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Formation of epoxides and *N*-arylaziridines via a simple Mg-Barbier reaction in DMF

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ABSTRACT

The Mg-activation of benzal bromide **2b** in DMF in the presence of carbonyl compounds **1** or imines **4** leads to epoxides **3** and *N*-arylaziridines **5**, respectively, with acceptable isolated yields. It was found that DMF is likely involved in this process to form a nucleophilic intermediate by reaction with a first generated electrophilic carbene. Results obtained in this chemical approach are compared to those obtained using electrochemical activation, also in DMF.

1. Introduction

The formation of epoxides and aziridines has attracted a lot of synthetic efforts because of their useful further transformations into more complex structures.[1] These small rings are also precursors of alcohol or amine functionalities by ring opening reactions. These rings are conventionally prepared by methods mentioned below.

Epoxides are mainly prepared either by epoxidation of C=C bond with peracids[2] or by nucleophilic addition of α-haloanions (Darzens reaction)[3] or sulfonium ylides[4] to carbonyl compounds.

Unlike to epoxides, the synthesis of aziridines[1f] has attracted less synthetic efforts due to the presence of an additional valency on the heteroatom thus rendering more complicated their further transformations. Whereas the synthesis of aziridines bearing an electron-withdrawing group at the nitrogen (i.e., sulfonyl, phosphoryl or carbonyl group) is well documented, the synthesis of *N*-arylaziridines has received less attention. The principal methods for the preparation of the latter compounds can be divided into four categories depending on the starting materials:

a *From N-arylimines*. Using diazo compounds[5a–c] or by nucleophilic additions of sulfur[6a–b] or arsenic[7] ylides. Addition of α-halogeno anions[8a–d] (Aza-Darzens reactions) or 1,3-dipolar additions[9] or nucleophilic additions of diazoic compounds[10a–d] are also involved.

b *From olefins*. The 1,3-dipolar addition of aryl azides and the subsequent photolysis or thermolysis of 1,2,3-triazolines[11a–b] are more commonly described than the reactions via an aryl nitrene.[12] In CF_3CO_2H, a diastereospecific addition of an aryl nitrenium cation on nucleophilic olefins is also mentioned.[13] Regarding electrophilic olefins, *N*-arylaziridines are obtained from *N*-acyl-*N*-arylhydroxylamines (hydroxamic acids),[14a,b] and possibly in an enantioselective manner.[14c]

c *From epoxides*. The ring opening by diethyl *N*-arylamidophosphates in basic medium leads to oxazaphospholidines, which are decomposed by heating in aziridines.[15]

d *From N-(2-haloethyl)anilines*[16a] *and more particularly from desylanilines, via the corresponding β-chloro secondary amines for the preparation of 1,2,3-triaryllaziridines*.[16b–i] This multistep synthesis is the most used process: first reported by Whittaker et al. in 1938[16b] and thereafter, frequently investigated to improve the yields in *N*-arylaziridines (1,2,3-triphenylaziridine: 40% overall yield, in five steps, from benzaldehyde).[16f]

We have previously reported[17,18] that small rings like cyclopropanes can be prepared in good yields via the magnesium activation of polyhalomethyl compounds (α,α,α-trichlorotoluene,[17] methyl trichloroacetate,[17,18] dichlorodiphenylmethane,[17] and benzal bromide[17]) in the presence of acyclic or cyclic activated olefins

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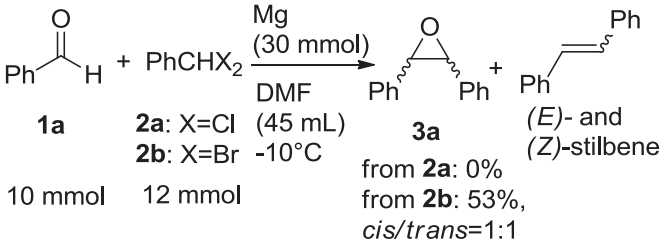
in DMF. In this study, our aim has been to determine the scope and limitations of such Mg-Barbier reaction for the access to epoxides and aziridines starting from carbonyl compounds or *N*-arylimines, respectively. Epoxide results obtained in this chemical approach are compared to those obtained using electrochemical activation, also in DMF.

