Chimica & Industria

# HOMOGENEOUS RUTHENIUM CATALYSTS FOR THE TRANSFORMATION OF PERFLUORINATED BUILDING BLOCKS

*Dario Lazzari*[a] *- Maria Cristina Cassani*[b] *- Maurizio Bertola*[a] *- Roberto Rossato*[a]
[a]*Miteni SpA*
*Trissino(VC)*
[b]*Dipartimento di Chimica Industriale "Toso Montanari"*
*Università di Bologna*
dario.lazzari@miteni.com
maria.cassani@unibo.it

*Commercially available homogeneous ruthenium catalysts are useful tools for the transformation of enviromentally compatible perfluorinated building blocks. This paper presents examples of reactions that make use of three different ruthenium complexes: the ruthenium(II) tri-chelated complex carbonylchlorohydrido[bis(2-(diphenylphosphinoethyl)amino]ruthenium(II) (a commercial catalyst known as Ru-MACHO), [RuClH(CO)(PPh*$_3$*)*$_3$*] and 2*$^{nd}$ *generation Grubbs' catalyst CatMETium_RF3*

**Catalizzatori omogenei a base di rutenio per la trasformazione di building blocks perfluorurati**

Catalizzatori omogenei, commercialmente disponibili, a base di complessi di rutenio sono strumenti fondamentali per la trasformazione di building blocks perfluorurati compatibili con l'ambiente. Questo articolo presenta alcuni esempi di reazioni che fanno uso di tre diversi complessi di rutenio(II): il complesso tris chelato carbonilcloroidruro[bis(2-(difenilfosfinoetil)ammino]rutenio(II) (un catalizzatore commerciale noto con il nome di Ru-MACHO), [RuClH(CO)(PPh$_3$)$_3$] e il catalizzatore di Grubbs di 2$^a$ generazione CatMETium_RF3.

The insertion of perfluorinated moieties within the structure of more traditional organic compounds confers unique properties that have been largely exploited in several application fields. To mention just a few: pharmaceuticals and agrochemicals, material science, surfactant chemistry, heat transfer fluids, additives for polymers as well as materials for lithium-ion batteries[1,2,3,4,5]. In this respect the synthesis and characterization of novel fluorinated building blocks containing suitable functional groups that can be easily transformed into a wide range of compounds represent an important industrial target. Nevertheless the existing concern towards long perfluorinated alkyl chains owing to their bioaccumulation, toxicity and environmental persistence is making more and more important the availability of fluorinated building blocks with shorter perfluorinated carbon chains. In the development of such new range of environmentally safe building blocks the fluorinated carbon chain moiety $R_F$ cannot be longer than six carbon atoms. Materials satisfying this requirement *do not* deliver, during service life, perfluoroctanoic acid (PFOA) via oxidative degradation.

The formation of PFOA is considered as the most detrimental aspect in the use $C_8$-fluorinated chains: PFOA is persistent in the environment, ubiquitously present in surface waters, and subject to long-range transport. It accumulates in bio-organisms, especially in top predators furthermore PFOA is increasingly analysed in food items, and in drinking water. PFOA's intrinsic properties such as its persistency, its potential for bioaccumulation and its toxicity suggest that PFOA is a promising candidate for being identified as a Substance of Very High Concern[6,7,8] .

