Synthesis of Three-, Five-, and Six-Membered Heterocycles Derived from New β-Amino-α-(trifluoromethyl) Alcohols

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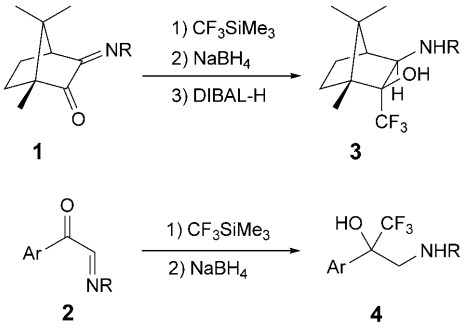
Dedicated to Professor *Rolf Huisgen* on the occasion of his 90th birthday

Nucleophilic trifluoromethylation of α-imino ketones **2**, derived from arylglyoxal, with *Ruppert–Prakash* reagent (CF_3SiMe_3) offers a convenient access to the corresponding *O*-silylated β-imino-α-(trifluoromethyl) alcohols. In a 'one-pot' procedure, by treatment with $NaBH_4$, these products smoothly undergo reduction and desilylation yielding the expected β-amino-α-(trifluoromethyl) alcohols **4**. The latter were used as starting materials for the synthesis of diverse trifluoromethylated heterocycles, including aziridines **5**, 1,3-oxazolidines **8**, 1,3-oxazolidin-2-ones **9**, 1,3,2-oxazaphospholidine 2-oxides **10**, 1,2,3-oxathiazolidine 2-oxides **11**, and morpholine-2,3-diones **12**. An optically active 5-(trifluoromethyl)-substituted 1,3-oxazolidin-2-one **9g** was also obtained.

1. Introduction. – A series of publications in the last two decades evidences the growing interest in the elaboration of new methods for the preparation of β-amino-α-(trifluoromethyl) alcohols in both chiral and achiral form (for a review, see [1]). In general, there are three main strategies applied. The first one is the *Henry* reaction of fluoral or hexafluoroacetone with nitro alkanes, followed by the reduction of the NO_2 group. The second method is based on the ring opening of (trifluoromethyl)oxiranes with primary or secondary amines. Finally, nucleophilic trifluoromethylation of α-amino aldehydes or α-amino ketones with trimethyl(trifluoromethyl)silane (*Ruppert–Prakash* reagent [2]) is probably the most frequently applied method [1]. In recent reports from our group, another approach was applied, and the chemoselective trifluoromethylation of the C=O group of α-imino ketones **1** and **2** derived from camphorquinone and arylglyoxals, respectively, was followed by treatment with $NaBH_4$ [3]. In the latter case, a one-pot procedure leads simultaneously to desilylation and selective reduction of the C=N bond yielding the corresponding β-amino-α-(trifluoromethyl) alcohols **4** (*Scheme 1*). On the other hand, α-imino ketones of type **1**, by treatment with $NaBH_4$, undergo only desilylation, and the reduction of the C=N bond, leading to amino alcohols **3**, was achieved only by using diisobutylaluminum hydride (DIBAL-H) for the final step of the procedure.

[1]) Part of the planned Ph.D. thesis of *E. O.*, University of Łódź.

Scheme 1



In the case of amino alcohol **3** (R = Me), the reaction of the major diastereoisomer with phosgene yielded the desired 1,3-oxazolidin-2-one [3a]. This preliminary result prompted us to explore a series of other easily available β-amino-α-(trifluoromethyl) alcohols **4** for the synthesis of trifluoromethylated heterocycles with various ring sizes.

2. Results and Discussion. – In general, β-amino alcohols of type **4** are crystalline and stable compounds, which can be stored for a long time without special precautions. In one of the studied cases, *i.e.*, **4a** (Ar = 4-$NO_2C_6H_4$, R = *t*-Bu), the crystal structure was established by X-ray crystallography (*Fig. 1*).

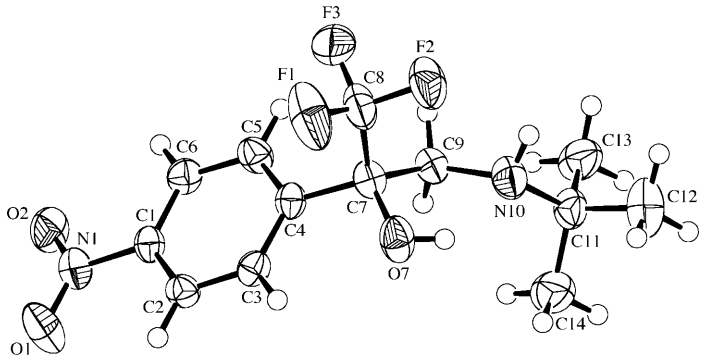


Fig. 1. *ORTEP Plot* [4] *of the molecular structure of* **4a** (with 50% probability ellipsoids; arbitrary numbering of the atoms)

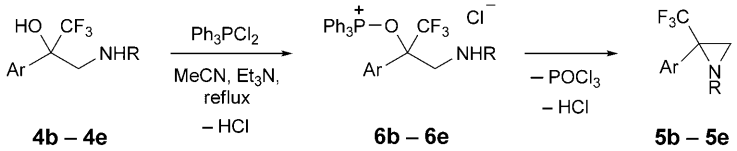
The OH group of **4a** forms an intramolecular H-bond with the amine N-atom, and thereby creates a five-membered loop which can be described by a graph set motif [5] of *S*(5). The NH group does not appear to form any significant H-bonds, although there might be a very weak intramolecular interaction with one of the F-atoms.

The three-membered aziridines are heterocyclic compounds with fundamental importance in organic synthesis [6]. Special interest is focused on aziridines, which contain F-atoms or perfluorinated alkyl groups. However, the limited availability of proper starting materials is reflected in a relatively low number of publications on syntheses of F-containing aziridines [7].

It is well-known that β-amino alcohols are convenient starting materials for the synthesis of aziridines *via* direct or multistep cyclization [6a]. For this reason, trifluoromethyl-substituted β-amino alcohols were studied as convenient substrates for the preparation of aziridines with a new substitution pattern. First attempts were made following *Gabriel*'s method, which is based on the initial conversion of a β-amino alcohol to the corresponding β-halogeno amine and subsequent treatment with a base [8]. In the case of **4b** (Ar = Ph, R = *t*-Bu), the attempted synthesis of the aziridine was unsuccessful[2]).

A successful preparation of the desired aziridines **5b**–**5e** was achieved by the cyclization reaction, using commercially available dichloro(triphenyl)phosphorane (Ph_3PCl_2) according to the procedure described in [7a] (*Scheme 2*). A likely intermediate for the ring closure is the zwitterion **6**.

