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A new preparation of trifluoromethanesulfinate salts

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Abstract

Trifluoromethanesulfinate (triflinate) salts can be prepared in an ecofriendly way by β-elimination of aliphatic triflones bearing an acidic hydrogen in β position. This technique allows the synthesis of various triflinate salts under mild conditions.

Keywords: Trihalomethyl sulfides; Trifluoromethyl sulfones; Trifluoromethanesulfinates; Trifluoromethylation; Halogen exchange; Alkyl thiocyanates; β-Elimination

1. Introduction

Sodium or potassium trifluoromethanesulfinates (triflinates) are very valuable compounds which can be used either as precursors of trifluoromethanesulfonic acid, by oxidation with hydrogen peroxide [1], or as generators of trifluoromethyl radicals by single electron oxidation with *tert*-butyl hydroperoxide [2a]. In this latter way, sodium triflinate can be used to transform disulfides into trifluoromethyl sulfides [2] or to trifluoromethylate, in the presence of catalytic Cu(II) salts, electron-rich aromatics [3], enol acetates [4] or vinyl sulfides [5], in a ''pseudo-electophilic'' process.

In the early 1990s, sodium triflinate has been prepared on a large scale by the Rhône-Poulenc Co., through single-electron reduction of bromotrifluoromethane, which is now banned because of its ozone depleting effect [1,6a]. This technique needs a heavy work up to extract triflinate from DMF without contamination by bromide [6b]. Thus, the Rhodia Co. further developed a new synthesis of potassium triflinate from potassium trifluoroacetate [7]. This process is ecologically friendly but, as its final goal is the manufacture of triflic acid, potassium triflinate is not separated from potassium trifluoroacetate and, consequently, cannot be easily available for trifluoromethylation purposes. Thus, we examined new ways to make various triflinates easily available, at least on the bench scale, with a high purity.

2. Results and discussion

Our general strategy was based on the generation of the triflinate anion, which is known to be a rather good leaving group [8], through β-elimination processes from trifluoromethyl sulfones (triflones). Two substrates were selected: ethyl 3-(trifluoromethanesulfonyl)propionates **1a,b** and α-(benzyl)-benzyl triflone **1c** (Scheme 1).

2.1. Synthesis of sodium triflinate *3a* from *1a*

The planed route is summarized in Scheme 2.

This study started with the synthesis of **2a** from trifluoromethylating reagents. Ten years ago, we reported a

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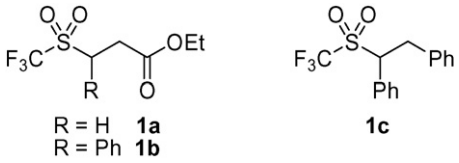


Scheme 1. Key intermediates.

very expedient route to trifluoromethyl sulfides, from the corresponding thiocyanates and (trifluoromethyl)trimethylsilane (Ruppert-Prakash's reagent) [9], but this method was inefficient with $NCS(CH_2)_2CO_2Et$ (**5**) because β-elimination of thiocyanate strongly competed with the expected reaction. The same β-elimination occurred when **5** was opposed to trifluoromethylcopper(I) species, produced from excess sodium trifluoroacetate and CuI in *N*,*N*-dimethylacetamide at 160 °C.

Two other preparations of **2a** were examined, first from sodium trifluoroacetate and ethyl 3-(benzenesulfonylthio)propionate **7** (obtained by analogy with [10]) but the yield was poor (Scheme 3, route A), and secondly from photolytic S_H2 decarbonylation of ethyl 3-(trifluoroacetylthio)propionate **8** [11] but this process was difficult to scale up (Scheme 3, route B).