In general, the reduction of the perfluorinated chain lengths on one hand decreases the toxicity and bioaccumulation potential but, on the other, leads to inferior performances in the applications where a large content of fluorine atoms is mandatory. Therefore, the synthetic strategies adopted by research groups working in this field are not simply consisting in a shortening of the fluorocarbon chains but also include a complete molecule redesign and a common approach is to replace a single long chain with branched structures containing short fluorocarbon alkyl groups. The seek for modern synthetic tools aimed at transforming fluorinated building blocks in a selective and efficient way is a key industrial target[9,10,11,12]. In this research account, which is the combined effort of an industrial and academic research group, we summarize some recently reported examples that make use of three different ruthenium(II) complexes in the transformation of perfluorinated organic compounds[13,14]. The ruthenium(II) tri-chelated complex carbonylchlorohydrido[bis(2-(diphenylphosphinoethyl)amino]ruthenium(II) (known as Ru-MACHO), has been successfully applied in the hydrogenation of perfluorinated methyl esters $C_3F_7C(O)OMe$ under *very mild* conditions ($pH_2$=10 bar, T=40 °C) and represents a valid alternative to the use of metal hydrides especially for the minimum amount of waste generated during the process. The two ruthenium(II) complexes $[RuClH(CO)(PPh_3)_3]$ and 2nd generation Grubbs' catalyst CatMETium_RF3 are instead very active in the solvent-free double bond isomerization of perfluoroalkyl allyl ethers $R_FCH_2OCH_2CH=CH_2$ ($R_F=C_3F_7$, $C_5F_{11}$) to the corresponding propen-1-yl ethers (*E*+*Z* isomers). Finally preliminary studies regarding the isomerization of *N*-allylsulfonamides with $[RuClH(CO)(PPh_3)_3]$ are also reported.

## Synthesis of fluorinated alcohols via homogeneous catalytic hydrogenation

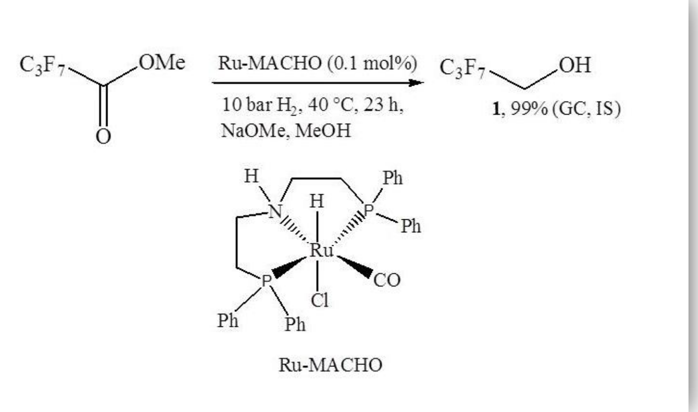
The need for short fluorinated alcohols is becoming a pressing request for several industries in the development of new fluorinated additives, surfactants and reagents for surface treatment. The production of fluorinated alcohols of the type $R_fCH_2OH$ where $R_f=C_3F_7$ and $C_5F_{11}$ from the reduction of the corresponding perfluoro methyl esters is part of the core competence of Miteni SpA. The traditional method reported in the literature for the reduction of perfluoro esters to alcohols of formula $R_fCH_2OH$ is based on the use of $NaBH_4$[15,16,17]. The yields of hydrogenation are in the range of 80%, and although sodium borohydride is a versatile reagent, its hazardous nature, complex postreaction workup procedures, and high level of residual waste are matters of concern in industrial operations. Moreover the postreaction workup generates boric acid and borates that according to the IUCLID Dataset published by the European Commission, in high doses show significant developmental toxicity and teratogenicity in rabbits, rats, and mouse fetuses[18,19,20,21]. Replacing hydride reductions with hydrogenations enables companies to implement simple and convenient processes. For this purpose, catalysts which work under mild conditions would have significant industrial advantages. To the best of our knowledge very few examples have been recently reported on this topic[22,23,24]; for example in the hydrogenation ($pH_2$=50 bar, 140 °C, 24 h) of $C_3F_7CO_2Me$ reported by Clarke *et al.*, the ruthenium catalyst bearing a chiral tridendate amine functionalized phosphine (0.5%) must be activated by a three-fold excess (1.5%) of $LiHBEt_3$[22]. In our group several attempts were also done carrying out the hydrogenation reaction under heterogeneous conditions: several systems such as Pd, Pt and Ru on a variety of supports (activated carbon, aluminia, titania) were tested with, at least under the same relatively harsh experimental conditions described by Clarke, negligible or no results.

