

[Supporting Information to accompany the corrigendum for:]
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**Sc(OTf)₃-Catalyzed Condensation of 2-Alkyl-*N*-tosylaziridine with Aldehydes or Ketones:
An Efficient Synthesis of 5-Alkyl-1,3-oxazolidines**

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General information. All reactions were set up in a nitrogen-filled dry box. All flash-chromatography was carried out using silica gel (MP siliotech 60-200 mesh) or basic aluminum oxide (EMD 80-200 mesh) under a positive pressure of nitrogen, unless otherwise noted. Dichloromethane (Fisher Scientific) was dried over neutral alumina in a Dow-Grubbs solvent system.¹ Acetone was purified by vacuum distillation over anhydrous CaSO₄ and other carbonyls were used without further purification. Finely ground 4Å molecular sieve powder was baked at 300 °C for 2 days under vacuum and flame-dried using a propane gastorch (three times) prior to use. Zn(OTf)₂ was newly purchased from Strem Chemicals (Newburyport, MA, USA) and Alfa Aesar (Ward Hill, MA, USA) for the current study. An old Aldrich Chemicals (Milwaukee, WI, USA) sample of Zn(OTf)₂ that has been stored on the bench top (under air) for a prolonged period time was also used.

Discussion

Reproducibility of Results. Our reproduced results and those of Singh and coworkers, both previously reported² and in recent reproductions, for the Zn(OTf)₂-catalyzed condensation of 2-phenyl-*N*-tosylaziridine with three different organic carbonyls are shown below in Tables CS1 and CS2. We failed to observe enhanced reactivity of Zn(OTf)₂, regardless of the source, for ketone substrates in the presence of activated 4Å molecular sieve (MS) powder (Table CS1, entries 2 and 5). This is in contrast to the high reactivity consistently observed by Singh and coworkers, either previously² or in recently reproduced results (Table CS2, entries 1-2 and 4-5). Interestingly, we found that Zn(OTf)₂ from two different sources (Strem and Alfa Aesar) showed variability in conversion and isolated yield for ketone substrates in the absence of 4Å MS powder (Table CS1, entries 1 and 4). For example, Zn(OTf)₂ from Strem Chemicals gave significantly lower conversion and yield for acetone substrate than that from Aldrich (Table CS1, entry 1), whereas the use of Zn(OTf)₂ from Alfa Aesar for cyclohexanone substrate increased the yield to 88% (Table CS1, entry 1).

Source of Zn(OTf)₂. Our hypothesis is that the source and quality of the Zn(OTf)₂ has significant influence on the formation and purity of oxazolidine. This is not the first instance where contrasting results have been reported with Zn(OTf)₂-catalyzed reactions. In the Zn(OTf)₂-catalyzed silylation of terminal alkyne and asymmetric alkynylation to aldehyde, several references reported inconsistent results with Zn(OTf)₂ from different sources. For example, see *J. Org. Chem.*, **2008**, *73*, 2912-2915 and *Tetrahedron*, **2005**, *61*, 7219-7232. The latter manuscript has a significant comment on this issue.

Indeed, an old batch of Zn(OTf)₂ from Aldrich that has been stored on the bench top (under air) for a prolonged period time showed very different product ratio between 5-substituted isomer (Fig. CS1) and ring-opened product (Fig. CS2) compared to new Zn(OTf)₂ from Strem under the same reaction conditions (Table CS1, entry 4; see also Fig. CS4), with the tosylamino alcohol ring-opened product being the major compound in the reaction using the Aldrich old materials (see also Fig. CS3).

The presence of Triflic Acid (HOTf) in An Old Sample of Zn(OTf)₂. We note that in Singh's reproducibility test (Table CS2) the 5-substituted isomer was isolated in quantitative yield. One potential source for the tosylamino alcohol ring-opened product in the crude reaction mixture that we obtained using the old Aldrich Zn(OTf)₂ sample is free HOTf. As zinc triflate is a hygroscopic white powder, it can potentially absorb water over time and release HOTf, which can catalyze the ring-opening of the aziridine substrate prior to oxazolidine formation.

