn$: C, 52.64; H, 6.73. Found: C, 52.29; H, 6.65.

3.4. 1-Tributylstannanyl-3,3,3-trifluoro-1,2-diphenylpropene **4**

3.4.1. 3,3,3-Trifluoro-1,2-diphenyl-1-phenylthiopropene **14**

To a dry THF (50 ml) solution of 1,1-bis(phenylthio)-2,2,3,3,3-pentfluoropropylbenzene (2.13 g, 5 mmol) was added phenyllithium (10 mmol) at −78 °C and the reaction mixture was slowly warmed to 0 °C. After quenching with 5% HCl, the reaction mixture was extracted with ether twice. The ether solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane provided **14** in 87% yield. **14**: oil; ^{1}H NMR ($CDCl_3$) δ 7.52–7.32 (m, 5H), 7.29–6.82 (m, 10H); ^{19}F NMR ($CDCl_3$) δ −55.49 (s, 3F, one isomer), −56.21 (s, 3F, the other isomer); MS, *m/z* (relative intensity) 356 (M^+, 100), 287 (15), 247 (74), 227 (97), 178 (24), 121 (22); IR (neat) 3058, 1605, 1583, 1309, 1238, 1159, 1114, 750, 707 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3S$: C, 70.77; H, 4.24. Found: C, 70.95; H, 4.18.

*3.4.2. 3,3,3-Trifluoro-1,2-diphenyl-1-phenylsulfonylpropene **15***

A mixture of **14** (1.49 g, 5 mmol) and MCPBA (8.6 g) in dry CH_2Cl_2 (100 ml) was heated to reflux for 24 h under nitrogen atmosphere. After cooling, the reaction mixture was washed with a mixture of saturated $NaHCO_3$ and 10% $NaHSO_3$ solution and extracted with CH_2Cl_2. The solution was dried and chromatographed on SiO_2 column. Elution with *n*-hexane and ethyl acetate (4:1) provided **15** in 87% yield. **15**: mp 149–150 °C; ^{1}H NMR ($CDCl_3$) δ 7.68–7.26 (m, 10H), 7.15–6.71 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −53.01 (s, 3F, one isomer), −54.05 (s, 3F, the other isomer); MS, *m/z* (relative intensity) 388 (M^+, 3), 263 (23), 247 (100), 227 (56), 178 (18); IR (KBr) 3058, 1490, 1444, 1302, 1252, 1167, 1124, 1087, 1052, 978, 748, 703 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3O_2S$: C, 64.94; H, 3.89. Found: C, 64.69; H, 3.82.

*3.4.3. 1-Tributylstannanyl-3,3,3-trifluoro-1,2-diphenylpropene **4***

To a dry benzene (50 ml) solution of 15 (1.94 g, 5 mmol) was added tributyltin hydride (20 mmol) and AIBN (catalytic amount) and the reaction mixture was heated at 80–90 °C for 24 h. After cooling, the reaction mixture was concentrated and then the residue was chromatographed on SiO_2 column. Elution with *n*-hexane and ethyl acetate (20:1) provided **4** in 38% yield. **4**: oil; ^{1}H NMR ($CDCl_3$) δ 7.35–6.60 (m, 10H), 1.67–1.16 (m, 27H, one isomer), 1.0–0.52 (m, 27H, the other isomer); ^{19}F NMR ($CDCl_3$) δ −56.04 (s, 3F, one isomer), −62.03 (s, 3F, the other isomer); MS, *m/z* (relative intensity) 481 ($M^+ - 56$, 13), 461 (35), 347 (13), 227 (16), 209 (100), 177 (14), 41 (20); IR (neat) 3025, 2985, 1300, 1134, 1106, 751, 697 cm^{-1}. Anal. Calcd. for $C_{27}H_{37}F_3Sn$: C, 60.36; H, 6.94. Found: C, 60.58; H, 7.03.

*3.5. General procedure for the preparation of **16**, **17**, **18**, **19**, **20** and **21***

To a DMF (5 ml) solution of aryl iodide (0.5 mmol) and vinylstannane **1**, **2a**, **3** or **4** (0.4 mmol) was added $Pd(PPh_3)_4$ (10 mol%) and CuI (10 mol%), and the reaction mixture was stirred at room temperature for 4 h under argon atmosphere. After the reaction mixture was quenched with water and then washed with 5% KF solution and brine, solution was extracted with ether twice. The ether solution was dried and chromatographed on SiO_2 column. Elution with a mixture of *n*-hexane and ethyl acetate (20:1) provided a desired product **16**, **17**, **18**, **19**, **20** or **21**.

16a: mp 63–65 °C; ^{1}H NMR ($CDCl_3$) δ 7.51–7.11 (m, 10H), 7.02–6.78 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −56.26 (s, 3F); MS, *m/z* (relative intensity) 324 (M^+, 100), 283 (19), 255 (40), 239 (18), 178 (10), 152 (5), 126 (9), 77 (5); IR (KBr) 3077, 3026, 2924, 1327, 1224, 1170, 1142, 1113, 757, 716, 697 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3$: C, 77.76; H, 4.66. Found: C, 77.55; H, 4.71.

16b: mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 7.93–7.84 (m, 2H), 7.54–7.10 (m, 12H); ^{19}F NMR ($CDCl_3$) δ −56.30 (s, 3F); MS, *m/z* (relative intensity) 404 ($M^+ + 2$, 100), 402 (M^+, 100), 323 (6), 283 (54), 254 (50), 246 (5), 141 (10), 126 (20); IR (KBr) 3063, 2924, 1462, 1224, 1367, 1260, 1116, 1013, 804, 590 cm^{-1}. Anal. Calcd. for $C_{21}H_{14}BrF_3$: C, 62.55; H, 3.50. Found: C, 62.31; H, 3.62.

16c: mp 67–68 °C; ^{1}H NMR ($CDCl_3$) δ 7.84–6.69 (m, 14H), 3.75 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −56.47 (s, 3F); MS, *m/z* (relative intensity) 354 (M^+, 100), 285 (7), 270 (11), 241 (8), 165 (5), 120 (3); IR (KBr) 3058, 2926, 1661, 1588, 1511, 1445, 1327, 1250, 1226, 1170, 1111, 1034, 757, 701 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3O$: C, 74.57; H, 4.84. Found: C, 74.29; H, 4.72.