Scheme 2



4b – 4e **6b – 6e** **5b – 5e**

b Ar = Ph, R = *t*-Bu
c Ar = Ph, R = i-Pr
d Ar = 4-MeO–C_6H_4, R = *t*-Bu
e Ar = 4-MeO–C_6H_4, i-Pr

In the case of **5b**, **5c**, and **5e**, the products were formed exclusively and were isolated as colorless oils in high yields (84–89%). Their structures were established on the basis of the spectroscopic data. In the low-resolution ^{1}H-NMR spectra (80 MHz) of the *N*-isopropyl derivatives **5c** and **5e**, the signal of the aziridine CH_2 group appears as a broad *singlet* at *ca.* 2.45 ppm and a *quadruplet* with $J(C,F) = 3-4$ Hz at higher field (*ca.* 2.05 ppm). The observed splitting of one of the signals results from a through-space coupling of the CF_3 group with the *cis*-oriented H-atom. Surprisingly, no geminal coupling could be detected for the nonequivalent H-atoms at C(3). The ^{1}H-NMR spectra of the *N*-(*tert*-butyl) derivatives **5b** and **5d** displayed a similar signal pattern for the CH_2 group, but, surprisingly, the difference of the chemical shifts in the case of **5b** was much smaller ($\Delta\delta < 0.1$ ppm) than in the other cases ($\Delta\delta = 0.38 - 0.46$ ppm). Moreover, the signal of the through-space coupled H-atom of **5b** appears at lower field, in contrast to the other examples.

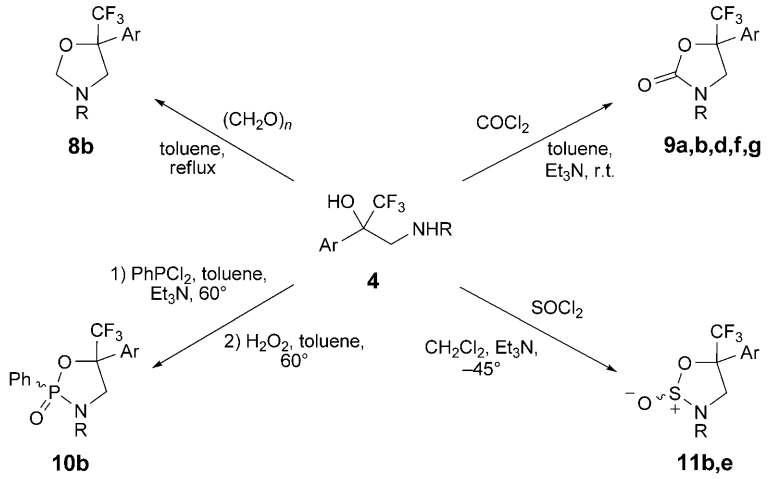
The reaction of **4c** under the same conditions (refluxing MeCN) led to a mixture of **5d** and a second product, in a ratio of *ca.* 1:1, which, in the ^{1}H-NMR spectrum, showed, in addition to a *singlet* for a *t*-Bu group (1.10 ppm), an *AB* system at 3.30 and 3.60 ppm with $J_{AB} = 9.7$ Hz. In a small-scale experiment, carried out in refluxing toluene, the aziridine **5d** was formed only in traces, and the second product was the major component of the reaction mixture. Several experiments, aimed at the optimization of the

[2]) Thionyl chloride ($SOCl_2$) was used as the chlorinating agent and Et_3N as the base. The starting material was consumed, but only a complex mixture of products was obtained [8].

reaction conditions and the formation of **5d** in higher yield, were unsuccessful. Chromatographic workup of the 1:1 mixture and distillation of the less-polar fraction yielded pure **5d** (42%). All attempts to isolate the other new product in pure form were in vain, and the sample was always contaminated with **5d**[3]). In an additional experiment, the isolated aziridine **5d** was heated in boiling toluene for 12 h, but, after cooling, no **7d** was found in the mixture (^{1}H-NMR analysis). Thus, the by-product **7d** was probably formed competitively from an intermediate appearing on the pathway to aziridine **5d**.

It is well-known that β-amino alcohols can be used for the synthesis of five-membered heterocycles *via* substitution or condensation reactions. Thus, the reaction of **4b** with paraformaldehyde in boiling toluene yielded the trifluoromethyl-substituted 1,3-oxazolidine **8b** in 62% yield (*Scheme 3*). On the other hand, the reaction of **4a**, **4b**, **4d**, and **4f** with phosgene in toluene at room temperature in the presence of Et_3N led to the corresponding 1,3-oxazolidin-2-ones **9** in excellent yields.

Scheme 3



a Ar = 4-NO_2–C_6H_4, R = *t*-Bu
b Ar = Ph, R = *t*-Bu
d Ar = 4-MeO–C_6H_4, R = *t*-Bu
e Ar = 4-MeO–C_6H_4, R = i-Pr
f Ar = 4-CF_3–C_6H_4, R = *t*-Bu
g Ar = 4-MeO–C_6H_4, R = (*S*)-PhCH(Me)

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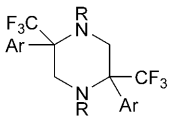
[3]) Based on the ^{1}H-NMR data, the structure of the second product was tentatively assigned as 2,2,5,5-tetrasubstituted piperazine derivative **7d**. It is worth mentioning that only one isomer of **7d** was formed in the described reaction. However, the configuration (*cis* or *trans*) of the substituents at C(2) and C(5) remains unknown.



7d Ar = 4-MeO–C_6H_4, R = *t*-Bu

Nucleophilic trifluoromethylation of the α-imino ketone **2**, with Ar = 4-MeOC$_6$H$_4$ and R = (*S*)-Ph(Me)CH, led to the formation of the β-amino alcohol **4g** as a 6:4 mixture of diastereoisomers [3b]. Chromatographic separation on silica gel yielded the pure diastereoisomers (according to ^{19}F-NMR), and the minor one (more polar fraction) was used for the reaction with phosgene. The corresponding 1,3-oxazolidin-2-one **9g** was obtained as a single product, and the absolute configuration of the two stereogenic centers was unambiguously established by a single-crystal X-ray diffraction analysis (*Fig. 2*).

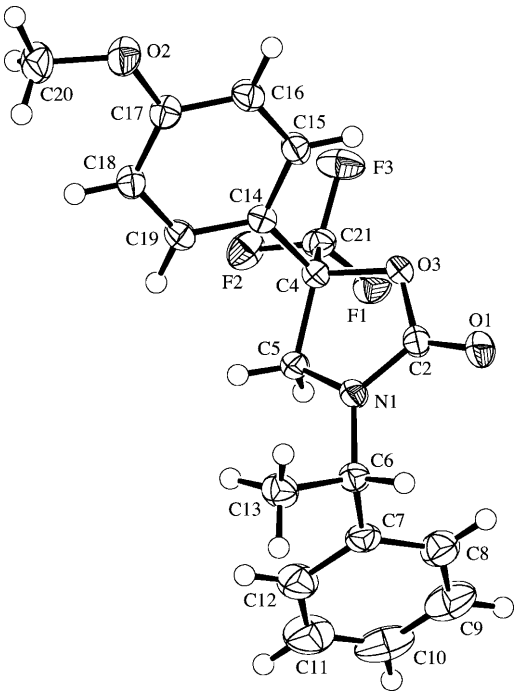


Fig. 2. *ORTEP Plot* [4] *of the molecular structure of* **9g** (with 50% probability ellipsoids; arbitrary numbering of the atoms)

The space group permits the compound in the crystal to be enantiomerically pure, but the absolute configuration of the molecule has not been determined. The enantiomer used in the refinement was based on the known (*S*)-configuration of the 1-phenylethyl substituent of the molecule. The compound thus has the (5*R*,1′*S*)-configuration.

