Preparation and Structures of 2-Substituted 5-Benzyl-3-methylimidazolidin-4-one-Derived Iminium Salts, Reactive Intermediates in Organocatalytic Transformations Involving α,β-Unsaturated Aldehydes

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Preparations of the title compounds, **5**–**7** (*Scheme 1* and *Table 1*), of their ammonium salts, **9**–**11** (*Scheme 2* and *Table 2*), and of the corresponding cinnamaldehyde-derived iminium salts **12**–**14** (*Scheme 3* and *Table 3*) are reported. The X-ray crystal structures of 15 cinnamyliminium PF_6 salts have been determined (*Table 4*). Selected ^{1}H-NMR data (*Table 5*) of the ammonium and iminium salts are discussed, and structures in solution are compared with those in the solid state.

1. Introduction. – We were the first[1]) to isolate and structurally characterize cinnamaldehyde-derived iminium salts prepared from 2-(*tert*-butyl)-3-methylimidazolidin-4-one (**2**), (5*S*)-5-benzyl-2,2,3-trimethylimidazolidin-4-one (**7e**), and (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-methylimidazolidin-4-one (**7c**)[2]). Such iminium ions are reactive intermediates in organocatalysis [4][5]. Details of our single-crystal X-ray structures revealed a striking resemblance with those of the corresponding DFT-calculated crotonaldehyde-derived reactive intermediates [6]. By NMR analyses, *Tomkinson* and co-workers and our group have also identified the preferred conformation in solution of the benzylic C,C-bond in these iminium ions [1][5]. The ensuing enthusiasm quickly resulted in the preparation of a statistically significantly large number of cinnamaldehyde-derived imidazolidin-1-ium salts. The obtained data raised questions, regarding the stereochemical models for additions to α,β-unsaturated aldehydes, on the role of the (*E*)- and (*Z*)-iminium intermediates [7][8], and the conformation of the benzyl (Bn) substituent [9]. In parallel, synthesis and structural

[1]) Independently, *Tomkinson* and co-workers have published preparation of the PF_6-iminium salt from **7e** and cinnamaldehyde [1].

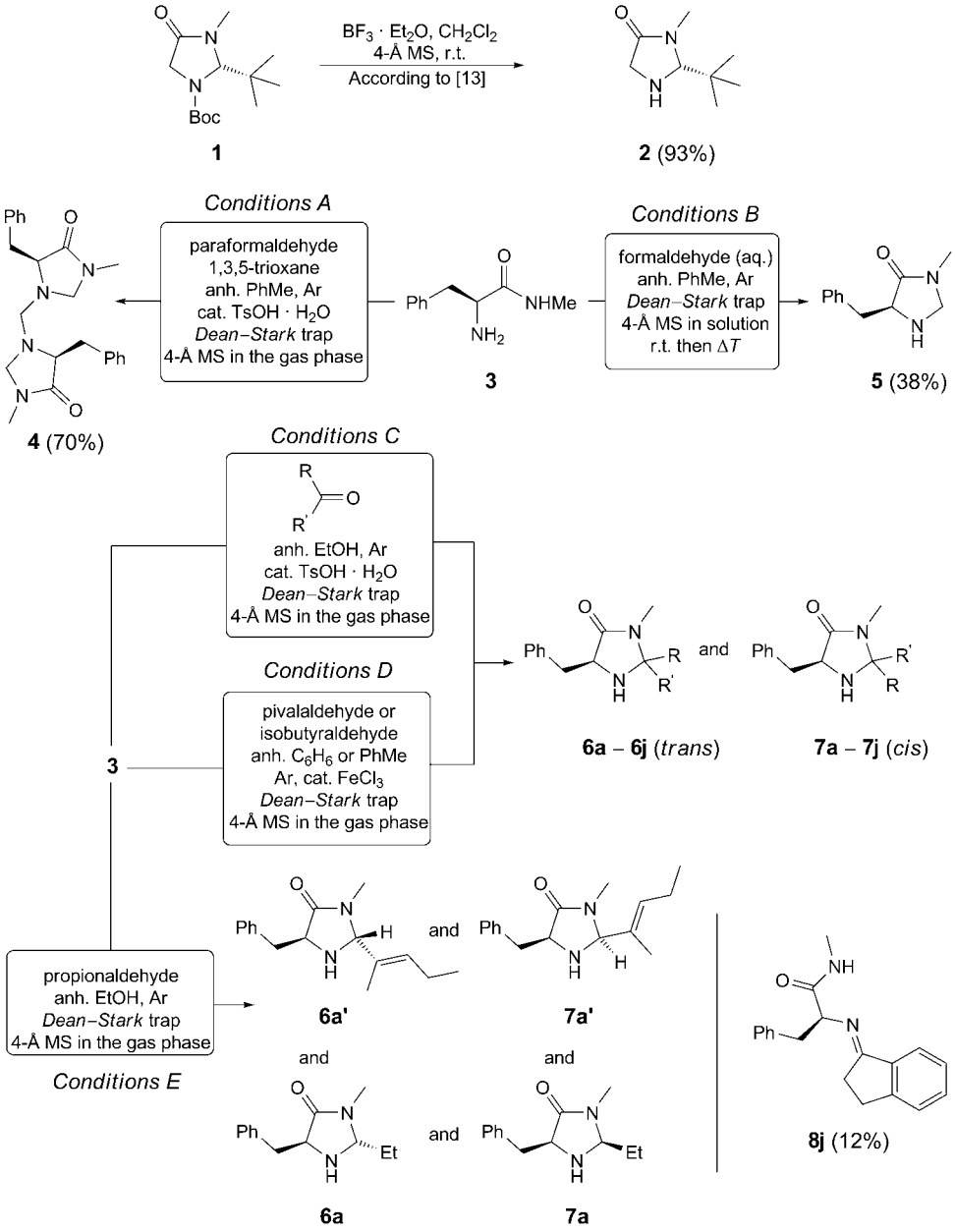
[2]) Compounds **7e** and **7c** are frequently referred to as *MacMillan*'s first- and second-generation (*cf.* [2] and [3], resp.) imidazolidinone organocatalysts, respectively.

characterization of diarylprolinol-derived iminium salts took place [10]. The ease of preparation of imidazolidinone- and diarylprolinol-derived reactive iminium intermediates and their stability were used in various mechanistic studies and for development of modified imidazolidinone- and diarylprolinol-based organocatalysts [11]. Herein, we report all experimental details regarding the synthesis and structural characterization of imidazolidinones, their ammonium salts, and cinnamaldehyde-derived iminium salts, having remained undisclosed in previous publications. We also discuss herein the conformations of the iminium salts in the solid state and in solution.

2. Preparation of Imidazolidinones, and Corresponding Ammonium Salts and Cinnamaldehyde-Derived Iminium Salts. – The only *C(5)*-unsubstituted imidazolidinone, 2-(*tert*-butyl)-3-methylimidazolidin-4-one [12] (**2**), was prepared *via* $BF_3 \cdot Et_2O$-mediated Boc deprotection [13] of Boc-BMI [12] (**1**) (*Scheme 1*). All 5-benzyl-3-methyl-1,3-imidazolidin-4-ones, **4**–**7**, were prepared from (*S*)-2-amino-*N*-methyl-3-phenylpropanamide, the *N*-methyl amide **3** of phenylalanine [14], in a cyclocondensation reaction with various aldehydes and ketones (*Conditions A*–*E*; *Scheme 1* and *Table 1*). The only *C(2)*-unsubstituted imidazolidinone, (*S*)-5-benzyl-3-methylimidazolidin-4-one (**5**) was prepared from **3** and aqueous HCHO in the presence of freshly activated 4-Å molecular sieves (MS) in toluene (*Conditions B*; *Scheme 1* and *Table 1*). An attempt to prepare **5** from a mixture of paraformaldehyde and 1,3,5-trioxane, and amide **3** under similar reaction conditions resulted in the formation of the bis-imidazolidinone **4** (*Conditions A*; *Scheme 1*). In most cases, the reaction of the phenylalanine amide **3** with an aldehyde or a ketone was carried out in anhydrous EtOH with or without catalytic amounts of $TsOH \cdot H_2O$ under Ar in the presence of freshly activated 4-Å MS (suspended in the gas phase [15]). In this manner, compounds **6a**, **6d**–**6j**, and **7a**, **7d**–**7j** were prepared (*Conditions C*; *Scheme 1* and *Table 1*). Similarly, 2-^{i}Pr- (**6b**, **7b**) and 2-^{t}Bu-substituted imidazolidinones, **6c** and **7c**, respectively [3], were prepared from **3** and isobutyraldehyde or pivalaldehyde, respectively, using a slightly modified literature procedure [16] in anhydrous benzene or toluene, in the presence of $FeCl_3$ (*Conditions D*; *Scheme 1* and *Table 1*). The reaction of **3** with propanal gave, besides the expected 2-Et-substituted imidazolidinones **6a** and **7a**, also the side-products **6a′** and **7a′**. The formation of **6a′**/**7a′** can be explained by the initial aldol condensation of propanal to (*E*)-2-methylpent-2-enal, followed by cyclization (*Conditions E*; *Scheme 1* and *Table 1*). The reaction of amide **3** with 2,3-dihydro-1*H*-inden-1-one furnished, besides the desired spiro-imidazolidinone **7j**, also the imine **8j**. The *trans*- and *cis*-diastereoisomers, **6** and **7**, respectively, could in all cases be separated by column chromatography, as a rule of thumb, the *trans*-isomer **6** is eluted first, followed by the *cis*-isomer **7**.

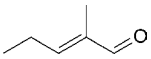
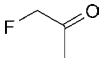
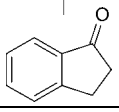
Most of the imidazolidinones prepared were converted to the corresponding BF_4^- and/or PF_6^- ammonium salts, **9** and **10**, and **11**, respectively, by simply mixing the corresponding Et_2O solutions of an imidazolidinone, **2**, **6**, or **7**, and of HBF_4 or HPF_6 (*Scheme 2* and *Table 2*); there was no *cis*/*trans*-equilibration in this salt-forming process. The vast majority of ammonium salts precipitated from the reaction mixture, the precipitate was collected by filtration, washed with Et_2O, and dried under high vacuum. For workup of the products that did not precipitate from the reaction mixture, see the *Exper. Part*. The BF_4^- ammonium salt of *cis*-5-benzyl-2-(*tert*-butyl)imidazoli-

Scheme 1. *Preparation of Imidazolidinones* **2**, **4**–**7**, *and of Amide* **8j**. For R and R′, see *Tables 1* and *2*, and *Exper. Part.*



dinone **10b** turned out to be very hygroscopic, and the *cis*-5-benzyl-2-(*tert*-butyl)-2-methylimidazolidinone-derived PF_6^- ammonium salt **11m** decomposed in solution but was stable in the solid state. After prolonged standing (6 months or more at r.t.) PF_6^-

Table 1. *Preparation of Imidazolidinones* **6** *and* **7**. For the particular procedure used, see *Scheme 1* and *Exper. Part.* Yields refer to isolated and purified products; enantiomer ratios (er) were determined by HPLC analysis with *Chiralcel OD-H* or *Chiralpak AD-H* columns and hexane/^{i}PrOH mixtures as mobile phase.

Reaction	Conditions	Ketone/aldehyde	*trans*-Product **6** (yield [%], er)	*cis*-Product **7** (yield [%], er)
3 → **6a**, **7a**, **6a′**, **7a′**	*E*		12, > 99.5 : 0.5	12, > 99.5 : 0.5
			7	4
3 → **6b**, **7b**	*D*		28	26
3 → **6c**, **7c** [16]	*D*		35	29
3 → **7d** [17]	*C*		–	13
3 → **7e** [2]	*C*		–	85
3 → **6f**, **7f**	*C*		29, > 99.5 : 0.5	24, > 99 : 1
3 → **6g**, **7g**	*C*		38	40
3 → **7h** [18]	*C*		–	41
3 → **6i**, **7i**	*C*		28	33
3 → **7j**	*C*		–	41

ammonium and iminium salts started to decompose (with formation of HF), in spite of their storage in an anhydrous Ar atmosphere.

According to a modified procedure of *Leonard* and *Paukstelis* [19], the BF_4^- and PF_6^- ammonium salts, **9** and **10**, and **11**, respectively, were used in the preparation of the corresponding iminium salts **12**–**14**. Thus, mixing of an ammonium salt in anhydrous EtOH with cinnamaldehyde in the presence of catalytic amounts of Et_3N under Ar afforded the iminium salt as a filterable solids. Only in the case of *trans*-5-benzyl-(2-*tert*-butyl)-imidazolidin-1-ium salt **11d**, the reaction with cinnamaldehyde, after prolonged reaction time, yielded transamination products: 5-benzyl-2-styrylimidazolidin-1-ium salts (*E*)- and (*Z*)-**14f**. Under thermodynamic conditions in solution, most of the isolated iminium salts existed as mixtures of the major (*E*)- and the minor (*Z*)-diastereoisomers (NMR analysis). Only in the *C(2)*-unsubstituted iminium salt **14a**, the

Scheme 2. *Preparation of the Ammonium Salts* **9**, **10**, *and* **11**. For R and R′, see *Tables 1* and *2*, and *Exper. Part*.

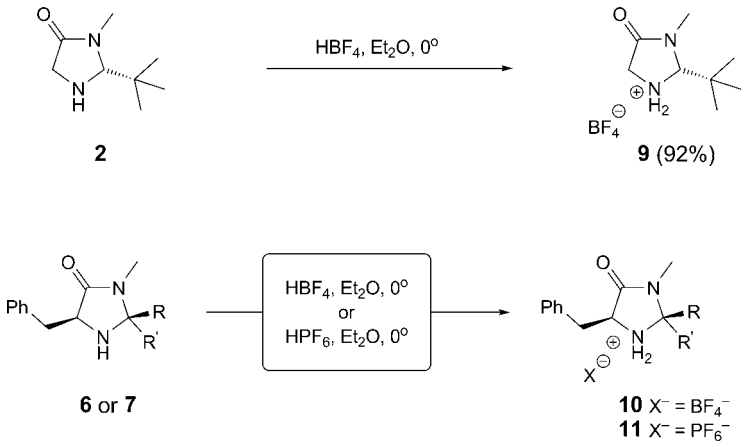
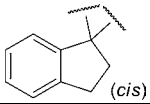
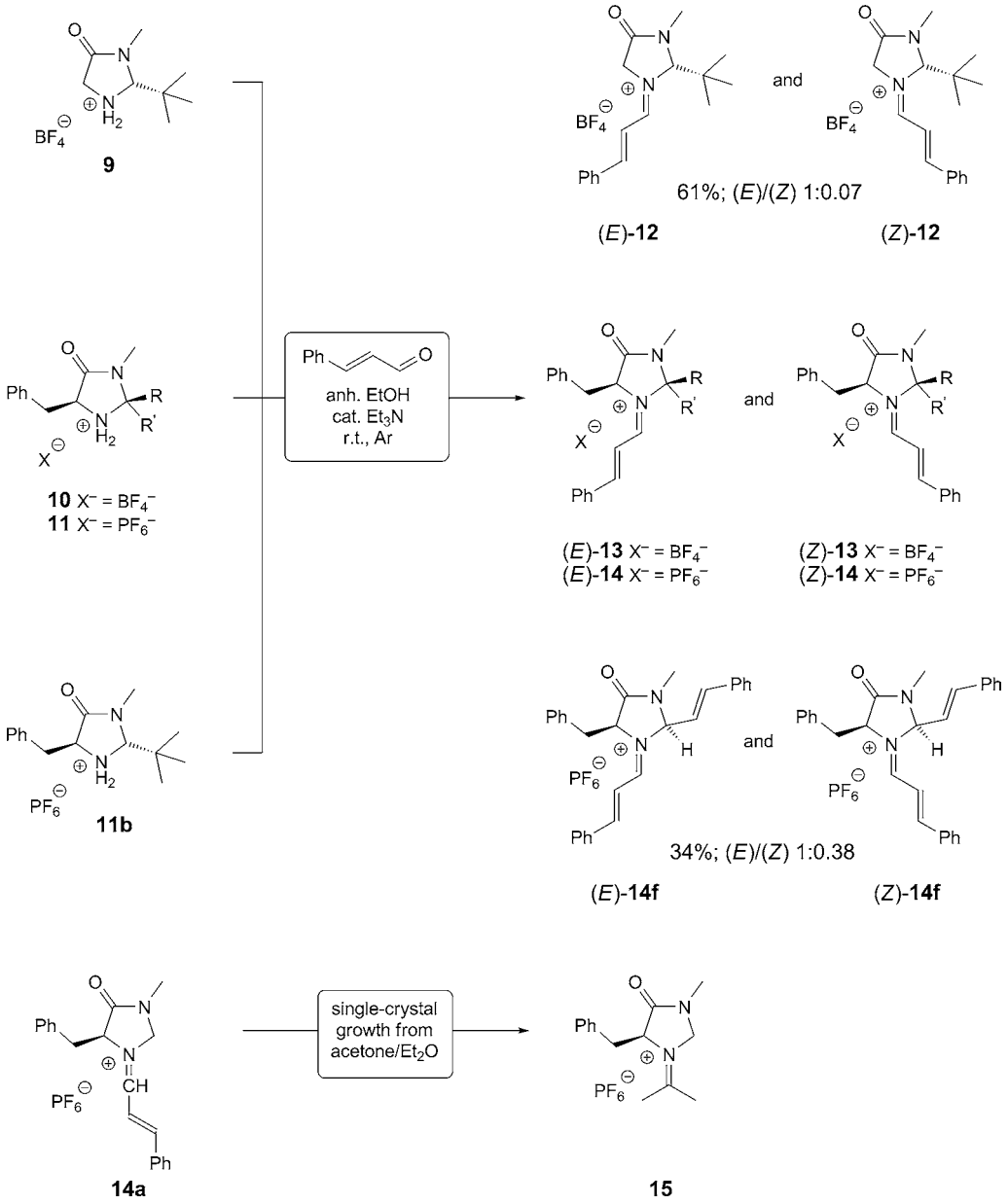


Table 2. *Prepared BF_4^- and PF_6^- Imidazolidin-2-ium Salts* **10** *and* **11** (*cf. Scheme 2*). The yields refer to isolated and purified products.

Reaction	X^-	R	R′	Yield [%]
6c → **10a**	BF_4^-	H	^{t}Bu	86
7c → **10b**	BF_4^-	^{t}Bu	H	67
7e → **10c**	BF_4^-	Me	Me	83
5 → **11a**	PF_6^-	H	H	83
7a → **11b**	PF_6^-	Et	H	85
7b → **11c**	PF_6^-	^{i}Pr	H	82
6c → **11d**	PF_6^-	H	^{t}Bu	97
7c → **11e**	PF_6^-	^{t}Bu	H	58
7a′ → **11f**	PF_6^-	(2*E*)-Pent-2-en-2-yl	H	56
7d → **11g**	PF_6^-	Ph	H	74
7e → **11h**	PF_6^-	Me	Me	93
6f → **11i**	PF_6^-	Me	CH_2F	71
7f → **11j**	PF_6^-	CH_2F	Me	86
6g → **11k**	PF_6^-	Me	^{i}Pr	88
7g → **11l**	PF_6^-	^{i}Pr	Me	87
7h → **11m**	PF_6^-	^{t}Bu	Me	87
6i → **11n**	PF_6^-	Me	Ph	38
7i → **11o**	PF_6^-	Ph	Me	97
7j → **11p**	PF_6^-	 (*cis*)		56

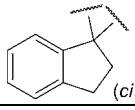
(*Z*)-isomer predominated (*Scheme 3* and *Table 3*). It is worth mentioning that all but one of the iminium salts **12**–**15** could be prepared in analytically pure form (see *Exper. Part*). In the solid state and if properly stored (pre-dried in high vacuum, stored under Ar), these cinnamaldehyde-derived iminium salts were 'bench-stable'. Under anhy-

Scheme 3. *Preparation of the Iminium salts* **12**–**15**. For R and R′, see *Table 3* and *Exper. Part.*



drous conditions, decomposition of the iminium salts was negligible even in solution. In an attempt to prepare single crystals for X-ray-analysis of the *C(2)*-unsubstituted iminium salt **14a** by slowly condensing Et_2O into an acetone solution, unexpectedly, the acetone-derived iminium salt **15** was obtained and characterized by single-crystal X-ray

Table 3. *Preparation of Imidazolidin-1-ium Salts* **13** *and* **14**. The yields refer to isolated and purified products. All products **13** and **14** are crystalline. The crystals generally consist of (*E*)-isomers (*cf. Table 4*). In solution, equilibration with the (*Z*)-isomers occurs. The (*E*)/(*Z*) ratios were determined in various NMR solvents (*cf. Table 5*); for details, see *Exper. Part.*

Reaction	X^-	R (*cis*)	R′ (*trans*)	Yield [%]	(*E*)/(*Z*)
10c → **13a**	BF_4^-	Me	Me	44	97 : 3
11a → **14a**	PF_6^-	H	H	83	31 : 69
11b → **14b**	PF_6^-	Et	H	77	79 : 21
11c → **14c**	PF_6^-	^{i}Pr	H	85	87 : 13
11e → **14d**	PF_6^-	^{t}Bu	H	58	95 : 5
11f → **14e**	PF_6^-	(2*E*)-Pent-2-en-2-yl	H	67	65 : 35
11d → **14f**	PF_6^-	(*E*)-2-Phenylethenyl)	H	34	72 : 28
11g → **14g**	PF_6^-	Ph	H	57	67 : 33
11h → **14h**	PF_6^-	Me	Me	76	98 : 2
11i → **14i**	PF_6^-	Me	CH_2F	86	> 99 : 1
11j → **14j**	PF_6^-	CH_2F	Me	76	> 99 : 1
11k → **14k**	PF_6^-	Me	^{i}Pr	73	> 99 : 1
11l → **14l**	PF_6^-	^{i}Pr	Me	92	> 99 : 1
11m → **14m**	PF_6^-	^{t}Bu	Me	20	> 99 : 1
11n → **14n**	PF_6^-	Me	Ph	95	89 : 11
11o → **14o**	PF_6^-	Ph	Me	91	76 : 24
11p → **14p**	PF_6^-	 (*cis*)		90	79 : 21

analysis (*Scheme 3*). This unique event has not been observed when preparing single crystals of any one of the other iminium salts, using acetone as one of the co-solvents for crystal growth.

From *Table 3*, one can clearly see how the substituents at C(2) control the configuration of the exocyclic N=C bond of the iminium salts (the (*E*)/(*Z*)-ratio under thermodynamic conditions). A good control of the configuration of the α,β-unsaturated iminium intermediate is one of the prerequisites for high stereoselectivity of corresponding imidazolidinone-catalyzed organocatalytic reactions. A large ^{t}Bu group at C(2) of iminium salts **12** and **14d** enforces predominantly the (*E*)-configuration of the exocyclic N=C bond (*Scheme 3* and *Table 3*). Not surprisingly, the corresponding imidazolidinones **2** [20] and **7c** [3][20] are well-established, commercially available organocatalysts. Reducing the steric bulk of the substituent at C(2) in the series ^{t}Bu, ^{i}Pr, Et, H results in decreased (*E*)/(*Z*)-control and eventually leads to the (*Z*)-diastereoisomer (R = H) as the major isomer. A substituent with a less bulky α-sp^2-hybridized C(2)-atom leads to diminished (*E*)/(*Z*)-control (**14e** – **14g** and **14n** – **14p**; *Table 3*). On the other hand, the reduction of steric strain (1,5-repulsion [21]) imposed by the substituent at C(2) is crucial for the performance of (2*S*,5*S*)-5-benzyl-3-methyl-2-(5-methylfuran-2-yl)imidazolidin-4-one [17], designed for enantioselective catalytic *Diels–Alder* reactions with simple α,β-unsaturated ketones. One can only guess how much fine-tuning has been invested in the 'design' of this catalyst. Two geminal substituents at C(2) provide perfect (*E*)/(*Z*)-control of the corresponding cinnamyl-iminium ion (**14h** – **14m**; *Table 3*), which is evident in the case of the

benchmark catalyst **7e** (→ **11h** → **14h**) [2]. Of course, placing a large group, such as ^{i}Pr, in the *2-trans*-position would counteract the selective attack of the nucleophile from the side *anti* to the Bn group. Finally, if one of the two geminal groups is replaced by a substituent bearing a α-sp^2-hybridized C-atom, the (*E*)/(*Z*)-control falters once again[3]).

