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Synthesis of optically active trifluoromethyl substituted diaziridines and oxaziridines

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ABSTRACT

(*E*)-Trifluoromethyl imines were considered as ideal substrates to be transformed into the corresponding diaziridines by a direct amination reaction with nosyloxycarbamates. The diastereoselective induction was strongly controlled by the *N*-substituent. Similar results were obtained in the epoxidation reactions performed on the same substrates using *m*-CPBA as oxidant. Starting from enantiopure imines chiral diaziridines or oxaziridines were obtained with very high enantiopurity.

1. Introduction

The presence in a molecule of fluorine atoms often leads to relevant modifications in the chemical and biological properties compared with unfluorinated parent compounds.[1] For some years now, a noteworthy development of methodologies to synthesize fluorinated organic compounds was observed, focusing the attention in particular on the preparation of trifluoromethylated systems[2] One of the most interesting aspects of organofluorine chemistry is that of asymmetric reactions often coupled with the unexpected reactivity and stereochemical outcome, due to the strongly electronegative nature of fluorine atoms, which can modify the asymmetric course of reactions.[3]

In this field, we have reported the results obtained by alkyl nosyloxycarbamates ($NsONHCO_2R$, $Ns{=}4\text{-}NO_2C_6H_4SO_2$) in the direct amination reaction of different trifluoromethylated compounds,[4] stressing the different reactivity observed with respect to the analogous unfluorinated compounds.[5]

Continuing our studies, we would like to report the reactivity of different trifluoromethyl imines[6] in the amination reaction performed by using $NsONHCO_2Et$ as aminating agent, focusing on the diastereoselective course of the reaction.

2. Results and discussion

Inspired by our previous studies performed on unfluorinated imines,[7] compounds (*E*)-**1a**–**j** were reacted with a twofold excess of $NsONHCO_2Et$ in CH_2C1_2 without added base at room temperature to give the corresponding diaziridines **2a**–**j**. The results are reported in Table 1.

In all cases, trifluoromethyl substituted diaziridines **2** were obtained in high yields[7] with total retention of the starting imine configurations as confirmed by NMR spectroscopy, and no further purifications were required after the work-up.

As we have previously reported,[7] the synthesis of diaziridines **2** could be explained either by the involvement of (ethoxycarbonyl) nitrene ($:NCO_2Et$, via a) or by a nucleophilic addition to imine carbon followed by a ring closure reaction (via b) involving an ionic pathway (Scheme 1).

To gain more information, imines **1a**,**c** were successfully tested in the amination reactions with $NsONHCO_2$*t*-Bu (Scheme 2), a carbamate, that is, known to give amination reactions only by an ionic pathway involving the corresponding aza-anion.[8]

Furthermore, a high regioselectivity was observed in the one-pot synthesis of the trifluoromethyl diaziridine **2k** (Scheme 3), starting from trifluoroacetaldehyde ethyl hemiacetal (90% aq solution) and allylamine, strengthening the hypothesis that the reaction proceeds by an ionic pathway.

Very interesting is the diastereoselective outcome of the amination reaction, as determined by ^1H NMR spectroscopy performed on the crude products.

As shown in Table 1, the stereoselective induction appears to be controlled by steric or electronic effects present on the β- or α-carbon of the aminic residue. In fact, while the presence of a *tert*-butyl group (entry 7) leads to the diastereomeric diaziridines with a 1.7:1 dr, **2e** was obtained as a 1:1 diastereomeric mixture (entry 5) and the isopropyl group leads to an induction decrease (entry 6). In

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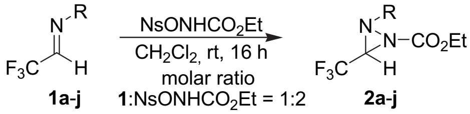
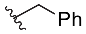
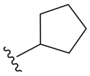
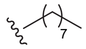
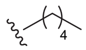
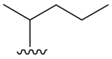
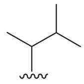
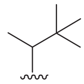
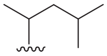
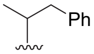
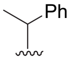
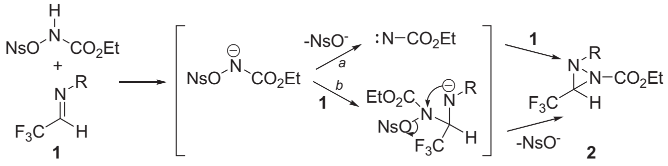
Table 1
Synthesis of trifluoromethyl diaziridines

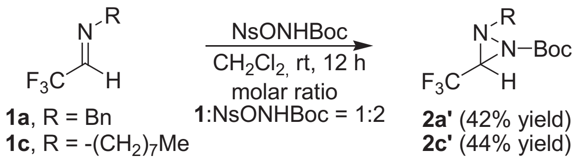


Entry	2	R	Yield %	dr[a]
1	a		48	—
2	b		40	—
3	c		50	—
4	d		50	—
5	e		49	1:1
6	f		37	1.3:1
7	g		38	1.7:1
8	h		44	1:1
9	i		40	1:1.7
10	j		35	100:1

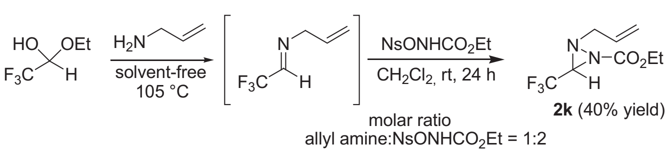
[a] By ^{1}H NMR spectroscopy.



Scheme 1. Possible pathways for the aziridination reaction.



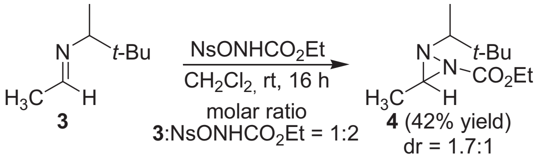
Scheme 2. Amination reactions with $NsONHCO_2t$-Bu.



Scheme 3. Regioselectivity in the amination giving trifluoromethyl diaziridine **2k**.

contrast, the same group present in the γ position does not give any induction (entry 8). Finally, a very good diastereomeric induction was observed when the phenyl group is present in the α position (entry 10), but if the same group is present in the β position a reversal of induction was observed leading to a 1:1.7 mixture of diastereomers (entry 9).

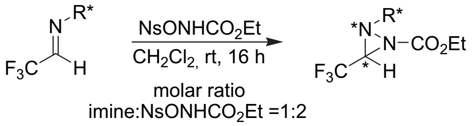
To exclude a possible influence of the CF_3 group on the stereochemical outcome of the aziridination reaction, imine **3**, an unfluorinated analogue of **1g**, was reacted with $NsONHCO_2Et$ (Scheme 4), and even in this case, the corresponding diaziridines **4** were obtained as a diastereomeric mixture (dr=1.7:1), as determined by its ^{1}H NMR spectrum.

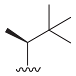
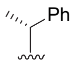
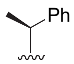


Scheme 4. Aziridination reaction of unfluorinated imine **3**.

Starting from these results, optically pure trifluoromethyl imines (*R*)- and (*S*)-**1g,j** were considered as suitable substrates to obtain the corresponding enantiopure diaziridines and the results are reported in Table 2.

