Tetrahedron xxx (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

Synthesis and reactivity of trifluoromethyl substituted oxaziridines

Serena Perrone [a], Francesca Rosato [a], Antonio Salomone [a,b], Luigino Troisi [a,*]

[a] Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, University of Salento, Via Prov.le Lecce-Monteroni, 73100 Lecce, Italy
[b] Dipartimento di Farmacia – Scienze del Farmaco, Università degli Studi di Bari "A. Moro", Consorzio C.I.N.M.P.I.S., Via E. Orabona, 4, 70125 Bari, Italy

ARTICLE INFO

Article history:
Received 20 November 2012
Received in revised form 19 February 2013
Accepted 11 March 2013
Available online xxx

This paper is dedicated to the memory of Professor Ludovico Ronzini for its precious contribution to the organic chemistry teaching

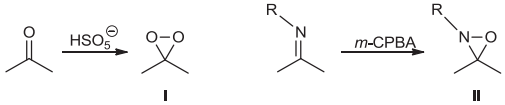
Keywords:
Oxaziridine
Trifluoromethyl group
Oxidation
Epoxide
Sulfoxide

ABSTRACT

This article reports a simple and efficient synthesis of methyl(trifluoromethyl)oxaziridines, a new family of organic oxidizing agents. A detailed study on their oxygen transfer capability with respect to styrene, thioanisole and benzyl alcohol as model substrates for the synthesis of epoxides, sulfoxides and aldehydes is described. Moreover, an oxaziridine auto-oxidation at nitrogen and/or *N*-benzylic carbon is also reported.

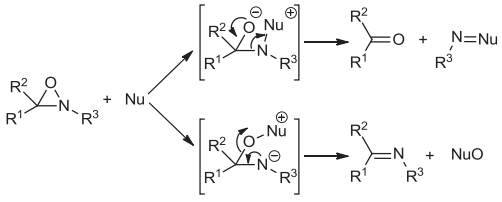
1. Introduction

Dioxiranes **I** and oxaziridines **II** are small heterocyclic compounds that can be prepared by oxidation of ketones and imines with peroxomonosulfate[1] and *meta*-chloroperbenzoic acid[2] (*m*-CPBA), respectively (Scheme 1). Due to the strained three membered ring, both heterocycles are versatile reagents in organic synthesis and their uses have rapidly grown in the past several years.



Scheme 1. Synthesis of dioxiranes and oxaziridines.

Dioxiranes are powerful oxygen atom donors.[3] Their reactivity ranges from the transfer of an oxygen atom to 'unactivated' C–H bonds of saturated hydrocarbons,[3] to epoxidations,[4] to the oxidation of heteroatoms containing a lone pair, such as amines[5] and sulfides.[2b,6] Oxaziridines play a central role in organic chemistry as usually aprotic, neutral species capable of transferring electrophilic oxygen or nitrogen to a plethora of nucleophiles (Scheme 2).[7] The predominance of one process over another can be affected by varying the substitution pattern on nitrogen. In general, oxaziridines with small groups on nitrogen (H, Me) act as aminating agents,[8] whereas those *N*-substituted with bulky or electron-withdrawing groups preferentially transfer the oxygen atom.[9]



Scheme 2. Oxaziridines as heteroatom transfer reagents.

Electron-deficient oxaziridines, such as *N*-sulfonyl oxaziridines,[7] have been widely used in the oxidation of sulfides to sulfoxides, in the epoxidation of alkenes and in the hydroxylation of enolates; amines, enamines and organometallic reagents can be oxygenated as well.

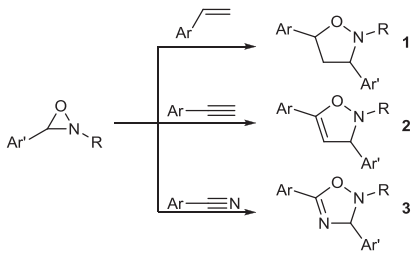
The versatility of oxaziridines extends far beyond their use as heteroatom transfer reagents. Indeed, oxaziridines have been

* Corresponding author. Fax: +39 0832 298732; e-mail address: luigino.troisi@unisalento.it (L. Troisi).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.03.048

shown also to undergo cycloaddition reactions with a variety of heterocumulenes, such as ketenes, ketenimines, isocyanates and isothiocyanates, to afford a diverse set of five-membered heterocycles.[10]

Moreover, recently, a highly efficient [3+2] cycloaddition reaction of 2-alkyl-3-aryloxaziridines with alkenes,[11,12] alkynes[13] and nitriles,[14] leading to isoxazolidines **1**, 4-isoxazolines **2** and 2,3-dihydro-1,2,4-oxadiazoles **3**, respectively, was described (Scheme 3).



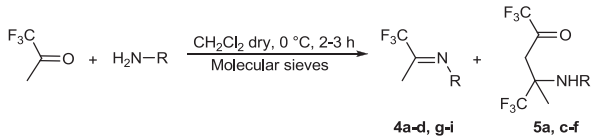
Scheme 3. [3+2] cycloaddition reactions between oxaziridines and dipolarophiles.

It is well known that methyl(trifluoromethyl)dioxirane (TFDO) is a more effective oxidizing agent than dimethyldioxirane (DDO). The substitution of a methyl- with a trifluoromethyl group results in a greater propensity of TFDO to act as an electrophilic oxidant with respect to DDO.[15] The introduction of a trifluoromethyl group in position 3 of the oxaziridine ring could lead to similar results increasing the reactivity of these compounds. For this reason, several novel methyl(trifluoromethyl)oxaziridines were synthesized and their reactivity as oxygen transfer reagents was studied. Herein, we report our findings.

2. Results and discussion

The Schiff bases **4a**–**d**, **g**–**i** were readily synthesized by the direct condensation of 1,1,1-trifluoropropanone and an appropriate primary amine (Table 1).

Table 1
(1,1,1-Trifluoropropanylidene)amines synthesis



4a-d, g-i **5a, c-f**

Entry	R	Product distribution (%)[a]		Yield (%)[b]
		4:**5**		
1	CH_2Ph	**4a** (97)	**5a** (3)	98
2	$CH(Ph)_2$	**4b** (100)	**5b** (—)	97
3	$CH(CH_3)Ph$	**4c** (95)	**5c** (5)	98
4	*n*-Butyl	**4d** (96)	**5d** (4)	96
5	*i*-Propyl	**4e** (—)	**5e** (100)	95
6	*t*-Butyl	**4f** (—)	**5f** (100)	98
7	Ph	**4g** (100)	**5g** (—)	96
8	4-Cl(C_6H_4)	**4h** (100)	**5h** (—)	97
9	4-CH_3(C_6H_4)	**4i** (100)	**5i** (—)	95

[a] Measured by ^{1}H NMR spectroscopic analysis.
[b] Isolated yields.

