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The general approach for the synthesis of substituted cyclobutenyl- and norbornadienyllithiums containing masked trifluoromethyl group

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ABSTRACT

α,β-Unsaturated trifluoromethylketones of cyclobutene number containing trimethylstannyl substituent in β-position were firstly prepared by the addition of trimethylstannyllithium to the corresponding trifluoromethylenaminoketones. The protection of carbonyl function under basic conditions conserving the organometallic substituent was elaborated. The generation of corresponding organolithiums by Sn–Li exchange and their reactivity was studied.

1. Introduction

The chemistry of α,β-unsaturated trifluoromethylketones, especially containing leaving groups in the β-position is a fascinating and quickly developing field of organic chemistry. This relative new class of extremely reactive compounds is a very valuable source for the different types of functionalization and heterocyclization reactions frequently giving the important biologically active compounds with a wide range of action. Owing to this reason the exhaustive and very interesting reports, and monographs dealing with α-fluorinated ketones regularly appear during two last decades.[1–5]

An important feature of all α,β-unsaturated trifluoromethylketones is the highly electrophilic character of the β-carbon atom of C=C bond, which is a driving force for the majority of their transformations.

An alternative potential approach to the novel fluorine containing building blocks is an umpolung strategy to convert the electrophilic center of the C=C bond to a strongly nucleophilic one with preliminary protection of the carbonyl function. Although alkenyllithums with a protected carbonyl group are widely used synthetic intermediates,[6–10] to the best of our knowledge their trifluoromethylated analogs stayed unknown until now. Recently we developed unusual [2+2]-cycloaddition reactions of 1-trifluoroacetyl-2-halogenoacetylenes with simple alkenes to afford substituted 1-trifluoroacetyl-2-halogeno-cyclobutenes,[11] which appeared to be versatile tools for further transformations including the nucleophilic substitution of halogen atoms.[12,13] The addition of organolithiums and Grignard reagents to the available pyrrolidine derivatives **1a–d** (Fig. 1) is a simple route for their β-functionalization.[12]

Herein we report the generation of novel β-alkenyl organolithiums with protected trifluoroacetyl group using enaminoketones **1a–f** as the starting compounds.

2. Results and discussion

2.1. The synthesis of β-trimethylstannyl-α,β-unsaturated trifluoromethylketones

Although trialkylstannyllithiums, sodiums, and magnesiums are reactive and frequently used nucleophiles,[14] they have never been exploited in the reactions with conjugated enaminoketones. Recently we have described a simple and preparative synthesis of hexamethyldistannan from trimethylstannylchloride on a large scale employing Li in THF as a coupling reagent. This method seemed to us more convenient and gave in our hands better results

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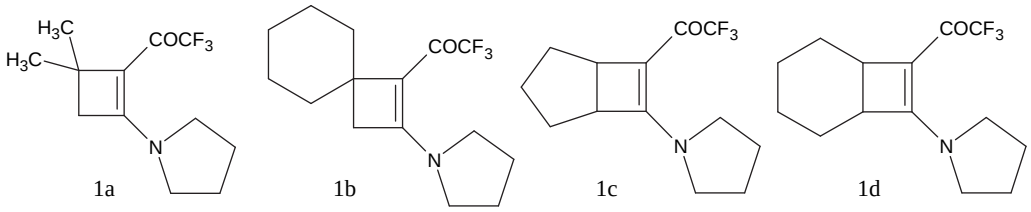
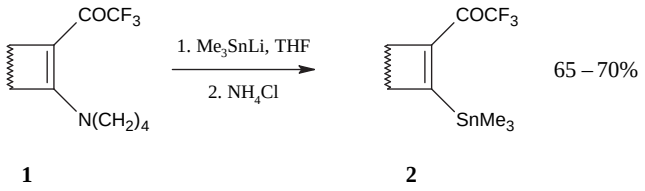


Fig. 1. The starting enaminoketones.

than traditionally used system Na in NH_3. The generation of trimethylstannyllithium from hexamethyldistannan was also carried out using Li in THF at ambient temperature.

It was shown that trimethylstannyllithium easily reacts with enaminoketones **1** to give β-trimethylstannyl-α,β-unsaturated trifluoromethylketones **2** in good yields after subsequent quench with NH_4Cl (Scheme 1). Interestingly, elimination of the protonated pyrrolidine moiety from the intermediate formed upon acidification does not require the presence of strong acid and forcing thermal conditions, and it allows the conservation of the trimethylstannyl substituent. The compounds obtained can be distilled under vacuum and exhibit moderate sensitivity to air although the short contact is not critical.



Scheme 1.

Using this method the following β-trimethylstannyl-α,β-unsaturated trifluoromethylketones **2a**–**d** were prepared (Fig. 2).

Previously in a short preliminary communication we reported that 1-trifluoroacetyl-2-trimethylstannylacetylene is an active dienophile and easily reacts with 1,3-cyclopentadiene, and 1,3-cyclohexadiene to furnish the corresponding cycloadducts **2e**,**f**.[15] Herein, for the further investigations these compounds were prepared according to slightly modified procedures (Scheme 2).

2.2. Protection of carbonyl group in trifluoromethylketones 2a–f

Initially we expected that compounds **2a**–**f** should be useful substrates in Stille cross-coupling and acylation reactions, however, even thorough variation of reagents, catalysts, and conditions gave only poor yields of coupled products, probably owing to the powerful deactivating mesomeric effect of trifluoroacetyl group. In order to realize an alternative approach we attempted to protect carbonyl function followed by the generation of organolithiums via of Sn–Li exchange. Our first endeavors to transform ketones **2** to the corresponding dimethylhydrazones or dioxolanes proved to be entirely unsuccessful since an acid, necessary as a catalyst rapidly affected Sn–C bond cleavage. Another carbonyl protection methodology including the addition of lithium dialkylamides to the carbonyl group[16] also failed. Eventually we found a very simple and preparative carbonyl protection procedure that proceeds at ambient temperature under weak basic conditions and retains the trimethylstannyl substituent. The addition of diisopropylamine to solutions of ketone **2** in chloroethanol results in an exothermic reaction and the formation of corresponding dioxolanes **3** in good