Table 2
Synthesis of chiral trifluoromethyl diaziridines



Entry	Imine	R	Diaziridine	Yield %	dr[a]
1	(*R*)-**1g**		(*R,S,S*)-**2g** (*R,R,R*)-**2g**	49	2.5:1
2	(*S*)-**1g**		(*S,R,R*)-**2g** (*S,S,S*)-**2g**	44	2:1
3	(*R*)-**1j**		(*R,S,S*)-**2j** (*R,R,R*)-**2j**	48	100:1
4	(*S*)-**1j**		(*S,R,R*)-**2j** (*S,S,S*)-**2j**	35	100:1

[a] By ^{1}H and ^{19}F NMR spectroscopy.

The diastereomeric mixtures were separated by HPLC and enantiomerically pure trifluoromethyl diaziridines were obtained.

Based on data reported in the literature for trifluoromethyl aziridines,[9] the absolute configuration of the obtained compounds was deduced from 2D-NOESY correlations performed on purified (*R,S,S*)- and (*R,R,R*)-**2g**. While no NOE interaction was observed in the minor isomer, a significant NOE interaction between $(CH_3)_3$–C and H_a (at δ 3.60) was detected in the major isomer, suggesting a 2*S*,3*S* absolute configuration for the diaziridine ring of the latter (Fig. 1).[10]

Consequently, the absolute configurations for all other diastereomers were assigned on the basis of the above reported NOE data.

Then, the synthesis of trifluoromethyl oxaziridines was considered, as an interesting extension of our studies. It is known that oxaziridines exhibit a remarkable stability[11] and can be used as both oxygenating and aminating agents in reactions with a wide

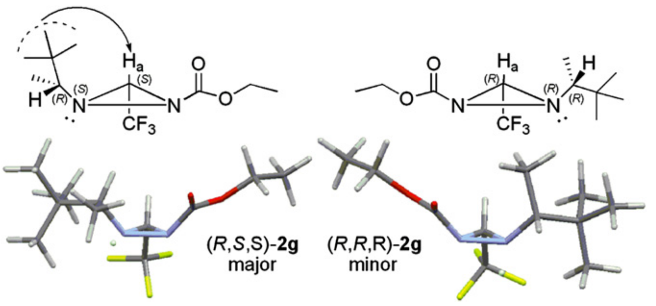
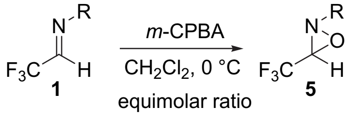


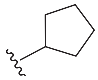
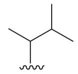
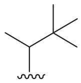
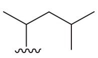
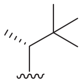
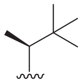
Fig. 1. Diaziridine (*R*,*S*,*S*)- and (*R*,*R*,*R*)-**2g**. NOE interaction and optimized geometries of both diastereomers.

variety of nucleophiles. On the other hand, these compounds, characterized by a reactive strained C,N,O three-membered ring, are very interesting reagents for their potential use in asymmetric induction,[12] and especially perfluorinated oxaziridines have been reported as effective and versatile oxidizing agents toward different substrates.[13] Recently *N*-unsubstituted oxaziridines were employed as sources of electrophilic nitrogen.[14]

The epoxidation reaction[15] was tested first on the imine **1b** and then on the imines **1f**–**h**, using *m*-CPBA as oxidant. The results are reported in Table 3.

Table 3
Synthesis of chiral trifluoromethyl diaziridines



Entry	Imine	R	Oxaziridine	Time h	Yield %	dr[a]
1	**1b**		**5b**	20	76	—
2	**1f**		**5f**	3	90	3.3:1
3	**1g**		**5g**	4	79	5:1
4	**1h**		**5h**	2	80	1.4:1
5	(*R*)-**1g**		(*R*,*S*,*S*)-**5g** (*R*,*R*,*R*)-**5g**	2	84	5:1
6	(*S*)-**1g**		(*S*,*R*,*R*)-**5g** (*S*,*S*,*S*)-**5g**	2	87	5:1

[a] By ^{1}H NMR spectroscopy.

As reported in Table 3, the expected compounds were obtained in good yield, the diastereoselectivity observed being related to the steric hindrance of the *N*-substituent (entries 2–4). In comparison to the aziridinations, the epoxidation reactions require shorter times and occur in all cases with a higher diastereoselectivity. Furthermore, the epoxidation reactions performed on enantiopure imines (*R*)- and (*S*)-**1g** lead to the corresponding fluorinated oxaziridines (R,S^*,S^*)**-** and (S,R^*,R^*)**-5g** with very high diastereoselectivity (entries 5–6). Products (*R*,*S*,*S*)**-** and (*R*,*R*,*R*)**-5g** were obtained as pure enantiomers after an easy purification.

Fluorinated oxaziridines are oxidants effective almost as much as dioxiranes and certainly more effective than unfluorinated analogues, as a consequence of the strong electron-withdrawing effect of fluoroalkyl groups.[13a] So, the optically pure oxaziridines can be regarded as interesting enantiopure oxygenating agents to be used in different reactions.[16]

3. Conclusions

In conclusion, trifluoromethyl aziridines can be prepared in a diastereoselective manner by direct aziridination of the corresponding imines. While in the past,[4] we observed a significant CF$_3$ group effect on the reactions between different trifluoromethyl alkenes and nosyloxycarbamates, the presence of the same group on the C=N bond does not seem to influence the outcome of the aziridination reactions, probably due to the major polarization of imine bond with respect to the C=C bond. A strong influence on the diastereoselective course of the reaction seems to be exerted by steric or electronic effects on the β- or α-carbon of the aminic residue. The same stereochemical trend was observed in the epoxidation reactions, obtaining the synthesis, also as pure enantiomers, of potentially effective oxygenating agents.

4. Experimental section

4.1. General

IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer in CHCl$_3$ as the solvent. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 instrument at 300 and 75 MHz, respectively. CDCl$_3$ was used as the solvent and CHCl$_3$ as the internal standard. ^{19}F NMR spectra were recorded at 282.2 MHz with a Varian XL-300 instrument, using CDCl$_3$ as the solvent and C$_6$F$_6$ as the internal standard; chemical shifts are given in parts per million relative to CFCl$_3$. The NOE experiments were performed at 400 MHz with a Bruker Advanced-three spectrometer using CDCl$_3$ as the solvent and CHCl$_3$ as the internal standard. HRMS analyses were performed using a Micromass Q-TOF Micro quadrupole-time of flight (TOF) mass spectrometer equipped with an ESI source and a syringe pump. The experiments were conducted in the positive ion mode. HPLC analyses were performed with a Varian 9002 instrument equipped with a Varian 9050 RI-4 differential refractometer or UV/vis detector using an analytical column (3.9×300 mm, flow rate 1.3 mL/min). Eluents were HPLC grade. Optical rotations were recorded at the Sodium D line with a Jasco Model DIP-370 polarimeter at room temperature, using a quartz cell of 1 cm lenght. The diastereomers (*R*,*S*,*S*)- and (*R*,*R*,*R*)-**2g** were separated by HPLC using 9:1 hexane/ethyl acetate mixture (flow 1.3 mL/min) as the eluent. The diastereomers (*R*,*S*,*S*)- and (*R*,*R*,*R*)-**5g** were separated by flash chromatography (silica gel, pentane/dichloromethane=9.5:0.5). The synthesis of imines[6] **1a**–**d**,**f**,**h**, (*R*)-**1g**,**j**, NsONHCO$_2$Et,[17] and NsONH/Boc[18] were performed following reported procedures.

