Tetrahedron 67 (2011) 3041–3045

Contents lists available at ScienceDirect

Tetrahedron

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

Preparation of (*E*)-1-aryl-3,3,3-trifluoro-1,2-di(trimethylsilyl)-1-propenes via stereoselective bissilylation of trifluoromethyl aryl acetylenes and electrophilic substitution of its TMS groups

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ARTICLE INFO

Article history:
Received 20 December 2010
Received in revised form 3 March 2011
Accepted 3 March 2011

Keywords:
Reductive bissilylation
Trifluoromethylated olefin
Trifluoropropene
Stereoselective *anti* addition

ABSTRACT

Preparations and reactions of (*E*)-1-aryl-3,3,3-trifluoro-1,2-di(trimethylsilyl)-1-propenes are described. (*E*)-1-Aryl-3,3,3-trifluoro-1,2-di(trimethylsilyl)-1-propene was prepared from aryl trifluoromethyl acetylenes via reductive bissilylation by TMSCl/Mg in good yields. The silyl groups of (*E*)-3,3,3-trifluoro-1,2-di(trimethylsilyl)-1-phenyl-1-propene were substituted by electrophiles in both a stepwise and stereoselective (and/or stereospecific) manner. This compound could be a building block for preparations of substituted trifluoropropenes.

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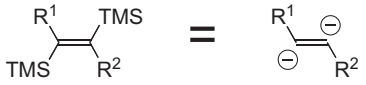
1. Introduction

Organosilicone compounds play an important role as carbanion synthons in the field of synthetic organic chemistry.[1] Di-silylated compounds are of high synthetic value because they work as dianion synthons.[2] Disilyl-olefin works as the dianion synthon in the synthesis of tetra-substituted olefins. Inexpensive and easy preparations of disilyl-olefin are in high demand.



To date, reductive bissilylation of imines,[2] ketones,[3] and nitriles[4] using TMSCl/Mg, an inexpensive silylating reagent has been reported. Meanwhile, only a few instances of the reductive bissilylation of alkynes with the reagent have been reported.[5] A reaction of methyl phenyl acetylene by TMSCl/Mg in HMPA resulted in the formation of only 1% (*E*)-1-phenyl-1,2-di(trimethylsilyl)-1-propene[5] and viscous black tar. In general, bissilylation of alkynes has been attained by transition metal-catalyzed *syn*-addition of disilanes.[6]

Difficulty in the bissilylation of alkynes by the TMSCl/Mg reagent could be caused by an intermediary composed of semi-stable anion radical species, which could be an initiator of radicalic oligomerizations to aromatic rings[7] and/or polymerizations.[8] Thus, after the first electron transfer, the bissilylation reaction would need a second one-electron transfer to generate the dianion species. However, although magnesium is a powerful reducing agent,[9] a dianion species of the 1-phenyl-1-propyne is not easily generated due to the possible localization of negative charges on the same π-system. Thus, stabilization of the dianion by delocalization of the negative charge is essential for the preparation of bissilylated olefins via reductive silylation by the TMSCl/Mg reagent. Here, the strong electron withdrawing effect of the trifluoromethyl group will stabilize the dianion species of the 1-aryl-3,3,3-trifluoro-1-propene (Scheme 1).

2. Results and discussion

The starting alkynes, 1-aryl-3,3,3-trifluoro-1-propenes (**1**), were prepared by a previously reported procedure.[10] The optimized condition for bissilylation of 3,3,3-trifluoro-1-phenyl-1-propene (**1a**) to an alkene **2a** is shown in Scheme 2.

The optimum conditions for bissilylation by excess amounts of TMSCl/Mg involved DMF as a solvent at a temperature of 0 °C. The reaction with reflux of THF resulted only in a recovery of starting material, but in DMI at 0 °C it resulted in the formation of black tar.