16d: mp 88–90 °C; ^{1}H NMR ($CDCl_3$) δ 7.32–6.89 (m, 14H), 2.27 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −56.37 (s, 3F); MS, *m/z* (relative intensity) 338 (M^+, 100), 323 (12), 297 (9), 269 (16), 252 (21), 189 (8), 165 (10), 126 (12); IR (KBr) 3027, 2923, 1491, 1445, 1327, 1226, 1171, 1141, 1112, 811, 756, 698 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3$: C, 78.09; H, 5.06. Found: C, 78.31; H, 4.95.

16e: mp 92–94 °C; ^{1}H NMR ($CDCl_3$) δ 8.12–8.03 (m, 2H), 7.46–6.91 (m, 12H); ^{19}F NMR ($CDCl_3$) δ −55.93 (s, 3F); MS, *m/z* (relative intensity) 369 (M^+, 100), 301 (5), 253 (28), 176 (4), 126 (8), 113 (4); IR (KBr) 3431, 3106, 1627, 1598, 1520, 1493, 1444, 1349, 1175, 1141, 1107, 848, 795, 765, 723, 701 cm^{-1}. Anal. Calcd. for $C_{21}H_{14}F_3NO_2$: C, 68.29; H, 3.82. Found: C, 68.01; H, 3.75.

16f: mp 79–81 °C; ^{1}H NMR ($CDCl_3$) δ 7.87–6.90 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.09 (s, 3F), −63.26 (s, 3F); MS, *m/z* (relative intensity) 392 (M^+, 100), 373 (10), 351 (14), 323 (23), 283 (25), 253 (18); IR (KBr) 3025, 1493, 1446, 1347, 1225, 1175, 1141, 1115, 799, 765, 701 cm^{-1}. Anal. Calcd. for $C_{22}H_{14}F_6$: C, 67.35; H, 3.60. Found: C, 67.07; H, 3.66.

16g: oil; ^{1}H NMR ($CDCl_3$) δ 7.33–6.96 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.20 (s, 3F); MS, *m/z* (relative intensity) 404 ($M^+ + 2$, 100), 402 (M^+, 100), 323 (8), 283 (46), 254 (66), 246 (11), 141 (21), 126 (17); IR (neat) 3063, 2924, 1462, 1224, 1367, 1260, 1116, 1013, 890, 782, 749, 690 cm^{-1}. Anal. Calcd. for $C_{21}H_{14}BrF_3$: C, 62.55; H, 3.50. Found: C, 62.21; H, 3.60.

16h: mp 61–63 °C; ^{1}H NMR ($CDCl_3$) δ 7.34–6.72 (m, 14H), 3.70 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −56.14 (s, 3F); MS, *m/z* (relative intensity) 354 (M^+, 100), 285 (14), 270 (65), 239 (14), 165 (10), 149 (8), 119 (7); IR (KBr) 3059, 2959, 1677, 1597, 1511, 1447, 1326, 1251, 1146, 1081, 889, 756, 695 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3O$: C, 74.57; H, 4.84. Found: C, 74.34; H, 4.76.

16i: mp 105–105 °C; ^{1}H NMR ($CDCl_3$) δ 7.33–6.96 (m, 14H), 2.24 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −56.20 (s, 3F); MS, *m/z* (relative intensity) 338 (M^+, 100), 283 (25), 254 (26), 226 (4), 165 (8), 126 (7); IR (KBr) 3026, 2924, 1336, 1244, 1194, 1159, 1122, 1092, 798, 752, 696 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3$: C, 78.09; H, 5.06. Found: C, 77.80; H, 4.98.

16j: oil; ^{1}H NMR ($CDCl_3$) δ 8.13–6.85 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.17 (s, 3F); MS, *m/z* (relative intensity) 369 (M^+, 100), 352 (7), 301 (7), 283 (16), 253 (36), 239 (8),

165 (6), 126 (9); IR (neat) 3430, 3105, 1625, 1595, 1524, 1490, 1442, 1347, 1175, 1107, 878, 795, 765, 723, 698 cm^{-1}. Anal. Calcd. for $C_{21}H_{14}F_3NO_2$: C, 68.29; H, 3.82. Found: C, 68.02; H, 3.88.

16k: oil; ^1H NMR ($CDCl_3$) δ 7.41–6.82 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.19 (s, 3F), −63.35 (s, 3F); MS, *m/z* (relative intensity) 392 (M^+, 100), 373 (7), 351 (11), 323 (17), 283 (23), 253 (15); IR (neat) 3025, 1492, 1445, 1348, 1224, 1173, 1143, 1113, 878, 795, 765, 701 cm^{-1}. Anal. Calcd. for $C_{22}H_{14}F_6$: C, 67.35; H, 3.60. Found: C, 67.01; H, 3.53.

17a: oil; ^1H NMR ($CDCl_3$) δ 7.57–7.13 (m, 10H), 1.79 (q, $J = 2.2$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −56.30 (s, 3F); MS, *m/z* (relative intensity) 262 (M^+, 100), 247 (35), 227 (36), 193 (46), 178 (59), 165 (10), 115 (25), 91 (11), 77 (10); IR (neat) 3060, 2962, 2853, 1578, 1445, 1325, 1260, 1215, 1156, 1110, 1014, 935, 760, 700 cm^{-1}. Anal. Calcd. for $C_{16}H_{13}F_3$: C, 73.27; H, 5.00. Found: C, 73.02; H, 4.87.

17b: oil; ^1H NMR ($CDCl_3$) δ 7.39–6.92 (m, 9H), 1.81 (q, $J = 2.2$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −56.30 (s, 3F); MS, *m/z* (relative intensity) 342 ($M^+ + 2$, 65), 340 (M^+, 66), 246 (51), 221 (8), 192 (100), 133 (8), 115 (11); IR (neat) 3146, 2951, 2927, 1711, 1349, 1249, 1153, 1127, 1035, 749, 695 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}BrF_3$: C, 56.33; H, 3.55. Found: C, 56.04; H, 3.63.

