# Catalytic enantioselective formation of aziridines from α-imino esters

**Karsten Juhl, Rita G. Hazell and Karl Anker Jørgensen***

*Center for Metal Catalyzed Reactions, Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark*

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A new catalytic enantioselective aziridination reaction of α-imino esters with diazo compounds catalyzed by chiral Lewis acid complexes is presented. A series of *N*-substituted α-imino esters has been tested as substrates for the aziridination reaction using trimethylsilyldiazomethane as the carbenoid fragment donor catalyzed by various chiral complexes. Both chiral BINAP and bisoxazoline† ligands, in combination with copper(I) salts in particular can catalyze the aziridination reaction leading to the *cis*-aziridine with up to 72% ee applying BINAP–copper(I) complexes as the catalyst, while the bisoxazoline–copper(I) catalysts give an aziridination reaction with lower diastereoselectivity, however, the *trans*-aziridine was formed in 69% ee. The influence of diazo compounds, Lewis acids, chiral ligands, solvents and counterion on the reaction course has been investigated and a mechanism for the reaction is discussed in which the α-imino ester coordinates to the chiral catalyst. For trimethylsilyldiazomethane, nucleophilic attack on the coordinated α-imino ester probably takes place in the case of copper(I) as the Lewis acid, while for ethyl diazoacetate the reaction course is dependent on the Lewis acid; for silver(I) a nucleophilic attack is probably also operating, while a metal–carbene intermediate is involved when copper(I) is used.

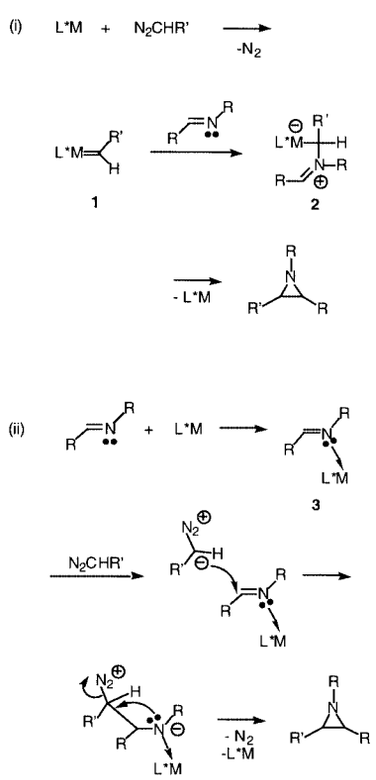
## Introduction

Optically active aziridines are attractive versatile organic molecules due to their ability to undergo highly regio- and stereoselective ring-opening reactions.[1] Aziridines are also found in molecules which exhibit biological activity[2] and, furthermore, synthetic aziridines are shown to exhibit useful biological properties.[3]

The synthesis of optically active aziridines can take its starting point from different types of substrates, such as amino alcohols, epoxides, alkenes and imines, or by resolution of racemic aziridines.[1]

A new and attractive procedure for the formation of aziridines is the metal-catalysed addition of a carbenoid fragment to an imine, and recently advances have been pursued in this area using different metal complexes as the catalyst.[4] Two different mechanisms can operate in the formation of aziridines from imines catalyzed by metal complexes (Scheme 1): one reaction path (i) is *via* a metal–carbene intermediate **1**, formed by reaction of the metal complex with a diazo compound. The metal–carbene intermediate reacts with the imine in the next step, probably *via* a zwitter-ion intermediate **2**, leading to the aziridine. The other reaction path (ii) involves coordination of the imine to the metal complex leading to an imine–metal complex **3**, which reacts with the diazo compound leading to elimination of $N_2$. In spite of many attempts to develop catalytic enantioselective aziridination of imines, only the former procedure, *via* a bisoxazoline–copper–carbene intermediate, has met with some success using bisoxazolines–copper(I) complexes as the catalyst.[4a] Under these reaction conditions up to 67% ee of *cis*-aziridines were formed in 23% yield and with low diastereoselectivity using aromatic imines.

This paper presents the first catalytic diastereo- and enantioselective aziridination reaction of imines derived from α-ethyl glyoxylate with diazo compounds in which the imine is activated by a chiral Lewis acid complex.