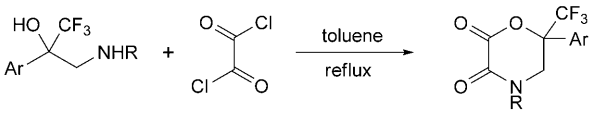
To obtain a derivative of a 1,3,2-oxazaphospholidine, a solution of the β-amino alcohol **4b** in toluene was treated with dichloro(phenyl)phosphane in the presence of Et_3N at 60°. The product obtained thereby decomposed during typical workup, and, therefore, the crude mixture was oxidized by addition of H_2O_2 at the same temperature. The oxidized product, 1,3,2-oxazaphospholidine 2-oxide **10b**, was isolated and purified by layer chromatography in 68% yield as a 1:1 mixture of diastereoisomers (*Scheme 3*). The attempted synthesis of the corresponding 2-sulfide by sulfurization

of the initially formed 1,3,2-oxazaphospholidine with elemental sulfur was achieved smoothly, but the obtained product spontaneously extruded sulfur during the workup and decomposed to give an intractable mixture.

Finally, β-amino alcohols **4b** and **4e** were reacted with $SOCl_2$ in CH_2Cl_2 in the presence of Et_3N at $-45°$ to yield the desired 1,2,3-oxathiazolidine 2-oxides **11b** and **11e**, respectively, as mixtures of diastereoisomers in good yields (*ca.* 4:1 and 1:1 ratio, resp.). In analogy to **10b**, the stereoisomers could not be separated by standard procedures.

As an example for the formation of a six-membered heterocycle, β-amino alcohols **4a** and **4e** were treated with oxalyl chloride in refluxing toluene. After crystallization from CH_2Cl_2/hexane and toluene, respectively, the morpholine-2,3-diones **12a** and **12e** were obtained as colorless crystals in 66 and 85% yield, respectively (*Scheme 4*).

Scheme 4



4a,e **12a,e**

a Ar = 4-NO_2–C_6H_4, R = *t*-Bu
e Ar = 4-MeO–C_6H_4, R = i-Pr

3. Conclusions. – The present study shows that the trifluoromethylated β-amino alcohols **4**, which can be prepared from monoimines of aryl glyoxals **2**, are attractive building blocks for the synthesis of trifluoromethyl-substituted three-, five-, and six-membered heterocycles. The presence of the CF_3 group, which is important for specific changes of physicochemical and biological properties of organic substances [9], enhances the attractiveness of the described approach. The examples of heterocycles selected in this report can be further explored for the preparation of more complex structures.

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Experimental Part

1. *General.* M.p.: *Melt-Temp. II* (*Aldrich*), in capillary; uncorrected. IR Spectra: *NEXUS FT-IR* spectrophotometer; in KBr; absorptions in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Avance III 600* instrument (600 and 150 MHz, resp.); in $CDCl_3$; δ in ppm (δ(TMS) 0 ppm), coupling constants *J* in Hz. The ^{13}C signals were assigned on the basis of HMQC experiments. ^{19}F- and ^{31}P-NMR spectra: *Varian Gemini BB 200* or *Bruker Avance III 600* spectrometers; in $CDCl_3$; with CCl_3F or H_3PO_4, resp., as references. Some spectra were also recorded with a *Tesla BS* spectrometer (80 MHz). HR-ESI-MS: *Finnigan MAT-95*.

2. *Starting Materials.* The commercially available dichloro(triphenyl)phosphorane (Ph_3PCl_2), dichloro(phenyl)phosphane ($PhPCl_2$), oxalyl chloride ($(COCl)_2$), paraformaldehyde ($(CH_2O)_n$), and thionyl chloride ($SOCl_2$) were purchased from *Sigma-Aldrich*, and soln. of phosgene in toluene (20%)

from *Fluka*. β-Amino-α-(trifluoromethyl) alcohols (**4**) were prepared according to the protocol described in [3b]. Toluene was dried over Na, MeCN and CH_2Cl_2 over CaH_2, and they were freshly distilled prior to use.

3. *Syntheses of Trifluoromethylated Aziridines; Reactions with Ph_3PCl_2. General Procedure.* To the soln. of the appropriate β-amino alcohol **4** (1 mmol) and Ph_3PCl_2 (646 mg, 2 mmol) in dry MeCN, Et_3N (505 mg, 5 mmol) was added while cooling the mixture in an ice-bath. Then, the mixture was heated to reflux for 10 h. The solvents were evaporated *in vacuo* (i.v.; for **5c** and **5e**, a water-bath at r.t. was used). The residue was washed with hexane, the precipitate was filtered off, and the solvent was evaporated. In the case of **5d**, the mixture of products was separated by prep. layer chromatography (PLC) on silica gel with hexane/CH_2Cl_2 1:1 as the mobile phase.

*1-(*tert*-Butyl)-2-phenyl-2-(trifluoromethyl)aziridine* (**5b**). Yield: 205 mg (84%). Colorless oil, purified by distillation at 90°/0.1 Pa (bulb-to-bulb). IR (film): 3062*m*, 3042*m*, 2976v*s*, 2934*s*, 2969v*s*, 2875*m*, 1604*w*, 1500*m*, 1474*m*, 1449*m*, 1364*s*, 1354*s*, 1334v*s*, 1217v*s*, 1173v*s*, 1147v*s*, 1114*s*, 1093*m*, 1052*s*, 1029*m*, 1010*m*, 826*w*. ^{1}H-NMR (600 MHz): 7.58–7.57 (*m*, 2 arom. H); 7.39–7.35 (*m*, 3 arom. H); 3.82 (*s*, MeO); 2.36 (br. *q*, ^4J(H,F) = 1.2, 1 H of CH_2); 2.30 (br. *s*, 1 H of CH_2); 0.88 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 131.8 (1 arom. CH); 131.2 (1 arom. C); 129.1, 128.4 (4 arom. CH); 124.8 (*q*, ^1J(C,F) = 276.2, CF_3); 54.5 (Me_3C); 47.0 (*q*, ^2J(C,F) = 34.7, C_q); 27.9 (Me_3C); 27.3 (*q*, ^3J(C,F) = 0.6, CH_2). ^{19}F-NMR (565 MHz): −76.4 (*s*, CF_3). HR-ESI-MS (MeOH + NaI): 266.11259 ($[M+Na]^+$, $C_{13}H_{16}F_3NNa^+$; calc. 266.11271); 244.13067 ($[M+1]^+$, $C_{13}H_{17}F_3N^+$; calc. 244.13076).