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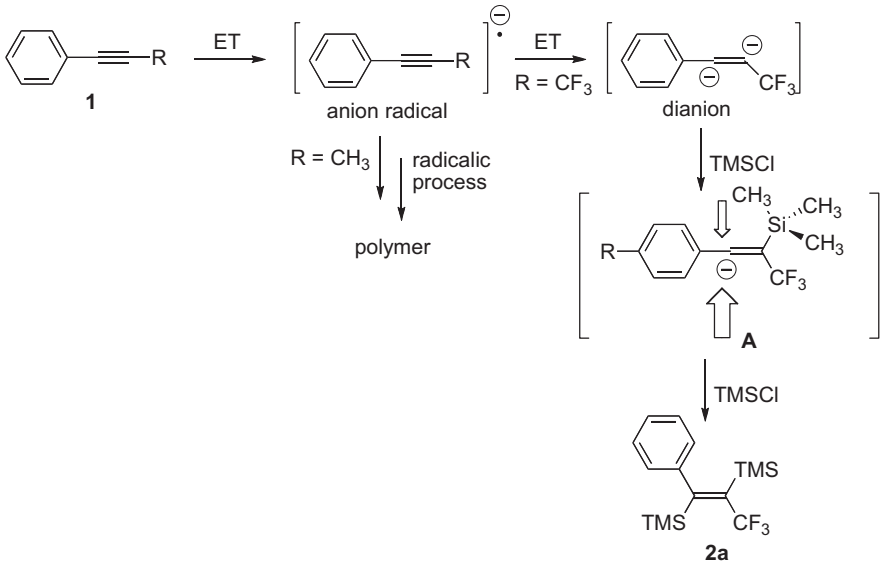
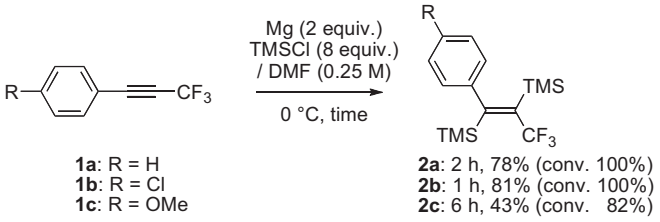
doi:10.1016/j.tet.2011.03.005



Scheme 1. Working hypothesis.



Scheme 2. Optimized bissilylation reaction of **1**.

In case of DMF solvent, the use of an excess amount (8 equiv) of TMSCl was needed for a good yield of the bissilylated product **2a**. The reaction with 4 equiv amounts of TMSCl resulted in a 10% lower yield of **2a**. The reaction of substrate **1c**, which has an electron-donating *para*-substituent on the phenyl group, required a longer reaction time and resulted in lower yield of the bissilylated olefin **2c**. The reactions of **1** with TMSCl/Mg gave rise to stereoisomers with *E*-configurations. The *E*-selective nature of the reaction was confirmed by a single crystal X-ray diffraction analysis of **2b** (Fig. 1).

The high stereoselectivity of the product (**2**) could be explained by the structure of the plausible intermediate **A** (Scheme 1), which was generated by the first addition of TMSCl to the dianion of the alkyne. Here, the bulky trimethylsilyl group covers one side of the sp carbanion center of the intermediate **A**. Thus, the second trimethylsilyl group can only attach to the carbanion center from the side of the trifluoromethyl group. This plausible mechanism is consistent with our experimental results; the reaction of the alkyne, **1b**, with a smaller silylating agent, $H(CH_3)_2SiCl$, led to two stereoisomers (major **2d** at 58%; minor **2e** at 7% Scheme 3).

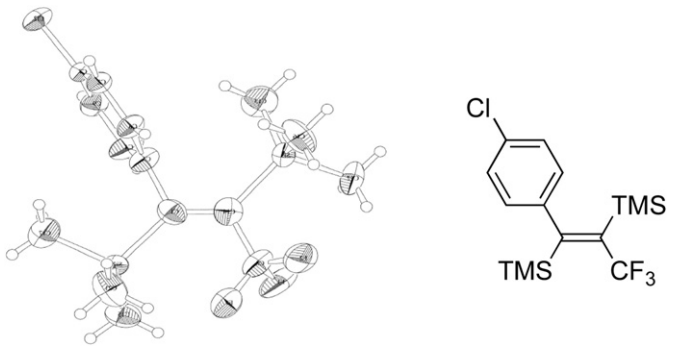


Fig. 1. ORTEP illustration of the bissilylated compound **2b** (CCDC 787293).

The two silyl groups of the compounds **2** were substituted regioselectively and stereoselectively. The reaction of compound **2a**, which involved two-step reactions with methyl iodide (58%), was followed by the reaction with PhCHO (43%) to produce the tetra-substituted olefin **4** (Scheme 4). The stereochemistry of the product was again confirmed by an X-ray crystallographic analysis of **5**, and the product was found to have maintained its configuration (Scheme 4).