17c: oil; ^1H NMR ($CDCl_3$) δ 7.26–6.84 (m, 9H), 3.78 (s, 3H), 1.84 (q, $J = 2.2$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −56.89 (s, 3F); MS, *m/z* (relative intensity) 292 (M^+, 100), 261 (4), 234 (3), 208 (22), 178 (8), 165 (13), 145 (8), 115 (17); IR (neat) 3038, 2956, 2924, 2871, 1513, 1463, 1249, 1161, 1117, 1040, 757, 697 cm^{-1}. Anal. Calcd. for $C_{17}H_{15}F_3O$: C, 69.85; H, 5.17. Found: C, 69.59; H, 5.05.

17d: mp 61–62 °C; ^1H NMR ($CDCl_3$) δ 7.34–7.23 (m, 9H), 2.40 (s, 3H), 1.88 (q, $J = 2.2$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −56.39 (s, 3F); MS, *m/z* (relative intensity) 276 (M^+, 100), 261 (59), 241 (52), 202 (59), 192 (89), 165 (19), 115 (18), 77 (10); IR (KBr) 3023, 2957, 1331, 1260, 1207, 1162, 1110, 1026, 801, 763, 699 cm^{-1}. Anal. Calcd. for $C_{17}H_{15}F_3$: C, 73.90; H, 5.47. Found: C, 73.61; H, 5.35.

17e: mp 110–112 °C; ^1H NMR ($CDCl_3$) δ 8.36–8.28 (m, 4H), 7.58–7.21 (m, 5H), 1.91 (q, $J = 2.1$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −55.97 (s, 3F); MS, *m/z* (relative intensity) 307 (M^+, 100), 246 (37), 192 (49), 165 (16), 151 (5), 115 (6), 77 (12), 51 (11); IR (KBr) 3080, 2994, 2359, 1653, 1520, 1350, 1264, 1216, 1162, 1106, 1013, 849, 765, 698 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}F_3NO_2$: C, 62.54; H, 3.94. Found: C, 62.29; H, 3.85.

17f: oil; ^1H NMR ($CDCl_3$) δ 7.33–7.15 (m, 9H), 3.40 (s, 3H), 1.86 (q, $J = 2.0$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −56.27 (s, 3F); MS, *m/z* (relative intensity) 292 (M^+, 100), 277 (21), 261 (9), 249 (4), 223 (10), 208 (20), 183 (9), 165 (20), 145 (5), 115 (12); IR (neat) 3022, 2958, 1600, 1580, 1487, 1334, 1248, 1155, 1117, 1031, 960, 732, 699 cm^{-1}. Anal. Calcd. for $C_{17}H_{15}F_3O$: C, 69.85; H, 5.17. Found: C, 69.59; H, 5.06.

17g: mp 50–52 °C; ^1H NMR ($CDCl_3$) δ 7.33–7.15 (m, 9H), 2.40 (s, 3H), 1.85 (q, $J = 2.1$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −56.27 (s, 3F); MS, *m/z* (relative intensity) 276 (M^+, 100), 261 (49), 241 (24), 192 (28), 183 (15), 165 (2), 129 (10), 115 (4), 77 (3), 51 (9); IR (KBr) 3056, 2923, 1638, 1605, 1488, 1444, 1327, 1265, 1222, 1172, 1113, 1075, 815, 760, 699 cm^{-1}. Anal. Calcd. for $C_{17}H_{15}F_3$: C, 73.90; H, 5.47. Found: C, 73.69; H, 5.34.

18a: oil; ^1H NMR ($CDCl_3$) δ 7.42–7.26 (m, 10H); ^{19}F NMR ($CDCl_3$) δ −64.87 (d, $J = 9.9$ Hz, 3F), −129.29 (q, $J = 9.8$ Hz, 1F); MS, *m/z* (relative intensity) 266 (M^+, 100), 245 (15), 196 (85), 177 (17), 165 (29), 98 (15), 51 (14); IR (CCl_4) 3062, 2959, 2927, 1731, 1549, 1344, 1282, 1195, 1143, 1100, 1010, 699 cm^{-1}. Anal. Calcd. for $C_{15}H_{10}F_4$: C, 67.67; H, 3.79. Found: C, 67.34; H, 3.75.

18b: oil; ^1H NMR ($CDCl_3$) δ 7.55–7.00 (m, 9H); ^{19}F NMR ($CDCl_3$) δ −64.95 (d, $J = 9.8$ Hz, 3F), −128.16 (q, $J = 9.9$ Hz, 1F); MS, *m/z* (relative intensity) 346 ($M^+ + 2$, 31), 344 (M^+, 32), 245 (20), 196 (100); IR (CCl_4) 3082, 3033, 2958, 2927, 1585, 1550, 1490, 1338, 1280, 1206, 1195, 1145, 1101, 1075, 1012, 700 cm^{-1}. Anal. Calcd. for $C_{15}H_9BrF_4$: C, 52.20; H, 2.63. Found: C, 52.01; H, 2.59.

18c: oil; ^1H NMR ($CDCl_3$) δ 7.68–7.12 (m, 9H); ^{19}F NMR ($CDCl_3$) δ −64.92 (d, $J = 9.9$ Hz, 3F), −128.35 (q, $J = 9.9$ Hz, 1F); MS, *m/z* (relative intensity) 302 ($M^+ + 2$, 33), 300 (M^+, 100), 265 (17), 245 (13), 196 (79). Anal. Calcd. for $C_{15}H_9ClF_4$: C, 59.92; H, 3.02. Found: C, 59.53; H, 3.05.

18d: oil; ^1H NMR ($CDCl_3$) δ 7.43–6.94 (m, 9H); ^{19}F NMR ($CDCl_3$) δ −64.83 (d, $J = 10.0$ Hz, 3F), −112.18 (s, 1F), −129.35 (q, $J = 9.9$ Hz, 1F); MS, *m/z* (relative intensity) 284 (M^+, 100), 214 (46), 183 (34), 107 (11). Anal. Calcd. for $C_{15}H_9F_5$: C, 63.34; H, 3.19. Found: C, 63.03; H, 3.14.

18e: oil; ^1H NMR ($CDCl_3$) δ 7.42–6.81 (m, 9H), 3.80 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −64.60 (d, $J = 10.1$ Hz, 3F), −131.01 (q, $J = 10.0$ Hz, 1F); MS, *m/z* (relative intensity) 296 (M^+, 100), 277 (4), 226 (7), 212 (10), 195 (35), 183 (31), 152 (6); IR (CCl_4) 3061, 3004, 2957, 2930, 2855, 1659, 1606, 1564, 1512, 1463, 1342, 1287, 1254, 1194, 1140, 1098, 1038, 700 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}F_4O$: C, 64.86; H, 4.08. Found: C, 64.73; H, 4.02.