3. Preparation of Single Crystals of Iminium Salts for X-Ray Analysis. – All the single crystals of iminium salts (BF_4^- and PF_6^-) for X-ray analysis have been prepared by slow diffusion of Et_2O or petroleum ether, in a large outer container, into a solution of the iminium salt in acetone and/or CH_2Cl_2 in a smaller container. The small container was positioned inside the larger one. The relative volume of Et_2O or petroleum ether was much bigger compared to that of acetone and/or CH_2Cl_2. All the solvents and glassware used were rigorously dried to ensure anhydrous conditions and prevent hydrolysis, and all crystallizations were performed under Ar at room temperature. The slow diffusion of Et_2O or petroleum ether caused gradual change in the solvent composition and thus polarity, which eventually induced the crystal formation and slow growth. The structures of the iminium ions, salts of which are described herein, have been discussed in our previous papers [4][5][7][9][10]. Besides the non-benzylated salt **12**, the altogether 14 structures of 5-benzyl-1-cinnamyl-3-methylimidazolidinone iminium salts, **14** and **15**, shown in *Table 4*, fall into three distinct categories **A** – **C** (*Fig. 1*), according to the conformation of the Bn group at C(5). A fourth conformation **D** with a pentafluoro-substituted Bn group has been discovered only recently [11g] (*Fig. 1*). In the acetone-derived *C(2)*-unsubstituted iminium salt **15**, the Bn group has conformation **A**, with the Ph group over the heterocycle. This same conformation is present in most other *C(2)*-substituted iminium salts. In the crystal of the enantiomerically pure form of the (*E*)-*cis*-2-Ph-substituted iminium salt **14g**, the Bn group adopts conformation **A** (non-centrosymmetric space group $P2_12_12_1$), while in the crystal of the racemate conformation **B** was adopted (centrosymmetric space group $P2_1/c$), with the benzene ring over the π-system. The substituents at C(2) affect, besides

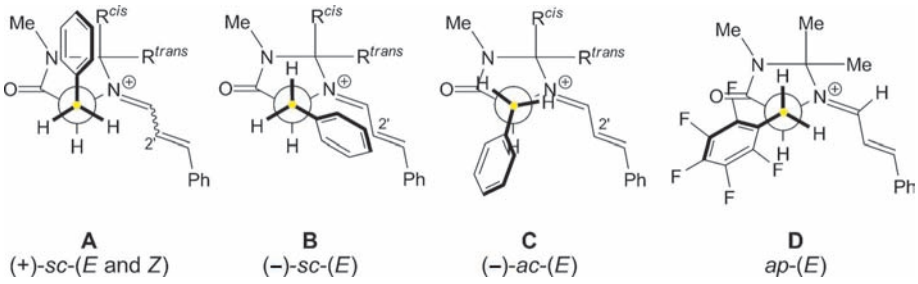


Fig. 1. *The four conformations* **A** – **D** *of the benzyl group of cinnamaldehyde-derived iminium salts found experimentally.* For discussion and DFT calculations of the conformations **A** – **D**, see our previous report and refs. cit. therein [9].

[3]) Note that this discussion is a 'thermodynamic one', suggesting that the thermodynamically more stable (*E*)-isomer dictates the stereochemical course of the catalytic reaction. We have, however, shown that the (*Z*)-isomer may be the kinetically preferred diastereoisomer [7].

Table 4. *X-Ray Crystal Structures of Cinnamaldehyde-Derived 4-Oxoimidazolidin-1-ium Salts* **12**, **14**, *and* **15**, *Ordered According to Their Conformations* **A** – **C**. PF_6 Counteranions are omitted for clarity.

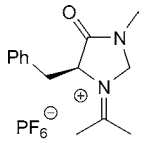
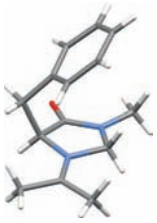
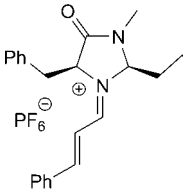
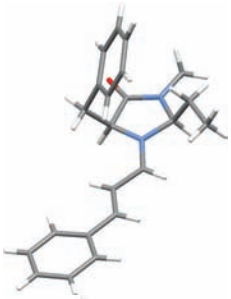
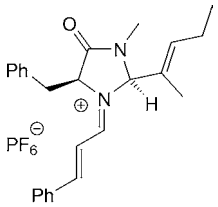
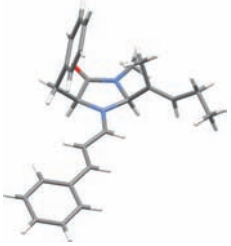
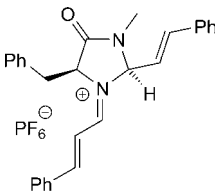
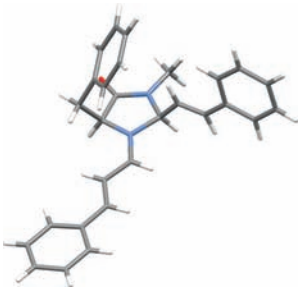
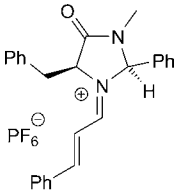
Crystal structures with conformation **A**		
 **15**	CCDC 990626	
 (*E*)-**14b**	CCDC 990627	
 (*E*)-**14e**	CCDC 990628	
 (*E*)-**14f**	CCDC 711496 [5]	
 (*E*)-**14g**	CCDC 990629	

Table 4 (cont.)

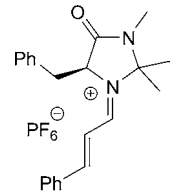
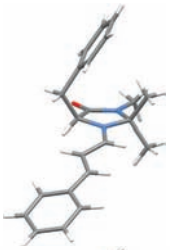
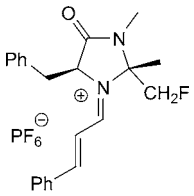
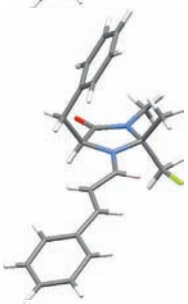
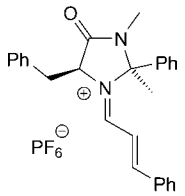
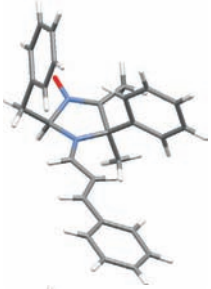
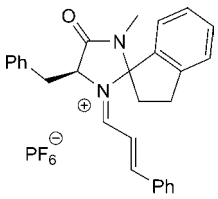
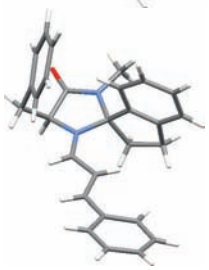
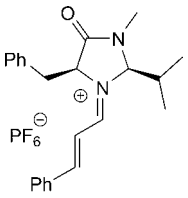
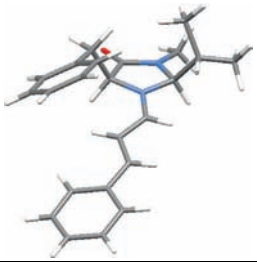
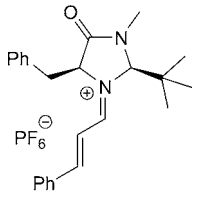
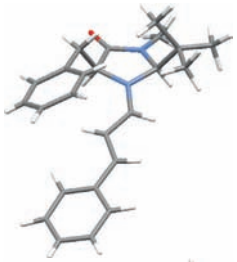
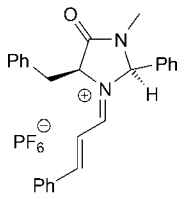
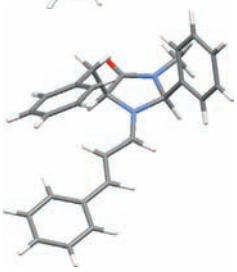
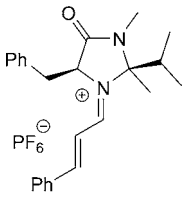
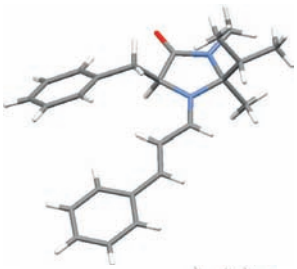
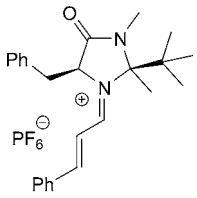
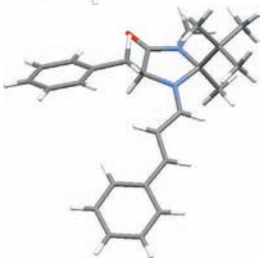
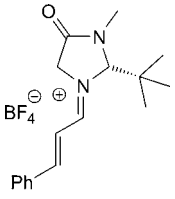
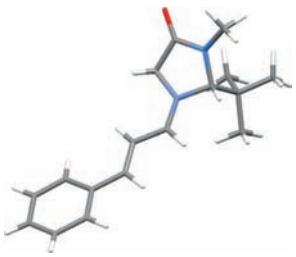
 (*E*)-**14h**	CCDC 711494 [5]	
 (*E*)-**14i**	CCDC 990630	
 (*Z*)-**14o**	CCDC 990631	
 (*Z*)-**14p**	CCDC 990632	
Crystal structures with conformation **B**		
 (*E*)-**14c**	CCDC 990633	

Table 4 (cont.)

 (*E*)-**14d**	CCDC 711495 [5]	
 *rac*-(*E*)-**14g**	CCDC 990634	
Crystal structures with conformation **C**		
 (*E*)-**14l**	CCDC 990635	
 (*E*)-**14m**	CCDC 990636	
Crystal structure without 5-Bn substituent		
 (*E*)-**12**	CCDC 695937 [4]	

the configuration of the N=C bond, also the conformation of the benzylic C–C bond, and thus the position of the Ph ring. In the case of the sterically bulky *cis*-^{i}Pr and *cis*-^{t}Bu groups of the iminium salts **14c** and **14d**, the Bn group adopted conformation **B**, with the Ph group above the cinnamyl-iminium π-system. Finally, the third, eclipsed conformation **C** was found in iminium salts bearing *trans*-Me/*cis*-^{i}Pr groups (*i.e.*, **14l**) and *trans*-Me/*cis*-^{t}Bu groups (*i.e.*, **14m**). In two cases with the conformation **A**, with the Ph group above the imidazolidinone ring, the exocyclic N=C bond had (*Z*)-configuration (**14o** and **14p**) (*Table 4*).

4. Comparison of Selected ^{1}H-NMR Data with Conformations A – C Observed in the Solid State. – As reported in [5] for the iminium salts of 2,2-dimethylimidazolidinone, (*E*)-**14h**, and of the 2-styrylimidazolidinone, (*E*)-**14f**, the conformation **A** of the Bn group, observed in the solid state, must also be populated in solution: there is a massive upfield shift of the signals from the *cis*-Me and the styryl H–C(1′) (*cf.* the corresponding signals of the ammonium salts **11h**, and Figs. 2 and 3 in [5]). The same observation was made in the NMR spectra of all iminium salts, of which conformation **A** was present in the crystal structure: depending on the solvent, there was a more or less strong shielding of H-atoms in the groups located *cis* to the Bn group (see the following pairs of ammonium and (*E*)- or (*Z*)-configured iminium salts: **11b**/(*E*)-**14b**, **11f**/(*E*)-**14e**, **11g**/(*E*)-**14g**, **11i**/(*E*)-**14i**, **11o**/(*Z*)-**14o**, **11p**/(*Z*)-**14p**; *Tables 4* and *5*, and *Exper. Part*). Based on these results, we assign the same configuration **A** of the Bn group from the ^{1}H-NMR data, also to those (*E*)- and/or (*Z*)-configured iminium salts that did not give suitable single crystals for X-ray-analysis (compare the data for **11f**/(*Z*)-**14e**, **11k**/(*E*)-**14k**, **11n**/(*E*/*Z*)-**14n**, **11o**/(*E*)-**14o**, **11p**/(*E*)-**14p** in *Table 5* and in the *Exper. Part*). In the case of (*E*)- and (*Z*)-iminium salt **14a**, the signals of the *cis*-H-atom at C(2) are not subject to an upfield shift, compared to those of the corresponding ammonium salt **11a**, conformation **A** was assigned, based on the X-ray structure of the acetone-derived iminium salt **15**. In two cases, iminium salts (*E*)-**14c** and (*E*)-**14d** [5], the sterically bulky ^{i}Pr and ^{t}Bu substituents cause the Ph group to be located over the iminium π-system in the solid state. That this conformation **B** was also populated in solution, could be deduced from the *ca.* 1-ppm upfield shift of the signal of H–C(2′) in the ^{1}H-NMR spectrum: H–C(2′) is situated underneath the Ph group in conformation **B**, but not in conformation **A** (compare the chemical shifts of H–C(2′) in (*E*)-**14c** and (*E*)-**14d** with that in (*E*)-**14h**, and also with that in (*Z*)-**14c**). Conformation **B** was tentatively assigned also to the *cis*-(CH_2F)-substituted *iminium* salt (*E*)-**14j** [8]. Finally, a similar degree of shielding of the H-atoms at C(2′) was observed for the iminium salts (*E*)-**14l** and (*E*)-**14m**, the solid-state structures of which have the eclipsed benzylic conformations **C**. As can be seen from space-filling representations of the crystal structures of these two compounds (Fig. 5 in [9]), the Ph ring is turned in such a way that it exerts anisotropy on H–C(2′). Thus, it appears that, from ^{1}H-NMR spectra alone, it is not possible to distinguish between conformations **B** and **C** in solution. An elaborate calculation of the potential energy for rotation around the benzylic C–C bond in the *cis*-^{t}Bu,2-Me-substituted iminium ion (*E*)-**14m** revealed a negligible energy difference between conformations **B** and **C** (Fig. 8 in [9]). In the (*Z*)-iminium salts **14n** – **14p** bearing a Ph group at C(2), the signals of H–C(2′) are subject to a strong upfield shift, as compared to the corresponding (*E*)-diastereoisomers (see *Table 5*).

Table 5. *Selected ^{1}H-NMR Data* (δ [ppm], multiplicity) *of Ammonium and Iminium Salts Derived from Imidazolidinones.*

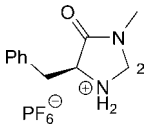
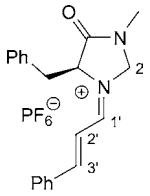
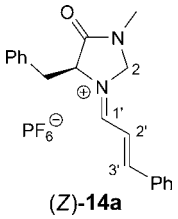
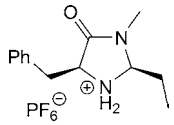
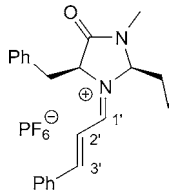
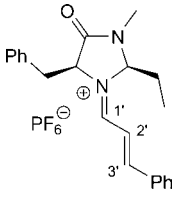
Compound	Solvent, conformation	H–C(1′), H–C(2′), H–C(3′)	H_a–C(2)	H_b–C(2)
 **11a**	(D_6)DMSO, –		4.50 (*d*)	4.54 (*d*)
 (*E*)-**14a**	(D_6)Acetone, –	8.97 (*d*), 7.38 (*dd*), 8.21 (*d*)	4.87 (*d*)	5.43 (*d*)
 (*Z*)-**14a**	(D_6)Acetone, –	8.85 (*dd*), ~7.58[a]); 8.25 (*d*)	4.99 (*dd*)	5.62 (*dt*)
		H–C(1′), H–C(2′), H–C(3′)	MeCH_2	MeCH_2
 **11b**	(D_6)DMSO, –		1.63 – 1.76 (*m*)	2.10 – 2.22 (*m*)
 (*E*)-**14b**	(D_6)Acetone, **A**	8.99 (*d*), ~7.33[a]), 8.31 (*d*)	1.19 – 1.31 (*m*)	1.83 – 1.95 (*m*)
 (*Z*)-**14b**	(D_6)Acetone, –	8.61 (*d*), ~7.65[a]), 8.16 (*d*)	[a])	[a])

Table 5 (cont.)

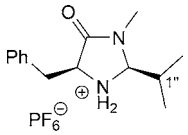
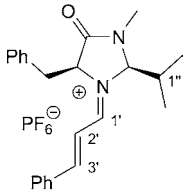
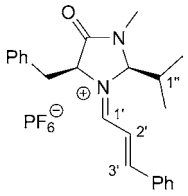
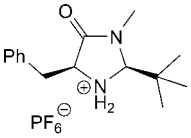
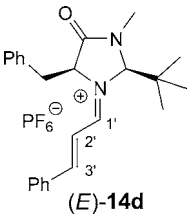
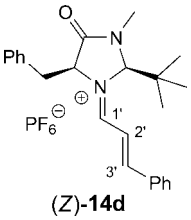
		H–C(1′), H–C(2′), H–C(3′)	H–C(1″)	Me_2CH	Me_2CH
 **11c**	(D_6)DMSO, –		2.29 – 2.41 (*m*)	0.92 (*d*)	1.04 (*d*)
 (*E*)-**14c**	(D_6)Acetone, **B**	8.92 (*d*), 6.80 (*dd*), 8.24 (*d*)	2.32 – 2.45 (*m*)	1.21 (*d*)	1.21 (*d*)
 (*Z*)-**14c**	(D_6)Acetone, –	8.46 (*d*), ~7.62[a]), 8.10 (*d*)	2.46 – 2.55 (*m*)	1.13 (*d*)	1.31 (*d*)
		H–C(1′), H–C(2′), H–C(3′)	^{t}Bu		
 **11e**	(D_6)DMSO, –		1.08 (*s*)		
 (*E*)-**14d**	(D_6)Acetone, **B** [5]	8.92 (*d*), 6.55 (*dd*), 8.27 (*d*)	1.34 (*s*)		
 (*Z*)-**14d**	(D_6)Acetone, –	8.49 (*d*), [b]), 8.11 (*d*)	[b])		

Table 5 (cont.)

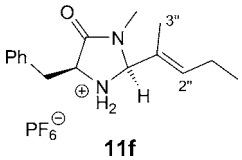
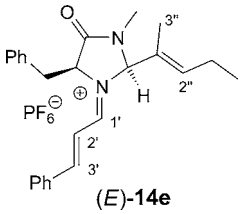
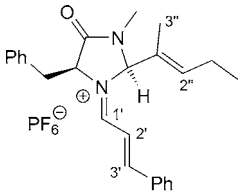
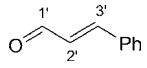
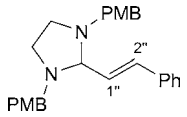
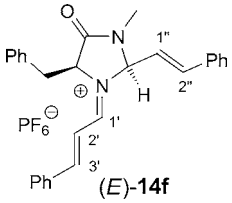
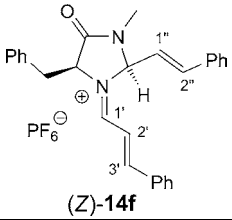
		H–C(1′), H–C(2′), H–C(3′)	Me(3″)	H–C(2″)
 **11f**	(D_6)DMSO, –		1.56 (*s*)	5.85 (*td*)
 (*E*)-**14e**	(D_6)Acetone, **A**	8.86 (*d*), ~7.42[a]), 8.34 (*d*)	1.12 (*d*)	6.19–6.23 (*m*)
 (*Z*)-**14e**	(D_6)Acetone, –	8.90 (*dt*), ~7.68[a]), 8.25 (*d*)	~1.07[a])	6.55 (*td*)
		H–C(1′), H–C(2′), H–C(3′)	H–C(1″)	H–C(2″)
	(D_6)Acetone	9.73 (*d*), 6.78 (*dd*), 7.65 (*d*)		
	$CDCl_3$ [22]		6.20 (*dd*)	6.61 (*d*)
 (*E*)-**14f**	(D_6)Acetone, **A** [5]	9.08 (*d*), 7.90 (*dd*), 8.42 (*d*)	4.27 (*dd*)	7.20 (*d*)
 (*Z*)-**14f**	(D_6)Acetone, – [5]	9.18 (*dt*), ~7.62[a]), 8.32 (*d*)	4.35 (*dd*)	~7.53[a])

Table 5 (cont.)

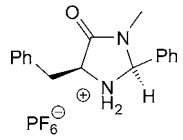
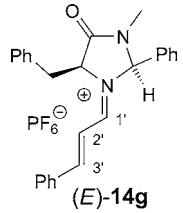
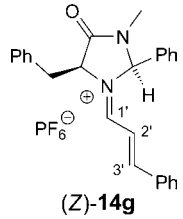
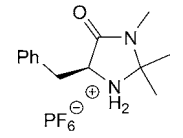
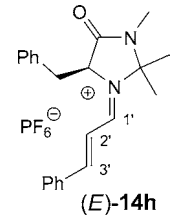
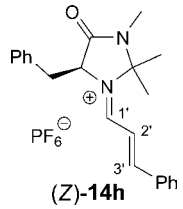
		H–C(1′), H–C(2′), H–C(3′)	H_{ortho} of Ph	
 **11g**	(D_6)DMSO, –		~7.43[c])	
 (*E*)-**14g**	(D_6)Acetone, **A**, (2*R*,5*S*), **B**, *rac*	8.88 (*d*), ~7.53[a]), 8.30 (*d*)	~6.95[c])	
 (*Z*)-**14g**	(D_6)Acetone, –	9.12 (*dt*), 7.19 (*dd*), 8.24 (*d*)	[b])	
		H–C(1′), H–C(2′), H–C(3′)	Me–C(2)	Me–C(2)
 **11h**	(D_6)DMSO, – [5]		1.52 (*s*)	1.66 (*s*)
 (*E*)-**14h**	(D_6)DMSO, **A** [5]	9.33 (*dd*), ~7.73[a]), 8.25 (*d*)	0.75 (*s*)	1.74 (*s*)
 (*Z*)-**14h**	(D_6)DMSO, – [5]	9.16 (*d*), [b]), [b])	[b])	[b])

Table 5 (cont.)

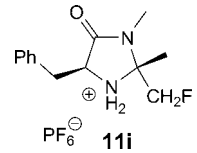
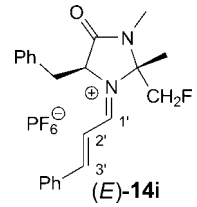
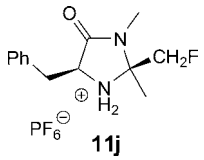
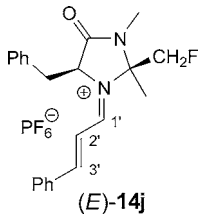
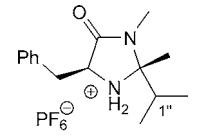
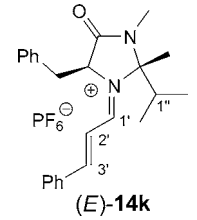
		H–C(1′), H–C(2′), H–C(3′)	H_aH_bCF	H_aH_bCF	Me–C(2)
 **11i**	(D_6)Acetone, –		4.90 (*dd*)	5.02 (*dd*)	1.90 (*d*)
 (*E*)-**14i**	(D_6)Acetone, **A**	9.27 (*dd*), 7.93 (*dd*), 8.53 (*d*)	4.86 (*dd*)	4.98 (*dd*)	0.94 (*d*)
		H–C(1′), H–C(2′), H–C(3′)	H_aH_bCF	H_aH_bCF	Me
 **11j**	(D_6)DMSO, –		4.70 (*dd*)	4.82 (*dd*)	1.55 (*d*)
 (*E*)-**14j**	(D_6)Acetone, –	9.19 (*d*), 7.20 (*dd*), 8.31 (*d*)	4.18 (*dd*)	4.68 (*dd*)	2.02 (*d*)
		H–C(1′), H–C(2′), H–C(3′)	H–C(1″)	Me–C(2)	
 **11k**	(D_6)DMSO, –		2.18 – 2.31 (*m*)	1.56 (*s*)	
 (*E*)-**14k**	(D_6)Acetone, –	9.15 (*dd*), 7.94 (*dd*), 8.55 (*d*)	2.39 – 2.52 (*m*)	0.99 (*s*)	

Table 5 (cont.)

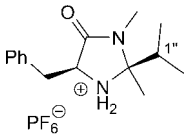
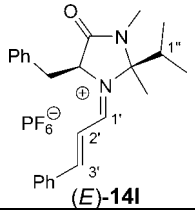
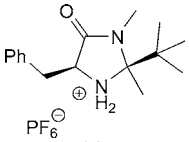
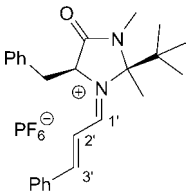
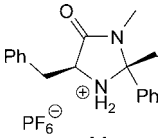
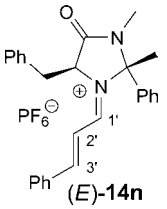
		H–C(1′), H–C(2′), H–C(3′)	H–C(1″)	Me–C(2)
 **11l**	(D_6)DMSO, –		2.23 – 2.37 (*m*)	1.57 (*s*)
 (*E*)-**14l**	(D_6)Acetone, **C**	9.09 (*dd*), 6.93 (*dd*), 8.37 (*d*)	2.34 – 2.46 (*m*)	2.01 (*s*)
		H–C(1′), H–C(2′), H–C(3′)	ᵗBu	Me–C(2)
 **11m**	(D_6)DMSO, –		1.09 (*s*)	1.53 (*s*)
 (*E*)-**14m**	(D_6)DMSO, **C**	9.26 (*d*), 6.59 (*dd*), 8.35 (*d*)	1.17 (*s*)	1.96 (*s*)
		H–C(1′), H–C(2′), H–C(3′)	H_{ortho} of Ph	Me–C(2)
 **11n**	(D_6)DMSO, –		[b])	2.11 (*s*)
 (*E*)-**14n**	(D_6)DMSO, –	8.86 (*dd*), ~7.72[a])[c]), 8.18 (*d*)	[b])	1.26 (*s*)

Table 5 (cont.)

