ELSEVIER



Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis of β -CF₃ ketones from trifluoromethylated allylic alcohols by ruthenium catalyzed isomerization

Vincent Bizet^a, Xavier Pannecoucke^a, Jean-Luc Renaud^{b,*}, Dominique Cahard^{a,*}

^a UMR 6014 CNRS de l'IRCOF, Université de Rouen et INSA de Rouen, Rue Tesnière, F-76821 Mont-Saint-Aignan Cedex, France ^b UMR CNRS 6507 LCMT, Université de Caen – ENSICAEN, Avenue du Maréchal Juin, 14050 Caen, France

ARTICLE INFO

ABSTRACT

Article history: Received 28 November 2012 Received in revised form 2 January 2013 Accepted 3 January 2013 Available online 31 January 2013

Keywords: Ruthenium Fluorinated compounds Catalysis Isomerization Atom economy This work describes the optimization process for the synthesis of β -trifluoromethylated ketones from trifluoromethylated allylic alcohols. This transformation proceeds through a ruthenium catalyzed isomerization under mild conditions with high atom economy. The effect of the CF₃ group was analyzed and it provides fundamental insights into the isomerization reaction.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The construction of $C(sp^3)$ – CF_3 stereogenic centers at the α position of a carbonyl function has been the subject of several successful investigations. Diastereoselective and enantioselective electrophilic trifluoromethylation have produced high level of asymmetric induction for mono- and dicarbonyl compounds [1]. Introducing a CF₃ group two carbons away from the carbonyl function at the remote β -position is a more challenging task because enolate chemistry is obviously not appropriate in this case. The direct $C(sp^3)$ -trifluoromethylation at the β -position of a carbonyl function is not known. Some rare examples of a $C(sp^2)$ -trifluoromethylation of α,β -unsaturated carbonyl compounds have been reported [2]. A unique case of nucleophilic conjugate addition of the CF₃ group to cyclohexenone is described by means of the Ruppert-Prakash reagent in the presence of one equivalent of the bulky Lewis acid aluminum tris(2,6-diphenylphenoxide) that activates the enone and masks the carbonyl function to allow the 1,4-addition to take place exclusively [3]. The radical iodotrifluoromethylation of acryloyl camphor sultams gave a 4:1 diastereomeric ratio (dr) but the new stereogenic center at α -position does not contain the CF₃ group [4]. It is only recently that Koksch, Czekelius and coworkers described a conjugate hydrotrifluoromethylation of α,β-unsaturated acyl-oxazolidinones featuring an internal olefin; however, the new C(sp³)–CF₃ stereogenic centers formed in the reaction is not at all controlled by the chiral auxiliary (1:1 dr) [5]. Thus, the direct introduction of a CF₃ group at the remote β-position with concomitant stereocontrol remains a topic to develop. Alternative synthetic approaches relies on asymmetric reactions of β-CF₃-α,β-unsaturated carbonyl compounds by transfer hydrogenation [6], hydrogenation [7], or conjugate addition [8]. These methods provide new C(sp³)–CF₃ stereogenic centers at the βposition by C–H, C–C, or C–heteroatom bond forming reactions with high enantioselectivities [9]. In addition, highly enantiospecific sigmatropic rearrangements of mixed ketene acetals [10] or allyloxyacetates [11] that proceed through well-defined cyclic transition states have demonstrated high level of chirality transfer.

We have recently developed a new approach to $C(sp^3)-CF_3$ stereogenic centers at the β -position of carbonyl functions by means of the catalytic isomerization of allylic alcohols (Fig. 1) [12]. The isomerization of allylic alcohols is an efficient, selective, atomeconomic, one-step process for isomerization of C=C bond of *O*allylic substrates into saturated carbonyl compounds. The overall process is equivalent to a sequential two-step oxidation and reduction reactions or vice versa. From a mechanistic point of view, a transition metal assists the migration of a hydrogen atom in the form of a hydride from C1 to C3, the intermediate enol then tautomerizes to the carbonyl compound [13]. Many transition metals have been employed in the isomerization of allylic alcohols; Ru, Rh and Ir catalysts dominate the field, in particular in the

^{*} Corresponding authors. Tel.: +33 2 35 52 24 66.

E-mail address: dominique.cahard@univ-rouen.fr (D. Cahard).