In particular, an excess of 1,1,1-trifluoropropanone (2.0 equiv) was added to an ice cooled solution of a primary amine (1.0 equiv) in CH_2Cl_2, in the presence of molecular sieves, according to Taguchi's protocol.[16] The reaction mixture was stirred for 2–3 h at 0–5 °C and monitored by gas chromatography. When the reaction was complete, the molecular sieves were filtered off and the solvent evaporated obtaining methyl(trifluoromethyl)imines **4a**–**d**, **g**–**i** and/or β-aminoketones **5a**, **c**–**f** (Table 1). The distribution of products **4**–**5** depends on the stereoelectronic nature of the starting amine.

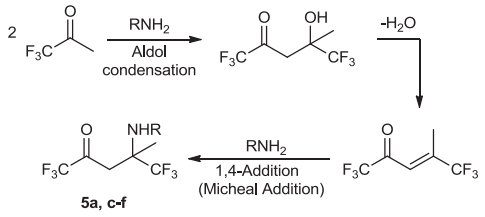
When benzyl-amines, such as benzylamine and 1-phenylethanamine, are reacted with 1,1,1-trifluoropropanone in the reaction conditions described above, they form the corresponding Schiff base and a trace amount of the β-aminoketone (Table 1, entries 1 and 3). Purification by chromatography on silica gel of the crude mixture afforded the (*E*)-methyl(trifluoromethyl) imines **4a**, **c** and β-aminoketones **5a**, **c** (Table 1, entries 1 and 3). The imine **4b** was instead the only product obtained in the reaction between *C*,*C*-diphenyl-methylamine and 1,1,1-trifluoropropanone (Table 1, entry 2). An important characteristic of the imines **4** is that they exist only as *E* isomers (verified by NOESY).[17]

A similar trend was found in the reaction carried out on *n*-butylamine as primary amine; after a 2 h period, the imine (*E*)-*N*-(1,1,1-trifluoropropan-2-ylidene)butan-1-amine **4d** together with small quantities of the β-aminoketone **5d** were identified in the reaction mixture, and subsequently isolated by chromatography in 96% total yield (Table 1, entry 4).

In the reaction with 1,1,1-trifluoropropanone, the aromatic amines, much less basic than aliphatic ones, provided only the Schiff bases **4g**–**i** in 95–97% total yield (Table 1, entries 7–9).

In contrast, isopropylamine and *tert*-butylamine, characterized by a high steric hindrance and thus by a poorer nucleophilicity compared with the other aliphatic amines, led to the exclusive formation of β-aminoketones **5e** and **5f**, in 95% and 98% yield, respectively (Table 1, entries 5–6).

A possible mechanism for the formation of the β-aminoketones **5a**, **c**–**f** is proposed in Scheme 4.



Scheme 4. Suggested mechanism for β-aminoketones formation.

We hypothesize that, among the aliphatic amines, the poor nucleophilicity of isopropylamine and *tert*-butylamine (Table 1, entries 5–6), determine the conditions for the aldol condensation of 1,1,1-trifluoropropanone to produce a β-hydroxyketone. The aldol product could dehydrate rather easily under the reaction conditions (presence of molecular sieves) to give a α,β-unsaturated carbonyl compound. Due to the presence a trifluoromethyl group on the β-carbon, this conjugated alkene is a reactive Michael acceptor, characterized by a very electrophilic conjugated C=C bond. For this reason, nucleophiles, such as the primary amine used in the reaction, could undergo 1,4-conjugate addition (Michael addition) with the α,β-unsaturated carbonyl compounds to give the β-aminoketones **5a**, **c**–**f** (Scheme 4).

By monitoring the reaction over time, no trace of imine was detected, also in the reaction carried out with an excess of amine.

For the other more nucleophilic aliphatic amines (Table 1, entries 1–4) and less basic aromatic amines (Table 1, entries 7–9) a prevalent nucleophilic attack to the ketone, could favour the imine formation instead of promoting the aldol condensation.

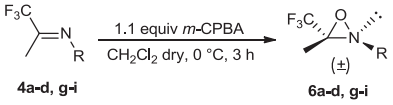
Novel methyl(trifluoromethyl)oxaziridines (**6a**–**d**, **g**–**i**) have been prepared from the corresponding imines according to a method previously reported.[2]

In particular, when *m*-CPBA (1.1 equiv) was added to a solution of **4a** in 20 mL of CH_2Cl_2 at 0 °C, after a 3 h period, GC and GC–MS

showed the total conversion of the starting imine into a new product.

The reaction work-up was performed in a non aqueous way, according to a modified Emmons's procedure:[2] the crude mixture was stirred with excess powdered anhydrous sodium carbonate with neutralization of the acid reaction mixture until carbon dioxide evolution ceased. After filtration, the solvent was evaporated in vacuo at room temperature affording the oxaziridine **6a** as a pure compound (yield=97%; Table 2, entry 1). NOESY revealed the configuration of the oxaziridine as *trans*-isomer.

Table 2
Methyl(trifluoromethyl)oxaziridines synthesis



Entry	Starting material	R	Product yield (%)[a]
1	**4a**	CH_2Ph	**6a** (97)
2	**4b**	$CH(Ph)_2$	**6b** (96)
3	**4c**	$CH(CH_3)Ph$	**6c** (94)
4	**4d**	*n*-Butyl	**6d** (93)
5	**4g**	Ph	**6g** (73)
6	**4h**	4-Cl(C_6H_4)	**6h** (77)
7	**4i**	4-CH_3(C_6H_4)	**6i** (79)

[a] Isolated yields.

The oxidation of the imines **4b**–**d** produced similar results giving the methyl(trifluoromethyl)oxaziridines **6b**–**d**, in a *trans*-configuration, in high yields (Table 2, entries 2–4).

Moreover, the same reactions performed with the Schiff bases **4g**, **4h** and **4i** led to an almost complete disappearance of the starting imine giving the *trans*-methyl(trifluoromethyl)oxaziridines **6g**, **6h** and **6i**, respectively, and small quantities of different by-products. The crude mixture was then purified by chromatography on silica gel to obtain the (trifluoromethyl)heterocycles **6g**–**i** as pure compounds (yield=73–79%; Table 2, entries 5–7).

All the reactions proceeded with a high stereoselectivity and, from each imine, only the *trans*-oxaziridine was generated. The observed *trans*-stereoselectivity (*trans*:*cis*=100:0) may be due to a synchronous oxygen transfer from the *m*-CPBA to the imine of *E*-structure.