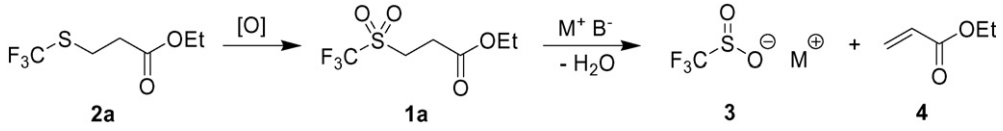
Thus, we turned to the synthesis of **2a** from the chlorinated precursor **9a**. Compound **9a** can be obtained from sodium trichloroacetate and **7**, according to Kloosterziel et al. [12], but more easily from **5**, as depicted in Scheme 5 (Makosza's process [13] from **5**, chloroform and a strong base is not possible because of extensive β-elimination). Then, **9a** was submitted to chlorine-fluorine exchange with Pyridine/10 HF (Olah's reagent), according to Saint-Jalmes [14], to provide, in a 50% unoptimized yield, **2a** which was further oxidized into **1a** with hydrogen peroxide,according to Kort and Löhmer [15]. Finally, **1a** was treated with sodium methoxide in methanol to provide, in a very short time, the expected sodium triflinate in a quantitative yield.

This successful approach is summarized in Scheme 4. Its advantage lies in the fact that cheap reagents are used and that thiocyanate **5** can be easily regenerated by a Michael addition of potassium thiocyanate upon ethyl acrylate **4**. However, four to five steps (if recycling of **4** into **5** is considered) are needed.

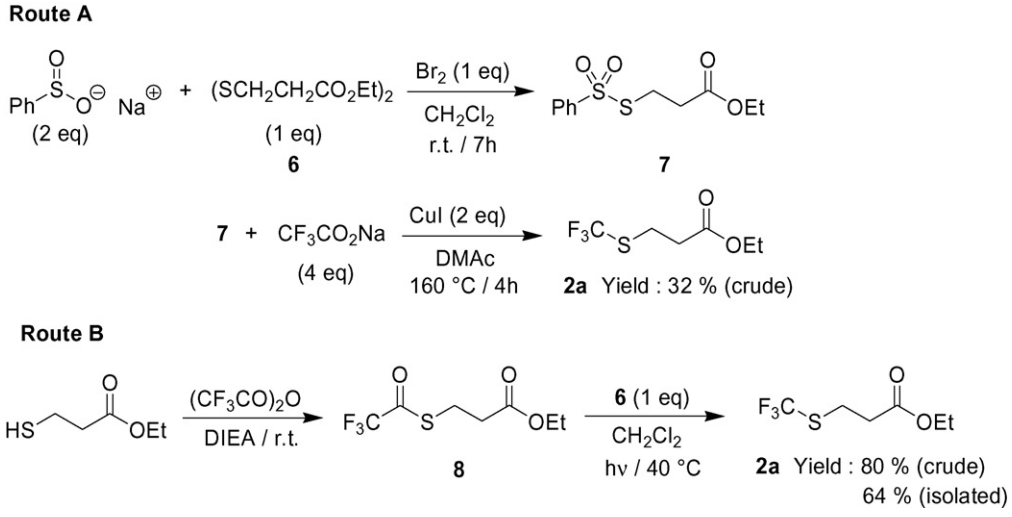
2.2. *Synthesis of alkaline triflinates **3a–b** from **1b** and **1c***

As most of troubles in the above strategy often came from extensive β-eliminations instead of the expected substitutions, we turned our attention to precursors of triflinates which could be prepared from a building block already containing the triflone moiety, especially benzyl trifluoromethyl sulfone **10** which could be easily alkylated then submitted to β-elimination (Scheme 5).

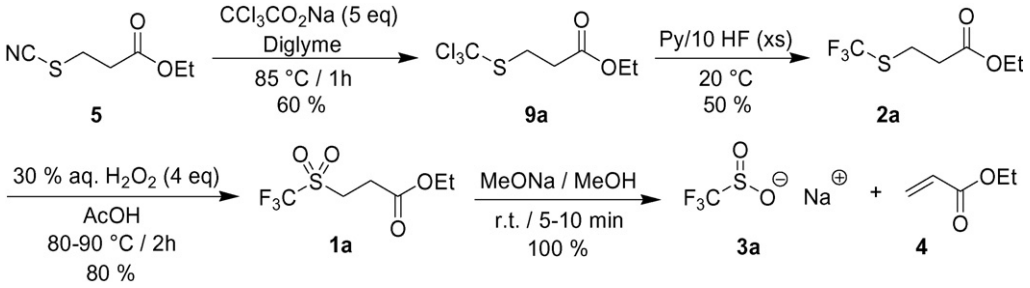
Compound **10** obviously results from the oxidation of benzyl trifluoromethyl sulfide **11**. This latter product can be efficiently synthesized from benzyl thiocyanate and (trifluoromethyl)trimethylsilane, as we previously published [9]. Alternatively, we based a cheaper strategy on an intermediate benzyl trichloromethyl sulfide **12**, which was easily prepared from benzyl thiocyanate **13**, chloroform and sodium hydroxide under phase transfer conditions (according to Makosza and Fedorynski [13]). Compound **12** was efficiently converted into **11** by