4.2. General procedure for the synthesis of (*E*)-trifluoromethyl imines (1)

A stirred equimolar solution (10 mmol) of trifluoroacetaldehyde ethyl hemiacetal (90% aq solution) and different primary amines was heated under solvent-free conditions in a flask fitted with a calcium chloride tube.

*4.2.1. N-[(E)-2,2,2-Trifluoroethylidene]pentan-2-amine (**1e**).* External bath: 105 °C; reaction time: 3 h; 1.22 g; 73% yield; yellow oil; IR: 1688 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.88 (t, ^{3}J=7.3 Hz, 3H) 1.00–1.05 (m, 2H), 1.22 (d, ^{3}J=6.3 Hz, 3H), 1.28–1.66

(m, 2H), 3.31–3.42 (m, 1H), 7.60 ($^{3}J_{H-F}$=3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 19.3, 21.6, 39.0, 65.6, 119.0 (q, $^{1}J_{C-F}$=274.6 Hz, CF_3), 147.3 (q, $^{2}J_{C-F}$=37.6 Hz, CCF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.1 (d, $^{3}J_{F-H}$=3.5 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_7H_{12}F_3NNa$: 190.0820; found: 190.0819.

4.2.2. *3,3-Dimethyl-N-[(E)-2,2,2-trifluoroethylidene]butan-2-amine (**1g**)*

External bath: 110 °C; reaction time: 30 min; 1.50 g; 83% yield; colorless oil; IR: 1682 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (s, 9H), 1.13 (d, ^{3}J=6.5 Hz, 3H), 3.01 (q, ^{3}J=6.5 Hz, 1H), 7.57 ($^{3}J_{H-F}$=3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.7, 26.2 (3C), 33.9, 74.8, 119.0 (q, $^{1}J_{C-F}$=274.9 Hz, CF_3), 147.2 (q, $^{2}J_{C-F}$=38.2 Hz, C−CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.4 (d, $^{3}J_{F-H}$=3.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_8H_{14}F_3NNa$: 204.0976; found: 204.0981.

4.2.3. *1-Phenyl-N-[(E)-2,2,2-trifluoroethylidene]propan-2-amine (**1i**)*

External bath: 105 °C, reaction time: 6 h; 1.96 g; 91% yield; yellow oil; IR: 1687 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.35 (d, ^{3}J=7.0 Hz, 3H), 3.21 (sextet, ^{3}J=7.0 Hz, 1H), 3.73–3.77 (m, 2H), 7.15–7.36 (m, 5H), 7.38–7.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.9, 40.0, 67.7, 118.6 (q, $^{1}J_{C-F}$=274.8 Hz, CF_3), 126.6, 127.2 (2C), 128.5 (2C), 143.8, 149.8 (q, $^{2}J_{C-F}$=38.0 Hz, C−CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.9 (d, $^{3}J_{F-H}$=3.5 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{11}H_{12}F_3NNa$: 238.0820; found: 238.0828.

4.2.4. *1-Phenyl-N-[(E)-2,2,2-trifluoroethylidene]ethanamine (**1j**)*

External bath: 115 °C; reaction time: 90 min; 1.51 g; 75% yield; yellow oil; IR: 1687 cm^{-1}; ^{1}H NMR (300 MHz, CDCl3): δ=1.59 (d, ^{3}J=6.7 Hz, 3H), 4.61 (q, ^{3}J=6.7 Hz, 1H), 7.27–7.40 (m, 5H), 7.65 ($^{3}J_{H-F}$=3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.8, 68.7, 119.0 (q, $^{1}J_{C-F}$=274.9 Hz, CF_3), 126.6 (2C), 127.6, 128.7 (2C), 142.2, 148.0 (q, $^{2}J_{C-F}$=38.2 Hz, C−CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.0 (d, $^{3}J_{F-H}$=3.5 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{10}H_{10}F_3NNa$: 224.0663; found: 224.0670.

4.2.5. *(2S)-3,3-Dimethyl-N-[(E)-2,2,2-trifluoroethylidene]butan-2-amine [(S)-**1g**]*

External bath: 110 °C; reaction time: 1 h; 1.28 g; 71% yield; colorless oil; $[\alpha]_D^{25}$ +35.8 (*c* 1.9, $CHCl_3$); IR ($CHCl_3$): 1681 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.88 (s, 9H), 1.13 (d, ^{3}J=6.5 Hz, 3H), 3.01 (q, ^{3}J=6.5 Hz, 1H), 7.57 ($^{3}J_{H-F}$=3.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.7, 26.2 (3C), 33.9, 74.8, 118 (q, $^{1}J_{C-F}$=274.9 Hz, CF_3), 147.2 (q, $^{2}J_{C-F}$=37.8 Hz, C−CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.6 (d, $^{3}J_{F-H}$=3.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_8H_{14}F_3NNa$: 204.0976; found: 204.0974.

4.2.6. *(1S)-1-Phenyl-N-[(E)-2,2,2-trifluoroethylidene]ethanamine [(S)-**1j**]*

External bath: 115 °C, reaction time: 4 h; 1.85 g; 92% yield; yellow oil; $[\alpha]_D^{25}$ −29.2 (*c* 1.2, $CHCl_3$); IR: 1685 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.59 (d, ^{3}J=6.7 Hz, 3H), 4.61 (q, ^{3}J=6.6 Hz, 1H), 7.27–7.40 (m, 5H), 7.65 ($^{3}J_{H-F}$=3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.8, 68.7, 119.0 (q, $^{1}J_{C-F}$=274.9 Hz, CF_3), 126.6 (2C), 127.6, 128.7 (2C), 142.2, 148.0 (q, $^{2}J_{C-F}$=38.2 Hz, C−CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.0 (d, $^{3}J_{F-H}$=3.5 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{10}H_{10}F_3NNa$: 224.0663; found: 224.0659.

4.3. General procedure for the synthesis of ethyl 2-alkyl-3-(trifluoromethyl)diaziridine-1-carboxylates (2a–j)

To a stirred solution of 1 mmol of trifluoromethyl imine in 2 mL of anhydrous CH_2Cl_2, 1 mmol of $NsONHCO_2Et$ was added batchwise at room temperature. After 1 h another 1 mmol of $NsONHCO_2Et$ was added and the mixture was kept stirring. After 16 h hexane was added, nosylate salts were filtered and the solvents were evaporated under vacuum.

4.3.1. *Ethyl 2-benzyl-3-(trifluoromethyl)diaziridine-1-carboxylate (**2a**)*

Orange oil; 0.13 g; IR: 1605, 1735 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.27 (t, ^{3}J=6.6 Hz, 3H), 3.57 (q, ^{3}J=4.3 Hz, 1H), 3.77 (d, ^{2}J=13.3 Hz, 1H), 3.97 (d, ^{2}J=13.3 Hz, 1H), 4.05–4.34 (m, 2H), 7.31–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 58.4 (q, $^{2}J_{C-F}$=41.0 Hz, C−CF_3), 63.6, 63.8, 121.6 (q, $^{1}J_{C-F}$=277.4 Hz, CF_3), 128.2, 128.5 (2C), 128.8 (2C), 132.2, 159.2; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.2 (d, $^{3}J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+H]$^+$ calcd for $C_{12}H_{14}F_3N_2O_2$: 275.1007; found: 275.1009.