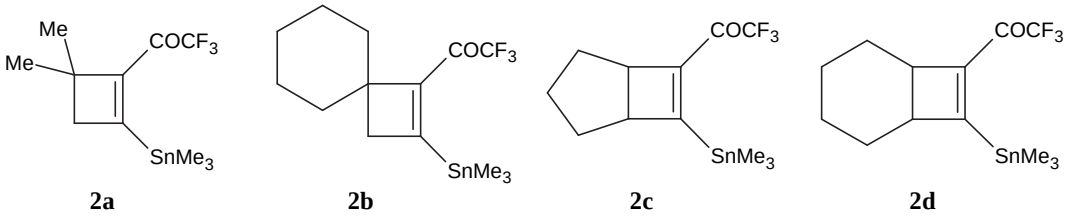
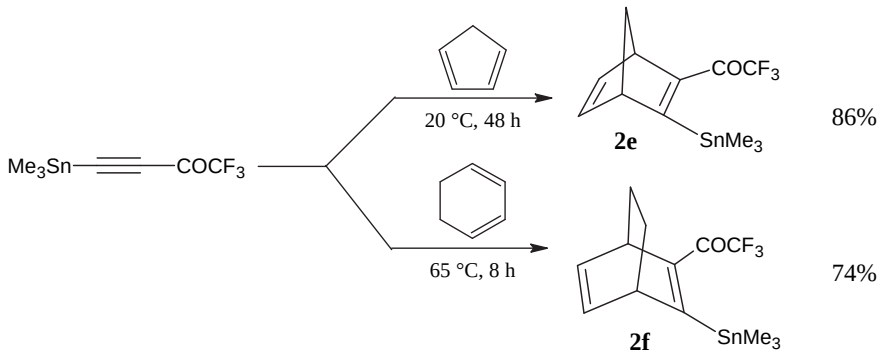
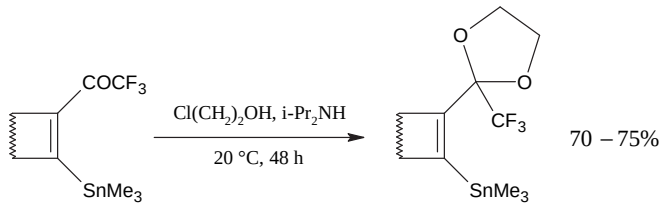


Fig. 2. The target β-trimethylstannyl-α,β-unsaturated trifluoromethylketones.



Scheme 2.

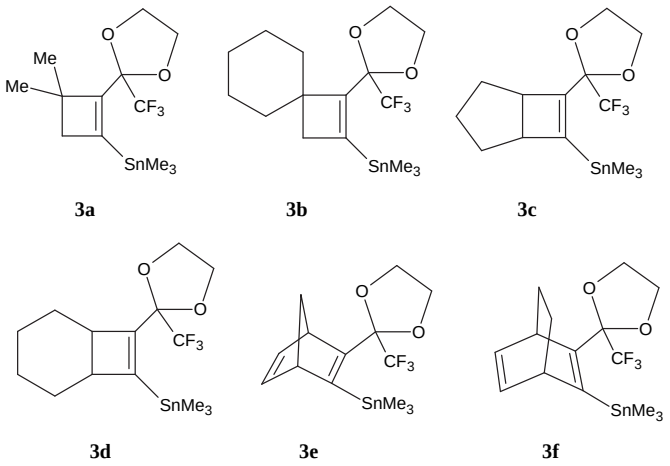
yields (Scheme 3). An elaborated protocol is possibly applicable for the various enolizable and non-enolizable ketones, and aldehydes having an activated carbonyl groups and different functions incompatible with acids. It is interesting to note that combination of chloroethanol with K_2CO_3 in DMF[17] gave lower yields, whereas chloroethanol with *t*-BuOK in DMF[18] afforded only traces of products.



2 **3**

Scheme 3.

Using this method the following dioxolanes **3a**–**f** were prepared (Fig. 3).



3a **3b** **3c**

3d **3e** **3f**

Fig. 3. The target trifluoromethyl dioxolanes.

Commencing the study of dioxolanes **3a**–**f** as a source of new organolithiums **4** we expected that MeLi in ether should be the best reagent for destannylation since the tetramethylstannan formed in parallel with organolithiums can be easily evaporated together with a solvent at work up stage. However, for reasons that are unclear, the completion of destannylation requires about 50% excess of MeLi, which can interfere in the further reactions with electrophiles. An employment of the more basic *n*-BuLi does not require a considerable excess of reagent and the lithiation smoothly proceeds even at −70 °C. The completion of lithiation was determined by the disappearance of the starting stannylated dioxolanes **3** in TLC. We have not closely studied the thermal stability of organolithiums **4**, but their acidification and reactions with chlorotrimethylsilan gave the corresponding products in nearly 90% yields, being performed even at −30 °C.

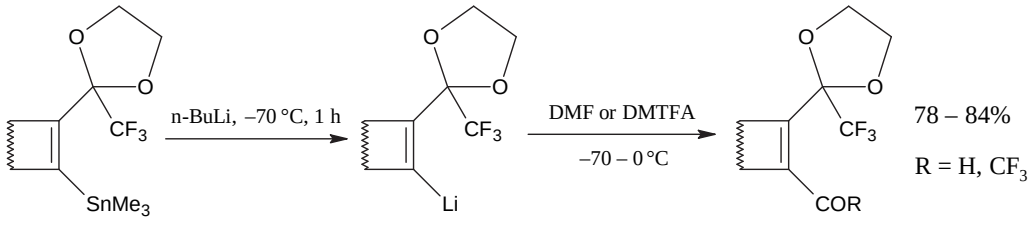
The organolithiums **4** were then subsequently functionalized with DMF to afford the corresponding unsaturated aldehydes **5** in good yields (Scheme 4). In order to extend the range of electrophiles we also studied the interaction of organolithiums **4** generated from **3a** and **3c** with dimethyltrifluoroacetamide (DMTFA). It was found that this addition proceeds much more faster than with DMF however after work up procedure very interesting and reactive ketones **6a**,**b** are formed in a mixture with their hydrates. The latter have been dehydrated by trifluoroacetic anhydride.

Using this method the following aldehydes **5a**–**f** and trifluoromethylketones **6a**,**b** were prepared (Fig. 4).

