First synthesis of *ortho*-trifluoromethylated aryl triflates

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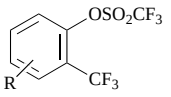
An efficient method for the preparation of trifluoromethylated aryl triflates (trifluoromethanesulfonates) has been developed. Treatment of 2-iodophenol with trifluoromethanesulfonic anhydride in the presence of triethylamine gives triflate 3. Then, reaction of compound 3 with $FSO_2CF_2CO_2Me$ and CuI in DMF–HMPA affords trifluoromethylated aryl triflate 2. This reaction sequence is also successful for *meta*- and *para*-trifluoromethylated aryl triflates. Based on this methodology, the trifluoromethylated aryl triflate 11, a key intermediate for the preparation of the conformationally restricted retinoid 8 containing a trifluoromethyl group, has been synthesized. The cross-coupling of aryl triflate 11 with vinylstannane 17 under palladium catalysis provides compound 18, the methyl ester of retinoid 8, in moderate yield.

Introduction

Since a trifluoromethyl group possesses high lipophilicity, powerful electron-withdrawing properties and small size, this group is an increasingly popular aromatic substituent in compounds synthesized for biological application.[1] Classical methods for the synthesis of trifluoromethylated aromatics include the use of antimony fluorides (conversion of $-CCl_3$ to $-CF_3$) and sulfur tetrafluoride (transformation of $-CO_2H$ into $-CF_3$).[2] Emphasis is now being placed on the use of less harsh reagents and mild conditions. A review of the methods of introducing the trifluoromethyl group into organic molecules has been published.[3] Owing to the discovery of cross-coupling reactions of aryl triflates with different organometallic compounds which proceed with high regioselectivity under mild conditions and which tolerate the presence of various functional groups,[4] the trifluoromethylated aryl triflates **1** would be



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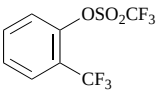

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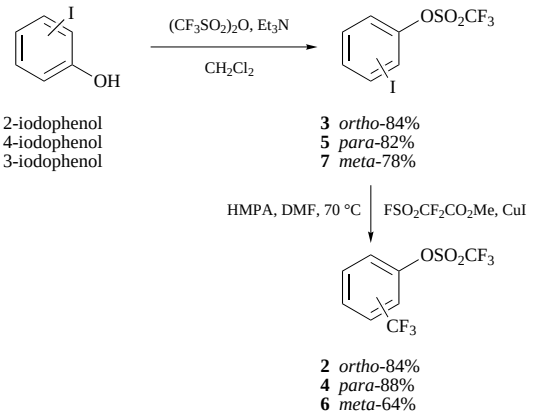
ideal intermediates for the synthesis of biologically active trifluoromethylated aromatic compounds. Aryl triflates are usually prepared from the phenols in excellent yields by treating them with trifluoromethanesulfonic anhydride in the presence of a base such as pyridine or triethylamine.[5] The synthesis of some special substituted aryl triflates could be accomplished by fluoride-anion-catalyzed reaction of aryl silyl ethers with trifluoromethanesulfonyl fluoride[6] and thermal or photochemical decomposition of arenediazonium salts in trifluoromethanesulfonic acid.[7] However, to the best of our knowledge, *ortho*-trifluoromethylated aryl triflates, even the simplest example, compound **2**, have not yet been reported. Herein, we report an efficient synthesis of trifluoromethylated aryl triflates.