^{0022-1139/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jfluchem.2013.01.004



Fig. 1. Isomerization of CF₃ allylic alcohols.

development of the asymmetric version [12,14]. Before our work, the reaction has never been investigated with fluorinated allylic alcohols; consequently, we undertook an in-depth study with allylic alcohols that feature a CF₃ olefin moiety. Ruthenium catalysts were selected for this purpose because many ruthenium complexes, which are stable in many oxidation states, have already demonstrated high efficiency in the isomerization and because of their lower cost compared to Rh or Ir catalysts. In addition to the screening of various reaction parameters (catalyst, solvent, base, temperature, concentration), the impact of the CF₃ group position either at the α - or the β -position of the allylic alcohol was evaluated. Importantly, all the data collected through this study provided new insights in the reaction mechanism clearly highlighting the specific effect of the fluorine atoms in the isomerization.

2. Results and discussion

All the allylic alcohols required for the study were readily synthesized from commercially available sources of trifluoromethylated reactants (Scheme 1). Allylic alcohol **1** featuring an α -CF₃ group and a disubstituted olefin moiety was prepared via a

α -CF₃ disubstituted secondary allylic alcohols

PhCHO +
$$H_{CF_3}^{Br}$$
 $H_{S1\%}^{Zn, CuCl_{cat}}$ $H_{CF_3}^{OH}$ $H_{CF_3}^{OH}$ $H_{CF_3}^{OH}$ $H_{CF_3}^{OH}$ $H_{CF_3}^{OH}$

a-CF₃ trisubstituted secondary allylic alcohols

$$\begin{array}{c} O \\ Ph \\ HO \\ OH \\ CI^{-} \end{array} + \begin{array}{c} Ph_{3}P^{+} \\ HO \\ CI^{-} \end{array} + \begin{array}{c} NaNH_{2}, THF \\ HMDS_{cat} \\ 76\% \\ CF_{3} \end{array} \begin{array}{c} Ph \\ OH \\ CF_{3} \end{array} O \\ Ph \\ CF_{3} \\ CF_{3} \end{array} \begin{array}{c} DIBAL-H, CH_{2}CI_{2} \\ -78^{\circ}C, 5 \\ 68\% \\ CF_{3} \\ 2 \end{array} \begin{array}{c} Ph \\ OH \\ CF_{3} \\ CF_{3} \\ 2 \end{array}$$

β-CF₃ disubstituted secondary allylic alcohols

$$\begin{array}{c} & & \\$$

β-CF₃ trisubstituted secondary allylic alcohols

OH

(See Table 3 for the nature of R¹ and R² groups)

.

β-CF₃ tetrasubstituted secondary allylic alcohols

$$\begin{array}{cccc} Ph_{3}P^{+} & Ph & \overbrace{CF_{3}CO_{2}Et}^{NaNH_{2}, THF} & F_{3}C & H & \underbrace{t\text{-BuLi / TMEDA}}_{EtO & Ph} & \underbrace{t\text{-BuLi / TMEDA}}_{37\%} & F_{3}C & OH & 6 \end{array}$$

β-CF₃ trisubstituted primary allylic alcohols

$$\begin{array}{c} O \\ R^{1} \\ CF_{3} \end{array}^{+} (EtO)_{2}P \\ OEt \\ \end{array} \begin{array}{c} NaH, THF \\ 70-99\% \\ \end{array} \\ F_{3}C \\ \hline \begin{array}{c} R^{1} \\ Hm-n \\ \end{array} \\ OEt \\ \hline \begin{array}{c} DIBAL-H \\ CH_{2}CI_{2}, 0^{\circ}C \\ 92-99\% \\ \end{array} \\ F_{3}C \\ \hline \begin{array}{c} DIBAL-H \\ Sm-n \\ \end{array} \\ F_{3}C \\ \hline \begin{array}{c} Sm-n \\ Sm-n \\ \end{array} \\ \end{array}$$

Scheme 1. Preparation of a library of allylic alcohols.

literature procedure from 2-bromo-3,3,3-trifluoropropene [15]. Compound **2** having a trisubstituted olefin was obtained through a Wittig olefination of the hydrate of 3,3,3-trifluoro-1-phenylpropane-1,2-dione followed by DIBAL-H reduction of the carbonyl function. This synthetic route was developed in our laboratory and is applicable to other substitution patterns of α -CF₃- α , β -unsaturated carbonyl compounds [16]. Secondary allylic alcohol 3 featuring a β -CF₃ group and a disubstituted double bond was prepared from 2-bromo-3.3.3-trifluoropropene via the addition of the intermediate lithium acetylide to 2-phenylacetaldehyde followed by a stereoselective Red-Al reduction [17]. A series of trisubstituted derivatives of B-CF₃ allylic alcohols were synthesized from the corresponding trifluoromethylketones by a Wittig-Horner olefination that provides stereoselectively E-enones 4a-l and a further reduction by DIBAL-H to end up with products 5a-l [18]. One tetrasubstituted derivative **6** was also prepared by a literature procedure [19] even if this type of fully substituted allylic alcohol has rarely been successfully transposed because of the high steric hindrance [20]. It would be a great achievement if the trifluoromethylated substrate 6 could provide the isomerization product. Finally, β-CF₃ trisubstituted primary allylic alcohols **5m** and **5n** were obtained by a straightforward sequence olefination/ reduction [21].