The choice of DMF and DMTFA as electrophiles allowed us to estimate the reactivity of organolithiums **4**, furthermore, highly functionalyzated compounds **5**,**6** bearing the unsaturated aldehyde or trifluoromethylketone fragments and the masked trifluoroacetyl group, should be potentially useful reagents in a variety of transformations. They proved to be relatively stable compounds and can be purified even by distillation under high vacuum. A probable limitation of their further employment consents the necessity of using an extremely strong Lewis or Bronsted acids for the deprotection of the carbonyl group adjacent to so strong inductive acceptor as trifluoromethyl substituent.[1] We are currently studying a specific mild acidolysis of dioxolanes **5** with anhydrous formic acid via a preliminary conversion of free aldehydes **5a**,**b** to the corresponding dimethylhydrazones **7a**,**b** (obtained in almost quantitative yields). As a preliminary report, two selected examples of this transformation are shown (Scheme 5). The dimethylhydrazono group itself does not undergo acidolysis at these conditions. The resulting ketohydrazones **8a**,**b** (Scheme 5) were purified by column chromatography.

3. Conclusion

In conclusion, β-trimethylstannyl-α,β-unsaturated trifluoromethylketones prepared in high yields by the addition of trimethylstannyllithium to the corresponding enaminoketones. They proved to be relatively stable compounds, even distillable under vacuum. The simple and effective method for protection of their carbonyl function in mild basic conditions conserving trimethylstannyl substituent was also proposed. It was subsequently discovered that the resulting dioxolanes are convenient sources of the corresponding organolithiums, that react with DMF and DMTFA to afford unsaturated aldehydes and trifluoromethylketones of cyclobutene and norbornadiene (also containing the masked trifluoroacetyl group). Their polyfunctional structure makes them potentially useful reagents in organic synthesis.



3 **4** **5, 6**

Scheme 4.

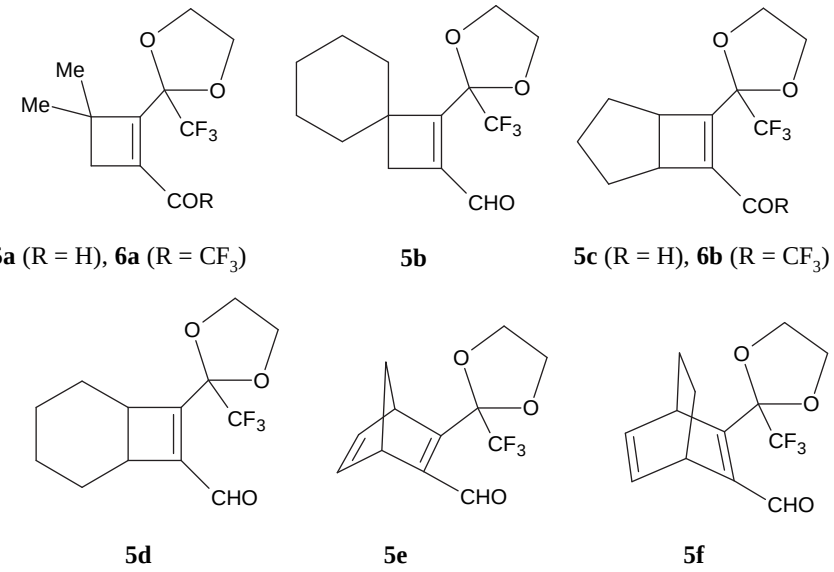
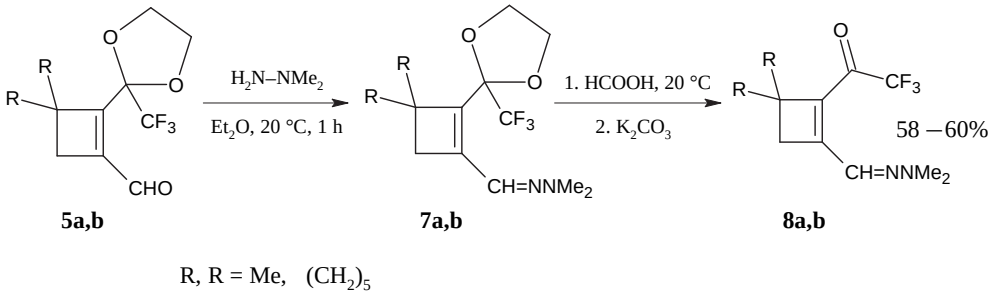


Fig. 4. The target α,β-unsaturated aldehydes and trifluoromethylketones.



Scheme 5.

4. Experimental

4.1. General

Enaminoketones **1** have been prepared according to described procedure.[12] Diisopropylamine and chloroethanol were distilled prior to use. Manipulations with organolithiums and organotins were carried out under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 'Bruker AMX 400' spectrometer at 400 and 100 MHz, respectively, chemical shifts are reported in parts per million relative to 0 for TMS. IR spectra were recorded on 'Bruker IFS 25' spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

4.2. Preparation of hexamethyldistannan in THF

To a stirred suspension of small thin strips of lithium (2.29 g, 0.33 mol) in THF (300 mL) at 25 °C a solution of Me_3SnCl (59.8 g, 0.3 mol) in THF (70 mL) was added dropwise. An exothermic reaction started after several minutes and then the addition was performed in such a rate to maintain the internal temperature around 30 °C. The strips of lithium completely disappeared in 2 h of stirring after which the reaction mixture was stirred for a further 2 h. The majority of the THF was distilled off under vacuum and the residue was diluted with hexane. The resulting mixture was stirred for 15 min, the resulting precipitate of LiCl was filtered off and after evaporation of hexane the residue was distilled under vacuum to afford 45.2 g (92%) of hexamethyldistannan as colorless liquid, bp 75 °C (15 Torr), lit.[19] bp 73 °C (12 Torr).

4.3. General procedure for preparation of β-trimethylstannyl-α,β-unsaturated trifluoromethylketones 2a–d

To a stirred suspension of small thin strips of lithium (0.04 g, 5.7 mmol) in THF (10 mL) containing 0.05 g (0.4 mmol) of naphthalene, hexamethyldistannan (0.82 g, 2.5 mmol) was added in one portion, and the reaction mixture was stirred at 25 °C until dissolution of lithium was completed (5–6 h). The resulting solution of organolithium was cooled to −70 °C and a solution of enaminoketones **1a–d** (5 mmol) in THF (5 mL) was added dropwise. The resulting mixture was allowed to warm to 0 °C (30–40 min) and then was quickly poured into vigorously stirred saturated solution of NH_4Cl (15 mL). After the additional 5 min of vigorous stirring the organic layer was separated, the aqueous phase was extracted with ether (3×10 mL), the combined organic solution was dried over Na_2SO_4, and the solvent was removed under vacuum. The residue was diluted with hexane (15 mL) and kept at 10 °C for 1 h. The insoluble material was filtered off and after solvent evaporation the residue was distilled under high vacuum.