In view of these findings we have therefore decided to focus our efforts on homogenous catalytic hydrogenation and we considered the commercial catalyst Ru-MACHO produced in bulk by the Takasago Company[25]. This catalyst is active in the hydrogenation of esters although no information were available regarding his activity in the hydrogenation of perfluorinated methyl esters[26,27,28,29]. As shown in Tab. 1, the hydrogenation of fully fluorinated methyl esters $C_3F_7C(O)OMe$ was carried out under a variety of reaction conditions in the presence of Ru-MACHO and NaOMe in methanol and Scheme 1 sum up the best reaction conditions found for the reduction of $C_3F_7C(O)OMe$[13].

**Tab. 1**
**Reduction of $C_3F_7C(O)OMe$[a]**

| Entry | T (°C) | *p*$H_2$ (bar) | Cat. (mol%) | Yield[b] | TON |
|---|---|---|---|---|---|
| 1 | 40 | 10 | 0.1 | 99 | 990 |
| 2 | 40 | 10 | 0.05 | 89 | 1,780 |
| 3 | 40 | 10 | 0.045 | 65 | 1,444 |
| 4 | 20 | 10 | 0.05 | 17 | 340 |
| 5 | 60 | 10 | 0.05 | 97 | 1,940 |
| 6 | 60 | 10 | 0.025 | 89 | 3,560 |
| 7 | 60 | 10 | 0.0125 | 74 | 5,920 |
| 8 | 60 | 10 | 0.005 | 46 | 9,200 |
| 9 | 80 | 10 | 0.0125 | 66 | 5,280 |
| 10[c] | 100 | 30 | 0.05 | - | - |
| 11[d] | 50 | 10 | 0.005 | 43 | 8,600 |
| 12[e] | 60 | 10 | 0.005 | 36 | 7,200 |

[a] *Reaction conditions: MeOH, $p(H_2)$=10 bar, 23 h, ester/$NaOCH_3$ molar ratio=0.25, in a 100 ml autoclave;* [b] *Determined by GC analysis (internal standard: decane);* [c] *$p(H_2)$=30 bar, 5 h;* [d] *Perfluorobutanol;* [e] *Isopropyl alcohol*



*Scheme 1*
*Hydrogenation of perfluorinated methyl esters with Ru-MACHO in a 100 ml autoclave (see entry 1, Tab. 1)*

In order to make the entire process as simple and straightforward as possible and keep the waste to a minimum level, a great effort has been also placed on the work-up optimization. For instance, when a 0.05 mol% of catalyst loading was employed the yields dropped to 89% (TON=1,780) and as a consequence at the end of the reaction the crude material was made of **1** together with ca. 8-10% of perfluorobutanoic acid sodium salt, methanol and sodium methoxide. In this case concentrated sulphuric acid (96%) is added in an amount equal to 10% w/w of the entire mass and a fractional distillation is carried out at atmospheric pressure. In the distillation conditions adopted the perfluorobutanoic acid sodium salt is reconverted into the original methyl ester that form with methanol an 80:20 azeotrope collected as the first fraction in the temperature range 42-63 °C. A second fraction composed by a mixture of perfluorobutanol **1** (94% w/w), methanol (4% w/w) and water (2% w/w) is collected in the temperature range 68-96 °C. Finally a 99% pure alcohol **1** was obtained by further distilling this second fraction on sulphuric acid (in this case the amount of sulphuric acid used is equal to the mass to be distilled). The perfluorobutanoic methyl ester obtained from the first distillation is added to the reduction reactor and recycled.