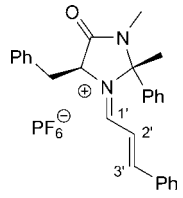
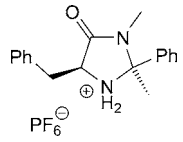
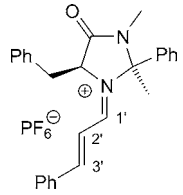
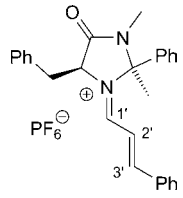
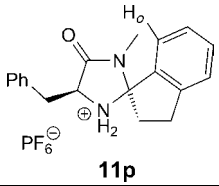
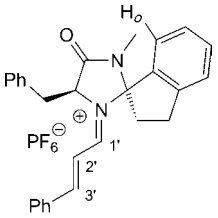
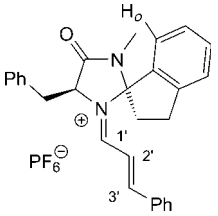
		H–C(1′), H–C(2′), H–C(3′)	H_{ortho} of Ph	Me–C(2)
 (*Z*)-**14n**	(D_6)DMSO, –	9.16 (*d*), 6.67 (*dd*), 8.13 (*d*)	[b])	1.36 (*s*)
		H–C(1′), H–C(2′), H–C(3′)	H_{ortho} of Ph	Me–C(2)
 **11o**	(D_6)DMSO, –		~7.49[c])	2.02 (*s*)
 (*E*)-**14o**	(D_6)Acetone, –	9.17 (*dd*), ~7.40[a]), 8.26 (*d*)	~7.09[c])	2.37 (*s*)
 (*Z*)-**14o**	(D_6)Acetone, **A**	9.35 (*dd*), 6.73 (*dd*), 8.37 (*d*)	[b])	2.40 (*s*)
		H–C(1′), H–C(2′), H–C(3′)	H_{ortho} of Ph	
 **11p**	(D_6)DMSO, –		~7.40[b])	

Table 5 (cont.)

		H–C(1′), H–C(2′), H–C(3′)	H_{ortho} of Ph
 (*E*)-**14p**	(D_6)Acetone, –	8.61 (*dd*), 7.91 (*dd*), 8.44 (*d*)	5.13 (*d*)
 (*Z*)-**14p**	(D_6)Acetone, **A**	9.41 (*dd*), 6.25 (*dd*), 8.37 (*d*)	4.90 (*d*)

[a]) Extracted from 2D HSQC spectra. [b]) Overlapped by other signals or not detected. [c]) Extracted from 1D-NOE recordings in (D_6)Acetone.

The configurational assignments of the key compounds, the iminium salts **14**, and the assignments of *ortho*-H-atoms of the Ph group of compounds **11g** and **11o** were derived from steady-state NOE difference NMR experiments (for details see *Fig. 2* and *Exper. Part*).

Novel imidazolidinones were characterized only partially. On the other hand, ammonium and iminium salts were fully characterized, in most cases with correct elemental analyses. The *cis*/*trans*-configurations of the 2,5-disubstituted imidazolidinones and the corresponding ammonium salts were confirmed indirectly *via* X-ray structural characterization of the respective iminium salts.

5. Conclusions. – The preparation of a large number of phenylalanine-derived *cis*- and *trans*-imidazolidinones in pure form and of the corresponding ammonium and cinnamyl iminium salts has enabled us to perform a detailed structural analysis by X-ray-diffraction and NMR methods. The X-ray data of altogether 15 iminium salts provide statistically relevant information[4]) about the structural energy minima of the

[4]) In several publications, a single, accidentally obtained X-ray structure is used to draw general structural and mechanistic conclusions. In the present case, the many X-ray structures (this paper and [1][4][5][7–9][11g]) led to the discovery of four different conformations (*Fig. 1*) around the benzylic bond, and of the two different configurations of the exocyclic C=N bond of cinnamylidene imidazolidinones.

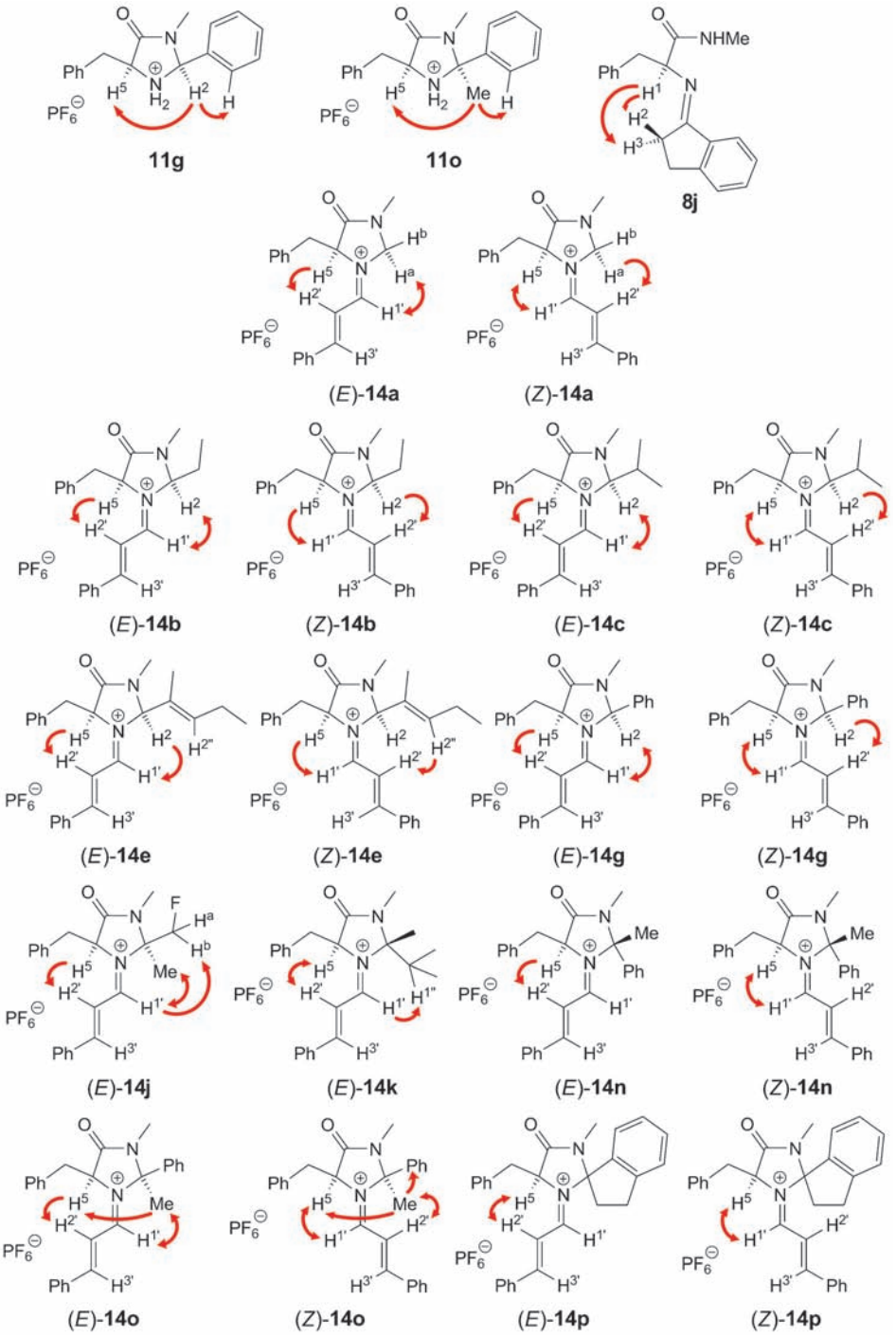


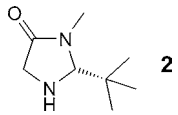
Fig. 2. *Configurational assignments of compounds* **8j**, **11**, *and* **14**, *derived from steady-state NOE difference NMR recordings* (see the red arrows)

iminium ions, which are intermediates of organocatalytic *Michael* additions to, and *Diels–Alder* reactions of cinnamaldehydes. Delicate effects of the substitution pattern on the configuration of the exocyclic iminium bond ((*E*) or (*Z*)) and on the conformation of the benzylic bond ((+)-*sc*, (−)-*sc*, *ac*, or *ap*) in solution have been unraveled by the NMR analysis.

Experimental Part

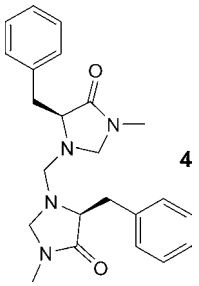
General. All reactions were performed under Ar in dried glassware using anh. solvents except when using aq. reagents. All chemicals were reagent grade and used as supplied, unless stated otherwise. Solvents for extractions and chromatography were technical grade and were distilled prior to use. Sat. hydrocarbon solvents were kept over Na wire. Extracts were dried over technical-grade $MgSO_4$. TLC: Precoated *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 *PerkinElmer Precisely Universal ATR Sampling Accessory*; in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AVANCE* (at 300 and 75 MHz, resp.), *DRX* (at 400 and 101 MHz, resp.), *AV* (at 400 and 101 MHz, resp.), or *Varian Gemini-300* (at 300 and 75 MHz, resp.) spectrometer; chemical shifts (δ) are reported in ppm relative to TMS (0.00 ppm). High-resolution (HR) MS: performed by the MS service at the Laboratory for Organic Chemistry, ETH Zürich on a *IonSpecUltima 4.7-T-FT Ion Cyclotron Resonance* (*ICR*; HR-MALDI, in 2,5-dihydroxybenzoic acid matrix) spectrometer. Elemental analyses: performed in the Microanalytical Laboratory at the Laboratory for Organic Chemistry, ETH Zürich.

*(*S*)-2-Amino*-N-*methyl-3-phenylpropanamide* (**3**) was prepared as described in [14].



2

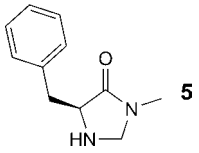
*(2*R*)-2-(*tert-*Butyl)-3-methylimidazolidin-4-one* (**2**) [12]. Prepared from Boc-BMI (**1**; 5.12 g, 20.0 mmol) as described in [13]. The crude product was purified by CC (AcOEt/hexane 2 : 1). Fractions containing the product were combined, and volatile components were evaporated *in vacuo* to give **2**. Yield: 2.91 g (93%). Yellowish oil. ^1H-NMR (300 MHz, $CDCl_3$): 0.98 (*s*, ^{t}Bu); 2.02 (br. *s*, NH); 2.96 (*s*, MeN); 3.44 (*d*, $J = 16.1$, 1 H, CH_2); 3.52 (*d*, $J = 16.2$, 1 H, CH_2); 4.13 (*s*, 1 H).



4

(5S,5′S)-1,1′-Methanediylbis(5-benzyl-3-methylimidazolidin-4-one) (**4**). A mixture of **3** (4.50 g, 25.25 mmol), paraformaldehyde (1.15 g), 1,3,5-trioxane (2.00 g, 22.20 mmol), and $TsOH \cdot H_2O$ (480 mg, 2.52 mmol) in anh. toluene (50 ml) under Ar was heated under reflux under *Dean–Stark* conditions using freshly activated 4-Å molecular sieves (MS) for 12 h. The reaction mixture was diluted with AcOEt (200 ml), and the resulting mixture was washed with $NaHCO_3$ (aq. sat., 50 ml) and twice with H_2O (30 ml). The org. phase was dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*.

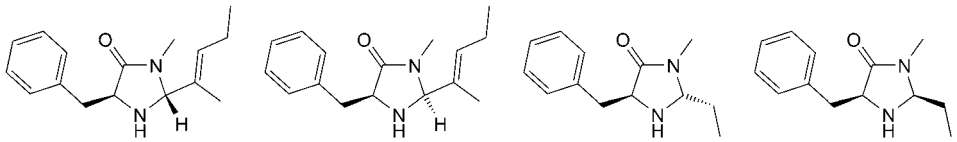
The residue was purified by CC: with 1. AcOEt/hexane 1:1 to elute the nonpolar impurities; 2. AcOEt to elute the product. Fractions containing the product were combined, and volatile components were evaporated *in vacuo* to give **4**. Yield: 3.50 g (70%). White solid. M.p. 62–70°. $[\alpha]_D^{r.t.} = -134.5$ ($c = 0.61$, CH_2Cl_2). IR: 2932*w*, 1635*s*, 1496*w*, 1452*m*, 1396*w*, 1357*m*, 1305*m*, 1274*w*, 1228*m*, 1144*w*, 1064*m*, 992*m*, 954*m*, 875*w*, 815*w*, 725*s*, 697*s*, 634*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.79 (*s*, 2 × MeN); 2.87 (*dd*, $J =$ 9.5, 14.6, 2 × 1 H, CH_2); 3.14 (*dd*, $J = 5.2$, 14.7, 2 × 1 H, CH_2); 4.01 (*s*, CH_2); 4.07 (*dd*, $J = 5.3$, 9.6, 2 × H–C(5)); 4.33 (*d*, $J = 15.2$, 2 × 1 H, H_2–C(2)); 4.80 (*d*, $J = 15.1$, 2 × 1 H, CH_2(2)); 7.11–7.18 (*m*, 1 arom. H); 7.20–7.32 (*m*, 4 arom. H). ^{13}C-NMR (101 MHz, (D_6)DMSO): 34.0; 36.3; 62.5; 64.0; 80.4; 125.6; 127.8; 129.0; 140.0; 174.5. HR-ESI-MS: 415.2104 (100, $[M + Na]^+$, $C_{23}H_{28}N_4NaO_2^+$; calc. 415.21045). Anal. calc. for $C_{23}H_{28}N_4O_2$ (392.49): C 70.38, H 7.19, N 14.27; found: C 70.14, H 7.31, N 13.89.



5

*(5*S*)-5-Benzyl-3-methylimidazolidin-4-one* (**5**). To a soln. of **3** (1.84 g, 10.35 mmol) in anh. toluene (50 ml), containing freshly activated 4-Å MS (20 g), was added HCHO (0.8 ml, 37% in H_2O), and the mixture was stirred at r.t. for 3 d. A white precipitate formed. Then, the mixture was heated under reflux for 5 h, the white precipitate dissolved, and the reaction mixture turned yellow. The mixture was filtered through a short plug of *Celite*® and washed up with AcOEt (100 ml). Volatile components were evaporated *in vacuo* and the residue was purified/separated by CC with 1. AcOEt to elute the nonpolar impurities; 2. AcOEt/EtOH 10:1 to elute **5**. Yield: 754 mg (38%). Yellow-orange solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.04 (br. *s*, NH); 2.77 (*s*, MeN); 2.93 (*dd*, $J = 7.2$, 14.0, 1 H, CH_2); 3.11 (*dd*, $J = 4.2$, 14.1, 1 H, CH_2); 3.71 (*dd*, $J = 4.3$, 6.9, H–C(5)); 4.00 (*dd*, $J = 0.7$, 7.0, 1 H, CH_2(2)); 4.19 (*d*, $J = 6.9$, 1 H, CH_2(2)); 7.14–7.32 (*m*, 5 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 27.7; 37.3; 60.5; 65.0; 126.7; 128.5; 129.5; 137.4; 174.3.

Preparation of Compounds **6a**, **6a′**, **6f**, **6g**, **6i**, **7a**, **7a′**, **7d**, **7e**, **7f**, **7g**, **7h**, **7i**, *and* **7j** *and Omide* **8j**. *General Procedure 1* (*GP 1*). To a soln. of **3** (1 equiv.) with or without $TsOH \cdot H_2O$ (0.1 equiv.) in anh. EtOH (V_1) under Ar was added the corresponding aldehyde/ketone (*x* equiv.), and the resulting mixture was heated under reflux under *Dean–Stark* conditions using freshly activated 4-Å MS for t_1 h. Volatile components were evaporated *in vacuo* and the residue was purified/separated by CC to give the desired compounds.



6a' **7a'** **6a** **7a**

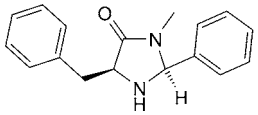
*(2*R*,5*S*)-5-Benzyl-3-methyl-2-[(2*E*)-pent-2-en-2-yl]imidazolidin-4-one* (**6a′**), *(2*S*,5*S*)-5-Benzyl-3-methyl-2-[(2*E*)-pent-2-en-2-yl]imidazolidin-4-one* (**7a′**), *(2*R*,5*S*)-5-Benzyl-2-ethyl-3-methylimidazolidin-4-one* (**6a**), *and (2*S*,5*S*)-5-Benzyl-2-ethyl-3-methylimidazolidin-4-one* (**7a**). Prepared from **3** (3.38 g, 18.96 mmol) and propanal (1.82 ml, 24.65 mmol). *GP 1:* V_1 50 ml; t_1 21 h; CC (AcOEt) to elute/separate **6a′**, **7a′**, **6a**, and **7a**.

Data of **6a′**. Eluted first. Yield: 350 mg (7%). Light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.95 (*t*, $J = 7.6$, *Me*CH_2); 1.45 (*d*, $J = 1.1$, Me); 1.93 (br. *s*, NH); 1.98–2.07 (*m*, Me*C*H_2); 2.59 (*s*, MeN); 2.86 (*dd*, $J = 7.6$, 13.8, 1 H, CH_2); 3.09 (*dd*, $J = 3.9$, 13.8, 1 H, CH_2); 3.89–3.94 (*m*, CH); 4.33 (*d*, $J = 2.0$, CH); 5.41 (*td*, $J = 1.2$; 7.1, CH); 7.18–7.30 (*m*, 5 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 9.2; 13.6; 20.9; 26.3; 39.0; 60.2; 81.2; 126.5; 128.3; 129.4; 132.1; 133.8; 137.7; 173.6.

Data of **7a′**. Eluted second. Yield: 204 mg (4%). Light-yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.94 (*td*, *J* = 1.6, 7.5, *Me*CH_2); 1.15 (*s*, Me); 1.77 (br. *s*, NH); 1.96–2.08 (*m*, MeC*H*$_2$); 2.62 (*s*, MeN); 2.96–3.20 (*m*, CH_2); 3.75 (br. *s*, CH); 4.57 (*s*, CH); 5.50 (*t*, *J* = 7.0, CH); 7.15–7.32 (*m*, 5 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 8.8; 13.7; 21.1; 26.7; 37.7; 59.9; 80.9; 126.7; 128.6; 129.6; 131.3; 135.1; 137.5; 174.1.

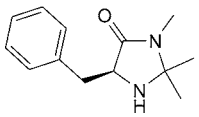
Data of **6a**. Eluted third. Yield: 506 mg (12%, <99% ee). Yellow oil. $[\alpha]_D^{r.t.} = -94.4$ (*c* = 0.30, CH_2Cl_2). HPLC (*Chiralpak AD-H*; hexane/^{i}PrOH 98:2; flow rate, 1.0 ml/min; λ 205 nm): t_R [min] 22.2 (minor); 27.5 (major). IR (NaCl): 3322, 2965, 2925, 2876, 1694, 1496, 1454, 1434, 1403, 1347, 1277, 1116, 1089, 990, 937, 750, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.4, *Me*CH_2); 1.42–1.52 (*m*, 1 H, MeC*H*$_2$); 1.63–1.72 (*m*, 1 H, MeC*H*$_2$); 1.92 (br. *s*, NH); 2.73 (*s*, MeN); 2.93 (*dd*, *J* = 7.1, 13.9, 1 H, CH_2); 3.08 (*dd*, *J* = 4.2, 13.9, 1 H, CH_2); 3.82–3.86 (*m*, CH); 4.02–4.06 (*m*, CH); 7.21–7.32 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 6.9; 25.9; 26.3; 37.8; 59.6; 74.7; 126.1; 127.9; 129.1; 137.3; 173.7. HR-EI-MS: 219.1493 $[M+H]^+$, $C_{13}H_{19}N_2O$; calc. 219.1497.

Data of **7a**. Eluted fourth. Yield: 514 mg (12%, <99% ee). Yellow oil. $[\alpha]_D^{r.t.} = -56.3$ (*c* = 0.32, CH_2Cl_2). HPLC (*Chiralpak AD-H*; hexane/^{i}PrOH 96:4; flow rate, 1.0 ml/min, λ 205 nm): t_R [min] 14.9 (major); 16.0 (minor). IR (NaCl): 3332, 2965, 2926, 1694, 1496, 1481, 1454, 1436, 1405, 1349, 1277, 1089, 995, 748, 701.^{1}H-NMR (300 MHz, $CDCl_3$): 0.66 (*t*, *J* = 7.5, *Me*CH_2); 1.23–1.39 (*m*, 1 H, MeC*H*$_2$); 1.63–1.77 (*m*, 1 H, MeC*H*$_2$); 2.22 (br *s*, NH); 2.76 (s, MeN); 3.01 (*dd*, *J* = 6.8; 14.1, 1 H, CH_2); 3.16 (*dd*, *J* = 4.4, 14.1, 1 H, CH_2); 3.70–3.76 (*m*, CH); 4.29 (*ddd*, *J* = 1.2; 2.6; 6.5, CH); 7.19–7.33 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 6.2; 25.6; 26.6; 37.3; 59.9; 74.2; 126.5; 128.3; 129.3; 137.1; 174.2. EI-HRMS: 219.1490 $[M+H]^+$, $C_{13}H_{19}N_2O^+$; calc. 219.1497.



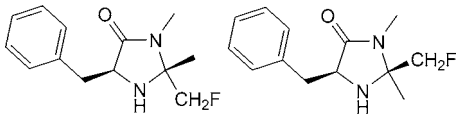
7d

(2S,5S)-5-Benzyl-3-methyl-2-phenylimidazolidin-4-one (**7d**) [17]. Prepared from **3** (4.84 g, 27.18 mmol) and PhCHO (3.57 ml, 35.33 mmol). *GP 1:* V_1 50 ml; t_1 20 h; CC with 1. AcOEt/hexane 2:1 to elute unreacted PhCHO and other nonpolar impurities; 2. AcOEt to elute **7d**. Yield: 978 mg (13%) Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.83 (*t*, *J* = 8.5, NH); 2.55 (*s*, MeN); 3.14 (*dd*, *J* = 4.7, 14.1, 1 H, CH_2); 3.25 (*dd*, *J* = 5.7, 14.1, 1 H, CH_2); 3.82–3.91 (*m*, H–C(5)); 5.13 (*d*, *J* = 6.8, H–C(2)); 6.80–6.86 (*m*, 2 arom. H); 7.19–7.35 (*m*, 8 arom. H).



7e

(5S)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one (**7e**) [2]. Prepared from **3** (2.20 g, 12.35 mmol) and Me_2CO (3 ml, 40.9 mmol). *GP 1:* V_1 30 ml; t_1 18 h; CC (AcOEt/hexane 2:1): **7e**. Yield: 2.29 g (85%) Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*s*, Me); 1.26 (*d*, *J* = 1.7, Me); 1.66 (br *s*, NH); 2.75 (*d*, *J* = 0.6, MeN), 3.00 (*dd*, *J* = 6.8, 14.1, 1 H, CH_2); 3.15 (*dd*, *J* = 4.5, 14.1, 1 H, CH_2); 3.79 (*dd*, *J* = 4.7, 6.5, CH); 7.18–7.33 (*m*, 5 arom. H).



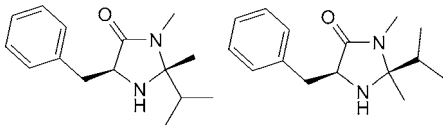
6f **7f**

(2R,5S)-5-Benzyl-2-(fluoromethyl)-2,3-dimethylimidazolidin-4-one (**6f**) *and (2S,5S)-5-Benzyl-2-(fluoromethyl)-2,3-dimethylimidazolidin-4-one* (**7f**). Prepared from **3** (2.02 g, 11.33 mmol) and 1-

fluoropropan-2-one (1.00 g, 13.15 mmol). *GP 1:* V_1 50 ml; t_1 16 h; **6f**/**7f** 1:0.64; CC with 1. AcOEt/hexane 2:1 to elute **6f**; 2. AcOEt to elute **7f**.