Similarly, the reaction of compound **2a** with 1.1 equiv amount of PhCHO gave mono-substituted product **6** in 53% isolate yield, and that with 2.0 equiv amount of PhCHO gave double substituted product **7** as a mixture of the diastereomer in 84% yield (Scheme 5).

The regioselectivity of the first step of the TMS substitution would be due to rather stable nature of the carbanion **A** in Scheme 1. More stable π-carbanion would be generated at first. Thus, the first substitution would be stereoselective reaction caused by the steric hindrance of the other TMS group. Meanwhile, the second substitution of the TMS group would be underwent via sp^2-carbanion type species, thus the reaction would be stereospecific.

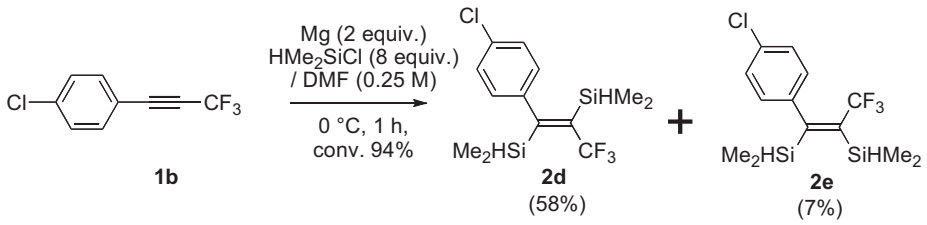
3. Conclusion

In conclusion, we prepared disilyl olefins (**2**) from the corresponding alkynes (**1**). The reaction with TMSCl/Mg was found to be highly stereoselective; it only resulted in the *E*-stereoisomer. The two silyl groups of **2** were substituted by electrophiles in both a regioselective and stereoselective (and/or stereospecific) manner. Further utilizations of the reductive silylation agent (TMSCl/Mg) are currently under investigation.