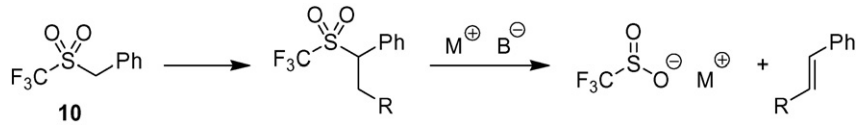
Scheme 2. Synthesis of sodium triflinate from **1a**.



Scheme 3. Synthesis of **2a** from thiosulfonate **7** and thioacetate **8**.



Scheme 4. Synthesis of sodium triflinate from thiocyanate **5**.



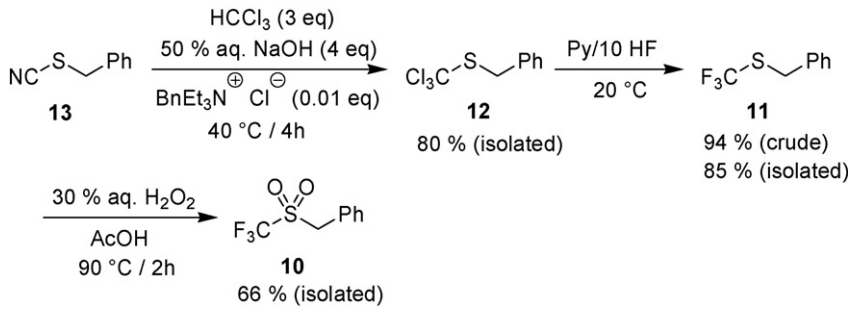
Scheme 5. Preparation of triflinates from benzyl trifluoromethyl sulfone **10**.

halogen exchange with Pyridine/10 HF (Olah's reagent), according to Saint-Jalmes [14] then **11** was oxidized by aqueous hydrogen peroxide into **10** [15] (Scheme 6).

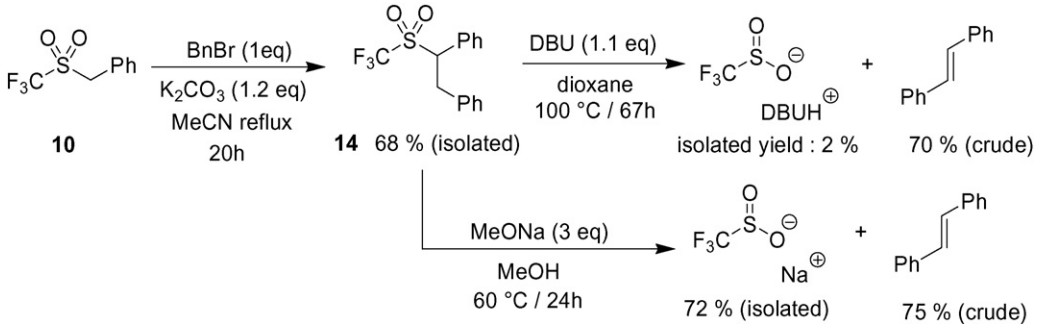
As expected, potassium triflinate could not be displaced from **10** by potassium thiocyanate. Thus, **10** was first alkylated with benzyl bromide to provide 1-triflyl-1,2-diphenylethane **14**, according to Hendrickson *et al.* [16]. When treated with 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU) at 100 °C, **14** was selectively but slowly converted (conversion = 70% after 72 h) into *trans*-stilbene and triflinate $CF_3SO_2^-$ DBU-H^+, which, however, was too soluble in organic solvents to be efficiently recovered. In contrast, treatment of **14** with sodium methoxide in methanol offered **3a** in a satisfactory yield but in a rather long time (Scheme 7).