Results and discussion

Triflate **2** was used as model target molecule to enable us to explore the reaction conditions. Initial attempts to synthesize compound **2** were carried out by treatment of the commercially available 2-(trifluoromethyl)phenol with trifluoromethanesulfonic anhydride[5] or *N*-phenyltrifluoromethanesulfonimide[8] in the presence of triethylamine in dichloromethane. The reaction failed to give the expected product **2**, and only 2-hydroxybenzoic acid was isolated after work-up. This implied that 2-(trifluoromethyl)phenol was sensitive to the reaction conditions, in accord with previously reported results.[9] Therefore, an alternative route, to introduce a triflate first, followed by incorporation of a trifluoromethyl group, was investigated (Scheme 1). Reaction of the commercially available 2-iodophenol with trifluoromethanesulfonic anhydride in the presence of triethylamine gave triflate **3** in high yield. Various methods of trifluoromethylation of the triflate **3** using trifluoromethylcopper as the trifluoromethylating agent have been evaluated. Treatment of compound **3** with CF_3SiMe_3–CuI in a sealed tube[10] or Burton's reagent (CF_2Br_2/Cd, CuBr)[11] were unsuccessful, and starting material **3** was recovered. Slow addition of $ClCF_2CO_2CH_3$ to the mixture of triflate **3**, CuI, KF and *N*,*N*-dimethylformamide (DMF) at 120 °C[12] also failed and only 2-(trifluoromethyl)phenol was obtained. If the reaction temperature was below 120 °C, methyl chlorodifluoroacetate ($ClCF_2CO_2CH_3$) was recovered unchanged. The isolated 2-(trifluoromethyl)phenol revealed that the formed triflate **2** was attacked by halides, with sulfur–oxygen cleavage at higher temperatures.[13] When we employed $FSO_2CF_2CO_2Me$[14]–CuI in DMF as the trifluoromethylating agent and followed Chen's procedure,[15] the trifluoromethylation took place slowly and compound **3** was only partly converted. Furthermore, we were unable to separate compounds **2** and **3** by column chromatography or by distillation. With longer reaction times (*e.g.*, 8 h) and higher reaction temperatures (*e.g.*, 90 °C), serious decomposition occurred to give 2-(trifluoromethyl)phenol. Burton and co-workers[11] reported that trifluoromethylcopper, produced *via in situ* metathesis of trifluoromethyl-cadmium and -zinc reagents with copper(I) salts, might exist in two forms: one would be a reactive species, the reagent to be employed in subsequent coupling-type chemistry; another one would be a less reactive species, produced with longer reaction times or higher temperatures. In addition, the reactive species could be stabilized by addition of hexamethylphosphoric triamide (HMPA). In accordance with this hypothesis, addition of HMPA to a solution of $FSO_2CF_2CO_2Me$–CuI and **3** in DMF, followed by stirring of the resultant mixture for 4 h at 70 °C, provided **2** in 84% isolated yield and the decomposition product 2-(trifluoromethyl)phenol was not detected by ^{19}F NMR spectroscopy used to monitor the reaction. This success suggested that the stabilization of reactive species of trifluoromethylcopper by HMPA was important. It should be noted that compound **2** at room

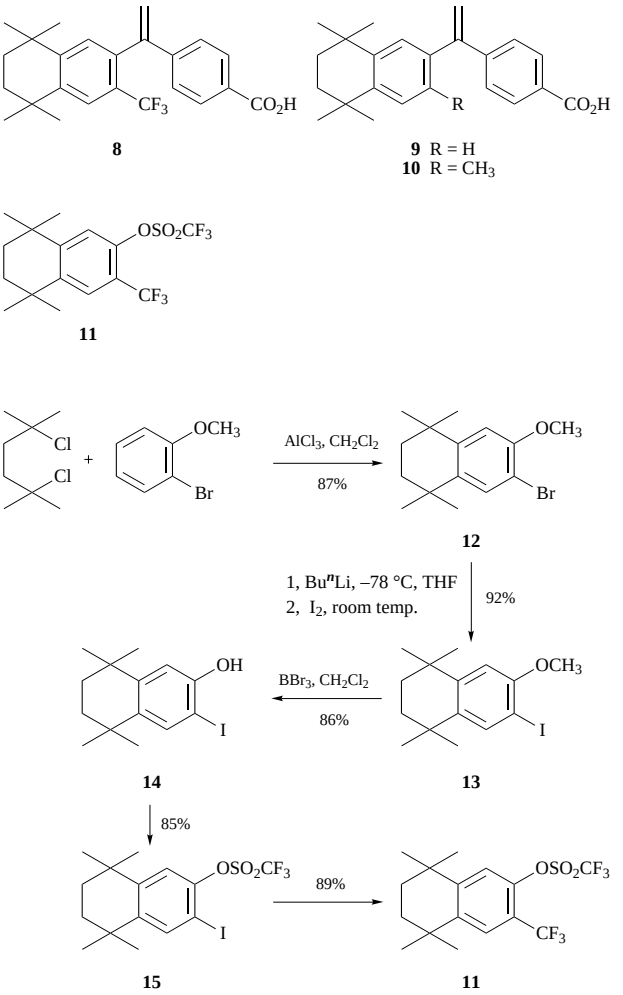
temperature and even at 110 °C for 8 h, was very stable in the absence of nucleophiles. Similarly, the *para*- and *meta*-trifluoromethylaryl triflates **4** and **6** can be prepared from 4- and 3-iodophenol, respectively, using this reaction sequence, in high yields (Scheme 1). Compounds **2**, **4** and **6** are fairly volatile and can be distilled.