We tested the HOTf-impurity hypothesis by employing as catalyst Zn(OTf)₂ samples (both the new Strem sample and the old Aldrich sample) that were pre-washed with anhydrous dichloromethane (DCM) in the dry box prior to use. In both cases (compare Fig. CS5 vs. CS3 for the old Aldrich samples and Fig. CS4 vs. CS6 for the new Strem samples), the DCM-washed Zn(OTf)₂ samples give less ring-opened products than the unwashed Zn(OTf)₂ samples, thereby suggesting that washing with DCM largely removes the impurity (believed to be HOTf) that gives rise to the ring-opened product.

¹ A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.

² S. Gandhi, A. Bisai, B. A. B. Prasad and V. K. Singh, *J. Org. Chem.*, 2007, **72**, 2133-2142.

Table CS1. The activity test of Zn(OTf)₂ from different sources for the condensation of 2-phenyl-*N*-tosylaziridine with carbonyls

Entry	R ¹	R ²	Additive	Time (h)	With Strem Zn(OTf) ₂ ^a		With Strem Zn(OTf) ₂ washed with DCM ^a		With Alfa Aesar Zn(OTf) ₂ ^a		With Aldrich Zn(OTf) ₂ ^d	
					Conv. (%) ^b	Yield (%)	Conv. (%) ^b	Yield (%) ^g	Conv. (%) ^b	Yield (%) ^g	Conv. (%) ^e	GC yield (%) ^f
					1	CH ₃	CH ₃	none	2	55	28	53
2	CH ₃	CH ₃	4Å MS	2	18	0	<2	0	7	0	27	0
3 ^c	CH ₃	CH ₃	4Å MS	2	-	80 ^e						
4	-(CH ₂) ₅ -		none	0.5	32	22	31	28	96	88	26	25
5	-(CH ₂) ₅ -		4Å MS	0.5	13	2	<2	0	5	0	17	13
6 ^c	-(CH ₂) ₅ -		4Å MS	0.5	-	96 ^e						
7	Ph	H	none	3.5	94	79					91	88
8	Ph	H	4Å MS	3.5	96	87					90	88
9 ^c	Ph	H	4Å MS	3.5	-	52 ^e						

^aReaction conditions: 2-phenyl-*N*-tosylaziridine (136.7 mg, 0.5 mmol), carbonyl compound (1.5 mmol), Zn(OTf)₂ (36.4 mg, 20 mol%), 4Å MS (150 mg), CH₂Cl₂ (2.5 mL, 0.2 M), rt, N₂ atmosphere. All reactions were performed in the absence of undecane and products were isolated using silica gel chromatography, unless otherwise noted. ^bConversion based on the recovered aziridine. ^cReported results by Singh and coworkers.² (source of Zn(OTf)₂ = Lancaster, India). Prof. Singh reported in private communication that his group activated 4Å MS only at 120 °C for 3 h. As such, our results in entry 2, 5, and 8 should not be directly compared to their reported results in entry 3, 6, and 9. ^dResults quoted from our original manuscript³ where undecane was used as an internal standard. ^eConversion determined by GC analysis based on aziridine. ^fGC yield was determined with internal standard. ^gIsolated yield via basic alumina.

Table CS2. Reproducibility test for the cycloaddition of 2-phenyl-*N*-tosylaziridine with carbonyl compounds carried out by Singh and coworkers.

Entry	R ¹	R ²	Product	Time	Yield (%) ^b
1 ^a		-(CH ₂) ₅ -	1a	30 min	95 ^c
2 ^a		-(CH ₂) ₅ -	1a	30 min	90 ^d
3 ^e		-(CH ₂) ₅ -	1a	30 min	96 ^e
4 ^a	CH ₃	CH ₃	1b	2 h	90 ^c
5 ^a	CH ₃	CH ₃	1b	2 h	82 ^d
6 ^e	CH ₃	CH ₃	1b	2 h	80 ^e

^aData provided by Prof. Singh in a private communication. Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.25 mmol), carbonyl compound (0.375 mmol), Zn(OTf)₂ (0.05 mmol; source = Lancaster, India), 4Å MS (140 mg, activated at 120 °C for 3 h), CH₂Cl₂ (1.25 mL). ^bIsolated yield. ^cResults of experiment done by a first student. ^dResults of experiment done by a second student. ^ePreviously reported results from *J. Org. Chem.*, **2007**, *72*, 2133-2142.