2. Results and discussion

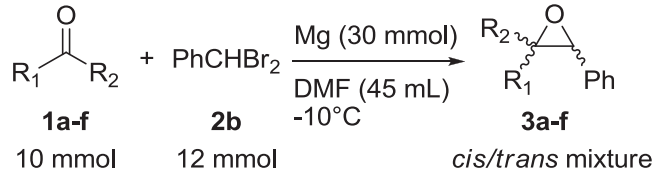
We initially applied the reaction conditions used for the cyclopropane formation[17] as follows: 50–150 mesh-magnesium grits (30 mmol) are suspended in DMF (40 mL) in a three-neck flask fitted with a dropping funnel and a thermometer, and cooled to −10 °C; half of the solution containing benzaldehyde **1a** (10 mmol), benzal chloride **2a** (12 mmol) and DMF (5 mL) was rapidly introduced into the flask, and one hour later the remaining of the reactants was added within 5 min. The expected epoxide **3a** was not detected, neither (*E*) nor (*Z*)-stilbenes (Scheme 1). The change of either the reaction temperature (50 °C), or the amount of DMF (20 mL), or even the solvent itself (DMAC), did not favour the cyclocondensation. We then decided to replace benzal chloride by the more reactive benzal bromide, and this allowed the formation of 2,3-diphenyloxirane **3a** in 53% yield in 1/1 *cis*/*trans* ratio along with (*E*)- and (*Z*)-stilbenes as by-products (Scheme 1).



Scheme 1. Formation of epoxide **3a** under Mg-Barbier conditions.

Several epoxides were thus prepared from benzal bromide **2b** and a variety of carbonyl compounds **1a–f** (aldehydes or ketones) (Table 1). All products gave satisfactory IR, NMR and mass spectra according to the spectral references data.[19,20] Results previously obtained using an electrochemical approach are given comparatively in Table 1.

Table 1
Epoxide formation by Mg-Barbier reaction in DMF from aldehydes or ketones and benzal bromide

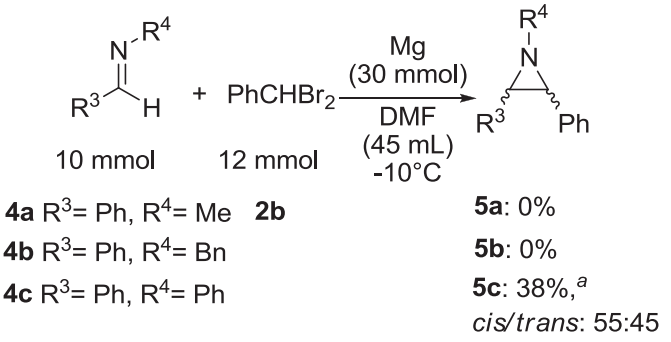


Entry	1	R^1	R^2	3	Mg-Barbier[a] yield % (*cis*/*trans*)	Electroreduction[b] yield % (*cis*/*trans*)
1	**1a**	C_6H_5	H	**3a**	53 (49/51)	40 (25/75)
2	**1b**	2-Me-C_6H_4	H	**3b**	50[c] (47/53)	36 (22/78)
3	**1c**	4-CNC_6H_4	H	**3c**	0	Traces
4	**1d**	C_6H_5	Me	**3d**	46 (50/50)	54 (56/44)
5	**1e**	C_6H_5	Et	**3e**	51 (48/52)	70 (50/50)
6	**1f**	$(CH_2)_5$		**3f**	22	32

[a] According to the structure of the carbonyl compound, the reaction time is range from 5 to 40 h.
[b] See Ref. 19
[c] 5 mmol of benzal bromide is added to ensure the complete consumption of the carbonyl compound.

It comes out that the Mg-Barbier reaction and the electroreductive coupling lead similarly to moderate isolated yields in epoxides **3**. Furthermore, in the two processes, the reaction is prevented by an electron-withdrawing group at the *para* position in benzaldehyde **1c** (Table 1, entry 3) and the yields are lower with cyclohexanone **1f** than with the two aromatic ketones **1d–e** (Table 1, entries 6 vs 4–5). It is noteworthy that with ketones, the yields are lower with this method as compared to electrochemical process. Consequently, we did not extend the application of this Mg-Barbier reaction to epoxide formation.

Our first investigations on the preparation of aziridines were made from three commercially available imines (*N*-benzylidenemethylamine **4a**, *N*-benzylidenebenzylamine **4b**, *N*-benzylideneaniline **4c**) and benzal bromide **2b**, using the same reaction conditions as for epoxides formation (Scheme 2).