Data of **6f**. Yield: 794 mg (29%, < 99% ee). Yellowish oil. $[\alpha]_D^{r.t.} = -65.2$ ($c = 0.32$, CH_2Cl_2). HPLC (*Chiralcel OD-H*, hexane/^{i}PrOH 95:5; flow rate, 1.0 ml/min; λ 205 nm): t_R [min] 18.0 (major); 25.8 (minor). IR (NaCl): 3492, 3320, 3028, 2980, 2931, 1694, 1496, 1454, 1430, 1402, 1283, 1145, 1086, 1031, 750, 702. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*d*, $J = 2.4$, Me); 1.78 (br. *s*, NH); 2.82 (*s*, MeN); 3.04 (*dd*, $J =$ 6.3, 14.2, 1 H, CH_2); 3.12 (*dd*, $J = 4.7$, 14.2, 1 H, CH_2); 3.85 (*t*, $J = 5.5$, H–C(5)); 4.13 (*dd*, $J = 9.6$, 17.4, 1 H, CH_2F); 4.29 (*dd*, $J = 9.6$, 17.6, 1 H, CH_2F); 7.18–7.34 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0 (*d*, $J = 2.5$); 25.6 (*d*, $J = 2.0$); 37.6; 59.4 (*d*, $J = 0.8$); 75.9 (*d*, $J = 18.3$); 86.1 (*d*, $J = 180.0$); 126.8; 128.5; 129.4; 136.7; 173.7. HR-EI-MS: 237.1410 $[M + H]^+$, $C_{13}H_{18}FN_2O$; calc. 237.1403).

Data of **7f**. Yield: 657 mg (24%, < 98% ee) Yellowish oil. $[\alpha]_D^{r.t.} = -93.8$ ($c = 0.18$, CH_2Cl_2). HPLC (*Chiralcel OD-H*; hexane/^{i}PrOH 95:5; flow rate, 1.0 ml/min, λ 205 nm): t_R [min] 22.0 (major); 25.4 (minor). IR (NaCl): 3332, 3029, 2980, 2931, 1694, 1496, 1454, 1434, 1402, 1288, 1088, 1032, 1006, 750, 701. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.32 (*d*, $J = 2.8$, Me); 1.97 (br. *s*, NH); 2.81 (*dd*, $J = 8.6$, 13.9, 1 H, CH_2); 2.85 (*s*, MeN); 3.18 (*dd*, $J = 3.8$, 13.9, 1 H, CH_2); 3.85–3.92 (*m*, H–C(5)); 3.95 (*dd*, $J = 10.0$; 47.8, 1 H, CH_2F); 4.15 (*dd*, $J = 10.0$, 47.6, 1 H, CH_2F); 7.19–7.33 (*m*, 5 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.0 (*d*, $J =$ 1.7); 25.7 (*d*, $J = 2.4$); 39.0; 59.4; 76.3 (*d*, $J = 18.9$); 86.2 (*d*, $J = 180.6$); 126.6; 128.5; 129.6; 138.0; 173.2. HR-EI-MS: 237.1406 $[M + H]^+$, $C_{13}H_{18}FN_2O^+$; calc. 237.1403.

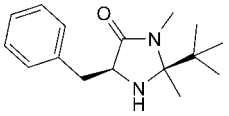


6g **7g**

*(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-(propan-2-yl)imidazolidin-4-one* (**6g**) *and (2*S*,5*S*)-5-Benzyl-2,3-dimethyl-2-(propan-2-yl)imidazolidin-4-one* (**7g**). Prepared from **3** (3.42 g, 19.19 mmol), 3-methylbutan-2-one (2.47 µl, 23.03 mmol), and $TsOH \cdot H_2O$ (130 mg, 0.863 mmol). *GP 1:* V_1 50 ml; t_1 24 h; CC with 1. AcOEt/hexane 1:1 to elute **6g**; 2. AcOEt to elute **7g**.

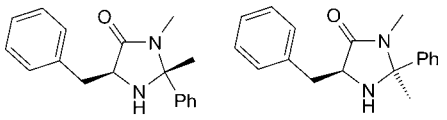
Data of **6g**. Yield: 1.80 g (38%). Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.74 (*d*, $J = 6.7$, 3 H, Me_2CH); 0.89 (*d*, $J = 6.7$, 3 H, Me_2CH); 0.91 (*s*, Me); 1.38 (br. *s*, NH); 1.75–1.86 (*m*, Me_2CH); 2.69 (*d*, $J = 0.6$, MeN); 3.03 (*dd*, $J = 5.0$, 14.1, 1 H, CH_2); 3.09 (*dd*, $J = 5.6$, 14.1, 1 H, CH_2); 3.79 (*t*, $J = 5.1$, H–C(5)); 7.18–7.25 (*m*, 3 arom. H); 7.26–7.32 (*m*, 2 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 16.4; 16.7; 25.3; 25.3; 35.1; 38.3; 60.6; 80.3; 126.8; 128.6; 129.8; 137.1; 173.2.

Data of **7g**. Yield: 1.90 g (40%). Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.44 (*d*, $J = 6.8$, 3 H, Me_2CH); 0.87 (*d*, $J = 6.9$, 3 H, Me_2CH); 1.27 (*s*, Me); 1.54 (br. *d*, $J = 6.4$, NH); 1.76–1.88 (*m*, Me_2CH); 2.70 (*d*, $J = 0.5$, MeN); 3.00 (*dd*, $J = 7.0$, 13.8, 1 H, CH_2); 3.13 (*dd*, $J = 4.2$; 13.8, 1 H, CH_2); 3.79 (br. *d*, $J =$ 3.2, H–C(5)); 7.17–7.32 (*m*, 5 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 15.5; 16.4; 23.1; 25.3; 33.6; 37.3; 58.7; 79.8; 126.7; 128.6; 129.7; 137.7; 173.2.



7h

*(2*S*,5*S*)-5-Benzyl-2-(*tert*-butyl)-2,3-dimethylimidazolidin-4-one* (**7h**) [18]. Prepared from **3** (3.22 g, 18.06 mmol) and 3,3-dimethylbutan-2-one (4.48 ml, 36.11 mmol; *GP 1:* V_1 50 ml; t_1 23 h; CC with 1. AcOEt/hexane 1:1 to elute nonpolar impurities; 2. AcOEt to elute **7h**. Yield: 1.95 g (41%). Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.81 (*s*, ^{t}Bu); 1.24 (*s*, Me); 1.61 (br. *d*, $J = 9.5$, NH); 2.86 (*s*, MeN); 3.04 (*dd*, $J = 6.8$, 13.7, 1 H, CH_2); 3.13 (*dd*, $J = 4.4$; 13.7, 1 H, CH_2); 3.68–3.78 (*m*, CH); 7.18–7.34 (*m*, 5 arom. H).

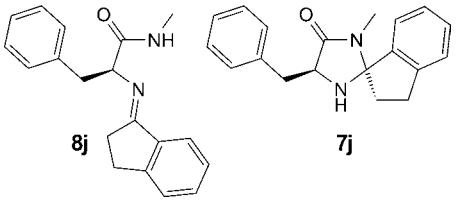


6i **7i**

*(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-phenylimidazolidin-4-one* (**6i**) *and (2*S*,5*S*)-5-Benzyl-2,3-dimethyl-2-phenylimidazolidin-4-one* (**7i**). Prepared from **3** (4.46 g, 25.05 mmol), acetophenone (3.22 µl, 27.56 mmol), and TsOH · H_2O (200 mg, 1.051 mmol). *GP 1:* V_1 50 ml; t_1 23 h; CC with 1. AcOEt/hexane 1:2 to elute nonpolar impurities; 2. AcOEt/hexane 1:1 to elute **6i**; 3. AcOEt to elute **7i**.

Data of **6i**. Yield: 2.03 g (28%). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.55 (*s*, Me); 2.02 (br. *s*, NH); 2.73 (*d*, *J* = 0.4, MeN); 3.00 (*dd*, *J* = 7.2, 13.9, 1 H, CH_2); 3.15 (*dd*, *J* = 4.2, 13.9, 1 H, CH_2); 3.86 (*dd*, *J* = 4.3, 7.0, H–C(5)); 7.17–7.36 (*m*, 10 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 26.1; 26.2; 38.3; 59.3; 78.6; 125.1; 126.7; 128.1; 128.5; 128.9; 129.7; 137.6; 142.8; 173.7.

Data of **7i**. Yield: 2.32 g (33%). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.70 (*s*, Me); 1.98 (br. *s*, NH); 2.52 (*s*, MeN); 3.08 (*dd*, *J* = 4.7, 14.0, 1 H, CH_2); 3.26 (*dd*, *J* = 5.6, 14.0, 1 H, CH_2); 3.91 (br. *s*, H–C(5)); 6.85–6.90 (*m*, 2 arom. H); 7.16–7.32 (*m*, 8 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 22.8; 26.2; 36.5; 59.6; 79.0; 126.0; 126.9; 128.5; 128.8; 128.9; 129.9; 136.8; 142.0; 173.7.

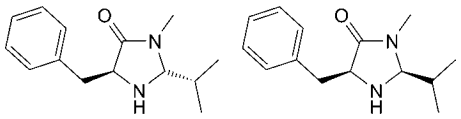


8j **7j**

*(2*S*)-2-[(*E*)-2,3-Dihydro-1*H*-inden-1-ylideneamino]-*N*-methyl-3-phenylpropanamide* (**8j**) *and (2*S*,5*S*)-5-Benzyl-2′,3′-dihydro-3-methyl-4*H*-spiro[imidazolidine-2,1′-inden]-4-one* (**7j**). Prepared from **3** (3.53 g, 19.81 mmol), 2,3-dihydro-1*H*-inden-1-one (3.14 g, 23.77 mmol), and TsOH · H_2O (160 mg, 0.841 mmol). *GP 1:* V_1 70 ml; t_1 24 h; CC with 1. AcOEt/hexane 1:1 to elute nonpolar impurities; 2. AcOEt to elute/separate **8j** (first fraction) and **7j** (second fraction). Mixed fractions of compounds **8j** and **7j** were re-separated by CC (AcOEt).

Data of **8j**. Yield: 700 mg (12%). Colorless oil that turns black after some time even when stored under Ar. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.46 (*ddd*, *J* = 4.0, 9.0, 18.0, 1 H, CH_2); 2.37 (*ddd*, *J* = 3.8, 8.9, 18.0, 1 H, CH_2); 2.60–2.70 (*m*, 1 H, CH_2); 2.78–2.87 (*m*, 1 H, CH_2); 2.85 (*d*, *J* = 5.0, *Me*NH); 2.93 (*dd*, *J* = 9.7, 13.1, 1 H, CH_2); 3.41 (*dd*, *J* = 2.9, 13.1, 1 H, CH_2); 4.18 (*dd*, *J* = 2.9, 9.7, H–C(5)); 7.08 (br. *s*, MeN*H*); 7.09–7.18 (*m*, 5 arom. H); 7.25–7.33 (*m*, 2 arom. H); 7.39 (*td*, *J* = 1.2, 7.4, 1 arom. H); 7.85 (*d*, *J* = 7.6, 1 arom. H). ^{13}C-NMR (101 MHz, CDCl3): 25.9; 28.1; 28.2; 41.2; 68.5; 122.4; 125.7; 126.4; 126.9; 128.1; 130.0; 131.6; 138.7; 139.3; 150.0; 173.6; 175.6. HR-ESI-MS: 293.1648 (100, $[M + H]^+$, $C_{19}H_{21}N_2O^+$; calc. 293.16484).

Data of **7j**. Yield: 2.40 g (41%). Orange-brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.84 (br. *s*, NH); 2.16–2.21 (*m*, CH_2); 2.57 (*d*, *J* = 0.5, MeN); 2.84–2.92 (*m*, 1 H, CH_2); 2.98–3.08 (*m*, 1 H, CH_2); 3.08 (*dd*, *J* = 5.0, 14.1, 1 H, CH_2); 3.31 (*dd*, *J* = 5.1, 14.1, 1 H, CH_2); 3.88 (*t*, *J* = 4.9, H–C(5)); 6.19 (*d*, *J* = 7.5, 1 arom. H); 7.02–7.09 (*m*, 1 arom. H); 7.18–7.33 (*m*, 7 arom. H). ^{13}C-NMR (101 MHz, $CDCl_3$): 26.0; 29.1; 35.5; 36.5; 59.4; 88.0; 122.5; 125.3; 127.0; 127.4; 128.9; 129.7; 130.0; 136.5; 141.7; 144.3; 174.1.

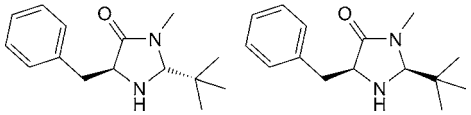


6b **7b**

*(2*R*,5*S*)-5-Benzyl-3-methyl-2-(propan-2-yl)imidazolidin-4-one* (**6b**) *and (2*S*,5*S*)-5-Benzyl-3-methyl-2-(propan-2-yl)imidazolidin-4-one* (**7b**). Prepared according to a slightly modified procedure described in [16]. To a soln. of **3** (2.22 g, 12.44 mmol) in anh. benzene (50 ml) under Ar at r.t., isobutyraldehyde (1.15 ml, 12.44 mmol) and $FeCl_3$ (400 mg, 2.47 mmol) were added, and the resulting mixture was heated under reflux under *Dean–Stark* conditions using freshly activated 4-Å MS for 18 h. The mixture was diluted with AcOEt (150 ml), washed with aq. sat. $NaHCO_3$ soln. (50 ml) and twice with brine (30 ml). The org. phase was dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*. ^{1}H-NMR of the residue showed a ratio **6b**/**7b** of 1:0.80. The residue was purified by CC with 1. AcOEt/hexane 1:1 to elute nonpolar impurities; 2. AcOEt/hexane 2:1 to elute **6b**; 3. AcOEt to elute **7b**. Fractions containing the product were combined, and volatile components were evaporated *in vacuo* to give **6b** and **7b**, resp.

Data of **6b**. Yield: 816 mg (28%). Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.80 (*d*, *J* = 6.7, Me); 0.96 (*d*, *J* = 6.9, Me); 1.90–2.02 (*m*, CH); 2.73 (*s*, MeN); 3.01 (*dd*, *J* = 6.1; 13.3, 1 H, CH_2); 3.15 (*dd*, *J* = 4.3, 14.0, 1 H, CH_2); 3.91 (br. *s*, CH); 4.06 (br. *s*, CH); 7.20–7.41 (*m*, 5 arom. H).

Data of **7b**. Yield: 770 mg (26%). Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.45 (*d*, *J* = 6.9, Me); 0.94 (*d*, *J* = 7.0, Me); 1.94–2.05 (*m*, CH); 2.78 (*s*, MeN); 3.15 (*dd*, *J* = 2.6, 5.4, CH_2); 3.87 (*t*, *J* = 5.2, CH); 4.39 (*d*, *J* = 2.6, CH); 7.20–7.35 (*m*, 5 arom. H).



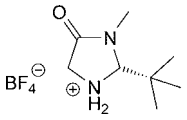
6c **7c**

*(2*R*,5*S*)-5-Benzyl-2-(*tert*-butyl)-3-methylimidazolidin-4-one* (**6c**) *and (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-methylimidazolidin-4-one* (**7c**) [16]. Prepared according to a slightly modified procedure described in [16]. To a soln. of **3** (2.32 g, 13.02 mmol) in anh. toluene (50 ml) under Ar at r.t., pivalaldehyde (1.46 ml, 13.02 mmol) and $FeCl_3$ (422 mg, 2.60 mmol) were added, and the resulting mixture was heated under reflux under *Dean–Stark* conditions using freshly activated 4-Å MS for 14 h. The mixture was diluted with AcOEt (200 ml), and the resulting mixture was washed with aq. sat. $NaHCO_3$ soln. (50 ml) and twice with brine (30 ml). The org. phase was dried ($MgSO_4$), filtered, and volatile components were evaporated *in vacuo*. The residue was purified by CC (AcOEt/hexane 1:1). Fractions containing the product were combined, and volatile components were evaporated *in vacuo* to give **6c** and **7c**, resp.

Data of **6c**. Eluted first. Yield: 1.12 g (35%). Yellowish solid. ^{1}H-NMR (300 MHz, $CDCl_3$): ^{1}H-NMR (300 MHz, $CDCl_3$): 0.90 (*s*, ^{t}Bu); 1.87 (br. *s*, NH); 2.89 (*dd*, *J* = 7.1, 14.0, 1 H, CH_2); 2.89 (*d*, *J* = 0.6, MeN); 3.11 (*dd*, *J* = 4.2, 14.0, 1 H, CH_2); 3.80 (*d*, *J* = 1.8, CH); 3.82–3.87 (*m*, CH); 7.19–7.33 (*m*, 5 arom. H).

Data of **7c**. Eluted second. Yield: 930 mg (29%). Yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.83 (*s*, ^{t}Bu); 1.68 (br. *s*, NH); 2.91 (*d*, *J* = 0.5, MeN); 2.93 (*dd*, *J* = 7.6, 13.7, 1 H, CH_2); 3.15 (*dd*, *J* = 4.0, 13.7, 1 H, CH_2); 3.70 (br. *s*, CH); 4.05 (br. *s*, CH); 7.16–7.34 (*m*, 5 arom. H).

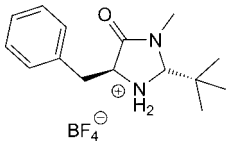
Preparation of BF_4^- *Salts* **9**, **10a**, **10b**, *and* **10c**. *General Procedure 2* (*GP 2*). To a soln. of a imidazolidin-4-one (1 equiv.) in dry Et_2O (V_1) at 0° under Ar was added a soln. of $HBF_4 \cdot Et_2O$ (1 equiv.) in dry Et_2O (V_2) at r.t. during 10 min. The reaction mixture was stirred for additional t_1 min at 0° and t_2 min at r.t. The precipitate was collected by filtration, washed with dry Et_2O (30 ml), and dried on high vacuum to give BF_4^- salts **9**, **10a**, **10b**, and **10c**.



9

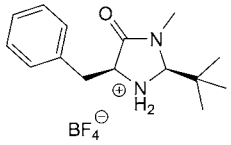
*(2*R*)-2-(*tert*-Butyl)-3-methyl-4-oxoimidazolidin-1-ium Tetrafluoroborate* (**9**). Prepared from **2** (827 mg, 5.29 mmol) and $HBF_4 \cdot Et_2O$ (726 µl, 5.29 mmol). *GP 2:* V_1 60 ml; V_2 20 ml; t_1 60 min; t_2 60 min. Yield: 1.19 g (92%). Light-yellow solid. M.p. 118–123°. $[\alpha]_D^{r.t.} = -3.6$ (*c* = 0.75, EtOH). IR:

3202*w*, 3132*w*, 2975*w*, 1716*s*, 1591*m*, 1478*w*, 1449*w*, 1435*w*, 1405*w*, 1382*m*, 1371*w*, 1364*w*, 1334*m*, 1259*w*, 1152*w*, 1099*s*, 1030*s*, 998*s*, 984*s*, 947*s*, 913*s*, 830*m*, 767*w*, 673*s*, 653*w*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 1.01 (*s*, ^{t}Bu); 2.89 (*s*, MeN); 3.71 (*d*, $J = 15.6$, 1 H, CH_2); 3.80 (*d*, $J = 15.6$, 1 H, CH_2); 4.62 (*s*, CH); 8.34 (br. *s*, NH_2^+). ^{13}C-NMR (75 MHz, (D_6)DMSO): 24.6; 31.0; 36.0; 45.1; 81.5; 168.2. HR-ESI-MS: 157.1335 (100, M^+, $C_8H_{17}N_2O^+$; calc. 157.13354). Anal. calc. for $C_8H_{17}BF_4N_2O$ (244.04): C 39.37, H 7.02, N 11.48; found: C 39.09, H 6.94, N 11.48.



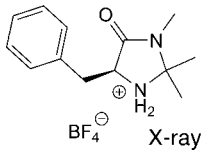
10a

*(2*R*,5*S*)-5-Benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-ium Tetrafluoroborate* (**10a**). Prepared from **6c** (1.45 g, 5.88 mmol) and $HBF_4 \cdot Et_2O$ (807 µl, 5.88 mmol). *GP 2:* V_1 60 ml; V_2 20 ml; t_1 60 min; t_2 15 min. Yield: 1.70 g (86%). Light-brown solid. M.p. 120–122°. $[\alpha]_D^{r.t.} = -50.0$ ($c = 0.23$, EtOH). IR: 2977*w*, 1723*m*, 1707*s*, 1570*w*, 1484*w*, 1458*w*, 1430*w*, 1406*w*, 1372*w*, 1352*w*, 1332*w*, 1261*w*, 1234*w*, 1091*s*, 1063*s*, 1035*s*, 1006*s*, 983*s*, 752*s*, 715*w*, 702*s*, 664*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*s*, ^{t}Bu); 2.95 (*s*, MeN); 3.33 (*dd*, $J = 6.8, 14.5$, 1 H, CH_2); 3.47 (*dd*, $J = 3.8, 14.6$, 1 H, CH_2); 4.38 (*s*, CH); 4.43 (br. *s*, CH); 7.28–7.41 (*m*, 5 arom. H); 7.70 (br. *s*, 1 H, NH_2^+); 7.88 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (75 MHz, (D_6)DMSO): 24.6; 31.7; 35.4; 36.3; 57.9; 80.2; 127.2; 128.6; 129.5; 135.6; 168.5. HR-ESI-MS: 247.1805 (100, M^+, $C_{15}H_{23}N_2O^+$; calc. 247.18049). Anal. calc. for $C_{15}H_{23}BF_4N_2O$ (334.16): C 53.91, H 6.94, N 8.38; found: C 53.63, H 6.79, N 8.33.



10b

*(2*S*,5*S*)-5-Benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-ium Tetrafluoroborate* (**10b**). Prepared from **7c** (1.07 g, 4.35 mmol) and $HBF_4 \cdot Et_2O$ (597 µl, 4.35 mmol). *GP 2:* V_1 50 ml; V_2 20 ml; t_1 10 min. The resulting precipitate was quickly collected on a dry ceramic frit under Ar, washed with dry Et_2O (20 ml), dried on high vacuum, and stored under Ar (the product is highly hygroscopic!). Yield: 980 mg (67%). Light-brown solid. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.75 (*s*, ^{t}Bu); 2.98 (*s*, MeN); 3.34 (*dd*, $J = 6.3, 14.7$, 1 H, CH_2); 3.69 (*dd*, $J = 2.4, 14.7$, 1 H, CH_2); 4.56 (br. *s*, CH); 4.83 (*d*, $J = 6.4$, CH); 5.50 (br. *s*, 1 H, NH_2^+); 7.29–7.46 (*m*, 5 arom. H); 8.85 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (75 MHz, (D_6)DMSO): 25.0; 30.5; 33.7; 33.8; 58.2; 79.4; 127.0; 128.6; 129.1; 136.5; 169.6.



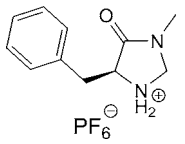
10c

X-ray

*(5*S*)-5-Benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-ium Tetrafluoroborate* (**10c**). Prepared from **7e** (463 mg, 2.12 mmol) and $HBF_4 \cdot Et_2O$ (291 µl, 2.12 mmol). *GP 2:* V_1 100 ml; V_2 20 ml; t_1 10 min; t_2 20 min. Yield: 540 mg (83%). White solid. M.p. 125–127°. $[\alpha]_D^{r.t.} = -59.3$ ($c = 0.18$, CH_2Cl_2). IR: 3067*w*, 1725*s*, 1612*w*, 1456*w*, 1435*w*, 1411*m*, 1397*s*, 1388*m*, 1371*m*, 1316*w*, 1272*w*, 1259*w*, 1154*w*, 1122*s*, 1058*s*, 1029*s*, 999*s*, 965*s*, 915*m*, 762*m*, 744*m*, 700*s*, 672*w*, 612*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.47 (*s*, Me); 1.60 (*s*, Me); 2.79 (*s*, MeN); 2.93 (*dd*, $J = 10.5, 15.1$, 1 H, CH_2); 3.32 (*dd*, $J = 3.3, 15.1$, 1 H, CH_2); 4.57 (br. *d*, $J = 5.6$, CH); 7.26–7.42 (*m*, 5 arom. H); 9.05 (br. *s*, 1 H, NH_2^+); 10.17 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 22.0; 24.2; 24.9; 34.1; 57.4; 76.7; 127.0; 128.6; 129.1; 136.2; 166.9. HR-ESI-MS:

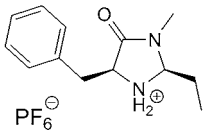
219.1492 (100, M^+, $C_{13}H_{19}N_2O^+$; calc. 219.14919). Anal. calc. for $C_{13}H_{19}BF_4N_2O$ (306.11): C 51.01, H 6.26, N 9.15; found: C 50.79, H 6.22, N 9.08.

Preparation of PF_6^- Salts **11a**–**11p**. *General Procedure 3* (*GP 3*). To a soln./emulsion of HPF_6 (*ca.* 60% in H_2O, 1.05 equiv.) in Et_2O (V_1) at 0° was added a soln. of imidazolidin-4-one (1 equiv.) in Et_2O (V_2) at r.t. during t_1 minutes. The reaction mixture was stirred for additional t_2 min at 0°. The precipitate was collected by filtration, washed with Et_2O (50 ml), and dried: in high vacuum to give **11a**–**11p**.