4.3.2. *Ethyl 2-cyclopentyl-3-(trifluoromethyl)diaziridine-1-carboxylate (**2b**)*

Yellow oil; 0.10 g; IR: 1737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.29 (t, ^{3}J=7.1 Hz, 3H), 1.56–2.02 (m, 8H), 2.51–2.58 (m, 1H), 3.45 (q, $^{3}J_{H-F}$=4.3 Hz, 1H), 4.10–4.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 24.3, 24.6, 28.8, 31.6, 58.3 (q, $^{2}J_{C-F}$=39.0 Hz, C−CF_3), 63.5, 70.8, 120.2 (q, $^{1}J_{C-F}$=275.0 Hz, CF_3), 159.3; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.5 (d, $^{3}J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{10}H_{15}F_3N_2NaO_2$: 275.0983; found: 275.0988, *m/z* [M+H]$^+$ calcd for $C_{10}H_{16}F_3N_2O_2$: 253.1164; found: 253.1170.

4.3.3. *Ethyl 2-octyl-3-(trifluoromethyl)diaziridine-1-carboxylate (**2c**)*

Yellow oil; 0.15 g; IR: 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.87 (t, ^{3}J=6.6 Hz, 3H), 1.19–1.42 (m, 13H), 1.56–1.76 (m, 2H), 2.51–2.77 (m, 2H), 3.44 (q, $^{3}J_{H-F}$=4.3 Hz, 1H), 4.19–4.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 14.0, 22.6, 26.8, 27.7, 29.1, 29.3, 31.9, 59.2 (q, $^{2}J_{C-F}$=40.0 Hz, C−CF_3), 60.6, 63.7, 121.6 (q, $^{1}J_{C-F}$=277.0 Hz, CF_3), 159.4; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.8 (d, $^{3}J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{13}H_{23}F_3N_2NaO_2$: 319.1609; found: 319.1613.

4.3.4. *Ethyl 2-pentyl-3-(trifluoromethyl)diaziridine-1-carboxylate (**2d**)*

Colorless oil; 0.13 g; IR: 1741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.9 (t, ^{3}J=7.1 Hz, 3H), 1.21–1.46 (m, 7H), 1.62–1.72 (m, 2H), 2.54–2.72 (m, 2H), 3.44 (q, $^{3}J_{H-F}$=4.4 Hz, 1H), 4.18–4.36 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 13.9, 22.4, 27.3, 28.9, 59.2 (q, $^{2}J_{C-F}$=40.0 Hz, C−CF_3), 60.5, 63.7, 121.6 (q, $^{1}J_{C-F}$=277.0 Hz, CF_3), 159.5; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.8 (d, $^{3}J_{F-H}$=4.4 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{10}H_{17}F_3N_2NaO_2$: 277.1140; found: 277.1139; *m/z* [M+H]$^+$ calcd for $C_{10}H_{18}F_3N_2O_2$: 255.1320; found: 255.1328.

4.3.5. *Ethyl 2-(1-methylbutyl)-3-(trifluoromethyl)diaziridine-1-carboxylate (**2e**)*

Orange oil; 0.12 g; IR: 1748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.90 (t, ^{3}J=7.1 Hz, 3H, diastereomer I), 0.91 (t, ^{3}J=7.3 Hz, 3H, diastereomer II), 1.09–1.81 (m, 20H), 1.92–2.03 (m, 2H), 3.43 (q, $^{3}J_{H-F}$=4.3 Hz, 1H, diastereomer I), 3.49 (q, $^{3}J_{H-F}$=4.3 Hz, 1H, diastereomer II), 4.14–4.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (2C), 14.1 (2C), 16.5, 18.5, 18.7, 18.8, 35.8, 37.4, 58.4 (q, $^{2}J_{C-F}$=40.2 Hz, C−CF_3, diastereomer I), 59.3 (q, $^{2}J_{C-F}$=39.9 Hz, C−CF_3, diastereomer II), 63.7 (2C), 65.1, 65.3, 121.6 (q, $^{1}J_{C-F}$=277.3 Hz, CF_3, diastereomer I), 121.7 (q, $^{1}J_{C-F}$=276.7 Hz, CF_3, diastereomer II), 159.6 (2C); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.7 (d, $^{3}J_{F-H}$=4.4 Hz, 3F, diastereomer I), −70.4 (d, $^{3}J_{F-H}$=4.3 Hz, 3F, diastereomer II); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{10}H_{17}F_3N_2NaO_2$: 277.1140; found: 277.1143.

4.3.6. *Ethyl 2-(1,2-dimethylpropyl)-3-(trifluoromethyl)diaziridine-1-carboxylate (**2f**)*

Orange oil; 0.09 g; IR: 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.93–1.04 (m, 12H), 1.12–1.20 (m, 6H), 1.24–1.30 (m, 6H), 1.74–1.89 (m, 2H), 1.96–2.07 (m, 2H), 3.39 (q, $^{3}J_{H-F}$=4.3 Hz, 1H, minor), 3.52 (q, $^{3}J_{H-F}$=4.3 Hz, 1H, major), 4.14–4.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.1, 13.9 (2C), 14.9, 16.5, 17.6, 19.0, 19.3, 31.3 (major), 31.6 (minor), 58.4 (q, $^{2}J_{C-F}$=40.2 Hz, C−CF_3, minor), 59.7 (q, $^{2}J_{C-F}$=39.8 Hz, CCF_3, major), 63.6 (minor), 63.7 (major), 70.0 (minor), 70.5 (major), 121.4

(q, $^1J_{C-F}$=277.4 Hz, CF_3, minor), 121.7 (q, $^1J_{C-F}$=277.2 Hz, CF_3, major), 157.9 (2C); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.5 (d, $^3J_{F-H}$=4.3 Hz, 3F, minor), −70.1 (d, $^3J_{F-H}$=4.3 Hz, 3F, major); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{10}H_{17}F_3N_2NaO_2$: 277.1140; found: 277.1149, *m*/*z* [M+H]$^+$ calcd for $C_{10}H_{18}F_3N_2O_2$: 255.1320; found: 255.1324.