With eighteen allylic alcohols at hand, our initial investigation started with a survey of the catalytic activity of different ruthenium complexes in the isomerization of the β -CF₃ secondary allylic alcohol **5a** (Table 1). The reactions were performed at temperatures comprised between 30 and 60 °C using 10 mol % of catalyst in toluene (0.5 M) in the presence of one equivalent of Cs₂CO₃ to give the ketone **7a** as the expected product accompanied

OН

Bn





Entry	Catalyst	Time (h)	<i>T</i> (°C)	7a (yield %) ^a	4a (yield %) ^a
1	$RuCl_2(PPh_3)_3$	1	30	90	9
2	$RuCl_2(PPh_3)_3$ (1 mol%)	2	30	90	<1
3	$[Ru(Cp^*)(MeCN)_3]PF_6$	3	50	56	<1
4	$(\operatorname{RuCl}_2(\operatorname{C}_6\operatorname{H}_6))_2$	3	50	94	2
5	$(\operatorname{RuCl}_2(p-\operatorname{Cym}))_2$	6	50	72	6
6	$RuCl_2(p-Cym)(PMe_3)$	6	50	30	4
7	$[RuCl(p-Cym) (PMe_3)_2]PF_6$	5	48	4	
8	$RuCl_3 \cdot xH_2O$	5	60	2	4
9	(RuCl ₂ (Indenyl)) ₂	15	50	61	4
10	$[RuCl_2(R-BINAP)]_x$	8	50	77	3

(Table 1, entry 2).

the catalyst loading to 1 mol%; furthermore, the reaction became

very clean and quantitative without detection of side product

whereas other solvents, e.g. CH₃CN, CH₂Cl₂, THF, *i*-PrOH, PhCF₃,

failed to produce the target β -CF₃ ketone in good yields (Table 2,

entries 1-6) as it is also the case for a deviation of the concentration

of the reaction mixture (Table 2, entries 7–9). Indeed, an optimized

0.5 M toluene solution of the substrate permits full conversion. It is

worth noting that the use of wet toluene does not impede the

reaction course [22]. The amount and the nature of the base are

important parameters since in the absence of base there is no

conversion and inorganic bases, in particular Cs₂CO₃, are preferred

to organic ones (Table 2, entries 10-15). A catalytic amount of

Cs₂CO₃ should theoretically allows the reaction to go to comple-

tion, but in practice, one equivalent of base is really needed

carbonyl compounds, we next examined the scope of the reaction with different β -CF₃ substituted secondary allylic alcohols and we

undertook a comparison of our trifluoromethylated allylic alcohols

with non-fluorinated substrates. From all the β -CF₃ substituted

Encouraged by the discovery of this new route to β -CF₃

probably due to the heterogeneity of the system [23].

Toluene is the most appropriate solvent for this isomerization

^a Yields were determined by ¹⁹F NMR using trifluorotoluene as internal standard.

by 1-9% of enone 4a. Application of a threshold temperature appeared necessary to allow the reaction to happen within a reasonable time. Unlike the isomerization of B-disubstituted substrates with Ru or Rh complexes that typically required temperatures in the range 70–100 °C, it is noteworthy that we conduct the reactions between 30 and 60 °C for sterically more hindered trisubstituted substrates. Concerning the nature of the ruthenium complexes, ruthenium(II) are suitable while ruthenium(III) is not active in this isomerization reaction. From Table 1, we can also conclude that electron rich ancillary ligands, such as pentamethylcyclopentadienyl or trimethylphosphine, have a detrimental effect in this process (entries 3, 6, 7 or 5 versus 4). Although the dimeric $(RuCl_2(C_6H_6))_2$ gave a high conversion at 50 °C for 3 h (Table 1, entry 4), a good comprise was found with the ruthenium(II) complex RuCl₂(PPh₃)₃, which is much cheaper, and provides a complete conversion after one hour at 30 °C (Table 1, entry 1). The desired β -CF₃ saturated ketone **7a** is always accompanied by the corresponding enone 4a resulting of an incomplete redox process. In this case, the abstraction of the hydrogen α to the OH group by the metal is not followed by a subsequent 1,4-hydride addition. Fortunately, we were able to minimize the proportion of enone 4a to less than 1% by lowering

Table 2

Screening of solvent, concentration and base.



