Structures of the Reactive Intermediates in Organocatalysis with Diarylprolinol Ethers

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Structures of the reactive intermediates (enamines and iminium ions) of organocatalysis with diarylprolinol derivatives have been determined. To this end, diarylprolinol methyl and silyl ethers, **1**, and aldehydes, Ph–CH_2–CHO, ^{t}Bu–CH_2–CHO, Ph–CH=CH–CHO, are condensed to the corresponding enamines, **A** and **3** (*Scheme 2*), and cinnamoylidene iminium salts, **B** and **4** (*Scheme 3*). These are isolated and fully characterized by melting/decomposition points, $[\alpha]_D$, elemental analysis, IR and NMR spectroscopy, and high-resolution mass spectrometry (HR-MS). Salts with BF_4, PF_6, SbF_6, and the *weakly coordinating* $Al[OC(CF_3)_3]_4$ anion were prepared. X-Ray crystal structures of an enamine and of six iminium salts have been obtained and are described herein (*Figs. 2* and *4–8*, and *Tables 2* and *7*) and in a previous preliminary communication (*Helv. Chim. Acta* **2008**, *91*, 1999). According to the NMR spectra (in $CDCl_3$, (D_6)DMSO, (D_6)acetone, or CD_3OD; *Table 1*), the major isomers **4** of the iminium salts have (*E*)-configuration of the exocyclic N=C(1′) bond, but there are up to 11% of the (*Z*)-isomer present in these solutions (*Fig. 1*). In all crystal structures, the iminium ions have (*E*)-configuration, and the conformation around the exocyclic N-C–C-O bond is *synclinal-exo* (*cf.* **C** and **L**), with one of the phenyl groups over the pyrrolidine ring, and the RO group over the π-system. One of the *meta*-substituents (Me in **4b**, CF_3 in **4c** and **4e**) on a 3,5-disubstituted phenyl group is also located in the space above the π-system. DFT Calculations at various levels of theory (*Tables 3–6*) confirm that the

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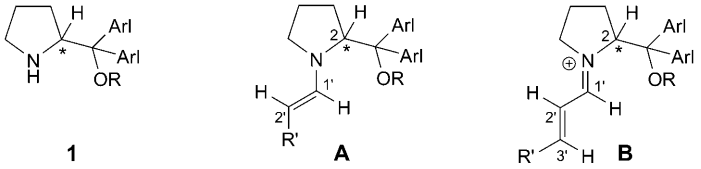
experimentally determined structures (*cf. Fig. 10*) are by far (up to 8.3 kcal/mol) the most stable ones. Implications of the results with respect to the mechanism of organocatalysis by diarylprolinol derivatives are discussed.

1. Introduction. – In the year 2005, the field of organocatalysis experienced a boost when several groups started to use diarylprolinol[3]) (= diarylpyrrolidine-2-methanol) ethers **1** as catalysts [4]. Since then, the formulae of enamines **A** and of iminium ions **B**, the reactive intermediates involved in activating nucleophilic α-carbonyl positions and electrophilic β-carbonyl positions, have been presented in dozens of publications. The big ('obese' [5]) diarylmethanol-ether substituent was assumed *a*) to enforce an s-*trans*-conformation around the exocyclic N–C(1′) bond of an enamine **A**, *b*) to secure (*E*)-configuration of the iminium N=C(1′) bond in **B**, and *c*) to direct incoming reactants to approach the π-system of **A** and **B** from the face *anti* to the large substituent at C(2) of the pyrrolidine, in agreement with the experimental results. For the (*S*)-forms, this corresponds to a relative topicity[4]) *like* (*lk*) for reactions of the enamines **A** (*Si* on C(2′)) and of the iminium ions **B** with R′ = Arl (*Si* on C(3′)). Besides some *in-situ* NMR spectra[5]), there were no experimental structural data of the reactive intermediates **A** and **B** available, as of July 2008. On the other hand, DFT calculations of the structures of a diarylprolinol-derived dienamine and of an iminium ion had been published in 2006 [7].



1, **4** (**B**, R' = Ph)	Arl	R	Absolute configuration
a	Ph	H	(*S*)
b	3,5-$Me_2C_6H_3$	Me	(*S*)
c	3,5-$(CF_3)_2C_6H_3$	Me	(*S*)
d	Ph	Me_3Si	(*S*)
e	3,5-$(CF_3)_2C_6H_3$	Me_3Si	(*S*)
f	Ph	$Me_2(Ph)Si$	(*S*)
g	4-^{t}BuC$_6$H$_4$	$Me_2(Ph)Si$	(*R*)
h	Ph	$Me(Ph)_2Si$	(*S*)
i	4-^{t}BuC$_6$H$_4$	$Me(Ph)_2Si$	(*R*)

While there are only a few enamine structures recorded in the *Cambridge Crystallographic Data Base*[6]), there is a rich history of isolation and structure

[3]) The parent compound *rac*-**1**, Arl = Ph, R = H was first described 75 years ago [1], the enantiomerically pure form 45 years ago [2]. For further references, see Footnote 16 and Scheme 1 of [3].

[4]) For the definition of relative topicities of stereoselective reactions, see [6].

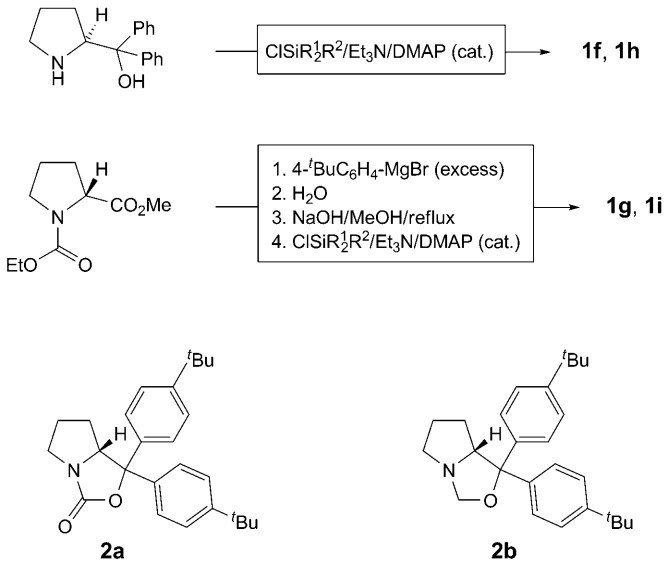
[5]) See Footnote 14 in our preliminary communication [3].

[6]) See Footnote 11 in [3] and discussion in Sect. 9, with Footnote 60 in [5].

determination of iminium salts[7]). As discussed in a seminal work by *Böhme et al.* [9], *J. von Braun* and *E. Röver* were probably the first to isolate dimethyl(methylidene)-iminium bromide ('dimethyl-bromomethyl amine')[8]) in 1903 [14]. There are numerous protocols for preparing and isolating iminium salts. We used a modified procedure of *Leonard* and *Paukstelis* [15][9]).

2. Preparation of the Enamines 3 and of the Iminium Salts 4, and Growing of Single Crystals. – The diarylprolinol derivatives **1a**–**1e** are commercially available, and the new compounds **1f**–**1i** were prepared as depicted in *Scheme 1*[10]). From the *Grignard* reaction with the *N*-(ethoxycarbonyl)proline ester substantial amounts of the

Scheme 1. *Preparation of the Diarylprolinol Silyl Ethers* **1f**–**1i** *and Isolation of the Oxazolidine Derivatives* **2**



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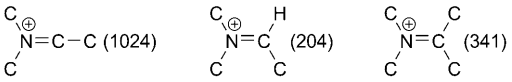
[7]) A search in the *Cambridge Structural Data File* (CSD [8]) as of March 2009 provided the following number of structures:



[8]) For the relationship α-halo-amines/dialkyl-iminium halide salts, see [10]. For a monograph and a review on α-aminoalkylations (*Mannich* reactions), see [11][12]. The iminium salt Me_2NCH_2I (*Eschenmoser* salt [13]) is very stable, sublimes at 120°/10^{-3} Torr, and decomposes at *ca.* 240°.

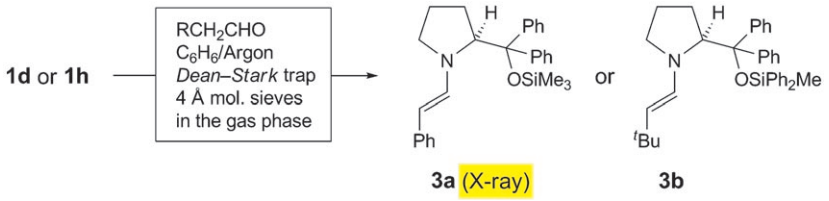
[9]) Besides our group [3][5][16], *Mayr* and co-workers [17], *Tompkinson* and co-workers [18], and *Gilmour* and co-workers [19] have recently reported isolations and structural identifications of iminium salts of relevance to organocatalysis.

[10]) For a discussion and leading references about the various methods of preparing diarylprolinols, see *Scheme 1* in [3].

oxazolidinone **2a** were isolated and subsequently hydrolyzed with NaOH in MeOH. Trace amounts of the oxazolidine **2b** were also obtained after this step[11]).

The enamines **3a** and **3b** were prepared as shown in *Scheme 2*[12]). Suitable single crystals for X-ray analysis could be prepared only of the enamine **3a**. For characterization of the enamines, see data in the *Exper. Part*.

Scheme 2. *Preparation of the Enamines* **3a** *and* **3b** *by Condensation of 2-Phenylacetaldehyde or 3,3-Dimethylbutanal with the Diphenyl Prolinol Silyl Ethers* **1d** *and* **1h**, *Respectively*



The preparation of cinnamaldehyde-derived[13]) iminium salts **4** is outlined in *Scheme 3*. First, the ammonium salts **1** · HX were prepared from the prolinol ethers and HCl or HBF_4[14]). With the hydrochloride, an anion exchange could be achieved by adding a Ag salt (*cf.* **1c** · HCl → **1c** · HPF_6). The ammonium salts were allowed to react with cinnamaldehyde in EtOH, in the presence of catalytic amounts of Et_3N. This led to precipitation of the iminium salts **4**, X = BF_4, PF_6, which, after filtering, washing with Et_2O and drying under high vacuum, gave correct elemental analyses.

The chlorides **4**, X = Cl, are converted to PF_6, SbF_6, and $Al[OC(CF_3)_3]_4$ salts by adding the corresponding Ag salt to the EtOH solution. The salts **4c** and **4e** derived from the bis[3,5-bis(trifluoromethyl)phenyl]prolinols **1c** and **1e** do not precipitate. Especially the salts with the complex aluminate anion, a so-called weakly-coordinating anion [21][15]), are extremely well soluble, even in a nonpolar solvent such as Et_2O[16]). In these cases, analytically pure samples are obtained by removing the AgCl precipitate by suction of the supernatant solution through an HPLC filter, stripping off the EtOH solvent, dissolving the residue in Et_2O, precipitating with heptane, washing with hexanes, and drying under high vacuum.

Single crystals were produced by the so-called diffusion method or by slow solvent evaporation. Thus, vials with solutions of the salts, for instance, in THF/heptane, were put in a sealed container, together with a reservoir of Et_2O/petroleum ether (b.p. 30–

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[11]) It is not clear to us how the aromatic *Grignard* reagent could have caused the reduction to **2b**; maybe MeONa functioned as a hydride source in step 3.

[12]) For the setup with a molecular-sieve bag in the gas phase, see [20].

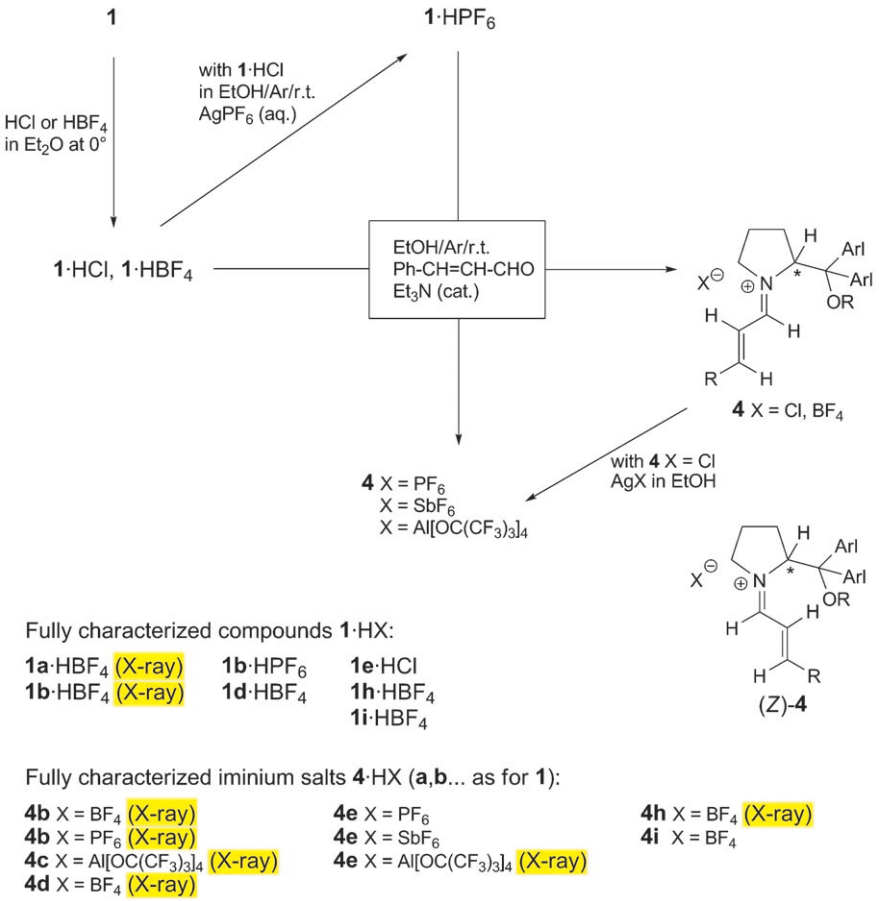
[13]) All attempts with unsaturated aliphatic aldehydes, such as crotonaldehyde, failed to produce crystalline iminium salts of this type, which would have been suitable for crystal structure analysis.

[14]) In the salt-forming process with HBF_4 and prolinol silyl ethers, up to 35% loss of the silyl group was observed, which complicated the subsequent step of iminium-salt formation and isolation.

[15]) Positively charged counter-ions do not abstract a small anion ($(CF_3)_3CO^-$) from the complex aluminate anion $Al[OC(CF_3)_3]_4^-$, a process which can happen with BF_4^-, PF_6^-, or SbF_6^- anions by transfer of F^-.

[16]) On the other hand, these $Al[OC(CF_3)_3]_4^-$ salts have much higher melting/decomposition points than the corresponding BF_4^-, PF_6^-, or SbF_6^- salts (see *Exper. Part*).

Scheme 3. *Preparation of the Ammonium Salts* **1** · *HX and of the Iminium Salts* **4**. The structure of the ammonium salt **1a** · HBF_4 and of the iminium salt **4h**, X = BF_4, have been published in [3].



50°). One of the crystals which had grown on the wall of one of the vials was picked and transferred to the X-ray diffractometer.

3. NMR Spectra of the Iminium Salts 4. – Selected NMR data are collected in *Table 1*. Besides the signals from the iminium salts **4** of (*E*)-configuration around the N=C bond (*cf.* the crystal structures), the NMR spectra of the analytically pure samples contain a set of signals that must arise from an isomer to which we assign the (*Z*)-configuration ((*Z*)-**4**). The amount of this 'impurity' can be as high as 8% (see *Fig. 1*; *Table 1* contains only data of the major isomers **4**). There are two noticeable features of the chemical shift data in *Table 1*: *i*) The H-atoms at C(2) of the pyrrolidine ring, and H–C(1′,2′,3′) in the iminium side chain of the bis(trifluoromethyl)phenyl-substituted compounds **4c** and **4e** resonate at *lower* field (by up to 0.8 ppm) than those of the other four compounds (**4b**, **4d**, **4h**, and **4i**); comparison of spectra obtained with

Table 1. *Selected [1]H-NMR Data of the Iminium Salts* **4**. The spectra were recorded on different NMR instruments. Multiplicities and coupling constants could not be determined in the case of the starred (*) signals because of overlap with signals from other H-atoms. [1]H-NMR Chemical shifts of the overlapping signals were extracted from the corresponding 2D-HSQC spectra recorded in the same solvent on the same instrument. For NMR spectra of *in situ* observed iminium salts of type **4**, see [4a][22]. For an NMR and a high-resolution mass spectrum of **4d**, $X = OSO_2CF_3$, see supplementary material of [17a]; the NMR spectra of this salt with BF_4 and triflate anions are more or less identical.

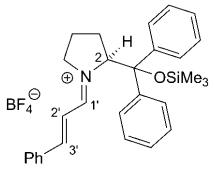
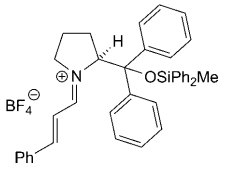
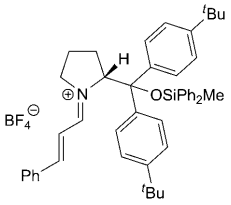
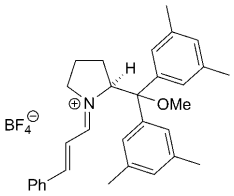
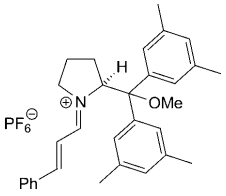
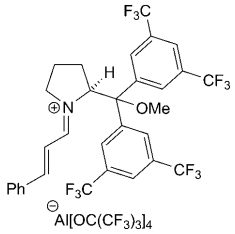
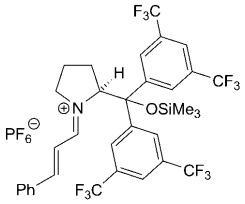
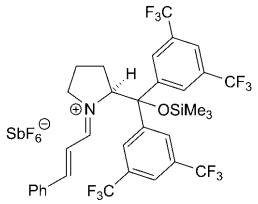
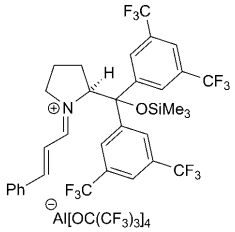
Chemical shifts δ [ppm], multiplicities, and coupling constants J [Hz]						
	Iminium salt	Solvent	H–C(2)	H–C(1′)	H–C(2′)	H–C(3′)
4d (X-ray)		$CDCl_3$	5.46 (*d*, $J = 7.4$)	8.53 (*d*, $J = 10.6$)	7.00 (*dd*, $J = 10.7, 15.2$)	*ca.* 7.70*
4h (X-ray)		(D_6)DMSO	5.61 (*d*, $J = 8.2$)	8.40 (*d*, $J = 10.5$)	*ca.* 7.14*	6.85 (*d*, $J = 15.2$)
4i		$CDCl_3$	5.53 (*d*, $J = 7.6$)	8.33 (*d*, $J = 10.3$)	6.88 (*dd*, $J = 10.6, 15.0$)	6.49 (*d*, $J = 15.1$)
4b (X-ray)		$CDCl_3$	5.27 (*dd*, $J = 3.1, 8.9$)	8.58 (*d*, $J = 10.5$)	7.04 (*dd*, $J = 10.5, 15.3$)	8.00 (*d*, $J = 15.2$)
4b (X-ray)		$CDCl_3$	5.24 (*dd*, $J = 3.7, 9.2$)	8.51 (*d*, $J = 10.6$)	6.93 (*dd*, $J = 10.7, 15.2$)	7.91 (*d*, $J = 15.2$)

Table 1 (cont.)