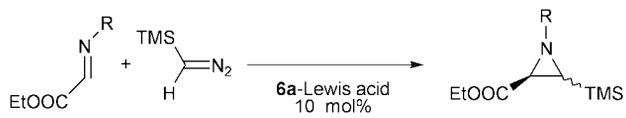

**Scheme 1**

## Results and discussion

The potential of the α-imino esters **4a**,**b** as possible substrates for the aziridination reaction with trimethylsilyldiazomethane **5a** [eqn. (1)] has been investigated.[5] A variety of chiral ligands, such as the BINAP's **6a**,**b**, the bisoxazolines **7a**–**c** and the phosphino oxazoline ligands **8a**,**b** have, in combination with different Lewis acid complexes, been tested as catalysts for the aziridination reaction.

† IUPAC name for oxazoline is 4,5-dihydro-1,3-oxazole.

**Table 1** The results for the reaction of the α-imino esters **4a**,**b** with trimethylsilyldiazomethane **5a** catalyzed by the complexes derived from (*R*)-Tol-BINAP **6a** and $Sn(OTf)_2$, $Zn(OTf)_2$, $Yb(OTf)_3$, $AgSbF_6$ and $CuClO_4$ in THF



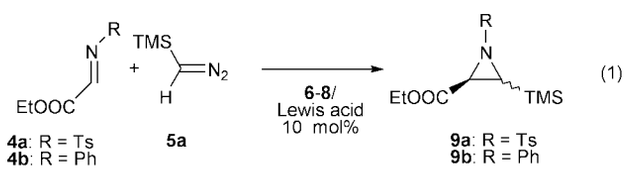

**4a**: R = Ts
**4b**: R = Ph

**5a**

**9a**: R = Ts
**9b**: R = Ph

| Entry | Catalyst | Catalytic load (%) | Imine | Solvent | Temp/°C | Yield (%) | *cis*:*trans*[a] | Ee[b] *cis* | Ee[b] *trans* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **6a**–$Sn(OTf)_2$ | 10 | **4a** | THF | −78 | **9a** (34) | 2:1 | 0 | 0 |
| 2 | **6a**–$Sn(OTf)_2$ | 10 | **4b** | THF | −78 | **9b** (33) | 1.2:1 | 0 | 0 |
| 3 | **6a**–$Yb(OTf)_3$ | 10 | **4a** | THF | −15 | **9a** (8) | 1:3.3 | 0 | 0 |
| 4 | **6a**–$Zn(OTf)_2$ | 10 | **4a** | THF | −78 | **9a** (22) | 3:1 | 0 | 0 |
| 5 | **6a**–$AgSbF_6$ | 10 | **4a** | THF | −78 | **9a** (88) | >20:1 | 12 | nd[c] |
| 6 | **6a**–$CuClO_4$ | 10 | **4a** | THF | −78 | **9a** (55) | 19:1 | 72 | nd[c] |

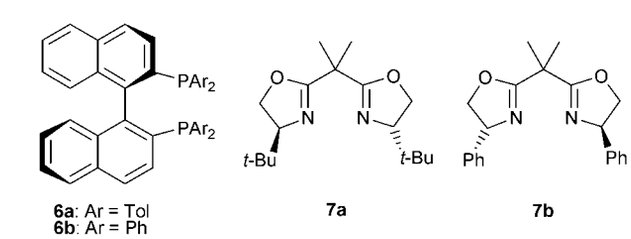
[a] *Cis*:*trans* ratio determined by $^1H$ NMR spectroscopy of the crude reaction mixture. [b] Ee determined by HPLC on Chiralcel AD column. [c] nd: not determined.