Entry	Solvent	Concentration (M)	Base	7a (yield %) ^a	4a (yield %) ^a
1	toluene	0.5	Cs ₂ CO ₃	90	9
2	CH ₃ CN	0.5	Cs ₂ CO ₃	4	2
3	CH ₂ Cl ₂	0.5	Cs ₂ CO ₃	<1	<1
4	THF	0.5	Cs ₂ CO ₃	<1	<1
5	<i>i</i> -PrOH	0.5	Cs ₂ CO ₃	<1	<1
6	PhCF ₃	0.5	Cs ₂ CO ₃	37	4
7	toluene	1	Cs ₂ CO ₃	18	10
8	toluene	0.25	Cs ₂ CO ₃	15	4
9	toluene	0.1	Cs ₂ CO ₃	0	<1
10	toluene	0.5	Et ₃ N	<1	<1
11	toluene	0.5	DBU	<1	<1
12	toluene	0.5	<i>t</i> -BuOK	28	<1
13	toluene	0.5	K ₂ CO ₃	0	0
14	toluene	0.5	K ₃ PO ₄	16	1
15	toluene	0.5	without	0	0

^a Yields were determined by ¹⁹F NMR using trifluorotoluene as internal standard.

. .

Table 3

Isomerization of various β -CF₃ substituted allylic alcohols.

$$F_{3}C \xrightarrow{R^{1} OH} R^{2} \xrightarrow{1 \text{ mol}\% \text{ RuCl}_{2}(\text{PPh}_{3})_{3}}_{\text{toluene (0.5 M)}} F_{3}C \xrightarrow{R^{1} O} R^{2}$$

Entry		Allylic alcohol		Time (h)	T (°C)	Ketone (yield %) ^a
		R ¹	R ²			
1	5a	Ph	Ph	2	30	7a , 95
2	5b	Me	Ph	4	30	7b , 76
3	5c	Bn	Ph	5	30	7c , 65
4	5d	p-MeOC ₆ H ₄	Ph	3	30	7d , 73
5	5e	$p-CF_3C_6H_4$	Ph	2	30	7e , 66
6	5f	Ph	Me	2	60	7f , 93
7	5g	Bn	Me	3	30	7g , 63
8	5h	o-MeOC ₆ H ₄	Me	2	60	7h , 71
9	5i	p-MeOC ₆ H ₄	Me	3	60	7i , 76
10	5j	$p-BrC_6H_4$	Ph	2	30	7 j, 77
11	5k	Ph	t-Bu	12	70	7k , 75
12	51	$(H_3C)_2C=CH(CH_2)_2$	Ph	24	50	71 , 93
13	3	Н	Bn	3	40	8 , 40

Yields for analytically pur products (all conversions determined by ¹⁹F NMR using trifluorotoluene as internal standard were >99% with less than 5% side-products). Yields are not optimized except for entry 1.

secondary allylic alcohols, the reaction lead to saturated ketones quantitatively (Table 3). Substrates featuring a rather sterically hindered trisubstituted alkene moiety (Table 3, entries 1-12) behave equally well to one with a disubstituted alkene (Table 3. entry 13), clearly demonstrating that the steric bulk of the CF_3 group, whose molar volume is similar to that of an isopropyl group, is not detrimental to the reactivity. Attempts to isolate the isomerization product of β-CF₃ substituted primary allylic alcohols **5m** ($R^1 = Ph$) or **5n** ($R^1 = Bn$) led to the corresponding saturated alcohol as the main product along with aldol condensation products. In these two cases, the isomerization took place giving the expected aldehydes, which are prone to reduction under the reaction conditions leading to the saturated alcohols and to α -CH deprotonation leading to aldol products. The highly sterically hindered β -CF₃ tetrasubstituted secondary allylic alcohol **6** was also submitted to the isomerization conditions but no desired rearranged product was observed even after 15 h at 110 °C. The isomerization of allylic alcohols is fostered thanks to the CF₃ group; however, this capability of the CF₃ group is annihilated in the special case of a tetrasubstituted alkene.