Chemical shifts δ [ppm], multiplicities, and coupling constants J [Hz]

	Iminium salt	Solvent	H–C(2)	H–C(1′)	H–C(2′)	H–C(3′)
4c (X-ray)		(D_6)DMSO	5.99 (*dd*, $J = 3.6, 9.0$)	8.91 (*d*, $J = 10.4$)	7.46 (*dd*, $J = 10.5, 15.1$)	8.51 (*d*, $J = 15.0$)
4e		(D_6)Acetone	6.02 (*dd*, $J = 3.1, 9.4$)	9.05 (*d*, $J = 10.7$)	*ca.* 7.59*	*ca.* 8.30*
4e		(D_6)Acetone	6.04 (*dd*, $J = 2.6, 9.1$)	9.07 (*d*, $J = 10.7$)	*ca.* 7.61*	*ca.* 8.31*
4e (X-ray)		(D_6)Acetone	6.11 (*d*, $J = 6.6$)	9.14 (*d*, $J = 10.7$)	*ca.* 7.65*	8.34 (*d*, $J = 15.2$)

$CDCl_3$, (D_6)DMSO, and (D_6)acetone solutions would suggest that this is not just a solvent or counterion effect. *ii*) In the case of **4h** and **4i**, the signals from H–C(3′), the C-atom of nucleophilic attack on such iminium ions, are shifted to higher fields (by up to 2 ppm) as compared to those of the other salts **4**; this effect is compatible with the X-ray crystal structure of **4h**, X = BF_4 [3], where the H–C(3′) resides in the shielding cone of one of the Si-bound phenyl groups (*Fig. 2*).

4. Crystal Structures of the Ammonium Salt 1b · HBF$_4$, of the Enamine 3a, and of Five Iminium Salts 4. – The crystal structure of the ammonium salt **1b** · HBF_4 (*Fig. 3*), precursor to the iminium salts **4**, X = BF_4 and PF_6, is shown in *Fig. 3*. While essentially all known diarylprolinols **1**, R = H, have a *sc*(synclinal)-*endo*-conformation **D** around

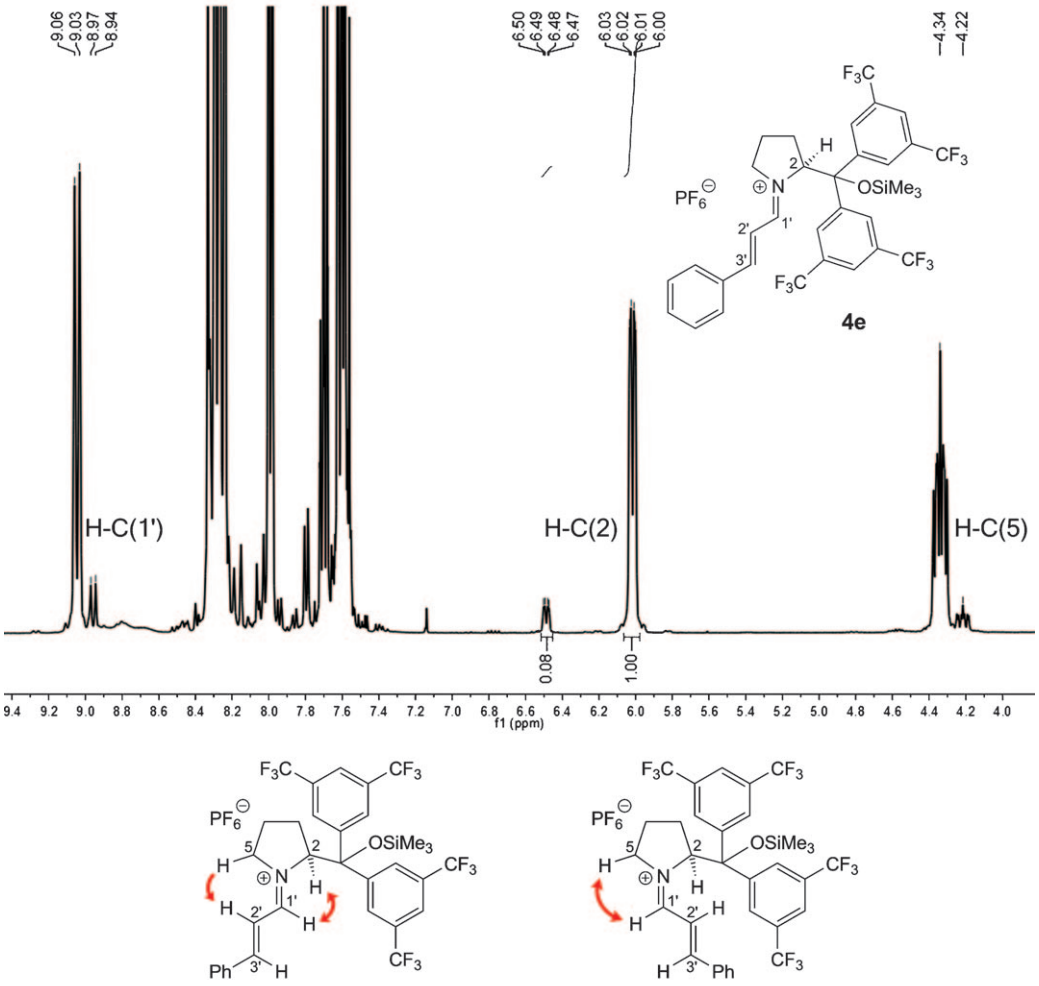
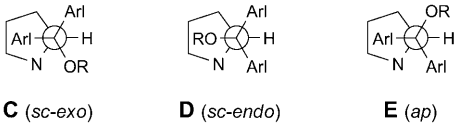


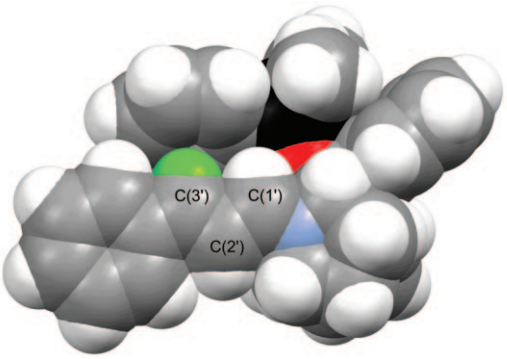
Fig. 1. *Section of the ^{1}H-NMR spectrum of the iminium salt* **4e**, *X* = PF_6, *in* (D_6)*acetone.* The *doublet* signal at 8.96 ppm, the *doublet* of *doublet* signal at 6.49 ppm, and the *multiplet* signal at 4.22 ppm are assigned to the isomer of (*Z*)-configuration of the N=C bond. A nuclear-*Overhauser*-effect was observed between H–C(2) and H–C(1′), and between H–C(5) and H–C(2′) in **4e**, and between H–C(5) and H–C(1′) in (*Z*)-**4e**.

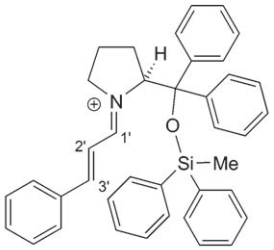
the exocyclic ethane bond[17]), all eight diarylprolinol ether derivatives, of which we have determined crystal structures[18]), have a *sc-exo*-conformation **C** around this bond, and so has the ammonium salt **1b** · HBF_4. The antiperiplanar (*ap*) conformation **E** has

[17]) See the result of a search in the *Cambridge Structural Data File* (CSD) as of May 2008 [3].
[18]) This work and [3].



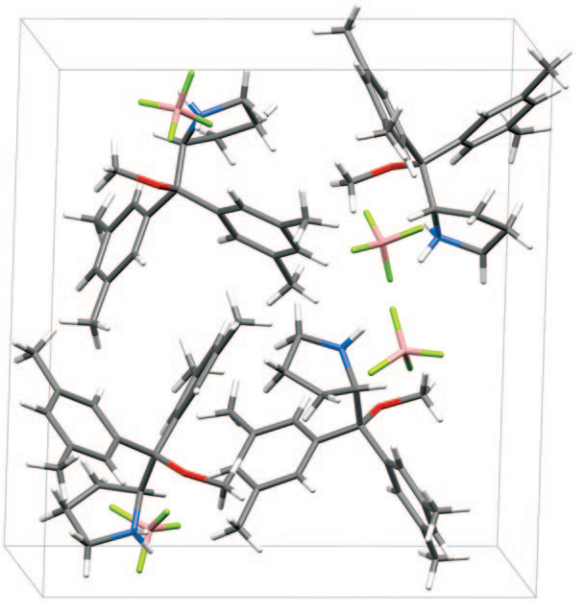
C (*sc-exo*) **D** (*sc-endo*) **E** (*ap*)

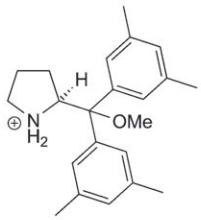




4h X = BF_4

Fig. 2. *Space-filling model of the X-ray crystal structure of iminium salt* **4h**, *X* = BF_4. *Cf. Fig. 2* in [3] and the accompanying discussion. The shielding of H–C(3′) (green label) in the NMR spectrum of this salt (*Table 1*) is compatible with the assumption that the conformation seen in the crystal is also populated in (D_6)DMSO solution.





1b·HBF_4

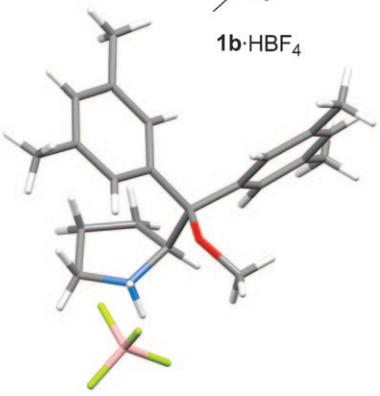
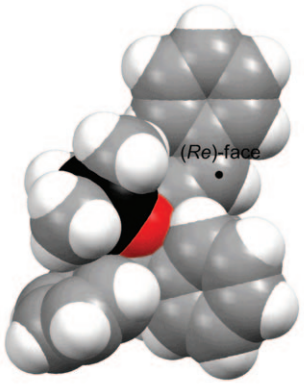


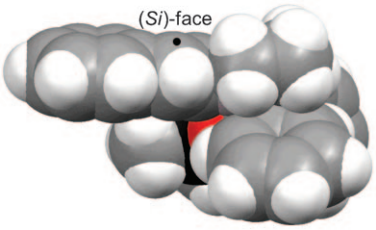
Fig. 3. *Crystal structure of the ammonium salt* **1b** · HBF_4. The exocyclic CH–C bond has *sc-exo*-conformation.

been found only in hydrazones derived from *N*-amino-diphenylprolinol methyl ethers [23][19]).

The crystal structure of enamine **3a** has been discussed in our previous work [3]. From a view at the face of the plane containing the Ph–CH=CH–N moiety of the molecule (see **F**), it is apparent that a Me group of Me_3Si and one of the phenyl groups cause massive shielding of the enamine N=C bond *Re*-face, while the *Si*-face is wide open for electrophilic attack (see **G**)[20]).



F



G

The crystal structures of the iminium salts **4d**, X = BF_4, **4b**, X = BF_4 and PF_6, **4c** and **4e**, X = $Al[OC(CF_3)_3]_4$, are shown in *Figs. 4–7*, and some selected structural data are listed in *Table 2* (for more details, see *Table 7* in the *Exper. Part*). The iminium N-atoms are slightly pyramidalized (0.02–0.04 Å) towards the large substituent, the conformation of the pyrrolidine ring is such that the C(1′)=N–C(2)–C(2″) torsion angle becomes 'as large as possible' (–73 to –79°), there is a slight distortion of the C=N bond (C(2′)–C(1′)=N–C(2): 174–179°)[21]). As mentioned above, the exocyclic C–C bond has *sc-exo* conformation, with the R group (Me or R_3Si) at the O-atom pointing up and away (torsion angles C(2)–C(2″)–O–R: 85–170°). These structural features may be considered as the result of repulsion minimization between the two substituents at N(1) and C(2) of the pyrrolidine ring. One of the aryl groups (the Ar^{Re} in an (*S*)-diarylprolinol, where it causes especially strong steric shielding in the enamine intermediate) *and* the RO group are located above one face of the π-system.

Of special interest are the diarylprolinol derivatives with *meta*-substituted phenyl groups, 3,5-$(H_3C)_2C_6H_3$ (*Fig. 5*) and 3,5-$(F_3C)_2C_6H_3$ (*Figs. 6* and *7*). Clearly, one of the *meta*-substituents and (in the case of the trimethylsilyl ether) one of the Me groups at

---

19) If we could consider the nitrogen of the hydrazone a σ-donor and the oxygen of the MeO group a σ-acceptor, a $\sigma \rightarrow \sigma^*$ interaction would be at work to stabilize the *ap* conformation **E** in these derivatives; see entries 21 and 22 in Table 1 of [3].

20) *Cf.* Fig. 1 in [3] and the discussion in Sect. 2.1. of that work, and compare with the presentations of three iminium salts in *Fig. 8*, below.

21) This is hardly caused by intramolecular forces, as the two extreme values are observed in the two symmetry-independent molecules of the **4d** crystal structure.

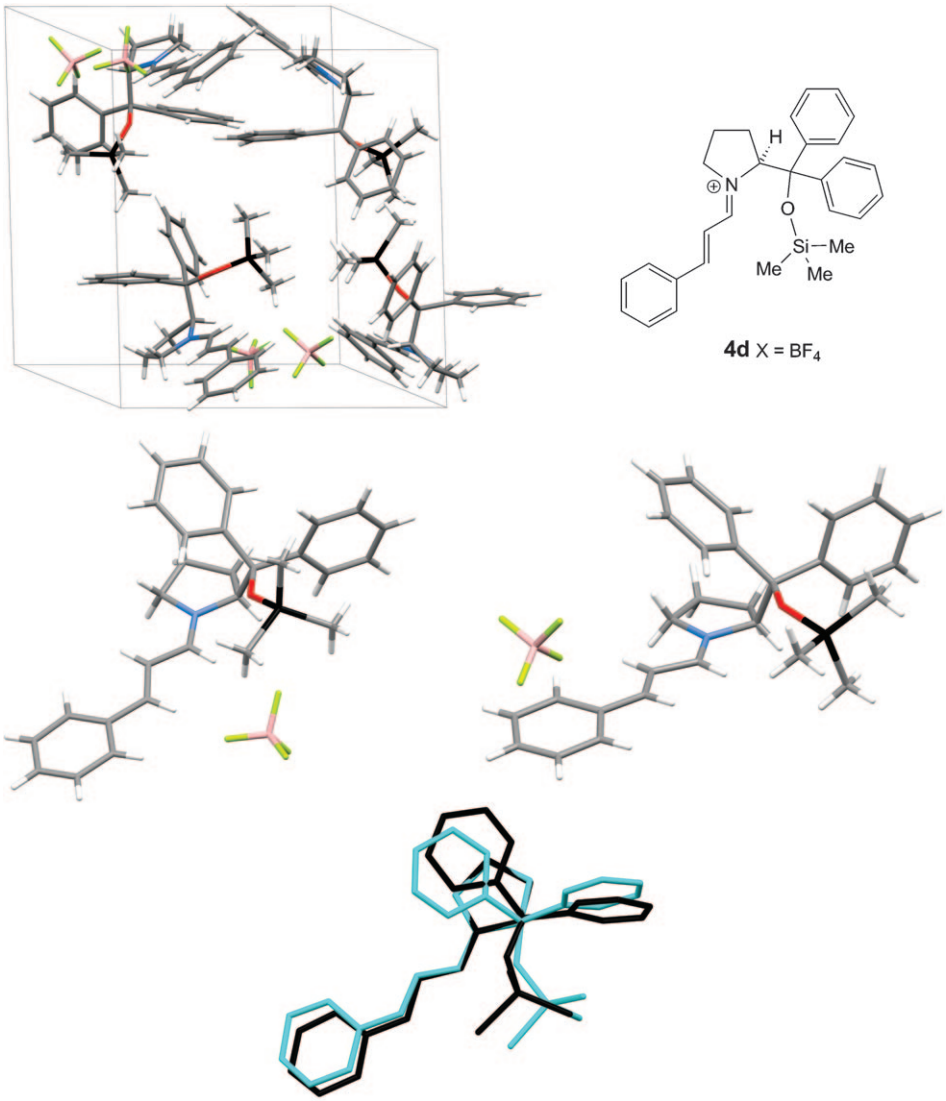


Fig. 4. *Crystal structure of the iminium salt* **4d**, $X = BF_4$. The asymmetric unit contains two somewhat different conformations of the cation. As can be seen from the overlay, in which the five-membered ring and the π-system are superimposed as closely as possible, the torsion angle around the exocyclic C–C bond differs by a few degrees in these two conformations.

the Si-atom are the major contributors to steric shielding of the iminium π-face *Si*(C(1′))/*Re*(C(2′))/*Re*(C(3′)) (*Fig. 8*). The superior performance of the organocatalyst **1e** with *geminal* 3,5-$(F_3C)_2C_6H_3$ groups is thus understandable, and it would appear reasonable to suggest that the CF_3 groups (volume of the hemisphere *ca.* 43 Å^3) [24] are

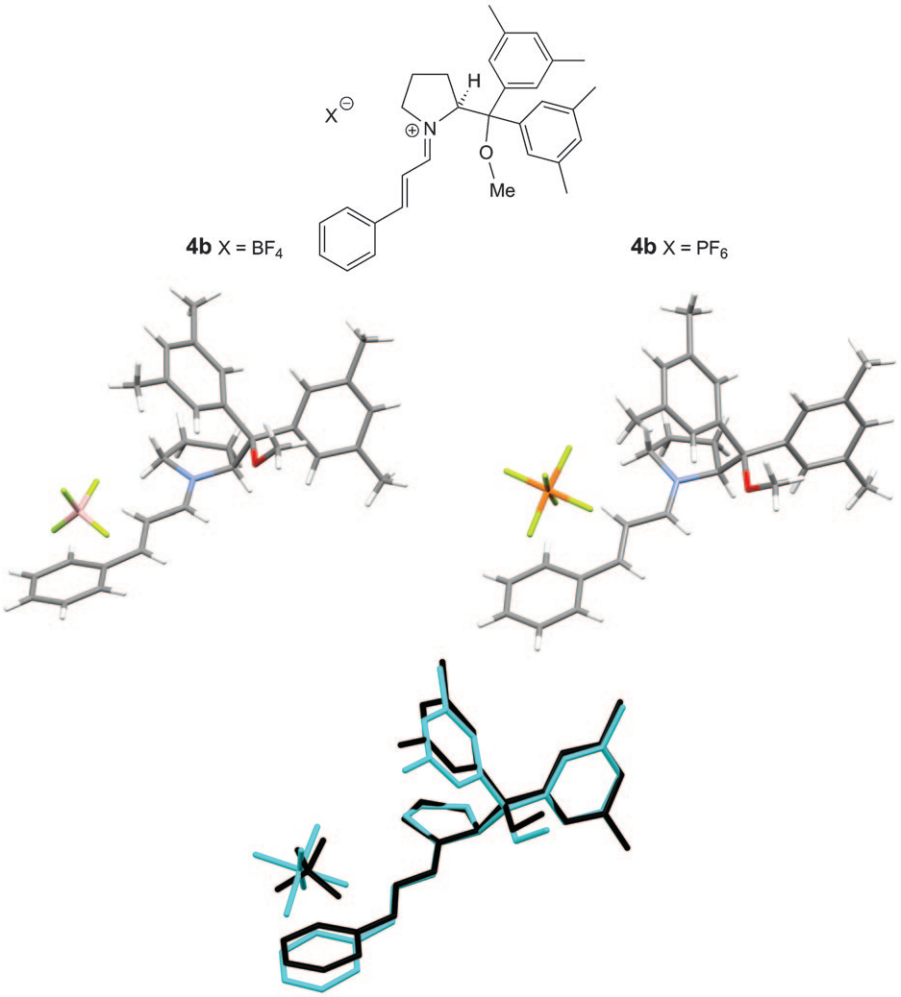


Fig. 5. *Crystal structures of the BF_4 and PF_6 salts of* **4b**. The crystal structures have the same spacegroup *P*1 with very similar cell dimensions and are almost superimposable.

primarily acting as '*big*' methyl groups (volume of the hemisphere *ca.* 17 Å^3), and that electronic or 'lipophilic' effects of the CF_3 groups are of less importance[22]).