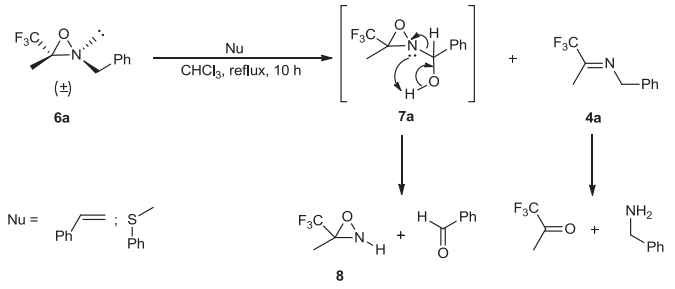
Subsequently, the reactivity of the electron-deficient oxaziridines **6a**–**d**, **g**–**i** towards electron-rich compounds, such as styrene and methyl phenyl sulfide, was investigated.

Oxaziridine **6a** (1.0 equiv) was dissolved in $CHCl_3$ and heated at reflux in the presence of methyl phenyl sulfide as nucleophile (1.0 equiv). The reaction was monitored by GC that showed the progressive decrease of **6a** that, after a 10 h period, reacted completely.

Then a portion of the reaction mixture (1 mL) was concentrated under vacuum and $CDCl_3$ added before ^1H NMR spectroscopic analysis was performed; the spectrum showed that oxaziridine **6a** did not oxidize the sulfide, but benzaldehyde and benzylamine (ratio 1:1), were the only products detected in the reaction mixture.

In similar experiments, performed by using styrene as nucleophile or in the absence of a nucleophile, oxaziridine **6a** behaved similarly.

The production of benzaldehyde and benzylamine, identified also by GC–MS, probably occurs via **6a** auto-oxidation: oxaziridine **6a** could transfer oxygen to another oxaziridine molecule at the benzylic position to produce an unstable compound **7a** and the starting Schiff base **4a**. The intermediate **7a** subsequently rearranges to form benzaldehyde and, presumably, 3-methyl-3-trifluoromethyl-oxaziridine **8**; imine **4a** hydrolyzes generating the benzylamine and 1,1,1-trifluoropropanone (Scheme 5). 3-Methyl-3-

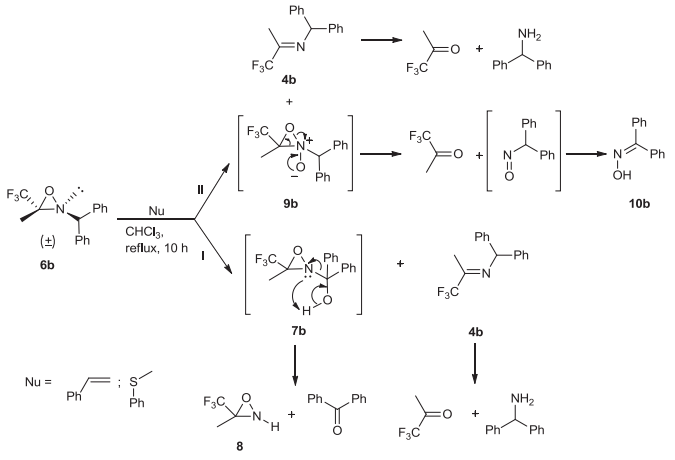


Scheme 5. Reactivity of oxaziridine **6a** in the presence of a nucleophile, such as methyl phenyl sulfide or styrene. No oxidation of the nucleophile was observed.

trifluoromethyl-oxaziridine **8** and 1,1,1-trifluoropropanone were not identified in the mixture by ^1H NMR spectroscopy, presumably due to their high volatility.

Recently, a copper-catalysed transformation of oxaziridines to allylic and benzylic alcohols via intramolecular C–H bond oxidation has been described.[18]

Slightly different results were obtained in a reaction carried out on oxaziridine **6b** and styrene or methyl phenyl sulfide as the electron-rich substrates. In both cases, after a 10 h period, ^1H NMR spectroscopic analysis of the mixture revealed no trace of epoxide or sulfoxide and different molecules, such as diphenyl-methanone oxime (**10b**),[19] benzophenone and *C*,*C*-diphenyl-methylamine were detected as the only reaction products (Scheme 6).



Scheme 6. Reactivity of oxaziridine **6b**. Auto-oxidation at the *N*-benzylic position (pathway I) and at the nitrogen atom of the heterocycle (pathway II) was observed.

The same result was achieved in a similar reaction performed without nucleophiles.

The formation of these compounds, identified also by GC–MS, could be explained through two different ways of **6b** auto-oxidation. Oxaziridine **6b** could transfer oxygen to another oxaziridine molecule, at the benzylic position, to produce benzophenone and the starting *C*,*C*-diphenylmethylamine, through a similar mechanism described for compound **6a** (Scheme 6, pathway I).

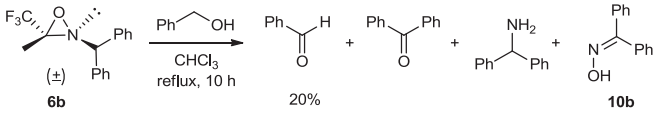
Moreover, **6b** could transfer oxygen at the heterocyclic nitrogen atom of another oxaziridine molecule to generate *N*-oxide **9b**, as a transient intermediate, which subsequently rearranges to the oxime **10b**, and the Schiff base **4b**. The latter hydrolyzes giving the *C*,*C*-diphenylmethylamine and the volatile 1,1,1-trifluoropropanone (Scheme 6, pathway II).

Previously, the oxidation at the oxaziridine nitrogen by a peroxy acid to give *C*-nitroso compounds and/or their tautomeric oximes was described.[20]

Please cite this article in press as: Perrone, S.; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.03.048

By assessing the relative quantities of the products benzophenone and oxime **10b** via ^{1}H NMR spectroscopy and GC, a 2/1 ratio between pathway I/II has been estimated.

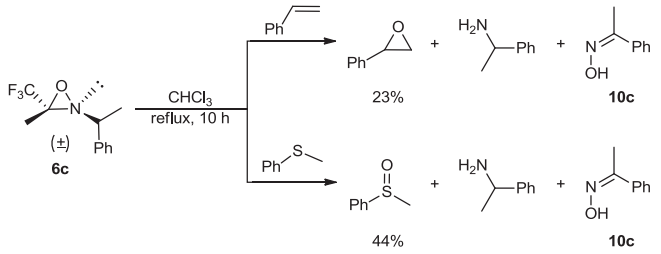
Furthermore, the ability of **6b** to transfer the electrophilic oxygen to the benzyl position of other substrates was evaluated. In particular, in the reaction with benzyl alcohol (1.0 equiv), the oxaziridine **6b** (1.0 equiv), treated under the same conditions, led to benzaldehyde (20%) and the aforementioned products benzophenone, *C*,*C*-diphenyl-methylamine and oxime **10b** (Scheme 7).



Scheme 7. Oxidation of benzyl alcohol by **6b**.

A solution of (trifluoromethyl)oxaziridine **6c** (1.0 equiv) and methyl phenyl sulfide or styrene (1.0 equiv) in $CHCl_3$ was also heated at reflux.