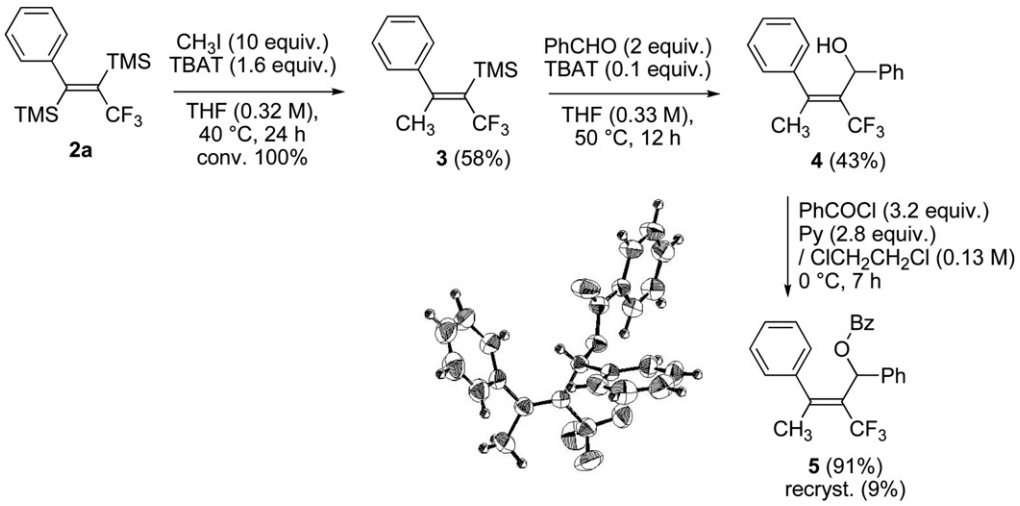
4. Experimental section

4.1. General

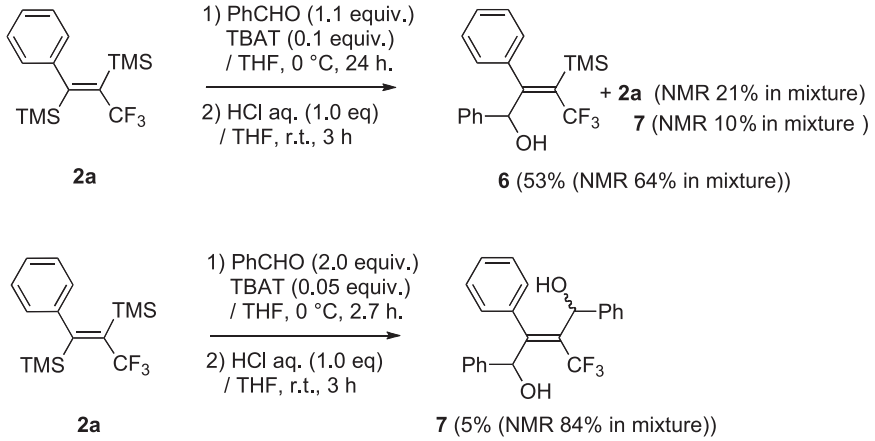
Reagents and solvents were purchased from TCI, WAKO, and Aldrich. IR spectra were measured on a Hitachi Model 270–30 Infrared Spectrophotometer. Elemental analyses were performed on a Perkin–Elmer series II CHNS/O Analyzer 2400. GC/MS analyses were carried out on a Shimadzu GCMS-QP5050A. Melting points



Scheme 3. Bissilylation by $H(CH_3)_2SiCl$.



Scheme 4. Regio- and stereo-selective substitutions of TMS groups (CCDC 786885).



Scheme 5. Stepwise substitutions of TMS groups.

were recorded by a Yanako MP-S3 melting point measurement apparatus. ^1H (300 MHz), ^{19}F (282 MHz), and ^{13}C (75 MHz) NMR spectra were recorded on a Varian MERCURY 300 instrument and the chemical shifts are reported in δ (ppm) values relative to $CDCl_3$ (δ 7.26 ppm for ^1H NMR in $CDCl_3$), C_6F_6 (δ 0 ppm for ^{19}F NMR in $CDCl_3$), and $CDCl_3$ (δ 77 ppm for ^{13}C NMR in $CDCl_3$). Coupling constants are reported in hertz (Hz).

4.2. Reductive bissilylation of alkynes (1) to disilylalkenes (2)

TMSCl (16 mmol, 2 mL) and alkyne **1a** (2 mmol, 0.34 g) were added to a suspension of magnesium powder (4 mmol, 0.097 g) in dry DMF (8 mL) at 0 °C under an argon atmosphere. After being stirred for 2 h, the reaction mixture was quenched with 10% HCl aq and extracted with Et_2O (5 mL) three times. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography eluted with hexane. The ^{19}F NMR estimated the yield of the crude product **2a** to be 84%. Further distillation of the crude product (100 °C/0.5 mmHg) provided **2a** as a colorless oil (0.497 g, 78% yield).

*4.2.1. (E)-3,3,3-Trifluoro-1-phenyl-1,2-ditrimethylsilyl-1-propene (**2a**, Scheme 2).* Isolate yield (78%), colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ −0.19 (q, J=1 Hz, 9H), 0.02 (q, J=2 Hz, 9H), 6.83–6.87 (m, 2H), 7.17–7.30 (m, 3H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 108.7 (s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.7 (q, J=4 Hz), 1.0 (s), 126.6 (d,

J=3 Hz), 127.0 (q, J=275 Hz), 127.3 (q, J=6 Hz), 128.0 (s), 143.7 (q, J=27 Hz), 144.1 (s), 169.6 (q, J=7 Hz) ppm; MS m/z (rel Int.)=209 (6), 132 (100), 73 (68); IR (neat): 1690 cm^{-1}. Anal. Calcd for $C_{15}H_{23}F_3Si_2$: C, 56.92; H, 7.32; N, 0.00. Found: C, 56.91; H, 7.42; N, 0.00.