The role of the $Al[OC(CF_3)_3]_4$ anion in the salts **4c** and **4e** warrants comments: when going from **4e**, X = PF_6 or SbF_6, to **4e**, X = $Al[OC(CF_3)_3]_4$, there is a jump of the melting point by *ca.* 100°; while we could not prepare single crystals of the phosphate and antimonate salts of **4c** and **4e** (carrying *meta*-CF_3-substituents on the phenyl groups), the aluminate salts gave nice crystals in the first attempt. Large

[22]) See, however, the low-field shifts observed in the NMR spectra of the CF_3-substituted iminium salts (*Table 1* and *Sect. 3*, *i*, above).

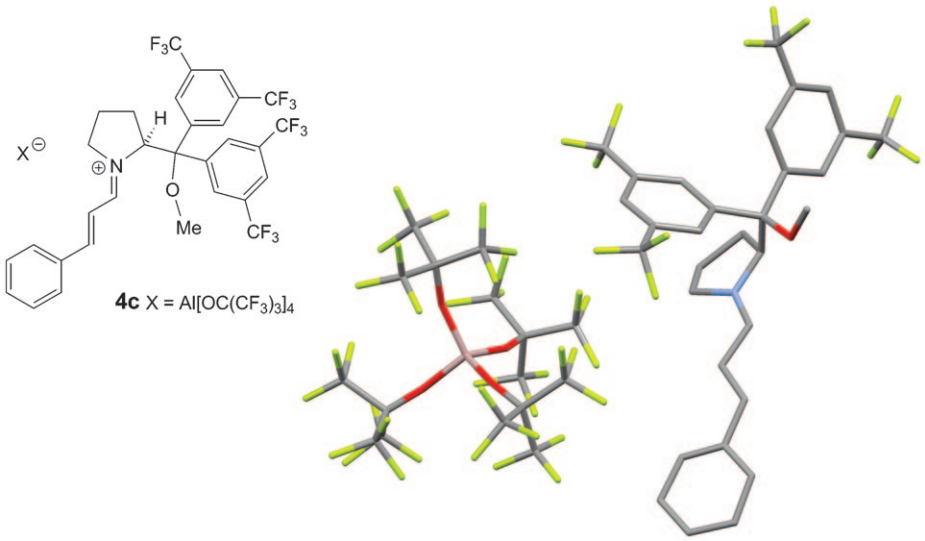


Fig. 6. *X-Ray crystal structure of the bis(trifluoromethyl)phenyl derivative* **4c**, *X* = *Al[OC(CF$_3$)$_3$]$_4$*. The counter-anion is almost as large as the iminium ion! There is a massive disorder of all CF_3 groups, especially in the anion where two CF_3 fragments could not be localized in the electron density map and had to be included as rigid groups (*cf.* the Me_3SiO analog in *Fig. 7*).

lipophilic anions, such as this aluminate, are called *weakly-coordinating* anions (WCAs), and it has been suggested that their counterparts, the cations, attain structures similar to gas-phase structures (which have *no* counter-ion at all); such anions are thought to create *pseudo-gas-phase conditions in condensed phases* [21]. Thus, the similarity of the iminium-ion structures with 'normal' counterions (BF_4^-, PF_6^-, and SbF_6^-) and with the WCA $Al[OC(CF_3)_3]_4$ is compatible with the assumption that there is at least no pronounced counterion effect to be considered in the structures reported herein (see NMR chemical shift 'similarities' of the selected NMR signals for the three **4e** iminium salts in *Table 1*). If so, a comparison with DFT-calculated ('gas-phase') structures appears to be appropriate at this point.

5. Density-Functional Theory (DFT) Calculations of the Structures of [3,5-(F$_3$C)$_2$C$_6$H$_3$]$_2$-Substituted Prolinol-Derived Enamines and Iminium Ions. – DFT Calculations of the diarylprolinol-derived dienamine **5** and of the iminium ion **6** (*Fig. 9*) were first reported by *Jørgensen* and co-workers in 2006 and 2007 [7][25]. In these calculated structures, the exocyclic CH–C bond has *sc-endo*-conformation **D**, which leads to essentially complete coverage of the π-faces, *syn* to the large substituent at C(2) of the pyrrolidine ring by a bis(trifluoromethyl)phenyl group (see the space-filling representations[23]) in *Fig. 9* and compare with *Fig. 8*). It looks like the *sc-exo-*

[23]) For another presentation, see Fig. 5 in [3].

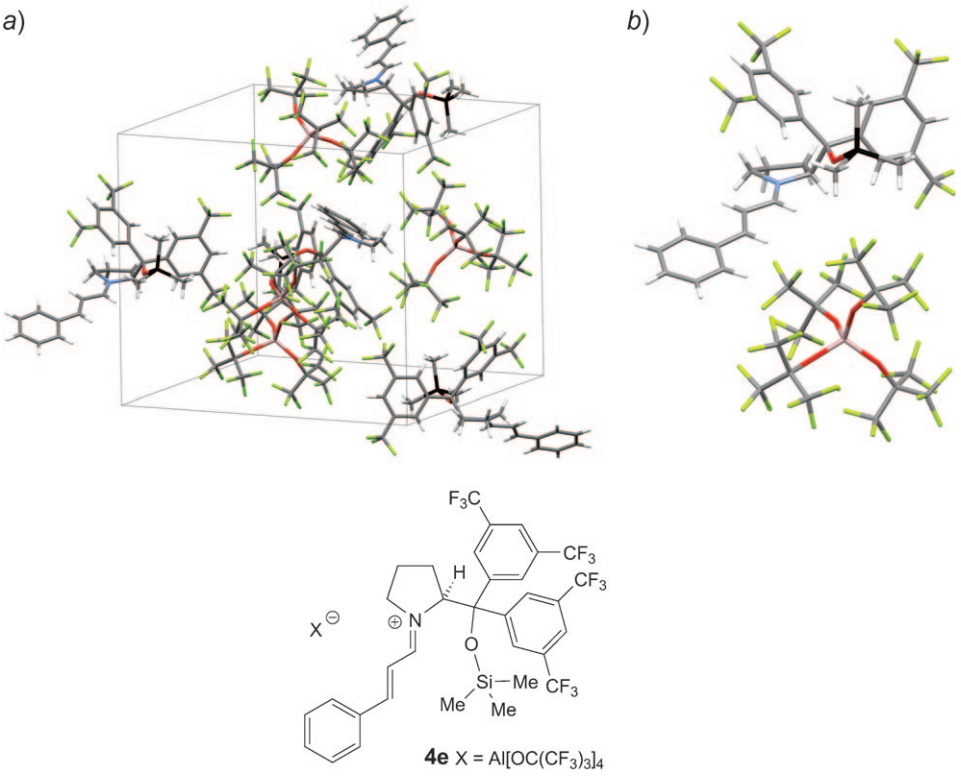


Fig. 7. *Crystal structure of the bis[3,5-bis(trifluoromethyl)phenyl]prolinol trimethylsilyl ether-derived iminium salt* **4e**, $X = Al[OC(CF_3)_3]_4$. *a*) Unit cell, *b*) cation/anion pair.

conformation, which we see in all diarylprolinol-ether crystal structures, has nowhere been considered in these calculations.

We have now performed DFT calculations with the three possible conformations **C**, **D**, and **E** of the exocyclic ethane bond for *Jørgensen*'s dienamine **5** and for our cinnamoylidene iminium ion **4e**[24]).

We first recalculated [27–31] *Jørgensen*'s dienamine structure **5** with s-*trans*-conformation around the N–C-bond and *sc-endo*-conformation (type **D**) of the exocyclic C–C bond at the B3LYP/6-31G(d) level: as can be seen from *Table 3*, the energy, as well as the detailed structure [7], was completely reproduced (*cf. Fig. 9*). We next calculated the structures of the dienamine **5** with *sc-exo*- and *ap*-conformations. The results listed in *Table 3* show that the conformation of type **C** with the N-atom and the Me_3SiO group in *sc-exo*-relationship is the most stable one and the *ap*-arrangement

[24]) We performed geometry optimizations at the same computational level, B3LYP/6-31G(d), as the *Jørgensen* group, and then B3LYP and MP2 single-point energy evaluations using a little bit larger basis set, 6-311G(d,p), were carried out at the optimized geometries. The B3LYP calculations do not reproduce dispersion effects [26], but the MP2 calculations do consider them, at least partly. We thank Prof. *S. Grimme* (Universität Münster) for pointing this out to us.

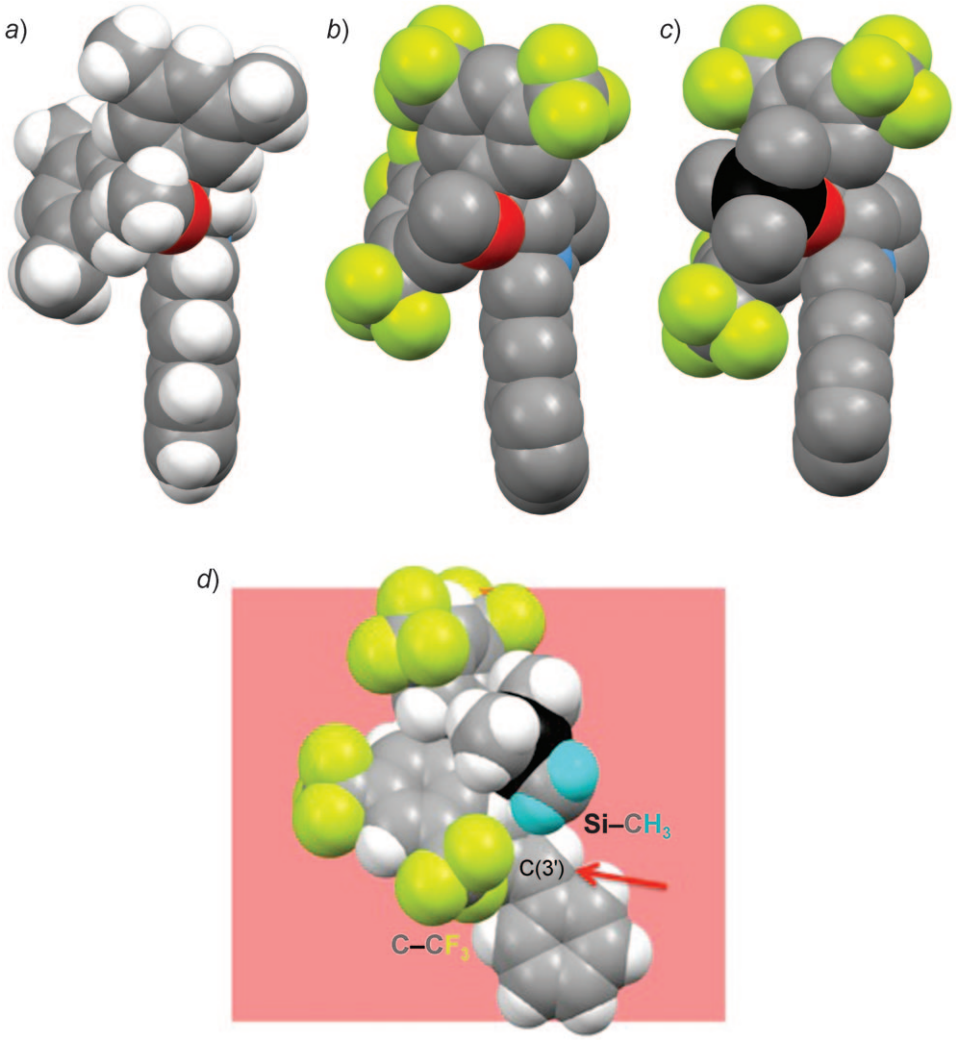
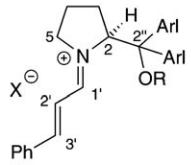
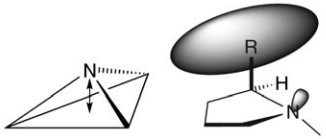


Fig. 8. *View along the iminium π-plane in the salts* a) **4b**, $X = PF_6$, b) **4c**, $X = Al[OC(CF_3)_3]_4$, c) *and* d) **4e**, $X = Al[OC(CF_3)_3]_4$. A *meta*-CH_3 and a *meta*-CF_3 group are sitting above one face of the π-plane, with increasing steric shielding from *a*) (*meta*-Me/MeO) to *b*) (*meta*-CF_3/MeO) to *c*) (*meta*-CF_3/Me_3SiO). The pink plane in *d* is the average plane of the enoyliminium π-system in **4e**; C(3′) is the atom of nucleophilic attack (red arrow).

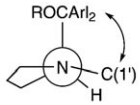
(type **E**) the least stable one of the three conformations. This conclusion remains unchanged in single-point energy evaluations at the B3LYP/6-31G(d)-optimized geometries. Thus, the most stable calculated structure of dienamine **5** and the X-ray structure of enamine **3a** have the same conformation around the exocyclic C−C bond (*Table 3*, top). The order of calculated stabilities of the three enamine conformations is the same in the gas phase and in toluene solution (*Table 3*, bottom). The dienamine **5**

Table 2. *Some Selected Structural Data of Iminium Salts* **4** *and of Enamine* **3a**. Pyramidalization on the N-atom and various torsion angles in the crystal structures are given.

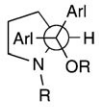




pyramidalization on N



C=N–C–C



sc-exo

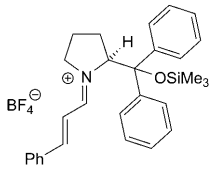
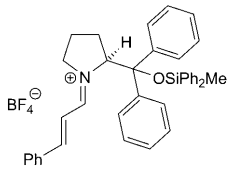
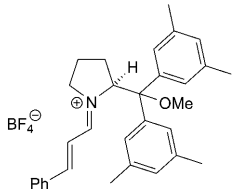
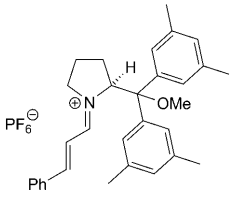
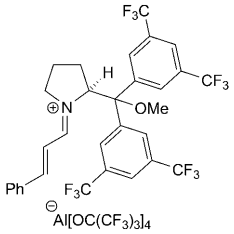
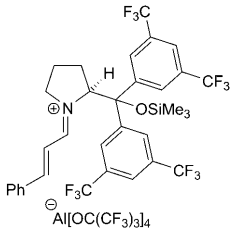
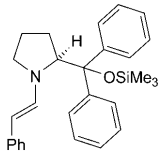
	Structure	[ref.]	N-Pyramidality Δ [Å]	Torsion angles [°]			
				C(1′)=N–C(2)–C(2″)	C(2)–C(2″)–O–R	C(2′)–C(1′)=N–C(2)	O–C(2″)–C(2)–N *sc-exo*
4d		This work	0.030 – 0.018	– 76.9 – 73.0	134.0 84.9	178.1 174.0	54.0 72.7
4h		[3]	0.022 0.027	– 76.4 – 79.1	132.9 135.0	177.7 178.8	57.2 56.2
4b		This work	0.021	– 78.5	169.9	– 176.4	64.9

Table 2 (cont.)

	Structure	[ref.]	N-Pyramidality Δ [Å]	Torsion angles [°]			
				C(1′)=N–C(2)–C(2″)	C(2)–C(2″)–O–R	C(2′)–C(1′)=N–C(2)	O–C(2″)–C(2)–N *sc-exo*
4b		This work	0.038	–78.4	170.5	–175.9	69.2
4c		This work	0.001	–73.2	167.6	177.6	69.4
4e		This work	0.021	–76.0	166.0	178.9	67.2
3a		[3]	0.037	–76.8	86.9	174.7	61.0

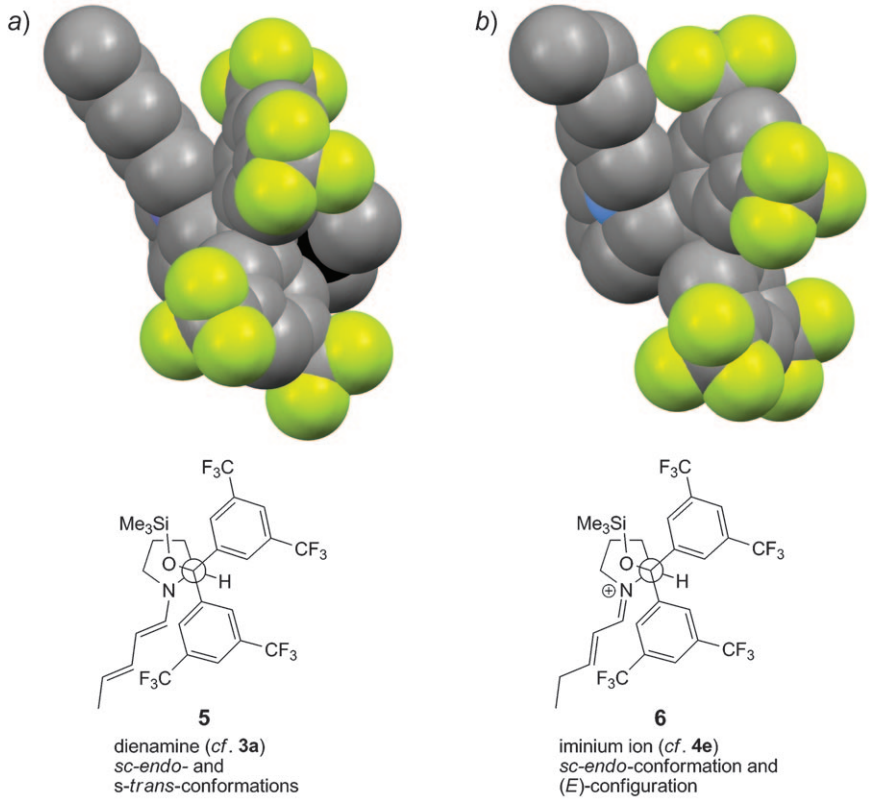


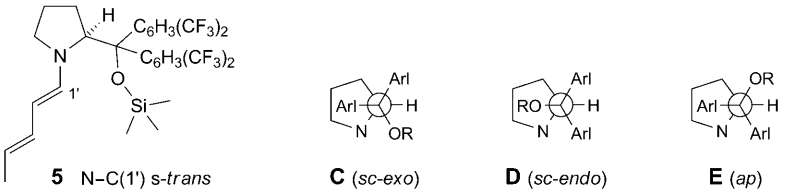
Fig. 9. Jørgensen*'s DFT-calculated structures of the dienamine* **5** (*a*), *and of an iminium ion* **6** (*b*) *derived from diarylprolinol* **1e** *and pentenal.* The coordinates for generating these pictures are taken from [7]. With the *sc-endo*-conformation around the O–C–C–N bond the (*Si*)-aryl group winds up right on top of the dienamine and enoyliminium π-planes, with steric shielding much stronger than in the measured structures with *sc-exo*-conformation (*cf. Fig. 8*).

structure with s-*cis*-conformation of the exocyclic N–C bond was also calculated. All s-*cis*-structures are found to be less stable than the s-*trans*-*sc*-*exo*-form (by 1.6–5.9 kcal/mol; see *Table 4*, and compare with *Table 3*).