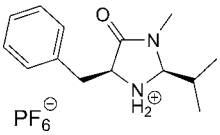
11a

*(5*S*)-5-Benzyl-3-methyl-4-oxoimidazolidin-1-ium Hexafluorophosphate* (**11a**). Prepared from **5** (611 mg, 3.21 mmol) and HPF_6 (497 µl, 3.37 mmol). (*GP 3*): V_1 80 ml; V_2 80 ml; t_1 10 min; t_2 20 min. Yield: 900 mg (83%). Yellow solid. M.p. 162–166°. $[\alpha]_D^{r.t.} = -55.2$ ($c = 0.13$, EtOH). IR: 1689*m*, 1501*w*, 1458*w*, 1417*w*, 1387*w*, 1365*w*, 1287*w*, 870*m*, 822*s*, 750*m*, 719*w*, 700*m*, 677*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.84 (*s*, MeN); 2.96 (*dd*, $J = 10.4$, 15.0, 1 H, CH_2); 3.31 (*dd*, $J = 3.9$, 15.0, 1 H, CH_2); 4.31 (*dd*, $J = 3.8$, 10.3, H–C(5)); 4.50 (*d*, $J = 7.4$, 1 H, CH_2(2)); 4.54 (*d*, $J = 7.4$, 1 H, CH_2(2)); 7.27–7.43 (*m*, 5 arom. H); 9.90 (*s*, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 27.7; 33.8; 58.4; 59.5; 127.3; 128.8; 129.1; 135.6; 166.9. HR-ESI-MS: 191.1179 (100, M^+, $C_{11}H_{15}N_2O^+$; calc. 191.11789). Anal. calc. for $C_{11}H_{15}F_6N_2OP$ (336.21): C 39.30, H 4.50, N 8.33; found: C 40.35, H 4.44, N 8.28.



11b

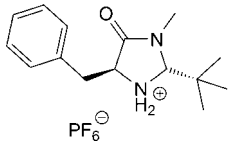
*(2*S*,5*S*)-5-Benzyl-2-ethyl-3-methyl-4-oxoimidazolidin-1-ium Hexafluorophosphate* (**11b**). Prepared from **7a** (500 mg, 2.29 mmol) and HPF_6 (354 µl, 2.41 mmol). *GP 3:* V_1 60 ml; V_2 60 ml; t_1 20 min; t_2 40 min. An oily precipitate was formed. The reaction mixture was decanted, and Et_2O (100 ml) was added to the oily residue, followed by scratching with spatula until the oily residue turned to a solid. The mixture was decanted again, Et_2O (100 ml) was added to the residue, followed by vigorous stirring at r.t. for 15 min. The process was repeated once more, until a fine filterable precipitate was formed. Yield: 710 mg (85%). White solid. M.p. 142–145°. $[\alpha]_D^{r.t.} = -29.1$ ($c = 0.28$, EtOH). IR: 2922*w*, 1695*m*, 1497*w*, 1457*w*, 1399*w*, 1353*w*, 1284*w*, 1259*w*, 1234*w*, 1090*w*, 1037*w*, 950*w*, 934*w*, 831*s*, 791*m*, 756*m*, 743*m*, 706*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.97 (*t*, $J = 7.4$, *Me*CH_2); 1.63–1.76 (*m*, 1 H, MeCH_2); 2.10–2.22 (*m*, 1 H, MeCH_2); 2.83 (*s*, MeN); 2.98 (*dd*, $J = 10.5$, 15.3, 1 H, CH_2); 3.36 (*dd*, $J = 3.6$, 15.4, 1 H, CH_2); 4.35 (*dd*, $J = 3.2$, 10.4, CH); 4.66 (*dd*, $J = 3.0$, 9.6, CH); 7.28–7.46 (*m*, 5 arom. H); 9.08 (br. *s*, 1 H, NH_2^+); 10.68 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 7.9; 23.2; 26.9; 33.6; 58.8; 72.7; 127.1; 128.7; 129.0; 136.0; 167.5. HR-ESI-MS: 219.1492 (100, M^+, $C_{13}H_{19}N_2O^+$; calc. 219.14919). Anal. calc. for $C_{13}H_{19}F_6N_2OP$ (364.27): C 42.86, H 5.26, N 7.69; found: C 43.14, H 5.24, N 7.60.



11c

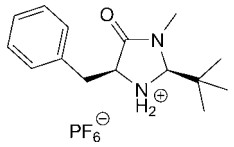
*(2*S*,5*S*)-5-Benzyl-3-methyl-4-oxo-2-(propan-2-yl)imidazolidin-1-ium Hexafluorophosphate* (**11c**). Prepared from **7b** (750 mg, 3.23 mmol) and HPF_6 (499 µl, 3.39 mmol). *GP 3:* V_1 100 ml; V_2 50 ml; t_1 20 min; t_2 30 min. Yield: 1.01 g (82%). Orange-yellow solid. M.p. 163–167°. $[\alpha]_D^{r.t.} = -19.6$ ($c = 0.37$, EtOH). IR: 1689*m*, 1466*w*, 1402*w*, 1362*w*, 1323*w*, 1263*w*, 1229*w*, 1111*w*, 1044*w*, 938*w*, 830*s*, 771*m*, 747*w*,

711*m*, 615*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.92 (*d*, *J* = 7.0, Me); 1.04 (*d*, *J* = 7.1, Me); 2.29 – 2.41 (*m*, CH); 2.83 (*s*, MeN); 3.09 (*dd*, *J* = 9.3, 15.6, 1 H, CH_2); 3.32 (*dd*, *J* = 4.0, 15.6, CH_2); 4.38 (*dd*, *J* = 3.8, 9.1, H–C(5)); 4.72 (*d*, *J* = 3.7, H–C(2)); 7.26 – 7.34 (*m*, 1 arom. H); 7.35 – 7.44 (*m*, 4 arom. H); 8.23 (br. *s*, 1 H, NH_2^+); 10.60 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 13.8; 16.5; 27.3; 27.6; 33.7; 58.3; 75.7; 127.0; 128.5; 128.9; 136.2; 168.3. HR-ESI-MS: 233.1648 (100, M^+, $C_{14}H_{21}N_2O^+$; calc. 233.16484). Anal. calc. for $C_{14}H_{21}F_6N_2OP$ (378.29): C 44.45, H 5.60, N 7.41; found: C 44.74, H 5.69, N 7.14.



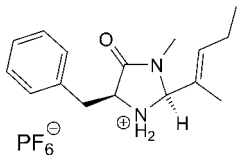
11d

*(2*R*,5*S*)-5-Benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-ium Hexafluorophosphate* (**11d**). Prepared from **6c** (832 mg, 3.38 mmol) and HPF_6 (522 µl, 3.55 mmol). *GP 3:* V_1 100 ml; V_2 80 ml; t_1 30 min; t_2 10 min. Yield: 1.29 g (97%). White solid. M.p. 148 – 150°. $[\alpha]_D^{rt.} = -62.8$ (*c* = 0.91, EtOH). IR: 3184*w*, 1718*m*, 1705*m*, 1572*w*, 1482*w*, 1457*w*, 1410*w*, 1381*w*, 1342*w*, 1257*w*, 1118*w*, 1054*w*, 832*s*, 790*w*, 756*w*, 741*m*, 719*w*, 701*m*, 659*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.03 (*s*, ^{t}Bu); 2.96 (*s*, MeN); 2.97 (*dd*, *J* = 8.7, 15.1, 1 H, CH_2); 3.28 (*dd*, *J* = 4.6, 15.1, 1 H, CH_2); 4.40 (*dd*, *J* = 4.5, 8.2, CH); 4.60 (*s*, CH); 7.27 – 7.43 (*m*, 5 arom. H); 9.29 (br. *s*, 1 H, NH_2^+); 9.84 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 24.6; 31.6; 35.3; 36.2; 57.8; 80.2; 127.1; 128.5; 129.5; 135.6; 168.5. HR-ESI-MS: 247.1805 (100, M^+, $C_{15}H_{23}N_2O^+$; calc. 247.18049). Anal. calc. for $C_{15}H_{23}F_6N_2OP$ (392.32): C 45.92, H 5.91, N 7.14; found: C 46.19, H 5.74, N 7.12.



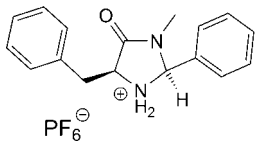
11e

*(2*S*,5*S*)-5-Benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-ium Hexafluorophosphate* (**11e**). Prepared from **7c** (451 mg, 1.83 mmol) and HPF_6 (283 µl, 1.92 mmol). *GP 3:* V_1 50 ml; V_2 30 ml; t_1 40 min; t_2 10 min. Yield: 420 mg (58%). Light-brown solid. M.p. 128 – 130°. $[\alpha]_D^{rt.} = -23.0$ (*c* = 0.49, EtOH). IR: 2956*w*, 1711*m*, 1694*s*, 1479*w*, 1457*w*, 1412*w*, 1394*m*, 1345*w*, 1331*w*, 1254*w*, 1234*w*, 1128*w*, 1049*w*, 1029*w*, 879*w*, 857*m*, 830*s*, 762*w*, 742*m*, 707*m*, 626*w*, 617*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.08 (*s*, ^{t}Bu); 2.93 (*s*, MeN); 3.13 (*dd*, *J* = 8.6, 15.3, 1 H, CH_2); 3.28 (*dd*, *J* = 4.4, 15.4, 1 H, CH_2); 4.24 (*dd*, *J* = 3.9, 7.8, CH); 4.52 (*s*, CH); 7.26 – 7.41 (*m*, 5 arom. H); 7.97 (br. *s*, 1 H, NH_2^+); 10.40 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 24.9; 30.4; 33.7; 58.1; 79.5; 126.9; 128.5; 129.0; 136.5; 169.7. HR-ESI-MS: 247.1805 (100, M^+, $C_{15}H_{23}N_2O^+$; calc. 247.18049). Anal. calc. for $C_{15}H_{23}F_6N_2OP$ (392.32): C 45.92, H 5.91, N 7.14; found: C 46.12, H 5.90, N 7.07.



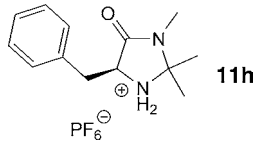
11f

*(2*S*,5*S*)-5-Benzyl-3-methyl-4-oxo-2-[(2*E*)-pent-2-en-2-yl]imidazolidin-1-ium Hexafluorophosphate* (**11f**). Prepared from **7a′** (200 mg, 0.774 mmol) and HPF_6 (120 µl, 0.813 mmol). *GP 3:* V_1 40 ml; V_2 50 ml; t_1 15 min; t_2 15 min. Yield: 176 mg (56%). White solid. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.98 (*t*, *J* = 7.5, *Me*CH_2); 1.56 (*s*, Me); 2.08 – 2.19 (*m*, MeCH_2); 2.66 (*s*, MeN); 3.04 (*dd*, *J* = 9.8, 15.5, 1 H, CH_2); 3.32 (*dd*, *J* = 3.7, 15.5, 1 H, CH_2); 4.36 (*dd*, *J* = 3.5, 9.8, H–C(5)); 5.10 (*s*, H–C(2)); 5.85 (*td*, *J* = 1.3, 7.2, CH); 7.26 – 7.42 (*m*, 5 arom. H); 8.67 (br. *s*, 1 H, NH_2^+); 10.34 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 10.3; 13.1; 20.9; 27.1; 34.0; 58.2; 77.2; 126.0; 126.9; 128.5; 128.9; 136.0; 139.9; 168.1.



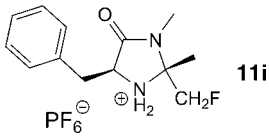
11g

(2S,5S)-5-Benzyl-3-methyl-4-oxo-2-phenylimidazolidin-1-ium Hexafluorophosphate (**11g**). Prepared from **7d** (877 mg, 3.29 mmol) and HPF_6 (510 µl, 3.46 mmol). *GP 3:* V_1 70 ml; V_2 50 ml; t_1 15 min; t_2 15 min. An oily precipitate was formed. The reaction mixture was decanted, and Et_2O (100 ml) was added to the oily residue, followed by scratching with spatula, until the oily residue turned to a (semi)solid. The mixture was decanted, the (semi)solid residue was dried in high vacuum, then crushed into powder, the powder was suspended in Et_2O (100 ml) and vigorously stirred at r.t. for 20 min, followed by filtration of the solid on a ceramic frit and drying in high vacuum. Yield: 1.01 g (74%). Light-yellow solid. M.p. 122–124°. $[\alpha]_D^{r.t.} = -77.1$ ($c = 0.17$, EtOH). IR: 1698*s*, 1610*w*, 1466*w*, 1438*w*, 1377*w*, 1341*w*, 1277*m*, 1236*w*, 1212*w*, 1144*m*, 1081*w*, 1052*w*, 1003*w*, 887*w*, 845*s*, 829*s*, 756*s*, 743*m*, 701*s*, 692*m*, 639*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.68 (*s*, MeN); 3.11 (*dd*, $J = 10.4, 15.2$, 1 H, CH_2); 3.40 (*dd*, $J = 3.1, 15.2$, 1 H, CH_2); 4.49 (*dd*, $J = 2.8, 10.1$, H–C(5)); 5.78 (*s*, H–C(2)); 7.26–7.64 (*m*, 10 arom. H); 9.56 (s, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 28.0; 33.7; 59.2; 73.5; 127.0; 128.6; 128.9; 129.0; 129.1; 130.8; 131.1; 136.1; 168.7. HR-ESI-MS: 267.1492 (100, M^+, $C_{17}H_{19}N_2O^+$; calc. 267.14919). Anal. calc. for $C_{17}H_{19}F_6N_2OP$ (412.31): C 49.52, H 4.64, N 6.79; found: C 51.99, H 4.85, N 7.06.



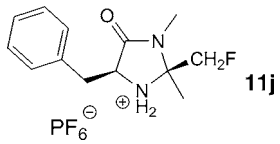
11h

(5S)-5-Benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-ium Hexafluorophosphate (**11h**). Prepared from **7e** (1.79 mg, 8.22 mmol) and HPF_6 (1.27 ml, 8.63 mmol). *GP 3:* V_1 100 ml; V_2 50 ml; t_1 40 min; t_2 20 min. Yield: 2.80 g (93%). White solid. M.p. 157–159°. $[\alpha]_D^{r.t.} = -64.2$ ($c = 0.52$, EtOH). IR: 3207*w*, 3163*w*, 2893*w*, 1702*s*, 1596*w*, 1501*w*, 1485*w*, 1456*w*, 1415*m*, 1397*m*, 1380*m*, 1314*w*, 1266*w*, 1194*w*, 1157*w*, 1061*w*, 829*s*, 765*w*, 748*m*, 739*m*, 705*m*, 699*m*, 686*m*, 615*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.52 (*s*, Me); 1.66 (*s*, Me); 2.81 (*s*, MeN); 2.98 (*dd*, $J = 10.7, 15.2$, 1 H, CH_2); 3.37 (*dd*, $J = 3.5, 15.2$, 1 H, CH_2); 4.69 (*dd*, $J = 3.0, 10.5$, CH); 7.29–7.47 (*m*, 5 arom. H); 9.36 (br. *s*, 1 H, NH_2^+); 10.38 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 21.7; 23.8; 24.9; 33.7; 57.3; 77.0; 127.2; 128.7; 129.2; 135.9; 166.2. HR-ESI-MS: 219.1492 (100, M^+, $C_{13}H_{19}N_2O^+$; calc. 219.14919). Anal. calc. for $C_{13}H_{19}F_6N_2OP$ (364.27): C 42.86, H 5.26, N 7.69; found: C 42.88, H 5.32, N 7.55.



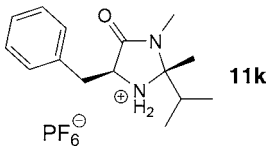
11i

(2R,5S)-5-Benzyl-2-(fluoromethyl)-2,3-dimethyl-4-oxoimidazolidin-1-ium Hexafluorophosphate (**11i**). Prepared from **6f** (794 mg, 3.36 mmol) and HPF_6 (520 µl, 3.53 mmol). *GP 3:* V_1 80 ml; V_2 70 ml; t_1 10 min; t_2 20 min. Yield: 922 mg (71%). White solid. M.p. 166–170°. $[\alpha]_D^{r.t.}{}_D^{r.t.} = -60.0$ ($c = 0.67$, EtOH). IR: 1704*m*, 1572*w*, 1477*w*, 1459*w*, 1409*w*, 1391*m*, 1360*w*, 1285*w*, 1186*w*, 1050*w*, 822*s*, 758*m*, 740*m*, 708*m*, 680*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): 1.90 (*d*, $J = 2.8$, Me); 3.04 (*s*, MeN); 3.22 (*dd*, $J = 10.6, 15.2$, 1 H, CH_2); 3.61 (*dd*, $J = 3.9, 15.3$, 1 H, CH_2); 4.79 (*dd*, $J = 3.0, 10.2$, H–C(5)); 4.90 (*dd*, $J = 11.8, 34.8$, 1 H, CH_2F); 5.02 (*dd*, $J = 11.7, 34.0$, 1 H, CH_2F); 7.28–7.44 (*m*, 5 arom. H); 8.93 (br. *s*, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 17.7 (*d*, $J = 3.5$); 25.4; 34.7; 59.1 (*d*, $J = 3.8$); 77.7 (*d*, $J = 16.7$); 82.0 (*d*, $J = 176.9$); 127.4; 128.8; 129.3; 136.1; 167.5. HR-ESI-MS: 237.1398 (100, M^+, $C_{13}H_{18}FN_2O^+$; calc. 237.13977). Anal. calc. for $C_{13}H_{18}F_7N_2OP$ (382.26): C 40.85, H 4.75, N 7.33; found: C 41.13, H 4.84, N 7.10.



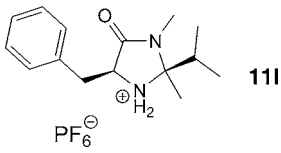
11j

(2S,5S)-5-Benzyl-2-(fluoromethyl)-2,3-dimethyl-4-oxoimidazolidin-1-ium Hexafluorophosphate (**11j**). Prepared from **7f** (657 mg, 2.78 mmol) and HPF_6 (430 µl, 2.92 mmol). *GP 3:* V_1 70 ml; V_2 60 ml; t_1 10 min; t_2 20 min. Yield: 915 mg (86%). White solid. M.p. 176–180°. $[\alpha]_D^{r.t.} = -56.7$ ($c = 0.50$, EtOH). IR: 1703*m*, 1480*w*, 1457*w*, 1445*w*, 1397*w*, 1385*w*, 1355*w*, 1265*w*, 1136*w*, 1050*m*, 936*w*, 835*s*, 754*m*, 746*m*, 706*m*, 675*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.55 (*d*, $J = 2.7$, Me); 2.84 (*s*, MeN); 2.97 (*dd*, $J =$ 10.3, 15.5, 1 H, CH_2); 3.32 (*dd*, $J = 3.6$, 15.5, 1 H, CH_2); 4.61 (*dd*, $J = 3.6$, 10.4, H–C(5)); 4.70 (*dd*, $J = 11.4$, 42.5, 1 H, CH_2F); 4.82 (*dd*, $J = 11.3$, 42.9, 1 H, CH_2F); 7.28–7.34 (*m*, 1 arom. H); 7.36–7.44 (*m*, 4 arom. H); 10.01 (br. *s*, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 17.1; 25.4; 34.4; 57.5; 77.9 (*d*, $J = 17.9$); 81.6 (*d*, $J = 177.3$); 127.2; 128.7; 129.1; 136.2; 167.3. HR-ESI-MS: 237.1398 (100, M^+, $C_{13}H_{18}FN_2O^+$; calc. 237.13977). Anal. calc. for $C_{13}H_{18}F_7N_2OP$ (382.26): C 40.85, H 4.75, N 7.33; found: C 41.12, H 4.75, N 7.20.



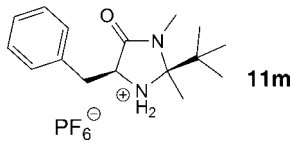
11k

(2R,5S)-5-Benzyl-2,3-dimethyl-4-oxo-2-(propan-2-yl)imidazolidin-1-ium Hexafluorophosphate (**11k**). Prepared from **6g** (1.70 g, 6.90 mmol) and HPF_6 (1.07 ml, 7.25 mmol). *GP 3:* V_1 100 ml; V_2 80 ml; t_1 10 min; t_2 20 min. Yield: 2.39 g (88%). White solid. M.p. 165–170°. $[\alpha]_D^{r.t.} = -56.6$ ($c = 0.27$, EtOH). IR: 1708*m*, 1694*m*, 1578*w*, 1478*w*, 1457*w*, 1411*w*, 1387*w*, 1356*w*, 1344*w*, 1268*w*, 1135*w*, 864*w*, 830*s*, 756*m*, 740*m*, 707*m*, 684*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.89 (*d*, $J = 7.0$, 3 H, Me_2CH); 1.03 (*d*, $J =$ 7.0, 3 H, Me_2CH); 1.56 (*s*, Me); 2.18–2.31 (*m*, Me_2CH); 2.79 (*s*, MeN); 3.11 (*dd*, $J = 8.3$; 15.5, 1 H, CH_2); 3.31 (*dd*, $J = 4.5$, 15.4, 1 H, CH_2); 4.46 (*dd*, $J = 4.6$, 8.2, H–C(5)); 7.27–7.46 (*m*, 5 arom. H); 9.52 (*s*, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 15.7; 15.9; 22.3; 26.1; 34.0; 35.6; 58.5; 83.1; 127.3; 128.6; 129.5; 135.8; 166.6. HR-ESI-MS: 247.1807 (100, M^+, $C_{15}H_{23}N_2O^+$; calc. 247.1805). Anal. calc. for $C_{15}H_{23}F_6N_2OP$ (392.32): C 45.92, H 5.91, N 7.14; found: C 45.90, H 5.68, N 7.21.



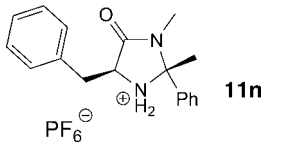
11l

(2S,5S)-5-Benzyl-2,3-dimethyl-4-oxo-2-(propan-2-yl)imidazolidin-1-ium Hexafluorophosphate (**11l**). Prepared from **7g** (1.90 g, 7.71 mmol) and HPF_6 (1.19 ml, 8.10 mmol). *GP 3:* V_1 90 ml; V_2 90 ml; t_1 10 min; t_2 10 min. Yield: 2.66 g (87%). White solid. M.p. 170–175°. $[\alpha]_D^{r.t.} = -32.1$ ($c = 0.20$, EtOH). IR: 1706*m*, 1694*m*, 1455*w*, 1413*w*, 1404*w*, 1395*w*, 1376*w*, 1352*w*, 1338*w*, 1255*w*, 1134*w*, 1083*w*, 1049*w*, 1033*w*, 871*w*, 832*s*, 761*m*, 740*m*, 707*m*, 683*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.95 (*d*, $J = 7.0$, 3 H, Me_2CH); 1.07 (*d*, $J = 7.0$, 3 H, Me_2CH); 1.57 (*s*, Me); 2.23–2.37 (*m*, Me_2CH); 2.80 (*s*, MeN); 3.09 (*dd*, $J =$ 9.2; 15.7, 1 H, CH_2); 3.35 (*dd*, $J = 3.8$, 15.7, 1 H, CH_2); 4.71 (*dd*, $J = 3.2$, 8.8, H–C(5)); 7.25–7.48 (*m*, 5 arom. H); 8.15 (br. *s*, 1 H, NH_2^+);10.47 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 15.4; 15.9; 19.0; 26.0; 32.9; 33.8; 56.8; 82.5; 127.0; 128.5; 129.1; 136.3; 167.1. HR-ESI-MS: 247.1805 (100, M^+, $C_{15}H_{23}N_2O^+$; calc. 247.1805). Anal. calc. for $C_{15}H_{23}F_6N_2OP$ (392.32): C 45.92, H 5.91, N 7.14; found: C 45.85, H 5.99, N 7.14.