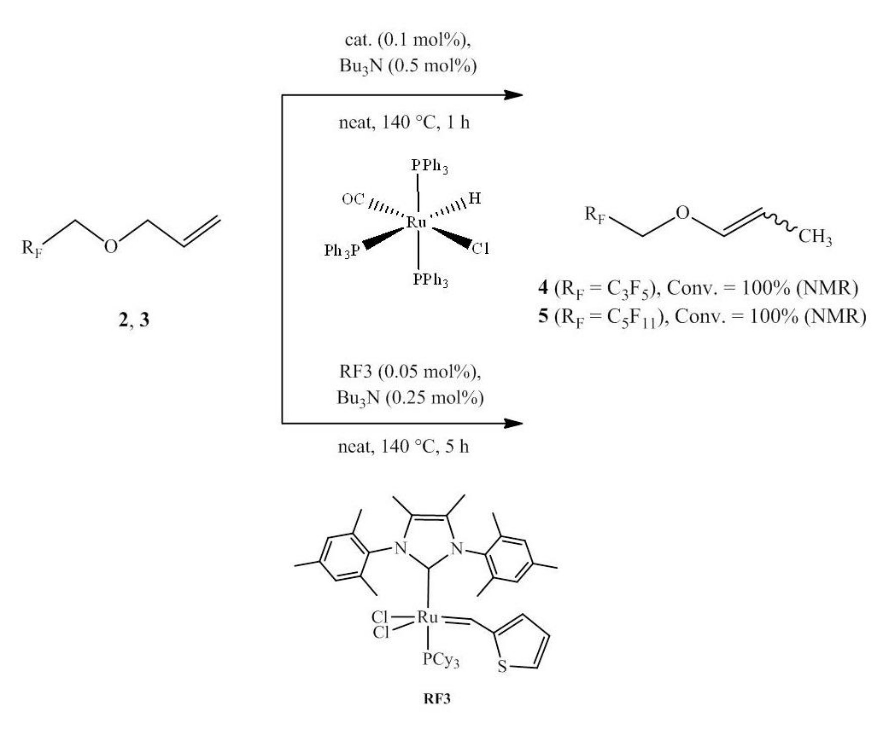
## Synthesis of perfluoroalkyl propen-1-yl ethers via homogeneous catalytic isomerization

In this framework perfluoroalkyl allyl ethers[30] easily formed from the corresponding alcohols (vide supra), represent an important class of starting materials that can be easily converted into perfluoroalkyl propen-1-yl ethers derivatives via a versatile and convenient double-bond isomerization reaction. These molecules are among the most reactive monomers in the cationic photopolymerization and are increasingly being used in resin production. Allyl ethers are reluctant to undergo free radical, cationic and anionic polymerization thus they have only limited value as monomers for the production of polymers. To the best of our knowledge the allyl ethers either polymerize after being isomerized to propen-1-yl ethers or they do not react at all[31,32,33].

The isomerization reaction of allyl ethers can be catalyzed by transition metal complexes and represents an example of an atom-economical process offering useful industrial synthetic applications. Various low-valent ruthenium complexes, particularly hydrides, act as very efficient pre-catalysts for the homogeneously catalyzed double-bond isomerization[34,35,36,37,38,39,40]. We have investigated the isomerization of the primary allyl ethers **2** ($R_F=C_3F_5$) and **3** ($R_F=C_5F_7$) into the corresponding propen-1-yl derivatives **4** and **5** catalyzed by two ruthenium complexes: $[RuClH(CO)(PPh_3)_3]$ (a well known efficient catalyst for this kind of reactions), and the second generation Grubb's type catalyst dichloro[1,3-bis-(2,4,6-trimethylphenyl)-4,5-dimethylimidazol-2-ylidene](thien-2-ylmethylidene)($PCy_3$) ruthenium(II) (known as CatMETium_RF3™ and hereafter abbreviated in RF3).