*4.2.2. (E)-1-(4-Chlorophenyl)-3,3,3-trifluoro-1,2-ditrimethylsilyl-1-propene (**2b**, Scheme 2).* Isolate yield (81%), colorless block; mp 53.0–54.0 °C; ^1H NMR (300 MHz, $CDCl_3$): δ −0.16 (d, J=1 Hz, 9H), 0.02 (d, J=1 Hz, 9H), 6.81 (d, J=8 Hz, 2H), 7.27 (d, J=8 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 108.6 (s) ppm; ^{13}C NMR (75 MHz, $CDCl_3$); δ 0.4 (q, J=4 Hz), 0.9 (br), 127.0 (q, J=275 Hz), 128.0 (s), 128.5 (s), 132.4 (s), 142.3 (s), 144.4 (q, J=27 Hz), 168.2 (q, J=7 Hz) ppm; MS m/z (rel Int.)=258 (tr), 243 (6), 166 (58), 73 (100); IR (KBr): 1490 cm^{-1}. Anal. Calcd for $C_{15}H_{22}ClF_3Si_2$: C, 51.33; H, 6.32; N, 0.00. Found: C, 51.23; H, 6.55; N, 0.07.

Crystallographic data for **2b** (CCDC 787293): $C_{15}H_{22}ClF_3Si_2$, M=350.96, triclinic, space group $P\bar{1}$, a=9.295(3), b=9.319(5), c=11.820(7) Å, α=95.09(2), β=108.339(7), γ=99.11(3)°, V=949.0 (8) $Å^3$, Z=2, D_c=1.228 g cm^{-3}, λ (Mo Kα)=0.7107 nm, 7208 reflections measured, 3949 unique, final R=0.1095 using 2444 reflections with $I>2.0(I)$, R(all data)=0.1815, T=296 K.

*4.2.3. (E)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1,2-ditrimethylsilyl-1-propene (**2c**, Scheme 2).* Isolate yield (43%), colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ −0.17 (q, J=1 Hz, 9H), 0.03 (q, J=1 Hz, 9H), 3.81 (s, 3H), 6.76 (d, J=9 Hz, 2H), 6.82 (d, J=9 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 108.8 (s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.5 (q, J=4 Hz), 0.9 (q, J=1 Hz), 55.1 (s), 113.1 (s), 126.8 (q, J=275 Hz), 128.3 (s), 136.2 (s), 144.0 (q, J=27 Hz), 158.4 (s), 169.4 (q, J=7 Hz) ppm; MS m/z (rel Int.)=346 (tr), 239 (41), 162 (85), 73 (100); IR (neat): 1610, 1510 cm^{-1}. Anal. Calcd for $C_{16}H_{25}OF_3Si_2$: C, 55.46; H, 7.27; N, 0.00. Found: C, 55.48; H, 7.29; N, 0.03.

*4.2.4. (E)-3,3,3-Trifluoro-1-(4-chlorophenyl)-1,2-di(dimethylsilyl)-1-propene (**2d**, Scheme 3).* With compound **2e** as a small impurity. ^1H NMR (300 MHz, $CDCl_3$): δ 0.07 (d q, J=4, 1 Hz, 6H), 0.10 (q d, J=4, 1 Hz, 6H), 3.56 (septet q, J=4, 2 Hz, 1H), 4.28 (q septet, J=7, 4 Hz, 1H), 6.85 (d, J=4 Hz, 2H), 7.30 (d, J=4 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 108.0 (d, J=7 Hz) ppm; MS m/z (rel Int.)=213 (3), 187 (5), 166 (15), 128 (23), 77 (100).

*4.2.5. (Z)-3,3,3-Trifluoro-1-(4-chlorophenyl)-1,2-di(dimethylsilyl)-1-propene (**2e**, Scheme 3).* Obtained as a mixture with **2d**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.07 (d, J=4 Hz, 6H), 0.36 (q d, J=4, 1 Hz, 6H), 4.50 (septet, J=4 Hz, 1H), 4.57 (septet q, J=4, 1 Hz, 1H), 6.81 (d, J=9 Hz, 2H), 7.26 (d, J=9 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 110.4 (s) ppm; MS m/z (rel Int.)=213 (2), 197 (5), 166 (16), 128 (20), 77 (100).

4.3. Stepwise substitutions of TMS groups of disilyl alkene 2a

*4.3.1. (Z)-1,1,1-Trifluoro-3-phenyl-2-trimethylsilyl-2-butene (**3**, Scheme 4).* Methyl iodide (5 mmol, 0.62 mL) and **2a** (0.48 mmol, 0.151 g) were added to a suspension of TBAT (0.75 mmol, 0.404 g) in dry THF (1.5 mL) at room temperature under an argon atmosphere. After the mixture was stirred for 24 h at 40 °C, an internal standard (α,α,α-trifluorotoluene) was added into the reaction mixture at room temperature. The ^{19}F NMR yield of compound **3** was 62%. And, isolate yield was 58%.