*4.3.7. Ethyl 3-(trifluoromethyl)-2-(1,2,2-trimethylpropyl)diaziridine-1-carboxylate (**2g**).* Brown oil; 0.10 g; IR: 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.97 (s, 9H, major), 1.02 (s, 9H, minor), 1.18 (d, ^3J=6.5 Hz, 6H), 1.27 (t, ^3J=7.1 Hz, 6H), 1.78 (q, ^3J=6.5 Hz, 2H), 3.34 (q, $^3J_{H-F}$=4.4 Hz, 1H, minor), 3.59 (q, $^3J_{H-F}$=4.2 Hz, 1H, major), 4.13–4.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.9 (minor), 13.8 (minor), 13.9 (major), 14.8 (major), 26.5 (3C, major), 26.6 (3C, minor), 34.0 (major), 34.3 (minor), 57.1 (q, $^2J_{C-F}$=40.3 Hz, C–CF_3, minor), 61.4 (q, $^2J_{C-F}$=39.8 Hz, C–CF_3, major), 63.5 (2C), 73.0 (minor), 73.4 (major), 121.7 (q, $^1J_{C-F}$=277.9 Hz, CF_3, major), 122.0 (q, $^1J_{C-F}$=277.1 Hz, CF_3, minor), 159.9 (2C); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.2 (d, $^3J_{F-H}$=4.3 Hz, 3F, minor), −70.4 (d, $^3J_{F-H}$=4.3 Hz, 3F, major); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{11}H_{19}F_3N_2NaO_2$: 291.1296; found: 291.1292, *m*/*z* [M+H]$^+$ calcd for $C_{11}H_{20}F_3N_2O_2$: 269.1477; found: 269.1479.

*4.3.8. Ethyl 2-(1,3-dimethylbutyl)-3-(trifluoromethyl)diaziridine-1-carboxylate (**2h**).* Yellow oil; 0.12 g; IR: 1745 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.83 (d, ^3J=6.5 Hz, 3H), 0.84 (d, ^3J=6.4 Hz, 3H), 1.91 (d, ^3J=6.5 Hz, 6H), 1.11 (d, ^3J=6.5 Hz, 3H), 1.24–1.31 (m, 9H), 1.39–1.50 (m, 2H), 1.60–1.86 (m, 4H), 1.98–2.11 (m, 2H); 3.44 (q, $^3J_{H-F}$=4.3 Hz, 1H, diastereomer I), 3.47 (q, $^3J_{H-F}$=4.3 Hz, 1H, diastereomer II), 4.13–4.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9 (2C), 17.0, 18.8, 22.1, 22.2, 23.2, 23.3, 24.4 (2C), 42.7, 44.6, 58.3 (q, $^2J_{C-F}$=40.2 Hz, C–CF_3, diastereomer I), 59.3 (q, $^2J_{C-F}$=40.1 Hz, C–CF_3, diastereomer II), 63.4, 63.6, 63.7 (2C), 121.6 (q, $^1J_{C-F}$=277.4 Hz, CF_3, diastereomer I), 121.7 (q, $^1J_{C-F}$=277.4 Hz, CF_3, diastereomer II), 159.7 (2C); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.9 (d, $^3J_{F-H}$=4.4 Hz, 3F, diastereomer II), −70.5 (d, $^3J_{F-H}$=4.3 Hz, 3F, diastereomer I); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{11}H_{19}F_3N_2NaO_2$: 291.1296; found: 291.1289, *m*/*z* [M+H]$^+$ calcd for $C_{11}H_{20}F_3N_2O_2$: 269.1477; found: 269.1471.

*4.3.9. Ethyl 2-(1-methyl-2-phenylethyl)-3-(trifluoromethyl)diaziridine-1-carboxylate (**2i**).* Orange oil; 0.12 g; IR: 1608, 1743 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.19 (t, ^3J=7.1 Hz, 3H, major), 1.20 (t, ^3J=7.0 Hz, 3H, minor), 1.29 (d, ^3J=7.0 Hz, 3H, major), 1.41 (d, ^3J=6.9 Hz, 3H, minor), 2.49 (dd, ^2J=4.6 Hz, ^3J=11.6 Hz, 1H), 2.66–2.90 (m, 3H), 3.00–3.16 (m, 2H), 3.20 (q, $^3J_{H-F}$=4.3 Hz, 1H, major), 3.39 (q, $^3J_{H-F}$=4.3 Hz, 1H, minor), 4.07–4.24 (m, 4H), 7.09–7.25 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (2C), 18.9 (minor), 19.8 (major), 39.0 (minor), 39.1 (major), 59.0 (q, $^2J_{C-F}$=40.3 Hz, C–CF_3, major), 59.5 (q, $^2J_{C-F}$=40.2 Hz, C–CF_3, major), 63.7 (4C), 67.4 (minor), 67.5 (major), 121.4 (q, $^1J_{C-F}$=277.6 Hz, CF_3, major), 121.6 (q, $^1J_{C-F}$=277.4 Hz, CF_3, minor), 126.5 (minor), 126.7 (major), 127.1 (4C), 128.5 (minor), 128.6 (major), 144.1, 144.2, 159.3, 159.4; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.2 (d, $^3J_{F-H}$=4.3 Hz, 3F, minor), −70.4 (d, $^3J_{F-H}$=4.3 Hz, 3F, major); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{14}H_{17}F_3N_2NaO_2$: 325.1140; found: 325.1137, *m*/*z* [M+H]$^+$ calcd for $C_{14}H_{18}F_3N_2O_2$: 303.1320; found: 303.1327.

*4.3.10. Ethyl 2-(1-phenylethyl)-3-(trifluoromethyl)diaziridine-1-carboxylate (**2j**).* Yellow oil; 0.10 g; IR: 1740, 1607 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.12 (t, ^3J=7.1 Hz, 3H), 1.41 (d, ^3J=6.8 Hz, 3H), 3.17 (q, ^3J=6.7 Hz, 1H), 3.47 (q, $^3J_{H-F}$=4.3 Hz, 1H), 3.98–4.15 (m, 2H), 7.18–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 20.0, 58.8 (q, $^2J_{C-F}$=40.4 Hz, C–CF_3), 63.6, 68.5, 121.7 (q, $^1J_{C-F}$=277.3 Hz, CF_3), 127.3 (2C), 127.8, 128.3 (2C), 140.4, 159.1; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.5 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{13}H_{15}F_3N_2NaO_2$: 311.0983; found: 311.0991.

4.4. General procedure for the synthesis of *tert*-butyl 2-alkyl-3-(trifluoromethyl)diaziridine-1-carboxylates (2a′,c′)

To a stirred solution of 1 mmol of trifluoromethyl imine in 2 mL of anhydrous CH_2Cl_2, 1 mmol of NsONHCO$_2$*t*-Bu was added batchwise at room temperature. After 1 h another 1 mmol of NsONHCO$_2$*t*-Bu was added and the mixture was kept stirring. After 24 h hexane was added, nosylate salts were filtered and the solvents were evaporated under vacuum.

*4.4.1. tert-Butyl 2-benzyl-3-(trifluoromethyl)diaziridine-1-carboxylate (**2a′**).* Colorless oil; 0.13 g; IR: 1738, 1604 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.45 (s, 9H), 3.57 (q, $^3J_{H-F}$=4.3 Hz, 1H), 3.77 (d, ^2J=13.3 Hz, 1H), 3.97 (d, ^2J=13.3 Hz, 1H), 7.26–7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.5 (3C), 58.3 (q, $^2J_{C-F}$=41 Hz, C–CF_3), 63.2, 80.5, 121.0 (q, $^1J_{C-F}$=276 Hz, CF_3), 127.3, 127.8 (2C), 128.5 (2C), 139.2, 158.6; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.0 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{14}H_{17}F_3N_2NaO_2$: 325.1140; found: 325.1137.