18f: oil; ^1H NMR ($CDCl_3$) δ 7.42–7.00 (m, 9H), 2.35 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −64.80 (d, $J = 10.0$ Hz, 3F), −130.01 (q, $J = 9.9$ Hz, 1F); MS, *m/z* (relative intensity) 280 (M^+, 100), 265 (24), 245 (12), 211 (26), 196 (86), 179 (27), 133 (5), 128 (6), 91 (11); IR (CCl_4) 3063, 3028, 2960, 2928, 2873, 2857, 1730, 1579, 1549, 1463, 1379, 1340, 1284, 1206, 1140, 1121, 1073, 1006, 977, 702 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}F_4$: C, 68.57; H, 4.32. Found: C, 68.70; H, 4.24.

18g: oil; ^1H NMR ($CDCl_3$) δ 8.31–7.26 (m, 9H); ^{19}F NMR ($CDCl_3$) δ −64.90 (d, $J = 9.8$ Hz, 3F, one isomer), −65.10 (q, $J = 9.9$ Hz, 3F, other isomer), −125.30 (q, $J = 9.7$ Hz, 1F, one isomer), −126.30 (q, $J = 9.8$ Hz, 1F, other isomer); MS, *m/z* (relative intensity) 311 (M^+, 100), 264 (18), 245 (6), 225 (5), 214 (5), 196 (33), 183 (7); IR (CCl_4) 3060, 3028, 2958, 2926, 2855, 1728, 1665, 1603, 1527, 1494, 1447, 1341, 1284, 1261, 1196, 1149, 1103,

1101, 938, 701 cm^{-1}. Anal. Calcd. for $C_{15}H_9F_4NO_2$: C, 57.89; H, 2.91. Found: C, 57.60; H, 2.97.

18h: oil; ^1H NMR ($CDCl_3$) δ 7.42–6.80 (m, 9H), 3.77 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −64.92 (d, $J = 9.6$ Hz, 3F), −128.41 (q, $J = 9.5$ Hz, 1F); MS, *m/z* (relative intensity) 296 (M^+, 100), 277 (9), 265 (11), 245 (9), 227 (23), 212 (37), 196 (47), 183 (62), 165 (6), 152 (8); IR (CCl_4) 3086, 3064, 2957, 2854, 2837, 1580, 1551, 1488, 1464, 1447, 1431, 1394, 1339, 1289, 1201, 1196, 1143, 1101, 1054, 1008, 975, 698 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}F_4O$: C, 64.86; H, 4.08. Found: C, 64.58; H, 4.00.

18i: oil; ^1H NMR ($CDCl_3$) δ 7.38–7.10 (m, 9H), 2.32 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −64.90 (d, $J = 10.0$ Hz, 3F), −129.02 (q, $J = 9.9$ Hz, 1F); MS, *m/z* (relative intensity) 280 (M^+, 100), 265 (31), 245 (10), 196 (45), 179 (10); IR (CCl_4) 3061, 3028, 2958, 2925, 2856, 1729, 1583, 1549, 1493, 1445, 1338, 1310, 1288, 1201, 1143, 1103, 1002, 978, 880, 663 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}F_4$: C, 68.57; H, 4.32. Found: C, 68.76; H, 4.27.

18j: oil; ^1H NMR ($CDCl_3$) δ 7.37–7.03 (m, 9H), 2.28 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −65.20 (d, $J = 10.2$ Hz, 3F), −123.70 (q, $J = 10.2$ Hz, 1F); MS, *m/z* (relative intensity) 280 (M^+, 52), 196 (413), 179 (100), 133 (7); IR (CCl_4) 3065, 3024, 2927, 2857, 1555, 1446, 1439, 1340, 1292, 1267, 1145, 1123, 1094, 695 cm^{-1}. Anal. Calcd. for $C_{16}H_{12}F_4$: C, 68.57; H, 4.32. Found: C, 68.33; H, 4.21.

19: oil; ^1H NMR ($CDCl_3$) δ 7.51–6.86 (m, 8H); ^{19}F NMR ($CDCl_3$) δ −64.14 (d, $J = 9.8$ Hz, 3F), −124.44 (q, $J = 9.7$ Hz, 1F); MS, *m/z* (relative intensity) 272 (M^+, 100), 202 (43), 171 (25). Anal. Calcd. for $C_{13}H_8F_4S$: C, 57.35; H, 2.96. Found: C, 57.11; H, 2.87.

20: oil; ^1H NMR ($CDCl_3$) δ 8.62–7.07 (m, 8H); ^{19}F NMR ($CDCl_3$) δ −65.42 (d, $J = 9.1$ Hz, 3F), −124.92 (q, $J = 9.1$ Hz, 1F); MS, *m/z* (relative intensity) 268 (M^+, 51), 267 (100), 217 (11), 199 (41). Anal. Calcd. for $C_{13}H_8F_4N_2$: C, 58.21; H, 3.01. Found: C, 57.97; H, 3.07.

21a: mp 72–73 °C; ^1H NMR ($CDCl_3$) δ 7.34–6.85 (m, 15H); ^{19}F NMR ($CDCl_3$) δ −56.27 (s, 3F); MS, *m/z* (relative intensity) 324 (M^+, 100), 283 (18), 255 (38), 178 (11), 126 (13), 113 (7), 77 (7); IR (KBr) 3081, 3022, 1621, 1491, 1444, 1326, 1222, 1168, 1100, 1034, 757, 695 cm^{-1}. Anal. Calcd. for $C_{21}H_{15}F_3$: C, 77.76; H, 4.66. Found: C, 77.69; H, 4.62.

21b: mp 78–80 °C; ^1H NMR ($CDCl_3$) δ 7.36–6.72 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.22 (s, 3F, *Z* isomer), −56.31 (s, 3F, *E* isomer), −113.44 (m, 1F, *Z* isomer); MS, *m/z* (relative intensity) 342 (M^+, 100), 301 (10), 273 (33), 253 (18), 151 (10), 135 (10). Anal. Calcd. for $C_{21}H_{14}F_4$: C, 73.68; H, 4.09. Found: C, 73.51; H, 4.03.