We then calculated the structures of the (*E*)-iminium ion **4e** with the three conformations **C**, **D**, and **E** of the exocyclic C–C bond in the gas-phase, at the B3LYP and MP2 levels, using 6-31G(d) and 6-311G(d,p) basis sets. Again, the *sc-exo*-conformation is by far the most stable one: the *sc-endo*-conformation (*cf.* **6** in *Fig. 9*) is up to 4 and the *ap*-conformation up to 8 kcal/mol less stable (*Table 5*).

An overlay of the calculated and measured *sc-exo*-structures of iminium ion **4e** is shown in *Fig. 10*. For comparison, the three conformations **C**, **D**, and **E** of the isomeric (*Z*)-iminium ion **4e** were also calculated. At all three levels of theory, all three conformers came out at higher energies than those of the (*E*)-*sc-exo*-form (by 1.7–8.7 kcal/mol; see *Table 6* and compare with *Table 5*).

Table 3. *Selected Results of a Computational Search for the Most Stable Structure of* Jørgensen*'s Dienamine* **5** (*cf. Fig. 9,a*) *with s*-trans-*N–C(1′) Conformation, and Conformations of Type* **C**, **D**, *and* **E** *of the Exocyclic C–C Bond*. Various basis functions were used. For further details, see *Exper. Part*. For a comparison with the calculated structures of s-*cis* N–C(1′) conformation, see *Table 4*.



5 N–C(1') s-*trans* **C** (*sc-exo*) **D** (*sc-endo*) **E** (*ap*)

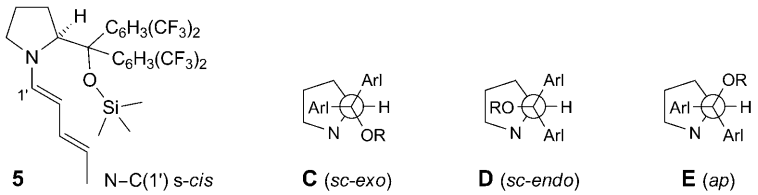
		sc-exo	*sc-endo*	*ap*
Dihedral angle N–C–C–NO [°]		60.3	– 68.2	– 177.1
Gas-phase calculations:				
B3LYP/6-31G(d)	E_{elec} [au][a])	– 2740.185713	– 2740.183693	– 2740.179526
	E_{elec} [kcal/mol][b])	0.00	1.27	3.88
B3LYP/6-311G(d,p)[c])	E_{elec} [au][a])	– 2740.899766	– 2740.897333	– 2740.893299
	E_{elec} [kcal/mol][b])	0.00	1.53	4.06
MP2/6-311G(d,p)[c])	E_{elec} [au][a])	– 2734.266005	– 2734.262795	– 2734.257087
	E_{elec} [kcal/mol][b])	0.00	2.01	5.60
CPCM Calculations (toluene soln.):				
B3LYP/6-31G(d)[c])	E_{elec} [au][a])	– 2740.191460	– 2740.189261	– 2740.184696
	E_{elec} [kcal/mol][b])	0.00	1.38	4.24
MP2/6-31G(d)[c])	E_{elec} [au][a])	– 2732.861831	– 2732.859738	– 2732.853455
	E_{elec} [kcal/mol][b])	0.00	1.31	5.26

[a]) Absolute energies for calculated compounds. [b]) Potential-energy differences between each conformer and the *sc-exo*-conformer are given. [c]) Single-point calculations at the B3LYP/6-31G(d)-optimized geometries.

6. Discussion and Conclusions. – The isolation and structural characterization, supported by DFT calculations, of the diarylprolinol-ether derivatives **3** and **4**, the reactive intermediates in organocatalyses by (diarylpyrrolidin-2-yl)methanol ethers, confirm the generally accepted assumption [4] that the large ('obese' [5]) $Arl_2(RO)C$ substituent at C(2) of the pyrrolidine ring *a*) sterically blocks one face of the nucleophilic and electrophilic π-systems of these intermediates, and *b*) causes a preference for the s-*trans*-conformation of the enamine and for the (*E*)-configuration of the iminium ion. The thus derived topical attack of electrophiles and of nucleophiles, as indicated in **H** and **I**, is compatible with the observed stereochemical course of the corresponding reactions. There are, however, two new aspects concerning details of the general mechanistic model.

a) *The (*E*)/(*Z*) Ratio*. When we dissolved the precipitated, analytically pure iminium salts **4** in $CDCl_3$, (D_6)DMSO, or (D_6)acetone, and recorded NMR spectra, we detected between 3 and 8% of the (*Z*)-isomers, besides the major (*E*)-isomers (see *Exper. Part)*. To see whether the two geometrical isomers are in equilibrium with each other, we dissolved the CF_3-substituted iminium salt **4e**, X = PF_6, in CD_3OD, recorded ^{1}H-NMR spectra at temperatures between -15 and $+45°$ and deduced the (*E*)/(*Z*)-

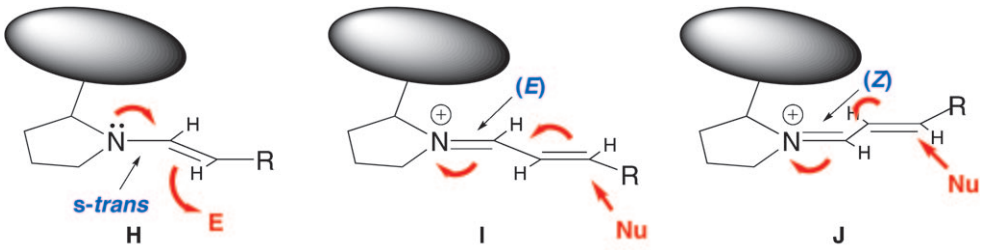
Table 4. *Results of Calculations of the Dienamine* **5** *Structures with s*-cis-*Conformation around the N–C(1′) Bond and* sc-exo, sc-endo-, *and* ap-*Conformations of the Exocyclic C–C Bond in the Gas Phase and in Toluene Solution* (*cf.* the corresponding s-*trans*-structures in *Table 3*). Note that, while all structures of s-*cis*-conformation are less stable than that of the s-*trans-sc-exo*-form, the s-*cis-sc-endo* form is slightly (0.1–0.6 kcal/mol) more stable than the s-*cis-sc-exo*-form in this calculation. While this small energy difference is within the error limit of the calculation, it is consistent throughout all levels of theory, in the gas phase as well as in toluene solution. More elaborate calculations (*cf. Footnote 24*) could possibly clarify this issue and might very well lead to the conclusion that there is an interaction between one of the CF_3-substituted benzene rings and the electron-rich dienamine π-system in the s-*cis-sc-endo*-form.



5 N–C(1′) s-*cis* **C** (*sc-exo*) **D** (*sc-endo*) **E** (*ap*)

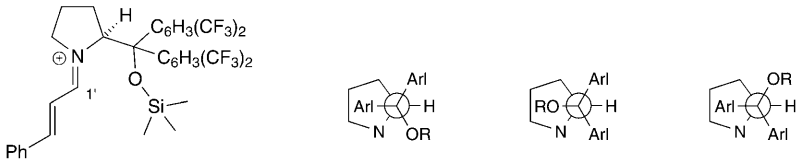
		sc-exo	*sc-endo*	*ap*
Dihedral angle N–C–C–NO [°]		57.0	– 70.8	167.3
Gas-phase calculations:				
B3LYP/6-31G(d)	E_{elec} [au][a])	– 2740.180850	– 2740.181521	– 2740.176885
	E_{elec} [kcal/mol][b])	3.05	2.63	5.54
B3LYP/6-311G(d,p)[c])	E_{elec} [au][a])	– 2740.894569	– 2740.895660	– 2740.891303
	E_{elec} [kcal/mol][b])	3.26	2.58	5.31
MP2/6-311G(d,p)[c])	E_{elec} [au][a])	– 2734.263245	– 2734.263474	– 2734.257871
	E_{elec} [kcal/mol][b])	1.73	1.59	5.10
CPCM Calculations (toluene solution):				
B3LYP/6-31G(d)[c])	E_{elec} [au][a])	– 2740.186025	– 2740.186410	– 2740.182023
	E_{elec} [kcal/mol][b])	3.41	3.17	5.92
MP2/6-31G(d)[c])	E_{elec} [au][a])	– 2732.858173	– 2732.858865	– 2732.853681
	E_{elec} [kcal/mol][b])	2.30	1.86	5.11

[a]) Absolute energies for calculated compounds. [b]) Potential-energy differences between each conformer and the *sc-exo*-conformer with s-*trans*-conformation of the exocyclic N–C bond are given (*cf. Table 3*). [c]) Single-point calculations at the B3LYP/6-31G(d)-optimized geometries.



ratios from the signals at 5.67 and 6.06 ppm (H–C(2); *cf. Fig. 1*). The content of (*Z*)-isomer (11 ± 1%) did not vary within the detection limit of NMR-peak integration. Furthermore, inversion-transfer NMR experiments (*a*) with the same solution at 45° or

Table 5. *Theoretical Structures Calculated at Various Levels of Theory for the* sc-exo-, sc-endo-, *and* ap-*Conformations of the Iminium Ion* **4e**. For an overlay of the measured (*cf. Fig. 8*, *c* and *d*) and the lowest-energy calculated structure, see *Fig. 10*. For a comparison with the analogous structures of (*Z*)-configuration, see *Table 6*.



4e N–C(1') (*E*) **C** (*sc-exo*) **D** (*sc-endo*) **E** (*ap*)

		sc-exo	*sc-endo*	*ap*
Dihedral angle N–C–C–NO [°]		61.4	– 59.6	– 177.6
Gas-phase calculations:				
B3LYP/6-31G(d)	E_{elec} [au][a])	– 2893.026143	– 2893.021057	– 2893.018802
	E_{elec} [kcal/mol][b])	0.00	3.19	4.61
B3LYP/6-311G(d,p)[c])	E_{elec} [au][a])	– 2893.764039	– 2893.757877	– 2893.754698
	E_{elec} [kcal/mol][b])	0.00	3.87	5.86
MP2/6-311G(d,p)[c])	E_{elec} [au][a])	– 2886.685493	– 2886.679220	– 2886.672259
	E_{elec} [kcal/mol][b])	0.00	3.94	8.30

[a]) Absolute energies for calculated compounds. [b]) Potential-energy differences between each conformer and the *sc-exo*-conformer are given. [c]) Single-point calculations at the B3LYP/6-31G(d)-optimized geometries.

b) in the presence of Et_3N at room temperature) showed that the rate constant of equilibration must be $\leq 0.05\ s^{-1}$[25]). This means that we can not detect equilibration (*Scheme 4*)[26]) between (*E*)- and (*Z*)-iminium salt **4** under these conditions and with the experiments carried out so far[27]). If the (*Z*)-isomer would also be present in organocatalytic applications of the CF_3-substituded prolinol Me_3Si ether **1e**, we would expect an erosion of the enantioselectivity (see **I** *vs.* **J**): with a 9:1 (*E*)/(*Z*) ratio the enantiomer excess of a compound produced in such a process would be 80%. This is inconsistent with the generally observed [4] high enantioselectivities (er up to 99.5:0.5) of the reactions catalyzed by **1e** (carried out in solvents such as CH_2Cl_2, MeCN, dioxane, sometimes in the presence of a benzoic acid Arl-CO_2H [4])[27]).

Three lines of rationalization come to mind: *i*) The (*Z*)-content in the samples of the iminium salts **4** may be an 'artifact' of our salt preparation in EtOH, in the presence

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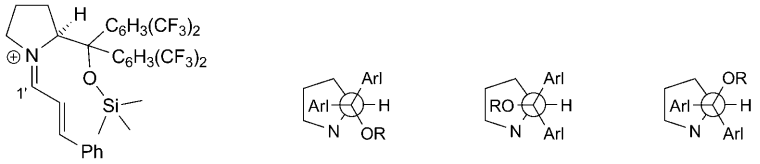
[25]) We thank Drs. *G. Deniau*, and *M.-O. Ebert*, as well as Prof. *B. Jaun* (ETH-Zürich) for carrying out and interpreting the temperature-dependent NMR measurements.

[26]) An energy difference of 1.4 kcal/mol corresponds to a 10:1 ratio at room temperature. The (*E*)/(*Z*)-ratio of *ca.* 89:11 happens to be in reasonable agreement with the DFT-calculated 1.7 kcal/mol energy difference between (*E*)-*sc-exo*- and (*Z*)-*sc-exo*-**4e** (*cf. Tables 5* and *6*).

[27]) It is intriguing that, according to NMR spectra, the iminium salt derived from 2-[fluoro(diphenyl)methyl]pyrrolidine is present as a 1:1 mixture of (*E*)- and (*Z*)-forms in solution, while the pyrrolidine itself catalyzes the epoxidation by H_2O_2 of α,β-unsaturated aldehydes with enantioselectivities ranging from er 90:10 to 98:2 [19].

Table 6. *Theoretical Structures Calculated at Various Levels of Theory for the* sc-exo-, sc-endo-, *and* ap-*Conformations of the Iminium Ion* (*Z*)-**4e** *of* (*Z*)-*Configuration of the Exocyclic N=C Bond*. For comparison with the corresponding conformations with (*E*)-configuration, see *Table 5*.



(*Z*)-**4e** N–C(1') (*Z*) **C** (*sc-exo*) **D** (*sc-endo*) **E** (*ap*)

		sc-exo	*sc-endo*	*ap*
Dihedral angle N–C–C–NO [°]		64.6	– 62.5	179.0
Gas-phase calculations:				
B3LYP/6-31G(d)	E_{elec} [au][a])	– 2893.020342	– 2893.019821	– 2893.013816
	E_{elec} [kcal/mol][b])	3.64	3.97	7.74
B3LYP/6-311G(d,p)[c])	E_{elec} [au][a])	– 2893.757508	– 2893.756427	– 2893.750149
	E_{elec} [kcal/mol][b])	4.10	4.78	8.72
MP2/6-311G(d,p)[c])	E_{elec} [au][a])	– 2886.682738	– 2886.682497	– 2886.676750
	E_{elec} [kcal/mol][b])	1.73	1.88	5.49

[a]) Absolute energies for calculated compounds. [b]) Potential-energy differences between each conformer and the *sc-exo*-conformer with (*E*)-configuration of the exocyclic N=C bond (see *Table 5*) are given. [c]) Single-point calculations at the B3LYP/6-31G(d)-optimized geometries.

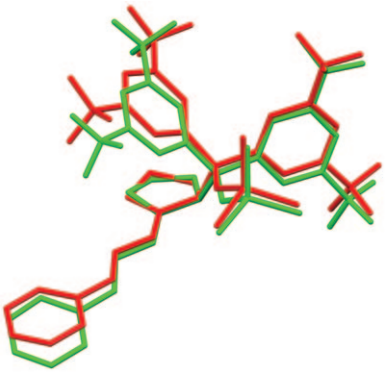
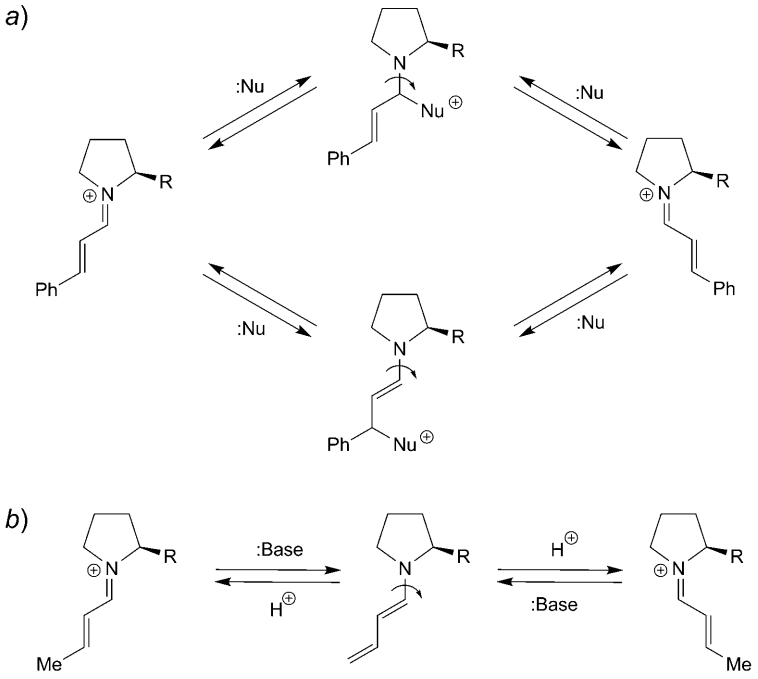


Fig. 10. *Overlay of the measured* (green) *and calculated* (red) *structures of the iminium ion* **4e**

of Et_3N, followed by precipitation from this solvent or from Et_2O (see *Sect.* 2 and *Exper. Part*). *ii*) Under the conditions of catalytic applications, the (*E*)-isomers **4** may be generated preferentially, equilibrate slowly or not at all with the (*Z*)-isomer, and react rapidly with nucleophiles (kinetic control) to give the precursors (see **I**) of the isolated products. *iii*) Both (*E*)- and (*Z*)-isomer are formed in the catalytic process, and the (*E*)-isomer is a much more reactive electrophile [17b] than the (*Z*)-isomer.

Detailed mechanistic and, possibly, theoretical investigations will be necessary in order to elucidate the apparent discrepancy between our results and the high performance of the diarylprolinol ethers as organocatalysts.

Scheme 4. *Possible Modes of Iminium (*E*) ⇌ (*Z*) Equilibration. a*) Iminium ions of type **4**; *b*) an iminium salt derived from crotonaldehyde (*cf. Fig. 9* and *Tables 3–6*).



b) *The* sc-exo-*Conformation*. In the generally accepted mechanistic model, 'wishful thinking' has placed an aryl group above the π-system in the reactive intermediates of catalysis by diarylprolinol ethers (see, for instance, the presentation **K** used in a recent – anonymous – publication on the subject and the calculation by the *Jørgensen* group presented in *Fig. 9*). From the crystal structures and from the DFT calculations, we are now led to assume that the C–C bond between the diaryl(methoxy)methyl or diaryl(silyloxy)methyl group and the pyrrolidine-ring C-atom adopts preferentially ($\geq$ 3.2 kcal/mol) a *sc-exo*-conformation, **C**, in the reactive electrophilic intermediates, such as the iminium ions **4** (see **L**)[28]). In this conformation, it is *not so much* the benzene ring of the aryl group itself, but a *meta*-substituent on one of the aryl groups *and* the RO group, which provide the major contributions to steric hindrance of approach to one of the faces of the iminium π-system (see especially *Fig. 8*).

In conclusion, the structure determination of reactive intermediates of organocatalysis by diarylprolinol ethers has provided new insights and, at the same time, raised some interesting questions concerning details of the mechanism.

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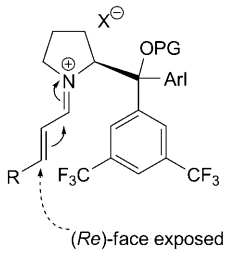
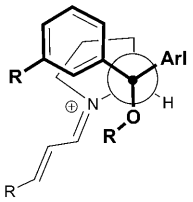
[28]) We do not know the barrier to rotation around this bond, but we may assume that it is substancial (*cf.* the discussion of the *geminal*-diaryl effect in stereoselective organic syntheses in [3] and [32]).



K



L (*cf.* **C**)

We thank *P. Kälin* and *M. Schneider* (Elemental Analyses), *R. Häfliger*, *L. Bertschi*, and *O. Greter* (MS Service), Prof. *B. Jaun*, Dr. *M.-O. Ebert*, *R. Frankenstein*, and *P. Zumbrunnen* (NMR Service), and *M. Solar* (X-Ray Service), as well as the Laboratory of Organic Chemistry (ETHZ) and the *Novartis Pharma AG* for all their help and support.