*4.4.2. tert-Butyl 2-octyl-3-(trifluoromethyl)diaziridine-1-carboxylate (**2c′**).* Colorless oil; 0.14 g; IR: 1737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86 (t, ^3J=6.6 Hz, 3H), 1.20–1.41 (m, 10H), 1.46 (s, 9H), 1.55–1.79 (m, 2H), 2.45–2.77 (m, 2H), 3.42 (q, $^3J_{H-F}$=4.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 22.5, 26.2, 27.4 (2C), 28.4 (3C), 30.5, 32.6, 50.3, 59.1 (q, $^2J_{C-F}$=41 Hz, C–CF_3), 80.4, 121.8 (q, $^1J_{C-F}$=277 Hz, CF_3), 159.3; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.9 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_{15}H_{27}F_3N_2NaO_2$: 347.1922; found: 347.1931.

4.5. Synthesis of ethyl 2-allyl-3-(trifluoromethyl)diaziridine-1-carboxylate (2k)

A stirred solution of 0.5 mmol of trifluoroacetaldehyde ethyl hemiacetal (90% aq solution) and 0.5 mmol of allylamine was heated at 105 °C under solvent-free conditions in a flask fitted with a calcium chloride tube. After the reaction was completed (^{1}H NMR, 4 h), 2 mL of anhydrous CH_2Cl_2 and 0.5 mmol of NsONHCO$_2$Et were added batchwise at room temperature. After 1 h another 1 mmol of NsONHCO$_2$Et was added and the mixture was kept stirring. After 24 h hexane was added, nosylate salts were filtered and the solvents were evaporated under vacuum. Orange oil; 0.04 g; IR: 1745, 1650 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.30 (t, ^3J=7.1 Hz, 3H), 3.21 (dd, ^3J=6.5 Hz, ^2J=13.6 Hz, 1H), 3.41 (dd, ^3J=6.5 Hz, ^2J=13.6 Hz, 1H), 3.51 (q, $^3J_{H-F}$=4.3 Hz, 1H), 4.21–4.37 (m, 2H), 5.27–5.40 (m, 2H), 5.87–6.00 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 58.5 (q, $^2J_{C-F}$=40 Hz, C–CF_3), 62.4, 62.9, 119.9, 121.6 (q, $^1J_{C-F}$=278 Hz, CF_3), 130.9, 159.5; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.4 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_8H_{11}F_3N_2NaO_2$: 247.0670; found: 247.0667, *m*/*z* [M+H]$^+$ calcd for $C_8H_{12}F_3N_2O_2$: 225.0851; found: 225.0849.

4.6. Synthesis of *N*-[(*E*)-ethylidene]-3,3-dimethylbutan-2-amine (3)

To a stirred solution of 1 mmol of 3,3-dimethylbutan-2-amine in 3 mL of CH_2Cl_2, 2 mmol of acetaldehyde was added at room temperature, reaction time 10 min; 0.09 g; 68% yield; yellow oil; IR: 1668 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.74 (s, 9H), 0.95 (d, ^3J=6.5 Hz, 3H), 1.83 (d, ^3J=4.8 Hz, 3H), 2.61 (q, ^3J=6.5 Hz, 1H), 7.53 (q, ^3J=5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.9, 23.9, 25.7 (3C), 42.8, 70.3, 156.7; HRMS: *m*/*z* [M+Na]$^+$ calcd for $C_8H_{17}NNa$: 150.1259; found: 150.1264.

4.7. Synthesis of ethyl 3-methyl-2-(1,2,2-trimethylpropyl) diaziridine-1-carboxylate (4)

To a stirred solution of imine **3** (1 mmol) in 2 mL in anhydrous CH_2Cl_2, 1 mmol of $NsONHCO_2Et$ was added batchwise at room temperature. After 30 min another 1 mmol of $NsONHCO_2Et$ was added and the mixture was kept stirring. After the reaction was completed (^1H NMR, 2 h), hexane was added, nosylate salts were filtered and the solvent was evaporated under vacuum. Colorless oil; 0.09 g; IR ($CHCl_3$): 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=0.87 (s, 9H, major), 0.94 (s, 9H, minor), 1.12 (d, ^3J=6.5 Hz, 6H), 1.26 (t, ^3J=7.1 Hz, 3H, major), 1.27 (t, ^3J=7.1 Hz, 3H, minor), 1.33 (d, ^3J=6.5 Hz, 6H), 1.58 (q, ^3J=6.4 Hz, 1H, major), 1.65 (q, ^3J=6.7 Hz, 1H, minor), 2.92 (q, $^3J_{H-F}$=5.2 Hz, 1H, minor), 3.07 (q, $^3J_{H-F}$=5.1 Hz, 1H, major), 4.09–4.29 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.2 (minor), 14.2 (2C), 14.8 (major), 16.0 (major), 16.3 (minor), 26.7 (3C, minor), 26.8 (3C, major), 33.8 (major), 34.3 (minor), 58.7 (2C), 62.5 (minor), 63.8 (major), 72.6 (minor), 73.1 (major), 162.0, 162.6; HRMS: *m/z* [M+Na]$^+$ calcd for $C_{11}H_{22}N_2NaO_2$: 237.1579; found: 237.1582, *m/z* [M+H]$^+$ calcd for $C_{11}H_{23}N_2O_2$: 215.1760; found: 215.1768.

4.8. General procedure for the synthesis of enantiopure ethyl 2-alkyl-3-(trifluoromethyl)diaziridine-1-carboxylate

To a stirred solution of 1 mmol of trifluoromethyl imine in 2 mL of anhydrous CH_2Cl_2, 1 mmol of $NsONHCO_2Et$ was added batchwise at room temperature. After 1 h another 1 mmol of $NsONHCO_2Et$ was added and the mixture was kept stirring. After 16 h hexane was added, nosylate salts were filtered and the solvents were evaporated under vacuum.

*4.8.1. Ethyl (2S,3S)-3-(trifluoromethyl)-2-[(R)-1,2,2-trimethylpropyl] diaziridine-1-carboxylate [(R,S,S)-**2g**].* Colorless oil; 0.09 g; [α]$_D^{25}$ −18.2 (*c* 1.6, $CHCl_3$); IR: 1742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=0.98 (s, 9H), 1.19 (d, ^3J=6.5 Hz, 3H), 1.28 (t, ^3J=7.1 Hz, 3H), 1.79 (q, ^3J=6.6 Hz, 1H), 3.60 (q, $^3J_{H-F}$=4.2 Hz, 1H), 4.22 (q, ^3J=7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 14.8, 26.5 (3C), 34.0, 61.4 (q, $^2J_{C-F}$=40.0 Hz, C–CF_3), 63.5, 73.4, 121.6 (q, $^1J_{C-F}$=277.0 Hz, CF_3), 159.9; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−70.4 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{11}H_{19}F_3N_2NaO_2$: 291.1296; found: 291.1291.

*4.8.2. Ethyl (2R,3R)-3-(trifluoromethyl)-2-[(R)-1,2,2-trimethylpropyl] diaziridine-1-carboxylate [(R,R,R)-**2g**].* Colorless oil; 0.04 g; [α]$_D^{25}$ +16.6 (*c* 1.6, $CHCl_3$); IR: 1742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.04 (s, 9H), 1.12 (d, ^3J=6.5 Hz, 3H), 1.29 (t, ^3J=7.1 Hz, 3H), 1.79 (q, ^3J=6.5 Hz, 1H), 3.35 (q, $^3J_{H-F}$=4.4 Hz, 1H), 4.25 (q, ^3J=7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.9, 13.8, 26.6 (3C), 34.2, 57.2 (q, $^2J_{C-F}$=40.0 Hz, C–CF_3), 63.6, 72.9, 122.1 (q, $^1J_{C-F}$=277.0 Hz, CF_3), 160.3; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.1 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{11}H_{19}F_3N_2NaO_2$: 291.1296; found: 291.1289.