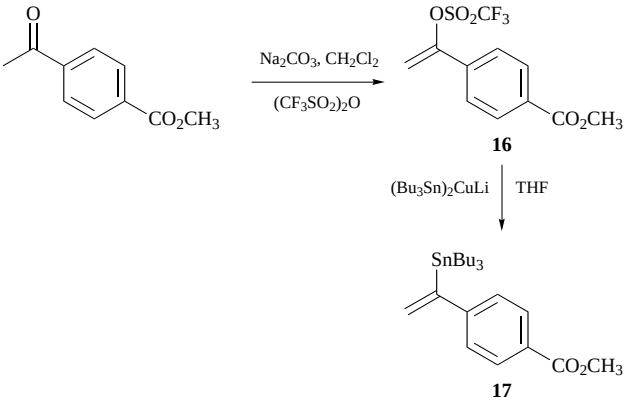
Scheme 1

To demonstrate further the versatility and effectiveness of the above method, synthesis of the conformationally restricted retinoid **8** containing a trifluoromethyl group was undertaken. Retinoids, natural and synthetic analogues of vitamin A, exert profound effects on many important cellular processes by regulating gene expression mediated by two classes of nuclear receptors: the retinoic acid receptor family (RAR) and the retinoid X receptor family (RXR).[16] Within the last three years, novel classes of RXR-selective retinoids have emerged. Among them, the introduction of a 3-methyl substituent to the weakly active retinoid **9** resulted in the most potent RXR selective compound **10** which is currently undergoing clinical trials for the treatment of cancer.[17] Considering the fact that many performance chemicals benefit from the presence of a trifluoromethyl group, we became interested in incorporating a 3-trifluoromethyl substituent into retinoid **9**. Trifluoromethylated aryl triflate **11** was chosen as a key intermediate for the preparation of 3-trifluoromethyl-substituted retinoid **8**. Based on the methodology we developed for the preparation of compound **2**, the synthesis of intermediate **11** was carried out as depicted in Scheme 2. Reaction of 2-bromoanisole with 2,5-dichloro-2,5-dimethylhexane in the presence of aluminium chloride gave the tetralin bromide **12**. Bromide **12** was treated with *n*-butyllithium at −78 °C, followed by iodine at room temperature to afford iodide **13**. Demethylation of the ether **13** with boron tribromide (1 M in dichloromethane) gave the phenol **14** which was then smoothly converted *via* triflate **15** into the intermediate **11** according to the procedures described in Scheme 1.

With the trifluoromethylated aryl triflate **11** available, we turned our attention to an examination of its utility as a partner for the preparation of the conformationally restricted retinoid **8** containing a trifluoromethyl group. Commercially available methyl 4-acetylbenzoate was converted *via* the vinyl triflate **16**[18] into the vinylstannane **17**[19] (Scheme 3). To our knowledge no example exists in the literature of the use of the vinylstannane **17** in a palladium-catalyzed coupling. A variety of experiments were carried out to find the best reaction conditions [$Pd(PPh_3)_4$, CuCl, K_2CO_3, tetrahydrofuran (THF), 25 °C;[20] $Pd(PPh_3)_4$, LiCl, THF, 65 °C;[21] $Pd(PPh_3)_4$, LiCl, 1,4-dioxane, 95 °C;[22] $Pd_2(dba)_3$,† $AsPh_3$, CuI, 1-methyl-2-pyrrolidone (NMP), 50 °C;[23] $Pd(PPh_3)_4$, CuI, LiCl, DMF, room temp.[24]] for the formation of the heterocoupling product **18**.