The low velocity of the reaction could be explain by the fact that the hydrogen in α-position of the triflyl group is more acidic than those of the methylene group. Consequently, a proton shift was required before β-elimination but, as this migration was not favoured, heating was necessary to speed up the reaction.

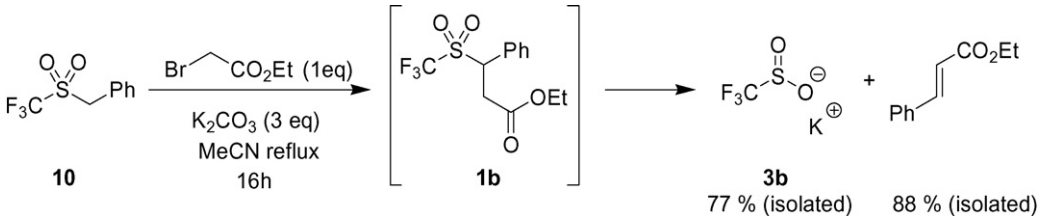
Thus, we turned to the alkylation of **10** with a reagent bearing more acidic hydrogens, that is ethyl bromoacetate **15**, under the conditions used to synthesize **14**, except that potassium carbonate was used in excess. Surprisingly, the



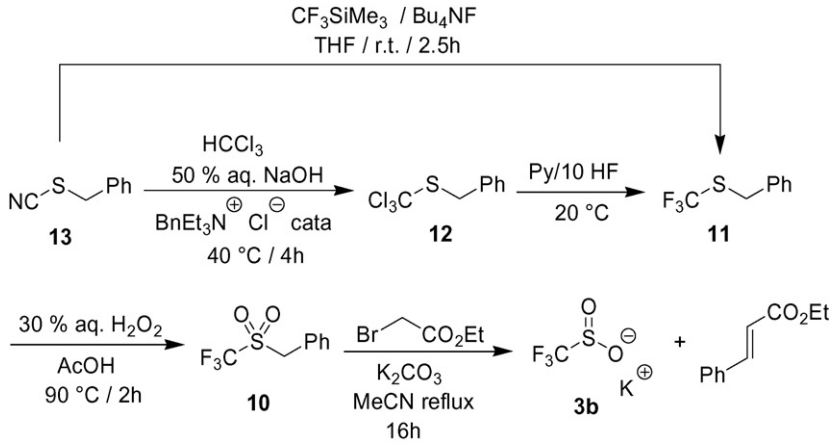
Scheme 6. Synthesis of benzyl triflone **10** from benzyl thiocyanate **13**.



Scheme 7. Synthesis of sodium triflinate from **14**.



Scheme 8. One pot formation of potassium triflinate from **1b**.



Scheme 9. Synthesis of potassium triflinate from benzy thiocyanate.

alkylated compound **1b** was not observed since K_2CO_3 was basic enough to promote β-elimination from **1b**, more rapidly than **1b** was formed, and deliver potassium triflinate **3b** in one pot with a high purity and a satisfactory yield which could be improved by optimizing the final solid–liquid extraction (Scheme 8).

This final approach to potassium triflinate involves a three step route (if using Ruppert-Prakash's reagent on the bench scale) or a four step route (if using chloroform on a larger scale) starting from benzyl thiocyanate **13** and transiting (optionally) by benzyl trichloromethyl sulfide **9a**, then benzyl trifluoromethyl sulfide **11** and benzyl trifluoromethyl sulfone **10** (Scheme 9). This method obviously allows the synthesis of various triflinates, depending on the base which is used. It is more interesting than the previous one since it is shorter and involves cheaper reagents and more efficient reactions. Its only drawback, compared to the former one, is that co-produced ethyl cinnamate cannot be reused for this purpose.

3. Conclusion

In conclusion, alkaline (or alkaline earth) trifluoromethanesulfinates can be obtained in four steps from thiocyanates, either ethyl 3-thiocyanatopropionate or benzyl thiocyanate. The latter starting substrate allows a easy and expedient route to trifinate whereas, from the former one, a more expensive but "greener" route is possible, since co-produced ethyl acrylate can be recycled. It can be also noticed that, for bench purposes, alkaline triflinate can be produced in a three step process from benzyl thiocyanate and (trifluoromethyl)trimethylsilane.