*4.3.1. 1-[4,4-Dimethyl-2-(trimethylstannyl)cyclobut-1-en-1-yl]-2,2,2-trifluoroethanone (**2a**).* From (**1a**). Colorless liquid, bp 60–61 °C (1 Torr); yield 1.18 g (69%); Found: C, 38.9; H, 5.0; F, 16.5; Sn, 34.7. $C_{11}H_{17}F_3OSn$ requires: C, 38.8; H, 5.0; F, 16.7; Sn, 34.8%; IR

(neat) 3004, 2995, 1700, 1605, 1245, 1175 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.74 (2H, s, CH_2–C=C), 1.42 (6H, s, $(CH_3)_2C$), 0.22 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 178.0 (q, *J* 38 Hz), 172.7, 146.6, 116.9 (q, *J* 290 Hz), 44.1, 41.7, 28.0, −8.6.

*4.3.2. 2,2,2-Trifluoro-1-[2-(trimethylstannyl)spiro[3.5]non-1-en-1-yl]ethanone (**2b**).* From (**1b**). Yellowish liquid, bp 87–88 °C (1 Torr); yield 1.26 g (66%); Found: C, 44.3; H, 5.6; F, 14.8; Sn, 31.0%. $C_{14}H_{21}F_3OSn$ requires: C, 44.1; H, 5.6; F, 15.0; Sn, 31.2%; IR (neat) 3015, 2999, 1700, 1602, 1240, 1172 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.76 (2H, s, CH_2–C=C), 2.11–1.90 (2H, m), 1.82–1.58 (4H, m), 1.54–1.37 (4H, m) (total 10H, $-(CH_2)_5-$), 0.24 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 178.3 (q, *J* 38 Hz), 172.8, 147.0, 116.5 (q, *J* 290 Hz), 50.9, 47.2, 33.2, 25.5, 24.7, −8.5.

*4.3.3. 2,2,2-Trifluoro-1-[7-(trimethylstannyl)bicyclo[3.2.0]hept-6-en-6-yl]ethanone (**2c**).* From (**1c**). Colorless liquid, bp 71–72 °C (1 Torr); yield 1.23 g (70%); Found: C, 40.9; H, 4.8; F, 16.2; Sn, 33.6%. $C_{12}H_{17}F_3OSn$ requires: C, 40.8; H, 4.9; F, 16.2; Sn, 33.6%; IR (neat) 3020, 2995, 1702, 1598, 1237, 1177 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.58 (1H, dd, *J* 7.9, 3.5 Hz, HC–C=C), 3.40 (1H, dd, *J* 7.9, 3.5 Hz, HC–C=C), 1.77–1.71 (2H, m), 1.70–1.64 (2H, m), 1.48–1.42 (2H, m) (total 6H, $-(CH_2)_3-$), 0.24 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 179.0, 178.8 (q, *J* 39 Hz), 147.9, 116.7 (q, *J* 288 Hz), 56.6, 46.1, 25.2, 23.8, 22.8, −8.0.

*4.3.4. 2,2,2-Trifluoro-1-[8-(trimethylstannyl)bicyclo[4.2.0]oct-7-en-7-yl]ethanone (**2d**).* From (**1d**). Colorless liquid, bp 80–81 °C (1 Torr); yield 1.19 g (65%); Found: C, 42.6; H, 5.3; F, 15.4; Sn, 32.3%. $C_{13}H_{19}F_3OSn$ requires: C, 42.6; H, 5.2; F, 15.5; Sn, 32.3%; IR (neat) 3020, 2990, 1700, 1595, 1237, 1180 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.46 (1H, dd, *J* 9.6, 4.8 Hz, HC–C=C), 3.11 (1H, dd, *J* 9.6, 4.8 Hz, HC–C=C), 1.80–1.60 (4H, m), 1.49–1.31 (4H, m) (total 8H, $-(CH_2)_4-$), 0.21 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 179.5, 177.5 (q, *J* 38 Hz), 145.9, 117.0 (q, *J* 290 Hz), 44.6, 40.2, 23.2, 22.0, 17.9, 16.4, −8.3.

4.4. Preparation of bicyclic ketones (2e,f)[15]

*4.4.1. 2,2,2-Trifluoro-1-[3-(trimethylstannyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]ethanone (**2e**).* To the solution of 1-trifluoroacetyl-2-trimethylstannylacetylene[11,15] (2.85 g, 10 mmol) in ether (2 mL) freshly distilled 1,3-cyclopentadiene (1.00 g, 15 mmol) was added in one portion and the resulting mixture was kept at 25 °C for 48 h. The solution was concentrated and the residue was distilled to afford **2e** as a yellowish liquid, bp 76–77 °C (1 Torr); yield 3.02 g (86%); Found: C, 41.2; H, 4.4; F, 16.1%. $C_{12}H_{15}F_3OSn$ requires: C, 41.1; H, 4.3; F, 16.2%; IR (neat) 3035, 3000, 1700, 1610, 1240, 1162 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.87 (1H, dd, *J* 5.6, 2,7 Hz, H–C=C), 6.63 (1H, dd, *J* 5.6, 2,7 Hz, H–C=C), 4.11 (2H, m, H–C^1, H–C^4), 2.20 (1H, d, *J* 7.5 Hz, $-CH_2-$), 2.09 (1H, d, *J* 7.5 Hz, $-CH_2-$), 0.25 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 195.5, 178.6 (q, *J* 38 Hz), 158.9, 144.0, 140.7, 117.2 (q, *J* 290 Hz), 72.9, 58.2, 51.4, −7.8.