21c: mp 89–90 °C; ^1H NMR ($CDCl_3$) δ 7.32–6.93 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.22 (s, 3F, *Z* isomer), −56.41 (s, 3F, *E* isomer); MS, *m/z* (relative intensity) 360 ($M^+ + 2$, 33), 358 (M^+, 100), 289 (12), 283 (28), 254 (60), 151 (12), 141 (15), 126 (30). Anal. Calcd. for $C_{21}H_{14}F_3Cl$: C, 70.39; H, 3.91. Found: C, 70.14; H, 3.83.

21d: mp 96–97 °C; ^1H NMR ($CDCl_3$) δ 7.55–6.86 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.22 (s, 3F, *Z* isomer), −56.81 (s, 3F, *E* isomer); MS, *m/z* (relative intensity) 404 ($M^+ + 2$, 74), 402 (M^+, 76), 323 (6), 283 (46), 254 (100), 227 (11), 141 (30), 126 (39); IR (KBr) 3057, 1616, 1486, 1444, 1393, 1326, 1268, 1224, 1171, 1115, 1013, 811, 758, 698 cm^{-1}. Anal. Calcd. for $C_{21}H_{14}BrF_3$: C, 62.55; H, 3.50. Found: C, 62.37; H, 3.56.

21e: oil; ^1H NMR ($CDCl_3$) δ 7.53–6.51 (m, 14H), 3.83 (s, 3H, *Z* isomer), 3.65 (s, 3H, *E* isomer); ^{19}F NMR ($CDCl_3$) δ −55.91 (s, 3F, *Z* isomer), −56.20 (s, 3F, *E* isomer); MS, *m/z* (relative intensity) 354 (M^+, 100), 289 (19), 270 (14), 239 (12), 195 (9), 126 (8), 119 (6); IR (neat) 3055, 2959, 2861, 1656, 1484, 1390, 1321, 1265, 1142, 1105, 1029, 755, 696 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3O$: C, 74.57; H, 4.84. Found: C, 74.36; H, 4.77.

21f: oil; ^1H NMR ($CDCl_3$) δ 7.60–7.02 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.29 (s, 3F, *Z* isomer), −56.64 (s, 3F, *E* isomer), −63.11 (s, 3F, *Z* isomer), −63.28 (s, 3F, *E* isomer); MS, *m/z* (relative intensity) 392 (M^+, 100), 351 (12), 323 (31), 283 (39), 253 (22). Anal. Calcd. for $C_{22}H_{14}F_6$: C, 67.35; H, 3.60. Found: C, 67.26; H, 3.55.

21g: oil; ^1H NMR ($CDCl_3$) δ 8.29–8.20 (m, 2H), 7.93–6.83 (m, 12H); ^{19}F NMR ($CDCl_3$) δ −56.33 (s, 3F, *Z* isomer), −56.93 (s, 3F, *E* isomer); MS, *m/z* (relative intensity) 369 (M^+, 100), 300 (16), 253 (54), 178 (7), 126 (24), 113 (11); IR (neat) 3060, 1598, 1521, 1444, 1348, 1280, 1225, 1172, 1118, 847, 757, 701 cm^{-1}. Anal. Calcd. for $C_{21}H_{14}F_3NO_2$: C, 68.29; H, 3.82. Found: C, 68.11; H, 3.77.

21h: mp 53–55 °C; ^1H NMR ($CDCl_3$) δ 7.33–6.95 (m, 14H), 2.35 (s, 3H, *Z* isomer), 2.09 (s, 3H, *E* isomer); ^{19}F NMR ($CDCl_3$) δ −56.17 (s, 3F, *E* isomer), −56.28 (s, 3F, *Z* isomer); MS, *m/z* (relative intensity) 338 (M^+, 100), 297 (10), 283 (19), 254 (28), 126 (10). Anal. Calcd. for $C_{22}H_{17}F_3$: C, 78.09; H, 5.06. Found: C, 77.80; H, 4.99.

21i: mp 81–82 °C; ^1H NMR ($CDCl_3$) δ 7.34–6.85 (m, 14H), 3.80 (s, 3H, *Z* isomer), 3.54 (s, 3H, *E* isomer); ^{19}F NMR ($CDCl_3$) δ −56.23 (s, 3F, *E* isomer), −56.42 (s, 3F, *Z* isomer); MS, *m/z* (relative intensity) 354 (M^+, 100), 285 (19), 270 (21), 253 (21), 239 (15). Anal. Calcd. for $C_{22}H_{17}F_3O$: C, 74.57; H, 4.84. Found: C, 74.39; H, 4.79.

21j: oil; ^1H NMR ($CDCl_3$) δ 7.57–7.03 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −56.26 (s, 3F, *Z* isomer), −56.65 (s, 3F, *E* isomer), −63.12 (s, 3F, *Z* isomer), −63.46 (s, 3F, *E* isomer); MS, *m/z* (relative intensity) 392 (M^+, 100), 351 (10), 323 (31), 283 (31), 253 (10). Anal. Calcd. for $C_{22}H_{14}F_6$: C, 67.35; H, 3.60. Found: C, 67.17; H, 3.52.

*3.6. General procedure for the preparation of **22**, **25**, **26**, **29** and **30***

To a toluene (5 ml) solution of acyl chloride (1.12 mmol) and **1**, **2a** or **4** (0.75 mmol) was added $Pd(PPh_3)_2Cl_2$ (10 mol%) and CuCN (10 mol%), and the reaction mixture was heated at 50–80 °C for 6 h under argon atmosphere. After the reaction mixture was quenched with water and then washed with 5% KF solution and brine, aqueous solution was extracted with ether twice. The ether solution was dried

and chromatographed on SiO_2 column. Elution with a mixture of hexane and ethyl acetate (20:1) provided **22**, **25**, **26**, **29** or **30**.

22a: mp 65–66 °C; ^{1}H NMR ($CDCl_3$) δ 7.41–7.18 (m, 10H), 2.03 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −55.42 (s, 3F); MS, *m/z* (relative intensity) 290 (M^+, 100), 255 (27), 213 (36), 178 (36), 151 (16), 127 (24), 105 (40), 77 (16); IR (KBr) 3059, 2926, 1704, 1619, 1492, 1357, 1322, 1261, 1216, 1145, 1078, 1042, 952, 759, 699 cm^{-1}. Anal. Calcd. for $C_{17}H_{13}F_3O$: C, 70.34; H, 4.51. Found: C, 70.18; H, 4.60.