Experimental Part

General. All reactions were performed under Argon in dried glassware using anh. solvents except when using aq. reagents. All chemicals were of reagent grade and used as supplied, unless stated otherwise. Solvents for extractions and chromatography were of technical grade and were distilled prior to use. Sat. hydrocarbon solvents were kept over Na wire. Extracts were dried over technical grade $MgSO_4$. Anal. TLC: pre-coated *Merck* silica gel *60* F_{254} plates (0.25 mm). Column chromatography (CC): *Fluka* silica gel *60* (230–400 mesh). M.p.: *Büchi 510* melting-point apparatus and are uncorrected. Optical rotations: *Jasco P-2000* polarimeter. IR Spectra: as neat solid/oil on a *Perkin-Elmer precisely Universal ATR Sampling Accessory*; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AVANCE* (^1H: 300 MHz, ^{13}C: 75 MHz), *DRX* (^1H: 400 MHz, ^{13}C: 101 MHz), and *AV* (^1H: 400 MHz, ^{13}C: 101 MHz) spectrometer, or *Varian Gemini-300* (^1H: 300 MHz, ^{13}C: 75 MHz) spectrometer; chemical shifts (δ) are reported in ppm rel. to Me_4Si (0.00 ppm). High-resolution (HR) MS: *IonSpecUltima 4.7-T-FT Ion Cyclotron Resonance* (ICR; HR-MALDI, in 2,5-dihydroxybenzoic acid matrix) spectrometer. Elemental analyses: by the Microanalytical Laboratorium at the Laboratory for Organic Chemistry, ETH Zürich.

Preparation of Diphenylprolinols **1** *and Oxazolidines* **2**. *(*R*)-Bis[4-*tert*-butyl)phenyl](pyrrolidin-2-yl)methanol* (**1**; Arl = 4-^{t}BuC$_6$H$_4$, R = H) *and (*R*)-1,1-bis[4-(*tert*-butyl)phenyl]tetrahydro-1*H*-pyrrolo[1,2-*c*][1,3]oxazol-3-one* (**2a**). *a*) To a soln. of [4-(*tert*-butyl)phenyl]magnesium bromide (2M in Et_2O, 50 ml, 100 mmol) at 0° was added a soln. of *N*-(ethoxycarbonyl)-D-proline methyl ester[29]) (6.3 g, 31.27 mmol) in anh. THF (40 ml, r.t.) during 40 min. After the addition, the mixture was stirred for 1 h at 0° and 24 h at r.t. The reaction of the ice-cold (0°) mixture was carefully quenched by slow addition of aq. sat. NH_4Cl (30 ml). After stirring for 1 h at r.t., the mixture was filtered through a short plug of *Celite* and thoroughly washed with CH_2Cl_2. Volatile components were evaporated *in vacuo*, and the residue was treated with H_2O (100 ml) and extracted with CH_2Cl_2 (4 × 100 ml). The combined org. phase was dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*. The residue was dissolved in MeOH (120 ml), KOH (19 g) was added, and the resulting mixture was heated under reflux for 4 h. Volatile components were carefully evaporated *in vacuo*. The residue was treated with CH_2Cl_2 (200 ml) upon which a gel-like mixture was formed. The mixture was filtered through a short plug of *Celite* and thoroughly washed with CH_2Cl_2 (4 × 100 ml). The filtrate was washed with H_2O (100 ml) and brine (100 ml), and dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*. The residue was purified by CC: 1st eluate: AcOEt/hexane 1:2 to elute **2a** (*ca.* 10–15 mmol of **2a** containing several

[29]) *N*-(Ethoxycarbonyl)-D-proline methyl ester was prepared from D-proline methyl ester according to the literature procedure used for the preparation of its L-enantiomer, *N*-(ethoxycarbonyl)-L-proline methyl ester [33].

other by-products, in tubes containing the highest concentration of the product, **2a** tends to precipitate from the soln.); 2nd eluate: AcOEt/Et_3N 50:1 to give 2.98 g of **1** (Arl = 4-^{t}BuC_6H_4, R = H) as a white solid containing *ca.* 20% of *(*R*)-1,1-bis[4-(*tert*-butyl)phenyl]tetrahydro-1*H*-pyrrolo[1,2-c][1,3]oxazole* (**2b**), that could not be separated from **1** (Arl = 4-^{t}BuC_6H_4, R = H) under these conditions. Fractions containing the product were evaporated *in vacuo* to give crude **2a** and **1** (Arl = 4-^{t}BuC_6H_4, R = H). The so isolated **2a** was used for the preparation of anal. pure **1** (Arl = 4-^{t}BuC_6H_4, R = H; see *procedure b*). A small amount of **2a** was purified by CC (two times CC, AcOEt/hexane 1:5) to obtain an anal. pure sample of **2a**. Crude **1** (Arl = 4-^{t}BuC_6H_4, R = H) was used to prepare compound **1i** and to isolate the side-product **2b**.

b) Crude **2a** (4.5 g, *ca.* 10 mmol, see *a*, above) in MeOH (100 ml) and KOH (27 g) were heated under reflux for 9 h. Volatile components were carefully evaporated *in vacuo*. The residue was treated with CH_2Cl_2 (150 ml) upon which a gel-like mixture was formed. The mixture was filtered through a short plug of *Celite* and thoroughly washed with CH_2Cl_2 (4 × 100 ml). The filtrate was washed with H_2O (100 ml) and brine (100 ml), and dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*. To a cold soln. of the residue in Et_2O (200 ml, 0°) was added a cold soln. of H_2SO_4 in Et_2O (0.1M, 100 ml, 0°) during 10 min. The white precipitate was collected by filtration and washed with Et_2O (300 ml) and H_2O (200 ml). The solid was suspended in a mixture of NaOH (aq., 2M, 150 ml) and THF (100 ml) and vigorously stirred for 5 h at r.t. The bulk of the THF from the mixture was carefully evaporated *in vacuo*. The remaining soln. was extracted with CH_2Cl_2 (4 × 100 ml), and the combined org. phase was washed with brine (100 ml), dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo* to give **1** (Arl = 4-^{t}BuC_6H_4, R = H). Yield: 2.47 g (*ca.* 70%).

Data of **1** (Arl = 4-^{t}BuC_6H_4, R = H). White solid. M.p. 160–162°. $[\alpha]_D^{r.t.} = +52.2$ ($c = 0.18$, CH_2Cl_2). IR: 2965*m*, 2866*w*, 2843*w*, 1508*w*, 1462*w*, 1403*m*, 1365*m*, 1324*w*, 1267*m*, 1203*w*, 1188*w*, 1110*m*, 1101*m*, 1019*w*, 997*m*, 915*m*, 874*m*, 844*m*, 836*s*, 823*s*, 810*m*, 707*m*, 693*m*, 655*m*, 637*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.23 (*s*, ^{t}Bu); 1.24 (*s*, ^{t}Bu); 1.41–1.55 (*m*, CH_2); 1.57–1.68 (*m*, CH_2); 2.81–2.94 (*m*, CH_2); 3.30 (br. *s*, NH); 4.24 (*t*, *J* = 7.7, H–C(2)); 7.20–7.27 (*m*, 4 arom. H); 7.34–7.38 (*m*, 2 arom. H); 7.45–7.50 (*m*, 2 arom. H). ^{13}C-NMR (101 MHz, (D_6)DMSO): 25.3; 26.4; 31.0; 33.8; 46.7; 64.0; 76.7; 124.2; 124.3; 124.8; 125.6; 143.3; 144.9; 147.8; 148.0. HR-MS (MALDI): 366.2791 (100, $[M + H]^+$, $C_{25}H_{36}NO^+$; calc. 366.27914). Anal. calc. for $C_{25}H_{35}NO$ (365.55): C 82.14, H 9.65, N 3.83; found: C 81.87, H 9.72, N 3.83.

Data of **2a**. White solid. M.p. 240–243°. $[\alpha]_D^{r.t.} = +124.5$ ($c = 0.44$, CH_2Cl_2). IR: 2961*m*, 2902*w*, 2869*w*, 1747*s*, 1510*w*, 1475*w*, 1462*w*, 1391*m*, 1362*w*, 1345*w*, 1325*w*, 1266*m*, 1230*m*, 1199*w*, 1110*w*, 1064*m*, 1021*w*, 999*s*, 969*m*, 861*w*, 843*w*, 823*s*, 771*m*, 720*w*, 709*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.05–1.21 (*m*, 1 H, CH_2); 1.29 (*s*, 2 ^{t}Bu); 1.67–1.77 (*m*, 1 H, CH_2); 1.78–2.04 (*m*, CH_2); 3.22 (*ddd*, *J* = 3.8; 9.3; 11.4, 1 H, CH_2); 3.71 (*dt*, *J* = 8.1, 11.4, 1 H, CH_2); 4.49 (*dd*, *J* = 5.4, 10.5, CH); 7.26–7.38 (*m*, 6 arom. H); 7.41–7.46 (*m*, 2 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 25.1; 29.2; 31.39; 31.43; 34.63; 34.64; 46.1; 69.8; 86.1; 125.2; 125.3; 125.6; 125.7; 137.5; 140.8; 150.6; 151.2; 160.8. HR-MS (MALDI): 391.2510 (100, M^+, $C_{26}H_{33}NO_2^+$; calc. 391.2506). Anal. calc. for $C_{26}H_{33}NO_2$ (391.55): C 79.76, H 8.49, N 3.58; found: C 79.64, H 8.57, N 3.55.

*(*S*)-2-[{[Dimethyl(phenyl)silyl]oxy}(diphenyl)methyl]pyrrolidine* (**1f**). According to a literature procedure [34] $Me_2PhSiCl$ (392 µl, 2.37 mmol) was added to a soln. of the *(*S*)-diphenyl(pyrrolidin-2-yl)methanol* (**1a**; 500 mg, 1.97 mmol), Et_3N (550 µl, 3.97 mmol), and 4-(dimethylamino)pyridine (DMAP; 17 mg, 5.9 µmol) in anh. CH_2Cl_2 (18 ml) under Ar in a 50-ml two-necked round-bottomed flask fitted with stirrer bar, stopper, and gas inlet (dried by heat gun at 0.3 mbar). The resulting colorless soln. was stirred for 20 h, after which it had become pink. TLC indicated the reaction was complete, and the reaction was quenched by pouring into ice/H_2O (25 ml). This mixture was extracted with AcOEt (3 × 25 ml), and the org. layers were combined and washed with H_2O (25 ml), resulting in an emulsion. This was broken up by washing with brine (3 × 25 ml). The org. layer was dried ($MgSO_4$) and concentrated to give a yellow oil (*ca.* 860 mg). The crude material was purified by CC (3 × 25 cm; AcOEt/hexane 1:1) to give a yellow oil which crystallized on standing to give **1f** (682 mg, 89%). Large yellow cubes. M.p. 59–61°. $[\alpha]_D^{r.t.} = -46.0$ ($c = 1.27$, $CHCl_3$). IR (neat): 3017*w*, 2955*m*, 2872*w*, 1599*w*, 1490*m*, 1446*m*, 1428*m*, 1401*m*, 1290*w*, 1256*m*, 1243*m*, 1197*m*, 1141*s*, 1118*s*, 1074*s*, 936*m*, 920*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.09 (*s*, Me_2Si); 1.18–1.28 (*m*, 1 H, CH_2); 1.40–1.80 (*m*, 3 H, CH_2, NH); 2.64–2.71 (*m*, 1 H, CH_2); 2.76–2.84 (*m*, 1 H, CH_2); 4.02 (*t*, *J* = 7.2, H–C(2)); 7.19–7.55 (*m*, 15 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 1.13; 1.28; 24.8; 27.5; 47.1; 65.4; 83.6; 126.7; 127.0, 127.6 (2×); 128.2; 128.4; 128.9; 133.3;

140.5; 145.6; 146.6. ESI-MS: 107 (12); 149 (25); 310 (22); 181 (100); 207 (12); 236 (88); 310 (21); 388 (18); 391 (12). HR-ESI-MS: 388.2088 ($C_{25}H_{30}NOSi^+$; calc. 388.2091).

*(*S*)-2-[{[Methyl(diphenyl)silyl]oxy}(diphenyl)methyl]pyrrolidine* (**1h**). Same procedure as for the synthesis of **1f** (see above), except that $MePh_2SiCl$ (534 µl, 2.37 mmol) was used for the silylation. The resulting colorless soln. was stirred for 16.5 h, after which it had become yellow. Workup gave a yellow foam (1.10 g). The crude material was purified by CC (3 × 25 cm; AcOEt/hexane 1:1) to give **1h** (787 mg, 89%). Amorphous yellow solid. M.p. 88–90°. $[\alpha]_D^{r.t.} = -48.2$ ($c = 1.02$, $CHCl_3$). IR (neat): 2867*w*, 1491*m*, 1448*m*, 1427*s*, 1400*m*, 1245*m*, 1196*w*, 1137*s*, 1115*s*, 1073*s*, 1020*m*, 930*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.20 (*s*, MeSi); 0.92–1.05 (*m*, 1 H, CH_2); 1.24–1.46 (*m*, CH_2); 1.54–1.67 (*m*, 1 H, CH_2); 1.70 (br. *s*, NH); 2.55 (*ddd*, $J = 5.2$; 7.6; 9.8, 1 H, CH_2); 2.73 (*dt*, $J = 6.4$; 9.8, 1 H, CH_2); 4.00 (*t*, $J =$ 7.4, H–C(2)); 7.18–7.39 (*m*, 14 arom. H); 7.48–7.54 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −0.8; 24.3; 27.3; 46.8; 65.2; 83.9; 126.9; 127.2; 127.5; 127.6 (2×); 127.8 (2×); 128.5; 129.1; 134.3; 134.5; 139.2; 139.5; 145.7; 146.6. EI-MS: 70 (100); 165 (3); 197 (14); 434 (0.3). HR-EI-MS: 434.1935 ($[M - Me]^+$, $C_{29}H_{28}NOSi^+$; calc. 434.1935).

Preparation of $R^1_2R^2SiO$-Protected Prolinole Derivatives **1g**, **1i**, *and* **2b**. *General Procedure 1* (*GP 1*)[30]). To a soln./suspension of diarylprolinol (1 equiv.) in anh. CH_2Cl_2 (V_1) at r.t. under Ar were added Et_3N (2 equiv.), DMAP (0.06 equiv.) and $R^1_2R^2SiCl$ (1.2 equiv.). After stirring at r.t. for hours (t_1), the reaction was quenched with ice cold H_2O (25–50 ml), and the resulting mixture was extracted with AcOEt (2 × 100 ml). The combined org. phase was dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*. The residue was purified by CC to give **1g** and **1i** (or **1i** and **2b**).

*(*R*)-2-(Bis[(4*-tert*-butyl)phenyl][{[dimethyl(phenyl)silyl]oxy}methyl)pyrrolidine* (**1g**). Prepared according to *GP 1* from **1** (Arl = 4-^{t}BuC_6H_4, R = H; 215 mg, 0.59 mmol) and $Me_2PhSiCl$ (120 µl, 0.71 mmol): CH_2Cl_2 (6 ml), Et_3N (164 µl, 1.18 mmol), DMAP (4 mg, 0.035 mmol); $t_1 = 22$ h; CC (AcOEt/hexane 1:4). Yield: 224 mg (76%). Colorless oil. $[\alpha]_D^{r.t.} = +45.3$ ($c = 0.15$, CH_2Cl_2). IR: 2960*m*, 2904*w*, 2869*w*, 1509*w*, 1475*w*, 1461*w*, 1428*w*, 1403*w*, 1363*w*, 1268*w*, 1249*m*, 1202*w*, 1144*w*, 1112*s*, 1075*m*, 1037*m*, 1015*m*, 934*w*, 877*m*, 825*s*, 801*m*, 780*s*, 726*m*, 699*s*, 648*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.25 (*s*, 2 Me); 1.31–1.38 (*m*, 1 H, CH_2); 1.44 (*s*, ^{t}Bu); 1.45 (*s*, ^{t}Bu); 1.56–1.67 (*m*, CH_2); 1.70–1.80 (*m*, 1 H, CH_2); 1.87 (br. *s*, NH); 2.78–2.86 (*m*, 1 H, CH_2); 2.88–2.95 (*m*, 1 H, CH_2); 4.15 (*t*, $J = 7.5$, H–C(2)); 7.35–7.46 (*m*, 9 arom. H); 7.50–7.56 (*m*, 2 arom. H); 7.63–7.68 (*m*, 2 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 1.0; 1.1; 24.8; 27.4; 31.5; 34.43; 34.45; 47.0; 65.6; 83.4; 124.4; 124.5; 127.3; 127.6; 128.1; 128.9; 133.4; 140.8; 142.6; 143.5; 149.5; 149.7. HR-MS (MALDI): 499.3259 (100, M^+, $C_{33}H_{45}NOSi^+$; calc. 499.3265). Anal. calc. for $C_{33}H_{45}NOSi$ (499.80): C 79.30, H 9.07, N 2.80; found: C 78.34, H 9.01, N 2.75.

*(*R*)-2-(Bis[(4*-tert*-butyl)phenyl][{[methyl(diphenyl)silyl]oxy}methyl)pyrrolidine* (**1i**) *and* **2b**. Prepared according to *GP 1* from crude **1** (Arl = 4-^{t}BuC_6H_4, R = H; 310 mg, *ca.* 0.700 mmol, containing *ca.* 20% of **2b**) and $MePh_2SiCl$ (183 µl, 0.84 mmol): CH_2Cl_2 (7 ml), Et_3N (195 µl, 1.4 mmol), DMAP (5 mg, 0.042 mmol); $t_1 = 20$ h; CC (AcOEt/hexane 1:4) afforded **1i** (300 mg, 76%) and **2b** (47 mg, *ca.* 88%).

Large-Scale Preparation of **1i**. Prepared according to *GP 1* from anal. pure **1** (Arl = 4-^{t}BuC_6H_4, R = H; 1.65 g, 4.52 mmol) and $MePh_2SiCl$ (1.18 ml, 5.42 mmol) (*GP 5*): CH_2Cl_2 (45 ml), Et_3N (1.26 ml, 9.03 mmol), DMAP (33 mg, 0.27 mmol); $t_1 = 23$ h; CC (AcOEt/hexane 1:4). Yield: 2.04 g (80%).

Data of **1i** (elutes first). White solid. M.p. 61–65°. $[\alpha]_D^{r.t.} = +61.0$ ($c = 0.25$, CH_2Cl_2). IR: 2961*m*, 2904*w*, 2867*w*, 1509*w*, 1475*w*, 1461*w*, 1428*m*, 1403*w*, 1363*w*, 1269*w*, 1251*w*, 1190*w*, 1143*w*, 1109*s*, 1063*m*, 1014*m*, 936*w*, 874*m*, 842*w*, 824*m*, 788*s*, 734*s*, 715*s*, 698*s*, 666*m*. ^{1}H-NMR (400 MHz, $CDCl_3$)[31]): 0.31 (*s*, Me); 0.98–1.09 (*m*, 1 H, CH_2); 1.34 (*s*, ^{t}Bu); 1.34 (*s*, ^{t}Bu); 1.38–1.47 (*m*, CH_2); 1.60–1.73 (*m*, 2 H, C*H*H, NH); 2.56–2.67 (*m*, 1 H, CH_2); 2.70–2.79 (*m*, 1 H, CH_2); 4.04 (*t*, $J = 7.2$, H–C(2)); 7.22–7.37 (*m*, 12 arom. H); 7.45–7.49 (*m*, 2 arom. H); 7.52–7.58 (m, 4 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): −0.6; 24.3; 27.3; 31.51; 31.52; 34.40; 34.43; 46.7; 65.4; 83.7; 124.45; 124.46; 127.2; 127.47; 127.48; 128.1; 128.93; 128.95; 134.3; 134.5; 139.4; 139.6; 142.6; 143.4; 149.4; 149.7. HR-MS (MALDI): 561.3425 (100, M^+,

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30) The volumes (in ml) of H_2O or solvents given in all *General Procedures* refer to the batch sizes (1–4 mmol) given in the corresponding individual procedures.