1-Isopropyl-2-phenyl-2-(trifluoromethyl)aziridine (**5c**). Yield: 188 mg (82%). Colorless oil, purified by distillation at *ca.* 30°/0.1 Pa (bulb-to-bulb). IR (film): 3062*m*, 3033*m*, 2973v*s*, 2934*s*, 2873*s*, 1604*w*, 1581*w*, 1501*s*, 1463*s*, 1449*s*, 1369v*s*, 1356v*s*, 1444*m*, 1324*s*, 1281*w*, 1203v*s*, 1174v*s*, 1139v*s*, 1051*s*, 1027*s*, 1011*s*, 896*w*, 855*w*. ^{1}H-NMR (600 MHz): 7.54–7.53 (*m*, 2 arom. H); 7.41–7.39 (*m*, 3 arom. H); 2.48 (br. *s*, 1 H of CH_2); 2.05 (br. *s*, 1 H of CH_2); 1.62 (br., Me_2CH); 1.13 (*d*, ^3J(H,H) = 6.0, 1 Me of Me_2CH); 1.08 (*d*, ^3J(H,H) = 4.2, 1 Me of Me_2CH). ^{1}H-NMR (80 MHz): 7.63–7.28 (*m*, 5 arom. H); 2.45 (br. *s*, 1 H of CH_2); 2.05 (*q*, *J*(H,F) = 3.6, 1 H of CH_2); 1.86–1.45 (br. *m*, Me_2CH); 1.14 (*d*, ^3J(H,H) = 6.0, 1 Me of Me_2CH); 1.05 (*d*, ^3J(H,H) = 4.2, 1 Me of Me_2CH). ^{13}C-NMR (150 MHz): 131.8 (1 arom. CH); 129.6 (1 arom. C); 128.6 (4 arom. CH); 124.8 (*q*, ^1J(C,F) = 276.2, CF_3); 52.2 (Me_2CH); 49.0 (*q*, ^2J(C,F) = 34.7, C_q); 33.1 (CH_2); 22.6, 22.4 (Me_2CH). ^{19}F-NMR (565 MHz): −71.6 (*s*, CF_3). HR-ESI-MS (MeCN + NaI): 230.11510 ($[M+1]^+$, $C_{12}H_{15}F_3N^+$; calc. 230.11511).

*1-(*tert*-Butyl)-2-(4-methoxyphenyl)-2-(trifluoromethyl)aziridine* (**5d**; less-polar fraction). Yield: 110 mg (40%). Colorless semi-solid; distilled at 140°/0.1 Pa (bulb-to-bulb). IR (film): 3046*m*, 2973v*s*, 2937v*s*, 2909*s*, 2841*m*, 1604v*s*, 1579*m*, 1518v*s*, 1466*s*, 1444*m*, 1391*m*, 1364*s*, 1336v*s*, 1295v*s*, 1254v*s*, 1217v*s*, 1171v*s*, 1146v*s*, 1111*s*, 1052v*s*, 1035*s*, 1009*m*, 861*m*. ^{1}H-NMR (600 MHz): 7.39–7.35 (*m*, 3 arom. H); 7.48–7.47, 6.89–6.87 (2*m*, 2 arom. H); 3.82 (*s*, MeO); 2.69 (br. *s*, 1 H of CH_2); 2.31 (*q*, ^4J(H,F) = 0.6, 1 H of CH_2); 0.88 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 124.9 (*q*, ^1J(C,F) = 276.2, CF_3); 160.1, 123.0 (2 arom. C); 139.2, 113.8 (4 arom. CH); 55.2 (MeO); 54.4 (Me_3C); 46.3 (*q*, ^2J(C,F) = 34.7, C_q); 27.9 (Me_3C); 27.4 (*q*, ^3J(C,F) = 0.6, CH_2). ^{19}F-NMR (565 MHz): −71.6 (*s*, CF_3). CI-MS (isobutane): 274 (100, $[M+1]^+$). HR-ESI-MS (MeCN + NaI): 274.14131 ($[M+1]^+$, $C_{14}H_{19}F_3NO^+$; calc. 274.14133).

*1,4-Di(*tert*-Butyl)-2,5-bis(4-methoxyphenyl)-2,5-bis(trifluoromethyl)piperazine* (**7d**; more-polar fraction, partially contaminated with **5d**). Decomposes at r.t. Yield: 100 mg (36%). Pale yellow oil. ^{1}H-NMR (80 MHz): 7.65–7.49, 7.00–6.81 (2*m*, 8 arom. H); 3.81 (*s*, 2 MeO); 3.60, 3.30 (*AB*, J_{AB} = 9.7, 2 CH_2); 1.09 (*s*, 2 *t*-Bu).

1-Isopropyl-2-(4-methoxyphenyl)-2-(trifluoromethyl)aziridine (**5e**). Yield: 198 mg (84%). Colorless oil, distilled at 70°/0.1 Pa (bulb-to-bulb). IR (film): 3046*m*, 2973v*s*, 2937v*s*, 2909*s*, 2841*m*, 1604v*s*, 1579*m*, 1518v*s*, 1466*s*, 1444*m*, 1391*m*, 1364*s*, 1336v*s*, 1295v*s*, 1254v*s*, 1217v*s*, 1171v*s*, 1146v*s*, 1111*s*, 1052v*s*, 1035*s*, 109*m*, 861*m*. ^{1}H-NMR (600 MHz): 7.46–7.45 (*m*, 2 arom. H); 6.93–6.91 (*m*, 2 arom. H); 3.83 (*s*, MeO); 2.46 (br. *s*, 1 H of CH_2); 2.00 (br. *s*, 1 H of CH_2); 1.62 (br., Me_2CH); 1.11, 1.08 (2*d*, ^3J(H,H) = 6.0, Me_2CH). ^{1}H-NMR (80 MHz): 7.53–7.36 (*m*, 2 arom. H); 6.99–6.80 (*m*, 2 arom. H); 3.81 (*s*, MeO); 2.42 (br. *s*, 1 H of CH_2); 1.99 (*q*, *J*(H,F) = 3.3, 1 H of CH_2); 1.85–1.42 (br. *m*, 1 H, Me_2CH); 1.12, 1.05 (2*d*, ^3J(H,H) = 6.0, Me_2CH). ^{13}C-NMR (150 MHz): 160.4, 127.6 (2 arom. C); 133.0, 113.9 (4 arom. CH); 124.8 (*q*, ^1J(C,F) = 273.0, CF_3); 55.3 (MeO); 52.2 (Me_2CH); 48.3 (*q*, ^2J(C,F) = 35.0, C_q); 33.2 (CH_2); 22.5, 22.4

(Me_2CH). ^{19}F-NMR (565 MHz): −71.9 (s, CF_3). HR-ESI-MS (MeOH + NaI): 260.12581 ([M+1]$^+$, $C_{13}H_{17}F_3NO^+$; calc. 260.12568).