*4.4.2. 2,2,2-Trifluoro-1-[3-(trimethylstannyl)bicyclo[2.2.2]octa-2,5-dien-2-yl]ethanone (**2f**).* The solution of 1-trifluoroacetyl-2-trimethylstannylacetylene (2.85 g, 10 mmol) and 1,3-cyclohexadiene (1.61 g, 20 mmol) in THF (6 mL) was heated to reflux for 6 h. The solution was concentrated and the residue was distilled to afford **2f** as a yellowish liquid, bp 84–85 °C (1 Torr); yield 2.48 g (68%); Found: C, 43.0; H, 4.8; F, 15.6%. $C_{13}H_{17}F_3OSn$ requires: C, 42.8; H, 4.7; F, 15.6%; IR (neat) 3026, 2998, 1702, 1602, 1236, 1177 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.40 (1H, t, *J* 6.5 Hz, H–C=C), 6.23 (1H, t, *J* 6.5 Hz, H–C=C), 4.25–4.19 (2H, m, H–C^1, H–C^4), 1.47–1.42 (2H, m, $-CH_2-$), 1.40–1.33 (2H, m, $-CH_2-$), 0.24 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 184.8, 178.6 (q, *J* 38 Hz), 147.4, 133.9, 132.4, 116.9 (q, *J* 290 Hz), 45.0, 40.0, 24.6, 22.6, −8.4.

4.5. General procedure for preparation of dioxolanes (3a–f)

To a solution of cycloadduct **2a**–**f** (10 mmol) in 2-chloroethanol (8 mL) diisopropylamine (1.52 g, 15 mmol) was added in one portion (the solution became red and exothermic process was observed) and the reaction mixture was exposed at 25 °C for 48 h. The excess of 2-chloroethanol and diisopropylamine was distilled off in vacuum and the residue was diluted with a mixture ether–hexane 1:1 (25 mL). The amine salt was filtered off and the organic solution was consequently washed with cold solution of $NaHCO_3$, dried over Na_2SO_4 and concentrated. The residue was distilled under vacuum to afford one of dioxolanes **3a**–**f**. Dioxolanes **3b**,**e**,**f**, which crystallized soon after distillation were additionally purified by low-temperature crystallization (−20 °C) from hexane.

*4.5.1. {3,3-Dimethyl-2-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]cyclobut-1-en-1-yl}(trimethyl)-stannane (**3a**).* From **2a**. Yellowish oil; bp 73–74 °C (1 Torr); yield 3.04 g (79%); Found: C, 40.7; H, 5.6; F, 14.7; Sn, 30.8%. $C_{13}H_{21}F_3O_2Sn$ requires: C, 40.6; H, 5.5; F, 14.8; Sn, 30.8%; IR (neat) 3020, 2935, 1644, 1318, 1180 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.12–3.98 (2H, m, $-CH_2O-$), 3.97–3.84 (2H, m, $-CH_2O-$), 2.36 (2H, s, CH_2–C=C), 1.40 (6H, s, $(CH_3)_2C$), 0.16 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 142.6, 139.0, 122.3 (q, *J* 290 Hz), 104.7 (q, *J* 33 Hz), 65.8, 43.0, 42.2, 25.4, −7.7.

*4.5.2. Trimethyl{1-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]spiro[3.5]non-1-en-2-yl}stannane (**3b**).* From **2b**. Yellowish solid; mp 46–47 °C, bp 108–109 °C (0.5 Torr); yield 3.1 g (73%); Found: C, 45.2; H, 6.1; F, 13.2; Sn, 28.1%. $C_{16}H_{25}F_3O_2Sn$ requires: C, 45.2; H, 5.9; F, 13.4; Sn, 27.9%; IR (mineral oil) 3026, 2980, 1644, 1320, 1178 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.15–4.04 (2H, m, $-CH_2O-$), 3.96–3.85 (2H, m, $-CH_2O-$), 2.39 (2H, s, CH_2–C=C), 2.03–1.81 (4H, m), 1.76–1.55 (4H, m), 1.45–1.33 (2H, m) (total 10H, $-(CH_2)_5-$), 0.16 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 143.0, 139.9, 120.9 (q, *J* 290 Hz), 105.1 (q, *J* 33 Hz), 66.3, 46.8, 43.4, 34.7, 25.3, 24.3, −8.0.

*4.5.3. Trimethyl{7-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[3.2.0]hept-6-en-6-yl}stannane (**3c**).* From **2c**. Colorless oil; bp 80–81 °C (1 Torr); yield 3.18 g (80%); Found: C, 42.5; H, 5.4; F, 14.3; Sn, 29.8%. $C_{14}H_{21}F_3O_2Sn$ requires: C, 42.4; H, 5.3; F, 14.4; Sn, 29.9%; IR (neat) 3044, 2975, 1650, 1320, 1180 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.16–4.05 (2H, m, $-CH_2O-$), 4.02–3.91 (2H, m, $-CH_2O-$), 3.53 (1H, dd, *J* 7.7, 3.2 Hz, HC–C=C), 3.37 (1H, dd, *J* 7.7, 3.2 Hz, HC–C=C), 1.81–1.67 (2H, m), 1.67–1.55 (2H, m), 1.49–1.38 (2H, m) (total 6H, $-(CH_2)_3-$), 0.17 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 145.8, 142.0, 122.4 (q, *J* 290 Hz), 105.7 (q, *J* 34 Hz), 67.5, 52.6, 48.1, 25.1, 23.7, 22.7, −8.2.

*4.5.4. Trimethyl{8-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[4.2.0]oct-7-en-7-yl}stannane (**3d**).* From **2d**. Colorless oil; bp 84–85 °C (1 Torr); yield 2.92 g (71%); Found: C, 44.0; H, 5.8; F, 13.8; Sn, 28.8%. $C_{15}H_{23}F_3O_2Sn$ requires: C, 43.8; H, 5.6; F, 13.9; Sn, 28.8%; IR (neat) 3050, 2960, 1638, 1322, 1165 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.19–4.08 (2H, m, $-CH_2O-$), 3.98–3.87 (2H, m, $-CH_2O-$), 3.39 (1H, dd, *J* 9.4, 4.6 Hz, HC–C=C), 3.19 (1H, dd, *J* 9.4, 4.6 Hz, HC–C=C), 1.80–1.56 (4H, m), 1.54–1.36 (4H, m) (total 8H, $-(CH_2)_4-$), 0.15 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 146.0, 142.3, 121.9 (q, *J* 289 Hz), 105.3 (q, *J* 34 Hz), 66.9, 43.3, 40.9, 23.6, 22.6, 17.0, 15.5, −8.3.