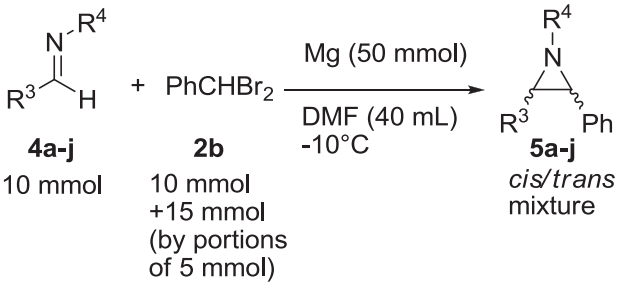


Scheme 2. Preliminary results for the aziridines **5** formation under Mg-Barbier conditions. [a]Incomplete conversion even when an extra amount of **2b** (18 mmol) was added.

Unfortunately, imines **4a** and **4b** bearing a methyl and a benzyl group on the nitrogen, respectively, failed to furnish the expected azidines, and only the stilbene by-products were obtained. When the more electrophilic imine **4c** was used, we were pleased to observe the formation of the aziridine **5c** in 38% yield and poor diastereomeric ratio (*cis*/*trans* ratio of 55 to 45). One should note that despite the addition of an extra amount of **2b** during the reaction, complete conversion was not reached. In order to improve the yield of the reaction, an extensive survey of the reaction conditions was undertaken thus allowing to set up new optimized conditions for the Mg-Barbier formation of imines. With these new conditions in hands (excess of benzal bromide and 50 mmol of Mg powder instead of 30 mmol), we moved to the examination of the scope of the Barbier reaction with various imines (Table 2).

From a general viewpoint, imines bearing aromatic substituents on the nitrogen of imines were found to give the best results in terms of isolated yield (Table 2, entries 4–8 vs 1–2 and 10). Among them, those having a halogen at the *meta* or *para* position of the phenyl ring allowed to increase the yield by 10–13% in comparison with the unsubstituted phenyl ring (Table 2, entries 4–6 vs 3). Moreover, the steric hindrance of the *ortho*-halogen, seems to somehow impede the formation of the aziridine (Table 2, entries 4 vs 5–6). The donating mesomeric effect of the *para*-methoxy in the benzylidene group prevents the approach of the nucleophilic species (Table 2, entry 9). Consequently, in this case, the (*E*)-stilbene was the major product. It appears that this Mg-Barbier process for the preparation of aziridines is efficient in the presence of sufficiently electrophilic imines. In addition, the *N*-phenylsulfonyl imine **4j** that is somewhat more electrophilic than the *N*-aryl imine **4c**, failed to provide the corresponding aziridine in our reaction conditions despite its complete consumption (Table 2, entry 10). This result could be explained by the fact that **4j** bearing a strong electron-withdrawing group allowing its easy reduction by Mg

Table 2
Formation of aziridines by Mg-Barbier reaction from imines **4a**–**j** and benzal bromide **2b**

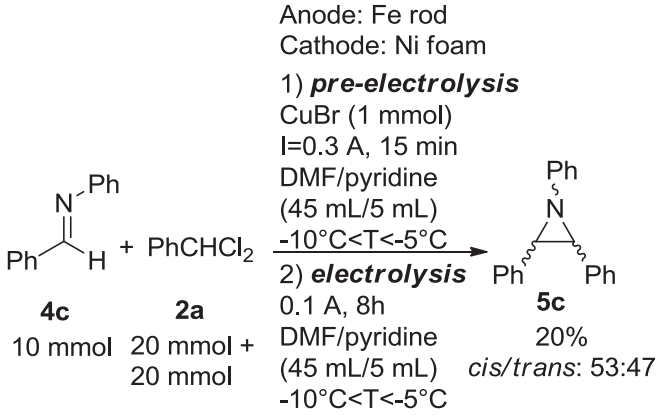


Entry	4	R^3	R^4	5	Yield % (*cis*/*trans*)
1	**4a**	C_6H_5	Me	**5a**	—
2	**4b**	C_6H_5	Bn	**5b**	—
3	**4c**	C_6H_5	C_6H_5	**5c**[b]	42 (53/47)
4	**4d**[a]	C_6H_5	2-BrC_6H_4	**5d**	40 (53/47)
5	**4e**[a]	C_6H_5	3-BrC_6H_4	**5e**[c]	57 (53/47)
6	**4f**[a]	C_6H_5	4-BrC_6H_4	**5f**	57 (56/44)
7	**4g**[a]	C_6H_5	4-ClC_6H_4	**5g**[d]	54 (54/46)
8	**4h**[a]	C_6H_5	2,4-$F_2C_6H_3$	**5h**[c]	46 (70/30)
9	**4i**[a]	4-MeOC_6H_4	C_6H_5	**5i**	Traces (GC)
10	**4j**	Ph	SO_2Ph	**5j**	—