4. *Synthesis of Five-Membered Heterocycles.* 4.1. *Reaction with* $(CH_2O)_n$. In a round-bottom flask with a *Dean–Stark* trap, a mixture of **4a** (261 mg, 1 mmol) and paraformaldehyde (45 mg, 1.5 mmol) in toluene (*ca.* 10 ml) was heated to reflux for 12 h. Then, the solvent was evaporated, and the crude product was purified by filtration through a pad of neutral Al_2O_3 (eluent: hexane/CH_2Cl_2 9:1).

*3-(*tert*-Butyl)-5-phenyl-5-(trifluoromethyl)-1,3-oxazolidine* (**8b**). Yield: 169 mg (62%). Colorless, viscous oil. IR (film): 3063*w*, 2972*m*, 2939*m*, 2876*w*, 1643*w*, 1496*w*, 1450*w*, 1389*w*, 1367*m*, 1307*m*, 1258*m*, 1176v*s*, 1164v*s*, 1086*s*, 1062*m*, 1030*m*, 1019*m*, 992*w*, 920*w*, 859*w*. ^{1}H-NMR (600 MHz): 7.43–7.42 (*m*, 2 arom. H); 7.30–7.25 (*m*, 3 arom. H); 4.63, 4.59 (2*d*, ^2J(H,H) = 10.2, CH_2); 3.52, 3.31 (2*d*, ^2J(H,H) = 10.2, CH_2); 0.95 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 137.7 (1 arom. C); 128.7, 128.5, 126.8 (5 arom. CH); 125.5 (*q*, ^1J(C,F) = 285.3, CF_3); 84.2 (*q*, ^2J(C,F) = 28.7, C_q); 83.1, 53.3 (2 CH_2); 52.6 (Me_3C); 25.7 (Me_3C). ^{19}F-NMR (188 MHz): −77.03 (*s*, CF_3). HR-ESI-MS (MeOH + NaI): 296.12297 ([M + Na]$^+$, $C_{14}H_{18}F_3NNaO^+$; calc. 296.12327), 274.14134 ([M+1]$^+$, $C_{14}H_{19}F_3NO^+$; calc. 274.14133).

4.2. *Cyclization with* $COCl_2$. *General Procedure.* To the soln. of an appropriate amino alcohol **4** (1 mmol) in dry toluene (2 ml), Et_3N (253 mg, 2.5 mmol) was added; an enantiomerically pure diastereoisomer **4g** [3b] was used for preparation of **9g**. Then, a soln. of phosgene was added dropwise while cooling the mixture in an ice bath, and the mixture was magnetically stirred overnight. Next day, the solvent was evaporated, and crude products were purified by filtration through a plug of neutral Al_2O_3 using hexane/CH_2Cl_2 7:3 as an eluent.

*3-(*tert*-Butyl)-5-(4-nitrophenyl)-5-(trifluoromethyl)-1,3-oxazolidin-2-one* (**9a**). Yield: 316 mg (95%). Colorless crystals. M.p. 154–156° (petroleum ether/CH_2Cl_2). IR (KBr): 3116*w*, 3078*w*, 2983*m*, 2939*w*, 1767v*s* (C=O), 1608*m*, 1522v*s*, 1478*m*, 1416*m*, 1352v*s*, 1459*w*, 1310*s*, 1295v*s*, 1272*s*, 1238*s*, 1212*s*, 1192v*s*, 1177v*s*, 1141*m*, 1073*s*, 1041*m*, 1001*s*, 861*m*, 849*s*. ^{1}H-NMR (600 MHz): 8.32–8.30, 7.73–7.71 (2*m*, 4 arom. CH); 4.28, 3.86 (2*d*, ^2J(H,H) = 9.6, CH_2); 1.42 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 153.3 (CO); 149.0, 141.4 (2 arom. C); 127.6, 124.5 (4 arom. CH); 123.5 (*q*, ^1J(C,F) = 285.3, CF_3); 77.5 (*q*, ^2J(C,F) = 31.7, C_q); 54.9 (Me_3C); 50.5 (CH_2); 27.5 (Me_3C). ^{19}F-NMR (565 MHz): −81.0 (*s*, CF_3). ESI-MS (MeOH): 355 (100, [M + Na]$^+$). HR-ESI-MS (MeOH + NaI): 355.08775 ([M + Na]$^+$, $C_{14}H_{15}F_3N_2NaO_4^+$; calc. 355.08761), 333.10557 ([M+1]$^+$, $C_{14}H_{16}F_3N_2O_4^+$; calc. 333.10567).

*3-(*tert*-Butyl)-5-phenyl-5-(trifluoromethyl)-1,3-oxazolidin-2-one* (**9b**). Yield: 275 mg (96%). Colorless crystals. M.p. 53–55° (petroleum ether). IR (KBr): 2980*w*, 2913*w*, 1767v*s* (C=O), 1635*w*, 1452*w*, 1412*w*, 1370*w*, 1291*w*, 1238*m*, 1171*s*, 1050*w*, 1035*w*, 1011*w*, 758*w*. ^{1}H-NMR (600 MHz): 7.51–7.49 (*m*, 2 arom. H); 7.45–7.43 (*m*, 3 arom. H); 4.23, 3.88 (2*d*, ^2J(H,H) = 9.3, CH_2); 1.41 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 153.8 (CO); 134.6 (1 arom. C); 129.7, 128.7, 125.9 (5 arom. CH); 123.8 (*q*, ^1J(C,F) = 283.7, CF_3); 77.6 (*q*, ^2J(C,F) = 30.9, C_q); 54.3 (Me_3C); 50.5 (CH_2); 27.3 (Me_3C). ^{19}F-NMR (188 MHz): −80.5 (*s*, CF_3). ESI-MS (MeOH): 310 (100, [M + Na]$^+$). HR-ESI-MS (MeOH + NaI): 310.10266 ([M + Na]$^+$, $C_{14}H_{16}F_3NNaO_2^+$; calc. 310.10253), 288.12028 ([M+1]$^+$, $C_{14}H_{17}F_3NO_2^+$; calc. 288.12059).

*3-(*tert*-Butyl)-5-(4-methoxyphenyl)-5-(trifluoromethyl)-1,3-oxazolidin-2-one* (**9d**). Yield: 310 mg (97%). Colorless crystals. M.p. 107–109° (petroleum ether/CH_2Cl_2). IR (KBr): 2982*w*, 2942*w*, 1763v*s* (C=O), 1611*m*, 1518*s*, 1459*w*, 1411*m*, 1294*s*, 1252v*s*, 1205*s*, 1171v*s*, 1073*m*, 1023*s*, 1011*m*, 844*w*. ^{1}H-NMR (600 MHz): 7.42–7.40, 6.96–6.93 (2*m*, 4 arom. H); 4.19 (*d*, ^2J(H,H) = 9.6, 1 H of CH_2); 3.84 (*dq*, ^2J(H,H) = 9.6, ^4J(H,F) = 0.6, 1 H of CH_2); 3.82 (*s*, MeO); 1.40 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 160.5 (CO); 153.9, 126.6 (2 arom. C); 127.3, 114.1 (4 arom. CH); 123.8 (*q*, ^1J(C,F) = 283.5, CF_3); 77.5 (*q*, ^2J(C,F) = 30.2, C_q); 55.3 (MeO); 54.2 (Me_3C); 50.5 (CH_2); 27.3 (Me_3C). ^{19}F-NMR (188 MHz): −80.8 (*s*, CF_3). ESI-MS (MeOH): 340 (100, [M + Na]$^+$), 318 (45, [M+1]$^+$). HR-ESI-MS (MeOH + NaI): 340.11330 ([M + Na]$^+$, $C_{15}H_{18}F_3NNaO_3^+$; calc. 340.1310), 318.113083 ([M+1]$^+$, $C_{15}H_{19}F_3NO_3^+$; calc. 318.13115).