4. Experimental

Prior to use, THF and dioxane were distilled over sodium-benzophenone then stored over 3 Å molecular sieves under N_2. Other solvents were also distilled and stored over 3 Å molecular sieves under N_2. Other reagents were used as received. TLC analyses were carried out on silica gel (Kieselgel 60F 254) deposited on aluminum plates, detection being by UV (254 nm). Flash-chromatographies were performed on silica gel Geduran SI 60. Unless stated otherwise, NMR spectra were recorded in $CDCl_3$. ^1H NMR were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 50 or 75 MHz. The substitution pattern of the different carbons were determined by a "DEPT 135" sequence. ^{19}F NMR spectra were recorded at 188 MHz. Chemical shifts (δ) are given in ppm versus TMS (^1H, ^{13}C) or $CFCl_3$ (^{19}F) used as internal references. Coupling constants are given in hertz. Crude yields were determined by ^{19}F NMR versus $PhOCF_3$ ($\delta_F = -58.3$ ppm) used as standard. GC was carried out on an apparatus fitted with a semi-capillary column (length: 15 m, diameter: 0.53 mm, film thickness (DB1): 1 μm) and a catharometric detector. Mass spectrometry, coupled with gas chromatography, was carried out under electron impact at 70 eV.

Compounds **5** [17], **6** [2,11] and **12** [13] were prepared according to the literature. Trichloromethyl sulfides **9a** and **12** have been fluorinated with Olah's reagent at the Rhodia Co., according to the literature [14].

4.1. Synthesis of ethyl 3-(phenylsulfonylthio)propionate 7

Diethyl 3,3′-dithio-di(propionate) **6** (1.33 g, 5 mmol), dissolved in CH_2Cl_2 (5 mL), was mixed with sodium

benzenesulfinate (1.64 g, 10 mmol), dissolved in CH_2Cl_2 (5 mL). Then, a 1 M solution of bromine in CH_2Cl_2 was dropped under stirring within 45 min. After stirring for 6.5 h at room temperature, the reaction mixture was filtered, the filtrate was washed with water (20 mL) and the organic phase was dried over $MgSO_4$ then evaporated in vacuo. The crude residue was purified by column chromatography over silica gel (eluent: petroleum ether/diethyl ether 4:1) and 1.92 g (7 mmol, 70%) of **7** was isolated as a colorless oil. ^{1}H NMR (200 MHz): δ 8.0–7.6 (m, 5H), 4.1 (q, J = 7.1, 2H), 3.2 (t, J = 6.9, 2H), 2.7 (t, J = 6.9, 2H), 1.2 (t, J = 7.1, 3H). ^{13}C NMR (50 MHz): δ 170.9, 144.5, 133.9, 129.4, 126.9, 61.0, 34.0, 30.7, 14.0. MS: *m/z* 229 (4%, $M^{\bullet+}$–OEt), 157, 141, 133 (100%, $M^{\bullet+}$–$PhSO_2$), 77, 51, 45, 29.

4.2. Reaction of ethyl 3-(phenylsulfonylthio)propionate 7 with sodium trifluoroacetate

A solution of **7** (0.27 g, 1 mmol) in DMAc (8 mL) was added to CuI (0.39 g, 2 mmol) and sodium trifluoroacetate (0.56 g, 4.1 mmol). The resulting mixture was stirred at 160 °C for 4 h, then filtered. The filtrate was washed with water (10 mL) then extracted with diethyl ether (3 × 20 mL). The gathered organic phases were dried over $MgSO_4$ then evaporated under vacuo at room temperature. ^{19}F NMR analysis of the crude residue, with $PhOCF_3$ as internal standard, indicated the formation of **2a** in a 32% crude yield. ^{19}F NMR and ^{1}H NMR data for **2a** were identical with those already reported [2,11].