We additionally verified the HOTf-impurity hypothesis by adding a small amount of HOTf (2 mol%) to a sample of new Strem Zn(OTf)₂ that has been pre-washed with anhydrous DCM in the dry box and using the resulting mixture to catalyze

³ B. Kang, A. W. Miller, S. Goyal, and S. T. Nguyen, *Chem. Commun.* 2009, 3928-3930.

the reaction shown in entry 4 of Table CS1. The ^1H NMR spectrum of the crude product mixture obtained from this reaction (Fig. CS7) clearly shows an increase in the proportion of the ring-opened product in comparison to the ^1H NMR spectrum of the crude product mixture obtained with DCM-washed new Strem $\text{Zn}(\text{OTf})_2$ (no-HOTf-added, Fig. CS6). The presence of the ring-opened product is thus attributed to the presence of HOTf in $\text{Zn}(\text{OTf})_2$.

The Effect of 4Å Molecular Sieve. Unfortunately, while our yields for acetone and cyclohexanone substrates improved when DCM-washed new Strem $\text{Zn}(\text{OTf})_2$ was used in the absence of 4Å MS powder, the observed conversions remained the same as in the unwashed new Strem $\text{Zn}(\text{OTf})_2$ sample and are much lower than those reported in the ESI of our original manuscript³ using an old Aldrich $\text{Zn}(\text{OTf})_2$ sample (cf columns 6, 7, and 9, entries 1 and 4 in Table CS1). In the presence of activated 4Å MS powder (cf columns 6, 7, and 9, entries 2 and 5 in Table CS1), not only did the new Strem $\text{Zn}(\text{OTf})_2$ catalyst give lower conversions and yields of the oxazolidine products than observed in our original experiments using Aldrich $\text{Zn}(\text{OTf})_2$, the DCM-washed new Strem $\text{Zn}(\text{OTf})_2$ sample also gave very low conversions and yields. As such, our isolated yields for acetone and cyclohexanone substrates never reach the level reproduced by Singh and coworkers.

We note that our data for reactions carried out in the presence of activated 4Å MS powder should not be directly compared to the data reported by Singh and coworkers in the presence of activated 4Å MS powder. Our activated 4Å MS powder was baked at 300 °C for 2 days under vacuum and flame-dried using a propane gastorch (three times) prior to use. On the other hand, the Singh group activated 4Å MS only for 3 h at 120 °C (Table CS1, footnote c). India's significantly more humid climate may additionally impact the reactions.

In conclusion, the source and purity of $\text{Zn}(\text{OTf})_2$ must have played very important roles in the outcome of experiments carried out by our lab vs. Singh's. With the newly purchased $\text{Zn}(\text{OTf})_2$ sample from Alfa-Aesar, our herein-reported yield data for the $\text{Zn}(\text{OTf})_2$ -catalyzed condensation of 2-phenyl-*N*-tosylaziridine with acetone and cyclohexanone approach closer to the data reported by Singh and coworkers using a Lancaster $\text{Zn}(\text{OTf})_2$ sample.² As the Lancasters brand was recently purchased by Alfa-Aesar, the two $\text{Zn}(\text{OTf})_2$ samples in questions are probably the closest in origin and it probably is not a surprise that they afford similar results.

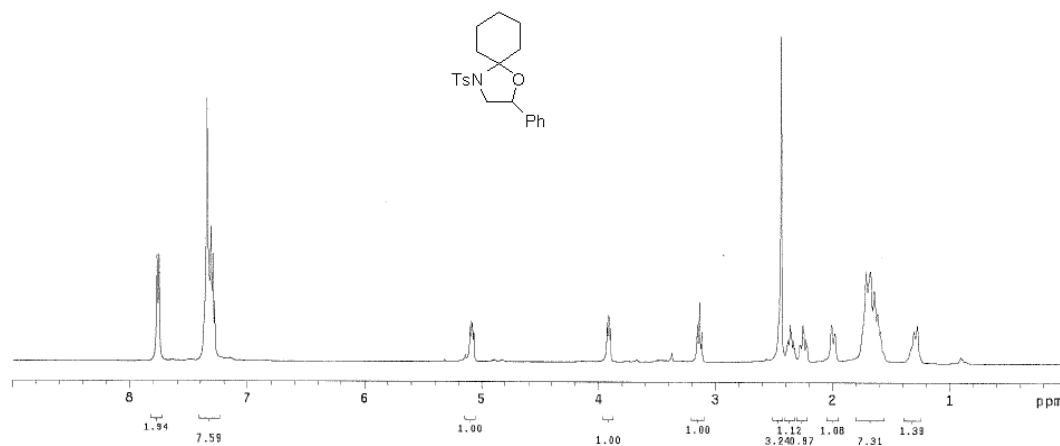


Figure CS1. ^1H NMR spectrum of the isolated main product in entry 4 of Table CS1.