After a reaction time of 10 h the oxaziridine totally reacted and GC–MS and ^{1}H NMR spectroscopic analysis provides us with the evidence for the formation of styrene oxide (conversion=23% by ^{1}H NMR spectroscopy) together with other compounds (1-phenylethanamine and acetophenone oxime **10c**[21]) resulting from auto-oxidation to **6c** *N*-oxide and subsequent ring-opening. According to the suggested mechanism, oxaziridine **6c** acts as an oxygenating agent both for nucleophilic substrates and for itself at the heterocyclic nitrogen to provide the detected compounds (Scheme 8).



Scheme 8. Oxidation of styrene and methyl phenyl sulfide by oxaziridine **6c**.

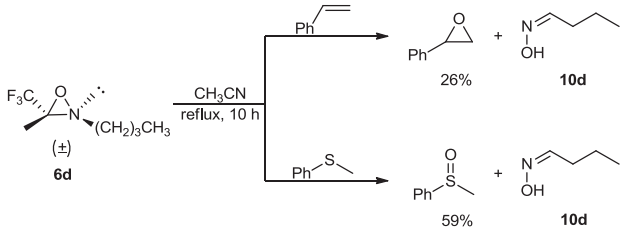
Similarly, by using methyl phenyl sulfide as nucleophile, methyl phenyl sulfoxide (conversion=44% by ^{1}H NMR spectroscopy), 1-phenylethanamine and oxime **10c** were obtained. Oxaziridine **6c** selectively oxidize methyl phenyl sulfide to the corresponding sulfoxide without over-oxidation to sulfone (Scheme 8).

No oxygen transfer at the benzylic position of **6c** with formation of acetophenone was observed. An increase of the steric hindrance is believed to prevent the oxidation of **6c** at the benzylic carbon.

Moreover, according to our results, a decreased ability to auto-oxidation corresponds to an increase in the ability of the methyl(-trifluoromethyl)oxaziridines to oxidize electron-rich substrates.

Furthermore, in a reaction performed without nucleophiles, oxaziridine **6c**, treated under the same conditions described above, led to 1-phenylethanamine and acetophenone oxime **7c** as the only detected products (conversion>90% by ^{1}H NMR spectroscopy).

No reaction product was instead found in a reaction carried out between 2-butyl-3-methyl-3-trifluoromethyl-1,2-oxaziridine **6d** (1.0 equiv) and methyl phenyl sulfide or styrene (1.0 equiv) in $CHCl_3$ at reflux. However, as shown in Scheme 9, the same reaction performed in CH_3CN as solvent, at reflux, after 10 h, resulted in the oxidation of the nucleophile and in a **6d** auto-oxidation at the heterocyclic nitrogen. In particular, ^{1}H NMR spectroscopic analysis of the reaction mixture showed the presence of methyl phenyl sulfoxide or styrene oxide in 59% or 26% yield, respectively, and



Scheme 9. Oxidation of methyl phenyl sulfoxide or styrene oxide by oxaziridine **6d** using CH_3CN as reaction solvent.

butyraldehyde oxime **10d** (Scheme 9). Probably due to its volatility, 1-butanamine was not identified by GC–MS and ^{1}H NMR spectroscopic analysis of the mixture.

Oxime **10d** was the only product observed when a solution of (trifluoromethyl)oxaziridine **6d** in CH_3CN, without nucleophiles, was heated at reflux.

Finally, a high thermal stability was instead observed for the oxaziridines **6g–i** characterized by an aromatic group at the nitrogen atom. Oxaziridines **6g–i** heated at reflux in $CHCl_3$, or in CH_3CN, both in the presence and in the absence of nucleophiles, retained their structure and after a 24 h period of reflux they were fully recovered.

3. Conclusions

In conclusion, this work shows that CF_3-substituted oxaziridines can be easily prepared and constitute a new family of organic oxidizing agents; some of them are able to oxidize, in mild conditions, styrene, thioanisole and benzyl alcohol obtaining useful synthons like styrene oxide, methyl phenyl sulfoxide and benzaldehyde. Due to their reactivity in neutral medium, they could be used for the oxygenation of acid-sensitive substrates. Moreover, we found a new behaviour of oxaziridines that can undergo auto-oxidation reactions at the nitrogen of the ring and/or *N*-substituent (benzylic carbon). Finally, their easy preparation as well as a more pronounced oxidizing capability, with respect to non-fluorinated oxaziridines, renders CF_3-substituted oxaziridines promising reagents for asymmetric oxidation.

4. Experimental section

4.1. General methods

All reactions involving air-sensitive reagents were performed under an atmosphere of nitrogen in oven-dried glassware by using syringe/septum cap techniques. CH_2Cl_2 was distilled from calcium hydride before use. Petroleum ether refers to the 40–60 °C boiling fraction. 1,1,1-Trifluoropropanone, primary amines (phenylmethanamine, diphenylmethanamine, 1-phenyl-ethanamine, butan-1-amine, propan-2-amine, 2-methylpropan-2-amine, aniline, 4-chloroaniline, *p*-toluidine) *m*-chloroperbenzoic acid (*m*-CPBA), styrene, thioanisole, acetonitrile, diethyl ether and chloroform were of commercial grade (Aldrich) and used without further purification. The ^{1}H and the ^{13}C NMR spectra were recorded with a Bruker Avance 400 apparatus (400.13 and 100.62 MHz, for ^{1}H and ^{13}C, respectively) with $CDCl_3$ as the solvent and TMS as an internal standard (δ=7.26 ppm for ^{1}H spectra; δ=77.0 ppm for ^{13}C spectra). ^{19}F spectra were recorded in $CDCl_3$ on Bruker Avance 600 spectrometer (564.68 MHz) using trichlorofluoromethane as an internal standard. The IR spectra were recorded with an FTIR spectrophotometer Digilab Scimitar Series FTS 2000. Gas chromatography (GC) was conducted on an Rt_x-5 30-m fused silica capillary column (split ratio 100:1). The following program was used: method *A*=initial temperature of 100 °C for 0.0 min, ramp 10 °C/min to 280 °C, and hold

for 15 min; the standard operating conditions were 300 °C injector temperature and 290 °C detector temperature. GC–MS analyzes, conducted using method *A* temperature programme , were performed with an Agilent Technologies 6850 series II gas chromatograph (5% phenylpolymethylsiloxane capillary column, 30 m, 0.25 mm i.d.), equipped with a 5973 Network mass-selective detector operating at 70 eV. The electrospray ionization [HRMS (ESI)] experiments were carried out in a hybrid QqTOF mass spectrometer (PE SCIEX–QSTAR) equipped with an ion-spray ionisation source. MS (+) spectra were acquired by direct infusion (5 μL min^{-1}) of a solution containing the appropriate sample (10 pmol μL^{-1}) dissolved in a solution 0.1% acetic acid, methanol/water (50:50) at the optimum ion voltage of 4800 V. The nitrogen gas flow was set at 30 psi (pounds per square inch) and the potentials of the orifice, the focussing ring and the skimmer were kept at 30, 50 and 25 V relative to ground, respectively. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. TLC was performed on Merck silica gel plates with F-254 indicator; viewing was by UV light (254 nm) or *p*-anisaldehyde and phosphomolybdic acid staining solutions. Column chromatographies were performed on silica gel (63–200 mm) using petroleum ether/diethyl ether (Et_2O) mixture as eluent.