*4.5.5. Trimethyl{3-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[2.2.1]hepta-2,5-dien-2-yl}stannane (**3e**).* From **2e**. White crystals; mp 37–38 °C; bp 87–88 °C (1 Torr); yield 3.16 g (80%); Found: C, 42.7; H, 4.9; F, 14.4%. $C_{14}H_{19}F_3O_2Sn$ requires: C, 42.6; H, 4.9; F, 14.4%;

IR (mineral oil) 2985, 2908, 1312, 1174 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.77 (1H, d, *J* 5.1 Hz, H–C=C), 6.61 (1H, d, *J* 5.1 Hz, H–C=C), 4.18–4.04 (2H, m, $-CH_2O-$), 4.03–3.91 (2H, m, $-CH_2O-$), 3.82 (1H, s, H–C^1), 3.72 (1H, s, H–C^4), 1.93 (2H, d, *J* 5.6 Hz, $-CH_2-$), 0.15 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 159.0, 157.7, 142.9, 142.1, 122.9 (q, *J* 290 Hz), 105.8 (q, *J* 34 Hz), 73.0, 66.6, 66.3, 56.1, 53.0, −8.3.

*4.5.6. Trimethyl{3-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[2.2.2]octa-2,5-dien-2-yl}stannane (**3f**).* From **2f**. White needles; mp 32–33 °C; bp 99–100 °C (1 Torr); yield 2.78 g (68%); Found: C, 44.2; H, 5.3; F, 13.9%. $C_{15}H_{21}F_3O_2Sn$ requires: C, 44.1; H, 5.2; F, 13.9%; IR (mineral oil) 3060, 2973, 1298, 1168 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.35 (1H, t, *J* 7.0 Hz, H–C=C), 6.29 (1H, t, *J* 7.0 Hz, H–C=C), 4.20–4.09 (2H, m, $-CH_2O-$), 4.06–3.95 (2H, m, $-CH_2O-$), 3.92–3.80 (2H, m, H–C^1, H–C^4), 1.38–1.10 (4H, m, $-(CH_2)_2-$), 0.18 (9H, s, Me_3Sn); δ_C (100.6 MHz, $CDCl_3$) 149.5, 147.4, 134.3, 134.2, 123.0 (q, *J* 290 Hz), 105.2 (q, *J* 34 Hz), 66.6, 66.4, 43.1, 39.0, 24.6, 24.0, −8.0.

4.6. General procedure for generation of organolithiums (4) and for preparation of aldehydes (5a–f) and trifluoromethylketones (6a,b)

To a stirred solution one of dioxolanes **3a**–**f** (10 mmol) in THF (12 mL) at −70 °C a solution of *n*-BuLi in hexane (6.9 mL of 1.6 M solution, 11 mmol) was added dropwise and the mixture was additionally stirred at −60 °C for 1.5 h. To the resulting solution of organolithium **4** (sometimes precipitate formation was observed) a solution of DMF or DMTFA (14 mmol) in THF (5 mL) was added dropwise at −70 °C and the reaction mixture was allowed gradually to warm to 0 °C (about 1 h) after which it was poured into stirred saturated NaH_2PO_4 (25 mL). The organic layer was separated and the aqueous phase extracted with ether (2×20 mL). The combined organic solution was dried over Na_2SO_4, concentrated, and the residue was distilled under vacuum (in the cases of **6a**,**b** the residue was additionally stirred in trifluoroacetic anhydride (10 mL) for 15 min before the distillation) to afford compounds **5**,**6** in preparative yields.

*4.6.1. 3,3-Dimethyl-2-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]cyclobut-1-ene-1-carbaldehyde (**5a**).* From **3a** and DMF. Yellowish oil, bp 62–63 °C (1 Torr); yield 1.90 g (76%); Found C, 54.0; H, 5.9; F, 25.6%. $C_{11}H_{13}F_3O_3$ requires: C, 54.1; H, 5.9; F, 25.8%; IR (neat) 3018, 1665, 1603, 1370, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 10.38 (1H, s, H–CO), 4.29–4.19 (2H, m, $-CH_2O-$), 4.15–4.03 (2H, m, $-CH_2O-$), 2.88 (2H, s, CH_2), 1.49 (6H, s, $(CH_3)_2C$); δ_C (100.6 MHz, $CDCl_3$) 192.6, 157.0, 143.8, 124.9 (q, *J* 290 Hz), 108.1 (q, *J* 32 Hz), 68.3, 49.9, 44.6, 27.0.

*4.6.2. 1-[2-(Trifluoromethyl)-1,3-dioxolan-2-yl]spiro[3.5]non-1-ene-2-carbaldehyde (**5b**).* From **3b** and DMF. Yellowish oil, bp 94–95 °C (1 Torr); yield 2.03 g (70%); Found: C, 58.0; H, 6.0; F, 19.7%. $C_{14}H_{17}F_3O_3$ requires: C, 57.9; H, 5.9; F, 19.6%; IR (neat) 3045, 3000, 1664, 1600, 1377, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 10.36 (1H, s, H–CO), 4.32–4.19 (2H, m, $-CH_2O-$), 4.16–4.06 (2H, m, $-CH_2O-$), 2.85 (2H, s, CH_2C=C), 2.13–2.01 (2H, m), 1.91–1.69 (2H, m), 1.66–1.43 (2H, m) (total 10H, $-(CH_2)_5-$); δ_C (100.6 MHz, $CDCl_3$) 193.3, 157.5, 140.0, 124.7 (q, *J* 290 Hz), 107.6 (q, *J* 32 Hz), 68.5, 48.3, 45.0, 33.8, 25.4, 25.1.

*4.6.3. 7-[2-(Trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[3.2.0]hept-6-ene-6-carbaldehyde (**5c**).* From **3c** and DMF. Yellowish oil, bp 67–68 °C (1 Torr); yield 1.91 g (73%); Found: C, 55.1; H, 5.1; F, 21.7%. $C_{12}H_{13}F_3O_3$ requires: C, 55.0; H, 5.0; F, 21.7%; IR (neat) 3050, 2990, 1670, 1600, 1348, 1165 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 10.40 (1H, s, H–CO), 4.26–4.15 (2H, m, $-CH_2O-$), 4.13–4.04 (2H, m, $-CH_2O-$), 3.82 (1H, dd, *J* 7.4, 3.6 Hz, HC–C=C), 3.54 (1H, dd, *J* 7.4, 3.6 Hz, HC–C=C), 2.02–1.82 (2H, m), 1.79–1.61 (2H, m), 1.58–1.39 (2H, m) (total 6H, $-(CH_2)_3-$); δ_C (100.6 MHz, $CDCl_3$) 195.3, 156.0, 145.7, 124.0 (q, *J* 290 Hz), 106.3 (q, *J* 34 Hz), 67.6, 54.9, 50.6, 25.8, 23.8, 22.7.