[a] Imines prepared according to literature procedure.[20]
[b] Trans CAS n°: [34310-77-5]/*cis* CAS n°: [7042-42-4].
[c] New products.
[d] Cis CAS n°: [58265-18-1].

during the reaction according to a desulfonylation process ($PhCHBr_2$ being totally recovered).

We also tried to prepare aziridine **5c** electrochemically according to the method used for the preparation of epoxides.[19] The results were disappointing (no more than 20% isolated yield) partly due to the difficult separation of the aziridine **5c** from a raw mixture containing large amounts of iron salts (Scheme 3).



Scheme 3. Synthesis of aziridine **5c** by electrochemical process.

Nevertheless, our simple Mg-Barbier conditions led to 1,2,3-triarylaziridines **5** from *N*-benzylideneanilines **4** and benzal bromide **2b** with global isolated yields about 40% (two steps from benzaldehyde including the formation of the imine and the aziridination reaction). This method can be considered as an interesting alternative of the use of diazo compounds that are well known for their unpredictable explosive behaviour[21] and the acidic hydrolysis of organic azides forms highly toxic hydrogen azide[22] (toxicity similar to that of hydrogen cyanide).

From a mechanistic point of view, Fry et al. have already described a Mg-Barbier reaction from benzal bromide or α-bromo-α-chlorotoluene and *N*-propylimines in Et_2O and under ultrasonic irradiations.[23] The mechanism postulated by the authors relies on the first generation of an electrophilic phenylcarbene, which is then attacked by nucleophilic imines leading to *cis*-aziridines as major products. As key difference, our process is conducted in DMF known to have a Lewis base behaviour. Thus, we postulated that the first step would be the generation of the same electrophilic carbenoid species **A** as reported by Fry et al.[23] The generation of such an intermediate could explain the formation of the observed stilbene by-products through a dimerization pathway. As main difference from Fry's mechanism, in our case, the intermediate **A** would then be trapped by DMF to form a nucleophilic species **B**[18], which would be able to react with the carbonyl compounds **1** or imines **4** to furnish the corresponding epoxides **3** or aziridines **5**, respectively, according to an 1,2-addition/intramolecular nucleophilic substitution sequence (Fig. 1). Nevertheless, the influence of DMF only as an appropriate polar solvent (without the formation of covalent bond) allowing the reaction to proceed cannot be ruled out.

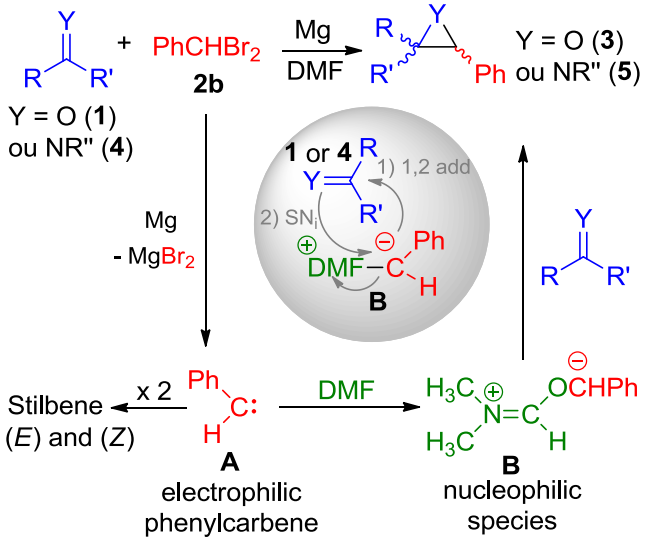


Fig. 1. Postulated mechanism for the formation of nucleophilic species **B** and its subsequent reaction with carbonyl compounds **1** or imines **4**.