22b: oil; ^{1}H NMR ($CDCl_3$) δ 7.90–7.81 (m, 2H), 7.54–7.09 (m, 13H); ^{19}F NMR ($CDCl_3$) δ −54.78 (s, 3F); MS, *m/z* (relative intensity) 352 (M^+, 60), 275 (13), 227 (5), 178 (6), 127 (5), 105 (100), 77 (86); IR (neat) 3083, 3060, 3030, 2926, 1670, 1621, 1597, 1492, 1447, 1326, 1249, 1193, 1147, 1081, 943, 834, 758, 695, 610 cm^{-1}. Anal. Calcd. for $C_{22}H_{15}F_3O$: C, 74.99; H, 4.29. Found: C, 74.83; H, 4.26.

22c: oil; ^{1}H NMR ($CDCl_3$) δ 8.08–6.96 (m, 14H), 2.36 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −55.04 (s, 3F); MS, *m/z* (relative intensity) 366 (M^+, 16), 346 (17), 297 (53), 119 (81), 91 (100), 65 (39). Anal. Calcd. for $C_{23}H_{17}F_3O$: C, 75.40; H, 4.68. Found: C, 75.26; H, 4.60.

22d: mp 149–151 °C; ^{1}H NMR ($CDCl_3$) δ 7.81–7.10 (m, 14H), 2.34 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −54.75 (s, 3F); MS, *m/z* (relative intensity) 366 (M^+, 97), 289 (13), 119 (100), 91 (36). Anal. Calcd. for $C_{23}H_{17}F_3O$: C, 75.40; H, 4.68. Found: C, 75.19; H, 4.56.

22e: oil; ^{1}H NMR ($CDCl_3$) δ 7.91–6.78 (m, 14H), 3.82 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −54.78 (s, 3F); MS, *m/z* (relative intensity) 382 (M^+, 41), 135 (100), 107 (10), 92 (19), 77 (31). Anal. Calcd. for $C_{23}H_{17}F_3O_2$: C, 72.24; H, 4.48. Found: C, 72.15; H, 4.45.

22f: oil; ^{1}H NMR ($CDCl_3$) δ 8.61–7.07 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −54.93 (s, 3F); MS, *m/z* (relative intensity) 397 (M^+, 100), 320 (25), 150 (41), 104 (20), 76 (14). Anal. Calcd. for $C_{22}H_{14}F_3NO_3$: C, 66.50; H, 3.55. Found: C, 66.32; H, 3.47.

22g: oil; ^{1}H NMR ($CDCl_3$) δ 7.66–7.09 (m, 14H), 2.44 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −54.70 (s, 3F); MS, *m/z* (relative intensity) 366 (M^+, 100), 289 (17), 119 (90), 91 (42). Anal. Calcd. for $C_{23}H_{17}F_3O$: C, 75.40; H, 4.68. Found: C, 75.28; H, 4.75.

22h: mp 76–78 °C; ^{1}H NMR ($CDCl_3$) δ 7.93–7.10 (m, 14H); ^{19}F NMR ($CDCl_3$) δ −54.81 (s, 3F); MS, *m/z* (relative intensity) 432 ($M^+ + 2$, 100), 430 (M^+, 99), 355 (21), 353 (21), 275 (14), 227 (11), 185 (72), 183 (72), 155 (46), 105 (13), 76 (19). Anal. Calcd. for $C_{22}H_{14}BrF_3O$: C, 61.27; H, 3.27. Found: C, 61.44; H, 3.22.

22i: oil; ^{1}H NMR ($CDCl_3$) δ 7.34–7.19 (m, 10H), 3.96 (q, $J = 7.1$, 2H), 0.89 (t, $J = 7.1$, 3H); ^{19}F NMR ($CDCl_3$) δ −56.04 (s, 3F); MS, *m/z* (relative intensity) 320 (M^+, 97), 275 (72), 255 (35), 247 (100), 227 (58), 204 (24), 178 (66), 165 (23), 127 (23), 105 (43), 77 (20), 51 (12). Anal. Calcd. for $C_{18}H_{15}F_3O_2$: C, 67.49; H, 4.72. Found: C, 67.35; H, 4.69.

22j: oil; ^{1}H NMR ($CDCl_3$) δ 7.49–7.16 (m, 12H), 6.39 (m, 1H); ^{19}F NMR ($CDCl_3$) δ −54.93 (s, 3F); MS, *m/z* (relative intensity) 342 (M^+, 78), 274 (26), 265 (26), 245 (28), 215 (22), 202 (15), 170 (22), 151 (36), 144 (21), 95 (100). Anal. Calcd. for $C_{20}H_{13}F_3O_2$: C, 70.17; H, 3.83. Found: C, 70.15; H, 3.77.

22k: mp 118–120 °C; ^{1}H NMR ($CDCl_3$) δ 8.40–6.99 (m, 17H); ^{19}F NMR ($CDCl_3$) δ −54.65 (s, 3F); MS, *m/z* (relative intensity) 402 (M^+, 100), 155 (60), 127 (69), 77 (12). Anal. Calcd. for $C_{26}H_{17}F_3O$: C, 77.60; H, 4.26. Found: C, 77.75; H, 4.21.

25: oil; ^{1}H NMR ($CDCl_3$) δ 7.46–7.13 (m, 5H), 2.46 (s, 3H), 2.12 (q, $J = 2.1$, 3H); ^{19}F NMR ($CDCl_3$) δ −57.36 (s, 3F); MS, *m/z* (relative intensity) 228 (M^+, 100), 213 (45), 193 (10), 165 (14), 123 (37), 115 (22), 77 (9); IR (neat) 3059, 2958, 2856, 1709, 1642, 1492, 1444, 1319, 1250, 1219, 1162, 1121, 1036, 765, 700 cm^{-1}. Anal. Calcd. for $C_{12}H_{11}F_3O$: C, 63.15; H, 4.86. Found: C, 63.03; H, 4.84.

