USE OF CYCLIC α,β-UNSATURATED TRIFLUOROMETHYL SULFONES IN DIELS–ALDER REACTIONS AND MICHAEL ADDITIONS

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Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.

Vinylic trifluoromethyl triflones, in particular cyclic ones, constitute potentially valuable building-blocks for further syntheses. Their uses in Diels–Alder cycloadditions as dienophiles or dienes led only to moderate yields of expected products. However, under fluoride activation, they afforded unexpected tricycle compounds.

Keywords: α,β-Unsaturated trifluoromethyl sulfones; Vinyl triflones; Michael additions; Diels–Alder cycloaddition; Trifluoromethanesulfinate; Bicyclic compounds; Spirocyclic compounds.

Olefins substituted by electron-withdrawing moieties are very useful substrates for cycloadditions, in particular Diels–Alder reactions, and also for Michael additions. Thus, because of the strong inductive electron-withdrawing effect of the sulfonyl group, α,β-unsaturated sulfones have been previously used as dienophiles[1], particularly in combination with 2,3-dimethyl-1,3-butadiene[2] and Danishefsky's diene[3]. Nevertheless, very few Michael additions of unsaturated sulfones have been reported[4].

α,β-Unsaturated trifluoromethyl sulfones (triflones) should be of great interest in such reactions because of the high electronic withgrawing properties of trifluoromethylsulfonyl (triflyl) group. However, only few examples are available in the literature since, until recently, α,β-unsaturated triflones

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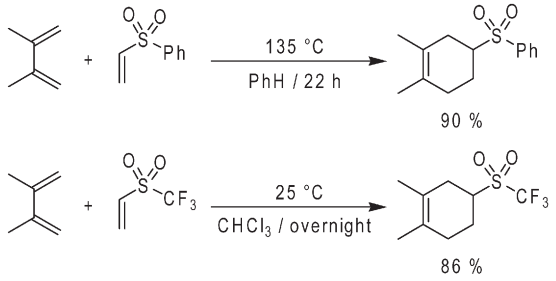
were not readily accessible. Thus, three examples of Diels–Alder cycloadditions, involving β-unsubstituted α,β-unsaturated triflones (vinyl triflone, α-phenylvinyl triflone and isopropenyl triflone), have been reported[2,5]. As expected, the trifluoromethylsulfonyl (triflyl) group strongly facilitates the reaction, compared with benzenesulfonyl[2], because of the much higher inductive electron-withdrawing effect of the former group[6] (σ_m = 0.79, σ_p = 0.93)[6b] (Scheme 1).

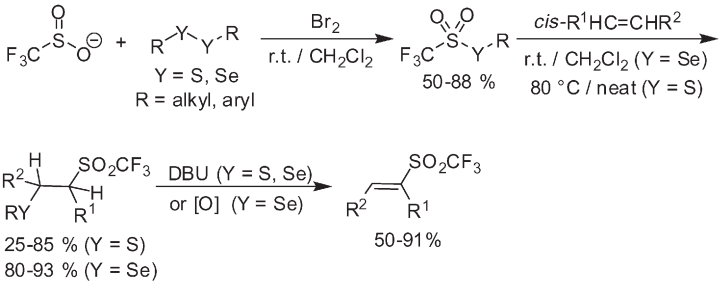


SCHEME 1
Cycloadditions with vinyl sulfones[2,5]

Concerning Michael additions, very few results have been published, again, with α,β-unsaturated trifluoromethyl sulfones, except the slow addition of piperidine and the non-chemoselective addition of diethyl malonate onto $PhCH_2CH{=}CHSO_2CF_3$[7]. Some years ago, it has been demonstrated that the fluorine atoms modify the energy level of the sulfonyl system to such an extent that it could stabilize an anion in α-position not only by an inductive effect but also by conjugation[4,6b]. Such results have been balanced by more recent work which suggested a dominant role of the strongly electron withdrawing effect of triflyl group to stabilize negative charge[6d]. Nevertheless, this two results let to anticipate that α,β-unsaturated trifluoromethyl sulfones could be suitable adducts for Michael additions.