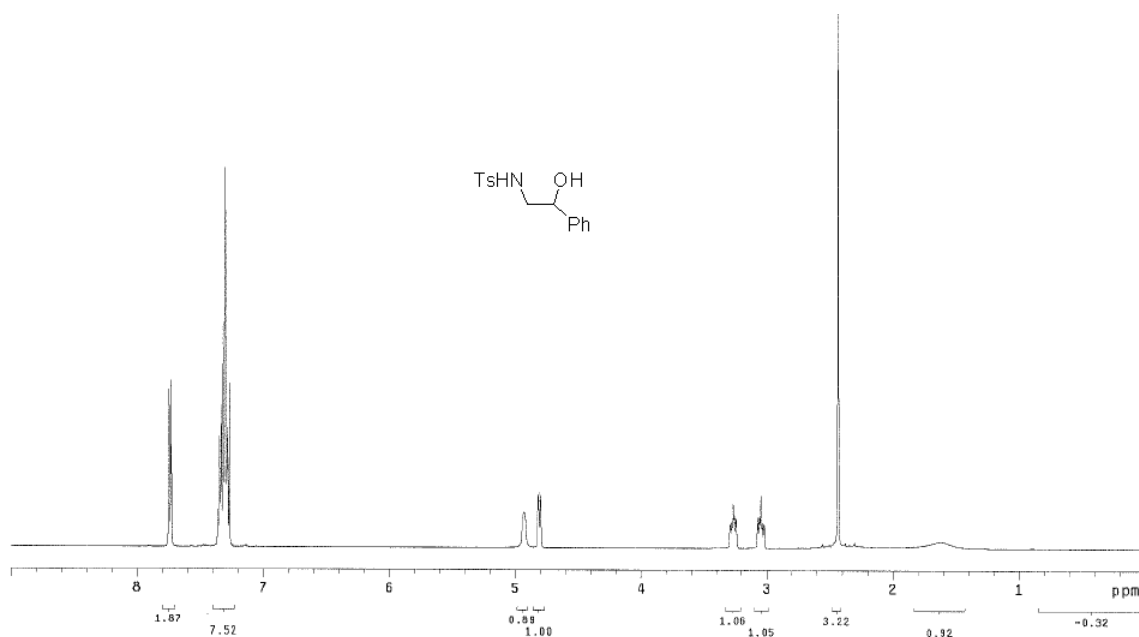


Figure CS2. ^1H NMR spectrum of the isolated ring-opened product in entry 4 of Table CS1.