4.3. Reaction of ethyl 3-(phenylsulfonylthio)propionate 7 with sodium trichloroacetate

A solution of **7** (0.27 g, 1 mmol) in diglyme (2 mL) was added to sodium trichloroacetate (0.37 g, 2 mmol). The resulting mixture was stirred at 80–85 °C for 1 h, then filtered. The precipitate was washed with ether and this extract joined to the diglyme solution. The resulting mixture was extracted with water (10 × 10 mL) then dried over $MgSO_4$ and evaporated under vacuo at room temperature. GC analysis of the crude residue, with an internal standard, indicated the formation of **9a** in a 75% crude yield. ^{1}H NMR (200 MHz): δ 4.2 (q, J = 7.1, 2H), 3.4 (t, J = 7.0, 2H), 2.8 (t, J = 7.0, 2H), 1.3 (t, J = 7.1, 3H). ^{13}C NMR (50 MHz): δ 171.1, 97.9, 61.1, 33.0, 31.8, 14.2. MS: *m/z* 215 (6%, $M^{\bullet+}$–Cl), 133, 117, 87, 73, 45, 29 (100%, Et).

4.4. Reaction of ethyl 3-(thiocyanato)propionate 5 with sodium trichloroacetate

A solution of **5** (1 mmol) in diglyme (2 mL) was added to sodium trichloroacetate (5 mmol). The resulting mixture was stirred at 80–85 °C for 1 h, then filtered. The precipitate was washed with ether and this extract joined to the diglyme solution. Diethyl ether and a solution of K_2CO_3 were added to the resulting mixture which was then extracted with water (10 × 10 mL) then dried over $MgSO_4$ and evaporated under vacuo at room temperature. The aqueous solution was treated with aqueous sodium hypochlorite to oxidize cyanide ions. Chromatography of the crude residue over silica gel offered pure **9a** as an oil in a 60% yield.

4.5. Oxidation of ethyl 3-(trifluoromethylthio)propionate 2a into (trifluoromethanesulfonyl)propionate 1a

A 30% (w/w) aqueous solution of H_2O_2 (0.26 mL, 2.55 mmol) was dropped at room temperature onto a solution of **2a** (0.13 g, 0.64 mmol) in acetic acid (0.5 mL). The mixture was brought to 80–90 °C for 2 h then poured into water (5 mL) and extracted with diethyl ether (3 × 20 mL). The gathered organic phases were washed with 1N aqueous NaOH until pH 8, then with water until neutral, dried over $MgSO_4$ and concentrated under vacuo at room temperature. A colorless oil was recovered (0.12 g, 80%). ^{1}H NMR (200 MHz): δ 4.2 (q, J = 7.1, 2H), 3.6 (t, J = 7.5, 2H), 2.9 (t, J = 7.5, 2H), 1.3 (t, J = 7.1, 3H). ^{13}C NMR (50 MHz): δ 169.1, 119.5 (q, J = 327), 62.0, 45.4, 26.3, 14.1. ^{19}F NMR (188 MHz): δ −78.5 (s). MS: *m/z* 235 (1%, $M^{\bullet+}$+1), 189, 165, 101, 73, 69, 55 (100%), 45, 29.

4.6. Formation of sodium triflinate 3a from (trifluoromethanesulfonyl)propionate 1a

A solution of **1a** (0.21 g, 0.9 mmol) in methanol (6 mL) was treated at room temperature with sodium methoxide (0.05 g, 0.9 mmol). GC monitoring of the reaction indicated that it was complete after 5–10 min. Then, methanol was evaporated under vacuum at 40 °C and the pasty residue was dried in a dessicator over P_2O_5 and under vacuum. Sodium triflinate **3a** was obtained as a white solid (0.14 g) in a quantitative yield. ^{13}C NMR (50 MHz): δ 125.5 (q, J = 346). ^{19}F NMR (188 MHz): δ −87.9 (s).

4.7. Oxidation of benzyl trifluoromethyl sulfide 11 into benzyl trifluoromethyl sulfone 10

A 30% (w/w) aqueous solution of H_2O_2 (12.7 mL, 124.3 mmol) was dropped at room temperature onto a solution of **11** (59.6 g, 31.06 mmol) in acetic acid (23 mL). The mixture was brought to 90 °C for 2 h then poured into water (5 mL) and extracted with diethyl ether (3 × 100 mL). The gathered organic phases were washed with water (3 × 75 mL), saturated aqueous $NaHCO_3$ (2 × 75 mL) and water again (2 × 75 mL), then dried over $MgSO_4$ and concentrated under vacuum at room temperature. The resulting solid was recrystalyzed in CCl_4 (25–30 mL) to offer a white and pure product (4.60 g, 66%). ^{1}H NMR (200 MHz): δ 7.43 (m, 5H), 4.47 (s, 2H). ^{19}F NMR (188 MHz): δ −76.91 (s).