Some years ago, we published an expedient two-step route to α,β-unsaturated trifluoromethyl sulfones from non-functionalized olefins and trifluoromethanethiosulfonates or trifluoromethaneselenosulfonates[8], the latter reagents being easily prepared in one step from sodium trifluoromethanesulfinate[9] (Scheme 2). This procedure was highly stereoselective for cyclic olefins and has been optimized for cyclopentene and cyclohexene. Moreover, when applied to 1,3-cyclohexadiene, it cleanly afforded 2-[(trifluoromethyl)sulfonyl]-1,3-cyclohexadiene[8]. This efficient synthesis of cy-

clic vinylic triflones led us to the study of their reactivity in Diels–Alder cycloadditions and Michael reactions.



SCHEME 2
Synthesis of α,β-unsaturated trifluoromethyl sulfones[8]

RESULTS AND DISCUSSION

Having an efficient method for the preparation of α,β-unsaturated trifluoromethyl sulfones in hand, we studied their applicability in Diels–Alder reactions and Michael additions. Preliminary results of our investigations with compounds **1**–**3** listed in Fig. 1 are presented below.

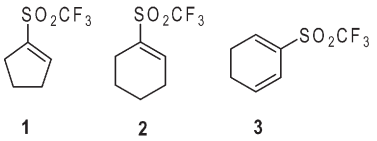
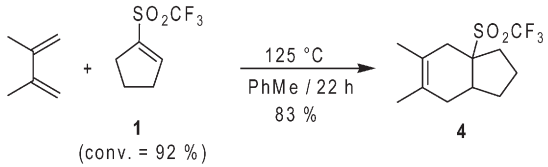


FIG. 1
Substrates used for Diels–Alder and Michael additions

In contrast to vinyl triflone itself, which reacts smoothly with 2,3-dimethylbutadiene at room temperature, **1** was unreactive towards the latter or Danishefsky's diene at room temperature for four days or at 60 °C for 72 h. Even at 110 °C in toluene for 28 h, no reaction was observed between **1** and Danishefsky's diene. The lack of reactivity under the conditions employed shows that, as far as cycloaddition is concerned, the reactivity of triflones is strongly sensitive to steric hindrance. Indeed, this observation is supported by previously published results: while vinyl triflone reacts efficiently with dimethylbutadiene at room temperature overnight, seven days are necessary for α-phenylvinyl triflone. Isopropenyl triflone must even be

reacted at 100 °C for ten days[2]. Accordingly, we were pleased to find that conducting the [4+2]-cycloaddition of **1** and dimethylbutadiene in toluene at 125 °C for 22 h resulted in the expected cycloadduct in good yield (Scheme 3).

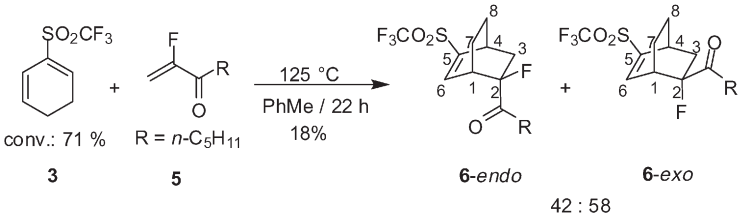


SCHEME 3
Cycloaddition between **1** and 2,3-dimethyl-1,3-butadiene

Besides being of interest itself, compound **4** should be also a potentially valuable intermediate since we can reasonably supposed that the trifluoromethylsulfonyl group could be substituted either by hydrogen, through reduction with sodium amalgam or other reducing agents[6c], or by nucleophiles because of the significant leaving ability of this moiety[5,6c,7,10,11]. This could allow for the synthesis of bicycles bearing a functionality on a quaternary carbon, which is generally a challenging task. Moreover, trifluoromethanesulfinic acid might be eliminated under basic conditions to afford a bis-unsaturated bicycle.