*4.6.4. 8-[2-(Trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[4.2.0]oct-7-ene-7-carbaldehyde (**5d**).* From **3d** and DMF. Yellowish oil, bp 79–80 °C (1 Torr); yield 1.77 g (64%); Found: C, 56.7; H, 5.5; F, 20.5%. $C_{13}H_{15}F_3O_3$ requires: C, 56.5; H, 5.5; F, 20.6%; IR (neat) 3050, 2996, 1670, 1604, 1360, 1177 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 10.35 (1H, s, H–CO), 4.26–4.16 (2H, m, $-CH_2O-$), 4.15–4.06 (2H, m, $-CH_2O-$), 3.44 (1H, dd, *J* 9.1, 4.5 Hz, HC–C=C), 3.26 (1H, dd, *J* 9.1, 4.5 Hz, HC–C=C), 2.02–1.78 (4H, m), 1.74–1.51 (4H, m) (total 8H, $-(CH_2)_4-$); δ_C (100.6 MHz, $CDCl_3$) 195.1, 155.4, 142.2, 123.8 (q, *J* 290 Hz), 106.0 (q, *J* 34 Hz), 67.8, 47.7, 43.9, 25.3, 22.9, 17.0, 15.0.

*4.6.5. 3-[2-(Trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde (**5e**).* From **3e** and DMF. Yellow oil, bp 82–83 °C (1 Torr); yield 1.95 g (75%); Found: C, 55.5; H, 4.3; F, 21.9%. $C_{12}H_{11}F_3O_3$ requires: C, 55.4; H, 4.3; F, 21.9%; IR (neat) 3033, 2990, 1658, 1380, 1177 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 10.48 (1H, s, H–CO), 6.84 (1H, dd, *J* 5.3, 1.0 Hz, H–C=C), 6.64 (1H, d, *J* 5.3, 1.0 Hz, H–C=C), 4.30–4.22 (2H, m, $-CH_2O-$), 4.20–4.11 (2H, m, $-CH_2O-$), 3.94 (1H, d, *J* 1.0 Hz, H–C^1), 3.81 (1H, d, *J* 1.0 Hz, H–C^4), 2.28 (1H, d, *J* 7.2 Hz, $-CH_2-$), 2.14 (1H, d, *J* 7.2 Hz, $-CH_2-$); δ_C (100.6 MHz, $CDCl_3$) 195.0, 176.9, 160.9, 147.9, 144.7, 122.4 (q, *J* 288 Hz), 107.3 (q, *J* 34 Hz), 71.0, 67.5, 67.2, 58.8, 53.6.

*4.6.6. 3-[2-(Trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[2.2.2]octa-2,5-diene-2-carbaldehyde (**5f**).* From **3f** and DMF. Yellow oil, bp 94–95 °C (1 Torr); yield 1.89 g (69%); Found: C, 57.1; H, 4.6; F, 20.8%. $C_{13}H_{13}F_3O_3$ requires: C, 57.0; H, 4.8; F, 20.8%; IR (neat) 3038, 2990, 1665, 1600, 1380, 1177 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 10.35 (1H, s, H–CO), 6.52 (1H, t, *J* 6.3 Hz, H–C=C), 6.38 (1H, t, *J* 6.3 Hz, H–C=C), 4.34–4.25 (2H, m, H–C^1, H–C^4), 4.20–4.12 (2H, m, $-CH_2O-$), 4.03–3.92 (2H, m, $-CH_2O-$),1.48–1.42 (2H, m, $-CH_2-$), 1.40–1.34 (2H, m, $-CH_2-$); δ_C (100.6 MHz, $CDCl_3$) 189.0, 164.1, 145.7, 135.9, 135.2, 124.0 (q, *J* 290 Hz), 105.5 (q, *J* 34 Hz), 67.0, 66.7, 46.8, 41.0, 26.5, 24.5.

*4.6.7. 1-{3,3-Dimethyl-2-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]cyclobut-1-en-1-yl}-2,2,2-trifluoroethanone (**6a**).* From **3a** and DMTFA. Yellowish oil, bp 59–60 °C (1 Torr); yield 2.61 g (82%); Found: C, 45.2; H, 3.9; F, 35.6%. $C_{12}H_{12}F_6O_3$ requires: C, 45.3; H, 3.8; F, 35.8%; IR (neat) 3010, 2985, 1700, 1602, 1277, 1170 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.30–4.20 (2H, m, $-CH_2O-$), 4.18–4.09 (2H, m, $-CH_2O-$), 2.90 (2H, s, CH_2), 1.46 (6H, s, $(CH_3)_2C$); δ_C (100.6 MHz, $CDCl_3$) 178.4 (q, *J* 38 Hz), 155.9, 146.0, 124.3 (q, *J* 290 Hz), 116.6 (q, *J* 288 Hz), 109.4 (q, *J* 34 Hz), 68.9, 48.0, 44.2, 27.0.

*4.6.8. 2,2,2-Trifluoro-1-{7-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]bicyclo[3.2.0]hept-6-en-6-yl}ethanone (**6b**).* From **3c** and DMTFA. Yellowish oil, bp 64–65 °C (1 Torr); yield 2.64 g (80%); Found: C, 47.1; H, 3.6; F, 34.6%. $C_{13}H_{12}F_6O_3$ requires: C, 47.3; H, 3.7; F, 34.5%; IR (neat) 3026, 2990, 1700, 1277, 1184 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.29–4.18 (2H, m, $-CH_2O-$), 4.17–4.07 (2H, m, $-CH_2O-$), 3.84 (1H, dd, *J* 7.3, 3.3 Hz, HC–C=C), 3.54 (1H, dd, *J* 7.3, 3.3 Hz, HC–C=C), 2.02–1.88 (2H, m), 1.74–1.60 (2H, m), 1.53–1.41 (2H, m) (totally 6H, $-(CH_2)_3-$); δ_C (100.6 MHz, $CDCl_3$) 178.8 (q, *J* 38 Hz), 152.6, 148.5, 124.5 (q, *J* 290 Hz), 117.1 (q, *J* 288 Hz), 108.8 (q, *J* 34 Hz), 68.2, 68.0, 52.9, 50.9, 26.3, 24.5, 22.5.