**4a**: R = Ts
**4b**: R = Ph

**5a**

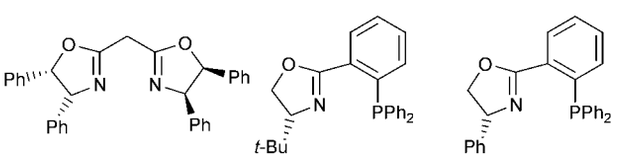
**9a**: R = Ts
**9b**: R = Ph




**6a**: Ar = Tol
**6b**: Ar = Ph

**7a**

**7b**




**7c**

**8a**

**8b**

The chiral catalysts derived from (*R*)-Tol-BINAP [2,2′-bis(di-tolylphosphino)binaphthyl] **6a** and the Lewis acids $Sn(OTf)_2$, $Zn(OTf)_2$, $Yb(OTf)_3$, $AgSbF_6$ and $CuClO_4$ were tested for the reaction of the α-imino esters **4a**,**b** with trimethylsilyldiazomethane **5a** in THF. The experimental details are given in the Experimental section. All the catalysts tested were able to catalyze the reaction of **4a** with **5a** giving aziridine **9a** in low to good yields, whereas, only the catalyst derived from **6a** and $Sn(OTf)_2$ could also catalyze the aziridination reaction of **4b** under the present reaction conditions. The results are presented in Table 1.

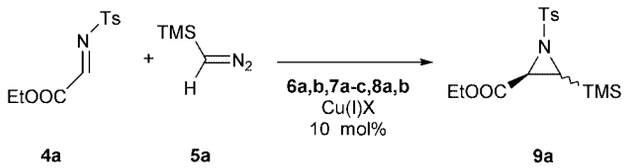
It appears from Table 1, that the catalyst obtained from (*R*)-Tol-BINAP **6a** and $AgSbF_6$ gives the highest yield and diastereoselectivity (*cis*:*trans* >20:1) of aziridine **9a**, however, the ee of *cis*-**9a** was only 12% (entry 5). The combination of $CuClO_4$ and **6a** gives a lower yield of **9a**, but the same high *cis*-selectivity and a large improvement in ee of *cis*-**9a** to 72% are found (entry 6), and according to our knowledge the highest ee obtained in a direct metal-catalyzed enantioselective aziridination reaction of imines with diazo compounds. The combination of **6a** with the other Lewis acids (entries 1–4) induces no enantioselectivity in the aziridination reaction.

The promising result with the (*R*)-Tol-BINAP–**6a**–$CuClO_4$ catalyst prompted us to further investigate the properties of copper(I) salts in this reaction. The results for the reaction of the *N*-tosyl α-imino ester **4a** with **5a** [eqn. (1)] catalyzed by $CuPF_6$ and $CuClO_4$ in combinations with the chiral ligands **6a**,**b**, **7a**–**c**, **8a**,**b** and various solvents are presented in Table 2.

In the absence of a chiral ligand the $CuClO_4$-catalyzed aziridination reaction of the *N*-tosyl α-imino ester **4a** proceeds giving a 66% yield of aziridine **9a** in THF at −15 °C with a *cis*:*trans* ratio of 2.5:1 (entry 1). With (*R*)-Tol-BINAP **6a** present as the chiral ligand and $CuClO_4$ as the Lewis acid at 0 °C, the yield of **9a** is lower, but the *cis*:*trans* ratio is improved to 5:1 and 60% ee is induced in the *cis*-aziridine **9a** (entry 2). By cooling the reaction mixture to −78 °C *cis*-aziridine **9a** is formed with only traces of the *trans* isomer (*cis*:*trans* 19:1) and the enantioselectivity is further enhanced to 72% ee (entry 3). Lowering the catalyst loading to 5 mol% only reduced the yield and selectivities moderately (entry 4), while 1 mol% catalyst load led to very low conversion. THF is the optimal solvent of the solvents tested; in toluene the *trans*-aziridine **9a** is the major isomer formed, however, this isomer was racemic, while the *cis*-aziridine **9a** was formed in 66% ee (entries 5, 6). Changing the counterion from $ClO_4$ to $PF_6$ causes a small decrease in the *cis*:*trans* ratio and in enantioselectivity (entry 7), so $CuClO_4$ remains the preferred Lewis acid. The use of the chiral ligand (*R*)-Ph-BINAP **6b** and $CuClO_4$ leads to a reduction in both the *cis*:*trans* ratio and ee of *cis*-aziridine **9a** (entry 8). Similar observations have been found for other reactions of the *N*-tosyl α-imino ester **4a** catalyzed by similar complexes.