Scheme 2

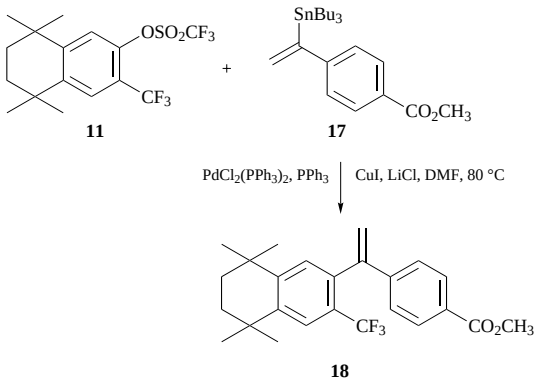


Scheme 3

Unfortunately, reaction of trifluoromethylated aryl triflate **11** with the vinylstannane **17** under the above conditions did not afford the desired heterocoupling product **18** due to the decomposition of substrates **11** and **17** or to the formation of homodimer of **17**. Finally, it was found that the cross-coupling reaction proceeded to provide the retinoid **18** in 60% yield in the presence of bis(triphenylphosphine)palladium(II) chloride, triphenylphosphine and copper(I) iodide (Scheme 4). The role of CuI and the reaction temperature were both crucial for the success of this reaction.

In conclusion, an efficient method for the preparation of *ortho*-trifluoromethylated aryl triflates has been developed for the first time. The cross-coupling reactions of trifluoromethylated aryl triflates **11** with the vinylstannane **17** under palladium

† dba = dibenzylideneacetonato.



Scheme 4

catalysis provided conformationally restricted retinoid **18** containing a trifluoromethyl group.

Experimental

Mps were determined on a commercially available apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-440 spectrometer. Mass spectra were recorded on a Finnigan-MAT-8430 instrument using electron impact (EI) ionization at 70 eV. ^{19}F NMR spectra were obtained on a 60 MHz spectrometer using trichlorofluoromethane as external standard, upfield negative. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer with tetramethylsilane as the internal standard. All chemical shifts (δ) are expressed in ppm. Coupling constants (J) are given in Hz.

All reactions were conducted under nitrogen in over-dried glassware. THF was freshly distilled under nitrogen from a purple solution of sodium and benzophenone. DMF, triethylamine and dichloromethane were freshly distilled from CaH_2. CuI was purified by a literature procedure.[25] Light petroleum refers to the fraction with distillation range 60–90 °C.

2-Iodophenyl triflate 3

$(CF_3SO_2)_2O$ (1.74 ml, 10.3 mmol) was added dropwise to a solution of 2-iodophenol (1.99 g, 9.05 mmol) and Et_3N (2.52 ml, 18.09 mmol) in CH_2Cl_2 (20 ml) at −78 °C. After being stirred for 1.5 h at −78 °C, the reaction mixture was warmed to room temperature overnight. After dilution with ice–water (10 ml) and Et_2O (100 ml), the organic layer was separated, washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo*. Flash chromatography of the residue with hexane afforded compound **3** (2.68 g, 84%) as an oil; $\delta_H(CDCl_3)$ 7.10–7.18 (m, ArH), 7.30–7.45 (m, ArH) and 7.80–7.92 (m, ArH); $\delta_F(CDCl_3)$ −80.8 (s, SO_2CF_3); *m*/*z* (EI) 352 (M^+, 61%), 219 (100), 191 (31), 92 (64) and 69 (17).

4-Iodophenyl triflate 5

$\delta_H(CDCl_3)$ 7.06 (dd, J_{HH} 8.84 and 1.98, ArH) and 7.78 (dd, J_{HH} 8.84 and 1.98, ArH); $\delta_F(CDCl_3)$ −81.9 (s, SO_2CF_3); *m*/*z* (EI) 352 (M^+, 47%), 219 (100), 191 (29) and 69 (21).

3-Iodophenyl triflate 7

$\delta_H(CDCl_3)$ 7.00–7.33 (m, ArH), 7.63–7.75 (m, ArH); $\delta_F(CDCl_3)$ −81.6 (s, SO_2CF_3); *m*/*z* (EI) (M^+, 100%), 219 (17), 191 (21), 95 (40) and 69 (20).

2-(Trifluoromethyl)phenyl triflate 2

A mixture of $FSO_2CF_2CO_2Me$ (0.97 ml, 8.55 mmol), CuI (391.2 mg, 2.05 mmol), HMPA (1.45 ml, 8.55 mmol) and iodide **3** (602 mg, 1.71 mmol) in DMF (5 ml) was stirred for 4 h at 70 °C. The reaction mixture was then cooled to room temperature, 5 ml of saturated aq. NH_4Cl were added and the mixture was extracted with Et_2O (3 × 20 ml). The organic layer was washed successively with saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. The solvent was removed *in vacuo*. Flash chromatography with hexane afforded title compound **2** (377 mg, 84%) as an oil, $\delta_H(CDCl_3)$ 7.48–7.53 (m, ArH), 7.65–7.74 (m, ArH) and 7.76–7.79 (m, ArH); $\delta_F(CDCl_3)$ −93.2 (s, CF_3) and −80.3 (s, SO_2CF_3); *m*/*z* (EI) 294 (M^+, 35%), 230 (50), 142 (99), 114 (100), 84 (86) and 69 (70).