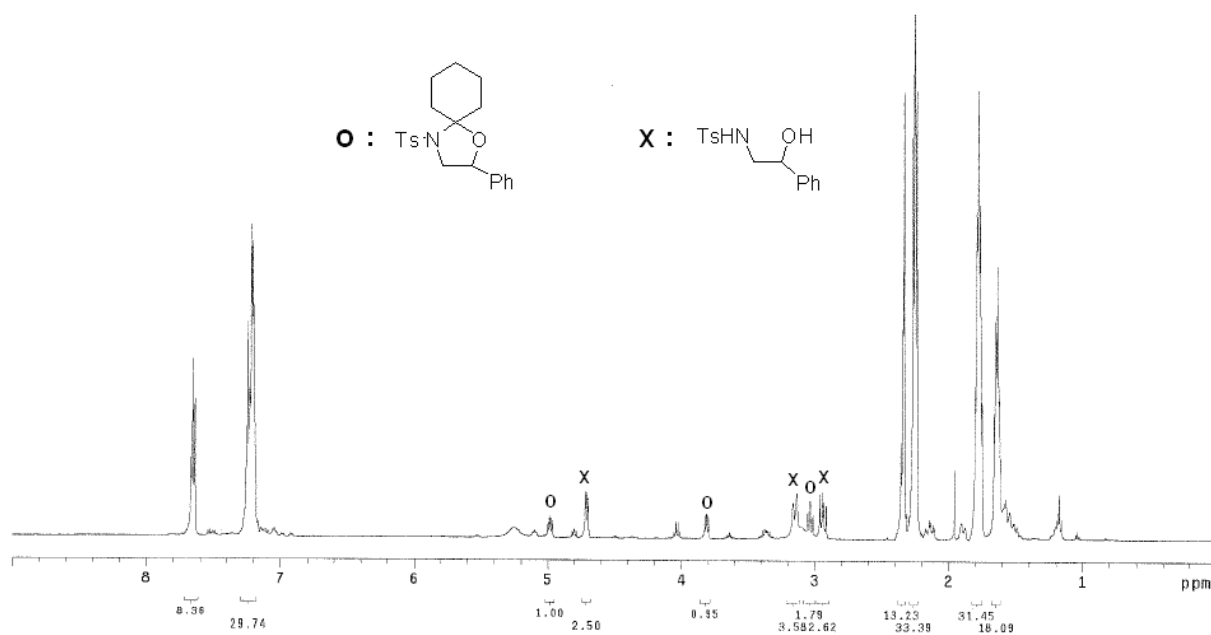


Figure CS3. ^1H NMR spectrum of the crude product mixture obtained using old Aldrich $\text{Zn}(\text{OTf})_2$. Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.25 mmol), cyclohexanone (0.75 mmol), old $\text{Zn}(\text{OTf})_2$ from Aldrich (20 mol%), CH_2Cl_2 (1.25 mL, 0.2 M), rt, N_2 atmosphere.

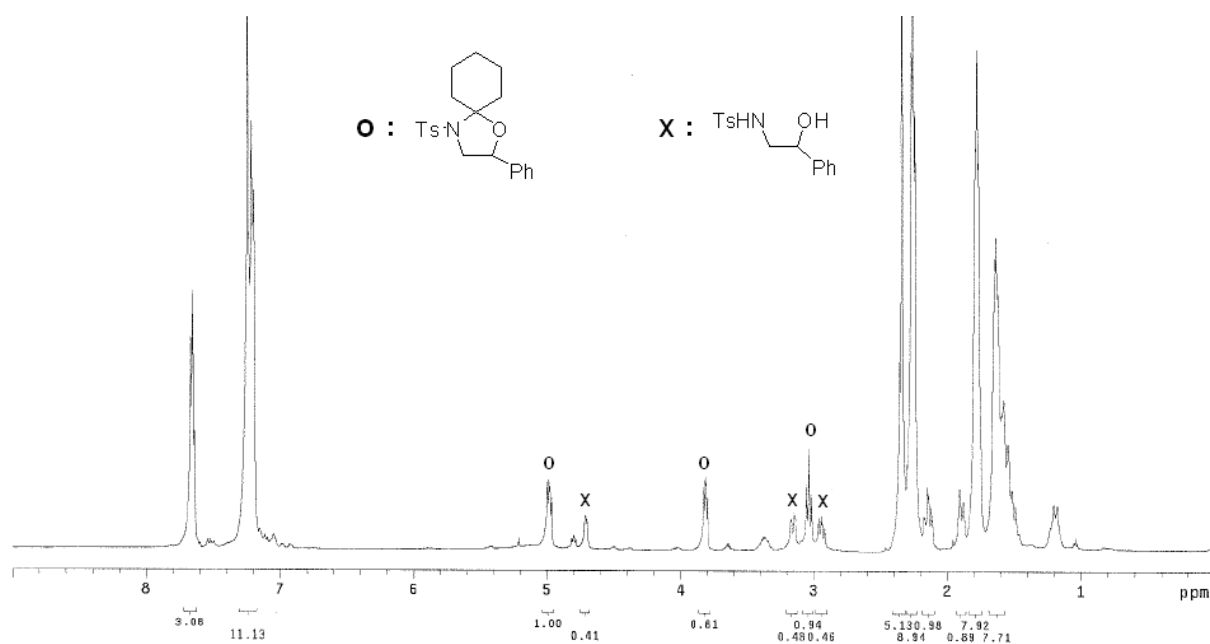


Figure CS4. ^1H NMR spectrum of the crude product mixture obtained using new Strem $\text{Zn}(\text{OTf})_2$. Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.25 mmol), cyclohexanone (0.75 mmol), new $\text{Zn}(\text{OTf})_2$ from Strem (20 mol%), CH_2Cl_2 (1.25 mL, 0.2 M), rt, N_2 atmosphere.