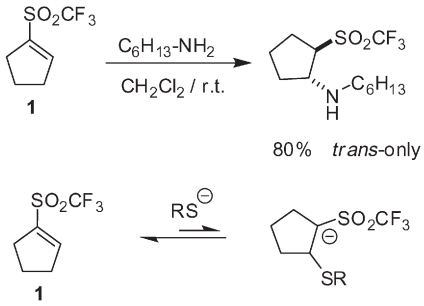
Having demonstrated the utility of vinyl triflones as dienophiles, now cyclohexadiene **3**, which is an electron-deficient diene due to the triflyl group, was proposed to be used as the diene component in a Diels–Alder cycloaddition with inverse electron demand. For this purpose, it was opposed to 2-fluorooct-1-en-3-one (**5**)[12]. This α-fluoro-α,β-unsaturated ketone was also used for Diels–Alder reactions with normal electron demand[13] and for the corresponding enantioselective reactions[14]. It is a captodative olefin, inductively deactivated by the carbonyl function and activated by conjugation with the unshared p-electrons of fluorine. Though proceeding with a high conversion of **3** (71%), this reaction provided only a modest isolated yield (18%) of adduct **6** as a mixture of two unseparable stereoisomers (*endo*/*exo* ratio 42:58), along with 12% of two unidentified compounds (as shown by GC of the crude mixture), which decomposed during work-up and purification. The structures of the two isolated stereoisomers were assigned mainly on the basis of the $^3J_{CF}$ coupling constants of C-6 to fluorine[15]. Observable coupling constants were found only in the *endo*-isomer because the (C-2)–F bond is in an *anti*-position towards the (C-1)–(C-6)

bond (Scheme 4). It should be noticed that the chemical shifts of the *exo*- (–139.6 ppm) and the *endo*-fluorine substituents (–155.6 ppm) differ by more than 15 ppm.



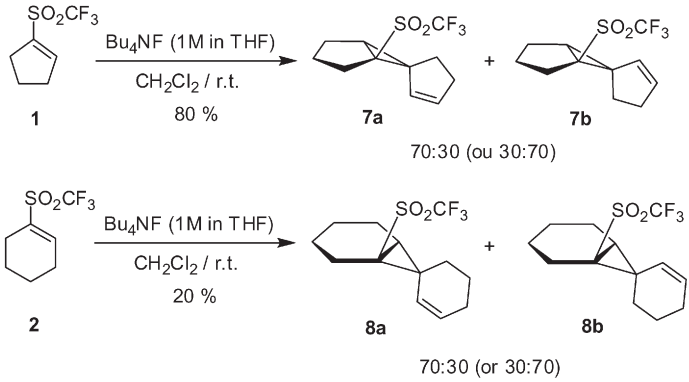
SCHEME 4
Reverse Diels–Alder cycloadditions of **3** and **5**

After cycloadditions, we examined selected Michael additions onto triflone **1**. In our previous article, we reported successful addition of *n*-hexylamine which occurred in a completely diastereoselective way and afforded the *trans*-adduct only[8]. The reaction succeeded due to the fact that a protic nucleophile was used so that the intermediate, bearing a stabilized negative charge in α position to the triflyl group, was protonated immediately after formation. However, when using a soft and charged nucleophile, such as thiolate, no addition occurred since the reverse elimination was probably as rapid (and maybe more rapid) than the expected addition. This point can be illustrated by the fact that thiolate elimination is the key step of the synthesis of vinylic triflones[9] (Scheme 5).



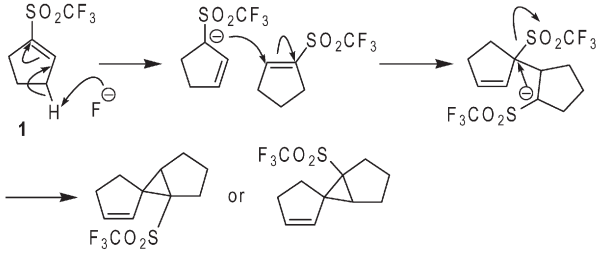
SCHEME 5
Conjugated addition of protic and aprotic nucleophiles onto **1** [9]

We expected that, the fluoride anion could form, after addition, a carbon–fluorine bond which would be strong enough to avoid elimination. Thus, we reacted **1** with tetrabutylammonium fluoride. Surprisingly, instead of the expected β-fluorotriflone, two unseparable diastereoisomers of tricycle **7** in a 70:30 ratio were obtained in a good yield. The same reaction occurred with cyclohex-1-en-1-yl triflone (**2**), but in a more modest yield, maybe because cyclohexene derivatives are conformationally more hindered than cyclopentene derivatives (Scheme 6).