The bisoxazoline (BOX) ligands **7a**–**c** in combination with $CuClO_4$ as the Lewis acid, have also been tested for aziridination of the *N*-tosyl α-imino ester **4a** applying trimethylsilyldiazomethane **5a**. In the presence of ligand (4*S*)-*t*-Bu-BOX **7a**, aziridine **9a** was formed with a *cis*:*trans* ratio of 4.3:1 and very low ee (entry 9). The ligand (4*R*)-Ph-BOX **7b** gave a lower *cis*:*trans* ratio (2:1), but higher optical activity was induced, especially for the *trans*-isomer which was formed with 63% ee (entry 10). It should be noted that using ligand **7b** and $CuClO_4$ as the catalyst gave excess of the opposite enantiomer of both the *cis*- and the *trans*-isomer of **9a** compared with the use of ligand **7a** and $CuClO_4$. This contradicts the results observed *e.g.* in addition reactions catalyzed by bisoxazoline–copper complexes where the same absolute configuration can be found in the product, although the absolute configuration is opposite in the ligands.[6] Finally the (4*R*,5*S*)-Ph-BOX **7c** ligand was

**Table 2** The results for the reaction of the *N*-tosyl α-imino ester **4a** with trimethylsilyldiazomethane **5a** catalyzed by the various chiral catalysts **6a**,**b**,**7a**–**c**,**8a**,**b**–Cu(I)X (X = $ClO_4$, $PF_6$) under various reaction conditions




4a 5a 9a

| Entry | Catalyst | Catalytic load (%) | Solvent | Temp/°C | Yield–**6a** (%) | *cis*:*trans*[a] | Ee[b] (%) *cis* | Ee[b] (%) *trans* |
|---|---|---|---|---|---|---|---|---|
| 1 | $CuClO_4$ | 10 | THF | −15 | 66 | 2.5:1 | 0 | 0 |
| 2 | **6a**-$CuClO_4$ | 10 | THF | 0 | 25 | 5:1 | 60 | 3 |
| 3 | **6a**-$CuClO_4$ | 10 | THF | −78 | 55 | 19:1 | 72 | nd[c] |
| 4 | **6a**-$CuClO_4$ | 5 | THF | −78 | 46 | 16:1 | 69 | nd[c] |
| 5 | **6a**-$CuClO_4$ | 10 | Toluene | −78 | 29 | 1:3 | 66 | 0 |
| 6 | **6a**-$CuClO_4$ | 10 | $CH_2Cl_2$ | −15 | 27 | 4.5:1 | 9 | 11 |
| 7 | **6a**-$CuPF_6$ | 10 | THF | −78 | 24 | 9:1 | 65 | nd[c] |
| 8 | **6b**-$CuClO_4$ | 10 | THF | −78 | 43 | 13:1 | 53 | nd[c] |
| 9 | **7a**-$CuClO_4$ | 10 | THF | −78 | 39 | 4.3:1 | 5 | 6 |
| 10 | **7b**-$CuClO_4$ | 10 | THF | −78 | 28 | 2:1 | 40 | 63 |
| 11 | **7c**-$CuClO_4$ | 10 | THF | −78 | 31 | 1.2:1 | 10 | 69 |
| 12 | **7c**-$CuClO_4$ | 10 | Toluene | −78 | 50 | 1:10 | 15 | 8 |
| 13 | **8a**-$CuClO_4$ | 10 | THF | −78 | 34 | 19:1 | 2 | nd[c] |
| 14 | **8b**-$CuClO_4$ | 10 | THF | −78 | 54 | 18:1 | 26 | nd[c] |

[a] *Cis*:*trans* ratio determined by $^1$H NMR spectroscopy of the crude reaction mixture. [b] Ee determined by HPLC on Chiralcel AD column. [c] nd: not determined.