*3-(*tert*-Butyl)-5-(trifluoromethyl)-5-[4-(trifluoromethyl)phenyl]-1,3-oxazolidin-2-one* (**9f**). Yield: 246 mg (92%). Colorless crystals. M.p. 117–119° (hexane/CH_2Cl_2). IR (KBr): 2989*w*, 2920*w*, 1766v*s* (C=O), 1622*w*, 1417*m*, 1371*w*, 1332*s*, 1291*w*, 1181*s*, 1135*m*, 1107*m*, 1072*m*, 1018*m*, 852*w*. ^{1}H-NMR (600 MHz): 7.73–7.71, 7.66–7.64 (2*m*, 4 arom. H); 4.26, 3.85 (2*d*, ^2J(H,H) = 9.6, CH_2); 1.41 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 153.6 (CO); 138.7 (1 arom. C); 132.3 (*q*, ^2J(C,F) = 33.2, 1 arom. C); 126.8 (2 arom. CH), 126.1 (*q*, ^3J(C,F) = 3.0, 2 arom. CH); 123.8 (*q*, ^1J(C,F) = 271.7, CF_3); 123.7 (*q*, ^1J(C,F) = 285.3,

CF_3); 77.6 (*q*, ^2J(C,F) = 31.7, C_q); 54.7 (Me_3C); 50.6 (CH_2); 27.5 (Me_3C). ^{19}F-NMR (565 MHz): −60.0 (*s*, CF_3); −81.3 (*s*, CF_3). ESI-MS: 378 (100, $[M+Na]^+$). HR-ESI-MS (MeOH + NaI): 378.08994 ($[M+Na]^+$, $C_{15}H_{15}F_6NNaO_2^+$; calc. 378.08992); 356.10780 ($[M+1]^+$, $C_{15}H_{16}F_6NO_2^+$; calc. 356.10797).

*(5*R*)-5-(4-Methoxyphenyl)-3-[(*S*)-1-phenylethyl]-5-(trifluoromethyl)-1,3-oxazolidin-2-one* (**9g**). Yield: 332 mg (91%). Colorless crystals. M.p. 120–122° (hexane/CH_2Cl_2). $[\alpha]_D^{20} = +31$ (*c* = 1, CH_2Cl_2). IR (KBr): 3066*w*, 3030*w*, 1755*vs* (C=O), 1612*w*, 1517*m*, 1439*w*, 1281*m*, 1254*s*, 1213*w*, 1182*vs*, 1034*s*, 1024*s*, 832*w*. ^{1}H-NMR (600 MHz): 7.43–7.39 (*m*, 4 arom. H); 7.36–7.34 (*m*, 3 arom. H); 6.96–6.95 (*m*, 2 arom. H); 5.27 (*q*, ^3J(H,H) = 7.2, CH); 3.84 (*s*, MeO); 3.72, 3.70 (2*d*, ^2J(H,H) = 9.5, CH_2); 1.55 (*d*, ^2J(H,H) = 7.2, Me). ^{13}C-NMR (150 MHz): 160.9 (C=O); 155.2, 138.7, 126.4 (3 arom. C); 123.8 (*q*, ^1J(C,F) = 283.7, CF_3); 128.5, 127.6, 127.1, 126.6, 114.4 (9 arom. CH); 79.2 (*q*, ^3J(C,F) = 31.7, C_q); 52.0 (CH_2); 48.0 (CH); 16.2 (Me). ^{19}F-NMR (565 MHz): −81.8 (*s*, CF_3). HR-ESI-MS (MeOH + NaI): 388.11329 ($[M+Na]^+$, $C_{19}H_{18}F_3NNaO_3^+$; calc. 388.11310).

Suitable crystals for a crystal-structure determination were obtained from hexane/CH_2Cl_2 by slow evaporation of the solvent.

4.3. *Cyclization with $PhPCl_2$.* To the soln. of **4a** (261mg, 1 mmol) in dry toluene (Ar atmosphere), a soln. of $PhPCl_2$ (286 mg, 1.6 mmol) in toluene was added dropwise while cooling the round-bottom flask in an ice-bath. Then, Et_3N (354 mg, 3.5 mmol) was added, and the mixture was heated for 3.5 h. The precipitate ($Et_3N \cdot HCl$) was filtered off, a 30% soln. of H_2O_2 (400 mg, 3.5 mmol) was added to the filtrate, and the mixture was heated at 60° for 3 h. The org. phases were diluted with H_2O and extracted with CH_2Cl_2. Org. layers were combined, dried (Na_2SO_4), and solvents were evaporated. The product was isolated, as a mixture of two diastereoisomers, by PLC on silica gel with CH_2Cl_2/hexane 1:1 as the eluent.

*3-(*tert*-Butyl)-5-phenyl-5-(trifluoromethyl)-1,3,2-oxazaphospholidine 2-Oxide* (**10b**). Yield: 260 mg (68%). Yellow oil. IR (film): 3062*w*, 2976*m*, 2940*w*, 2889*w*, 1683*w*, 1592*w*, 1485*w*, 1450*m*, 1440*m*, 1399*w*, 1369*w*, 1310*s*, 1270*vs*, 1244*vs*, 1226*vs*, 1174*vs*, 1140*s*, 1119*s*, 1071*s*, 1043*s*, 1014*s*, 923*w*, 861*s*. ^{1}H-NMR (600 MHz): major isomer: 7.97–7.93, 7.71–7.73, 7.58–7.54, 7.50–7.39, 7.33–7.32 (5*m*, 10 arom. H); 4.17 (*dd*, ^2J(H,H) = 9.6, ^3J(H,P) = 7.8, 1 H of CH_2); 4.00 (*dd*, ^2J(H,H) = 9.6, ^3J(H,P) = 9.6, 1 H of CH_2); 1.18 (*s*, *t*-Bu); minor isomer: 7.97–7.93, 7.71–7.73, 7.58–7.54, 7.50–7.39, 7.33–7.32 (5*m*, 10 arom. H); 4.32 (*dd*, ^2J(H,H) = 10.2, ^3J(H,P) = 7.8, 1 H of CH_2); 3.90 (*dd*, ^2J(H,H) = 10.2, ^3J(H,P) = 10.2, 1 H of CH_2); 1.28 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): major isomer: 123.9 (*qd*, ^1J(C,F) = 283.8, ^3J(C,P) = 9.1, CF_3); 113.90 (2 arom. CH); 81.3 (*q*, ^2J(C,F) = 31.7, C_q); 53.2 (*d*, ^2J(C,P) = 4.5, Me_3C); 51.5 (*d*, ^2J(C,P) = 9.1, CH_2); 28.4 (*d*, ^3J(C,P) = 3.0, Me_3C); minor isomer: 123.7 (*q*, ^1J(C,F) = 285.3, ^3J(C,P) = 3.6, CF_3); 80.9 (*q*, ^2J(C,F) = 31.7, C_q); 50.9 (*d*, ^2J(C,P) = 10.6, CH_2); 53.3 (*d*, ^2J(C,P) = 4.5, Me_3C); 50.9 (*d*, ^2J(C,P) = 10.6, CH_2); 28.5 (*d*, ^3J(C,P) = 3.0, Me_3C); complex signals attributed to aromatic C-atoms of both diastereoisomers were found between 126.2 and 135.3 ppm. ^{19}F-NMR (188 MHz): major isomer: −78.46 (*s*, CF_3); minor isomer: −79.31 (*s*, CF_3). HR-ESI-MS (MeOH + NaI): 406.11509 ($[M+Na]^+$, $C_{19}H_{21}F_3NNaO_2P^+$; calc. 406.11542), 384.13295 ($[M+1]^+$, $C_{19}H_{22}F_3NO_2P^+$; calc. 384.13347).