4.2. General procedure for the synthesis of methyl(trifluoromethyl)imines 4a–d, g–i and β-aminoketones 5a, c–f

An excess of 1,1,1-trifluoropropanone (2.0 mmol) was added to an ice cooled of the primary amine (1.0 mmol) in anhydrous CH_2Cl_2 (20 mL) in the presence of 7 g of molecular sieves (4 Å, 1.6 mm pellets) according to Taguchi's method.[16] The reaction was taken under magnetic stirring and cooling (0–5 °C) for 2–3 h and monitored by GC. After this time, the molecular sieves were filtered and the solvent was removed in vacuo to give a crude material.

By using this procedure, the imines **4b**, **g**–**i** and the β-aminoketones **5e**–**f** were obtained directly as pure products. For the reactions shown in the entries 1, 3–4 of Table 1, the crude material was than purified by flash chromatography (silica gel, eluent petroleum ether/diethyl ether 70:30) to afford, for each reaction, the corresponding imine **4a**, **c**–**d** and the β-aminoketone **5a**, **c**–**d** as pure compounds.

The compounds **4a**,[22,23] **4c**,[17] **4g**,[24] **4i**,[24] are known and their characterization data are in agreement with those reported in literature. The imines **4b**, **4d**, **4h** and β-aminoketones **5a**, **c**–**f** are unknown and their characterization is reported below.

*4.2.1. (E)-1,1-Diphenyl-N-(1,1,1-trifluoropropan-2-ylidene)methanamine (**4b**).* Yield: 268 mg (97%), white solid with mp 64.1–65.5 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.98 (3H, s, C*H*$_3$), 5.69 (1H, s, C*H*), 7.18 (2H, t, *J* 7.7 Hz, Ph), 7.26 (4H, t, *J* 7.7 Hz, Ph), 7.35 (4H, d, *J* 7.7 Hz, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=13.0 (*C*H$_3$), 68.0 (*C*H), 120.0 (q, *J* 278.6 Hz, *C*F$_3$), 127.1, 127.2, 128.6, 142.6, 155.8 (q, *J* 33.3 Hz, *C*=N) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−74.5 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=277 (5) $[M]^+$, 198 (8), 167 (100), 152 (28). FTIR ($CHCl_3$)=3332, 2920, 2850, 1640, 1210 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{15}F_3N$: (278.1156) $[M+H]^+$; found: (278.1154).

*4.2.2. (E)-N-(1,1,1-Trifluoropropan-2-ylidene)-butan-1-amine (**4d**).* Yield: 154 mg (92%), colourless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=0.95 (3H, t, *J* 7.3 Hz, CH$_2$–C*H*$_3$), 1.38 (2H, sext, *J* 7.3 Hz, C*H*$_2$–CH$_3$), 1.67 (2H, quintet, *J* 7.3 Hz, CH$_2$–C*H*$_2$–CH$_2$), 2.0 (3H, s, C*H*$_3$–C=N), 3.44 (2H, t, *J* 7.3 Hz, C*H*$_2$–N) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=12.3 (*C*H$_3$–C=N), 13.7 (*C*H$_3$–CH$_2$), 20.5 (CH$_3$–*C*H$_2$), 31.9 (CH$_2$–*C*H$_2$–CH$_2$), 51.4 (*C*H$_2$–N), 120.0 (q, *J* 279.0 Hz, *C*F$_3$), 156.0 (q, *J* 34.0 Hz, *C*=N) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−79.1 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=167 (3) $[M]^+$, 152 (13), 138 (7), 124 (92), 98 (100). FTIR ($CHCl_3$)=2960, 2930, 2860, 1645, 1212 cm^{-1}. HRMS (ESI): calcd for $C_7H_{13}F_3N$: (168.1001) $[M+H]^+$; found: (168.1003).

*4.2.3. (E)-4-Chloro-N-(1,1,1-Trifluoropropan-2-ylidene)aniline (**4h**).* Yield: 214 mg (97%), pale yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=2.02 (3H, s, C*H*$_3$), 6.73 (2H, d, *J* 8.5 Hz, Ph), 7.35 (2H, d, *J* 8.5 Hz, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=14.4 (*C*H$_3$), 119.7 (q, *J* 278.5 Hz, *C*F3), 118.2, 129.3, 130.7, 146.1, 158.1 (q, *J* 34.7 Hz, *C*=N) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−74.6 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=221 (36) $[M]^+$, 152 (100), 111 (90), 75 (62). FTIR ($CHCl_3$)=3030, 2960, 2860, 1640, 1213 cm^{-1}. HRMS (ESI): calcd for $C_9H_8^{35}ClF_3N$: (222.0297) $[M+H]^+$; found: (222.0295).

*4.2.4. 4-(Benzylamino)-1,1,1,5,5,5-hexafluoro-4-methylpentan-2-one (**5a**).* Yield: 9 mg (3%), pale yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.38 (3H, s, C–C*H*$_3$), 2.77 (1H, d, *J* 17.5 Hz, C*H*H), 3.18 (1H, d, *J* 17.5 Hz, CH*H*), 3.50 (1H, s, broad, N*H*). 4.52 (2H, s, C*H*$_2$–Ph), 7.22–7.33 (5H, m, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=20.0 (*C*H$_3$–C), 40.1 (*C*H$_2$–Ph), 46.2 (*C*H$_2$–CO), 69.9 (q, *J* 30.2 Hz, *C*–CF$_3$), 115.1 (q, *J* 292.7 Hz, C–*C*F3), 125.1 (q, *J* 286.3 Hz, OC–*C*F$_3$), 127.5, 128.5, 129.0, 140.3, 189.1 (q, *J* 37.5 Hz, *C*=O) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−81.1 (s), −85.1 (s) ppm. FTIR ($CHCl_3$)=3332, 3060, 3030, 2964, 2930, 2875, 1765, 1600, 1589, 1272, 1224, 1170 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{14}F_6NO$: (314.0979) $[M+H]^+$; found: (314.0978).