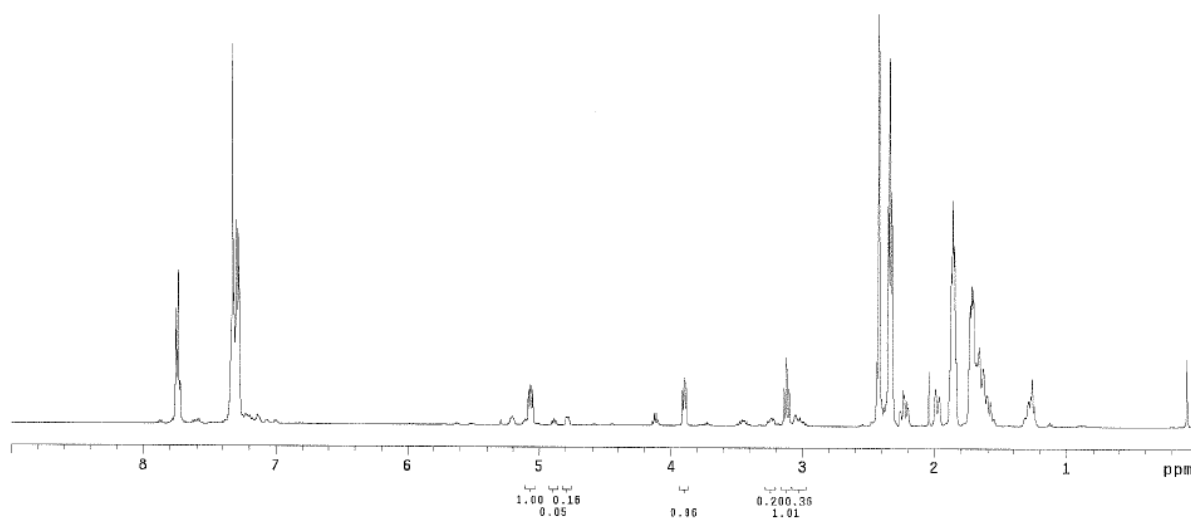


Figure CS5. ^1H NMR spectrum of the crude product mixture obtained using DCM-washed old Aldrich $\text{Zn}(\text{OTf})_2$. Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.25 mmol), cyclohexanone (0.75 mmol), old Aldrich $\text{Zn}(\text{OTf})_2$ (20 mol%, pre-washed with anhydrous DCM), CH_2Cl_2 (1.25 mL, 0.2 M), rt, N_2 atmosphere.