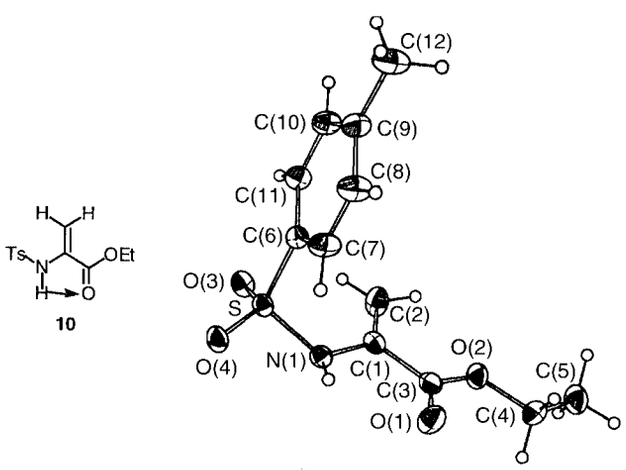



**Fig. 1** X-Ray structure of the by-product **10** formed in the aziridination reaction of the *N*-tosyl α-imino ester **4a** catalysed by various chiral ligand–Cu(I) complexes.

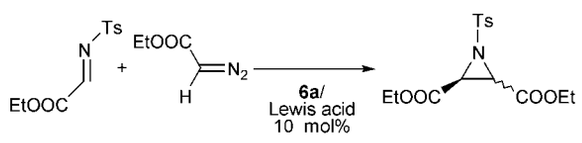
tested in the aziridination reaction and gave 69% ee of the *trans*-isomer of **9a**, while low ee of the *cis*-isomer and low *cis*:*trans* ratio were found (entry 11). Having established that good enantioselectivity was induced by ligand **7c** in forming the *trans*-isomer of **9a** and that high *trans*-selectivity was obtained in toluene (entry 5), a reaction combining these conditions was attempted. The **7c**–$CuClO_4$ catalyzed reaction in toluene did give the *trans*-isomer of **9a** as the predominant isomer (*cis*:*trans* = 1:10). However, poor enantioselectivity was observed (entry 12).

The phosphinooxazoline ligands **8a**,**b** have also been tested in combination with $CuClO_4$ as chiral catalysts for the aziridination reaction of the *N*-tosyl α-imino ester **4a** with trimethylsilyldiazomethane **5a**. High *cis*-selectivity of aziridine **9a** was found, but the ee of *cis*-**9a** was only 2% for the *tert*-butyl substituted ligand **8a** (entry 13) and 26% for the phenyl substituted analog **8b** (entry 14).

In the aziridination reactions of the *N*-tosyl α-imino ester **4a** with trimethylsilyldiazomethane **5a** catalysed by the different chiral ligand–Cu(I) complexes a by–product was formed in up to 10–15% yield (*vide infra*). The by-product **10** has been characterized by NMR spectroscopy and X-ray analysis, and is outlined in Fig. 1.

The reaction of the *N*-tosyl α-imino ester **4a** with trimethylsilyldiazomethane **5a** catalysed by chiral ligand–Cu(I) complexes proceeds without the formation of the carbene-coupling products (in the present reactions (*Z*)-1,2-di-TMS-ethylene and (*E*)-1,2-di-TMS-ethylene) observed in the bisoxazoline–copper(I) catalyzed reaction with ethyl diazoacetate.[4a] We have also performed trapping experiments with diethyl fumarate (up to two equivalents) in an attempt to obtain pyrrolidines formed by a reaction of diethyl fumarate with an azomethine ylide intermediate. It is suggested that the azomethine ylide intermediate is formed by an attack of the imine on the ligand–copper–carbene intermediate ((ii) in Scheme 1).[4a] However, pyrrolidines were not observed under these reaction conditions, indicating a reaction mechanism where a metal–carbene intermediate is not involved in the formation of the aziridine. A more likely mechanism is one by which the imine is activated by the Lewis acid and then exposed to a nucleophilic attack on the imine carbon atom by **5a** followed by elimination of $N_2$ leading to the formation of the aziridine (*vide infra*).

The aziridination reaction of the *N*-tosyl α-imino ester **4a** has also been investigated with other diazo compounds, such as ethyl diazoacetate (EDA) **5b** [eqn. (2)].