The effect of the CF₃ substituent was analyzed in a comparison of our trifluoromethylated allylic alcohols with non-fluorinated substrates. Replacement of the CF₃ group in **5a** by a methyl group (either the *E* or *Z* isomer) required both a much higher reaction temperature and a longer reaction time but the yields remained poor and some by-products were observed (Scheme 2, $9 \rightarrow 10$). Even, a less hindered disubstituted substrate failed to provide the isomerized product in good yield (Scheme 2, $11 \rightarrow 12$). These observations

$$\begin{array}{c} \begin{array}{c} Ph & OH \\ Me & & Ph \end{array} & \begin{array}{c} 1 \mod \% \operatorname{RuCl}_2(\operatorname{PPh}_3)_3 \\ \hline \text{toluene, } \operatorname{Cs}_2\operatorname{CO}_3 \\ 100^\circ\operatorname{C}, 15h \end{array} & \begin{array}{c} Ph & O \\ Me & Ph \end{array} & \begin{array}{c} 10 \\ Me & Ph \end{array} & \begin{array}{c} 10 \\ 10\% \text{ from } \textbf{Z-9} \\ 21\% \text{ from } \textbf{E-9} \end{array} \\ \begin{array}{c} OH \\ Ph & \begin{array}{c} 1 \mod \% \operatorname{RuCl}_2(\operatorname{PPh}_3)_3 \\ \hline \text{toluene, } \operatorname{Cs}_2\operatorname{CO}_3 \\ 30^\circ\operatorname{C}, 9h \end{array} & \begin{array}{c} O \\ Ph & \begin{array}{c} 0 \\ Ph & Ph \end{array} & \begin{array}{c} 12 \\ 33\% \end{array} & \begin{array}{c} 33\% \end{array} \end{array}$$

Scheme 2. Comparison with non-fluorinated substrates.

clearly indicate that the bulkiness of the CF₃ substituent does not impede the reaction and that the electron-withdrawing effect of the CF_3 very significantly enhances the rate of the reaction.

Although there are several methods in the literature for the direct trifluoromethylation of carbonyl compounds, the access to α -CF₃ carbonyls by isomerization is not known. An extension of the work done with β -CF₃ allylic alcohols would be the study of α -CF₃ allyl alcohols 1 and 2 (see Scheme 1 for their preparation). However, 1 and 2 appeared inert under the isomerization conditions. For this type of substrate, the strongly electronwithdrawing CF₃ group weakens the hydride character of the hydrogen atom at the alcohol function and prevents hydride abstraction by the ruthenium complex.

The mechanism of the isomerization has been investigated in details [13f,24]; however, the case of trifluoromethylated allylic alcohols deserves a specific interest. Indeed, we have demonstrated by kinetic studies, deuterium-labeling experiments, crossover experiments, and X-ray analyses that the isomerization of β -CF₃ allylic alcohols into the corresponding saturated ketones is a ruthenium-mediated syn-specific 1,3-hydrogen shift [12]. The main differences in reactivity between β -CF₃ allylic alcohols and non-fluorinated counterparts are: (i) the electron-withdrawing CF₃ group accelerates the overall reaction rate, (ii) the bulkiness of the CF₃ group does not impede the reaction even for trisubstituted substrates, (iii) the rate-determining step in the isomerization of β -CF₃ substituted substrates is the β -elimination while it is the insertion for non-fluorinated substrates. The successive steps of the mechanism are proposed in Fig. 2, which also illustrates the enantiospecificity of the process from optically pure (R)-5a.

The fact that the intermediate enone stays coordinated to the metal combined with a rapid insertion step make the enantiospecific isomerization highly efficient with complete retention of the chiral information. Since chiral optically enriched allylic alcohols are readily available, the enantiospecific approach is a convenient method to access chiral non-racemic β -CF₃ carbonyl compounds. However, the mechanism of the reaction does not argue in favor of a direct enantioselective version starting from racemic allylic alcohols by means of a chiral ruthenium catalyst. Indeed, all our attempts to use chiral Ru(II) complexes as catalyst in the isomerization failed to deliver a reasonable level of stereoinduction.



Fig. 2. Reaction mechanism

3. Conclusion

We have developed straightforward conditions for the isomerization of β -trifluoromethylated secondary allylic alcohols. The ruthenium(II) complex RuCl₂(PPh₃)₃ is suitable to conduct the intramolecular 1,3-hydrogen shift at temperatures comprised between 30 and 70 °C in toluene in the presence of Cs₂CO₃. The rather low reaction temperature for this transformation as well as the easy reaction with trisubstituted allylic alcohols are ascribed to the electron-withdrawing effect of the CF₃ group, which strongly accelerate the insertion step compared to non-fluorinated substrates. A mechanistic study revealed that the rate-determining step is the β -elimination and that the isomerization proceeds through a metal-mediated *syn*-specific 1,3-hydrogen shift allowing an enantiospecific version from optically enriched allylic alcohols with a total transfer of chirality. However, appropriate conditions for an enantioselective version remain to be found.