^1H NMR (300 MHz, $CDCl_3$): δ −0.16 (s, 9H), 2.28 (q, J=3 Hz, 3H), 7.1–7.2 (m, 2H), 7.3–7.4 (m, 3H) ppm; ^{19}F NMR ($CDCl_3$, 300 MHz): δ 109.5 (s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.6 (d, J=2 Hz), 25.8 (d, J=2 Hz), 126.9 (q, J=276 Hz), 127.7 (s), 128.1 (s), 128.2 (s), 144.8 (s), 161.1 (q, J=6 Hz) ppm; GC/MS m/z (rel Int.)=243 (23), 147 (100), 127 (69), 77 (34); IR (neat): 1600 cm^{-1}. Anal. Calcd for $C_{13}H_{17}F_3Si$: C, 60.44; H, 6.63. Found: C, 60.55; H, 6.52.

*4.3.2. (Z)-3-Trifluoromethyl-1-hydroxy-1,3-diphenyl-2-butene (**4**, Scheme 4).* To a suspension of TBAT (0.05 mmol, 0.027 g) in dry THF (1.5 mL) were added PhCHO (1 mmol, 0.117 g) and **3** (0.46 mmol, 0.118 g) at room temperature under an argon atmosphere. After the mixture was stirred for 12 h at 50 °C, to the reaction mixture was added TBAF (0.5 mL, 1 M THF solution). Reaction mixture was stirred for more 3 h at 50 °C. The reaction mixture was quenched with $NaHCO_3$ aq (3 mL) and extracted with Et_2O (2 mL) three times. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=20:1). After removal of the solvent, distillation (80 °C/0.5 mmHg,) provided colorless oil of **4** (0.198 mmol, 43% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 2.19 (br d, J=6 Hz, 1H), 2.32 (q, J=2 Hz, 3H), 5.46 (br d, J=6 Hz, 1H), 7.2–7.4 (m, 10H). ^{19}F NMR (282 MHz, $CDCl_3$): δ 107.3 (s, 3F) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 22.9 (d, J=2 Hz), 71.9 (d, J=2 Hz), 124.7 (q, J=279 Hz), 124.9 (s), 126.7 (s), 127.1 (s), 128.0 (s), 128.2 (s), 128.7 (s), 134.9 (s), 141.3 (d, J=7 Hz), 149.6 (q, J=4 Hz); IR (neat): 3500 cm^{-1}; GC/MS m/z (rel Int.)=293 (2), 292 (12), 205 (25), 105 (100), 77 (59). Anal. Calcd for $C_{17}H_{125}F_3O$: C, 69.85; H, 5.17; N, 0.00. Found: C, 70.09; H, 5.20; N, 0.04.

*4.3.3. (E)-1,3-Diphenyl-2-(trifluoromethyl)-2-butenyl benzoate (**5**, Scheme 4).* Pyridine (0.7 mmol, 0.060 mL) and BzCl (0.8 mmol, 0.090 mL) were added to a solution of **4** (0.0734 g, 0.25 mmol) in dry dichloroethane (2.0 mL) at 0 °C under an argon atmosphere. After the mixture was stirred for 7 h, water was added. The solution was extracted with Et_2O (2 mL) three times. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc=10:1). Removal of the solvent provided colorless plates of **5** (0.0907 g, 0.229 mmol, 91% yield).

Mp=127.0–128.0 °C, ^1H NMR (300 MHz, $CDCl_3$): 2.35 (q, J=28 Hz, 3H), 6.80 (br, 1H), 7.26–7.50 (m, 12H), 7.60 (t, J=8 Hz, 1H), 8.12 (d, J=7 Hz, 2H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 107.3 (s) ppm; IR (KBr): 1730 cm^{-1}; GC/MS m/z (rel Int.)=274 (29), 259 (8), 205 (50), 177 (9), 105 (100), 77 (35). Anal. Calcd for $C_{24}H_{19}F_3O_2$: C, 72.72; H, 4.83. Found: C, 72.73; H, 4.74.