*4.2.5. 1,1,1,5,5,5-Hexafluoro-4-methyl-4-[(1-phenylethyl)amino]-pentan-2-one (**5c**).* Yield: 16 mg (5%), pale yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.38 (3H, d, *J* 8.2 Hz, CH–C*H*$_3$), 1.51 (3H, s, C–C*H*$_3$), 2.80 (1H, d, *J* 17.5 Hz, C*H*H), 3.22 (1H, d, *J* 17.5 Hz, CH*H*), 3.40 (1H, s, broad, N*H*), 4.08 (1H, q, *J* 8.2 Hz, *C*H–CH$_3$), 7.22–7.35 (5H, m, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=20.9 (*C*H$_3$–C), 21.2 (CH–*C*H$_3$), 40.0 (*C*H–CH$_3$), 51.5 (*C*H$_2$–CO), 72.4 (q, *J* 30.1 Hz, *C*–CF$_3$), 114.0 (q, *J* 289.7.7 Hz, C–*C*F3), 125.0 (q, *J* 288.3 Hz, OC–*C*F$_3$), 127.8, 128.3, 128.4, 143.7, 193.6 (q, *J* 37.4 Hz, *C*=O) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−81.2 (s), −84.9 (s) ppm. FTIR ($CHCl_3$)=3331, 3062, 3030, 2965, 2933, 2876, 1763, 1600, 1589, 1271, 1224, 1172 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{16}F_6NO$: (328.1136) $[M+H]^+$; found: (328.1138).

*4.2.6. 4-(Butylamino)-1,1,1,5,5,5-hexafluoro-4-methylpentan-2-one (**5d**).* Yield: 11 mg (4%), pale yellow oil ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=0.95 (3H, t, *J* 7.3 Hz, CH$_2$–C*H*$_3$), 1.38 (2H, sext, *J* 7.3 Hz, C*H*$_2$–CH$_3$), 1.55 (3H, s, C–C*H*$_3$), 1.67 (2H, quintet, *J* 7.3 Hz, CH$_2$–C*H*$_2$–CH$_2$), 2.91 (1H, d, *J* 17.6 Hz C*H*H), 3.27 (1H, d, *J* 17.6 Hz CH*H*), 3.44 (2H, t, *J* 7.3 Hz, C*H*$_2$–N) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=13.1 (CH$_2$–*C*H$_3$), 14.2 (*C*H$_3$–C), 20.5 (*C*H$_2$–CH$_3$), 31.0 (CH$_2$–*C*H$_2$–CH$_2$), 40.1 (*C*H$_2$–CO), 51.4 (*C*H$_2$–N), 72.1 (q, *J* 30.2 Hz, *C*–CF$_3$), 117.1 (q, *J* 290.8 Hz, C–*C*F3), 127.0 (q, *J* 289.5 Hz, OC–*C*F$_3$), 190.1 (q, *J* 39.4 Hz, *C*=O) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−81.0 (s), −85.1 (s) ppm. FTIR ($CHCl_3$)=3332, 2964, 2930, 2872, 1765, 1587, 1466, 1381, 1270, 1226, 1170 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_{16}F_6NO$: (280.1136) $[M+H]^+$; found: (280.1134).

*4.2.7. 1,1,1,5,5,5-Hexafluoro-4-(isopropylamino)-4-methylpentan-2-one (**5e**).* Yield: 252 mg (95%), pale yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.19 (6H, d, *J* 6.3 Hz, CH–(C*H*$_3$)$_2$), 1.55 (3H, s, C–C*H*$_3$), 2.90 (1H, d, *J* 17.5 Hz, C*H*H), 3.26 (1H, d, *J* 17.5 Hz, CH*H*), 3.78 (1H, septet, *J* 6.3 Hz, C*H*–(CH$_3$)$_2$) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=20.9 (*C*H$_3$–C), 22.6 (CH–(*C*H$_3$)$_2$), 40.0 (*C*H$_2$), 51.5 (*C*H–(CH$_3$)$_2$), 72.7 (q, *J* 30.1 Hz, *C*–CF$_3$), 114.8 (q, *J* 294.7 Hz, C–*C*F3), 125.1 (q, *J* 285.3 Hz, OC–*C*F$_3$), 188.8 (q, *J* 38.6 Hz, *C*=O) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−81.0 (s), −85.0 (s) ppm. FTIR ($CHCl_3$)=3330, 2965, 2930, 2873, 1764, 1589, 1466, 1381, 1272, 1224, 1170 cm^{-1}. HRMS (ESI): calcd for $C_9H_{14}F_6NO$: (266.0979) $[M+H]^+$; found: (266.0978).

*4.2.8. 4-(tert-Butylamino)-1,1,1,5,5,5-hexafluoro-4-methylpentan-2-one (**5f**).* Yield: 273 mg (98%), colourless oil. ^{1}H NMR (400.13 MHz,

Please cite this article in press as: Perrone, S.; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.03.048

$CDCl_3$) δ=1.22 (9H, s, C–(CH_3)$_3$), 1.55 (3H, s, C–CH_3), 2.90 (1H, d, *J* 17.5 Hz, CH*H*), 3.26 (1H, d, *J* 17.5 Hz, C*H*H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=20.6 (CH_3), 30.5 (C–(CH_3)$_3$), 40.2 (CH_2), 49.0 (*C*–(CH_3)$_3$), 72.5 (q, *J* 30.2 Hz, *C*–CF_3), 114.9 (q, *J* 292.0 Hz, C–*C*F3), 125.2 (q, *J* 285.0 Hz, OC–*C*F_3), 188.8 (q, *J* 36.7 Hz, *C*=O) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−81.1 (s), −85.1 (s) ppm. FTIR ($CHCl_3$)= 3337, 2965, 2873, 1765, 1588, 1466, 1380, 1273, 1224, 1172 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_{16}F_6NO$: (280.1136) $[M+H]^+$; found: (280.1138).

4.3. General procedure for the synthesis of oxaziridines 6a–d, g–i

A small excess of *m*-CPBA (270 mg, 1.1 mmol, 70%) was added to an ice cooled solution of the methyl(trifluoromethyl)-imines **4a**–**d**, **g**–**i** (1.0 mmol) in anhydrous CH_2Cl_2 (20 mL). The reaction was taken under magnetic stirring and cooling (0–5 °C) for about 3 h and monitored by GC and GC–MS. When the reaction was complete, the solution was stirred at 0–5 °C with excess powdered anhydrous sodium carbonate until carbon dioxide evolution ceased. After filtration, the mixture was concentrated in vacuo affording the methyl(trifluoromethyl)oxaziridines **6a**–**d** as pure compounds; in particular, oxaziridine **6c** was obtained as only one diastereoisomer.

For the oxaziridines **6g**–**i**, after filtration and evaporation of the solvent in vacuo, the residue was purified by flash chromatography (silica gel, partly deactivated with triethyl-amine, eluent petroleum ether/diethyl ether 95:5 for **6g** and **6i**; petroleum ether/diethyl ether 90:10 for **6h**).