4-(Trifluoromethyl)phenyl triflate 4

$\delta_H(CDCl_3)$ 7.47 (d, J_{HH} 8.61, ArH), 7.78 (d, J_{HH} 8.61, ArH); $\delta_F(CDCl_3)$ −91.9 (s, CF_3), −81.8 (s, SO_2CF_3); *m*/*z* (EI) 294 (M^+, 65%), 230 (79), 145 (45), 133 (78) and 69 (100).

3-(Trifluoromethyl)phenyl triflate 6

$\delta_H(CDCl_3)$ 7.44–7.52 (m, ArH), 7.59–7.75 (m, ArH); $\delta_F(CDCl_3)$ −91.5 (s, CF_3) and −81.7 (s, SO_2CF_3); *m*/*z* (EI) 294 (M^+, 22%), 230 (45), 161 (32), 107 (72) and 69 (100).

6-Bromo-7-methoxy-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene 12

Anhydrous aluminium chloride (1.0 g) was added cautiously to a stirred solution of 2,5-dichloro-2,5-dimethylhexane (18.3 g, 0.1 mol) and 2-bromoanisole (18.7 g, 0.1 mol) in dry CH_2Cl_2 (200 ml) at 0 °C. The reaction mixture was warmed to room temperature, then was stirred overnight. The mixture was combined with 3 M hydrochloric acid, and the organic layer was washed with water until the aqueous phase was neutral to pH paper. This solution was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The solid residue was recrystallized from MeOH–acetone to give compound **12** as a solid (25.8 g, 87%), mp 75–76 °C; ν_{max}(KBr)/cm^{-1} 2965, 2928, 1596, 1490, 1313, 1252, 1080, 1047, 889, 848 and 706; δ_H 1.24 (s, CH_3), 1.27 (s, CH_3), 1.66 (s, CH_2), 3.86 (s, OCH_3), 6.79 (s, ArH), 7.42 (s, ArH); *m*/*z* (EI) 296 (M^+, 56%), 283 (100), 281 (99) and 202 (30).

6-Iodo-7-methoxy-1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene 13

n-BuLi (32 ml, 50 mmol; 1.6 M in hexanes) was added dropwise to a solution of bromide **12** (14.86 g, 50 mmol) in THF (60 ml) at −78 °C. Then the reaction mixture was warmed to room temperature and was stirred for 10 min before being recooled to −78 °C, and a solution of I_2 (12.6 g, 50 mmol) in THF (20 ml) was added. Then the reaction mixture was warmed to room temperature and stirred for 30 min. 100 ml of saturated aq. NH_4Cl were added and the mixture was extracted with Et_2O (3 × 50 ml). The organic layer was washed successively with water, saturated aq. $Na_2S_2O_3$ and brine. The solvent was removed *in vacuo*. The solid residue was recrystallized from MeOH to give *iodide* **13** as a solid (15.8 g, 92%), mp 87–88 °C (Found: C, 52.45; H, 6.19. $C_{15}H_{21}IO$ requires C, 52.35; H, 6.15%); ν_{max}(KBr)/cm^{-1} 2959, 2926, 1586, 1487, 1247, 1072, 1041, 853 and 695; $\delta_H(CDCl_3)$ 1.26 (s, CH_3), 1.30 (s, CH_3), 1.70 (s, CH_2), 3.90 (s, OCH_3), 6.74 (s, ArH) and 7.64 (s, ArH); *m*/*z* (EI) 344 (M^+, 50%), 330 (18), 329 (100) and 202 (13).