31) If one sees rotamers in NMR spectra recorded in $CDCl_3$, one should record the same spectra in DMSO to avoid that!

$C_{38}H_{47}NOSi^+$; calc. 561.3422). Anal. calc. for $C_{38}H_{47}NOSi$ (561.87): C 81.23, H 8.43, N 2.49; found: C 81.10, H 8.56, N 2.46.

Data of **2b** (elutes second). White solid. M.p. 162–167°. $[\alpha]_D^{r.t.} = +227.8$ ($c = 0.53$, CH_2Cl_2). IR: 2960*m*, 2867*w*, 1507*m*, 1475*w*, 1461*w*, 1404*w*, 1362*w*, 1268*m*, 1192*w*, 1172*w*, 1155*w*, 1131*w*, 1109*m*, 1091*w*, 1075*w*, 1023*w*, 1005*s*, 963*m*, 953*m*, 941*m*, 927*m*, 843*m*, 820*s*, 727*w*, 709*m*, 695*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.16–1.23 (*m*, 1 H, CH_2); 1.27 (*s*, ^{t}Bu); 1.27 (*s*, ^{t}Bu); 1.59–1.70 (*m*, 3 H, CH_2); 2.74–2.83 (*m*, 1 H, CH_2); 3.19–3.27 (*m*, 1 H, CH_2); 4.31 (*d*, $J = 6.1$, 1 H, CH_2); 4.36 (*t*, $J = 7.0$, CH); 4.48 (*d*, $J = 6.1$, 1 H, CH_2); 7.22–7.34 (*m*, 6 arom. H); 7.40–7.45 (*m*, 2 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 26.5; 30.6; 31.4; 31.5; 34.4; 34.5; 56.6; 71.4; 85.8; 88.1; 124.7; 125.1; 125.6; 126.7; 141.0; 141.8; 149.1; 149.8. HR-MS (MALDI): 378.2791 (100, $[M + H]^+$, $C_{26}H_{36}NO^+$; calc. 378.27914). Anal. calc. for $C_{26}H_{35}NO$ (377.56): C 82.71, H 9.34, N 3.71; found: C 82.49, H 9.34, N 3.75.

Preparation of the Ammonium Salts **1** · *HX. Preparation of* BF_4 *Salts of the Secondary Amines* **1a** · HBF_4 *and* **1b** · HBF_4. *General Procedure 2* (*GP 2*)[30]. To a soln. of a secondary amine (1 equiv.) in anh. Et_2O (V_1) at 0° under Ar was added a soln. of $HBF_4 \cdot Et_2O$ (1 equiv.) in anh. Et_2O (V_2) at r.t. during 10 min. The mixture was stirred for additional t_1 min. at 0° and t_2 min at r.t. The precipitate was collected by filtration, washed with anh. Et_2O (30 ml), and dried under high vacuum to give BF_4 salts **1a** · HBF_4 and **1b** · HBF_4.

*(*S*)-2-[Hydroxy(diphenyl)methyl]pyrrolidinium Tetrafluoroborate* (**1a** · HBF_4). Prepared according to *GP 2* from **1a** (510 mg, 2.01 mmol) and $HBF_4 \cdot Et_2O$ (276 µl, 2.01 mmol): $V_1 = 80$ ml; $V_2 = 30$ ml; $t_1 = 60$ min; $t_2 = 10$ min. Yield: 660 mg (96%). White solid. M.p. 207–209°. $[\alpha]_D^{r.t.} = +49.1$ ($c = 0.33$, EtOH). IR: 3469*w*, 3233*w*, 3193*w*, 1578*w*, 1495*w*, 1450*m*, 1395*w*, 1361*m*, 1328*w*, 1268*w*, 1185*m*, 1162*w*, 1112*s*, 1065*s*, 1043*s*, 981*s*, 956*s*, 944*s*, 882*m*, 861*w*, 771*s*, 753*s*, 698*s*, 641*s*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.79–1.98 (*m*, 2 CH_2); 3.04–3.20 (*m*, CH_2); 4.86 (deg. *t*, $J = 7.5$; 7.8, CH); 6.58 (*s*, OH); 7.21–7.28 (*m*, 2 arom. H); 7.31–7.40 (*m*, 4 arom. H); 7.51–7.63 (*m*, 4 arom. H); 7.89 (*s*, 1 H, NH_2^+); 8.85 (*s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 23.9; 25.8; 46.7; 65.4; 76.9; 125.56; 125.59; 127.1; 127.2; 128.2; 128.4; 144.4; 144.9. HR-MS (MALDI): 254.1539 (100, M^+, $C_{17}H_{20}NO^+$; calc. 254.15394). Anal. calc. for $C_{17}H_{20}BF_4NO$ (341.15): C 59.85, H 5.91, N 4.11; found: C 59.98, H 5.99, N 4.05.

*(*S*)-2-[Bis(3,5-dimethylphenyl)(methoxy)methyl]pyrrolidinium Tetrafluoroborate* (**1b** · HBF_4). Prepared according to *GP 2* from *(*S*)-2-[bis(3,5-dimethylphenyl)(methoxy)methyl]pyrrolidine* (**1b**; 1.39 mmol; which was quantitatively prepared from its HCl salt (500 mg, 1.39 mmol) by neutralization (aq. Na_2CO_3) and extraction with CH_2Cl_2 sequence) and $HBF_4 \cdot Et_2O$ (191 µl, 1.39 mmol): $V_1 = 60$ ml; $V_2 = 10$ ml; $t_1 = 10$ min; $t_2 = 30$ min. Yield: 460 mg (80%). White solid. M.p. 192–195°. $[\alpha]_D^{r.t.} = -37.2$ ($c = 0.28$, CH_2Cl_2). IR: 3118*w*, 1604*m*, 1457*w*, 1408*w*, 1371*w*, 1297*w*, 1270*w*, 1223*w*, 1177*w*, 1062*s*, 1021*s*, 922*m*, 865*m*, 857*m*, 811*m*, 760*m*, 720*m*, 700*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.16–1.28 (*m*, 1 H, CH_2); 1.86–2.00 (*m*, CH_2); 2.23–2.39 (*m*, 1 H, CH_2); 2.31 (*s*, 2 Me); 2.32 (*s*, 2 Me); 2.67–2.80 (*m*, 1 H, CH_2); 3.07 (*s*, MeO); 3.37–3.48 (*m*, 1 H, CH_2); 4.86–4.96 (*m*, H–C(2)); 6.54 (br. *s*, 1 H, NH_2^+); 6.90 (*s*, 2 arom. H); 6.97 (*s*, 2 arom. H); 7.00 (*s*, 2 arom. H); 7.79 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, $CDCl_3$): 21.5; 21.6; 24.0; 27.4; 47.4; 51.6; 63.4; 83.6; 126.1; 126.9; 130.4; 130.6; 138.1; 138.2; 138.5; 138.6. HR-MS (MALDI): 324.2322 (100, M^+, $C_{22}H_{30}NO^+$; calc. 324.23219). Anal. calc. for $C_{22}H_{30}BF_4NO$ (411.28): C 64.25, H 7.35, N 3.41; found: C 64.42, H 7.34, N 3.40.

Preparation of BF_4 *Salts of Secondary Amines* **1d** · HBF_4, **1h** · HBF_4, *and* **1i** · HBF_4. *General Procedure 3* (*GP 3*)[30]. According to *GP 2*, the initially obtained precipitate (in case the desired product did not precipitate readily, hexane (up to 50 ml) was added to the mixture, and vigorous stirring at 0° was continued until a fine precipitate was formed) consisted of the desired R_3SiO-protected prolinol-derived BF_4^- salt (major product) and various amounts (*ca.* 5–36%) of undesired R_3SiO-deprotected BF_4^- salt (minor product). The precipitate was suspended in anh. CH_2Cl_2 (V_3) or a mixture of anh. $CHCl_3$/hexane (V_3), where only the desired R_3SiO-protected prolinol-derived BF_4^- salt was soluble, and quickly filtered and washed through a short plug of *Celite* with the same solvent or solvent mixture. Volatile components were evaporated *in vacuo*, and the residue was dried under high vacuum. Et_2O and hexane were added to the residue, followed by intense 'scratching by spatula' until a nicely powdered, filterable solid was formed. The so formed solid was collected by filtration, washed with Et_2O (20 ml), and dried under high vacuum to give salts **1d** · HBF_4, **1h** · HBF_4, and **1i** · HBF_4.

(S)-2-{Diphenyl[(trimethylsilyl)oxy]methyl}pyrrolidinium Tetrafluoroborate (**1d**·HBF_4). Prepared according to *GP 3* from *(S)-2-{diphenyl[(trimethylsilyl)oxy]methyl}pyrrolidine* (**1d**; 1250 mg, 3.84 mmol) and $HBF_4 \cdot Et_2O$ (527 µl, 3.84 mmol): $V_1 = 60$ ml; $V_2 = 20$ ml; $t_1 = 60$ min; $V_3 = 40$ ml CH_2Cl_2. Yield: 860 mg (54%). White solid. M.p. 149–150°. $[\alpha]_D^{r.t.} = -9.3$ ($c = 0.19$, CH_2Cl_2). IR: 3199*w*, 1590*w*, 1494*w*, 1392*w*, 1362*w*, 1252*w*, 1199*w*, 1182*w*, 1130*m*, 1110*m*, 1078*s*, 1066*s*, 1050*s*, 1033*s*, 1000*s*, 990*s*, 980*s*, 894*w*, 871*s*, 837*s*, 762*s*, 751*s*, 704*s*, 642*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): −0.08 (*s*, Me_3Si); 1.41–1.53 (*m*, 1 H, CH_2); 1.92–2.06 (*m*, CH_2); 2.27–2.40 (*m*, 1 H, CH_2); 2.70–2.82 (*m*, 1 H, CH_2); 3.27–3.38 (*m*, 1 H, CH_2); 4.78–4.89 (*m*, H–C(2)); 6.32 (br. *s*, 1 H, NH_2^+); 7.28–7.64 (*m*, 11 H, 10 arom. H, N*H*H$^+$). ^{13}C-NMR (101 MHz, $CDCl_3$): 1.7; 24.1; 27.0; 47.6; 67.9; 81.8; 128.3; 128.5; 128.8; 128.85; 128.90; 129.0; 140.7; 141.5. HR-MS (MALDI): 326.1935 (100, M^+, $C_{20}H_{28}NOSi^+$; calc. 326.19347). Anal. calc. for $C_{20}H_{28}BF_4NOSi$ (413.33): C 58.12, H 6.83, N 3.39; found: C 58.41, H 6.76, N 3.24.

(S)-2-({[Methyl(diphenyl)silyl]oxy}(diphenyl)methyl)pyrrolidinium Tetrafluoroborate (**1h**·HBF_4). Prepared according to *GP 3* from *(S)-2-({[methyl(diphenyl)silyl]oxy}(diphenyl)methyl)pyrrolidine* (**1h**; 743 mg, 1.65 mmol) and $HBF_4 \cdot Et_2O$ (227 µl, 1.65 mmol): $V_1 = 60$ ml; $V_2 = 10$ ml; $t_1 = 30$ min; $V_3 = 20$ ml of $CHCl_3$/heptane 3:2. Yield: 460 mg (51%). White solid. M.p. 139–141°. $[\alpha]_D^{r.t.} = -8.7$ ($c = 0.21$, CH_2Cl_2). IR: 3237*w*, 1590*w*, 1491*w*, 1446*w*, 1429*w*, 1374*w*, 1263*w*, 1195*w*, 1109*m*, 1092*m*, 1058*s*, 1016*s*, 1001*s*, 934*w*, 920*w*, 898*w*, 847*m*, 833*m*, 796*m*, 788*m*, 775*m*, 751*m*, 739*s*, 722*s*, 711*m*, 698*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.32 (*s*, Me); 1.29–1.45 (*m*, 1 H, CH_2); 1.80–2.03 (*m*, CH_2); 2.18–2.34 (*m*, 1 H, CH_2); 2.46–2.61 (*m*, 1 H, CH_2); 3.13–3.27 (*m*, 1 H, CH_2); 4.77–4.90 (*m*, H–C(2)); 6.06 (br. *s*, 1 H, NH_2^+); 7.13–7.52 (*m*, 20 arom. H). ^{13}C-NMR (101 MHz, (D_6)DMSO): −1.9; 23.7; 26.8; 46.2; 65.9; 82.6; 127.57; 127.68; 127.74; 128.15; 128.16; 128.24; 128.5; 128.6; 129.7; 133.8; 133.9; 136.7; 136.8; 141.1; 142.1. HR-MS (MALDI): 450.2248 (100, M^+, $C_{30}H_{32}NOSi^+$; calc. 450.22477). Anal. calc. for $C_{30}H_{32}BF_4NOSi$ (537.47): C 67.04, H 6.00, N 2.61; found: C 66.90, H 6.12, N 2.64.

*(R)-2-(Bis[4-*tert*-butyl)phenyl]{[methyl(diphenyl)silyl]oxy}methyl)pyrrolidinium Tetrafluoroborate* (**1i**·HBF_4). Prepared according to *GP 3* from *(R)-2-(bis[(4-*tert*-butyl)phenyl]{[methyl(diphenyl)silyl]oxy}methyl)pyrrolidine* (**1i**; 559 mg, 0.99 mmol) and $HBF_4 \cdot Et_2O$ (137 µl, 0.99 mmol): $V_1 = 60$ ml; $V_2 = 20$ ml; $t_1 = 30$ min; only the desired product was formed (no R_3SiO deprotection occurred). Yield: 560 mg (86%). White solid. M.p. 181–183°. $[\alpha]_D^{r.t.} = +24.7$ ($c = 0.52$, CH_2Cl_2). IR: 2965*w*, 1591*w*, 1512*w*, 1477*w*, 1462*w*, 1429*w*, 1393*w*, 1363*w*, 1262*w*, 1101*m*, 1054*s*, 1012*s*, 954*w*, 916*w*, 860*m*, 834*m*, 792*m*, 777*m*, 736*m*, 722*m*, 697*m*, 669*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.36 (*s*, Me); 1.27 (*s*, ^{t}Bu); 1.24–1.39 (*m*, 1 H, CH_2); 1.31 (*s*, ^{t}Bu); 1.82–2.00 (*m*, CH_2); 2.16–2.28 (*m*, 1 H, CH_2); 2.39–2.51 (*m*, 1 H, CH_2); 3.22–3.35 (*m*, 1 H, CH_2); 4.83–4.92 (*m*, H–C(2)); 5.98 (br. *s*, 1 H, NH_2^+); 7.08 (*d*, $J = 8.6$, 2 arom. H); 7.16 (*d*, $J = 8.6$, 2 arom. H); 7.23–7.41 (*m*, 14 arom. H); 7.81 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, $CDCl_3$): −0.9; 24.1; 27.1; 31.3; 31.4; 34.66; 34.74; 47.9; 67.9; 82.5; 125.5; 125.7; 128.00; 128.03; 128.1; 128.5; 129.9; 130.0; 134.26; 134.30; 136.4; 137.0; 137.1; 152.1; 152.2. HR-MS (MALDI): 562.3500 (100, M^+, $C_{38}H_{48}NOSi^+$; calc. 562.34997). Anal. calc. for $C_{38}H_{48}BF_4NOSi$ (649.68): C 70.25, H 7.45, N 2.16; found: C 69.97, H 7.37, N 1.97.

(S)-2-[Bis(3,5-dimethylphenyl)(methoxy)methyl]pyrrolidinium Hexafluorophosphate (**1b**·HPF_6). To a soln. of *(S)-2-[bis(3,5-dimethylphenyl)(methoxy)methyl]pyrrolidinium hydrochloride* (**1b**·HCl; 474 mg, 1.32 mmol) in EtOH (5 ml) under Ar was added a soln. of $AgPF_6$ (333 mg, 1.32 mmol) in H_2O (2 ml). Upon addition of $AgPF_6$, a white precipitate formed immediately (AgCl). The mixture was stirred at r.t. for 10 min, then filtered through a short plug of *Celite* and washed with EtOH (30 ml). Volatile components were evaporated *in vacuo*, and the residue was dried under high vacuum. The solid residue was dissolved/suspended in anh. CH_2Cl_2, filtered through a short plug of *Celite*, and washed with anh. CH_2Cl_2. Volatile components were evaporated *in vacuo*, and the solid residue was dissolved in anh. CH_2Cl_2 and filtered through an HPLC filter to remove traces of insoluble by-products. Volatile components were evaporated *in vacuo*, and the residue was dried under high vacuum to give **1b**·HPF_6. Yield: 590 mg (95%). Light yellow-brownish solid. M.p. 206–208°. $[\alpha]_D^{r.t.} = -18.5$ ($c = 0.22$, EtOH). IR: 3246*w*, 2920*w*, 1599*m*, 1457*w*, 1382*m*, 1359*w*, 1333*w*, 1269*w*, 1186*w*, 1156*w*, 1096*w*, 1070*m*, 824*s*, 764*m*, 741*m*, 715*m*, 699*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.19–1.35 (*m*, 1 H, CH_2); 1.84–2.02 (*m*, CH_2); 2.19–2.42 (*m*, 1 H, CH_2); 2.31 (*s*, 2 Me); 2.32 (*s*, 2 Me); 2.67–2.82 (*m*, 1 H, CH_2); 3.06 (*s*, MeO); 3.30–3.44 (*m*, 1 H, CH_2); 4.77–4.91 (*m*, H–C(2)); 6.47 (br. *s*, 1 H, NH_2^+); 6.88 (*s*, 2 arom. H); 6.94 (*s*, 2 arom. H); 7.01 (*s*, 2 arom. H); 7.92 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, $CDCl_3$): 21.5; 21.6; 24.0; 27.4; 47.4; 51.7; 63.9;

83.6; 126.1; 126.8; 130.5; 130.7; 138.0; 138.26; 138.29; 138.7. HR-MS (MALDI): 324.2322 (100, M^+, $C_{22}H_{30}NO^+$; calc. 324.23219). Anal. calc. for $C_{22}H_{30}F_6NOP$ (469.44): C 56.29, H 6.44, N 2.98; found: C 56.48, H 6.38, N 2.97.

*(*S*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}pyrrolidinium Hydrochloride* (**1e**·HCl). To a soln. of *(*S*)-2-{bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}pyrrolidine* (**1e**; 1000 mg, 1.67 mmol) in anh. Et_2O (50 ml) under Ar at 0° was added a soln. of HCl (1.7 ml, 1M in anh. Et_2O, 1.7 mmol) diluted in anh. Et_2O (30 ml) during 20 min. Upon stirring at 0° for additional 15 min, volatile components were evaporated *in vacuo*, and the residue was dried under high vacuum to give **1e**·HCl in quant. yield. White solid. M.p. 85–93°. $[\alpha]_D^{r.t.} = +3.4$ ($c = 0.64$, CH_2Cl_2). IR: 1370*w*, 1276*s*, 1171*m*, 1127*s*, 1051*w*, 905*m*, 866*w*, 843*m*, 756*w*, 708*m*, 681*s*. ^{1}H-NMR (300 MHz, (D_6)DMSO: −0.03 (*s*, Me_3SiO); 1.68–1.89 (*m*, CH_2); 1.90–2.03 (*m*, 1 H, CH_2); 2.28–2.43 (*m*, 1 H, CH_2); 2.84–2.99 (*m*, 1 H, CH_2); 3.03–3.18 (*m*, 1 H, CH_2); 4.99–5.13 (*m*, H–C(2)); 7.94–8.29 (*m*, 7 H, 6 arom. H, N*H*H$^+$); 10.41 (br. *s*, 1 H, NH_2^+). HR-MS (MALDI): 598.1430 (100, M^+, $C_{24}H_{24}F_{12}NOSi^+$; calc. 598.14301). Anal. calc. for $C_{24}H_{24}ClF_{12}NOSi$ (633.97): C 45.47, H 3.82, N 2.21; found: C 45.48, H 3.90, N 2.15.