Such a mechanism is supported in one hand by Burton's work[24] showing the intermediate involving DMF, and in the other hand by different experimental observations. First, less nucleophilic imines such as *N*-benzylidenemethylamine (Table 2, entry 1) closely related to those used by Fry et al.[23] or *p*-methoxybenzylideneaniline (Table 2, entry 9) were unreactive in our conditions. Moreover, the conditions of Fry et al.[23] applied to our substrates did not provide any addition-cyclisation products (i.e., epoxides or aziridines) thus demonstrating the involvement of different pathways in DMF and in THF.

3. Conclusion

In conclusion, we have reported in this study that the intermediate, which is generated from benzal bromide **2b** and magnesium in DMF is a rather nucleophilic species that reacts with electrophiles, such as carbonyl compounds **1** or electrophilic imines **4**. Such an intermediate is not a mere carbene that would be electrophilic, as shown by Fry et al.,[23] but more likely an adduct between a carbene and DMF. This remains to be clearly demonstrated. We have also found that the access to epoxides is more

conveniently carried out electrochemically, whereas the chemical approach is more efficient for preparing aziridines. Furthermore, one should note that these two 'one pot' processes involve less pollutant and more user-friendly reagents than those previously described in the literature for the synthesis of epoxides or aziridines.

4. Experimental section

4.1. General information

Solvents and chemicals were used as received. Melting points were determined with an Electrothermal IA 9100 digital mp apparatus. ^{1}H, ^{13}C, ^{19}F, NMR spectra were recorded on a Bruker AM-300 (300, 75, 282 MHz) spectrometer. Mass spectra (electron impact) were obtained on a GCQ Thermoquest spectrometer coupled to a Finigan-GCQ, fitted with a DB5-ms capillary column. High-resolution mass spectral analyses and elemental analyses were carried out at Service Central d'Analyse du CNRS, Vernaison, France. Gas chromatography was performed on a Varian 3300 chromatograph fitted with a SIL-5 CP capillary column. Compounds labelled by (*) are, to the best of our knowledge, new compounds. The CAS numbers were given in square brackets for known compounds.

4.2. General procedures

4.2.1. Typical Mg-Barbier procedure for the preparation of epoxides ***3***. Magnesium grits (50–100 mesh) (30 mmol) are suspended in DMF (40 mL) in a three-neck flask fitted with a thermometer and a dropping funnel and cooled at −10 °C under an argon atmosphere. Half of the solution containing aldehyde or ketone **1** (10 mmol), benzal bromide **2b** (12 mmol), and DMF (5 mL) is rapidly introduced in the flask. The start of the reaction is clearly indicated by the rise of the temperature up to 0 °C and the mixture turning yellow. The remaining of the reactants is then added within 5 min and the reaction is allowed to proceed until the complete consumption of the carbonyl compound. Then the reaction mixture is filtered on a Buchner funnel. DMF is evaporated under reduced pressure. The reaction mixture is poured into a cold mixture of aq HCl (1 M, 50 mL) and Et_2O (50 mL). The layers are separated and extracted with Et_2O (three portions of 25 mL). The combined Et_2O extracts are washed with saturated aq NH_4Cl and $NaHCO_3$ solutions and brine. They are dried ($MgSO_4$) and evaporated after filtration. Products are isolated by column chromatography on silica gel (230–400 mesh) using pentane/Et_2O (95%/5%) as eluent and characterized by ^{1}H and ^{13}C NMR, GC–MS, and IR analysis. All isolated products described in the literature[5] show satisfactory physical characteristics and spectroscopic data.

4.2.2. Typical Mg-Barbier procedure for the preparation of aziridines ***5***. Magnesium grits (50–100 mesh) (50 mmol) are suspended in DMF (40 mL) in a three-neck flask fitted with a thermometer and a dropping funnel and cooled at −10 °C under an argon atmosphere. Half of the solution containing imine **4** (5 mmol), benzal bromide **2b** (10 mmol), and DMF (5 mL) is rapidly introduced in the flask. The start of the reaction is clearly indicated by the temperature rising up to 0 °C and the mixture turning yellow. The remaining of the reactants is then added within 5 min and the reaction allowed to proceed until the complete consumption of the imine obtained after addition of a large excess of benzal bromide **2b** (+15 mmol: 3×5 mmol). Then the reaction mixture is filtered on a Buchner funnel. The DMF is evaporated under reduced pressure and the residual mixture is solubilized in CH_2Cl_2 (50 mL) and hydrolysed with saturated aq NH_4Cl solution. The layers are separated and the aqueous layer is extracted with CH_2Cl_2 (three portions of 25 mL). The combined CH_2Cl_2 extracts are washed aq NH_3 solution (2 M), dried (Na_2SO_4) and evaporated after filtration. After this work-up, the products are isolated by flash-chromatography on silica gel (eluent: pentane/CH_2Cl_2) and characterized as above.