SCHEME 6
Reaction of **1** and **2** with Bu_4NF

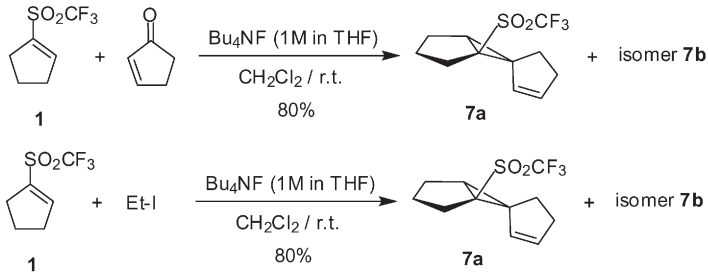
Owing to the facts that the triflyl moiety (i) is strongly electron-withdrawing, thus acidifiying the allylic hydrogens of **1**, (ii) is a good leaving group[5,6c,7,10,11], and (iii) the fluoride anion can behave as a strong base, and, for example, has been used to promote Michael additions of nitroalkanes[16], the following mechanism is proposed (Scheme 7).



SCHEME 7
Possible mechanism of formation of tricycle **7**

In the first step, fluoride could deprotonate **1** and thus provide an allylic anion in α-position of triflyl substituent, which enhances its stability. This stabilized soft anion subsequently undergoes an 1,4-addition onto another molecule of **1**. Finally, the resulting anion, which is also stabilized by a triflyl group, could displace the first triflyl moiety to form a strained spiro-tricyclic system.

In order to get some insight into this mechanism, **1** was reacted with tetrabutylammonium fluoride in the presence of other electrophiles such as cyclopent-2-en-1-one or ethyl iodide. However, no cross-coupling was observed (Scheme 8), suggesting that **1** is a better Michael acceptor than cyclopent-2-en-1-one and a better electrophile than ethyl iodide.



SCHEME 8
Attempted cross-coupling of **1**

In conclusion, the easy-to-synthesize cyclic α,β-unsaturated triflones behave as valuable substrates for Diels–Alder cycloadditions and, in particular, as very good Michael acceptors. Moreover, due to their propensity to undergo Michael additions combined with the acidifying properties of the triflyl moiety, cyclic α,β-unsaturated triflones can be transformed on fluoride activation into strained spiro tricycles in an unprecedented one-step reaction. The ensuing products should prove useful as scaffolds for more valuable synthetic targets.

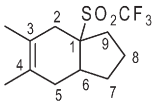
EXPERIMENTAL

All solvents were stored over 3 Å molecular sieves prior to use. Other reagents were used as received. TLC analyses were carried out on Kieselgel 60F 254 coated on aluminum plates, UV detection (254 nm). Flash chromatography was performed on silica gel Geduran SI 60 or silica gel 60 (Merck) (230–400 mesh). Unless stated otherwise, NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 50 or 75 MHz, on a Bruker Avance apparatus. The substitution patterns of the different carbons

were determined by a DEPT 135 sequence. To assign the stereochemistry, the results of TOCSY and NOE experiments were used. ^{19}F NMR spectra were recorded at 188 MHz. Chemical shifts (δ) are given in ppm vs TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F) as internal references. Coupling constants (*J*) are given in Hz. Crude yields were determined by ^{19}F NMR vs $PhOCF_3$ used as a standard. Gas chromatography (GC) was carried out on an apparatus fitted with a semi capillary column (length 15 m, Ø 0.53 mm; film thickness (DB1) 1 μm) and a catharometric or a FID detector. Mass spectrometry, coupled with GC, was carrried out under electron impact at 70 eV or chemical ionization with ammonia.

trans-1-(Hexylamino)-2-[(trifluoromethyl)sulfonyl]cyclopentane has been described in ref.[8]

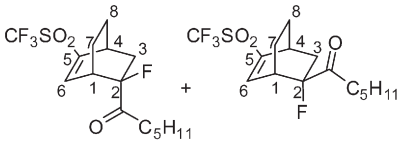
3,4-Dimethyl-1-[(trifluoromethyl)sulfonyl]bicyclo[4.3.0]non-3-ene (**4**)