4.8.3. Ethyl (2R,3R*)-3-(trifluoromethyl)-2-[(S)-1,2,2-trimethylpropyl]diaziridine-1-carboxylate [(S,R*,R*)-**2g**].* Yellow oil; 0.12 g; IR: 1743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=0.96 (s, 9H, major), 1.02 (s, 9H, minor), 1.12 (d, ^3J=7.1 Hz, 3H, minor), 1.18 (d, ^3J=6.5 Hz, 3H, major), 1.27 (t, ^3J=7.1 Hz, 6H), 1.78 (q, ^3J=6.6 Hz, 2H), 3.35 (q, $^3J_{H-F}$=4.4 Hz, 1H, minor), 3.60 (q, $^3J_{H-F}$=4.2 Hz, 1H, major), 4.13–4.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.9 (minor), 13.8 (minor), 13.9 (major), 14.8 (major), 26.5 (3C, major), 26.6 (3C, minor), 34.0 (major), 34.3 (minor), 57.1 (q, $^2J_{C-F}$=40.1 Hz, C–CF_3, minor), 61.4 (q, $^2J_{C-F}$=39.8 Hz, C–CF_3, major), 63.5 (2C), 72.9 (minor), 73.4 (major), 121.7 (q, $^1J_{C-F}$=277.9 Hz, CF_3, major), 122.0 (q, $^1J_{C-F}$=277.1 Hz, CF_3, minor), 159.9 (2C); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.2 (d, $^3J_{F-H}$=4.3 Hz, 3F, minor), −70.4 (d, $^3J_{F-H}$=4.3 Hz, 3F, major); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{11}H_{19}F_3N_2NaO_2$: 291.1296; found: 291.1294.

*4.8.4. Ethyl (2S,3S)-2-[(R)-1-phenylethyl]-3-(trifluoromethyl)diaziridine-1-carboxylate [(R,S,S)-**2j**].* Orange oil; 0.14 g; [α]$_D^{25}$ +27.1 (*c* 2.0, $CHCl_3$); IR: 1740, 1607 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.12 (t, ^3J=7.1 Hz, 3H), 1.41 (d, ^3J=6.8 Hz, 3H), 3.17 (q, ^3J=6.7 Hz, 1H), 3.47 (q, $^3J_{H-F}$=4.3 Hz, 1H), 3.98–4.15 (m, 2H), 7.18–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 20.0, 58.8 (q, $^2J_{C-F}$=40.4 Hz, C–CF_3), 63.6, 68.5, 121.7 (q, $^1J_{C-F}$=277.3 Hz, CF_3), 127.3 (2C), 127.8, 128.3 (2C), 140.4, 159.1; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.6 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{13}H_{15}F_3N_2NaO_2$: 311.0983; found: 311.0994.

*4.8.5. Ethyl (2R,3R)-2-[(S)-1-phenylethyl]-3-(trifluoromethyl)diaziridine-1-carboxylate [(S,R,R)-**2j**].* Orange oil; 0.10 g; [α]$_D^{25}$ −29.2 (*c* 1.2, $CHCl_3$); IR: 1607, 1740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.12 (t, ^3J=7.1 Hz, 3H), 1.41 (d, ^3J=6.8 Hz, 3H), 3.17 (q, ^3J=6.8 Hz, 1H), 3.47 (q, $^3J_{H-F}$=4.3 Hz, 1H), 3.97–4.14 (m, 2H), 7.17–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 20.0, 58.7 (q, $^2J_{C-F}$=40.3 Hz, C–CF_3), 63.6, 68.5, 121.7 (q, $^1J_{C-F}$=277.3 Hz, CF_3), 127.3 (2C), 127.8, 128.3 (2C), 140.4, 159.1; ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.5 (d, $^3J_{F-H}$=4.3 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_{13}H_{15}F_3N_2NaO_2$: 311.0983; found: 311.0989.

4.9. General procedure for the synthesis of 2-alkyl-3-(trifluoromethyl)oxaziridines

Trifluoromethyl imine (1 mmol) was dissolved in 1 mL of CH_2Cl_2 and was added dropwise to a stirred solution of 1 mmol of *m*-CPBA in 2 mL of CH_2Cl_2 at 0 °C. When the solution becomes clear was washed with 2 N Na_2CO_3 and the solvent was evaporated under vacuum after drying over Na_2SO_4.

*4.9.1. 2-Cyclopentyl-3-(trifluoromethyl)oxaziridine (**5b**).* Yellow oil; 0.14 g; IR: 1412 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.38–2.01 (m, 8H), 2.71–2.80 (m, 1H), 4.15 (q, $^3J_{H-F}$=3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.1 (2C), 31.3 (2C), 69.3, 74.6 (q, $^2J_{C-F}$=42.0 Hz, C–CF_3), 120.9 (q, $^1J_{C-F}$=277.4 Hz, CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.5 (d, $^3J_{F-H}$=3.4 Hz, 3F); HRMS: *m/z* [M+Na]$^+$ calcd for $C_7H_{10}F_3NNaO$: 204.0612; found: 204.0620.

*4.9.2. 2-(1,2-Dimethylpropyl)-3-(trifluoromethyl)oxaziridine (**5f**).* Yellow oil; 0.16 g; IR: 1421 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=0.98 (d, ^3J=6.7 Hz, 6H, minor), 0.99 (d, ^3J=6.7 Hz, 6H, major), 1.09 (d, ^3J=6.6 Hz, 3H, minor), 1.24 (d, ^3J=6.2 Hz, 3H, major), 1.80–2.01 (m, 4H), 4.17 (q, $^3J_{H-F}$=3.3 Hz, 1H, minor), 4.27 (q, $^3J_{H-F}$=3.3 Hz, 1H, major); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.7, 16.1, 17.7, 18.5, 18.8, 19.0, 31.8 (major), 32.4 (minor), 71.4 (minor), 71.5 (major), 73.9 (q, $^2J_{C-F}$=42.0 Hz, C–CF_3, minor), 76.2 (q, $^2J_{C-F}$=41.5 Hz, C–CF_3, major), 120.9 (q, $^1J_{C-F}$=277.8 Hz, CF_3, major), 121.1 (q, $^1J_{C-F}$=277.5 Hz, CF_3, minor); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.4 (d, $^3J_{F-H}$=3.4 Hz, 3F, minor), −70.2 (d, $^3J_{F-H}$=3.4 Hz, 3F, major); HRMS: *m/z* [M+Na]$^+$ calcd for $C_7H_{12}F_3NNaO$: 206.0769; found: 206.0774.