*4.2.2.1. 1,2,3-Triphenylaziridine (**5c**). cis* [7042-42-4], *trans* [34310-77-5].

Mp: *cis*: 98–99 °C; *trans*:[16e] 87–88 °C; isolated yield: 42%, *cis*/*trans*: 53/47. Purification by flash-chromatography: elution with pentane/CH_2Cl_2 (80/20) followed by (50/50). IRFT ($CDCl_3$, cm^{-1}): ν 3087, 3065, 3033, 2978, 1951–1666 (multiple bands with low intensity), 1598, 1488, 1454, 1411, 1316, 1269, 1234, 1140, 1075, 1027, 891, 882. ^{1}H NMR ($CDCl_3$, 300 MHz): *cis*[10a,b]: δ 7.55–7.15 (m, 15H), 4.0 (s, 2H). *trans*:[16e] δ 7.6–7.2 (m, 15H), 3.9 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*:[10a,b,25] δ 154.9, 136.1, 129.5, 128.1, 127.3, 123.0, 120.2, 49.3. *trans*: δ 148.3, 134.4, 128.2, 127.5, 127.3, 122.0, 120.9, 50.0. MS (EI, 70 eV): *m*/*z* (%): *cis*: 271 (47) $[M]^+$, 270 (100), 178 (27), 168 (12), 167 (41), 166 (16), 165 (24), 152 (13), 77 (9). *trans*: 271 (40) $[M]^+$, 270 (100), 178 (27), 167 (42), 166 (9), 165 (25), 152 (16), 77 (8).

*4.2.2.2. 1-(2-Bromophenyl)-2,3-diphenylaziridine (**5d**).*[26] *cis* [1048636-57-2], *trans* [1048636-62-9].

Mp: *cis*: 110–111 °C; *trans*: 51–55 °C (purity: 80%); isolated yield: 40%, *cis*/*trans*: 53/47. Purification by flash-chromatography: elution with pentane/CH_2Cl_2 (80/20) followed by (50/50), second purification for the *trans* isomer eluted with pentane/CH_2Cl_2 (60/40), pentane/CH_2Cl_2 (70/30). IRFT ($CDCl_3$, cm^{-1}): ν 3087, 3065, 3032, 2979, 1951–1766 (multiple bands with low intensity), 1590, 1568, 1495, 1473, 1455, 1426, 1411, 934, 913, 881. ^{1}H NMR ($CDCl_3$, 300 MHz): *cis*: δ 7.8–7.1 (m, 14H), 3.95 (s, 2H). *trans*: δ 7.25–7.0 (m, 14H), 3.75 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*: δ 151.6, 135.3, 127.7, 127.0, 123.9, 121.6, 116.5, 50.1. *trans*: δ 145.5, 136.4, 133.0, 128.1, 127.5, 127.0, 123.2, 121.9, 116.6, 51.0, 50.9. MS (EI, 70 eV): *m*/*z* (%): *cis*: 350 (88) $[M]^+$, 349 (48), 348 (100), 270 (12), 269 (18), 268 (23), 247 (22), 245 (25), 179 (10), 178 (38), 167 (18), 166 (45), 165 (42). *trans*: 350 (100) $[M]^+$, 349 (47), 348 (96), 270 (12), 269 (18), 268 (23), 267 (10), 247 (29), 245 (23), 179 (12), 178 (48), 167 (16), 166 (49), 165 (40), 152 (10).