Preparation of Enamines **3**. *(*S*)-2-{Diphenyl[(trimethylsilyl)oxy]methyl}-1-[(*E*)-2-phenylethenyl]-pyrrolidine* (**3a**). 2-Phenylacetaldehyde (339 µl, 2.90 mmol) was added to a soln. of *(*S*)-2-{diphenyl-[(trimethylsilyl)oxy]methyl}pyrrolidine* (**1d**; 944 mg, 2.90 mmol) in anh. benzene (20 ml) under Ar in a two-necked flask fitted with a stirrer bar, stopper, and a *Dean–Stark* trap filled with freshly activated 4-Å mol. sieves. Soln. went cloudy, and, after stirring at r.t. for 30 min, a slight emulsion resulted. The mixture was heated to reflux (120° bath temp.), and an orange soln. developed. After 2 h of reflux, the soln. was cooled to r.t., more anh. benzene (10 ml) was added, and the mixture was returned to reflux. After a further 2 h of reflux, the heating was stopped, and the flask was cooled under Ar. The *Dean–Stark* condenser was removed, and the mixture was concentrated under vacuum, resulting in a light orange foam. Recrystallization under Ar from anh. Et_2O gave **3a** (440 mg, 35%). Light yellow cubes. M.p. 152–154° (dec.). $[\alpha]_D^{r.t.} = -283.8$ ($c = 0.76$, $CHCl_3$). IR (neat) 2962*w*, 1630*s*, 1595*m*, 1491*w*, 1447*m*, 1387*s*, 1307*w*, 1250*m*, 1176*w*, 1149*m*, 1089*s*, 1063*s*, 1031*s*, 923*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): −0.11 (*s*, Me_3Si); 0.48–0.64 (*m*, 1 H, CH_2); 1.42–1.54 (*m*, 1 H, CH_2); 1.93–2.16 (*m*, CH_2); 2.57 (*td*, $J = 2.8$; 9.2, 1 H, CH_2); 2.94 (*q*, $J = 9.2$, 1 H, CH_2); 4.62 (*dd*, $J = 2.2$; 9.0, H–C(2)); 5.02 (*d*, $J = 13.8$, H–C(1′)); 6.95 (*tt*, $J = 1.2$; 7.4, 1 arom. H); 7.06 (br. *d*, $J = 7.4$, 2 arom. H); 7.19 (*t*, $J = 7.4$, 2 arom. H); 7.25 (*d*, $J = 13.8$, H–C(2′)); 7.33–7.43 (*m*, 6 arom. H); 7.48–7.54 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 2.2; 22.7; 28.0; 48.6; 70.0; 83.9; 97.2; 122.6; 123.1; 127.3; 127.6 (2×); 128.4 (2×); 129.5; 129.7; 137.4; 140.4; 142.2; 142.7. EI-MS: 172 (100); 173 (15); 255 (2.5); 338 (0.5); 412 (1); 427 (0.4). HR-EI-MS: 427.2328 ($C_{28}H_{33}NOSi^+$; calc. 427.2326).

*(*S*)-1-[(1*E*)-3,3-Dimethylbut-1-en-1-yl)-2-({[methyl(diphenyl)silyl]oxy}(diphenyl)methyl)pyrrolidine* (**3b**). To a soln. of *(*S*)-2-({[methyl(diphenyl)silyl]oxy}(diphenyl)methyl)pyrrolidine* (**1h**; 192 mg, 0.43 mmol) in anh. C_6D_6 (8 ml) under Ar was added 3,3-dimethylbutanal (56 µl, 0.43 mmol), and the resulting mixture was heated under reflux under *Dean–Stark* condition using freshly activated 4-Å mol. sieves. After 1 h, *ca.* 87% conversion was achieved according to ^{1}H-NMR analysis of the mixture (0.7-ml aliquot). Additional 3,3-dimethylbutanal (56 µl, 0.43 mmol) was added to the mixture, and heating under reflux was continued for further 3 h to give 100% conversion. Volatile components were evaporated *in vacuo*, and the residue was dried under high vacuum to remove all traces of volatile compounds to give **3b** as an orange-yellow semisolid. The product was stored under Ar. The product **3b** is highly sensitive to hydrolysis and should, therefore, always (during the synthesis, reaction workup, storage *etc.*) be kept under dry Ar in carefully dried glassware. ^{1}H-NMR (300 MHz, C_6D_6): 0.22 (*s*, Me); 0.40–0.58 (*m*, 1 H, CH_2); 1.00 (*s*, ^{t}Bu); 1.15–1.27 (*m*, 1 H, CH_2); 1.80–1.93 (*m*, 1 H, CH_2); 2.09–2.20 (*m*, 1 H, CH_2); 2.72 (*dd*, $J = 5.0$; 9.0, CH_2); 4.26 (*d*, $J = 14.0$, H–C(1′)); 4.43 (*dd*, $J = 1.8$; 8.9, H–C(2)); 6.14 (*d*, $J = 14.0$, H–C(2′)); 6.91–7.00 (*m*, 3 arom. H); 7.01–7.07 (*m*, 3 arom. H); 7.12–7.22 (*m*, 6 arom. H); 7.41–7.46 (*m*, 2 arom. H); 7.47–7.57 (*m*, 4 arom. H); 7.63–7.68 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, C_6D_6): −0.8; 23.3; 28.8; 29.8; 32.0; 49.9; 70.5; 85.1; 110.3; 117.3; 127.3; 127.4; 127.7; 127.8; 128.0; 129.57; 129.62; 129.9; 130.4; 133.8; 134.56; 134.63; 138.6; 139.1; 142.1; 143.7.

Preparation of the Iminium Salts **4**. *Preparation of* **4b**·BF_4, (E/Z)-**4b**·PF_6, **4d**·BF_4, (E/Z)-**4h**·BF_4, *and* **4i**·BF_4. *General Procedure 4* (*GP 4*)[30]). To a soln./suspension of a PF_6^- or BF_4^- salt of a secondary amine in anh. EtOH (V_1) under Ar was added cinnamaldehyde (1.05 equiv.), followed by

addition of Et_3N (V_2). The mixture was stirred vigorously at r.t. until a filterable precipitate was formed (t_1). The precipitate was collected on a dry ceramic frit under Ar and washed with anh. Et_2O (20 ml) to give iminium salts **4b** · BF_4, (*E*/*Z*)-**4b** · PF_6, **4d** · BF_4, (*E*/*Z*)-**4h** · BF_4, and **4i** · BF_4. The isolated products were dried under high vacuum and stored under Ar.

*(*S*)-2-[Bis(3,5-dimethylphenyl)(methoxy)methyl]-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]pyrrolidinium Tetrafluoroborate* (**4b** · BF_4). Prepared according to *GP 4* from *(*S*)-2-[bis(3,5-dimethylphenyl)(methoxy)methyl]pyrrolidinium tetrafluoroborate* (**1b** · BF_4; 330 mg, 0.80 mmol) and cinnamaldehyde (108 µl, 0.84 mmol): $V_1 = 2$ ml; $V_2 = 5$ µl; $t_1 = 3$ h. Yield: 322 mg (76%). Light yellow solid. M.p. 232–235°. $[\alpha]_D^{r.t.} = -194.6$ ($c = 0.59$, CH_2Cl_2). IR: 2960*w*, 1623*m*, 1608*m*, 1591*m*, 1450*w*, 1424*w*, 1330*w*, 1283*w*, 1189*w*, 1178*m*, 1075*s*, 1051*s*, 997*m*, 957*w*, 862*w*, 848*m*, 761*s*, 693*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.12–1.25 (*m*, 1 H, CH_2); 1.67–1.81 (*m*, 1 H, CH_2); 1.99–2.10 (*m*, 1 H, CH_2); 2.34–2.49 (*m*, 1 H, CH_2); 2.24 (*s*, 2 Me); 2.32 (*s*, 2 Me); 2.53–2.63 (*m*, 1 H, CH_2); 2.99 (*s*, MeO); 3.86–3.96 (*m*, 1 H, CH_2); 5.27 (*dd*, $J = 3.1$; 8.9, H–C(2)); 6.81 (*s*, 2 arom. H); 6.94 (*s*, 2 arom. H); 7.00 (*d*, $J = 14.8$, 2 arom. H); 7.04 (*dd*, $J =$ 10.5; 15.3, H–C(2′)); 7.42–7.54 (*m*, 3 arom. H); 7.81 (*d*, $J = 7.1$, 2 arom. H); 8.00 (*d*, $J = 15.2$, H–C(3′)); 8.58 (*d*, $J = 10.5$, H–C(1′)). ^{13}C-NMR (101 MHz, $CDCl_3$): 21.5; 21.6; 22.4; 26.8; 52.0; 52.8; 72.9; 86.0; 117.3; 126.8; 127.6; 129.5; 130.2; 130.4; 130.7; 133.6; 133.7; 136.9; 137.2; 137.8; 138.0; 161.9; 168.5. HR-MS (MALDI): 438.2791 (100, M^+, $C_{31}H_{36}NO^+$; calc. 438.27914). Anal. calc. for $C_{31}H_{36}BF_4NO$ (525.43): C 70.86, H 6.91, N 2.67; found: C 70.77, H 6.99, N 2.64.

*(*S*)-2-[Bis(3,5-dimethylphenyl)(methoxy)methyl]-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Hexafluorophosphate* (**4b** · PF_6; (*E*)/(*Z*) 1:0.06). Prepared *GP 4* from *(*S*)-2-[bis(3,5-dimethylphenyl)(methoxy)methyl]pyrrolidinium* hexafluorophosphate (**1b** · PF_6) (500 mg, 1.06 mmol) and cinnamaldehyde (144 µl, 1.12 mmol): $V_1 = 1.5$ ml; $V_2 = 10$ µl; $t_1 = 2$ h. Yield: 580 mg (93%; (*E*)/(*Z*) 1:0.06). Yellowish solid. M.p. 242–245°. $[\alpha]_D^{r.t.} = -178.8$ ($c = 0.23$, CH_2Cl_2). IR: 2956*w*, 1628*m*, 1608*m*, 1592*m*, 1454*w*, 1319*w*, 1281*w*, 1188*w*, 1177*m*, 1076*m*, 998*w*, 954*w*, 877*w*, 833*s*, 756*m*, 741*w*, 689*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): (*E*)-isomer: 1.16–1.29 (*m*, 1 H, CH_2); 1.70–1.83 (*m*, 1 H, CH_2); 2.01–2.11 (*m*, 1 H, CH_2); 2.25 (*s*, 2 Me); 2.32 (*s*, 2 Me); 2.38–2.50 (*m*, 1 H, CH_2); 2.51–2.62 (*m*, 1 H, CH_2); 2.97 (*s*, MeO); 3.77–3.89 (*m*, 1 H, CH_2); 5.24 (*dd*, $J = 3.7$; 9.2, H–C(2)); 6.82 (*s*, 2 arom. H); 6.93 (*dd*, $J = 10.7$; 15.2, H–C(2′)); 6.94 (*s*, 2 arom. H); 7.02 (*d*, $J = 9.9$, 2 arom. H); 7.42–7.48 (*m*, 2 arom. H); 7.49–7.55 (*m*, 1 arom. H); 7.73–7.79 (*m*, 2 arom. H); 7.91 (*d*, $J = 15.2$, H–C(3′)); 8.51 (*d*, $J = 10.6$, H–C(1′)); (*Z*)-isomer: 2.88 (*s*, MeO); 3.61–3.68 (*m*, 1 H, CH_2); 5.52 (*dd*, $J = 4.4$; 9.1, H–C(2)). ^{13}C-NMR (101 MHz, $CDCl_3$): (*E*)-isomer: 21.57; 21.63; 22.5; 26.8; 52.1; 52.8; 73.5; 86.2; 117.0; 126.9; 127.7; 129.6; 130.4; 130.6; 130.7; 133.6; 133.9; 136.7; 136.8; 138.0; 138.1; 162.1; 168.3. HR-MS (MALDI): 438.2791 (100, M^+, $C_{31}H_{36}NO^+$; calc. 438.27914). Anal. calc. for $C_{31}H_{36}F_6NOP$ (583.59): C 63.80, H 6.22, N 2.40; found: C 63.71, H 6.23, N 2.39.

*(*S*)-2-{Diphenyl[(trimethylsilyl)oxy]methyl}-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Tetrafluoroborate* (**4d** · BF_4). Prepared according to *GP 4* from *(*S*)-2-{diphenyl[(trimethylsilyl)oxy]methyl}pyrrolidinium tetrafluoroborate* (**1d** · BF_4) (327 mg, 0.79 mmol) and cinnamaldehyde (107 µl, 0.83 mmol): $V_1 = 1$ ml; $V_2 = 5$ µl; $t_1 = 24$ h. Yield: 105 mg (25%). Light yellow solid. M.p. 155–158°. $[\alpha]_D^{r.t.} = -110.9$ ($c = 0.13$, CH_2Cl_2). IR: 2953*w*, 1619*m*, 1608*m*, 1592*m*, 1446*w*, 1327*w*, 1288*w*, 1253*w*, 1182*m*, 1053*s*, 1001*m*, 928*w*, 915*w*, 870*m*, 839*s*, 764*s*, 704*s*, 690*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): −0.16 (*s*, Me_3Si); 1.15–1.29 (*m*, 1 H, CH_2); 1.67–1.82 (*m*, 1 H, CH_2); 1.99–2.09 (*m*, 1 H, CH_2); 2.44–2.56 (*m*, 1 H, CH_2); 2.62–2.73 (*m*, 1 H, CH_2); 3.85–3.95 (*m*, 1 H, CH_2); 5.46 (*d*, $J = 7.4$, H–C(2)); 7.00 (*dd*, $J = 10.7$; 15.2, H–C(2′)); 7.25–7.54 (*m*, 13 arom. H); 7.67–7.75 (*m*, 3 H, 2 arom. H, H–C(3′)); 8.53 (*d*, $J = 10.6$, H–C(1′)). ^{13}C-NMR (101 MHz, $CDCl_3$): 1.6; 22.6; 26.2; 52.4; 76.3; 83.5; 117.2; 128.3; 128.75; 128.86; 128.88; 129.1; 129.5; 129.6; 130.7; 133.6; 133.8; 140.1; 140.4; 161.5; 168.4. HR-MS (MALDI): 440.2404 (100, M^+, $C_{29}H_{34}NOSi^+$; calc. 440.24042). Anal. calc. for $C_{29}H_{34}BF_4NOSi$ (527.48): C 66.03, H 6.50, N 2.66; found: C 65.90, H 6.53, N 2.49.

*(*S*)-2-({[Methyl(diphenyl)silyl]oxy}(diphenyl)methyl)-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Tetrafluoroborate* (**4h** · BF_4; (*E*)/(*Z*) 1:0.03). Prepared according to *GP 4* from *(*S*)-2-({[methyl(diphenyl)silyl]oxy}(diphenyl)methyl)pyrrolidinium tetrafluoroborate* (**1h** · BF_4) (417 mg, 0.78 mmol) and cinnamaldehyde (105 µl, 0.82 mmol): $V_1 = 3$ ml; $V_2 = 10$ µl; $t_1 = 20$ h. Yield: 250 mg (49%; (*E*)/(*Z*) 1:0.03). Light yellow solid. M.p. 196–198°. $[\alpha]_D^{r.t.} = -160.2$ ($c = 0.79$, CH_2Cl_2). IR: 3071*w*, 1615*m*, 1589*m*, 1450*w*, 1430*w*, 1326*w*, 1285*w*, 1259*w*, 1181*m*, 1057*s*, 996*s*, 958*w*, 927*w*, 852*m*, 792*m*, 755*m*,

724*m*, 700*s*, 687*s*. ^{1}H-NMR (400 MHz, (D_6)DMSO): (*E*)-isomer: 0.24 (*s*, Me); 0.90–1.03 (*m*, 1 H, CH_2); 1.71–1.84 (*m*, 1 H, CH_2); 2.01–2.12 (*m*, 1 H, CH_2); 2.49–2.60 (*m*, 1 H, CH_2); 2.74–2.86 (*m*, 1 H, CH_2); 3.95–4.07 (*m*, 1 H, CH_2); 5.61 (*d*, *J* = 8.2, H–C(2)); 6.85 (*d*, *J* = 15.2, H–C(3′)); 7.16–7.48 (*m*, 19 H, 18 arom. H, H–C(2′)); 7.54–7.68 (*m*, 5 arom. H); 7.83 (*d*, *J* = 7.1, 2 arom. H); 8.40 (*d*, *J* = 10.5, H–C(1′)); (*Z*)-isomer: 3.89 (*t*, *J* = 9.8, 1 H, CH_2); 6.00 (*d*, *J* = 8.1, H–C(2)); 8.67 (*d*, *J* = 10.6, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)DMSO): (*E*)-isomer: −3.0; 21.7; 26.2; 52.6; 74.9; 83.4; 118.2; 127.76; 127.82; 128.1; 128.2; 128.4; 128.6; 128.9; 129.4; 129.8; 129.9; 130.5; 133.3; 133.7; 134.0; 136.3; 136.6; 139.4; 140.0; 160.1; 168.3. HR-MS (MALDI): 564.2717 (100, M^+, $C_{39}H_{38}NOSi^+$; calc. 564.27172). Anal. calc. for $C_{39}H_{38}BF_4NOSi$ (651.62): C 71.89, H 5.88, N 2.15; found: C 71.87, H 6.01, N 2.16.

*(*R*)-2-(Bis[4-(*tert*-butyl)phenyl][{[methyl(diphenyl)silyl]oxy}methyl)-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Tetrafluoroborate* (**4i** · BF_4). Prepared according to *GP 4* from *(*R*)-2-(bis[4-(*tert*-butyl)phenyl][{[methyl(diphenyl)silyl]oxy}methyl)pyrrolidinium tetrafluoroborate* (**1i** · BF_4) (330 mg, 0.51 mmol) and cinnamaldehyde (69 µl, 0.53 mmol): V_1 = 2 ml; V_2 = 5 µl; t_1 = 2 h. Yield: 210 mg (54%). Light yellow solid. M.p. 187–189°. $[\alpha]_D^{r.t.} = +191.4$ (*c* = 0.30, CH_2Cl_2). IR: 2960*w*, 1627*m*, 1607*m*, 1592*m*, 1577*w*, 1512*w*, 1456*w*, 1429*w*, 1406*w*, 1363*w*, 1273*w*, 1250*w*, 1183*m*, 1112*m*, 1054*s*, 999*m*, 944*w*, 862*m*, 832*w*, 790*m*, 766*m*, 739*m*, 748*m*, 720*w*, 705*m*, 700*m*, 690*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.31 (*s*, Me); 0.80–0.94 (*m*, 1 H, CH_2); 1.24 (*s*, ^{t}Bu); 1.34 (*s*, ^{t}Bu); 1.59–1.72 (*m*, 1 H, CH_2); 1.92–2.03 (*m*, 1 H, CH_2); 2.49–2.62 (*m*, 1 H, CH_2); 2.68–2.79 (*m*, 1 H, CH_2); 3.78–3.91 (*m*, 1 H, CH_2); 5.53 (*d*, *J* = 7.6, H–C(2)); 6.49 (*d*, *J* = 15.1, H–C(3′)); 6.88 (*dd*, *J* = 10.6; 15.0, H–C(2′)); 7.07 (*d*, *J* = 8.8, 2 arom. H); 7.10 (*d*, *J* = 8.8, 2 arom. H); 7.20–7.26 (*m*, 4 arom. H); 7.28–7.56 (*m*, 15 arom. H); 8.33 (*d*, *J* = 10.3, H–C(1′)). ^{13}C-NMR (101 MHz, $CDCl_3$): −2.1; 22.2; 26.7; 31.3; 31.4; 34.6; 34.7; 52.8; 75.8; 83.4; 117.0; 125.06; 125.09; 127.9; 128.1; 128.4; 129.4; 129.7; 129.82; 129.88; 130.6; 133.5; 134.4; 136.1; 136.2; 137.3; 137.5; 152.0; 152.1; 161.1; 168.6. HR-MS (MALDI): 676.3969 (100, M^+, $C_{47}H_{54}NOSi^+$; calc. 676.39692). Anal. calc. for $C_{47}H_{54}BF_4NOSi$ (763.83): C 73.91, H 7.13, N 1.83; found: C 73.76, H 7.19, N 1.87.