4. Experimental

4.1. General remarks

¹H (300 MHz), ¹³C (75.5 MHz) and ¹⁹F (282 MHz) NMR spectra were recorded on Bruker AVANCE 300. Chemical shifts in NMR spectra are reported in parts per million from TMS or CFCl₃ resonance as the internal standard. IR spectra were recorded on a Perkin-Elmer IRFT 1650 spectrometer. The conversion and ratio of the corresponding products were determined by ¹⁹F NMR analysis adopting α , α , α -trifluorotoluene as internal standard with D1 value = 5 s. Unless otherwise noted, all reagents were purchased from commercial sources and were used without further purification. Some ruthenium catalysts were generously provided by Johnson-Matthey (UK).

4.2. Representative procedure for the isomerization

In a Schlenk tube under inert atmosphere, were added the (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-ol **5a** (278.27 mg, 1 mmol), degassed toluene (2 mL), cesium carbonate (325.8 mg, 1 mmol), and $RuCl_2(PPh_3)_3$ (9.6 mg, 0.01 mmol). The reaction

mixture was heated for 2 h at 30 °C. Then, the reaction mixture was filtered through a pad of celite, concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate: 99/1) to give the desired 4,4,4-trifluoro-1,3-diphenylbutan-1-one **7a**. Yield: 95%; white solid (mp = 66 °C). ¹H NMR (CDCl₃) δ 3.52 (dd, ¹H, *J* = 17.8 Hz, *J* = 4.3 Hz), 3.64 (dd, ¹H, *J* = 17.8 Hz, *J* = 8.8 Hz), 4.11–4.25 (m, ¹H), 7.18–7.87 (m, ¹⁰H); ¹³C NMR (CDCl₃) δ 38.4 (q,*J* = 2.0 Hz), 44.9 (q, *J* = 27.4 Hz), 127.1 (q, *J* = 279.5 Hz), 128.2, 128.4, 128.8, 128.9, 129.2, 133.7, 134.7 (q, *J* = 1.9 Hz), 136.4, 195.4; ¹⁹F NMR (CDCl₃) δ –70.2 (d, *J* = 9.7 Hz); HRMS Calcd for C₁₆H₁₃F₃O (M+), 278.0918, Found 278.0920; IR (neat) ν 3068, 1680, 1300, 1250, 1187, 1153, 1103 cm⁻¹.

Acknowledgments

This work is promoted by the interregional CRUNCh network. V.B. thanks the Région Haute-Normandie for a fellowship. Johnson-Matthey is acknowledged for a generous loan of catalysts.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013. 01.004.

References

- [1] (a) J.-A. Ma, D. Cahard, J. Fluorine. Chem. 128 (2007) 975-996;
 - (b) J.-A. Ma, D. Cahard, Chem. Rev. 108 (2008) PR1-PR43;
 - (c) S. Noritake, N. Shibata, Y. Nomura, Y. Huang, A. Matsnev, S. Nakamura, T. Toru, D. Cahard, Org. Biomol. Chem. (2009) 3599–3604;
 - (d) D.A. Nagib, M.E. Scott, D.W.C. MacMillan, J. Am. Chem. Soc. 131 (2009) 10875-10877
 - (e) A.E. Allen, D.W.C. MacMillan, J. Am. Chem. Soc. 132 (2010) 4986–4987;
 - (f) P.V. Pham, D.A. Nagib, D.W.C. MacMillan, Angew. Chem. Int. 50 (2011) 6119-6122:
 - (g) A.T. Herrmann, L.L. Smith, A. Zakarian, J. Am. Chem. Soc. 134 (2012) 6976-6979;
 - (h) Q.-H. Deng, H. Wadepohl, L.H. Gade, J. Am. Chem. Soc. 134 (2012) 10769-10772;
 - (i) V. Matousek, A. Togni, V. Bizet, D. Cahard, Org. Lett. 13 (2011) 5762-5765.
- [2] (a) S. Large, N. Roques, B.R. Langlois, J. Org. Chem. 65 (2000) 8848–8856;
 (b) V.Y. Sosnovskikh, D.V. Sevenard, B.I. Usachev, G.-V. Röschenthaler, Tetrahedron Lett. 44 (2003) 2097–2099;

(c) V.Y. Sosnovskikh, B.I. Usachev, D.V. Sevenard, G.-V. Röschenthaler, J. Org. Chem. 68 (2003) 7747–7754;

(d) V.Y. Sosnovskikh, B.I. Usachev, D.V. Sevenard, G.-V. Röschenthaler, J. Fluorine Chem. 126 (2005) 779–784.