*4.2.2.3. 1-(3-Bromophenyl)-2,3-diphenylaziridine (**5e**). New product.* Mp: *cis*: 116–117 °C; *trans*: 100–101 °C, isolated yield: 57%, *cis*/*trans*: 53/47. Purification by flash-chromatography: elution with pentane/CH_2Cl_2 (80/20) followed by (50/50); purification of the *trans* isomer: elution with pentane/CH_2Cl_2 (60/40). IRFT ($CDCl_3$, cm^{-1}): ν 3085, 3061, 3034, 2980, 1590, 1560, 1493, 1472, 1450, 1422, 924–864 (multiple bands). ^{1}H NMR ($CDCl_3$, 300 MHz): *cis*: δ 7.3–7.0 (m, 14H), 3.6 (s, 2H). *trans*: δ 7.25–6.85 (m, 12H), 6.55–6.5 (m, 2H), 3.6 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*: δ 155.9, 135.1, 130.5, 127.2, 127.1, 125.7, 123.1, 122.9, 122.6, 118.5, 49.1. *trans*: δ 149.8, 135.7, 129.8, 128.3, 127.7, 127.2, 124.9, 123.6, 123.5, 122.3, 119.7, 50.1. MS (EI, 70 eV): *m*/*z* (%): *cis*: 350 (100) $[M]^+$, 349 (48), 348 (92), 269 (14), 268 (14), 247 (14), 245 (14), 179 (10), 178 (39), 167 (14), 166 (41), 165 (30). *trans*: 350 (97) $[M]^+$, 349 (44), 348 (100), 269 (17), 268 (12), 247 (16), 245 (15), 179 (10), 178 (44), 167 (15), 166 (42), 165 (27). HRMS (in electron ionization mode): *cis* isomer: *m*/*z* calculated for $C_{20}H_{16}BrN$ 348.0388; found: 348.0396.

*4.2.2.4. 1-(4-Bromophenyl)-2,3-diphenylaziridine (**5f**). cis* [1048636-56-1], *trans* [1048636-61-8].

Mp: *cis*: 99–100 °C; *trans*: oil (purity: 93%); isolated yield: 57%, *cis*/*trans*: 56/44. Purification by flash-chromatography: elution with pentane/CH_2Cl_2 (80/20) followed by (50/50), second purification for the *trans* isomer: elution with pentane/CH_2Cl_2 (60/40). IRFT ($CDCl_3$, cm^{-1}): ν 3090, 3061, 3025, 2982, 1595, 1570, 1496, 1465, 1450, 1409, 930–860 (multiple bands). ^{1}H NMR ($CDCl_3$, 300 MHz): *cis*: δ 7.55–7.1 (m, 14H), 3.8 (s, 2H). *trans*: δ 7.4–7.1 (m, 12H), 6.5–6.45 (m, 2H), 3.5 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*:

δ 153.5, 135.1, 131.8, 127.7, 127.5, 126.9, 121.5, 115.0, 49.0. *trans*: δ 147.4, 145.6, 135.8, 131.7, 128.3, 127.4, 122.5, 114.5, 50.0. MS (EI, 70 eV): *m*/*z* (%): *cis*: 350 (89) $[M]^+$, 349 (48), 348 (100), 269 (21), 268 (19), 247 (35), 245 (34), 179 (11), 178 (36), 167 (18), 166 (59), 165 (34). *trans*: 350 (100) $[M]^+$, 349 (53), 348 (99), 269 (18), 268 (18), 247 (31), 245 (31), 179 (12), 178 (36), 167 (15), 166 (53), 165 (32). HRMS (in electron ionization mode): *cis* isomer: *m*/*z* calculated for $C_{20}H_{16}BrN$ 348.0388; found: 348.0393.

*4.2.2.5. 1-(4-Chlorophenyl)-2,3-diphenylaziridine (**5g**). cis* [58268-18-1], *trans* compound was characterized by reference to the data of the *cis* known compound. Mp: *cis*: 95–96 °C;[16g] *trans*: oil (purity=94%), isolated yield: 54%, *cis*/*trans*: 54/46. Purification by flash-chromatography: elution with pentane/CH_2Cl_2 (80/20) followed by (50/50). IRFT ($CDCl_3$, cm^{-1}): ν 3089, 3065, 3033, 2977, 1951–1645 (multiple bands with low intensity), 1605, 1594, 1488, 1456, 1410, 1317, 1264, 1140, 1093, 1026, 932–886 (multiple band), 834. ^1H NMR ($CDCl_3$, 300 MHz): *cis*[16g]: δ 7.3–7.0 (m, 14H), 3.6 (s, 2H). *trans*: δ 7.45–7.0 (m, 12H), 6.8–6.7 (m, 2H), 3.75 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*: δ 153.0, 135.2, 128.9, 128.1, 127.6, 127.4, 126.9, 121.0, 49.1. *trans*: δ 146.8, 135.8, 128.7, 128.5, 128.3, 127.1, 126.8, 122.0, 50.1, 50.0. MS (EI, 70 eV): *m*/*z* (%): *cis*: 305 (47) $[M]^+$, 304 (100), 203 (10), 201 (25), 178 (25), 166 (21), 165 (22), 138 (10). *trans*: 305 (46) $[M]^+$, 304 (100), 203 (9), 201 (28), 178 (23), 166 (19), 165 (20), 138 (10).