*4.3.1. 2-Benzyl-3-methyl-3-(trifluoromethyl)-1,2-oxaziridine (**6a**).* Yield: 210 mg (97%), yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.79 (3H, s, CH_3), 3.96 (2H, s, CH_2–Ph), 7.28–7.38 (5H, m, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=9.8 (CH_3), 57.9 (CH_2), 79.1 (q, *J* 36.6 Hz, *C*–O). 122.2 (q, *J* 280.9 Hz, *C*F_3), 128.0, 129.3, 128.7, 134.8 ppm. GC–MS (70 eV): *m*/*z* (%)=217 (45) $[M]^+$, 202 (15), 148 (21), 91 (100). ^{19}F NMR (564.68 MHz, $CDCl_3$)=−80.2 (s) ppm. FTIR ($CHCl_3$)=3027, 2962, 2930, 2870, 1335, 1212, 1160 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_{11}F_3NO$: (218.0792) $[M+H]^+$; found: (218.0793).

*4.3.2. 2-Benzhydryl-3-methyl-3-(trifluoromethyl)-1,2-oxaziridine (**6b**).* Yield: 281 mg (96%), orange oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.68 (3H, s, CH_3), 4.64 (1H, s, C*H*), 7.20–7.35 (8H, m, Ph), 7.44 (2H, d, *J* 7.7 Hz, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=10.3 (CH_3), 70.7 (*C*H), 79.7 (q, *J* 36.8 Hz, *C*–O). 122.2 (q, *J* 281.2 Hz, *C*F_3), 128.2, 128.5, 128.9, 138.4 ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−81.3 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=293 (27) $[M]^+$, 292 (35), 180 (100), 165 (60). FTIR ($CHCl_3$)=3027, 2960, 2935, 2868, 1335, 1210, 1162 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{15}F_3NO$: (294.1105) $[M+H]^+$; found: (294.1103).

*4.3.3. 3-Methyl-2-(1-phenylethyl)-3-(trifluoromethyl)-1,2-oxaziridine (**6c**).* Yield: 217 mg (94%), yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=1.60 (3H, d, *J* 6.4 Hz, CH_3–CH), 1.63 (3H, s, CH_3–CO), 3.63 (1H, q, *J* 6.4 Hz, C*H*–CH_3), 7.27–7.36 (5H, m, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=9.9 (CH_3–CO), 23.1 (CH_3–CH), 63.1 (*C*H–CH_3), 79.6 (q, *J* 36.3 Hz, CH_3*C*–O). 122.1 (q, *J* 281.0 Hz, *C*F_3), 126.6, 128.1, 128.9, 139.6 ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−82.1 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=231 (<1) $[M]^+$, 120 (25), 105 (100), 77 (70). FTIR ($CHCl_3$)=3027, 2959, 2930, 2871, 1334, 1210, 1160 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{13}F_3NO$: (232.0949) $[M+H]^+$; found: (232.0948).

*4.3.4. 2-Butyl-3-methyl-3-(trifluoromethyl)-1,2-oxaziridine (**6d**).* Yield: 170 mg (93%), colourless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=0.95 (3H, t, *J* 7.3 Hz, CH_2–CH_3), 1.47 (2H, sext, *J* 7.3 Hz, CH_2–CH_3), 1.65 (2H, quintet, *J* 7.3 Hz, CH_2–CH_2–CH_2), 1.67 (3H, s, CH_3–CN), 2.74–2.81 (1H, m, NC–*H*H), 2.85–2.92 (1H, m, NC–CH*H*) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=9.6 (*C*H_3–CN), 13.7 (CH_3–CH_2), 20.3 (CH_3–*C*H_2), 29.9 (CH_2–CH_2–CH_2), 53.9 (CH_2–N), 78.8 (q, *J* 36.5 Hz, *C*–O), 122.2 (q, *J* 276.8 Hz, *C*F_3) ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−82.5 (s) ppm. FTIR ($CHCl_3$)=2962, 2934, 2875, 1335, 1209, 1166, 1110, 880 cm^{-1}. HRMS (ESI): calcd for $C_7H_{13}F_3NO$: (184.0949) $[M+H]^+$; found: (184.0947).

*4.3.5. 3-Methyl-2-phenyl-3-(trifluoromethyl)-1,2-oxaziridine (**6g**).* Yield: 148 mg (73%), yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=3.35 (3H, s, CH_3), 7.24–7.27 (2H, m, Ph), 7.41–7.45 (3H, m, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=17.9 (CH_3), 96.1 (q, *J* 32.1 Hz, *C*–O), 110.0 (q, *J* 286.0 Hz, *C*F_3), 127.3, 129.0, 129.5, 140.6 ppm. ^{19}F NMR (564.68 MHz, CDCl3)=−72.1 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=203 (100) $[M]^+$, 134 (48), 106 (75), 77 (90). FTIR ($CHCl_3$)=3027, 2955, 2927, 2850, 1490, 1210, 1161, 887 cm^{-1}. HRMS (ESI): calcd for $C_9H_9F_3NO$: (204.0636) $[M+H]^+$; found: (204.0639).

*4.3.6. 2-(4-Chlorophenyl)-3-methyl-3-(trifluoromethyl)-1,2-oxaziridine (**6h**).* Yield: 182 mg (77%), yellow oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=3.34 (3H, s, CH_3), 7.19 (2H, d, *J* 8.5 Hz, Ph), 7.41 (2H, d, *J* 8.5 Hz, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=20.3 (CH_3), 97.4 (q, *J* 31.9 Hz, *C*–O), 116.0 (q, *J* 285.9 Hz, *C*F_3), 128.8, 129.8, 135.0, 139.1 ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−67.5 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=237 (90) $[M]^+$, 168 (25), 140 (75), 110 (100). FTIR ($CHCl_3$)=3027, 2958, 2927, 2853, 1489, 1211, 1161, 888 cm^{-1}. HRMS (ESI): calcd for $C_9H_8^{35}ClF_3NO$: (238.0246) $[M+H]^+$; found: (238.0245).

*4.3.7. 3-Methyl-2-(p-tolyl)-3-(trifluoromethyl)-1,2-oxaziridine (**6i**).* Yield: 171 mg (79%), orange oil. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ=2.37 (3H, s, CH_3–Ph), 3.33 (3H, s, CH_3–CO), 7.10 (2H, d, *J* 8.2 Hz, Ph), 7.20 (2H, d, *J* 8.2 Hz, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$) δ=15.2 (*C*H_3–CO), 18.0 (*C*H_3–Ph), 95.5 (q, *J* 32.1 Hz, *C*–O), 108.1 (q, *J* 286.1 Hz, *C*F_3), 127.1, 130.1, 132.4, 139.0 ppm. ^{19}F NMR (564.68 MHz, $CDCl_3$)=−74.2 (s) ppm. GC–MS (70 eV): *m*/*z* (%)=217 (50) $[M]^+$, 198 (5), 148 (100). FTIR ($CHCl_3$)=3028, 2960, 2927, 2855, 1490, 1212, 1161, 890 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_{11}F_3NO$: (218.0792) $[M+H]^+$; found: (218.0794).