[3] (a) K. Maruoka, H. Imoto, S. Saito, H. Yamamoto, J. Am. Chem. Soc. 116 (1994) 4131–4132;

(b) D.V. Sevenard, V.Y. Sosnovskikh, A.A. Kolomeitsev, M.H. Königsmann, G.-V. Röschenthaler, Tetrahedron Lett. 44 (2003) 7623–7627.

- [4] T. Yajima, H. Nagano, Org. Lett. 9 (2007) 2513–2515.
- [5] H. Erdbrink, I. Peuser, U.I.M. Gerling, D. Lentz, B. Koksch, C. Czekelius, Org. Biomol. Chem. (2012) 8583–8586.
- [6] Y. Tsuchiya, Y. Hamashima, M. Sodeoka, Org. Lett. 8 (2006) 4851–4854.
- (7) (a) G. Szöllösi, T. Varga, K. Felföldi, S. Cserényi, M. Bartók, Catal. Commun. 9 (2008) 421–424;
 - (b) J.A. Pigza, T. Quach, T.F. Molinski, J. Org. Chem. 74 (2009) 5510-5515;

(c) A. Alimardanov, A. Nikitenko, T.J. Connolly, G. Feigelson, A.W. Chan, Z. Ding, M. Ghosh, X. Shi, J. Ren, E. Hansen, R. Farr, M. MacEwan, S. Tadayon, D.M. Springer, A.F. Kreft, D.M. Ho, J.R. Potoski, Org. Process Res. Devel. 13 (2009) 1161–1168;
 (d) C. Benhaim, L. Bouchard, G. Pelletier, J. Sellstedt, L. Kristofova, S. Daigneault, Org. Lett. 12 (2010) 2008–2011.

[8] (a) T. Yamazaki, N. Shinohara, T. Kitazume, S. Sato, J. Fluorine Chem. 97 (1999) 91–96;

(b) T. Konno, T. Tanaka, T. Miyabe, A. Morigaki, T. Ishihara, Tetrahedron Lett. 49 (2008) 2106–2110;

- (c) Y. Huang, E. Tokunaga, S. Suzuki, M. Shiro, N. Shibata, Org. Lett. 12 (2010) 1136-1138;
- (d) N. Shinohara, J. Haga, T. Yamazaki, T. Kitazume, S. Nakamura, J. Org. Chem. 60 (1995) 4363–4374;
- (e) V.A. Soloshonok, D.V. Avilov, V.P. Kukhar, L.V. Meervelt, N. Mischenko, Tetrahedron Lett. 38 (1997) 4903-4904;
- (f) W. Wang, X. Lian, D. Chen, X. Liu, L. Lin, X. Feng, Chem. Commun. 47 (2011) 7821-7823;

(g) H. Kawai, T. Kitayama, E. Tokunaga, T. Matsumoto, H. Sato, M. Shiro, N. Shibata, Chem. Commun. 48 (2012) 4067–4069;

(h) A. Morigaki, T. Tanaka, T. Miyabe, T. Ishihara, T. Konno, Org. Biomol. Chem. 11 (2013) 586-595

- [9] J. Nie, H.-C. Guo, D. Cahard, J.-A. Ma, Chem. Rev. 111 (2011) 455–529.
- [10] (a) T. Konno, H. Nakano, T. Kitazume, J. Fluorine Chem. 86 (1997) 81–87;
 (b) T. Konno, T. Ishihara, H. Yamanaka, Tetrahedron Lett. 41 (2000) 8467–8472;
 (c) T. Konno, T. Daitoh, T. Ishihara, H. Yamanaka, Tetrahedron Asymmet. 12 (2001) 2743–2748;
- (d) B. Jiang, Y. Liu, W.-S. Zhou, J. Org. Chem. 65 (2000) 6231–6236.
- [11] (a) T. Konno, T. Kitazume, Tetrahedron Asymmet. 8 (1997) 223–230;
 (b) T. Ichikawa, T. Kawasaki-Takasuka, S. Yamada, T. Yamazaki, T. Kubota, J. Fluorine Chem. (2012), http://dx.doi.org/10.1016/j.jfluchem. 2012.1010.1013;