26: oil; ^{1}H NMR ($CDCl_3$) δ 8.13–8.06 (m, 2H), 7.74–7.11 (m, 8H), 2.00 (q, $J = 2.0$, 3H); ^{19}F NMR ($CDCl_3$) δ −54.73 (s, 3F); MS, *m/z* (relative intensity) 290 (M^+, 41), 275 (11), 249 (7), 221 (12), 193 (4), 165 (6), 105 (100), 77 (70), 51 (20); IR (neat) 3099, 3061, 2995, 1673, 1596, 1450, 1325, 1239, 1171, 1127, 1102, 996, 764, 694 cm^{-1}. Anal. Calcd. for $C_{17}H_{13}F_3O$: C, 70.34; H, 4.51. Found: C, 70.29; H, 4.44.

29: oil; ^{1}H NMR ($CDCl_3$) δ 7.34–7.05 (m, 10H), 2.28 (s, 3H, *Z* isomer), 1.79 (s, 3H, *E* isomer); ^{19}F NMR ($CDCl_3$) δ −57.42 (s, 3F, *E* isomer), −59.93 (s, 3H, *Z* isomer); MS, *m/z* (relative intensity) 290 (M^+, 100), 247 (32), 227 (83), 178 (40), 151 (14), 126 (7), 77 (17), 51 (25); IR (neat) 3061, 2927, 1710, 1492, 1445, 1324, 1256, 1216, 1177, 1125, 759, 697 cm^{-1}. Anal. Calcd. for $C_{17}H_{13}F_3O$: C, 70.34; H, 4.51. Found: C, 70.22; H, 4.55.

30: oil; ^{1}H NMR ($CDCl_3$) δ 8.14–7.05 (m, 15H); ^{19}F NMR ($CDCl_3$) δ −56.85 (s, 3F, *E* isomer), −59.73 (s, 3F, *Z* isomer); MS, *m/z* (relative intensity) 352 (M^+, 17), 283 (2), 227 (2), 178 (3), 105 (100), 77 (33); IR (neat) 3059, 2923, 1671, 1596, 1447, 1326, 1248, 1193, 1146, 1080, 770, 693 cm^{-1}. Anal. Calcd. for $C_{22}H_{15}F_3O$: C, 74.99; H, 4.29. Found: C, 74.75; H, 4.22.

*3.7. General procedure for the preparation of **23**, **27** and **31***

To a ether (5 ml) solution of **22**, **26** or **30** (1.28 mmol) was slowly added $LiAlH_4$ (1.92 mmol) dissolved in ether and then the reaction mixture was heated to reflux for 3 h. After the reaction mixture was quenched with 10% HCl solution and then washed with water, aqueous solution was extracted with ether twice. The ether solution was dried and chromatographed on SiO_2 column. Elution with a mixture of hexane and ethyl acetate(4:1) provided **23**, **27** and **31**.

23a: oil; ^{1}H NMR ($CDCl_3$) δ 7.53–7.02 (m, 10H), 4.58 (m, 1H), 1.87 (d, $J = 6.1$ Hz, 1H), 1.48 (d, $J = 7.5$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −52.64 (s, 3F); MS, *m/z* (relative intensity) 292 (M^+, 44), 259 (15), 209 (26), 178 (18), 167 (100), 127 (59), 77 (22), 51 (17); IR (neat) 3395, 3059, 3028, 2963, 2932, 1622, 1492, 1445, 1318, 1260,

1130, 1077, 1018, 797, 759, 701 cm^{-1}. Anal. Calcd. for $C_{17}H_{15}F_3O$: C, 69.85; H, 5.17. Found: C, 69.69; H, 5.12.

23b: oil; ^1H NMR ($CDCl_3$) δ 7.44–7.19 (m, 15H), 5.71 (d, $J = 8.8$ Hz, 1H), 2.51 (d, $J = 8.7$ Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −51.74 (s, 3F); MS, *m/z* (relative intensity) 354 (M^+, 33), 336 (25), 285 (15), 267 (50), 207 (19), 178 (21), 151 (14), 105 (100), 77 (31); IR (neat) 3437, 3059, 3028, 2926, 2856, 1724, 1600, 1493, 1447, 1338, 1256, 1190, 1121, 1077, 1034, 926, 861, 767, 698 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3O$: C, 74.57; H, 4.84. Found: C, 74.42; H, 4.78.

23c: oil; ^1H NMR ($CDCl_3$) δ 7.35–7.13 (m, 14H), 5.63 (d, $J = 8.8$ Hz, 1H), 2.48 (d, $J = 8.6$ Hz, 1H), 2.36 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −51.61 (s, 3F); MS, *m/z* (relative intensity) 368 (M^+, 21), 350 (19), 281 (50), 207 (10), 178 (16), 165 (14), 119 (100), 91 (40), 77 (23). Anal. Calcd. for $C_{23}H_{19}F_3O$: C, 74.99; H, 5.20. Found: C, 74.70; H, 5.11.

23d: oil; ^1H NMR ($CDCl_3$) δ 7.88–6.95 (m, 14H), 5.59 (d, $J = 8.5$ Hz, 1H), 3.81 (s, 3H), 2.43 (d, $J = 8.4$ Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −51.57 (s, 3F); MS, *m/z* (relative intensity) 384 (M^+, 47), 366 (29), 315 (16), 297 (55), 207 (14), 178 (16), 165 (14), 135 (100), 109 (17), 94 (17), 77 (40). Anal. Calcd. for $C_{23}H_{19}F_3O_2$: C, 71.97; H, 4.98. Found: C, 71.86; H, 4.94.

23e: oil; ^1H NMR ($CDCl_3$) δ 7.90–7.26 (m, 17H), 5.83 (d, $J = 8.3$ Hz, 1H), 2.61 (d, $J = 8.2$ Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −51.82 (s, 3F); MS, *m/z* (relative intensity) 404 (M^+, 33), 386 (20), 317 (35), 275 (18), 257 (14), 229 (12), 207 (13), 165 (19), 155 (57), 127 (100), 77 (28). Anal. Calcd. for $C_{26}H_{19}F_3O$: C, 77.21; H, 4.74. Found: C, 77.01; H, 4.77.