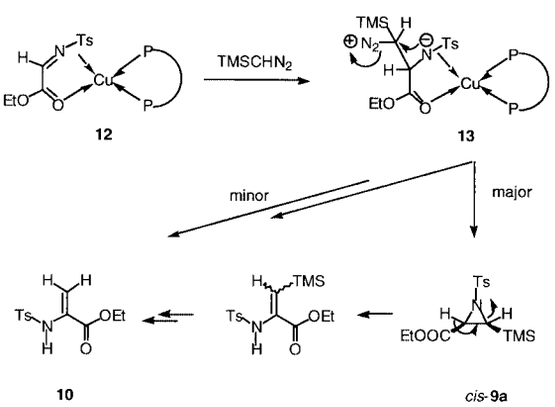



4a 5b 11

Reaction of the *N*-tosyl α-imino ester **4a** with EDA **5b** in the presence of (*R*)-Tol-BINAP–**6a**–$CuPF_6$ catalyst at rt in $CH_2Cl_2$

gives only 27% yield of aziridine **11** with a *cis*:*trans* ratio of 2.4:1. The *cis*-aziridine **11** is a *meso* compound while the *trans*-aziridine **11** is formed with only 16% ee. Application of $AgSbF_6$ as the Lewis acid in THF at −78 °C gives aziridine **11** in 32% yield with a *cis*:*trans* ratio of 1:1 and *trans*-**11** is formed in 20% ee. In these reactions the by-products ethyl fumarate and ethyl maleate are only observed in the copper(I)-catalyzed reaction. This indicates that the reaction in eqn. (2) probably proceeds by a mechanism where a copper–carbene is present along the reaction path ((i) in Scheme 1). This intermediate, probably a chiral Tol-BINAP–**6a**–copper(I)–carbene intermediate, is attacked by the imine in the next step leading to the aziridine. To keep the formation of ethyl fumarate and ethyl maleate to a minimum in these reactions EDA has to be added slowly (~9 h). The ethyl fumarate and ethyl maleate by-products are not observed in the silver(I)-catalyzed reaction, even though EDA is added instantaneously and it is thus unlikely that silver–carbene complexes are formed during the reaction.

Based on the experimental results for the aziridination reactions of the *N*-tosyl α-imino ester **4a** with trimethylsilyldiazomethane **5a** catalysed by different chiral ligand–Cu(I) complexes a tentative mechanism is proposed in Scheme 2.




**Scheme 2**

After the imine **4a** has coordinated to the chiral catalyst leading to intermediate **12**, the diazo compound **5a** attacks the imine-carbon atom as a nucleophile giving **13**. At the present stage of investigations we are not able to distinguish if it is the imine nitrogen atom, one of the oxygen atoms of the sulfonyl groups or both of them which are involved in coordination to the chiral catalyst and therefore the coordination mode of **4a** to the catalyst in **12** is shown with one of the coordination arrows to the nitrogen atom and one to the tosyl substituent. The major reaction path leads to *cis*-aziridine **9a** formed from intermediate **13** as outlined in Scheme 2. Compound **10** can be formed by an elimination reaction of the aziridine *cis*-**9a** followed by an exchange of the TMS substituent with a proton. However, a direct pathway from **13** (probably a minor pathway), an elimination reaction and an exchange of the TMS substituent with a proton, might also account for the formation of **10** (Scheme 2).[4f,7]

## Conclusion

The present work has shown that *N*-tosyl α-imino esters can react with trimethylsilyldiazomethane in the presence of BINAP– and bisoxazoline–copper salts as the catalyst giving *cis*- and *trans*-aziridines, respectively, with good enantioselectivity. The diastereoselectivity is best for the Tol-BINAP–Cu(I) catalyst which gives the *cis*-aziridine with high selectivity, while the bisoxazoline–copper(I) is less diastereoselective.

## Experimental

### General

The $^1$H NMR and $^{13}$C NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shifts for $^1$H and $^{13}$C NMR are recorded in $CDCl_3$ as the solvent and measured in ppm downfield from tetramethylsilane (TMS). HPLC was performed using a 4.6 mm × 25 cm Daicel Chiralcel AD column. TLC was performed on Merck analytical silica gel 60 $F_{254}$ plates. Solvents were dried using standard procedures. All glass equipment were oven- or flame-dried before use.