With regard to RF3, this ruthenium complex was used among the many catalysts available for the following reasons: i) it is a robust thermally stable catalyst, ii) it is produced on a large scale, iii) there are not licence fees on this catalyst and it can be acquired as any other raw material. Additionally, previous attempts of isomerization of perfluoroalkyl allyl ethers with the first generation Grubb's type complex $[RuCl_2(PCy_3)_2CHPh]$ always led to poor results with very low conversions (ca. 4%). The RF3 catalyst has been employed in cross methatesis (CM) and ring-closing methatesis (RCM) reactions however, as often found, the ruthenium-hydride species, that are formed from the decomposition of the ruthenium metathesis catalysts, also promote isomerization to a significant extent[41,42,43,44]. As the isomerization reactions reported in literature never involved perfluorinated substrates we have decided to study the behaviour of this catalysts also in consideration of the fact that self CM of perfluorinated olefins does not occur[45,46,47].

The most important results are highlighted in Scheme 2. All isomerizations were carried out in air under solvent-free conditions either using a 30 ml screw-capped ampoule or a 300 ml Parr autoclave equipped with a mechanical stirrer and a heating mantle. In all the examined cases the selectivity of the reaction was quantitative and the reported conversions were measured after the reactions had come to a complete standstill. The conversion of *O*-allyl groups to propen-1-yl derivatives as well as the ratios of the unseparated *E* and *Z* stereoisomers were determined from the analysis of $^1$H NMR spectra of the crude mixtures on the basis of vicinal $^3J$(HC=CH) coupling constants and confirmed by GC and GC-MS analyses[14].



*Scheme 2*
*Isomerization of perfluorinated allyl ethers catalyzed by [RuClH(CO)(PPh$_3$)$_3$] (top) and RF3 (bottom)*

In keeping with what reported by other authors[37,40,48,49], we observed that the presence of a base such as $Bu_3N$ (completely soluble in the reaction mixture and with b.p. 180 °C) can have dramatic effects on the final conversion: with a cat. loading of 0.1 mol% of [RuClH(CO)(PPh$_3$)$_3$] only in the presence of *n*-tributylamine the starting substrates are quantitatively converted in 1 h (TON=1,000). Under the same reaction conditions, with RF3 a total conversion (NMR) has been obtained with a cat. loading of 0.05 mol% (TON=2,000) moreover we never identified products deriving from a metathesis process. The better catalytic performance ensuing by the use of the Grubbs catalyst is evident in Fig. 1 in which the conversion profiles of the two catalysts were compared. In order to carry out the kinetic studies within a 24 h period of time a catalytic loading of 0.05 mol% was chosen for both RF3

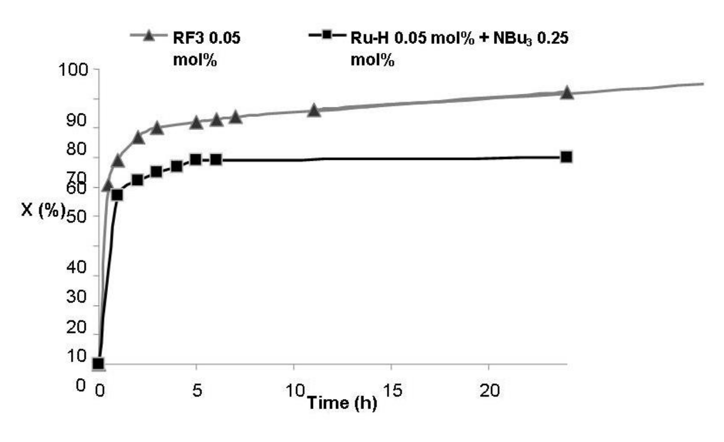
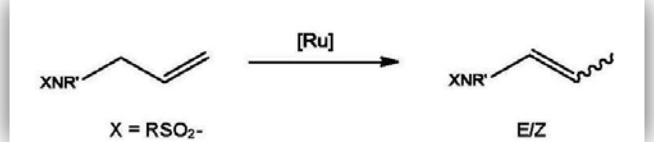


*Fig. 1*
*Isomerization of* ***2*** *in presence of 0.05 mol% of RF3 (▲) or with 0.05 mol% of [RuHCl(CO)(PPh$_3$)$_3$] with 0.25 mol% of n-tributylamine (■). Reaction conditions: 30 ml screw-capped ampoule, neat, 140 °C, 1 h*

and [RuHCl(CO)(PPh$_3$)$_3$] but for the latter the presence of 0.25 mol% *n*-tributylamine was necessary.