27: oil; ^1H NMR ($CDCl_3$) δ 7.48–7.15 (m, 10H), 5.92 (d, $J = 7.0$ Hz, 1H), 2.41 (d, $J = 6.8$ Hz, 1H), 2.10 (m, 3H); ^{19}F NMR ($CDCl_3$) δ −54.26 (s, 3F); MS, *m/z* (relative intensity) 292 (M^+, 38), 277 (10), 259 (8), 205 (45), 179 (20), 145 (14), 105 (100), 77 (76); IR (neat) 3408, 3060, 3029, 2921, 1648, 1601, 1493, 1450, 1377, 1337, 1249, 1173, 1121, 1027, 965, 917, 764, 699 cm^{-1}. Anal. Calcd. for $C_{17}H_{15}F_3O$: C, 69.85; H, 5.17. Found: C, 69.70; H, 5.13.

31: oil; ^1H NMR ($CDCl_3$) δ 7.58–6.74 (m, 15H), 5.00 (d, $J = 8.8$ Hz, 1H), 3.95 (d, $J = 8.8$ Hz, 1H); ^{19}F NMR ($CDCl_3$) δ −57.11 (s, 3F); MS, *m/z* (relative intensity) 354 (M^+, 15), 248 (76), 227 (16), 179 (33), 105 (100), 77 (71); IR (neat) 3418, 3029, 2923, 1663, 1601, 1493, 1453, 1326, 1170, 1112, 1040, 1034, 926, 861, 765, 700 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}F_3O$: C, 74.57; H, 4.84. Found: C, 74.35; H, 4.72.

*3.8. General procedure for the preparation of **24**, **28** and **32***

To a methylene chloride (5 ml) solution of **23**, **27** or **31** (0.28 mmol) was slowly added $AlCl_3$ (0.30 mmol) via solid addition tube at −78 °C and then the reaction mixture was slowly warmed to room temperature. After the reaction mixture was quenched with 10% HCl solution, aqueous solution was extracted with methylene chloride twice. The methylene chloride solution was dried and chromatographed on SiO_2 column. Elution with a mixture of hexane and ethyl acetate(20:1) provided **24**, **28** and **32**.

24a: mp 75–77 °C; ^1H NMR ($CDCl_3$) δ 7.41–7.10 (m, 9H), 4.90 (q, $J = 7.3$ Hz, 1H), 1.80 (d, $J = 7.4$ Hz, 1H), 1.48 (d, $J = 7.5$ Hz, 3H); ^{19}F NMR ($CDCl_3$) δ −52.50 (s, 3F); MS, *m/z* (relative intensity) 274 (M^+, 39), 233 (41), 205 (100), 177 (24), 165 (10), 151 (5), 127 (14), 101 (20), 91 (18), 77 (19); IR (KBr) 3058, 2929, 1598, 1445, 1320, 1194, 1137, 1034, 732, 700 cm^{-1}. Anal. Calcd. for $C_{17}H_{13}F_3$: C, 74.44; H, 4.78. Found: C, 74.27; H, 4.69.

24b: mp 69–70 °C; ^1H NMR ($CDCl_3$) δ 7.41–6.91 (m, 14H), 4.87 (s, 1H); ^{19}F NMR ($CDCl_3$) δ −55.07 (s, 3F); MS, *m/z* (relative intensity) 336 (M^+, 98), 267 (100), 189 (12), 165 (10); IR (KBr) 3063, 3027, 2959, 2924, 1600, 1494, 1453, 1359, 1264, 1144, 1110, 1072, 750, 699 cm^{-1}. Anal. Calcd. for $C_{22}H_{15}F_3$: C, 78.56; H, 4.50. Found: C, 78.45; H, 4.45.

24c: mp 74–76 °C; ^1H NMR ($CDCl_3$) δ 7.48–6.99 (m, 13H), 4.95 (s, 1H), 2.33 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −55.06 (s, 3F); MS, *m/z* (relative intensity) 350 (M^+, 100), 281 (88), 265 (15), 239 (4), 202 (4). Anal. Calcd. for $C_{23}H_{17}F_3$: C, 78.84; H, 4.89. Found: C, 78.59; H, 4.79.

24d: mp 79–81 °C; ^1H NMR ($CDCl_3$) δ 7.48–6.79 (m, 13H), 4.91 (s, 1H), 3.80 (s, 3H); ^{19}F NMR ($CDCl_3$) δ −55.10 (s, 3F); MS, *m/z* (relative intensity) 366 (M^+, 96), 297 (100), 282 (5), 252 (13), 239 (5). Anal. Calcd. for $C_{23}H_{17}F_3O$: C, 75.40; H, 4.68. Found: C, 75.31; H, 4.65.

24e: mp 88–90 °C; ^1H NMR ($CDCl_3$) δ 7.93–7.03 (m, 16H), 5.12 (s, 1H); ^{19}F NMR ($CDCl_3$) δ −55.19 (s, 3F); MS, *m/z* (relative intensity) 386 (M^+, 94), 317 (100), 189 (11), 165 (9). Anal. Calcd. for $C_{26}H_{17}F_3$: C, 80.81; H, 4.43. Found: C, 80.52; H, 4.51.

28: mp 75–77 °C; ^1H NMR ($CDCl_3$) δ 7.50–6.98 (m, 9H), 4.77 (s, 1H), 2.41 (m, 3H); ^{19}F NMR ($CDCl_3$) δ −56.58 (s, 3F); MS, *m/z* (relative intensity) 274 (M^+, 100), 259 (19), 233 (8), 205 (80), 189 (12), 127 (12), 101 (15), 77 (13); IR (KBr) 3065, 2957, 1786, 1632, 1494, 1453, 1358, 1258, 1158, 1111, 1015, 758, 697 cm^{-1}. Anal. Calcd. for $C_{17}H_{13}F_3$: C, 74.44; H, 4.78. Found: C, 74.72; H, 4.71.

32: mp 67–68 °C; ^1H NMR ($CDCl_3$) δ 7.55–6.59 (m, 14H), 4.96 (s, 1H); ^{19}F NMR ($CDCl_3$) δ −59.09 (s, 3F); MS, *m/z* (relative intensity) 336 (M^+, 100), 267 (62), 265 (32), 252 (17), 132 (20); IR (KBr) 3060, 3025, 2962, 1698, 1599, 1493, 1452, 1260, 1096, 1027, 800, 760, 699 cm^{-1}. Anal. Calcd. for $C_{22}H_{15}F_3$: C, 78.56; H, 4.50. Found: C, 78.21; H, 4.56.

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