*4.9.3. 3-(Trifluoromethyl)-2-(1,2,2-trimethylpropyl)-oxaziridine (**5g**).* Yellow oil; 0.16 g; IR: 1416 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=0.99 (s, 9H, major), 1.00 (s, 9H, minor), 1.07 (d, ^3J=6.9 Hz, 3H, minor), 1.21 (d, ^3J=6.4 Hz, 3H, major), 1.87–1.98 (m, 2H), 4.09 (q, $^3J_{H-F}$=3.3 Hz, 1H, minor), 4.31 (q, $^3J_{H-F}$=3.3 Hz, 1H, major); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.9 (minor), 14.7 (major), 26.3 (3C, minor), 26.6 (3C, major), 34.9 (major), 36.0 (minor), 73.2 (q, $^2J_{C-F}$=42.1 Hz, C–CF_3, minor), 74.2 (2C) 77.5 (q, $^2J_{C-F}$=41.1 Hz, CCF_3, major), 120.9 (q, $^1J_{C-F}$=277.5 Hz, CF_3, major), 121.2 (q, $^1J_{C-F}$=277.5 Hz, CF_3, minor); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.2 (d, $^3J_{F-H}$=3.4 Hz, 3F, minor),

−70.4 (d, $^{3}J_{F-H}$=3.4 Hz, 3F, major); HRMS: *m*/*z* [M+Na]$^{+}$ calcd for $C_8H_{14}F_3NNaO$: 220.0925; found: 220.0931.

*4.9.4. 2-(1,3-Dimethylbutyl)-3-(trifluoromethyl)oxaziridine (**5h**).* Orange oil; 0.16 g; IR: 1416 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86–0.95(m, 12H), 1.15 (d, ^{3}J=6.6 Hz, 3H, minor), 1.26 (d, ^{3}J=6.2 Hz, 3H, major), 1.34–1.45 (m, 2H), 1.61–1.87 (m, 4H), 2.19–2.30 (m, 2H), 4.17 (q, $^{3}J_{H-F}$=3.3 Hz, 1H, minor), 4.22 (q, $^{3}J_{H-F}$=3.2 Hz, 1H, major); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.6 (minor), 19.2 (major), 22.3, 26.6 (2C), 23.0, 24.5 (2C), 42.2 (minor), 44.9 (major), 64.4 (minor), 64.6 (major), 74.0 (q, $^{2}J_{C-F}$=42.1 Hz, C–CF_3, minor), 75.4 (q, $^{2}J_{C-F}$=41.8 Hz, C–CF_3, major), 120.8 (q, $^{1}J_{C-F}$=277.7 Hz, CF_3, minor), 120.9 (q, $^{1}J_{C-F}$=277.5 Hz, CF_3, major); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−72.9 (d, $^{3}J_{F-H}$=3.4 Hz, 3F, minor), −70.5 (d, $^{3}J_{F-H}$=3.4 Hz, 3F, major); HRMS: *m*/*z* [M+Na]$^{+}$ calcd for $C_8H_{14}F_3NNaO$: 220.0925; found: 220.0935.

*4.9.5. Ethyl (2S,3S)-3-(trifluoromethyl)-2-[(R)-1,2,2-trimethylpropyl] oxaziridine [(R,S,S)-**5g**].* Yellow oil; 0.13 g; $[\alpha]_D^{25}$ −22.0 (*c* 1.2, $CHCl_3$); IR: 1419 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.0 (s, 9H), 1.21 (d, ^{3}J=6.4 Hz, 3H), 1.94 (q, ^{3}J=6.4 Hz, 1H), 4.31 (q, $^{3}J_{H-F}$=3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.7, 26.6 (3C), 34.7, 74.3, 77.5 (q, $^{2}J_{C-F}$=41.1 Hz, C–CF_3), 120.9 (q, $^{1}J_{C-F}$=277.5 Hz, CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−70.4 (d, $^{3}J_{F-H}$=3.4 Hz, 3F); HRMS: *m*/*z* [M+Na]$^{+}$ calcd for $C_8H_{14}F_3NNaO$: 220.0925; found: 220.0931.

*4.9.6. Ethyl (2R,3R)-3-(trifluoromethyl)-2-[(1R)-1,2,2-trimethylpropyl]oxaziridine [(R,R,R)-**5g**].* Colorless oil; 0.03 g; $[\alpha]_D^{25}$ +18.4 (*c* 1.4, $CHCl_3$); IR: 1421 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.99 (s, 9H), 1.07 (d, ^{3}J=6.9 Hz, 3H), 1.90 (q, ^{3}J=6.9 Hz, 1H), 4.09 (q, $^{3}J_{H-F}$=3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.0, 26.4 (3C), 36.1, 73.2 (q, $^{2}J_{C-F}$=42.1 Hz, C–CF_3), 74.2, 121.1 (q, $^{1}J_{C-F}$=277.6 Hz, CF_3); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.2 (d, $^{3}J_{F-H}$=3.4 Hz, 3F); HRMS: *m*/*z* [M+Na]$^{+}$ calcd for $C_8H_{14}F_3NNaO$: 220.0925; found: 220.0929.

*4.9.7. Ethyl (2R*,3R*)-3-(trifluoromethyl)-2-[(S)-1,2,2-trimethylpropyl]oxaziridine [(S,R*,R*)-**5g**].* Orange oil; 0.17 g; IR: 1422 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.99 (s, 9H, minor), 1.00 (s, 9H, major), 1.07 (d, ^{3}J=6.9 Hz, 3H, minor), 1.21 (d, ^{3}J=6.4 Hz, 3H, major), 1.87–1.98 (m, 2H), 4.09 (q, $^{3}J_{H-F}$=3.3 Hz, 1H, minor), 4.31 (q, $^{3}J_{H-F}$=3.3 Hz, 1H, major); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.9 (minor), 14.7 (major), 26.3 (3C, minor), 26.6 (3C, major), 34.8 (major), 36.1 (minor), 73.2 (q, $^{2}J_{C-F}$=42.1 Hz, C–CF_3, minor), 74.2 (2C), 77.5 (q, $^{2}J_{C-F}$=41.1 Hz, C–CF_3, major), 120.9 (q, $^{1}J_{C-F}$=277.5 Hz, CF_3, major), 121.2 (q, $^{1}J_{C-F}$=277.5 Hz, CF_3, minor); ^{19}F NMR (282.2 MHz, $CDCl_3$): δ=−71.2 (d, $^{3}J_{F-H}$=3.4 Hz, 3F, minor), −70.4 (d, $^{3}J_{F-H}$=3.4 Hz, 3F, major); HRMS: *m*/*z* [M+Na]$^{+}$ calcd for $C_8H_{14}F_3NNaO$: 220.0925; found: 220.0931.

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Supplementary data

Supplementary data associated with this article [^{1}H and ^{13}C NMR spectra of (*E*)-trifluoromethyl imines **1e**,**g**,**i**,**j**, and (*S*)-**1g**,**j**, **3**; diaziridines **2a**–**k**, **2a′**,**c′**, (*R*,*S*,*S*)- and (*R*,*R*,*R*)-**2g**, (*S*,*R**,*R**)-**2g**, (*R*,*S*,*S*)- and (*S*,*R*,*R*)-**2j** and **4**; oxaziridines **5b**,**f**–**h**, (*R*,*S*,*S*)-**5g**, (*S*,*R*,*R*)-**5g**, and (*S*,*R**,*R**)-**5g**] can be found. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.05.097.

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