### Materials

Trimethylsilyldiazomethane **5a** in 2 M solution in hexanes, ethyl diazoacetate **5b**, 2,2′-(propane-2,2-diyl)bis[(4*S*)-4-*tert*-butyl-4,5-dihydro-1,3-oxazole] **7a**, 2,2′-(propane-2,2-diyl)bis-[(4*S*)-4-phenyl-4,5-dihydro-1,3-oxazole] **7b**, $AgSbF_6$, $Sn(OTf)_2$ $Yb(OTf)_3$ and $Zn(OTf)_2$ were purchased from Aldrich and used as received. (*R*)-Tol-BINAP **6a** and (*R*)-Ph-BINAP **6b** were purchased from Lancaster and used as received. *N*-Tosyl α-imino ester **4a**,[8] methylenebis[(*4R*,*5S*)-4,5-diphenyl-2-oxazoline] **7c**,[9] $CuClO_4$,[10] $CuPF_6$[11] and phosphinooxazoline ligands **8a**,**b**[12] were prepared according to literature procedures.

### General aziridination procedure

The Lewis acid (0.02 mmol) and ligand (0.022 mmol) were added to a flame dried Schlenk flask and evacuated twice and re-filled with $N_2$. Dry solvent (2 mL) was added and the solution was stirred for 0.5 h at rt followed by the addition of 0.2 mmol of the imine and the mixture was cooled to the desired temperature before diazo compound (1.2 eq.) was added (in the copper-catalyzed reaction of EDA **5b** and imine **4a**, EDA was dissolved in 0.5 mL of solvent and added over 9 h). The reaction mixture was stirred overnight and solvent was removed *in vacuo* and the aziridine was isolated by flash column chromatography (FC) (18 mm) on silica gel using 0.2–2% EtOAc in $CH_2Cl_2$ as the eluent.

***cis*-1-Tosyl-2-(trimethylsilyl)aziridine-3-carboxylic acid ethyl ester *cis*-9a.** $^1$H NMR $\delta$ 0.01 (s, 9H), 1.25 (t, $J$ = 7 Hz, 3H), 2.10 (d, $J$ = 9 Hz, 1H), 2.45 (s, 3H), 3.41 (d, $J$ = 9 Hz, 1H), 4.15 (m, 2H), 7.34 (d, $J$ = 9 Hz, 2H), 7.84 (d, $J$ = 9 Hz, 2H). $^{13}$C NMR $\delta$ 14.0, 21.7, 35.6, 40.4, 61.7, 128.2, 129.6, 134.4, 144.8, 167.1. MS *m*/*z* 341 ($M^{\bullet+}$, 1%), 325 (61), 297 (10), 205 (33), 186 (100), 158 (24), 73 (9).

***trans*-1-Tosyl-2-(trimethylsilyl)aziridine-3-carboxylic acid ethyl ester *trans*-9a.** $^1$H NMR $\delta$ 0.24 (s, 9H), 1.21 (t, $J$ = 7 Hz, 3H), 2.30 (d, $J$ = 6 Hz, 1H), 2.43 (s, 3H), 3.20 (d, $J$ = 6 Hz, 1H), 4.15 (m, 2H), 7.31 (d, $J$ = 8 Hz, 2H), 7.84 (d, $J$ = 8 Hz, 2H). $^{13}$C NMR $\delta$ 13.9, 21.6, 39.4, 41.0, 61.8, 127.7, 129.6, 136.2, 144.4, 167.8.

***cis*-1-Phenyl-2-(trimethylsilyl)aziridine-3-carboxylic acid ethyl ester *cis*-9b.** $^1$H NMR $\delta$ 0.20 (s, 9H), 1.34 (t, $J$ = 7 Hz, 3H), 1.65 (d, $J$ = 8 Hz, 1H), 2.89 (d, $J$ = 8 Hz, 1H), 4.25 (m, 2H), 6.96 (m, 3H), 7.24 (m, 2H). $^{13}$C NMR $\delta$ 14.2, 37.3, 42.5, 61.3, 120.5, 123.0, 128.9, 154.7, 170.5. MS *m*/*z* 263 ($M^{\bullet+}$, 17%), 234 (18), 220 (20), 190 (79), 176 (100), 162 (38), 146 (25), 117 (19), 77 (23), 75 (29), 73 (55). MS *m*/*z* 262.1342 ($M^{\bullet+}$), calc. for $C_{14}H_{21}NO_2Si$ 263.1341.

