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Stereoselective formation of quaternary carbon centres with chiral 3-sulfonyl-1,3-oxazolidines and titanium enolates

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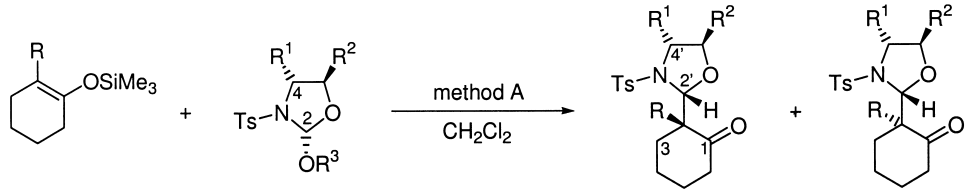
Abstract—The reaction of chiral 2-alkoxy-3-sulfonyl-1,3-oxazolidines and trichlorotitanium enolates was applied for the stereoselective construction of quaternary α-carbonyl stereocentres on cycloalkanones. The influence of different chiral 1,3-oxazolidines on the selectivity and yield of this reaction has been studied. 2-Alkoxy-3-sulfonyl-1,3-oxazolidines bearing one small group in the 4 position or two *trans*-arranged groups in the 4 and 5 position have been found to give the best results.

1. Introduction

The Lewis acid mediated asymmetric formylation of prochiral silyl enol ethers (e.g. **1**) with optically pure 2-alkoxy-3-sulfonyl-1,3-oxazolidines (e.g. **2**) has been elaborated by our group[1] and the group of C. Scolastico[2] since the early 1990s (Scheme 1, method A). The Lewis acid leads to the formation of a 1,3-oxazolidine cation,[2d] followed by the reaction with the nucleophilic silyl enol ether. The advantages of this reaction have been shown in many synthetic applications.[3] Beneficial properties of the obtained products (e.g. **3**,[‡] Table 1, entries 1 and 2) are the easy separation of diastereomers and compatibility and stability under many reaction conditions. The deprotection of the introduced formyl group can be accomplished by electrolysis,[3e] acetal exchange reactions[2b,3a] and subsequent hydrolysis or other transformations.[3f] During our synthesis of metachromin A[3k] we were challenged that the construction of quaternary carbon centres gives only poor selectivities[2b] (Table 1, entries 3–5). The previous conversion of the silyl enol ether **1b**[4a] into a titanium enolate led to much better stereoselection and allowed us the preparation of metachromin A in high overall yield. In this article we report our results dealing with this new method in detail.

2. Results and discussion

As shown in Scheme 2 we converted the silyl enol ether **1b** into the titanium enolates **4a**[5] and **4b**[6] (methods B and C); both species reacted subsequently with the cation of 2-ethoxy-1,3-oxazolidine **2c**. Due to the Lewis-acidic properties of enolate **4b** no addition of a Lewis acid[7] for



1a-b **2a-b** ***cl*-3a-d** ***cu*-3a-d**

for R, R^1, R^2 and R^3 see Table 1

Scheme 1.

Keywords: oxazolidines; enolates; titanium and compounds; asymmetric reactions.

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† X-Ray structure analyses.

‡ Nomenclature: the four possible diastereomers of this reaction are marked as *cl*, *cu*, *tl* and *tu*. *cis* or *trans* (*c* or *t*) indicates the relative configuration at the 1,3-oxazolidine ring (substituents in 2 and 4 position); *like* or *unlike* (*l* or *u*) stands for the relative configuration of the stereocentre in the 2 position of the 1,3-oxazolidine ring and its neighbouring stereogenic carbon centre.