4.4. General procedure for the oxidation reactions using oxaziridines 6a–d, g–i

A solution of the methyl(trifluoromethyl)oxaziridine (1.0 mmol) in $CHCl_3$ (20 mL) was heated at reflux in the presence of a nucleophile (1.0 mmol), such as styrene or thioanisole. The reaction was taken under magnetic stirring and heating for a 10 h period and monitored by TLC and GC. When it was complete, reaction products were identified by GC–MS and ^{1}H NMR spectroscopic analysis by comparison with literature characterization data.

Auto-oxidation reactions were performed by heating a solution of the oxaziridine (1.0 equiv) in $CHCl_3$ (20 mL) at reflux for 10 h.

The reactions involving oxaziridines **6d**, **g**–**i** were carried out using also CH_3CN (20 mL) as reaction solvent.

Acknowledgements

Thanks are due to the University of Salento and C.I.N.M.P.I.S. (Consorzio Interuniversitario Nazionale Metodologie e Processi Innovativi di Sintesi) for financial support.

References and notes

1. (a) Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63–70; (b) Murray, R. W.; Jeyaraman, R. *J. Organomet. Chem.* **1985**, *50*,

2847–2853; (c) Murray, R. W.; Singh, M.; Jeyaraman, R. *J. Am. Chem. Soc.* **1992**, *114*, 1346–1351; (d) Mello, R.; Gonzalez Nunez, M. E.; Asensio, G. *ChemInform* **2007**, *38*.
2. (a) Emmons, W. D. *J. Am. Chem. Soc.* **1956**, *78*, 6208–6209; (b) Widmer, J.; Keller-Schierlein, W.; Helv. *Chim. Acta* **1974**, *57*, 657–664.
3. For a recent review, see: Curci, R.; D'Accolti, L.; Fusco, C. *Acc. Chem. Res.* **2006**, *39*, 1–9.
4. (a) Murray, R. W.; Singh, M. *Org. Synth.* **1997**, *74*, 91–100; (b) Adam, W.; Saha-Moeller, C. R.; Cong-Gui, Z. *Organic Reactions*; John Wiley & Sons: Hoboken, NJ, United States, 2002; Vol. 61.
5. (a) Ferrer, M.; Sanchez-Baeza, F.; Messeguer, A.; Diez, A.; Rubiralta, M. *J. Chem. Soc., Chem. Commun.* **1995**, 293–294; (b) Miaskiewicz, K.; Teich, N. A.; Smith, D. A. *J. Organomet. Chem.* **1997**, *62*, 6493–6497.
6. Dieva, S. A.; Eliseenkova, R. M.; Efremov, Y. Y.; Sharafutdinova, D. R.; Bredikhin, A. A. *Russian J. Org. Chem.* **2006**, *42*, 12–16.
7. For reviews, see: (a) Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, *45*, 5703–5742; (b) Davis, F. A.; Chen, B.-C. *Chem. Rev.* **1992**, *92*, 919–934.
8. Blanc, S.; Bordogna, C. A. C.; Buckley, B. R.; Elsegood, M. R. J.; Bullman Page, P. C. *Eur. J. Org. Chem.* **2010**, 882–889.
9. Bullman Page, P. C.; Heer, J. P.; Bethell, D.; Collington, E. W.; Andrews, D. M. *Tetrahedron: Asymmetry* **1995**, *6*, 2911–2914.
10. (a) Komatsu, M.; Ohshiro, Y.; Hotta, H.; Sato, M.; Agawa, T. *J. Organomet. Chem.* **1974**, *39*, 948–956; (b) Komatsu, M.; Ohshiro, Y.; Yasuda, K.; Ichijima, S.; Agawa, T. *J. Organomet. Chem.* **1974**, *39*, 957–962; (c) Murai, N.; Komatsu, M.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1977**, *42*, 448–451; (d) Komatsu, M.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1986**, *51*, 407–409.
11. Fabio, M.; Ronzini, L.; Troisi, L. *Tetrahedron* **2007**, *63*, 12896–12902.
12. Troisi, L.; De Lorenzis, S.; Fabio, M.; Rosato, F.; Granito, C. *Tetrahedron: Asymmetry* **2008**, *19*, 2246–2251.
13. Fabio, M.; Ronzini, L.; Troisi, L. *Tetrahedron* **2008**, *64*, 4979–4984.
14. Troisi, L.; Ronzini, L.; Rosato, F.; Videtta, V. *Synlett* **2009**, 1806–1808.
15. (a) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Organomet. Chem.* **1988**, *53*, 3890–3891; (b) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749–6757; (c) D'Accolti, L.; Fusco, C.; Rella, M. R.; Curci, R. *Synth. Commun.* **2003**, *33*, 3009–3016; (d) Adam, W.; Curci, R.; Gonzalez Nunez, M. E.; Mello, R. *J. Am. Chem. Soc.* **1991**, *113*, 7654–7658.
16. Westheimer, F. H.; Taguchi, K. *J. Organomet. Chem.* **1971**, *36*, 1570–1572.
17. Soloshonok, V. A.; Ono, T. *J. Organomet. Chem.* **1997**, *62*, 3030–3031.
18. Motiwala, H. F.; Gülgeze, B.; Aubè, J. *J. Organomet. Chem.* **2012**, *77*, 7005–7022.
19. (a) Khazaei, A.; Rostami, A. *Org. Prep. Proced. Int.* **2006**, *38*, 484–490; (b) Liu, S.; Yu, Y.; Liebeskind, L. S. *Org. Lett.* **2007**, *9*, 1947–1950.
20. (a) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 6522–6524; (b) Perrone, S.; Pilati, T.; Rosato, F.; Salomone, A.; Videtta, V.; Troisi, L. *Tetrahedron* **2011**, *67*, 2090–2095.
21. Madabhushi, S.; Chinthala, N.; Vangipuram, V. S.; Godala, K. . R.; Jillella, R.; Mallu, K. K. R.; Beeram, C. R. *Tetrahedron Lett.* **2011**, *52*, 6103–6107.
22. Gulevich, A. V.; Shevchenko, N. E.; Balenkova, E. S.; Roeschenthaler, G.-V.; Nenajdenko, V. G. *Tetrahedron* **2008**, *64*, 11706–11712.
23. Ono, T.; Kukhar, V. P.; Soloshonok, V. A. *J. Organomet. Chem.* **1996**, *61*, 6563–6569.
24. Kino, T.; Nagase, Y.; Horino, Y.; Yamakawa, T. *J. Mol. Catal. A: Chem.* **2008**, *282*, 34–51.

Please cite this article in press as: Perrone, S.; et al., Tetrahedron (2013), http://dx.doi.org/10.1016/j.tet.2013.03.048