4.8. Synthesis of 14 from benzyl trifluoromethyl sulfone 10

K_2CO_3 (485 mg, 3.5 mmol) then benzyl bromide (0.365 mL, 3 mmol) were added to a solution of benzyl triflone **10** (673 mg, 3 mmol) in dry acetonitrile (12 mL). The mixture was brought to reflux (82 °C) for 20 h, then filtered, diluted with water and extracted with diethyl ether (2 × 25 mL). The gathered organic phases were washed with

water (2 × 20 mL) then saturated brine (20 mL). After drying over $MgSO_4$ and concentration under vacuum, a yellow oil was obtained. It was recrystalized in petroleum ether (3 mL) to provide a white solid (637–768 mg, 68–82%). ^{1}H NMR (200 MHz): δ 6.92–7.35 (m, 10H), 4.54 (dd, J = 3.2, J = 11.6, 1H), 3.77 (dd, J = 13.6, J = 11.6, 1H), 3.39 (dd, J = 13.6, J = 3.2, 1H). ^{19}F NMR (188 MHz): δ −73.80 (s).

*4.9. Formation of sodium triflinate **3a** from **14** and sodium methoxide*

A solution of **14** (760 mg, 2.42 mmol) in methanol (10 mL) was treated at room temperature with sodium methoxide (408 mg, 7.55 mmol). The mixture was stirred at 60 °C for 24 h then concentrated under vacuum and diluted with a mixture (45 mL) of diethyl ether and water (2:1). After decantation, the aqueous phase was extracted with CH_2Cl_2 (4 × 25 mL) and the gathered organic phases were washed with water (1 × 25 mL then 2 × 40 mL) and brine (40 mL). After drying over $MgSO_4$ and concentration under vacuum, the organic phase delivered a white solid (747 mg) which was found, by ^{1}H NMR, to be consituted of *trans*-stilbene (1.82 mmol, yield: 75%) and remaining **14** (0.58 mmol). All the gathered aqueous phases were acidified by 6N aqueous HCl until pH 5, then concentrated under vacuum. Sodium triflinate **3a** was obtained as a white solid (514 mg, 72%). Its spectral features were in accordance with the previous ones.

*4.10. Formation of potassium triflinate **3b** from benzyl triflone **10** and ethylbromoacetate*

Ethyl bromoacetate (300 μL, 2.65 mmol) was poured on a mixture of benzyl triflone **10** (559 mg, 2.5 mmol), K_2CO_3 (1043 mg, 7.55 mmol) and acetonitrile (10 mL). The reaction medium was stirred at 80 °C for 16 h. After cooling, it was diluted with water (30 mL) and diethyl ether (60 mL). After decantation, the aqueous phase was extracted with diethyl ether (40 mL) and the gathered organic phases were washed with water (4 × 40 mL). After drying over $MgSO_4$ and concentration under vacuum, an organic yellow liquid was obtained whose ^{1}H NMR spectrum was in accordance with that of ethyl cinnamate. ^{1}H NMR (200 MHz): δ 7.69 (d, J = 16, 1H), 7.35–7.53 (m, 5H), 6.43 (d, J = 16, 1H), 4.26 (q, J = 7, 2H), 1.33 (t, J = 7, 3H).

All the aqueous phases were gathered and neutralized with 0.1N aqueous HCl before being concentrated under vacuum at 65 °C. The remaining water was extracted by azeotropic distillation with toluene. A white solid (1.156 g) was obtained which was determined, by ^{19}F NMR, to contain potassium triflinate in a 68% yield. Extraction of this solid with ethyl acetate (8 × 10 mL) offered pure potassium triflinate **3b** (390 mg, 50%). ^{19}F NMR (188 MHz, H_2O): δ −87.4 (s).

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