4

A solution of 1-[(trifluoromethyl)sulfonyl]cyclopent-1-ene (**1**) (208 mg, 4.2 mmol) and 2,3-dimethylbutadiene (343 mg, 4.2 mmol) in toluene (1 ml) was stirred at 125 °C in a glass tube fitted with a Young-tap for 21.5 h. After cooling down to room temperature, GC analysis of the crude product indicated a 92% conversion of the dienophile. Toluene was removed and 3,4-dimethyl-1-[(trifluoromethyl)sulfonyl)]bicyclo[4.3.0]non-3-ene (**4**) was purified by column chromatography using a cyclohexane/ethyl acetate (20:1) mixture as eluent. Yield 244 mg (83%, oil), purity 93% (GC: 5% of **1**, 2% of an unknown impurity). ^{1}H NMR: 1.30–1.42 (m, 1 H); 1.71 (2 s, 6 H); 1.55–2.05 (m, 5 H); 2.17 (d, $^{2}J_{HH}$ = 15.9, 1 H); 2.29 (dm, $^{3}J_{HH}$ = 15.3, 1 H); 2.50 (m, 1 H); 2.62 (d, $^{2}J_{HH}$ = 15.9, 1 H); 2.97 (m, 1 H). ^{13}C NMR: 19.3, 19.7, 23.5, 32.2, 33.7, 34.8, 36.3, 39.6, 73.6, 120.8 (q, $^{1}J_{CF}$ = 331.36, CF_3); 121.9, 127.4. ^{19}F NMR: –71.1 (s). GC-MS (70 eV), *m/z* (%): 282 (4) [M^+], 149 (34) [$M^+ - SO_2CF_3$], 148 (100), 133 (65), 120 (29), 119 (62), 107 (25), 105 (49), 93 (24), 91 (30), 81 (10), 79 (20), 77 (15), 69 (9) [CF_3], 67 (15), 65 (10), 55 (13), 41 (22), 39 (10).

1-{2-Fluoro-5-[(trifluoromethyl)sulfonyl]bicyclo[2.2.2]oct-5-en-2-yl}hexan-1-one (**6**)



6-*endo* **6**-*exo*

42 : 58

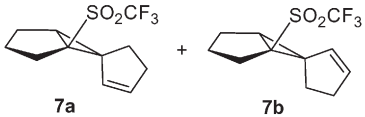
A solution of 2-[(trifluoromethyl)sulfonyl]cyclohexa-1,3-diene (**3**) (220 mg, 1.04 mmol) and 2-fluorooct-1-en-3-one (**5**) (432 mg, 3 mmol) in toluene (1 ml) was stirred at 125 °C in a glass tube fitted with a Young-tap. After 1 min, fumes evolved which lasted for a few minutes. After 21.5 h, the reaction mixture was cooled down to room temperature. The GC

analysis indicated a 71% conversion of **3**. The title compound **6** was obtained in an *exo*/*endo* ratio of 58:42 (GC). Two unidentified products (12%) were also detected by GC in the crude mixture but they mostly decomposed during work-up and column chromatography (cyclohexane/ethyl acetate 20:1). As the reaction mixture could not be sufficiently separated, preparative HPLC (Nucleosil 50-7, cyclohexane/$CHCl_3$ 10:1) was applied and afforded an oily mixture of the two isomers of **6**. Yield 65 mg (18%), 25% with respect to 71% conversion of **3**. For $C_{15}H_{20}SO_3F_4$ (356.4) calculated: 50.55% C, 5.66% H; found: 50.84% C, 5.96% H. Exact mass: calculated 379.0967 for $C_{15}H_{20}SO_3F_4 + Na^+$, found 379.0949. IR (film, NaCl), ν (cm^{-1}): 3429, 3085, 2963, 2933, 2875, 1729, 1605, 1467, 1367, 1219, 1190, 1130, 1067, 1047, 1027, 930, 765, 727, 720.