(c) T. Konno, H. Umetani, T. Kitazume, J. Org. Chem. 62 (1997) 137-150;

- (d) T. Yamazaki, N. Shinohara, T. Kitazume, S. Sato, J. Org. Chem. 60 (1995) 8140-8141.
- [12] V. Bizet, X. Pannecoucke, J.-L. Renaud, D. Cahard, Angew. Chem. Int. 51 (2012) 6467–6470.
- [13] (a) R. Uma, C. Crévisy, R. Grée, Chem. Rev. 103 (2003) 27–51;
 (b) v. RC, d. Drift, E. Bouwman, E. Drent, J. Organomet. Chem. 650 (2002) 1–24;
 (c) L. Mantilli, C. Mazet, Chem. Lett. 40 (2011) 341–344;
 - (d) V. Cadierno, P. Crochet, J. Gimeno, Synlett (2008) 1105-1124;
 - (e) B. Martin-Matute, K. Bogar, M. Edin, F.B. Kaynak, J.-E. Bäckvall, Chem. Eur. J. 11 (2005) 5832–5842;
 - (f) N. Ahlsten, A. Bartoszewicz, B. Martin-Matute, Dalton trans. 41 (2012) 1660–1670.
- [14] (a) M. Ito, S. Kitahara, T. Ikariya, J. Am. Chem. Soc. 127 (2005) 6172–6173;
 (b) L. Mantilli, D. Gérard, S. Torche, C. Besnard, C. Mazet, Chem. Eur. J. 16 (2010) 12736–12745;
 - (c) L. Mantilli, C. Mazet, Chem. Commun. 46 (2010) 445-447;
 - (d) K. Tanaka, G.C. Fu, J. Org. Chem. 66 (2001) 8177-8186;
 - (e) J.-Q. Li, B. Peters, P.G. Andersson, Chem. Eur. J. 17 (2011) 11143-11145;
 - (f) R. Wu, M.G. Beauchamps, J.M. Laquidara, J.R. Sowa Jr., Angew, Chem. Int. 51 (2012) 2106–2110.
- [15] F. Hong, X. Tang, C. Hu, J. Chem. Soc., Chem. Commun. (1994) 289–290.
- [16] V. Bizet, PhD thesis (2012).
- [17] T. Yamazaki, K. Mizutani, T. Kitazume, J. Org. Chem. 60 (1995) 6046-6056.
- [18] T. Konno, T. Takehana, M. Mishima, T. Ishihara, J. Org. Chem. 71 (2006) 3545-3550.
- [19] (a) J.P. Bégué, D. Bonnet-Delpon, D. Mesureur, G. Nee, S.W. Wu, J. Org. Chem. 57 (1992) 3807–3814;
- (b) D. Bouvet, H. Sdassi, M. Ourévitch, D. Bonnet-Delpon, J. Org. Chem. 65 (2000) 2104–2107.
- [20] L. Mantilli, C. Mazet, Tetrahedron Lett. 50 (2009) 4141-4144.
- M. Kimura, T. Yamazaki, T. Kitazume, T. Kubota, Org. Lett. 6 (2004) 4651–4654.
 (a) V. Cadierno, S.E. Garcia-Garrido, J. Gimeno, Chem. Commun. (2004) 232–233;
 (b) A. Bouziane, B. Carboni, C. Bruneau, F. Carreaux, J.-L. Renaud, Tetrahedron 64 (2008) 11745–11750;
 (c) N. Ahlsten, H. Lundberg, B. Martin-Matute, Green Chem. 12 (2010) 1628–
 - (c) N. Ahlsten, H. Lundberg, B. Martin-Matute, Green Chem. 12 (2010) 1628– 1633.
- [23] J. Garcia-Alvarez, J. Gimeno, F.J. Suarez, Organometallics 30 (2011) 2893-2896.
- [24] (a) A. Varela-Alvarez, J.A. Sordo, E. Piedra, N. Nebra, V. Cadierno, J. Gimeno, Chem. Eur. J. 17 (2011) 10583-10599;
 - (b) B.M. Trost, R.C. Livingston, J. Am. Chem. Soc. 130 (2008) 11970-11978;
 - (c) B.M. Trost, R.J. Kulawiec, Tetrahedron Lett. 32 (1991) 3039-3042;
 - (d) B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 115 (1993) 2027-2036;
 - (e) V. Cadierno, S.E. Garcia-Garrido, J. Gimeno, A. Varela-Alvarez, J.A. Sordo, J. Am. Chem. Soc. 128 (2006) 1360–1370.