4.7. Preparation of dimetylhydrazones 7a,b

To the stirred solution of *N*,*N*-dimethylhydazine (0.90 g, 15 mmol) and acetic acid (0.1 g) in ether (5 mL) at 20 °C the aldehydes **5a**,**b** (10 mmol) in ether (3 mL) was added dropwise. After 1 h the resulting cloudy, wet solution was dried over K_2CO_3 and solvent and an excess of dimethylhydrazine were removed under vacuum.

The crude dimethylhydrazones **6a**,**b** formed in almost quantitative yield were subjected to acidolysis without further purification. For analytical purposes they can be purified by column chromatography (silicagel, chloroform–methanol 20: 1) although it leads to some loss of material.

*4.7.1. 2-({3,3-dimethyl-2-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]cyclobut-1-en-1-yl}methylene)-1,1-dimethyl-1λ^5,2λ^5-diazyne (**7a**).* From **5a** and *N*,*N*-dimethylhydrazine. Yellowish oil; yield 2.42 g (83%) after chromatography; Found: C, 53.6; H, 6.7; F, 19.4; N, 9.4%. $C_{13}H_{19}F_3N_2O_2$ requires: C, 53.4; H, 6.6; F, 19.5; N, 9.5%; IR (neat) 3015, 2997, 1650, 1294, 1180 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.95 (1H, s, H–C=N), 4.30–4.19 (2H, m, $-CH_2O-$), 4.16–4.03 (2H, m, $-CH_2O-$), 2.76 (6H, s, Me_2N), 2.64 (2H, s, CH_2), 1.46 (6H, s, $(CH_3)_2C$); δ_C (100.6 MHz, $CDCl_3$) 144.2, 135.8, 133.7, 122.5 (q, *J* 290 Hz), 106.8 (q, *J* 32 Hz), 67.0, 46.3, 42.2, 40.7, 27.3.

*4.7.2. 1,1-Dimethyl-2-({1-[2-(trifluoromethyl)-1,3-dioxolan-2-yl]spiro[3.5]non-1-en-2-yl}methy-lene)-1λ^5,2λ^5-diazyne (**7b**).* From **5b** and *N*,*N*-dimethylhydrazine. Yellowish oil; yield 2.82 g (85%) after chromatography; Found: C, 57.9; H, 7.1; F, 17.1; N, 8.3%. $C_{16}H_{23}F_3N_2O_2$ requires: C, 57.8; H, 7.0; F, 17.2; N, 8.4%; IR (neat) 3034, 3000, 1650, 1290, 1178 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.91 (1H, s, H–C=N), 4.31–4.20 (2H, m, $-CH_2O-$), 4.17–4.05 (2H, m, $-CH_2O-$), 2.75 (6H, s, Me_2N), 2.66 (2H, s, $CH_2C=C$), 2.16–1.93 (2H, m), 1.80–1.51 (6H, m) (total 10H, $-(CH_2)_5-$); δ_C (100.6 MHz, $CDCl_3$) 145.0, 135.5, 134.1, 122.8 (q, *J* 290 Hz), 107.7 (q, *J* 32 Hz), 68.9, 48.4, 43.3, 41.0, 33.2, 26.0, 25.1.

4.8. Preparation of ketohydrazones 8a,b

A mixture of 90% formic acid (10 mL) and acetic anhydride (2.22 g) was kept overnight at ambient temperature. To the resulting stirred solution one of corresponding dimethylhydrazones **7a**,**b** (10 mmol) was added and the mixture was stirred at 20 °C for 1 h. The excess of formic and acetic acid was removed under vacuum, the residue was dissolved in THF (10 mL) and the resulting solution was vigorously stirred with 10% aqueous solution of K_2CO_3 (10 mL) for 2 h. The organic solvent was evaporated under vacuum and the aqueous phase was extracted with ether (3×10 mL). The ether solution was dried over K_2CO_3 and concentrated in vacuum. The residual crude ketohydrazones **8a**,**b** were purified by column chromatography (silicagel, chloroform–ethylacetate 5:1).

*4.8.1. 1-{2-[(2,2-dimethyl-1λ^5,2λ^5-diazynylidene)methyl]-4,4-dimethylcyclobut-1-en-1-yl}-2,2,2-trifluoroethanone (**8a**).* From **7a**. Yellow-orange oil; yield 1.44 g (58%); Found: C, 53.4; H, 6.2; F, 22.9%. $C_{11}H_{15}F_3N_2O$ requires: C, 53.2; H, 6.1; F, 23.0%; IR (neat) 3010, 2990, 1700, 1645, 1420, 1270, 1165 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.44 (1H, s, H–C=N), 3.40 (6H, s, Me_2N), 2.90 (2H, s, CH_2), 1.55 (6H, s, $(CH_3)_2C$); δ_C (100.6 MHz, $CDCl_3$) 178.0 (q, *J* 39 Hz), 160.7, 156.0, 152.2, 116.5 (q, *J* 290 Hz), 52.8, 48.2, 43.5, 27.9.

*4.8.2. 1-{2-[(2,2-dimethyl-1λ^5,2λ^5-diazynylidene)methyl]spiro[3.5]non-1-en-1-yl}-2,2,2-trifluoroethanone (**8b**).* From **7b**. Yellow-orange prisms, mp 40–41 °C; yield 1.73 g (60%); Found: C, 58.4; H, 6.7; F, 19.7%. $C_{14}H_{19}F_3N_2O$ requires: C, 58.3; H, 6.6; F, 19.8%; IR (mineral oil) 3012, 2990, 1700, 1650, 1277, 1170 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38 (1H, s, H–C=N), 3.36 (6H, s, Me_2N), 2.90 (2H, s, CH_2), 2.26–2.03 (2H, m), 1.82–1.60 (6H, m) (total 10H, $-(CH_2)_5-$); δ_C (100.6 MHz, $CDCl_3$) 177.2 (q, *J* 39 Hz), 161.1, 156.2, 152.7, 116.7 (q, *J* 290 Hz), 53.3, 49.0, 44.0, 33.4, 25.9, 25.3.

References and notes

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