6-*endo*: ^{1}H NMR: 0.89 (t, $^3J_{HH}$ = 6.7, 3 H); 1.18–1.42 (m, 6 H); 1.50–1.76 (m, 2 H); 1.78–2.00 (m, 3 H); 2.24 (pseudo ddt, J_{HH} = 12.9, 9.5, 3.1, 1 H); 2.47–2.78 (m, 2 H); 3.22 (dm, $^3J_{HH}$ = 7.1, 1 H); 3.38–3.41 (m, 1 H); 7.69 (ddd, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 3.9, $^4J_{HH}$ = 1.9, 1 H). ^{13}C NMR: 13.9, 18.2, 22.4, 22.7, 23.2, 31.2, 31.7, 37.2, 38.9 (t, $^2J_{CF}$ = 25.4); 39.9 (d, $^2J_{CF}$ = 21.7) [or 40.0 (d, $^2J_{CF}$ = 24.9)]; 101.0 (d, $^1J_{CF}$ = 190.9); 119.8 (q, $^1J_{CF}$ = 352.6); 137.0, 154.0 (d, $^3J_{CF}$ = 7.7); 208.3 (d, $^2J_{CF}$ = 31.3) [or 208.5 (d, $^2J_{CF}$ = 30.6)]. ^{19}F NMR: –78.8 (s, 3 F); –155.6 (dd pseudo quint., $^3J_{HF}$ = 32.1, $^3J_{HF}$ = 22.8, $^3J_{HF}$ = $^4J_{HF}$ = $^4J_{HF}$ = $^4J_{HF}$ = 4.6, 1 F). GC-MS (70 eV), *m/z* (%): 358 (0.3), 356 (0.4) [M^+], 336 (0.3), 299 (0.3), 287 (1.5), 271 (0.2), 145 (1), 143 (1), 99 (100), 71 (41), 43 (44). GC-MS-CI (NH_3), *m/z* (%): 374 (100) [M + NH_4^+], 354 (10), 335 (14), 240 (20), 223 (16), 205 (16), 203 (14), 175 (8).

6-*exo*: ^{1}H NMR: 0.91 (t, $^3J_{HH}$ = 6.9, 3 H); 1.18–1.42 (m, 5 H); 1.50–1.76 (m, 6 H); 2.40 (ddd, $^3J_{HF}$ = 18.6, $^2J_{HH}$ = 14.3, $^3J_{HH}$ = 2.3, 1 H); 2.47–2.78 (m, 2 H); 3.36 (dt, $^3J_{HH}$ = 6.6, $^3J_{HH}$ = 3.0, 1 H); 3.41–3.44 (m, 1 H); 7.65 (dd, $^3J_{HH}$ = 6.6, $^4J_{HH}$ = 1.8, 1 H). ^{13}C NMR: 13.9, 18.3, 22.4, 22.7, 23.2, 31.2, 31.9, 37.2, 38.1 (t, $^2J_{CF}$ = 22.9); 39.9 (d, $^2J_{CF}$ = 21.7) [or 40.0 (d, $^2J_{CF}$ = 24.9)]; 101.0 (d, $^1J_{CF}$ = 190.9); 119.8 (q, $^1J_{CF}$ = 325.6); 139.4, 152.7, 208.3 (d, $^2J_{CF}$ = 31.3) [or 208.5 (d, $^2J_{CF}$ = 30.6)]. ^{19}F NMR: –78.9 (s, 3 F); –139.6 (dd, $^3J_{HF}$ = 32.8, $^3J_{HF}$ = 18.6, 1 F). GC-MS (70 eV), *m/z* (%): 358 (0.2), 356 (0.3) [M^+], 336 (0.3), 307 (0.2), 287 (1), 144 (9), 99 (100), 71 (57), 43 (81). GC-MS-CI (NH_3), *m/z* (%): 374 (100) [M + NH_4^+], 354 (58), 337 (4), 335 (4), 332 (4), 324 (8), 238 (7), 207 (12), 205 (25), 203 (9), 177 (10), 175 (9).