*4.2.2.6. 1-(2,4-Difluorophenyl)-2,3-diphenylaziridine (**5h**). New product.* Mp: *cis*: 134–135 °C; *trans*: oil (purity=90%); isolated yield=46%, *cis*/*trans*: 70/30. Purification by flash-chromatography: elution with pentane/CH_2Cl_2 (80/20) followed by (50/50), second purification for the *trans* isomer: elution with pentane/CH_2Cl_2 (75/25). IRTF ($CDCl_3$, cm^{-1}): ν 3089, 3065, 3032, 2981, 1951–1764 (multiple bands with low intensity), 1599, 1505, 1455, 1433, 1412, 1366, 1317, 1264, 1217, 1141, 1100, 1027, 967, 908, 852. ^1H NMR ($CDCl_3$, 300 MHz): *cis*: δ 7.4–7.05 (m, 11H), 7.0–6.9 (m, 2H), 3.8 (s, 2H). *trans*: δ 7.4–6.5 (m, 13H), 3.7 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): *cis*: δ 158.2 (dd, ^1J=243.7 Hz, ^3J=10.6 Hz), 155.6 (dd, ^1J=250.1 Hz, ^3J=11.9 Hz), 138.4–138.2, 135.8, 127.9, 127.8, 127.2, 121.7, 111.0 (dd, ^2J=23.5 Hz, ^4J=3.8 Hz), 104.5 (dd, ^2J=26.7 Hz, ^2J=23.6 Hz), 49.5. *trans*: δ 157.7 (dd, ^1J=242.8 Hz, ^3J=10.6 Hz), 155.0 (dd, ^1J=248.9 Hz, ^3J=11.9 Hz), 135.8, 132.4 (dd, ^2J=11.1 Hz, ^4J=3.5 Hz), 128.3, 128.2, 127.8, 127.1, 122.4 (broad d, ^3J=9.1 Hz), 110.6 (dd, ^2J=21.7 Hz, ^4J=3.5 Hz), 104.2 (dd, ^2J=23.8 Hz, ^2J=23.6 Hz), 49.8. ^{19}F NMR ($CDCl_3$, 282 MHz): *cis*: δ −117.6, −122.0. *trans*: δ −118.0, −120.7. MS (EI, 70 eV): *m*/*z* (%): *cis*: 307 (46) $[M]^+$, 306 (100), 203 (17), 183 (14), 178 (31), 140 (9). *trans*: 307 (47) $[M]^+$, 306 (100), 203 (18), 183 (16), 178 (29), 140 (11). HRMS (in electron ionization mode): *cis* isomer: *m*/*z* calculated for $C_{20}H_{15}F_2N$ 307.1172; found: 307.1168.

*4.2.3. Typical electrochemical procedure for the preparation of aziridines **5c**.* The reactions are conducted in an undivided cell fitted with a Fe rod as the anode and a nickel foam as the cathode (area: ca. 40 cm^2). A solution of CuBr (144 mg, 1 mmol) and Bu_4NBr (300 mg) in DMF (45 mL) and pyridine (5 mL) is electrolysed at constant current intensity (0.3 A) during 15 min at −10 °C<*T*<−5 °C. Then, the activated imine **4a** (10 mmol) and benzal bromide **2b** (20 mmol) are added and electrolysed (0.1 A) until the complete consumption of the imine **4a** (20 mmol of **2b** were added in order to reach complete conversion). The DMF is evaporated under reduced pressure and the residual mixture is solubilized in CH_2Cl_2 (50 mL) and hydrolysed with saturated aq NH_4Cl solution. The layers are separated and the aqueous layer is extracted with CH_2Cl_2 (three portions of 25 mL). The combined CH_2Cl_2 extracts are washed aq NH_3 solution (2 M), dried (Na_2SO_4) and evaporated after filtration. After this work-up, the aziridines **5c** was obtained in 20% yield (*cis*/*trans* mixture: 53:47) after purification by flash-chromatography on silica gel (eluent: pentane/CH_2Cl_2).

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