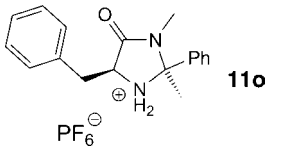
11m

*(2S,5S)-5-Benzyl-2-(*tert*-butyl)-2,3-dimethyl-4-oxoimidazolidin-1-ium Hexafluorophosphate* (**11m**). Prepared from **7h** (1.24 g, 4.77 mmol) and HPF_6 (1 equiv.!, 704 µl, 4.77 mmol). *GP 3:* V_1 100 ml; V_2 50 ml; t_1 20 min; t_2 10 min. Yield: 1.69 g (87%). White solid. The product was stable in the solid form (dry, under Ar), but decomposed in soln. ((D_6)Acetone, (D_6)DMSO, (D_4)MeOH) in *ca.* 24 hours! M.p. 99–101°. $[\alpha]_D^{rt.} = -23.5$ ($c = 0.74$, EtOH). IR: 2965*w*, 1693*m*, 1481*w*, 1455*w*, 1384*m*, 1372*w*, 1341*w*, 1252*w*, 1128*w*, 1112*w*, 831*s*, 781*w*, 760*w*, 739*m*, 707*m*, 670*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.09 (*s*, ^{t}Bu); 1.53 (*s*, Me); 2.91 (*s*, MeN); 3.14 (*dd*, $J = 8.7$, 15.5, 1 H, CH_2); 3.32 (*dd*, $J = 3.9$, 15.6, 1 H, CH_2); 4.66 (br. *s*, CH); 7.24–7.49 (*m*, 5 arom. H); 7.70 (br. *s*, 1 H, NH_2^+); 10.65 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 15.7; 24.8; 28.1; 33.8; 37.5; 56.3; 84.9; 126.8; 128.4; 129.1; 136.5; 168.0. HR-ESI-MS: 261.1961 (100, M^+, $C_{16}H_{25}N_2O^+$; calc. 261.19614). Anal. calc. for $C_{16}H_{25}F_6N_2OP$ (406.35): C 47.29, H 6.20, N 6.89; found: C 48.05, H 6.42, N 6.55.



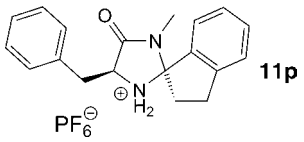
11n

(2R,5S)-5-Benzyl-2,3-dimethyl-4-oxo-2-phenylimidazolidin-1-ium Hexafluorophosphate (**11n**). Prepared from **6i** (2.03 mg, 7.23 mmol) and HPF_6 (1.12 µl, 7.59 mmol). *GP 3:* V_1 80 ml; V_2 80 ml; t_1 10 min; t_2 10 min. Yield: 1.18 g (38%). White solid. M.p. 141–143°. $[\alpha]_D^{rt.} = +4.1$ ($c = 0.10$, EtOH). IR: 1688*m*, 1577*w*, 1481*w*, 1453*w*, 1406*w*, 1384*w*, 1356*w*, 1288*w*, 1255*w*, 1196*w*, 1188*w*, 1137*w*, 1004*w*, 880*w*, 864*w*, 835*s*, 766*m*, 754*m*, 740*m*, 707*m*, 700*m*, 676*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.11 (*s*, Me); 2.79 (*s*, MeN); 3.06 (*dd*, $J = 9.8$, 15.2, 1 H, CH_2); 3.39 (*dd*, $J = 3.8$, 15.2, 1 H, CH_2); 4.36 (*dd*, $J = 3.4$, 9.6, H–C(5)); 7.23–7.44 (*m*, 7 arom. H); 7.49–7.58 (*m*, 3 arom. H); 9.63 (br. *s*, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 23.3; 26.2; 34.2; 57.2; 79.0; 126.7; 127.0; 128.4; 129.26; 129.28; 130.2; 134.8; 135.9; 167.5. HR-ESI-MS: 281.1645 (100, M^+, $C_{18}H_{21}N_2O^+$; calc. 281.1648). Anal. calc. for $C_{18}H_{21}F_6N_2OP$ (426.34): C 50.71, H 4.96, N 6.57; found: C 50.61, H 4.99, N 6.58.



11o

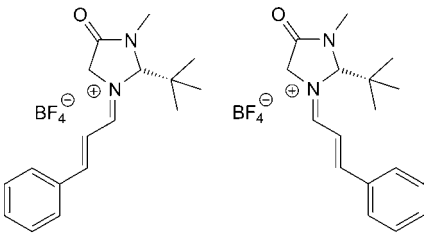
(2S,5S)-5-Benzyl-2,3-dimethyl-4-oxo-2-phenylimidazolidin-1-ium Hexafluorophosphate (**11o**). Prepared from **7i** (2.32 g, 8.26 mmol) and HPF_6 (1.28 µl, 8.68 mmol). *GP 3:* V_1 80 ml; V_2 100 ml; t_1 10 min; t_2 20 min. Yield: 3.42 g (97%). White solid. M.p. 132–134°. $[\alpha]_D^{rt.} = -76.6$ ($c = 3.8$, EtOH). IR: 1690*m*, 1564*w*, 1449*w*, 1404*w*, 1384*w*, 1345*w*, 1277*w*, 1258*w*, 1217*w*, 1134*w*, 1075*w*, 1021*w*, 829*s*, 754*m*, 738*m*, 712*m*, 699*m*, 679*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.02 (*s*, Me); 2.70 (*s*, MeN); 3.06 (*dd*, $J = 10.2$, 15.3, 1 H, CH_2); 3.41 (*dd*, $J = 3.2$, 15.3, 1 H, CH_2); 4.80 (*dd*, $J = 2.7$, 10.0, H–C(5)); 7.26–7.44 (*m*, 5 arom. H); 7.47–7.64 (*m*, 5 arom. H); 9.41 (br. *s*, 1 H, NH_2^+); 10.15 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 19.9; 26.8; 34.0; 57.8; 79.6; 127.1; 127.5; 128.5; 129.17; 129.24; 130.5; 135.1; 136.1; 167.9. HR-ESI-MS: 281.1648 (100, M^+, $C_{18}H_{21}N_2O^+$; calc. 281.16484). Anal. calc. for $C_{18}H_{21}F_6N_2OP$ (426.34): C 50.71, H 4.96, N 6.57; found: C 50.78, H 4.79, N 6.53.



11p

(2S,5S)-5-Benzyl-2′,3′-dihydro-3-methyl-4-oxospiro[imidazolidin-1-ium-2,1′-indene] Hexafluorophosphate (**11p**). Prepared from **7j** (700 mg, 2.39 mmol) and HPF_6 (370 µl, 2.51 mmol). *GP 3:* V_1 100 ml; V_2 100 ml; t_1 10 min; t_2 20 min. Yield: 594 mg (56%). White solid. M.p. 126–128°. $[\alpha]_D^{r.t.} = -86.8$ ($c = 0.87$, EtOH). IR: 1708*s*, 1480*w*, 1456*w*, 1408*w*, 1379*w*, 1344*w*, 1284*w*, 1261*w*, 1130*w*, 1082*w*, 1032*w*, 929*w*, 835*s*, 810*s*, 772*m*, 753*s*, 740*m*, 726*w*, 708*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.35–2.46 (*m*, 1 H, CH_2); 2.59–2.75 (*m*, 1 H, CH_2); 2.68 (*s*, MeN); 2.96–3.19 (*m*, 3 H, CH_2); 3.45 (*dd*, $J = 3.2$; 15.3, 1 H, CH_2); 4.84 (*dd*, $J = 2.8$; 10.0, H–C(5)); 7.26–7.58 (*m*, 9 arom. H); 9.52 (br. *s*, 1 H, NH_2^+); 10.39 (br. *s*, 1 H, NH_2^+). ^{13}C-NMR (101 MHz, (D_6)DMSO): 26.0; 28.2; 31.5; 33.9; 57.8; 87.6; 125.7; 125.8; 127.1; 127.2; 128.6; 129.2; 131.6; 134.1; 136.1; 145.8; 167.3. HR-ESI-MS: 293.1648 (100, M^+, $C_{19}H_{21}N_2O^+$; calc. 293.16484). Anal. calc. for $C_{19}H_{21}F_6N_2OP$ (438.35): C 52.06, H 4.83, N 6.39; found: C 51.93, H 4.88, N 6.23.

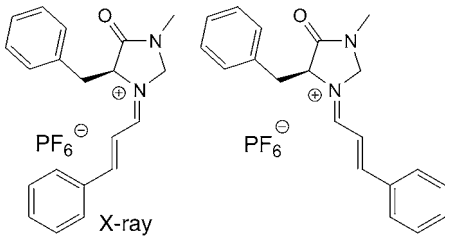
Preparation of Iminium Salts (E/Z)-**12** *and* (E/Z)-**14a**–(E/Z)-**14p**. *General Procedure 4* (*GP 4*). To a soln./suspension of PF_6 or BF_4 salt in anh. EtOH (V_1) under Ar, cinnamaldehyde was added (1.05 equiv.), followed by the addition of Et_3N (V_2). The reaction mixture was stirred vigorously 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 (*E*/*Z*)-**12** and (*E*/*Z*)-**14a**–(*E*/*Z*)-**14p**. The collected products were dried on high vacuum and stored under Ar.



(*E*)-**12**

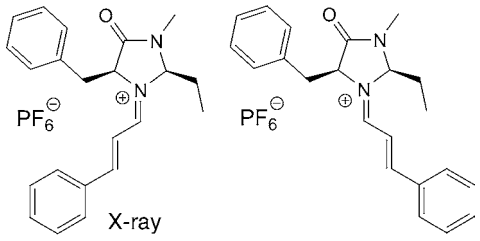
(*Z*)-**12**

(1E,2S)- and (1Z,2S)-2-(tert-*Butyl)-3-methyl-4-oxo-1-[(2E)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Tetrafluoroborate* ((*E*)-**12** and (*Z*)-**12**, resp.). Prepared from **9** (529 mg, 2.17 mmol) and cinnamaldehyde (292 µl, 2.28 mmol). *GP 4:* V_1 3 ml; V_2 5 µl; t_1 3 h. Yield: 474 mg (61%). Light-yellow solid. (*E*)-**12**/(*Z*)-**12** 1:0.07. M.p. 151–155°. $[\alpha]_D^{r.t.} = 0$ ($c = 0.24$, CH_2Cl_2). IR: 2966*w*, 1720*s*, 1633*s*, 1608*s*, 1593*s*, 1481*w*, 1457*m*, 1425*m*, 1395*m*, 1373*w*, 1346*w*, 1307*w*, 1282*m*, 1259*m*, 1233*m*, 1194*m*, 1182*m*, 1026*s*, 1045*s*, 997*s*, 980*m*, 960*s*, 915*m*, 866*m*, 844*w*, 831*w*, 762*s*, 688*m*, 665*m*. ^{1}H-NMR (300 MHz, (D_6)Acetone): (*E*)-**12**: 1.19 (*s*, ^{t}Bu); 3.13 (*s*, MeN); 4.83 (*dd*, $J = 1.7$; 18.1, 1 H, CH_2); 4.95 (*d*, $J = 18.1$, 1 H, CH_2); 5.58 (*s*, H–C(2)); 7.53–7.61 (*m*, 2 arom. H); 7.63–7.70 (*m*, 1 arom. H, H–C(2′)); 7.96–8.02 (*m*, 2 arom. H); 8.41 (*d*, $J = 15.2$, H–C(3′)); 8.94 (*d*, $J = 10.4$, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**12**: 25.5; 32.2; 39.9; 53.1; 90.7; 118.7; 130.4; 131.9; 134.9; 135.3; 165.3; 166.4; 170.1. ^{1}H-NMR (300 MHz, (D_6)Acetone): (*Z*)-**12**: 1.23 (*s*, ^{t}Bu); 3.11 (*s*, MeN); 4.66 (*d*, $J = 17.5$, 1 H, CH_2); 4.97 (*d*, $J = 17.6$, 1 H, CH_2); 6.11 (*d*, $J = 1.0$, H–C(2)); 7.81 (*dd*, $J = 10.7$; 15.0, H–C(2′)); 8.25 (*d*, $J = 15.1$, H–C(3′)). HR-ESI-MS: 271.1805 (100, M^+, $C_{17}H_{23}N_2O^+$; calc. 271.18049). Anal. calc. for $C_{17}H_{23}BF_4N_2O$ (358.18): C 57.01, H 6.47, N 7.82; found: C 57.05, H 6.54, N 7.78.



(*E*)-**14a** (*Z*)-**14a**

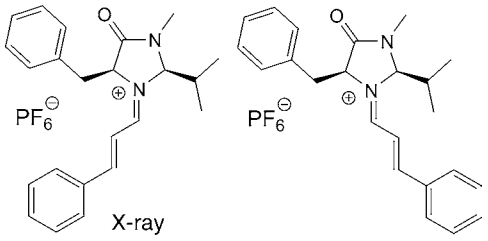
*(1*E*,5*S*)- and (1*Z*,5*S*)-5-Benzyl-3-methyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14a** and (*Z*)-**14a**, resp.). Prepared from **11a** (660 mg, 1.96 mmol) and cinnamaldehyde (265 µl, 2.06 mmol). *GP 4:* V_1 3 ml; V_2 10 µl; t_1 5 h. Yield: 740 mg (83%). Light-yellow solid. (*E*)-**14a**/(*Z*)-**14a** 0.44:1. M.p. 175–179°. $[\alpha]_D^{r.t.} = +331.1$ ($c = 0.11$, CH_2Cl_2). IR: 1729*m*, 1643*m*, 1614*w*, 1592*m*, 1575*w*, 1455*w*, 1407*w*, 1343*w*, 1288*w*, 1191*m*, 1181*m*, 1000*w*, 858*m*, 823*s*, 752*m*, 703*w*, 694*w*, 685*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14a**: 2.87 (*s*, MeN); 3.43 (*dd*, *J* = 5.8, 14.4, 1 H, CH_2); 3.68 (*dd*, *J* = 4.8, 14.4, 1 H, CH_2); 4.87 (*d*, *J* = 10.0, 1 H, CH_2(2)); 5.43 (*d*, *J* = 10.1, 1 H, CH_2(2)); 5.46 (*t*, *J* = 5.4, H–C(5)); 7.38 (*dd*, *J* = 10.8, 15.1, H–C(2′)); 7.86–7.89 (*m*, 2 arom. H); 8.21 (*d*, *J* = 15.2, H–C(3′)); 8.97 (*d*, *J* = 10.8, H–C(1′)). ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14a**: 2.90 (*s*, MeN); 3.50 (*dd*, *J* = 5.0, 14.5, 1 H, CH_2); 3.61 (*dd*, *J* = 5.5, 14.5, 1 H, CH_2); 4.99 (*dd*, *J* = 1.9, 10.8, 1 H, CH_2(2)); 5.18 (*t*, *J* = 5.1, H–C(5)); 5.62 (*dt*, *J* = 1.5, 10.8, 1 H, CH_2(2)); 7.23–7.36 (*m*, 5 arom. H); 7.53–7.61 (*m*, 2 arom. H, H–C(2′)); 7.66–7.71 (*m*, 1 arom. H); 7.94–7.99 (*m*, 2 arom. H); 8.25 (*d*, *J* = 15.2, H–C(3′)); 8.85 (*dd*, *J* = 1.4, 10.7, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14a** and (*Z*)-**14a**: 27.6; 27.7; 37.5; 38.2; 65.1; 67.3; 67.7; 70.6; 117.2; 117.8; 128.8; 129.0; 129.86; 129.87; 130.3; 130.5; 130.6; 130.7; 132.06; 132.1; 134.47; 134.50; 134.51; 134.8; 135.5; 135.7; 165.4; 165.5; 166.2; 166.5; 168.6; 170.3. HR-ESI-MS: 305.1648 (100, M^+, $C_{20}H_{21}N_2O^+$; calc. 305.16484). Anal. calc. for $C_{20}H_{21}F_6N_2OP$ (450.36): C 53.34, H 4.70, N 6.22; found: C 53.36, H 4.77, N 6.22.



(*E*)-**14b** (*Z*)-**14b**

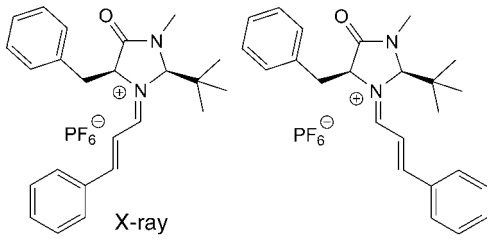
*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-2-ethyl-3-methyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14b** and (*Z*)-**14b**, resp.). Prepared from **11b** (590 mg, 1.62 mmol) and cinnamaldehyde (218 µl, 1.70 mmol). *GP 4:* V_1 1.5 ml; V_2 10 µl; t_1 3 d. No filterable precipitate was formed, but rather a two phase system with the product (thick orange liquid) on the bottom (bottom phase) and the soln. on the top (top phase) of the flask. The top phase was carefully removed with a syringe, followed by addition of anh. Et_2O (6 ml) to the remaining product (bottom phase). The so formed mixture was stirred vigorously whereby the product slowly solidified. The soln. was removed *via* a syringe and replaced by anh. Et_2O (6 ml), followed by vigorous stirring and scratching with a spatula. The process (removing solvent, adding anh. Et_2O, stirring/scratching) was repeated, until a finely powdered product was formed. The precipitate was collected on a dry ceramic frit under Ar and washed with anh. Et_2O (20 ml) to give (*E*)-**14b**/(*Z*)-**14b**. Yield: 600 mg (77%). Yellow solid. (*E*)-**14b**/(*Z*)-**14b** 1:0.26. M.p. 108–115°. $[\alpha]_D^{r.t.} = +335.9$ ($c = 0.32$, CH_2Cl_2). IR: 1718*m*, 1622*m*, 1605*m*, 1590*m*, 1456*w*, 1439*w*, 1406*w*, 1338*w*, 1282*w*, 1196*w*, 1181*m*, 1079*w*, 1001*w*, 829*s*, 755*m*, 702*m*, 685*m*. ^{1}H-NMR

(400 MHz, (D_6)Acetone): (*E*)-**14b**: 1.01 (*t*, *J* = 7.6, *Me*CH_2); 1.19–1.31 (*m*, 1 H, MeCH_2); 1.83–1.95 (*m*, 1 H, MeCH_2); 2.98 (*s*, MeN); 3.44 (*dd*, *J* = 6.1; 14.7, 1 H, CH_2); 3.76 (*dd*, *J* = 5.2, 14.7, 1 H, CH_2); 5.43 (*t*, *J* = 5.4, CH); 5.57 (*dd*, *J* = 4.9, 7.1, CH); 7.24–7.44 (*m*, 5 arom. H, H–C(2′)); 7.56–7.63 (*m*, 2 arom. H); 7.66–7.74 (*m*, 1 arom. H); 7.85 (*d*, *J* = 7.4, 2 arom. H); 8.31 (*d*, *J* = 15.0, H–C(3′)); 8.99 (*d*, *J* = 10.8, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14b**: 8.8; 27.2; 27.9; 38.2; 65.4; 83.6; 118.1; 129.1; 130.1; 130.4; 131.0; 132.2; 134.5; 135.7; 135.8; 166.2; 166.4; 170.9. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14b**: 3.01 (*s*, MeN); 3.63 (*dd*, *J* = 6.2, 14.5, 1 H, CH_2); 5.09 (*t*, *J* = 6.3, CH); 6.04 (*t*, *J* = 5.1, CH); 7.96 (*d*, *J* = 7.4, 2 arom. H); 8.16 (*d*, *J* = 15.0, H–C(3′)); 8.61 (*d*, *J* = 10.9, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*Z*)-**14b**: 9.0; 27.7; 28.4; 38.3; 68.1; 79.9; 117.5; 128.9; 130.0; 130.5; 134.5; 135.3; 166.0; 166.1; 170.3. HR-ESI-MS: 333.1961 (100, M^+, $C_{22}H_{25}N_2O^+$; calc. 333.19614). Anal. calc. for $C_{22}H_{25}F_6N_2OP$ (478.41): C 55.23, H 5.27, N 5.86; found: C 55.60, H 5.57, N 5.58.



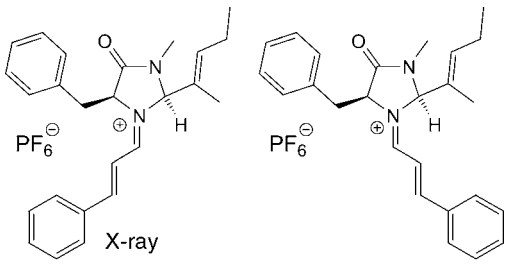
(*E*)-**14c** (*Z*)-**14c**

*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-3-methyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]-2-(propan-2-yl)imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14c** and (*Z*)-**14c**, resp.). Prepared from **11c** (880 mg, 2.33 mmol) and cinnamaldehyde (314 µl, 2.44 mmol). *GP 4:* V_1 2 ml; V_2 10 µl; t_1 18 h. Yield: 980 mg (85%). Yellow solid. (*E*)-**14c**/(*Z*)-**14c** 1:0.15. M.p. 175–178°. $[\alpha]_D^{r.t.} = +309.5$ (*c* = 1.89, CH_2Cl_2). IR: 1717*m*, 1621*w*, 1604*m*, 1588*m*, 1456*w*, 1433*w*, 1392*w*, 1375*w*, 1326*w*, 1282*w*, 1267*w*, 1229*w*, 1201*m*, 1178*w*, 1082*w*, 1000*w*, 965*w*, 876*w*, 840*s*, 828*s*, 755*m*, 732*w*, 699*m*, 688*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14c**: 1.21 (*d*, *J* = 7.0, 2 Me); 2.32–2.45 (*m*, CH); 3.09 (*s*, MeN); 3.38 (*dd*, *J* = 8.2, 14.8, 1 H, CH_2); 3.69 (*dd*, *J* = 4.8; 14.8, 1 H, CH_2); 5.32 (*dd*, *J* = 4.9, 7.9, H–C(5)); 5.55 (*d*, *J* = 5.3, H–C(2)); 6.80 (*dd*, *J* = 10.7, 15.0, H–C(2′)); 7.24–7.29 (*m*, 1 arom. H); 7.39–7.45 (*m*, 2 arom. H); 7.50–7.59 (*m*, 4 arom. H); 7.63–7.70 (*m*, 3 arom. H); 8.24 (*d*, *J* = 15.0, H–C(3′)); 8.92 (*d*, *J* = 10.8, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14c**: 17.7; 18.3; 29.9; 34.1; 38.8; 65.3; 87.6; 118.2; 129.0; 130.2; 130.3; 130.8; 132.1; 134.3; 135.7; 136.7; 166.3; 167.2; 171.7. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14c**: 1.13 (*d*, *J* = 6.7, Me); 1.31 (*d*, *J* = 7.2, Me); 2.46–2.55 (*m*, CH); 3.10 (*s*, MeN); 3.47 (*dd*, *J* = 7.8, 14.5, 1 H, CH_2); 3.64 (*dd*, *J* = 6.6, 14.5, 1 H, CH_2); 5.01 (*t*, *J* = 7.2, H–C(5)); 6.00 (*d*, *J* = 4.6, H–C(2)); 7.92–7.97 (*m*, 2 arom. H); 8.10 (*d*, *J* = 15.0, H–C(3′)); 8.46 (*d*, *J* = 10.9, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*Z*)-**14c**: 17.1; 19.8; 35.5; 38.6; 68.0; 83.6; 117.9; 165.9; 167.0; 171.3. HR-ESI-MS: 347.2118 (100, M^+, $C_{23}H_{27}N_2O^+$; calc. 347.21179). Anal. calc. for $C_{23}H_{27}F_6N_2OP$ (492.44): C 56.10, H 5.53, N 5.69; found: C 56.24, H 5.43, N 5.57.



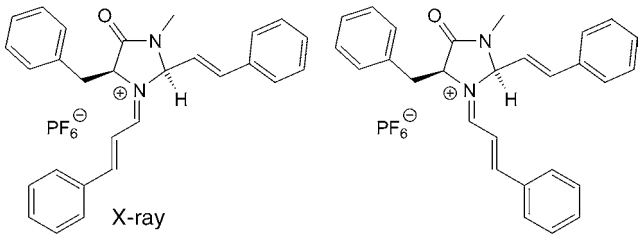
(*E*)-**14d** (*Z*)-**14d**

*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-2-(*tert*-butyl)-3-methyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14d** and (*Z*)-**14d**, resp.). Prepared from **11e** (320 mg, 0.82 mmol) and cinnamaldehyde (110 µl, 0.86 mmol). *GP 4:* V_1 0.8 ml; V_2 5 µl; t_1 24 h. Yield: 240 mg (58%). Yellow solid. (*E*)-**14d**/(*Z*)-**14d** 1:0.05. M.p. 177–178°. $[\alpha]_D^{r.t.} = +333.9$ ($c = 0.87$, CH_2Cl_2). IR: 2977*w*, 1720*m*, 1613*m*, 1601*m*, 1587*s*, 1575*m*, 1479*w*, 1456*w*, 1431*w*, 1396*w*, 1370*w*, 1325*w*, 1280*w*, 1260*w*, 1227*w*, 1198*m*, 1177*w*, 1081*w*, 1000*w*, 961*w*, 874*w*, 839*s*, 828*s*, 763m, 754*s*, 736*m*, 699*m*, 688*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14d**: 1.34 (*s*, ^{t}Bu); 3.17 (*s*, MeN); 3.41 (*dd*, $J = 8.7$, 14.9, 1 H, CH_2); 3.66 (*dd*, $J = 4.7$, 14.9, 1 H, CH_2); 5.23 (*dd*, $J = 4.7$, 8.5, H–C(5)); 5.58 (*s*, H–C(2)); 6.55 (*dd*, $J =$ 10.8; 15.0, H–C(2′)); 7.28–7.33 (*m*, 1 arom. H); 7.44–7.50 (*m*, 2 arom. H); 7.51–7.57 (*m*, 4 arom. H); 7.58–7.63 (*m*, 2 arom. H); 7.64–7.70 (*m*, 1 arom. H); 8.27 (*d*, $J = 15.0$, H–C(3′)); 8.92 (*d*, $J = 10.8$, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14d**: 26.8; 32.3; 38.2; 38.6; 65.4; 91.2; 118.2; 129.0; 130.3; 130.4; 130.7; 132.1; 134.2; 135.9; 137.3; 167.0; 168.0; 173.4. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14d**: 5.00 (*t*, $J = 7.5$, H–C(5)); 6.07 (*s*, H–C(2)); 7.94–7.99 (*m*, 2 arom. H); 8.11 (*d*, $J = 15.0$, H–C(3′)); 8.49 (*d*, $J = 10.8$, H–C(1′)). HR-ESI-MS: 361.2274 (100, M^+, $C_{24}H_{29}N_2O^+$; calc. 361.22744). Anal. calc. for $C_{24}H_{29}F_6N_2OP$ (506.46): C 56.92, H 5.77, N 5.53; found: C 56.99, H 5.82, N 5.54.