3-Iodo-5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-2-naphthol 14

BBr_3 (10 ml, 10 mmol; 1 M in CH_2Cl_2) was added to a solution of the ether **13** (3.0 g, 8.72 mmol) in CH_2Cl_2 (30 ml) at −78 °C. The reaction mixture was warmed to −10 °C and stirred for 1 h. The mixture was diluted with ice–water (30 ml) and extracted with Et_2O (100 ml); the organic layer was separated, washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo*. The solid residue was recrystallized from hexanes to give the naphthol **14** as a solid (2.47 g, 86%), mp 102–103 °C (Found: C, 51.23; H, 6.00. $C_{14}H_{19}IO$ requires C, 50.92; H, 5.80%); ν_{max}(KBr)/cm^{-1} 3489, 2956, 1559, 1481, 1290, 1196, 884 and 702; $\delta_H(CDCl_3)$ 1.24 (s, CH_3), 1.63 (s, CH_2) 5.08 (s, OH), 6.93 (s, ArH) and 7.53 (s, ArH); *m*/*z* (EI) 330 (M^+, 32%), 315 (100), 173 (25) and 146 (18).

3-Iodo-5,5,8,8-tetramethyl-3,5,6,7,8-tetrahydro-2-naphthyl triflate 15

Prepared according to the procedure described above, using substrate **14**. The *product* **15** was isolated as a solid in 85% yield, mp 60 °C (Found: C, 39.10; H, 3.91. $C_{15}H_{18}F_3IO_3S$ requires C, 38.97; H, 3.92%); ν_{max}(KBr)/cm^{-1} 2967, 1929, 1423, 1209, 1139, 941, 855, 637 and 603; δ_H($CDCl_3$) 1.25 (s, CH_3), 1.66 (s, CH_2), 7.17 (s, ArH) and 7.73 (s, ArH); δ_F($CDCl_3$) −81.6 (s, SO_2CF_3); *m*/*z* (EI) 462 (M^+, 45%), 447 (100), 187 (41) and 159 (33).

5,5,8,8-Tetramethyl-3-trifluoromethyl-5,6,7,8-tetrahydro-2-naphthyl triflate 11

Prepared according to the procedure described above, using substrate **15**. The *product* **11** was isolated as a solid in 89% yield, mp 57 °C (Found: C, 47.23; H, 4.47. $C_{16}H_{18}F_6O_3S$ requires C, 47.52; H, 4.49%); δ_H($CDCl_3$) 1.29 (s, CH_3) 1.30 (s, CH_3), 1.72 (s, CH_2), 7.35 (s, ArH) and 7.61 (s, ArH); δ_C($CDCl_3$) 30.7, 30.8, 33.4, 33.7, 34.1, 34.7, 118.4, 119.9, 120.6, 126.5, 142.7, 146.3, 152.7, 155.5, 159.9 and 164.5; δ_F($CDCl_3$) −94.6 (s, CF_3) and −81.3 (s, SO_2CF_3); *m*/*z* (EI) 404 (M^+, 7%), 398 (100), 327 (31), 227 (10), 213 (13) and 194 (12).

Methyl 4-[1-(trifluoromethylsulfonyloxy)ethenyl]benzoate 16

To a mixture of methyl 4-acetylbenzoate (3.56 g, 20 mmol) and anhydrous sodium carbonate (5.3 g, 50 mmol) in 120 ml of dichloromethane was added a solution of trifluoromethanesulfonic anhydride (5.1 ml, 30 mmol). The reaction mixture was stirred for 24 h. The mixture was filtered, and the filtrate was washed with dichloromethane. The organic layer was washed successively with aq. sodium hydrogen carbonate and water, and dried over sodium sulfate. The solvent was removed *in vacuo*. Purification of the residue by column chromatography on silica gel and elution with 10 : 1 light petroleum–ethyl acetate provided compound **16** (4.9 g, 80%) as a solid, mp 36–37 °C (Found: C, 42.55; H, 2.71. Calc. for $C_{11}H_9F_3O_5S$: C, 42.58; H, 2.92%); ν_{max}(KBr)/cm^{-1} 2958, 1730, 1464, 1424, 1285, 1227, 1143, 1114, 941, 712 and 608; δ_H($CDCl_3$) 3.90 (s, OCH_3), 5.49 (d, J_{HH} 4.3, CH_2=) 5.73 (d, J_{HH} 4.3, CH_2=), 7.60 (A_2B_2, J_{HH} 8.6, ArH), 8.07 (A_2B_2, J_{HH} 8.6, ArH); δ_F($CDCl_3$) −81.0 (s, SO_2CF_3); *m*/*z* (EI) 310 (M^+, 89%), 215 (100), 279 (75), 177 (43) and 149 (40).