4.4. *Reactions with $SOCl_2$. General Procedure.* To the soln. of an amino alcohol **4** (1 mmol) and Et_3N (253 mg, 2.5 mmol) in dry CH_2Cl_2, $SOCl_2$ (92 mg, 1.1 mmol) was added dropwise (Ar atmosphere), while cooling the mixture in an acetone/dry ice bath (*ca.* −45°). The mixture was stirred for 3 h, diluted with H_2O, and extracted with CH_2Cl_2. The org. layers were combined, dried (anh. Na_2SO_4), filtered, and the solvent was evaporated. Products were obtained as a mixture of diastereoisomers and, without separation, were purified by filtration through silica gel pad using hexane/CH_2Cl_2 1:1 as the eluent.

*3-(*tert*-Butyl)-5-phenyl-5-(trifluoromethyl)-1,2,3-oxathiazolidine 2-Oxide* (**11b**). Yield: 260–280 mg (85–91%, mixture of two diastereoisomers). Yellow oil. The ratio of the diastereoisomers (*ca.* 1:4) was determined for a freshly prepared sample, and no change of this ratio was observed during the storage. IR (film): 3063*w*, 2976*s*, 2935*m*, 1738*w*, 1603*w*, 1496*m*, 1450*m*, 1399*w*, 1372*m*, 1300*s*, 1269*s*, 1204*vs*, 1174*vs*, 1113*m*, 1074*m*, 1008*s*, 959*s*, 876*w*. ^{1}H-NMR (600 MHz): major isomer: 7.54–7.52 (*m*, 2 arom. H); 7.43–7.40 (*m*, 3 arom. H); 4.27 (*d*, ^2J(H,H) = 9.6, 1 H of CH_2); 3.87 (*dq*, ^2J(H,H) = 9.6, ^4J(H,F) = 0.6, 1 H of CH_2); 1.30 (*s*, *t*-Bu); minor isomer: 7.54–7.52 (*m*, 2 arom. H); 7.43–7.40 (*m*, 3 arom. H); 4.18 (*d*, ^2J(H,H) = 10.2, 1 H of CH_2); 3.98 (*dq*, ^2J(H,H) = 10.2, ^4J(H,F) = 1.2, 1 H of CH_2); 1.41 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): major isomer: 134.7 (1 arom. C); 129.4, 128.4, 125.9 (5 arom. CH); 123.1 (*q*, ^1J(C,F) = 282.3, CF_3); 89.8 (*q*, ^2J(C,F) = 30.8, C_q); 54.9 (Me_3C); 48.8 (CH_2); 28.4 (Me_3C); minor isomer:

135.7 (1 arom. C); 129.3, 128.5, 126.3 (5 arom. CH); 123.7 (*q*, ^1J(C,F) = 285.3, CF_3); 90.1 (*q*, ^2J(C,F) = 29.7, C_q); 54.8 (Me_3C); 49.5 (CH_2); 29.6 (Me_3C). ^{19}F-NMR (188 MHz): major isomer: − 75.2 (*s*, CF_3); minor isomer: − 78.8 (*s*, CF_3). HR-ESI-MS (MeOH + NaI): 330.07490 ($[M + Na]^+$, $C_{13}H_{16}F_3NNaO_2S^+$; calc. 330.07461).

3-Isopropyl-5-(4-methoxyphenyl)-5-(trifluoromethyl)-1,2,3-oxathiazolidine 2-Oxide (**11e**). Yield: 220 mg (71%). Yellow oil. Mixture of diastereoisomers; a ratio of *ca.* 15:85 was determined for a freshly prepared sample. After several weeks storage in the refrigerator, a *ca.* 1:1 mixture of both isomers was formed. IR (film): 3018*w*, 2972*m*, 2939*m*, 2845*w*, 1612*s*, 1518v*s*, 1467*m*, 1377*w*, 1297*s*, 1260v*s*, 1207*s*, 1173v*s*, 1145v*s*, 1092*s*, 1031*s*, 996*s*, 884*w*, 834*s*. ^{1}H-NMR (600 MHz): major isomer: 7.45 – 7.42 (*m*, 2 arom. H); 6.95 – 6.90 (*m*, 2 arom. H); 4.12, 3.83 (2*d*, ^2J(H,H) = 9.6, CH_2); 3.81 (*s*, MeO); 3.47 (*sept.*, ^3J(H,H) = 6.6, Me_2CH); 1.24, 1.23 (2*d*, ^3J(H,H) = 6.6, Me_2CH); minor isomer: 7.45 – 7.42 (*m*, 2 arom. H); 6.95 – 6.90 (*m*, 2 arom. H); 4.13, 3.84 (2*d*, ^2J(H,H) = 9.6, CH_2); 3.82 (*s*, MeO); 3.49 (*sept.*, ^3J(H,H) = 6.0, Me_2CH); 1.38, 1.30 (2*d*, ^3J(H,H) = 6.0, Me_2CH). ^{13}C-NMR (150 MHz): major isomer: 160.4 (1 arom. C); 127.3 (2 arom. CH); 126.6 (1 arom. C); 123.1 (*q*, ^1J(C,F) = 283.8, CF_3); 113.90 (2 arom. CH); 90.2 (*q*, ^2J(C,F) = 31.7, C_q); 55.3 (MeO); 51.8 (CH_2); 47.2 (Me_2CH); 21.6, 21.5 (Me_2CH); minor isomer: 160.3 (1 arom. C); 127.6 (2 arom. CH); 126.6 (1 arom. C); 123.7 (*q*, ^1J(C,F) = 285.3, CF_3); 113.86 (2 arom. CH); 90.5 (*q*, ^2J(C,F) = 30.2, C_q); 55.3 (MeO); 51.0 (CH_2); 47.23 (Me_2CH); 21.7, 21.4 (Me_2CH). ^{19}F-NMR (188 MHz): major isomer: − 79.1 (*s*, CF_3); minor isomer: − 75.7 (*s*, CF_3). HR-ESI-MS (MeOH + NaI): 346.06928 ($[M + Na]^+$, $C_{13}H_{16}F_3NNaO_3S^+$; calc. 346.06952).