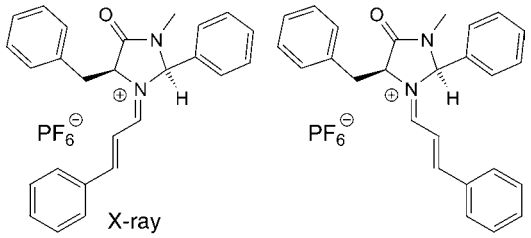
(*E*)-**14e** (*Z*)-**14e**

*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-3-methyl-4-oxo-2-[(2*E*)-pent-2-en-2-yl]-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14e** and (*Z*)-**14e**, resp.). Prepared from **11f** (150 mg, 0.37 mmol) and cinnamaldehyde (50 µl, 0.39 mmol). *GP 4:* V_1 1 ml; V_2 5 µl; t_1 2 d. Yield: 130 mg (67%). Yellow solid. (*E*)-**14e**/(*Z*)-**14e** 1:0.54. M.p. 168–171°. $[\alpha]_D^{r.t.} = +338.8$ ($c = 0.26$, CH_2Cl_2). IR: 1721*m*, 1708*m*, 1629*m*, 1605*m*, 1593*m*, 1575*w*, 1457*w*, 1403*w*, 1329*w*, 1306*w*, 1278*w*, 1194*m*, 1180*m*, 1068*w*, 1047*w*, 1010*w*, 948*w*, 872*w*, 829*s*, 788*m*, 756*m*, 738*m*, 702*m*, 683*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14e**: 1.05 (*t*, $J = 7.6$, CH_3CH_2); 1.12 (*d*, $J = 1.0$, Me); 2.16–2.32 (*m*, $MeCH_2$); 2.85 (*s*, MeN); 3.53 (*dd*, $J = 5.3$, 15.0, 1 H, CH_2); 3.86 (*dd*, $J = 5.4$, 15.0, 1 H, CH_2); 5.41 (*t*, $J = 5.1$, CH); 5.86 (*s*, CH); 6.19–6.23 (*m*, CH); 7.24–7.48 (*m*, 5 arom. H, H–C(2′)); 7.55–7.64 (*m*, 2 arom. H); 7.66–7.74 (*m*, 1 arom. H); 7.81–7.87 (*m*, 2 arom. H); 8.34 (*d*, $J = 15.0$, H–C(3′)); 8.86 (*d*, $J = 11.0$, H–C(1′)). ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14e**: 1.08 (*t*, $J = 7.5$, $MeCH_2$); 2.81 (*d*, $J = 0.7$, MeN); 3.63 (*dd*, $J = 5.3$, 14.9, 1 H, CH_2); 3.71 (*dd*, $J = 6.3$, 14.9, 1 H, CH_2); 5.18 (*t*, $J = 5.6$, CH); 6.55 (*td*, $J = 1.1$, 7.4, CH); 8.25 (*d*, $J =$ 15.1, H–C(3′)); 8.90 (*dt*, $J = 1.6$; 10.8, H–C(1)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14e** and (*Z*)-**14e**: 8.9; 9.2; 13.4; 13.5; 22.1; 22.2; 26.8; 27.3; 36.8; 38.0; 64.7; 67.0; 85.3; 88.3; 117.1; 118.6; 126.9; 128.4; 128.8; 129.0; 130.06; 130.08; 130.5; 130.7; 131.1; 131.3; 132.0; 132.3; 134.4; 134.5; 135.2; 135.7; 135.8; 136.0; 143.4; 145.4; 165.9; 166.3; 166.7; 166.8; 169.6; 170.4. HR-ESI-MS: 373.2274 (100, M^+, $C_{25}H_{29}N_2O^+$; calc. 373.22744). Anal. calc. for $C_{25}H_{29}F_6N_2OP$ (518.47): C 57.91, H 5.64, N 5.40; found: C 57.85, H 5.54, N 5.37.



(*E*)-**14f** (*Z*)-**14f**

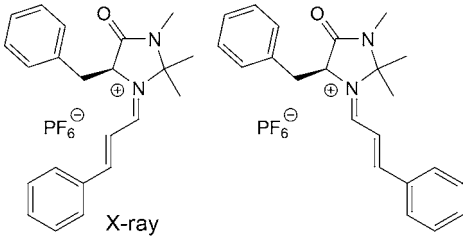
*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-3-methyl-4-oxo-2-[(*E*)-2-phenylethenyl]-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14f** and (*Z*)-**14f**, resp.). Prepared from **11d** (625 mg, 1.59 mmol) and cinnamaldehyde (215 µl, 1.67 mmol). *GP 4: V*$_1$ 2 ml; *V*$_2$ 10 µl; *t*$_1$ 15 d. Yield: 300 mg (34%). Yellow solid. (*E*)-**14f**/(*Z*)-**14f** 1:0.38. M.p. 175–190°. $[\alpha]_D^{r.t.} = +343.3$ (*c* = 0.09, CH_2Cl_2). IR: 1727*m* ,1644*w*, 1624*m*, 1607*m*, 1590*m*, 1496*w*, 1455*w*, 1402*m*, 1376*w*, 1331*w*, 1314*w*, 1282*m*, 1258*w*, 1182*m*, 1111*w*, 1081*w*, 1059*w*, 1013*w*, 1001*w*, 970*w*, 884*w*, 829*s*, 776*m*, 750*m*, 734*m*, 693*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14f**: 2.85 (*s*, MeN); 3.64 (*dd*, *J* = 3.1, 14.5, 1 H, CH_2); 3.84 (*dd*, *J* = 5.7, 14.6, 1 H, CH_2); 4.27 (*dd*, *J* = 9.3, 15.7, H–C(1″)); 5.58 (br. *s*, H–C(5)); 6.03 (*d*, *J* = 9.3, H–C(2)); 7.20 (*d*, *J* = 15.7, H–C(2″)); 7.25–7.34 (*m*, 3 arom. H); 7.35–7.49 (*m*, 5 arom. H); 7.50–7.58 (*m*, 2 arom. H); 7.60–7.65 (*m*, 2 arom. H); 7.70–7.76 (*m*, 1 arom. H); 7.90 (*dd*, *J* = 10.8, 15.0, H–C(2′)); 8.00–8.05 (*m*, 2 arom. H); 8.42 (*d*, *J* = 15.0, H–C(3′)); 9.08 (*d*, *J* = 11.0, H–C(1′)). ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14f**: 2.85 (*s*, MeN); 3.69 (*dd*, *J* = 2.8, 4.7, CH_2); 4.35 (*dd*, *J* = 9.2, 15.9, H–C(1″)); 5.31 (*t*, *J* = 4.6, H–C(5)); 6.41 (*d*, *J* = 9.2, H–C(2)); 8.32 (*d*, *J* = 15.1, H–C(3′)); 9.18 (*dt*, *J* = 1.3, 10.9, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14f** and (*Z*)-**14f**: 26.9; 27.1; 37.1; 37.5; 64.9; 67.9; 80.3; 83.7; 117.3; 118.3; 121.0; 121.2; 128.3; 128.5; 129.4; 129.6; 129.7; 130.1; 130.2; 130.5; 130.60; 130.63; 131.37; 131.44; 132.1; 132.5; 134.4; 134.7; 135.0; 135.20; 135.22; 135.9; 136.0; 142.2; 143.4; 165.6; 166.0; 166.3; 167.2; 170.2; 170.5. HR-ESI-MS: 407.2118 (100, M^+, $C_{28}H_{27}N_2O^+$; calc. 407.21179). Anal. calc. for $C_{28}H_{27}F_6N_2OP$ (552.49): C 60.87, H 4.93, N 5.07; found: C 60.91, H 5.08, N 5.03.



(*E*)-**14g** (*Z*)-**14g**

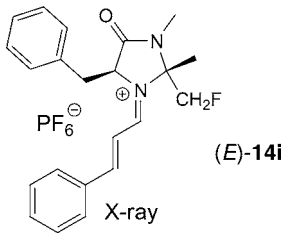
*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-3-methyl-4-oxo-2-phenyl-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14g** and (*Z*)-**14g**, resp.). Prepared from **11g** (560 mg, 1.36 mmol) and cinnamaldehyde (183 µl, 1.43 mmol). *GP 4: V*$_1$ 1.5 ml; *V*$_2$ 10 µl; *t*$_1$ 18 h. Yield: 408 mg (57%). Yellow solid. (*E*)-**14g**/(*Z*)-**14g** = 1:0.49. M.p. 151–154°. $[\alpha]_D^{r.t.} = +152.4$ (*c* = 0.21, CH_2Cl_2). IR: 1732*m*, 1614*w*, 1604*w*, 1589*m*, 1458*w*, 1434*w*, 1397*w*, 1353*w*, 1320*w*, 1281*w*, 1259*w*, 1196*w*, 1178*w*, 1135*w*, 1010*w*, 961*w*, 876*w*, 829*s*, 761*m*, 754*m*, 727*w*, 707*m*, 686*m*, 667*w*, 621*w*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14g**: 2.81 (*s*, MeN); 3.57 (*dd*, *J* = 5.4, 14.7, 1 H, CH_2); 3.88 (*dd*, *J* = 5.3, 14.8, 1 H, CH_2); 5.59 (*t*, *J* = 4.9, H–C(5)); 6.57 (*s*, H–C(2)); 6.98 (*d*, *J* = 7.3, 2 arom. H); 7.12–7.16 (*m*, 2 arom. H); 7.25–7.75 (*m*, 9 arom. H, H–C(2′)); 7.89 (*d*, *J* = 7.4, 2 arom. H); 8.30 (*d*, *J* = 15.0, H–C(3′)); 8.88 (*d*, *J* = 10.8, H–C(1′)). ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14g**: 2.68 (*s*, MeN); 3.83 (*d*, *J* = 5.0, CH_2); 5.40 (*t*, *J* = 4.6, H–C(5)); 6.80 (*s*, H–C(2)); 6.87 (*d*, *J* = 7.3, 2 arom. H); 7.19 (*dd*, *J* = 10.2; 14.2, H–C(2′)); 8.24 (*d*, *J* = 15.0, H–C(3′)); 9.12

(*dt*, *J* = 1.7; 10.9, H–C(1′)). HR-ESI-MS: 381.1961 (100, M^+, $C_{26}H_{25}N_2O^+$; calc. 381.19614). Anal. calc. for $C_{26}H_{25}F_6N_2OP$ (526.45): C 59.32, H 4.79, N 5.32; found: C 59.56, H 4.81, N 5.41.



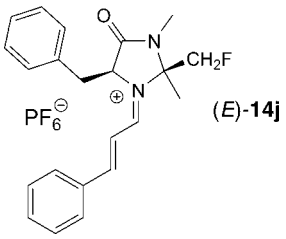
(*E*)-**14h** (*Z*)-**14h**

*(1*E*,5*S*)- and (1*Z*,5*S*)-5-Benzyl-2,2,3-trimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14h** and (*Z*)-**14h**, resp.). Prepared from **11h** (700 mg, 1.92 mmol) and cinnamaldehyde (259 µl, 2.02 mmol). *GP 4:* V_1 1 ml; V_2 10 µl; t_1 24 h. Yield: 702 mg (76%). Yellow solid. (*E*)-**14h**/(*Z*)-**14h** 1:0.02. M.p. 190–194°. $[\alpha]_D^{r.t.} = +613.6$ (*c* = 1.06, EtOH). IR: 1719*m*, 1630*m*, 1603*m*, 1592*m*, 1573*w*, 1459*w*, 1433*w*, 1423*w*, 1404*w*, 1392*w*, 1335*w*, 1291*w*, 1238*w*, 1208*w*, 1198*w*, 1181*w*, 1151*w*, 1121*w*, 1081*w*, 1051*w*, 1020*w*, 999*w*, 881*w*, 827*s*, 759*m*, 746*m*, 702*m*, 687*m*, 642*w*, 606*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): (*E*)-**14h**: 0.75 (*s*, Me); 1.74 (*s*, Me); 2.77 (*s*, MeN); 3.42 (*dd*, *J* = 2.8, 14.7, 1 H, CH_2); 3.61 (*dd*, *J* = 5.8, 14.6, 1 H, CH_2); 5.52 (br. *s*, H–C(5)); 7.04 (*d*, *J* = 6.7, 2 arom. H); 7.24–7.34 (*m*, 3 arom. H); 7.62–7.77 (*m*, 3 arom. H, H–C(2′)); 8.07 (*d*, *J* = 7.3, 2 arom. H); 8.25 (*d*, *J* = 14.9, H–C(3′)); 9.33 (*dd*, *J* = 1.6; 10.4, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)DMSO): (*E*)-**14h**: 23.6; 25.1; 26.5; 35.9; 63.8; 84.9; 118.6; 127.9; 128.9; 129.5; 129.9; 131.4; 133.5; 133.9; 134.6; 164.3; 164.5; 167.9. ^{1}H-NMR (400 MHz, (D_6)DMSO): (*Z*)-**14h**: 5.31 (*s*, H–C(5)); 9.16 (*d*, *J* = 11.1, H–C(1′)). HR-ESI-MS: 333.1961 (100, M^+, $C_{22}H_{25}N_2O^+$; calc. 333.19614). Anal. calc. for $C_{22}H_{25}F_6N_2OP$ (478.41): C 55.23, H 5.27, N 5.86; found: C 55.51, H 5.40, N 5.65.

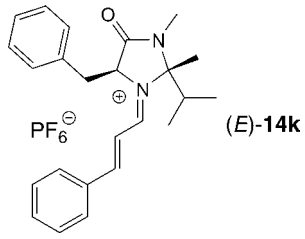


(*E*)-**14i**

*((1*E*,2*S*,5*S*)-5-Benzyl-2-(fluoromethyl)-2,3-dimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]-imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14i**). Prepared from **11i** (578 mg, 1.51 mmol) and cinnamaldehyde (204 µl, 1.59 mmol). *GP 4:* V_1 1.5 ml; V_2 10 µl; t_1 18 h. Yield: 650 mg (86%). Yellow solid. M.p. 170–172°. $[\alpha]_D^{r.t.} = +714.8$ (*c* = 0.51, CH_2Cl_2). IR: 1725*m*, 1620*m*, 1602*m*, 1590*m*, 1457*w*, 1432*w*, 1423*w*, 1393*w*, 1334*w*, 1315*w*, 1283*w*, 1236*w*, 1199*w*, 1187*w*, 1180*w*, 1165*w*, 1043*w*, 1021*w*, 881*w*, 829*s*, 761*m*, 750*m*, 703*m*, 688*m*, 648*w*, 640*w*. ^{1}H-NMR (400 MHz, (D_6)Acetone): 0.94 (*d*, *J* = 2.8, Me); 2.91 (*s*, MeN); 3.60 (*dd*, *J* = 2.7, 14.7, 1 H, CH_2); 3.86 (*dd*, *J* = 5.8, 14.7, 1 H, CH_2); 4.86 (*dd*, *J* = 11.7, 17.8, 1 H, CH_2F); 4.98 (*dd*, *J* = 11.7, 17.4, 1 H, CH_2F); 5.59–5.62 (*m*, H–C(5)); 7.14–7.19 (*m*, 2 arom. H); 7.31–7.38 (*m*, 3 arom. H); 7.61–7.68 (*m*, 2 arom. H); 7.73–7.78 (*m*, 1 arom. H); 7.93 (*dd*, *J* = 10.7, 14.9, H–C(2′)); 8.05–8.10 (*m*, 2 arom. H); 8.53 (*d*, *J* = 14.9, H–C(3′)); 9.27 (*dd*, *J* = 1.9, 10.7, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): 17.9 (*d*, *J* = 1.4); 25.8; 37.0; 65.2; 83.1 (*d*, *J* = 181.4); 86.7 (*d*, *J* = 17.0); 118.5; 129.1; 129.9; 130.6; 131.0; 132.8; 134.3; 134.5; 136.4; 166.0; 169.0; 169.1. HR-ESI-MS: 351.1867 (100, M^+, $C_{22}H_{24}FN_2O^+$; calc. 351.18672). Anal. calc. for $C_{22}H_{24}F_7N_2OP$ (496.40): C 53.23, H 4.87, N 5.64; found: C 53.34, H 4.90, N 5.54.

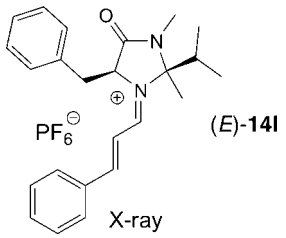


*(1*E*,2*R*,5*S*)-5-Benzyl-2-(fluoromethyl)-2,3-dimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]-imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14j**). Prepared from **11j** (632 mg, 1.65 mmol) and cinnamaldehyde (223 µl, 1.74 mmol). *GP 4: V*$_1$ 2 ml; *V*$_2$ 10 µl; *t*$_1$ 48 h. No filterable precipitate was formed, but rather a two-phase system with the product (thick orange liquid) on the bottom (bottom phase) and the soln. on the top (top phase) of the flask. The top phase was carefully removed *via* a syringe, followed by addition of anh. Et_2O (6 ml) to the remaining product (bottom phase). The so-formed mixture was stirred vigorously whereby the product slowly solidified. The soln. was again removed *via* a syringe and replaced by anh. Et_2O (6 ml), followed by vigorous stirring and scratching with spatula. The process (removing solvent, adding anh. Et_2O, stirring/scratching) was repeated, until a finely powdered product was formed. The precipitate was collected on a dry ceramic frit under Ar and washed with anh. Et_2O (20 ml) give (*E*)-**14j**. Yield: 630 mg (76%). Yellow solid. M.p. 90 – 97°. $[\alpha]_D^{rt}$ = +316.6 (*c* = 0.61, CH_2Cl_2). IR: 1721*m*, 1616*m*, 1604*m*, 1586*s*, 1456*w*, 1429*w*, 1394*m*, 1325*w*, 1282*w*, 1237*w*, 1200*m*, 1181*m*, 1052*w*, 1013*w*, 1000*w*, 826*s*, 754*m*, 702*m*, 684*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): 2.02 (*d*, *J* = 2.2, Me); 3.04 (*s*, MeN); 3.40 (*dd*, *J* = 7.0, 14.0, 1 H, CH_2); 3.72 (*dd*, *J* = 5.1, 14.7, 1 H, CH_2); 4.18 (*dd*, *J* = 11.0, 46.9, 1 H, CH_2F); 4.68 (*dd*, *J* = 11.0, 45.5, 1 H, CH_2F); 5.52 (*t*, *J* = 5.2, H–C(5)); 7.20 (*dd*, *J* = 10.6, 14.9, H–C(2′)); 7.21 – 7.26 (*m*, 1 arom. H); 7.33 – 7.38 (*m*, 4 arom. H); 7.55 – 7.61 (*m*, 2 arom. H); 7.67 – 7.73 (*m*, 1 arom. H); 7.78 (*d*, *J* = 7.5, 2 arom. H); 8.31 (*d*, *J* = 14.9, H–C(3′)); 9.19 (*d*, *J* = 10.5, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): 20.6 (*d*, *J* = 1.7); 26.4; 38.3 (*d*, *J* = 3.6); 64.9; 83.2 (*d*, *J* = 181.2); 86.4 (*d*, *J* = 18.5); 118.9; 129.1; 130.1; 130.4; 130.9; 132.4; 134.3; 135.9; 136.0; 166.3; 167.3; 170.4. HR-ESI-MS: 351.1867 (100, M^+, $C_{22}H_{24}FN_2O^+$; calc. 351.18672). Anal. calc. for $C_{22}H_{24}F_7N_2OP$ (496.40): C 53.23, H 4.87, N 5.64; found: C 53.45, H 4.91, N 5.44.

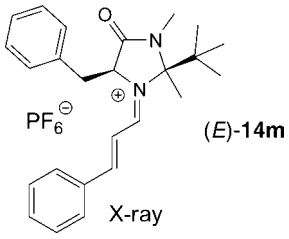


*(1*E*,2*S*,5*S*)-5-Benzyl-2,3-dimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]-2-(propan-2-yl)imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14k**). Prepared from **11k** (600 mg, 1.53 mmol) and cinnamaldehyde (236 µl, 1.83 mmol (1.2 equiv.)). *GP 4: V*$_1$ 3 ml; *V*$_2$ 10 µl; *t*$_1$ 4 d. No filterable precipitate was formed, but rather a two-phase system with the product (thick orange liquid) on the bottom (bottom phase) and the soln. on the top (top phase) of the flask. The top phase was carefully remover *via* a syringe, followed by addition of anh. Et_2O (10 ml) to the remaining product (bottom phase). The so-formed mixture was stirred vigorously whereby the product slowly solidified. The soln. was again removed *via* a syringe and replaced by anh. Et_2O (10 ml), followed by vigorous stirring and scratching with spatula. The process (removing solvent, adding anh. Et_2O, stirring/scratching) was repeated until a finely powdered product was formed. The precipitate was collected on a dry ceramic frit under Ar and washed with anh. Et_2O (20 ml) give (*E*)-**14k**. Yield: 570 mg (73%). Yellow solid. M.p. 105 – 120°. $[\alpha]_D^{rt}$ = +561.2 (*c* = 0.58, CH_2Cl_2). IR: 1714*m*, 1618*m*, 1603*m*, 1587*s*, 1456*w*, 1437*w*, 1389*w*, 1334*w*, 1310*w*, 1279*w*, 1234*w*, 1199*m*, 1180*m*, 1135*w*, 1113*w*, 1082*w*, 1055*w*, 1016*w*, 1000*w*, 876*w*, 827*s*, 756*m*, 741*m*, 703*m*, 684*m*.

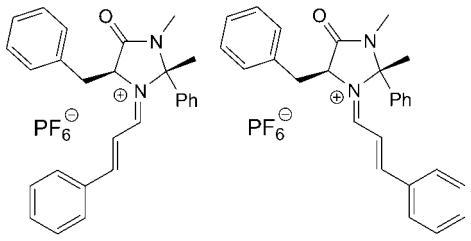
^{1}H-NMR (400 MHz, (D_6)Acetone): 0.99 (*s*, Me); 1.00 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH); 1.01 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH); 2.39 – 2.52 (*m*, Me$_2$C*H*); 2.89 (*s*, MeN); 3.60 (*d*, *J* = 14.2, 1 H, CH_2); 3.85 (*dd*, *J* = 5.7, 14.6, 1 H, CH_2); 5.61 (br. *s*, H–C(5)); 7.06 – 7.17 (*m*, 2 arom. H); 7.28 – 7.37 (*m*, 3 arom. H); 7.60 – 7.69 (*m*, 2 arom. H); 7.71 – 7.79 (*m*, 1 arom. H); 7.94 (*dd*, *J* = 10.8; 14.8, H–C(2′)); 8.07 (*d*, *J* = 7.5, 2 arom. H); 8.55 (*d*, *J* = 14.9, H–C(3′)); 9.15 (*dd*, 2.0; 10.7, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): 16.1; 17.0; 20.8; 27.3; 36.9; 40.1; 65.7; 91.0; 118.9; 129.1; 129.8; 130.6; 130.9; 132.7; 134.4; 134.7; 136.1; 166.1; 167.92; 167.94. HR-ESI-MS: 361.2274 (100, M^+, $C_{24}H_{29}N_2O^+$; calc. 361.22744). Anal. calc. for $C_{24}H_{29}F_6N_2OP$ (506.46): C 56.92, H 5.77, N 5.53; found: C 57.14, H 5.93, N 5.33.