Crystallographic data for **5** (CCDC 786885): $C_{24}H_{19}F_3O_2$, M=396.40, monoclinic, space group $P21/c$, a=9.8246(15), b=11.2322 (14), c=18.5397(17) Å, α=90.000, β=95.003(5), γ=90.000°, V=2038.1(4) $Å^3$, Z=4, D_c=1.292 g cm^{-3}, λ (Mo Kα)=0.7107 nm, 12,673 reflections measured, 4654 unique, final R=0.0674, using 3799 reflections with $I>2.0.(I)$, R(all data)=0.0920, T=296.1 K.

*4.3.4. (E)-1-Hydroxy-4,4,4-trifluoro-1,2-diphenyl-3-(trimethylsilyl)-2-butene (**6**, Scheme 5).* Compound **2a** (1 mmol, 0.315 g) was added to a suspension of TBAT (0.05 mmol, 0.027 g) and PhCHO (1.1 mmol, 0.116 g) in dry THF (0.33 mL) at 0 °C under an argon atmosphere after the mixture was stirred for 24 h at 0 °C. Then, 1.1 equiv amount of HCl aq (1 M, 1.1 mL) was added and stirred for more 5 h. The reaction mixture was added by satd $NaHCO_3$ aq and extracted by ether three times. The organic layer was washed by satd NaCl aq twice and dried over anhydrous $MgSO_4$. Further purification by silica gel column chromatography, followed by distillation (90 °C/7 mmHg) gave the product as a colorless oil in 53% yield.

^1H NMR (300 MHz, $CDCl_3$): δ 7.1–7.3 (m, 8H), 7.0 (m, 1H), 6.23 (d, J=7 Hz, 1H), 6.14(d, J=8 Hz, 1H), 1.94 (d, J=7 Hz, 1H), −0.19(d, J=1 Hz, 9H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 113.2 (s, 3F) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.5 (s), 72.6 (q), 126.0 (s), 126.3 (q, J=276 Hz), 127.0 (s), 127.3 (s), 127.9 (s), 128.2 (s), 129.7 (s), 130.7 (s), 131.8 (q, J=26 Hz), 136.5 (s), 139.9 (s), 162.6 (q, J=5 Hz), 227.5 (s) ppm; IR (neat): 3480 cm^{-1}; GC/MS m/z (rel Int.)=244 (18), 229 (36), 191 (18), 151 (58), 107 (100), 77 (60), 73 (42). Anal. Calcd for $C_{19}H_{21}F_3OSi$; C, 65.12; H, 6.04; N, 0.00. Found: C, 65.02; H, 6.26; N, 0.04.

*4.3.5. (Z)-1,2,4-Triphenyl-3-(trifluoromethyl)-2-butene-1,4-diol (**7**, Scheme 5).* Similar to the preparation of compound **6**, 2 equiv amount of PhCHO was allowed to react with **2a**. ^{19}F NMR yield was found 84% as the mixture of a pair of diastereomers (major/minor=6:4). The product was obtained as a white powder, and was purified by recrystallization from hexane/ether (ca. 5%) for elemental analysis.

Mp=216–217 °C, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2–7.4 (m, 15H), 6.26 (s, minor 1H), 6.24 (s, major 1H), 5.31 (s, minor 1H), 5.29 (s, major 1H), 2.22 (br, major 1H) 2.19 (br, minor 1H), 2.14 (s, major 1H), 2.12 (s, minor 1H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ 111.1 (s overlap, 3F) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.3 (s), 71.4 (s), 125.4 (q, J=276 Hz), 125.7 (s), 126.9 (s), 127.4 (s), 127.9 (s), 128.2 (s), 128.6 (s), 128.8 (s) 129.9 (br), 130.9 (s), 131.2 (q J=25 Hz), 136.0 (s), 142.1 (s), 143.0 (s), 153.4 (br) ppm; IR (KBr): 3300 cm^{-1}; GC/MS m/z (rel Int.)=366 (7), 278 (9), 260 (32), 191 (44), 107 (100), 105 (78), 79 (69), 77 (61). Anal. Calcd for $C_{26}H_{25}F_3O_2Si$; C, 71.85; H, 4.98. Found: C, 71.71; H, 4.94.

Acknowledgements

The authors express our gratitude to the SC-NMR Laboratory of Okayama University for NMR analysis and the VBL Laboratory for X-ray crystallographic analysis.

References and notes

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