***trans*-1-Phenyl-2-(trimethylsilyl)aziridine-3-carboxylic acid ethyl ester *trans*-9b.** $^1$H NMR $\delta$ 0.02 (s, 9H), 1.19 (t, $J$ = 7 Hz, 3H), 2.08 (d, $J$ = 4 Hz, 1H), 2.94 (d, $J$ = 4 Hz, 1H), 4.13 (m, 2H), 6.92 (m, 3H), 7.21(m, 2H). $^{13}$C NMR $\delta$ 14.1, 36.8, 39.4, 61.2, 120.5, 122.6, 128.7, 151.0, 169.9. MS *m*/*z* 263 ($M^{\bullet+}$, 23%), 190 (89), 176 (100), 162 (37), 75 (28), 73 (63). MS *m*/*z* 262.1342 ($M^{\bullet+}$), calc. for $C_{14}H_{21}NO_2Si$ 263.1341.

**2-(*p*-Tolylsulfonylamino)acrylic acid ethyl ester 10.** $^1$H NMR $\delta$ 1.27 (t, $J$ = 7 Hz, 3H), 2.42 (s, 3H), 4.19 (q, $J$ = 7 Hz, 2H), 5.64 (m, 2H), 7.30 (d, $J$ = 8 Hz, 2H), 7.75 (d, $J$ = 8 Hz, 2H). $^{13}$C NMR $\delta$ 14.0, 21.6, 62.5, 106.7, 127.6, 129.7, 131.0, 135.4, 144.3, 163.1.

***cis*-1-Tosylaziridine-2,3-dicarboxylic acid diethyl ester *cis*-11.** $^1$H NMR $\delta$ 1.23 (t, $J$ = 7 Hz, 6H), 2.45 (s, 3H), 3.55 (s, 2H), 4.17 (q, $J$ = 7 Hz, 4H), 7.35 (d, $J$ = 9 Hz), 7.89 (d, $J$ = 9 Hz). $^{13}$C NMR $\delta$ 13.9, 21.7, 40.6, 62.3, 128.3, 129.9, 133.4, 145.6, 164.1.

***trans*-1-Tosylaziridine-2,3-dicarboxylic acid diethyl ester *trans*-11.** $^1$H NMR $\delta$ 1.31 (t, $J$ = 7 Hz, 6H), 2.44 (s, 3H), 3.78 (s, 2H), 4.26 (q, $J$ = 7 Hz, 4H), 7.33 (d, $J$ = 8 Hz), 7.85 (d, $J$ = 8 Hz). $^{13}$C NMR $\delta$ 13.9, 21.7, 43.1, 62.6, 127.7, 129.7, 136.4, 144.8, 164.9.

### X-Ray analysis of 10‡

X-Ray analysis of crystals of **10** ($C_{12}H_{15}NO_4S$, $M$ 269.33) was carried out on a Siemens SMART CCD diffractometer at 120 K.[12] The crystal was triclinic, space group $P\bar{1}$, with unit cell $a$ = 8.195(1), $b$ = 9.437(2), $c$ = 9.663(2) Å, $\alpha$ = 98.890(3), $\beta$ = 105.927(3), $\gamma$ = 106.060(1)°, $V$ = 668.7(1) Å$^3$, $Z$ = 2, $D_x$ = 1.34 g cm$^{-3}$, $\mu$ = 0.248 mm$^{-1}$. Mo-Kα radiation ($\lambda$ = 0.71073 Å). 2859 reflections with $I > 3\sigma(I)$ gave $R$ = 0.033 in a full matrix least squares refinement with 224 parameters.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‡ CCDC reference number 207/344. See http://www.rsc.org/suppdata/p1/1999/2293 for crystallographic files in .cif format.

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