*(1*E*,2*R*,5*S*)-5-Benzyl-2,3-dimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]-2-(propan-2-yl)imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14l**). Prepared from **11l** (1.36 g, 3.46 mmol) and cinnamaldehyde (467 µl, 3.63 mmol). *GP 4: V*$_1$ 6 ml; *V*$_2$ 20 µl; *t*$_1$ 13 h. Yield: 1.63 g (92%). Yellow solid. M.p. 166 – 168°. $[\alpha]_D^{r.t.} = +189.8$ (*c* = 0.52, CH_2Cl_2). IR: 1709*m*, 1610*m*, 1585*s*, 1456*w*, 1431*w*, 1400*w*, 1392*m*, 1335*w*, 1321*w*, 1307*w*, 1291*w*, 1196*m*, 1180*m*, 1138*w*, 1114*w*, 1079*w*, 1052*w*, 1018*w*, 1000*w*, 875*w*, 827*s*, 766*m*, 758*s*, 750*m*, 711*m*, 697*m*, 687*m*, 647*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): 1.11 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH); 1.17 (*d*, *J* = 6.9, 3 H, *Me*$_2$CH); 2.01 (*s*, Me); 2.34 – 2.46 (*m*, Me$_2$C*H*); 3.08 (*s*, MeN); 3.42 (*dd*, *J* = 5.6, 15.3, 1 H, CH_2); 3.71 (*dd*, *J* = 5.4, 15.3, 1 H, CH_2); 5.37 (*t*, *J* = 4.9, H–C(5)); 6.93 (*dd*, *J* = 10.6, 15.0, H–C(2′)); 7.31 – 7.36 (*m*, 1 arom. H); 7.41 – 7.47 (*m*, 2 arom. H); 7.51 – 7.58 (*m*, 4 arom. H); 7.59 – 7.64 (*m*, 2 arom. H); 7.66 – 7.71 (*m*, 1 arom. H); 8.37 (*d*, *J* = 15.0, H–C(3′)); 9.09 (*dd*, *J* = 1.8; 10.6, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): 16.8; 17.6; 22.5; 27.4; 37.2; 38.7; 64.4; 91.5; 118.6; 128.4; 129.8; 130.07; 130.15; 131.7; 134.0; 135.4; 137.0; 166.1; 166.3; 169.1. HR-ESI-MS: 361.2274 (100, M^+, $C_{24}H_{29}N_2O^+$; calc. 361.22744). Anal. calc. for $C_{24}H_{29}F_6N_2OP$ (506.46): C 56.92, H 5.77, N 5.53; found: C 56.73, H 5.66, N 5.53.

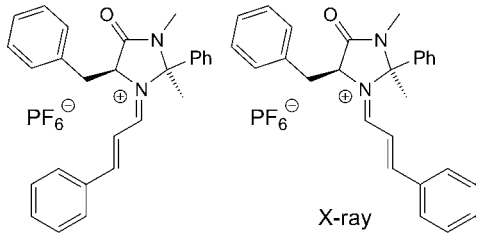


*(1*E*,2*R*,5*S*)-5-Benzyl-2-(*tert*-butyl)-2,3-dimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14m**). Prepared from **11m** (1.59 g, 3.90 mmol) and cinnamaldehyde (526 µl, 4.10 mmol). *GP 4: V*$_1$ 4 ml; *V*$_2$ 20 µl; *t*$_1$ 2 h. Yield: 420 mg (20%). Yellow solid. M.p. 195 – 198°. $[\alpha]_D^{r.t.} = +159.7$ (*c* = 0.32, CH_2Cl_2). IR: 1722*m*, 1616*m*, 1604*m*, 1590*m*, 1480*w*, 1455*w*, 1435*w*, 1411*w*, 1392*w*, 1281*w*, 1235*w*, 1199*m*, 1180*w*, 1134*w*, 1091*w*, 1080*w*, 1012*w*, 833*s*, 766*w*, 755*m*, 734*w*, 700*w*, 689*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.17 (*s*, ^{t}Bu); 1.96 (*s*, Me); 3.08 (*s*, MeN); 3.38 (*dd*, *J* = 4.3; 15.5, 1 H, CH_2); 3.51 (*dd*, *J* = 5.8, 15.3, 1 H, CH_2); 5.24 (*t*, *J* = 4.4, H–C(5)); 6.59 (*dd*, *J* = 10.4, 14.9, H–C(2′)); 7.35 – 7.72 (*m*, 10 arom. H); 8.35 (*d*, *J* = 14.9, H–C(3′)); 9.26 (*d*, *J* = 10.4, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)DMSO): 20.8; 26.2; 29.3; 37.1; 40.6; 63.4; 93.2; 118.8; 127.5; 129.1; 129.3; 129.6; 130.7; 133.1; 134.7; 137.4; 163.8; 166.9; 169.8. HR-ESI-MS: 375.2431 (100, M^+, $C_{25}H_{31}N_2O^+$; calc. 375.24309). Anal. calc. for $C_{25}H_{31}F_6N_2OP$ (520.49): C 57.69, H 6.00, N 5.38; found: C 57.43, H 6.02, N 5.34.



(*E*)-**14n** (*Z*)-**14n**

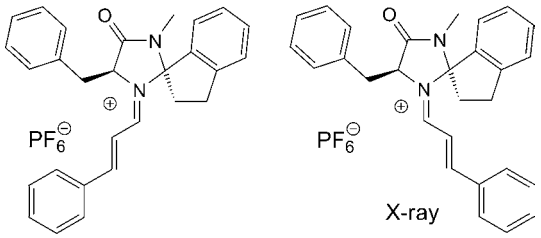
*(1*E*,2*S*,5*S*)- and (1*Z*,2*S*,5*S*)-5-Benzyl-2,3-dimethyl-4-oxo-2-phenyl-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14n** and (*Z*)-**14n**, resp.). Prepared from **11n** (806 mg, 1.89 mmol) and cinnamaldehyde (255 µl, 1.99 mmol). *GP 4: V*$_1$ 7 ml; *V*$_2$ 10 µl; *t*$_1$ 24 h. Yield: 974 mg (95%). Yellow solid. (*E*)-**14n**/(*Z*)-**14n** 1:0.12. M.p. 131–138°. $[\alpha]_D^{r.t.} = +543.5$ ($c = 0.26$, CH_2Cl_2). IR: 1721*m*, 1620*m*, 1602*m*, 1587*s*, 1455*w*, 1418*w*, 1392*w*, 1333*w*, 1313*w*, 1282*w*, 1234*w*, 1201*m*, 1181*m*, 1091*w*, 1014*w*, 1001*w*, 832*s*, 770*m*, 758*m*, 742*m*, 702*m*, 684*m*, 645*w*, 604*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): (*E*)-**14n**: 1.26 (*s*, Me); 2.49 (*s*, MeN); 3.54 (*dd*, *J* = 3.0, 14.7, 1 H, CH_2); 3.78 (*dd*, *J* = 5.8, 14.7, 1 H, CH_2); 5.93 (*s*, H–C(5)); 7.13 (*d*, *J* = 7.0, 2 arom. H); 7.30–7.42 (*m*, 3 arom. H); 7.46–7.75 (*m*, 8 arom. H, H–C(2′)); 8.00 (*d*, *J* = 7.5, 2 arom. H); 8.18 (*d*, *J* = 14.9, H–C(3′)); 8.86 (*dd*, *J* = 1.0; 10.5, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14n**: 22.1; 26.2; 37.4; 65.1; 88.6; 118.6; 128.0; 129.2; 130.1; 130.48; 130.54; 131.2; 131.8; 132.7; 134.4; 135.1; 136.2; 138.4; 165.7; 167.8; 170.3. ^{1}H-NMR (400 MHz, (D_6)DMSO): (*Z*)-**14n**: 1.36 (*s*, Me); 2.45 (*s*, MeN); 5.80 (br. *s*, H–C(5)); 6.67 (*dd*, *J* = 11.2, 14.8, H–C(2′)); 7.25 (*d*, *J* = 6.6, 2 arom. H); 8.13 (*d*, *J* = 14.9, H–C(3′)); 9.16 (*d*, *J* = 11.0, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*Z*)-**14n**: 20.8; 25.5; 37.6; 68.7; 87.2; 116.9; 128.1; 129.1; 131.2; 131.8; 132.3; 134.1; 137.2; 164.8; 167.5; 169.4. HR-ESI-MS: 395.2118 (100, M^+, $C_{27}H_{27}N_2O^+$; calc. 395.21179). Anal. calc. for $C_{27}H_{27}F_6N_2OP$ (540.48): C 60.00, H 5.03, N 5.18; found: C 59.74, H 4.81, N 5.16.



(*E*)-**14o** (*Z*)-**14o**

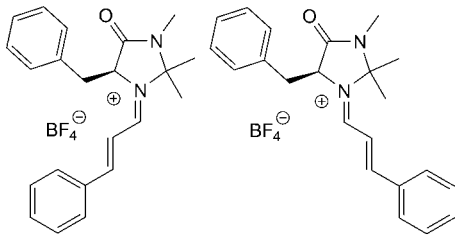
*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-2,3-dimethyl-4-oxo-2-phenyl-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Hexafluorophosphate* ((*E*)-**14o** and (*Z*)-**14o**, resp.). Prepared from **11o** (1.67 g, 3.92 mmol) and cinnamaldehyde (529 µl, 4.12 mmol). *GP 4: V*$_1$ 3 ml; *V*$_2$ 10 µl; *t*$_1$ 5 h. Yield: 1.94 g (91%). Yellow solid. (*E*)-**14o**/(*Z*)-**14o** 1:0.32. M.p. 178–183°. $[\alpha]_D^{r.t.} = +69.3$ ($c = 0.22$, CH_2Cl_2). IR: 1707*m*, 1625*m*, 1603*m*, 1593*m*, 1574*w*, 1447*w*, 1412*w*, 1397*w*, 1388*w*, 1339*w*, 1281*w*, 1258*w*, 1240*w*, 1183*m*, 1123*w*, 1100*w*, 1011*w*, 839*s*, 824*s*, 755*m*, 749*s*, 701*s*, 684*m*, 612*w*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14o**: 2.37 (*s*, Me); 2.86 (*s*, MeN); 3.32 (*dd*, *J* = 6.0, 14.7, 1 H, CH_2); 3.76 (*dd*, *J* = 5.4, 14.7, 1 H, CH_2); 5.71 (*t*, *J* = 5.0, H–C(5)); 6.92–6.97 (*m*, 2 arom. H); 7.11–7.27 (*m*, 4 arom. H); 7.36–7.55 (*m*, 5 arom. H, H–C(2′)); 7.57–7.71 (*m*, 2 arom. H); 7.88–7.92 (*m*, 2 arom. H); 8.26 (*d*, *J* = 14.9, H–C(3′)); 9.17 (*dd*, *J* = 1.8; 10.6, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14o**: 25.8; 26.9; 37.2; 64.2; 88.3; 119.1; 127.3; 129.7; 130.1; 130.2; 130.6; 132.0; 134.1; 134.9; 135.3; 136.0; 165.9; 166.1; 169.1. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14o**: 2.40 (*s*, Me); 2.53 (*s*, MeN); 3.82 (*dd*, *J* = 5.8, 15.1, 1 H, CH_2); 3.89 (*dd*, *J* = 2.7, 15.0, 1 H, CH_2); 5.64 (br. *s*, H–C(5)); 6.60 (*d*, *J* = 7.6, 2 arom. H); 6.73 (*dd*, *J* = 11.0, 14.9, H–C(2′)); 8.37 (*d*, *J* = 14.9, H–C(3′)); 9.35 (*dd*, *J* = 1.5, 11.0, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*Z*)-**14o**:

22.1; 25.4; 33.9; 66.6; 86.3; 116.8; 127.9; 128.6; 129.9; 131.0; 131.3; 131.7; 133.8; 134.7; 135.5; 136.0; 164.7; 165.9; 168.8. HR-ESI-MS: 395.2118 (100, M^+, $C_{27}H_{27}N_2O^+$; calc. 395.21179). Anal. calc. for $C_{27}H_{27}F_6N_2OP$ (540.48): C 60.00, H 5.03, N 5.18; found: C 59.79, H 5.20, N 5.12.



(*E*)-**14p** (*Z*)-**14p**

*(1*E*,2*R*,5*S*)- and (1*Z*,2*R*,5*S*)-5-Benzyl-2′,3′-dihydro-3-methyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]spiro[imidazolidin-1-ium-2,1′-indene] Hexafluorophosphate* ((*Z*)-**14p**). Prepared from **11p** (384 mg, 0.88 mmol) and cinnamaldehyde (118 µl, 0.92 mmol). *GP 4: V*$_1$ 1 ml; *V*$_2$ 5 µl; *t*$_1$ 3 h. Yield: 440 mg (90%). Yellow solid. (*E*)-**14p**/(*Z*)-**14p** = 1:0.26. M.p. 158–161°. $[\alpha]_D^{r.t.} = +44.4$ (*c* = 0.27, CH_2Cl_2). IR: 1717*m*, 1708*m*, 1625*m*, 1588*m*, 1573*m*, 1445*w*, 1417*w*, 1398*w*, 1336*w*, 1309*w*, 1286*w*, 1253*w*, 1195*w*, 1182*m*, 1130*w*, 1088*w*, 1010*w*, 873*w*, 835*s*, 776*w*, 760*m*, 745*m*, 701*m*, 685*m*. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*E*)-**14p**: 2.67 (*d*, *J* = 0.3, MeN); 2.80–3.04 (*m*, 2 H, CH_2); 3.17 (*ddd*, *J* = 3.7, 9.1; 17.0, 1 H, CH_2); 3.37–3.46 (*m*, 1 H, CH_2); 3.71 (*dd*, *J* = 3.0, 15.0, 1 H, CH_2); 3.94 (*dd*, *J* = 5.8, 14.9, 1 H, CH_2); 5.13 (*d*, *J* = 7.8, 1 arom. H); 5.75–5.80 (*m*, H–C(5)); 6.97–7.03 (*m*, 1 arom. H); 7.17–7.22 (*m*, 2 arom. H); 7.33–7.53 (*m*, 5 arom. H); 7.57–7.66 (*m*, 2 arom. H); 7.69–7.76 (*m*, 1 arom. H); 7.91 (*dd*, *J* = 10.7; 14.9, H–C(2′)); 8.00–8.05 (*m*, 2 arom. H); 8.44 (*d*, *J* = 14.9, H–C(3′)); 8.61 (*dd*, *J* = 2.2; 10.7, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**14p**: 26.3; 29.5; 36.7; 39.4; 64.9; 96.9; 119.7; 124.8; 126.8; 128.8; 128.9; 130.2; 130.4; 131.1; 132.5; 132.6; 134.6; 134.9; 135.8; 136.2; 147.5; 165.6; 167.4; 169.2. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**14p**: 2.58 (*d*, *J* = 0.5, MeN); 3.80 (*dd*, *J* = 5.9, 14.9, 1 H, CH_2); 3.88 (*dd*, *J* = 2.6, 15.0, 1 H, CH_2); 4.90 (*d*, *J* = 7.8, 1 arom. H); 5.58 (*d*, *J* = 5.1, H–C(5)); 6.25 (*dd*, *J* = 11.1, 14.9, H–C(2′)); 6.92–6.97 (*m*, 1 arom. H); 8.37 (*d*, *J* = 14.9, H–C(3′)); 9.41 (*dd*, *J* = 1.5, 11.1, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*Z*)-**14p**: 25.2; 35.0; 37.3; 67.4; 94.8; 116.5; 124.4; 126.9; 129.3; 129.4; 130.5; 131.5; 131.7; 132.8; 134.1; 134.8; 137.2; 146.2; 164.4; 166.1; 169.1. HR-ESI-MS: 407.2123 (100, M^+, $C_{28}H_{27}N_2O^+$; calc. 407.2118). Anal. calc. for $C_{28}H_{27}F_6N_2OP$ (552.49): C 60.87, H 4.93, N 5.07; found: C 60.98, H 5.18, N 4.90.



(*E*)-**13a** (*Z*)-**13a**

*(1*E*,5*S*)- and (1*Z*,5*S*)-5-Benzyl-2,2,3-trimethyl-4-oxo-1-[(2*E*)-3-phenylprop-2-en-1-ylidene]imidazolidin-1-ium Tetrafluoroborate* ((*E*)-**13a** and (*Z*)-**13a**, resp.). To a soln. of **10c** (445 mg, 1.45 mmol) in anh. CH_2Cl_2 (10 ml) under Ar were added 4 Å MS (3.6 g), cinnamaldehyde (243 µl, 1.89 mmol), and Et_3N (5 µl). The reaction mixture was stirred at r.t. for 4 d. Then, it was filtered through an HPLC filter into a syringe and, during 5 min, injected into a vigorously stirred mixture of anh. Et_2O (60 ml) and anh. petroleum ether (10 ml) in a *Schlenk* flask under Ar. The fine precipitate formed was stirred for additional 5 min and then collected on a dry ceramic frit under Ar and washed with anh. Et_2O (40 ml) to

Table 6. *Selected Experimental Details for X-Ray Structures*

	15[a])	**14b**[b])	**14c**	**14e**	**14g**[c])
CCDC No.	990626	990627	990633	990628	990629
Empirical Formula	$C_{14}H_{19}N_2O^+ \cdot F_6P^-$	$C_{22}H_{19}N_2O^+ \cdot F_6P^-$	$C_{23}H_{27}N_2O^+ \cdot F_6P^-$	$C_{25}H_{29}N_2O^+ \cdot F_6P^-$	$C_{26}H_{27}N_2O^+ \cdot F_6P^-$
Formula weight	376.28	478.42	492.44	518.48	611.39
Spacegroup	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$C2$	$P2_12_12_1$
Z	4	4	4	4	4
Unit cell parameter					
a [Å]	8.590(1)	10.656(1)	11.578(1)	18.784(1)	10.983(1)
b [Å]	8.815(1)	11.478(1)	13.975(1)	9.117(1)	12.475(1)
c [Å]	21.954(1)	22.674(1)	14.451(1)	16.164(1)	20.583(1)
α [°]					
β [°]				113.64(1)	
γ [°]					
V [Å]^3	1662.5(1)	2773.2(2)	2338.1(2)	2535.9(2)	2820.3(2)
D_x [g cm^{-3}]	1.503	1.146	1.399	1.358	1.440
Radiation	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
θ [°]	2.4 – 25.0	2.5 – 27.5	2.4 – 27.5	2.5 – 27.5	2.5 – 25.3
μ [mm^{-1}]	0.23	0.15	0.18	0.17	0.35
Temp. [K]	173	223	223	223	223
Crystal size [mm]	0.31 × 0.1 × 0.06	0.27 × 0.21 × 0.14	0.27 × 0.24 × 0.21	0.33 × 0.21 × 0.2	0.48 × 0.06 × 0.02
Reflections/$I > 2\sigma(I)$	2920/2556	6220/4618	5207/4336	5297/4473	5108/4136
Ref. parameters	217	289	328	320	438
$\Delta\rho_{max}$ [e Å^{-3}]	0.87	0.92	0.64	0.61	0.45
R_{obs}	0.087	0.099	0.058	0.074	0.065
wR_{all}	0.244	0.283	0.164	0.219	0.184
Flack parameter	0.2(3)	0.0(2)	− 0.1(2)	0.0(2)	0.0(1)

[a]) High $\Delta\rho$ close to disordered PF_6^- moiety. [b]) Channels parallel to a-axis contain totally disordered solvent molecules. OLEX2 [25] Calculation provides a volume of 356 A^3 and 15 electrons. Refining with solvent mask

give (*E*)-**13a**/(*Z*)-**13a**. Yield: 270 mg (44%). Orange yellow solid. (*E*)-**13a**/(*Z*)-**13a** 1 : 0.03. M.p. 95 – 115°. $[\alpha]_D^{r.t.} = +636.3$ ($c = 0.81$, CH_2Cl_2). IR: 1713*m*, 1623*m*, 1604*m*, 1590*s*, 1575*m*, 1456*w*, 1439*w*, 1403*m*, 1393*m*, 1333*w*, 1311*w*, 1282*w*, 1235*w*, 1199*m*, 1180*m*, 1153*w*, 1049*s*, 1033*s*, 998*s*, 935*w*, 869*w*, 754*m*, 703*m*, 685*m*. ^{1}H-NMR (300 MHz, (D_6)Acetone): (*E*)-**13a**: 0.90 (*s*, Me); 1.87 (*s*, Me); 2.87 (*d*, $J = 0.4$, MeN); 3.56 (*dd*, $J = 3.1, 14.6$, 1 H, CH_2); 3.78 (*dd*, $J = 5.7, 14.6$, 1 H, CH_2); 5.55 – 5.61 (*m*, H–C(5)); 7.12 – 7.18 (*m*, 2 arom. H); 7.25 – 7.35 (*m*, 3 arom. H); 7.56 – 7.64 (*m*, 2 arom. H); 7.67 – 7.73 (*m*, 1 arom. H); 7.82 (*dd*, $J =$ 10.6; 15.0, H–C(2′)); 8.01 – 8.07 (*m*, 2 arom. H); 8.52 (*d*, $J = 15.0$, H–C(3′)); 9.29 (*dd*, $J = 2.0$; 10.6, H–C(1′)). ^{13}C-NMR (101 MHz, (D_6)Acetone): (*E*)-**13a**: 24.4; 25.7; 27.3; 37.1; 65.0; 86.4; 118.9; 128.0; 129.9; 130.4; 131.0; 132.4; 134.8; 135.0; 135.6; 165.3; 166.8; 168.9. ^{1}H-NMR (400 MHz, (D_6)Acetone): (*Z*)-**13a**: 5.35 (*t*, $J = 4.0$, H–C(5)); 9.16 (*dd*, $J = 1.2$, 11.4, H–C(1′)). HR-ESI-MS: 333.1961 (100, M^+, $C_{22}H_{25}N_2O^+$; calc. 333.19614). Anal. calc. for $C_{22}H_{25}BF_4N_2O$ (420.25): C 62.88, H 6.00, N 6.67; found: C 62.33, H 6.07, N 6.59.

Determination of the X-Ray Crystal Structures (Table 6). Suitable single crystals were analyzed on a *Bruker Nonius Kappa CCD* diffractometer with MoK_α radiation (λ 0.71073 Å; graphite monochromator). Structures were solved by direct methods (SIR97) [23] and refined by full-matrix least-squares on F^2 (SHELXL97) [24]. If possible, the H-atoms were located from a difference electron density map or constrained at ideal positions and included in the refinement. *CIF* files of the data can be obtained free of charge on application to the *Cambridge Crystallographic Data Centre* (CCDC), 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

rac-**14g**	**14i**	**14l**	**14m**	**14o**	**14p**[d])
990634	990630	990635	990636	990631	990632
$C_{26}H_{25}N_2O^+$	$C_{22}H_{24}FN_2O^+$	$C_{24}H_{29}N_2O^+$	$C_{25}H_{31}N_2O^+$	$C_{27}H_{27}N_2O^+$	$C_{28}H_{27}N_2O^+$
$\cdot F_6P^-$	$\cdot F_6P^-$	$\cdot F_6P^-$	$\cdot F_6P^-$	$\cdot F_6P^-$	$\cdot CH_2Cl_2 \cdot F_6P^-$
526.46	496.41	506.47	520.50	540.49	637.43
$P2_1/c$	$P2_12_12_1$	$P1$	$P2_12_12_1$	$P2_12_12_1$	$C2$
4	4	2	4	4	4
11.282(1)	9.891(1)	9.995(1)	11.050(1)	9.073(1)	16.654(1)
8.844(1)	13.358(1)	11.795(1)	11.764(1)	11.227(1)	11.018(1)
25.432(2)	17.300(1)	11.980(1)	19.806(1)	25.277(1)	16.655(1)
		63.32(1)			
101.12(1)		77.07(1)			99.21(1)
		85.86(1)			
2490.0(2)	2285.6(1)	1229.3(1)	2574.5(2)	2574.8(1)	3016.7(2)
1.404	1.443	1.368	1.343	1.394	1.404
MoK_α	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
2.4 – 27.4	2.6 – 27.5	2.5 – 27.5	2.5 – 27.5	2.4 – 27.5	2.4 – 27.5
0.18	0.19	0.18	0.17	0.17	0.33
223	223	223	223	223	223
0.36 × 0.33 × 0.12	0.21 × 0.15 × 0.09	0.23 × 0.15 × 0.14	0.36 × 0.12 × 0.02	0.27 × 0.24 × 0.12	0.21 × 0.20 × 0.13
4640/3001	5231/4314	9357/7321	5839/3965	5661/4016	6093/4390
372	371	613	321	334	372
0.89	0.26	0.59	0.22	0.39	1.02
0.098	0.047	0.076	0.068	0.067	0.097
0.275	0.144	0.215	0.191	0.194	0.270
	0.0(1)	0.0(1)	0.0(2)	0.2(2)	0.2(2)

gives R of 0.061 and $\Delta\rho_{max}$ of 0.25. [c]) Small crystal did not allow to collect higher angle data. [d]) High $\Delta\rho$ close to disordered CH_2Cl_2 solvent molecule.

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