1-[(Trifluoromethyl)sulfonyl]spiro(bicyclo[3.1.0]hexane-6,1′-cyclopent-2-ene) **7a** and **7b**



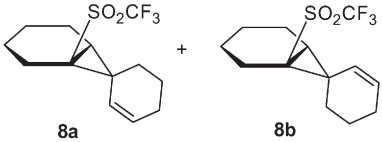
7a **7b**

70:30 (or 30:70)

A solution (6 ml) of 1 M tetrabutylammonium fluoride (6 mmol) in THF was added to a solution of **1** (1.6 g, 6 mmol) in dichloromethane (5 ml). The mixture was stirred at room temperature for 2 h. After evaporation of the solvents, the crude product was purified by column chromatography. A mixture of **7a** and **7b** was obtained as a yellow oil (1.28 g, 80%). For $C_{11}H_{13}F_3O_2S_2$ (266.3) calculated: 49.62% C, 4.92% H, 12.04% S; found: 49.48% C, 4.95% H, 12.21% S.

^{1}H NMR. Major diastereomer: 6.15 (dt, $^3J_{HH}$ = 5.9, $^3J_{HH}$ = 2.3, 1 H); 5.80 (dt, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 2.0, 1 H); 1.5–2.7 (m, 11 H). Minor diastereomer: 5.86 (dt, $^3J_{HH}$ = 5.7, $^3J_{HH}$ = 2.3, 1 H); 5.80 (dt, $^3J_{HH}$ = 5.7, $^4J_{HH}$ = 2.0, 1 H); 1.5–2.7 (m, 11 H). ^{13}C NMR. Major diastereomer: 138.16, 126.64, 119.79 (q, $^1J_{CF}$ = 327.2); 53.89, 49.66, 40.86, 31.38, 28.46, 28.11, 25.99, 24.98. Minor diastereomer: 132.43, 130.66, 119.69 (q, $^1J_{CF}$ = 327.5); 52.15, 48.32, 37.83, 31.25, 30.82, 28.16, 25.87, 24.25. ^{19}F NMR. Major diastereomer: –77.75 (s). Minor diastereomer: –77.52 (s). GC-MS, *m/z* (%). Major diastereomer: 133 (54) [CF_3SO_2] or [M^+ – CF_3SO_2], 105 (30), 91 (100), 79 (17), 77 (16), 67 (26), 55 (13), 41 (31), 39 (32), 27 (10). Minor diastereomer: 133 (57), [CF_3SO_2] or [M^+ – CF_3SO_2], 105 (29), 91 (100), 79 (18), 77 (15), 67 (24), 55 (11), 41 (28), 39 (28), 27 (10).

1-[(Trifluoromethyl)sulfonyl]spiro(bicyclo[4.1.0]heptane-7,1′-cyclohex-2-ene) **8a** and **8b**



70:30 (or 30:70)

The same procedure as above for **1** was carried out, but starting from **2** (1.76 g, 6 mmol) to obtain **8a** and **8b** (0.35 g, 20%).

^{1}H NMR. Major diastereomer: 6.08 (dt, $^3J_{HH}$ = 10.5, $^3J_{HH}$ = 3.6, 1 H); 5.44 (m, 1 H); 2.8–0.8 (m, 15 H). Minor diastereomer: 5.83 (dt, $^3J_{HH}$ = 10.15, $^3J_{HH}$ = 3.3, 1 H); 5.72 (m, 1 H); 2.8–0.8 (m, 15 H). ^{13}C NMR. Major diastereomer: 134.65, 123.40, 120.24 (q, $^1J_{CF}$ = 329.4); 47.74, 37.04, 27.90, 25.39, 22.14, 21.13, 20.96, 20.13, 18.67, 17.60. Minor diastereomer: 130.05, 128.56, 123.33 (q, $^1J_{CF}$ = 329.4); 45.72, 35.76, 27.37, 24.93, 24.79, 21.90, 20.91, 20.17, 20.06, 18.49. ^{19}F NMR. Major diastereomer: –74.91 (s). Minor diastereomer: –74.31 (s). GC-MS, *m/z* (%). Major diastereomer: 161 (94) [M^+ – CF_3SO_2], 133 (6), 105 (24), 91 (100), 81 (100), 79 (95), 77 (51), 67 (62), 55 (25), 41 (85), 39 (56), 27 (30). Minor diastereomer: 161 (72) [M^+ – CF_3SO_2], 133 (4), 105 (21), 91 (91), 81 (100), 79 (93), 77 (51), 67 (63), 55 (25), 41 (91), 39 (57), 27 (32).

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