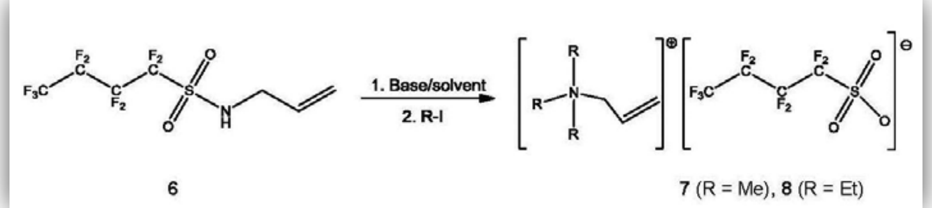
The double bond migration is not stereoselective and a *E/Z* ratio of ca. 40/60 was found in all cases. Propenyl ethers **4** and **5** are colourless liquid purified by distillation (bp of **4**=52-54 °C, bp of **5**=140-142 °C) with isolated yields in the range 65÷70%, though the solvent-free conditions employed for the synthesis make them suitable for direct use in the cationic polymerization without the necessity of removing the catalysts[14].

Successively, we focussed our attention on the synthesis of *N*-(1-propenyl)sulfonamides that are useful substrates for the synthesis of heterocyclic systems and are thoroughly investigated monomers and co-monomers. Generally the most convenient method for the synthesis of such systems consists of the isomerization of the appropriate *N*-allylsulfonamides catalyzed by transition metal complexes such as [RhCl(PPh$_3$)$_3$][50] or second generation Grubbs carbene ruthenium complexes as shown in Scheme 3[51,52].



*Scheme 3*
*Isomerization of N-allylsulfonamides*

However with regard to the latter class of catalysts, to the best of our knowledge, the examples reported in the literature always use high cat. loadings (5 mol%) making such synthetic procedure not appealing for an industrial scale-up. We therefore decided to investigate the isomerization of *N*-allyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide $C_4F_9SO_2NHCH_2CH=CH_2$ (**6**) with the less expensive [RuHCl(CO)(PPh$_3$)$_3$] with cat. loadings lower than 1 mol%[53]. The reaction was carried out under a variety of reaction conditions: using different solvents (THF, methanol; dioxane, 1-butanol, 2-butanol) or in neat with the molten product (150 °C); different cat. loadings (0.1-1.0 mol%) at different temperatures; absence or presence of Bu$_3$N. Nevertheless the outcome was either no reaction or a complex mixture of degradation products. We therefore decided to try also the isomerization reaction on the *N*-bis-alkylated sulfonamide $C_4F_9SO_2N(R)CH_2CH=CH_2$. Several attempts of alkylating **6** using first a base (KO$^t$Bu, K$_2$CO$_3$, Cs$_2$CO$_3$) and then an alkyl halide (MeI, EtI) were done, however analysis of the crude product obtained after addition of water to the reaction mixture followed by extraction in CH$_2$Cl$_2$, invariably showed the hitherto unreported allyltrialkylammonium salts **7** (R=Me) and **8** (R=Et) as the only identified products (Scheme 4)[54].



*Scheme 4*
*Reactions conditions: KO$^t$Bu in THF; K$_2$CO$_3$ or Cs$_2$CO$_3$ in DMF*

The last results made us clear that $C_4F_9SO_2N(R)CH_2CH=CH_2$ can be only obtained by condensation of $C_4F_9SO_2NHR$ with allyl bromide in the presence of a base.