5. *Syntheses of Six-Membered Heterocycles. Reaction with Oxalyl Chloride. General Procedure.* To a soln. of amino alcohol **4** (1 mmol) in dry toluene (5 ml), oxalyl chloride (207 mg, 1.3 mmol) was added dropwise. The mixture was refluxed for 4 h. Then, toluene was evaporated, and the crude product was crystallized from an appropriate solvent.

*4-(*tert*-Butyl)-6-(4-nitrophenyl)-6-(trifluoromethyl)morpholine-2,3-dione* (**12a**). Yield: 306 mg (85%). Colorless crystals. M.p. 143 – 144° (toluene). IR (KBr): 3120*w*, 3092*w*, 2979*w*, 2938*w*, 1792v*s* (C=O), 1693v*s* (C=O), 1610*w*, 1530v*s*, 1423*w*, 1355v*s*, 1293*m*, 1192v*s*, 1147v*s*, 1127*s*, 1059*w*, 944*m*, 855*m*. ^{1}H-NMR (200 MHz): 8.37 – 8.35, 7.75 – 7.74 (2*m*, 4 arom. H); 4.32, 4.22 (2*d*, ^2J(H,H) = 14.4, CH_2); 1.39 (*s*, *t*-Bu). ^{13}C-NMR (150 MHz): 154.3, 152.6 (2 CO); 149.3, 138.3 (2 arom. C); 127.8, 124.6 (4 arom. CH); 122.4 (*q*, ^1J(C,F) = 286.8, CF_3); 81.4 (*q*, ^2J(C,F) = 30.2, C_q); 59.8 (Me_3C); 45.2 (CH_2); 19.0 (Me_3C). ^{19}F-NMR (565 MHz): − 75.7 (*s*, CF_3). HR-ESI-MS (MeCN + NaI): 383.08240 ($[M + Na]^+$, $C_{15}H_{15}F_3N_2NaO_5^+$; calc. 383.08253).

4-Isopropyl-6-(4-methoxyphenyl)-6-(trifluoromethyl)morpholine-2,3-dione (**12e**). Yield: 210 mg, (66%). Colorless crystals. M.p. 148 – 150° (CH_2Cl_2/hexane). IR (KBr): 3026*w*, 2291*w*, 2978*w*, 2848*w*, 1776v*s* (C=O), 1689v*s* (C=O), 1609*m*, 1517*s*, 1481*m*, 1443*m*, 1342*m*, 1308*m*, 1263v*s*, 1180v*s*, 1160v*s*, 1137*s*, 1112*m*, 1028*m*, 991*m*, 835*m*. ^{1}H-NMR (600 MHz): 7.40 – 7.38, 6.96 – 6.94 (2*m*, 4 arom. H); 4.75 – 4.65 (*m*, Me_2CH); 4.12, 3.94 (2*d*, ^2J(H,H) = 14.1, CH_2); 3.83 (*s*, MeO); 1.21 (2*d*, ^3J(H,H) = 6.9, Me_2CH). ^{13}C-NMR (150 MHz): 161.1, 154.4 (2 CO); 151.8, 122.7 (2 arom. C); 122.6 (*q*, ^1J(C,F) = 285.3, CF_3); 114.7, 127.6 (4 arom. CH); 81.4 (*q*, ^2J(C,F) = 31.7, C_q); 55.42 (MeO); 46.1 (Me_2CH); 42.2 (CH_2); 19.0 (Me_2CH). ^{19}F-NMR (188 MHz): − 76.7 (*s*, CF_3). HR-ESI-MS (MeCN + NaI): 354.09216 ($[M + Na]^+$, $C_{15}H_{16}F_3NNaO_4^+$; calc. 354.09236).

6. *X-Ray Crystal-Structure Determination of* **4a** *and* **9g** (*Table*, and *Figs. 1* and *2*)[4]). All measurements were performed on a *Nonius KappaCCD* diffractometer [10] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1* and *2*. Data reduction was performed with *HKL Denzo* and *Scalepack* [11]. The intensities were corrected for *Lorentz* and polarization effects but not for absorption. Equivalent reflections were merged. The structures were solved by direct methods using SHELXS97 [12], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. The amine and OH H-atoms of **4a** were placed in the positions indicated by a difference electron-density map, and their

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[4]) CCDC-779928 and -779929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

positions were allowed to refine with individual isotropic displacement parameters, while the O–H and N–H distances were restrained to suitable values. All remaining H-atoms and all H-atoms of **9g** were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. In both cases, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [13a], and the scattering factors for H-atoms were taken from [14]. Anomalous dispersion effects were included in F_c [15]; the values for f' and f'' were those of [13b]. The values of the mass attenuation coefficients are those of [13c]. All calculations were performed using the SHELXL97 [16] program.

Table. *Crystallographic Data for Compound* **4a** *and* **9g**

	4a	**9g**
Crystallized from	hexane/Et_2O	hexane/CH_2Cl_2
Empirical formula	$C_{13}H_{17}F_3N_2O_3$	$C_{19}H_{18}F_3NO_3$
Formula weight	306.28	365.35
Crystal color, habit	colorless, tablet	colorless, prism
Crystal dimensions [mm]	$0.08 \times 0.15 \times 0.15$	$0.25 \times 0.28 \times 0.35$
Temperature [K]	160(1)	160(1)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1$
Z	2	2
Reflections for cell determination	2649	2045
2θ Range for cell determination [°]	4–50	4–55
Unit cell parameters a [Å]	6.8276(3)	6.4391(2)
b [Å]	9.3896(4)	14.7662(4)
c [Å]	12.7135(5)	9.0768(2)
α [°]	73.634(2)	90
β [°]	76.284(2)	93.755(2)
γ [°]	89.260(2)	90
V [Å^3]	758.45(6)	861.18(4)
D_x [g cm^{-3}]	1.341	1.409
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.119	0.116
Scan type	ω	ϕ and ω
$2\theta_{(max)}$ [°]	50	55
Total reflections measured	14693	20611
Symmetry-independent reflections	2674	2049
Reflections with $I > 2\sigma(I)$	1927	1930
Reflections used in refinement	2673	2048
Parameters refined; restraints	201; 2	238; 1
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0685	0.0309
$wR(F^2)$ (all data)	0.2083	0.0797
Weighting parameters [a; b][a])	0.1037; 0.7456	0.0481; 0.0874
Goodness-of-fit	1.031	1.075
Secondary extinction coefficient	–	0.044(6)
Final Δ_{max}/σ	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.59; −0.32	0.17; −0.17

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

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