Methyl 4-[1-(tributylstannyl)ethenyl]benzoate 17

Tributyltin hydride (5.4 ml, 20 mmol) was added to a solution of lithium diisopropylamide (LDA) (10 ml, 20 mmol; 2.0 M in heptane–THF) in 30 ml of THF at 0 °C. After being stirred for 10 min at 0 °C, the mixture was cooled to −15 °C and CuI (2.0 g, 10 mmol) was added. The resulting suspension was stirred at −15 °C for 30 min and then was cooled to −78 °C. A solution of triflate **16** (3.1 g, 10 mmol) in 10 ml of THF was added over a period of 5 min. After 40 min at −78 °C, the reaction mixture was quenched with saturated aq. ammonium chloride (60 ml), and was then extracted with diethyl ether. The combined extracts were washed successively with water and brine. The solution was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel and elution with 5% EtOAc–hexanes to afford the title stannane **17** (2.9 g, 65%) as a liquid (Found: C, 58.74; H, 8.05. Calc. for $C_{22}H_{36}O_2Sn$: C, 58.56; H, 8.04%); ν_{max}(liquid film)/cm^{-1} 2957, 2929, 2854, 1726, 1604, 1436, 1277, 1109, 1018, 861 and 723; δ_H($CDCl_3$) 0.86 (t, J_{HH} 7.0, CH_3), 0.95 (t, J_{HH} 7.0, $SnCH_2$), 1.23–1.28 (m, CH_2), 1.37–1.51 (m, CH_2), 3.91 (s, OCH_3), 5.51 (d, J_{HH} 2.4, =CH_2), 6.05 (d, J_{HH} 2.4, CH_2=), 7.19 (A_2B_2, J_{HH} 8.3, ArH) and 7.97 (A_2B_2, J_{HH} 8.3, ArH); *m*/*z* (EI) 452 (M^+ + 1, 6.4%), 395 (100), 339 (95), 281 (79), 283 (74) and 131 (69).

Methyl 4-[1-(5,5,8,8-tetramethyl-3-trifluoromethyl-5,6,7,8-tetrahydro-2-naphthyl)ethenyl]benzoate 18

A round-bottomed flask was charged with a mixture of triflate **11** (0.4 g, 1 mmol), anhydrous LiCl (0.12 g, 3 mmol), triphenylphosphine (0.006 g, 0.02 mmol), and $PdCl_2(PPh_3)_2$ (0.006 g, 0.01 mmol) suspended in DMF (10 ml) and the mixture was stirred at 80 °C for 10 min. Then organostannane **17** (1.8 g, 4 mmol) and CuI (1 g, 5 mmol) were added and the resulting mixture was stirred overnight at 80 °C. Water (20 ml) and diethyl ether (40 ml) were added, and the organic phase was washed successively with 1.5 M HCl and saturated aq. potassium fluoride, and dried over Na_2SO_4. Evaporation to dryness furnished a residue, which was suspended in ethyl acetate and then filtered off. The filtrate was evaporated, and the resulting crude material was purified by flash chromatography on silica gel and elution with 3% EtOAc–hexanes to afford *title compound* **18** (250 mg, 60%) as a solid, mp 124–126 °C (Found: C, 71.69; H, 6.95. $C_{15}H_{27}F_3O_2$ requires C, 72.09; H, 6.54%); ν_{max}(KBr)/cm^{-1} 2954, 2929, 1719, 1608, 1279, 1218, 1079, 913, 863, 785 and 717; δ_H($CDCl_3$) 1.26 (s, CH_3), 1.34 (s, CH_3), 1.72 (s, CH_2), 3.90 (s, OCH_3), 5.34 (s, CH_2=), 5.94 (s, CH_2=), 7.17 (s, ArH), 7.61 (s, ArH), 7.31 (A_2B_2, J_{HH} 8.5, ArH) and 7.95 (A_2B_2, J_{HH} 8.5, ArH); δ_C($CDCl_3$) 29.8, 30.4, 31.6, 31.7, 34.5, 34.9, 52.0, 117.9, 124.7, 126.2, 126.6, 127.7, 129.2, 129.6, 129.9, 130.2, 136.5, 144.8, 144.9, 146.3, 148.8 and 166.9; δ_F($CDCl_3$) −97.3 (s, CF_3); *m*/*z* (EI) 416 (M^+, 31%), 401 (100), 359 (18), 345 (19), 327 (18), 161 (81) and 43 (23).

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