## Conclusions

The ruthenium catalyst Ru-MACHO is an active catalyst for the hydrogenation of perfluorinated methyl esters under *very mild* conditions and represents a valid alternative to the use of metal hydrides. The double bound isomerization of environmentally compatible perfluoroalkyl allyl ethers to the corresponding propen-1-yl ethers (*E*+*Z* isomers) catalyzed by two ruthenium(II) complexes [RuClH(CO)(PPh$_3$)$_3$] and 2nd generation Grubbs' catalyst CatMETium_RF3 has been studied in solvent-free conditions. The latter, which has not been employed so far for the isomerization of allyl systems, presented a significantly higher efficiency in the studied reactions. In both cases the presence of an HCl scavenger such Bu$_3$N led to a dramatic improvement of the catalytic performances allowing 100% conversions with low catalytic loadings (down to 0.1 mol%) and short reaction times (1 h). Studies concerning the polymerization of the prepared perfluoroalkyl propen-1-yl ethers are under way.

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[53] *N*-allyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1 sulfonamide $C_4F_9SO_2NHCH_2CH=CH_2$ (6) is prepared in 86% yield by reacting 1,1,2,2,3,3,4,4,4-nonafluorobutane-1 sulfonyl fluoride with allylamine and sodium methoxide in methanol for 1 h at 40 °C. Successively methanol was removed with rotary evaporation and the white residue was dissolved in THF. The resulting suspension was filtered to eliminate NaF and dried again. No further purifications were needed; the product is a white solid

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with mp 145 °C. $^1$H NMR (300.1 MHz, $CD_3OD$): δ 5.93 (m, 1H, $CH_2CH=CH_2$), 5.42 (m, 2H, $CH_2CH=CH_2$), 3.55 (d, $^3J_{H,H}$=6,0 Hz, 2H, $CH_2CH=CH_2$); $^{13}$C NMR (75.5 MHz, $CD_3OD$): δ 130.9 ($CH_2CH=CH_2$), 121.6 ($CH_2CH=CH_2$), 120.5-105.5 ($C_3F_7$), 42.8 ($CH_2CH=CH_2$); $^{19}$F NMR (282.3 MHz, $CD_3OD$): δ -82.5 (t, $^3J_{F,F}$=9.5 Hz, $CF_3$), -115.9 (m, $CF_2$), -122.7 (s, $CF_2$), -127.2 (m, $CF_2$).

[54] In a typical procedure a flask with magnetic stirrer was charged with *N*-allyl-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide (1.500 g, 4.42 mmol) and 10 ml of anhydrous THF. After 5 min. 1.2 equivalents of KO$^t$Bu were added (0.623 g, 5.55 mmol) and after 1 hour, 5 equivalents of methyl iodide (22.10 mmol, 1.44 ml) were added to the suspension. The reaction was carried out at 25 °C for 18 h. The crude product was analyzed after addition of water and extraction in $CH_2Cl_2$ by NMR spectroscopy and ESI-MS spectrometry. Spectroscopic data for 7: $^1$H NMR (300.1 MHz, $CD_3OD$): δ 6.09 (m, 1H, =CH), 5.70 (m, 2H, =$CH_2$), 3.81 (d, $^3J_{H,H}$=4.0 Hz, 2H, $CH_2$), 3.12 (s, 9H, $NCH_3$). $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 129.5 (=CH), 126.4 (=$CH_2$), 69.5 (m, $NCH_2$), 53.1 (m, $NCH_3$). $^{19}$F NMR (282 MHz, $CDCl_3$): δ -81.2 (tt, $^3J$=10.0, $^4J$=2.8, $CF_3$), -111.8 (m, $CF_2$), -122.6 (m, $CF_2$), -127.2 (m, $CF_2$). ESI-MS (MeOH, m/z): 100 (100) $[N(CH_3)_3(CH_2CH=CH_2)]^+$; 299 (100) $[C_4F_9SO_3]^-$. The data for the cationic moiety are in perfect agreement with those reported for the chloride salt $[(CH_3)_3(allyl)N]Cl$ in Y.A. Lin, J.M. Chalker, B.G. Davis, *J. Am. Chem. Soc.,* 2010, **132**, 16805.