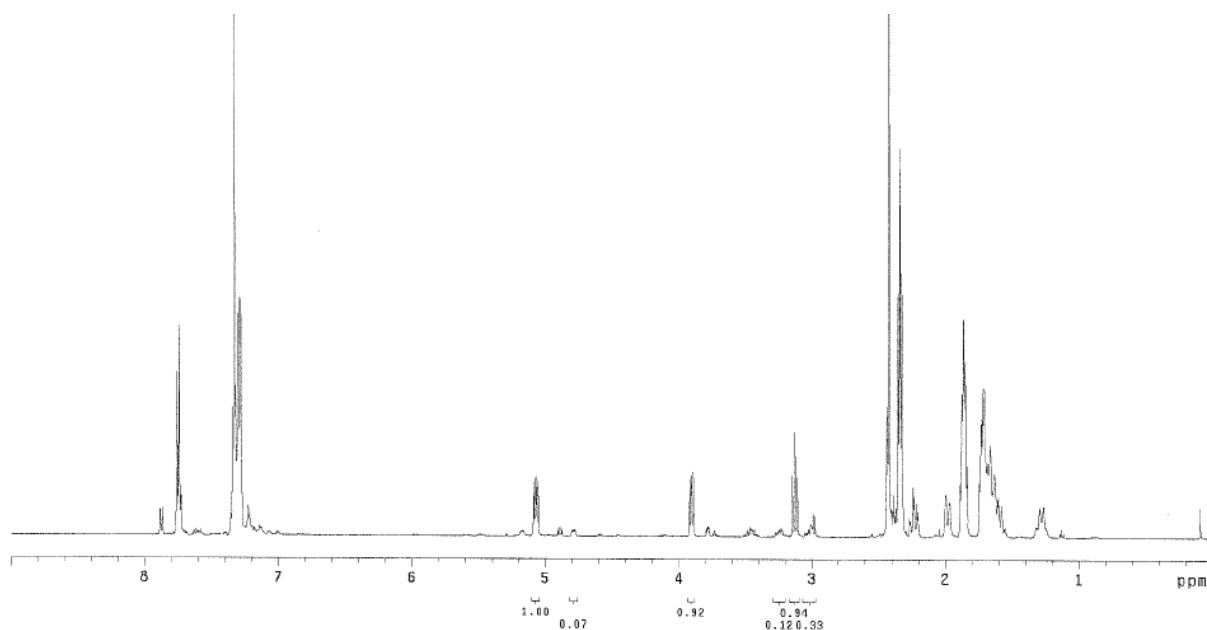


Figure CS6. ¹H NMR spectrum of the crude product mixture obtained using DCM-washed Strem's Zn(OTf)₂. Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.25 mmol), cyclohexanone (0.75 mmol), new Strem Zn(OTf)₂ (20 mol%, pre-washed with anhydrous DCM), CH₂Cl₂ (1.25 mL, 0.2 M), rt, N₂ atmosphere.

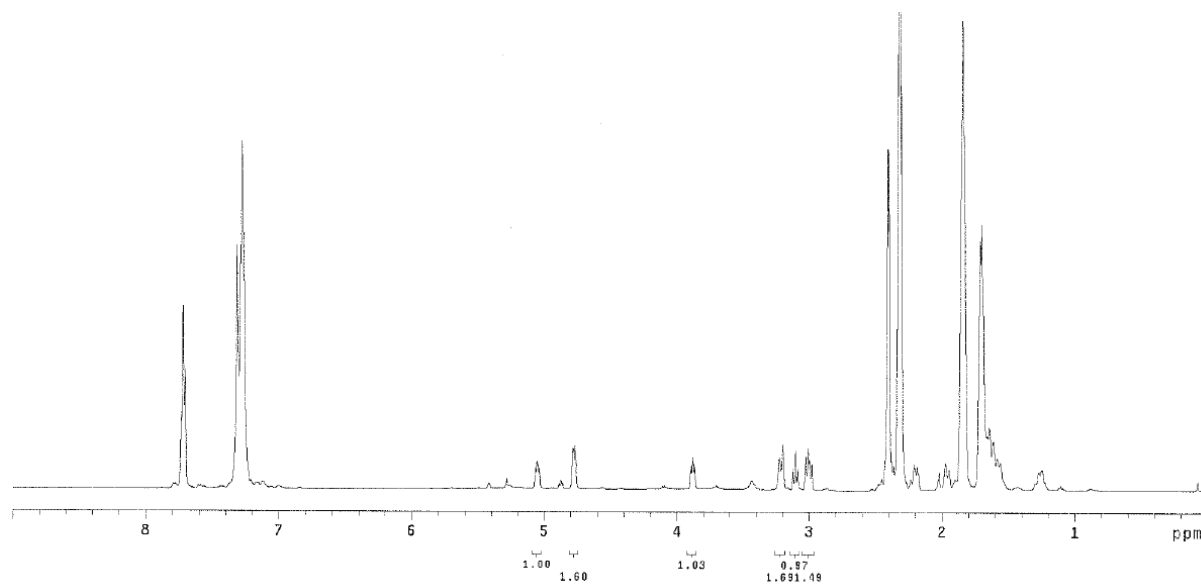


Figure CS7. ¹H NMR spectrum of the crude product mixture obtained using DCM-washed new Strem Zn(OTf)₂ and 2 mol% HOTf. Reaction conditions: 2-phenyl-*N*-tosylaziridine (0.25 mmol), cyclohexanone (0.75 mmol), new Strem Zn(OTf)₂ (20 mol%, pre-washed with anhydrous DCM), trifluoromethanesulfonic acid (2 mol %), CH₂Cl₂ (1.25 mL, 0.2 M), rt, N₂ atmosphere.