*Preparation of (*E/Z*)-***4c*** · Al[OC(CF$_3$)$_3$]$_4$, (*E/Z*)-***4e*** · Al[OC(CF$_3$)$_3$]$_4$, (*E/Z*)-***4e*** · PF$_6$, and (*E/Z*)-***4e*** · SbF$_6$. General Procedure 5 (GP 5)*[30]. To a soln./suspension of a secondary amine hydrochloride (1 equiv.) in anh. EtOH (V_1) under Ar was added cinnamaldehyde (1.05 equiv.), followed by the addition of Et_3N (V_2). The mixture was stirred vigorously at r.t. for 3 h, followed by the addition of AgX salt (1 equiv., either as a pure solid or as a soln. in anh. EtOH (2–3 ml)). After vigorous stirring for 15 h at r.t., the mixture was filtered through an HPLC filter to remove AgCl precipitate, volatile components were evaporated *in vacuo*, and the residue was dried under high vacuum. In the case of (*E/Z*)-**4c** · Al[$OC(CF_3)_3$]$_4$ and (*E/Z*)-**4e** · Al[$OC(CF_3)_3$]$_4$, the residue was dissolved in anh. Et_2O (2–4 ml) and the product precipitated by the addition of heptane (20–40 ml). The precipitate was vigorously stirred at r.t., until a fine precipitate was formed. If the precipitate did not deposit properly, the soln. was decanted, the precipitate was redissolved in anh. Et_2O (2–4 ml) and re-precipitated with heptane (20–40 ml). After a fine precipitate was formed (vigorous stirring), it was collected by filtration on a dry ceramic frit under Ar, washed with hexane (100 ml), dried under high vacuum, and stored under Ar. In the case of (*E/Z*)-**4e** · PF_6 and (*E/Z*)-**4e** · SbF_6, the residue was also dissolved in anh. Et_2O (2–4 ml), and the product was precipitated by the addition of heptane (20–40 ml). The soln. was decanted, the residue redissolved in anh. Et_2O (15 ml), filtered through an HPLC filter, and injected into vigorously stirred hexane (150 ml). The so formed precipitate was collected by filtration on a dry ceramic frit under Ar, washed with hexane (100 ml), dried under high vacuum, and stored under Ar. If in any of the isolated compounds a small amount of Ag appeared (gray to black color), the solid was redissolved in anh. Et_2O, filtered through an HPLC filter, and reprecipitated according to the procedures described above.

*(*S*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl](methoxy)methyl}-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)-pyrrolidinium Tetrakis{[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethyl]oxy}aluminate* (**4c** · Al[$OC(CF_3)_3$]$_4$; (*E/Z*) 1:0.06). Prepared according to *GP 5* from *(*S*)-2-{bis[3,5-bis(trifluoromethyl)phenyl](methoxy)-methyl}pyrrolidinium chloride* (**1c** · HCl; 324 mg, 0.56 mmol), silver tetrakis{[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethyl]oxy}aluminate (605 mg, 0.65 mmol, dissolved in 3 ml of anh. EtOH), and cinnamaldehyde (76 µl, 0.59 mmol): V_1 = 3 ml; V_2 = 10 µl. Yield: 627 mg (68%; (*E*)/(*Z*) 1:0.06). Yellow solid. M.p. 215–220°. $[\alpha]_D^{r.t.} = -59.7$ (*c* = 0.63, CH_2Cl_2). IR: 1605*w*, 1616*w*, 1590*m*, 1372*w*, 1353*w*, 1277*s*, 1240*m*, 1216*s*, 1181*m*, 1143*s*, 1116*m*, 1079*w*, 971*s*, 917*w*, 899*w*, 845*w*, 834*w*, 757*w*, 727*s*, 710*w*, 683*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): (*E*)-isomer: 1.11–1.25 (*m*, 1 H, CH_2); 1.83–1.96 (*m*, 1 H, CH_2); 2.19–2.31 (*m*,

1 H, CH_2); 2.43–2.66 (*m*, CH_2); 3.07 (*s*, MeO); 4.07–4.18 (*m*, 1 H, CH_2); 5.99 (*dd*, *J* = 3.6; 9.0, H–C(2)); 7.46 (*dd*, *J* = 10.5; 15.1, H–C(2′)); 7.57–7.70 (*m*, 3 arom. H); 7.95–8.01 (*m*, 4 arom. H); 8.07 (*s*, 2 arom. H); 8.21 (*d*, *J* = 9.6, 2 arom. H); 8.51 (*d*, *J* = 15.0, H–C(3′)); 8.91 (*d*, *J* = 10.4, H–C(1′)); (*Z*)-isomer: 3.96–4.06 (*m*, 1 H, CH_2); 6.23 (*d*, *J* = 6.4, H–C(2)); 9.02 (*d*, *J* = 10.4, H–C(1′)). HR-MS (MALDI): 654.1661 (100, M^+, $C_{31}H_{24}F_{12}NO^+$; calc. 654.16608). Anal. calc. for $C_{47}H_{24}AlF_{48}NO_5$ (1621.60): C 34.81, H 1.49, N 0.86; found: C 34.80, H 1.73, N 0.99.

*(*S*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Tetrakis{[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethyl]oxy}aluminate* (**4e** · Al[OC(CF_3)$_3$]$_4$; (*E*)/(*Z*) 1:0.09). Prepared according to *GP 5* from *(*S*)-2-{bis[3,5-bis(trifluoromethyl)-phenyl][(trimethylsilyl)oxy]methyl}pyrrolidinium chloride* (**1e** · HCl; 218 mg, 0.34 mmol), silver tetrakis{[2,2,2-trifluoro-1,1-bis(trifluoromethyl)ethyl]oxy}aluminate (370 mg, 0.34 mmol, dissolved in 2 ml of anh. EtOH), and cinnamaldehyde (46 µl, 0.36 mmol): V_1 = 3 ml; V_2 = 10 µl. Yield: 340 mg (58%, (*E*)/(*Z*) 1:0.09). Yellow solid. M.p. 189–192°. $[\alpha]_D^{r.t.} = -36.7$ (*c* = 0.57, CH_2Cl_2). IR: 1623*w*, 1604*w*, 1591*m*, 1577*w*, 1375*w*, 1352*w*, 1274*s*, 1239*s*, 1219*s*, 1186*s*, 1142*s*, 1119*m*, 1076*w*, 970*s*, 913*w*, 901*w*, 846*m*, 752*w*, 726*s*, 709*m*, 682*m*. ^{1}H-NMR (400 MHz, (D_6)acetone): (*E*)-isomer: 0.01 (*s*, Me_3SiO); 1.48–1.61 (*m*, 1 H, CH_2); 2.11–2.24 (*m*, 1 H, CH_2); 2.57–2.67 (*m*, 1 H, CH_2); 2.84–2.95 (*m*, 1 H, CH_2); 3.00–3.11 (*m*, 1 H, CH_2); 4.34–4.45 (*m*, 1 H, CH_2); 6.11 (*d*, *J* = 6.6, H–C(2)); 7.57–7.74 (*m*, 4 H, 3 arom. H, H–C(2′)); 7.99 (*d*, *J* = 7.3, 2 arom. H); 8.21–8.31 (*m*, 6 arom. H); 8.34 (*d*, *J* = 15.2, H–C(3′)); 9.14 (*d*, *J* = 10.7, H–C(1′)); (*Z*)-isomer: −0.06 (*s*, Me_3Si); 4.23–4.31 (*m*, 1 H, CH_2); 6.60 (*dd*, *J* = 2.3; 8.7, H–C(2)); 9.08 (*d*, *J* = 10.7, H–C(1′)). HR-MS (MALDI): 712.1900 (100, M^+, $C_{33}H_{30}F_{12}NOSi^+$; calc. 712.18996). Anal. calc. for $C_{49}H_{30}AlF_{48}NO_5Si$ (1679.76): C 35.04, H 1.80, N 0.83; found: C 34.81, H 2.00, N 1.06.

*(*S*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}-1-[(*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Hexafluorophosphate* (**4e** · PF_6; (*E*)/(*Z*) 1:0.07). Prepared according to *GP 5* from *(*S*)-2-{bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}pyrrolidinium chloride* (**1e** · HCl; 621 mg, 0.98 mmol), $AgPF_6$ (247 mg, 0.98 mmol), and cinnamaldehyde (132 µl, 1.03 mmol): V_1 = 15 ml; V_2 = 15 µl. Yield: 380 mg (45%, (*E*)/(*Z*) 1:0.07). Pinkish solid. M.p. 88–95°. $[\alpha]_D^{r.t.} = -61.7$ (*c* = 0.4, CH_2Cl_2). IR: 1622*w*, 1608*w*, 1592*m*, 1455*w*, 1373*w*, 1278*s*, 1178*m*, 1132*s*, 1010*w*, 1000*w*, 907*w*, 831*s*, 755*m*, 709*m*, 681*s*. ^{1}H-NMR (400 MHz, (D_6)acetone): (*E*)-isomer: 0.00 (*s*, Me_3SiO); 1.44–1.56 (*m*, 1 H, CH_2); 2.09–2.22 (*m*, 1 H, CH_2); 2.52–2.61 (*m*, 1 H, CH_2); 2.80–2.92 (*m*, 1 H, CH_2); 2.96–3.05 (*m*, 1 H, CH_2); 4.29–4.38 (*m*, 1 H, CH_2); 6.02 (*dd*, *J* = 3.1; 9.4, H–C(2)); 7.55–7.64 (*m*, 3 H, 2 arom. H, H–C(2′)); 7.67–7.73 (*m*, 1 arom. H); 7.97–8.02 (*m*, 2 arom. H); 8.21–8.35 (*m*, 7 H, 6 arom. H, H–C(3′)); 9.05 (*d*, *J* = 10.7, H–C(1′)); (*Z*)-isomer: −0.07 (*s*, Me_3Si); 1.79–1.92 (*m*, 1 H, CH_2); 4.18–4.26 (*m*, 1 H, CH_2); 6.49 (*dd*, *J* = 2.8, 9.0, H–C(2)); 8.96 (*d*, *J* = 10.6, H–C(1′)). HR-MS (MALDI): 712.1909 (100, M^+, $C_{33}H_{30}F_{12}NOSi^+$; calc. 712.1900). Anal. calc. for $C_{33}H_{30}F_{18}NOPSi$ (857.63): C 46.22, H 3.53, N 1.63; found: C 45.96, H 3.56, N 1.81.

*(*S*)-2-{Bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}-1-[(2*E*)-3-phenylprop-2-en-1-ylidene)pyrrolidinium Hexafluoroantimonate* (**4e** · SbF_6; (*E*)/(*Z*) 1:0.09). Prepared according to *GP 5* from *(*S*)-2-{bis[3,5-bis(trifluoromethyl)phenyl][(trimethylsilyl)oxy]methyl}pyrrolidinium hydrochloride* (**1e** · HCl) (308 mg, 0.49 mmol), $AgSbF_6$ (170 mg, 0.49 mmol), and cinnamaldehyde (66 µl, 0.51 mmol): V_1 = 3 ml; V_2 = 10 µl. Yield: 250 mg (54%; (*E*)/(*Z*) 1:0.09). Yellowish solid. M.p. 95–103°. $[\alpha]_D^{r.t.} = -24.3$ (*c* = 0.21, CH_2Cl_2). IR: 1621*w*, 1608*w*, 1592*m*, 1455*w*, 1373*w*, 1277*s*, 1178*s*, 1133*s*, 999*w*, 906*w*, 863*w*, 844*m*, 756*w*, 710*w*, 682*m*, 656*s*. ^{1}H-NMR (400 MHz, (D_6)acetone): (*E*)-isomer: 0.00 (*s*, Me_3SiO); 1.46–1.58 (*m*, 1 H, CH_2); 2.12–2.22 (*m*, 1 H, CH_2); 2.53–2.64 (*m*, 1 H, CH_2); 2.81–2.93 (*m*, 1 H, CH_2); 2.97–3.09 (*m*, 1 H, CH_2); 4.30–4.40 (*m*, 1 H, CH_2); 6.04 (*dd*, *J* = 2.6; 9.1, H–C(2)); 7.54–7.73 (*m*, 4 H, 3 arom. H, H–C(2′)); 7.95–8.02 (*m*, 2 arom. H); 8.23–8.36 (*m*, 7 H, 6 arom. H, H–C(3′)); 9.07 (*d*, *J* = 10.7, H–C(1′)); (*Z*)-isomer: −0.06 (*s*, Me_3Si); 4.19–4.27 (*m*, 1 H, CH_2); 6.53 (*dd*, *J* = 2.8; 9.0, H–C(2)); 9.00 (*d*, *J* = 10.6, H–C(1′)). HR-MS (MALDI): 712.1900 (100, M^+, $C_{33}H_{30}F_{12}NOSi^+$; calc. 712.18996). Anal. calc. for $C_{33}H_{30}F_{18}NOSbSi$ (948.41): C 41.79, H 3.19, N 1.48; found: C 41.95, H 3.34, N 1.65.

Determination of the X-Ray Structures (*Table 7*). Suitable single crystals were measured on a *Bruker Nonius Kappa CCD* diffractometer with MoK_α radiation (λ 0.71073 Å, graphite monochromator). Structures were solved by direct methods (SIR97) [35] and refined by full-matrix least-squares on F^2 (SHELXL97) [36]. If possible, H-atoms were located from a difference electron density map or constrained at ideal positions and included in the refinement. The absolute configurations were

Table 7. *Experimental Details for the X-Ray Structures of* **1b** *and* **4b**–**4e**

	1b	**4b** (PF_6)	**4b** (BF_4)	**4c**	**4d**	**4e**
CCDC No.[a])	732048	732049	732050	732051	732052	732053
Chemical formula	$C_{22}H_{30}NO^+\ BF_4^-$	$C_{31}H_{36}NO^+\ PF_6^-$	$C_{31}H_{36}NO^+\ BF_4^-$	$C_{31}H_{24}F_{12}NO^+\ C_{16}AlF_{36}O_4^-$	$C_{29}H_{34}NOSi^+\ BF_4^-$	$C_{33}H_{30}F_{12}NOSi^+\ C_{16}AlF_{36}O_4^-$
M_r	411.29	583.60	525.44	1621.60	527.49	1679.75
Crystal size [mm]	$0.37 \times 0.17 \times 0.06$	$0.3 \times 0.2 \times 0.08$	$0.28 \times 0.14 \times 0.12$	$0.27 \times 0.21 \times 0.21$	$0.22 \times 0.06 \times 0.004$	$0.34 \times 0.2 \times 0.11$
Space group	$P2_12_12_1$ orthorhombic	$P1$ triclinic	$P1$ triclinic	$P2_12_12_1$ orthorhombic	$P2_1$ monoclinic	$P2_12_12_1$ orthorhombic
a [Å]	8.1443(2)	7.9691(4)	7.843(4)	11.4517(2)	13.3972(12)	17.0600(3)
b [Å]	15.7263(5)	8.6946(4)	8.578(3)	14.8514(3)	14.5900(12)	19.0620(4)
c [Å]	16.9678(6)	11.5126(6)	11.138(5)	35.3534(6)	15.141(2)	19.7120(3)
α [°]		106.224(2)	104.52(2)			
β [°]		102.553(2)	100.88(2)		102.011(4)	
γ [°]		94.470(2)	93.99(2)			
Z	4	1	1	4	4	4
ρ_{calc} [g cm^{-3}]	1.257	1.311	1.234	1.791	1.210	1.741
μ [mm^{-1}]	0.099	0.156	0.091	0.229	0.128	0.236
Temp. [K]	223	223	223	223	173	223
θ_{max} [°]	27.5	27.6	27.5	25.0	21.7	27.5
$I > 2\sigma(I)$ Reflexions:						
measured	9660	12765	4342	17934	8342	54897
independent	4992	6043	3844	9317	6053	14440
observed	3860	5184	2487	6839	3696	10486
R_{int}	0.058	0.046	0.07	0.05	0.18	0.05
Ref. parameters	284	361	343	663	667	914
H-Atom treatment	mixed	calc.	calc.	calc.	calc.	calc.
R(gt)	0.064	0.069	0.094	0.183	0.088	0.086
R(all)	0.088	0.081	0.156	0.212	0.165	0.114
Δ/σ_{max}	0.029	0.029	0.00	0.06	0.02	0.03
$\Delta\rho_{max}$ (e Å^3)	0.38	0.55	0.28	0.97	0.39	0.557
Flack parameter, (*) unreliable	−0.1(12)	−0.05(13)	1(2)*	0.5(7)*	0.1(4)*	0.0(2)*

[a]) Copies of the data can be obtained, free of charge, on application to the *Cambridge Crystallographic Data Centre* (*CCDC*), 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

determined by refining the *Flack* [37] parameter. The five-memered ring in **1b** shows an envelope form with the out-of-plane C(5) disordered on opposite sides of the ring plane (0.7:0.3). In **4b**·BF_4, the F-atoms of the BF_4 are disordered. In **4c**, all the CF_3 groups are heavily disordered. In the anion, two CF_3 groups could not be localized by electron-density map and are included as fixed groups with ideal geometry. The other CF_3 fragments in the anion have constrained distances and angles, and were all refined isotropically. There is also major disorder in the five-membered ring and the phenyl ring of **4c**; **4d** shows two symmetry-independent molecules with both BF_4 groups disordered; **4e** shows all CF_3 groups disordered, some of them refined at two positions.

Theoretical Calculations of Structures. Structures of iminium ion **4e** and dienamine **5** were fully optimized at the B3LYP/6-31G(d) level [27]. Each structure was verified as an energy minimum by a frequency calculation, *i.e.*, having no imaginary frequency. Energy evaluations of the B3LYP/6-31G(d)-optimized structures were carried out at the B3LYP and MP2 [28] levels using a larger basis set, 6-311G(d,p) [29]. The B3LYP calculations do not reproduce dispersion effects [26], but the MP2 calculations do consider them, at least partly. For aromatic systems, the dispersion energies tend to be overestimated at the MP2 basis set limit. However, MP2 calculations in conjunction with a medium-size basis set such as 6-311G(d,p) provide a dispersion interaction energy close to a CCSD(T) basis set limit value in most cases [38]. We, thus, also considering practical aspects, chose the MP2/6-311G(d,p) level for single-point energy evaluations in the present study. We thank Prof. *S. Grimme* (Universität Münster) and Dr. *S. Tsuzuki* (AIST) for helpful discussion on evaluation of dispersion energies.

In addition, we estimated solvation effect in toluene solution by using the conductor-like polarizable continuum model (CPCM) [30]. Single-point CPCM calculations were performed at the gas-phase B3LYP/6-31G(d)-optimized geometries. The Gaussian 03 program [31] was used for all theoretical calculations.

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