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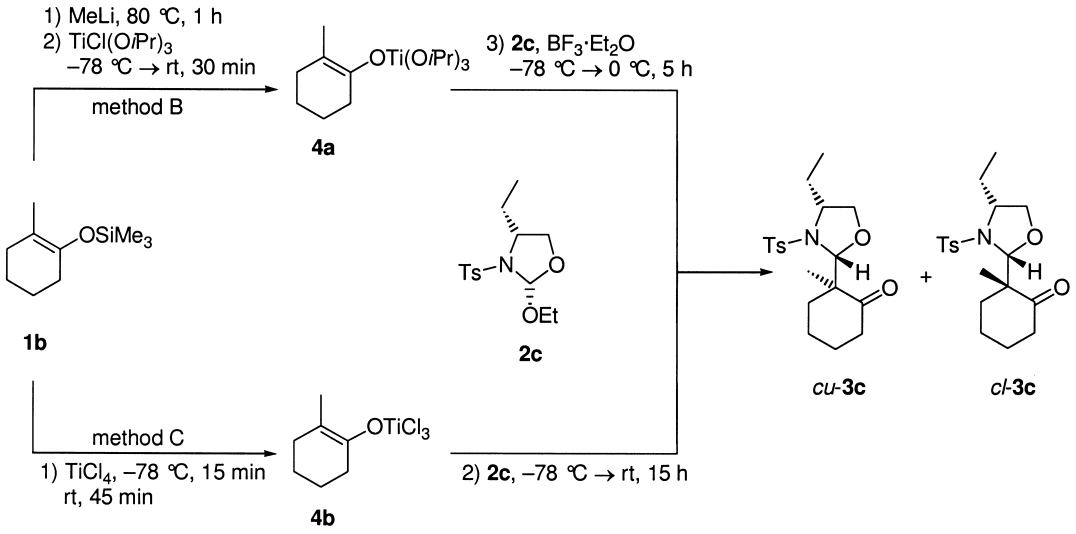
Table 1. Reactions of silyl enol ethers **1** and 2-alkoxy-3-sulfonyl-1,3-oxazolidines **2**

Entry	R	R^1	R^2	R^3	Educts	Lewis-acid	Temperature (°C)	Product	Yield (%)[a]	dr (*cl*/*cu*)[b]
1	H	Et	H	Me	**1a**+**2a**	$ZnCl_2{\cdot}Et_2O$	0	**3a**[3c]	75	84:16
2	H	Me	Ph	Me	**1a**+**2b**	$ZnCl_2{\cdot}Et_2O$	0	**3b**[1b]	91	>95:5
3	Me	Et	H	Et	**1b**+**2c**	$ZnCl_2{\cdot}Et_2O$	0	**3c**[1j]	83	51:49
4	Me	Me	Ph	Me	**1b**+**2b**	$ZnCl_2{\cdot}Et_2O$	0	**3d**[1b]	78	50:50
5	Me	Et	H	Me	**1b**+**2a**	$TiCl_4$	−78	**3c**[1e]	–[c]	50:50

[a] All yields were determined after flash column chromatography.
[b] All diastereomeric ratios were determined by ^1H NMR spectroscopy of the crude products.
[c] Not determined.



Scheme 2.

the generation of the 1,3-oxazolidine cation was necessary in that case. Method B provided the product **3c** with the best selectivity (dr=85:15, Table 2, entry 1) but only with a moderate yield (51%). Because of the much better yield (79%) and the easier practical performance, method C (dichloromethane as the solvent, Table 2, entry 3) was superior.

Table 2. Reactions of titanium enolates **4** and 2-ethoxy-3-sulfonyl-1,3-oxazolidine **2c**

Entry	Method	Enolate	Solvent	Yield (%)[a]	dr (*cu*/*cl*)[b]
1	B	**4a**	PhMe	51	85:15
2	C	**4b**	PhMe	44	78:22
3	C	**4b**	CH_2Cl_2	79	81:19

[a] All yields were determined after flash column chromatography.
[b] All diastereomeric ratios were determined by ^1H NMR spectroscopy of the crude products.

It is noteworthy that the same reagents were used earlier in reverse order;[1e] only a poor selectivity was observed that case (Table 1, entry 5). This indicates that the previous formation of a titanium enolate is essential. This kind of reaction has not been studied before.

To get a further insight into this reaction (Table 2, entry 3) temperature-dependent NMR experiments were done. The reaction was carried out in a carefully sealed NMR tube and the temperature was slowly increased from −80 to 10°C. ^1H NMR spectra were recorded periodically and are depicted in Fig. 1. A signal at 9.41 ppm (2-H) appearing right from the beginning of the reaction indicates the presence of a 1,3-oxazolidine cation,[2d] formed by the abstraction of the ethoxy group of **2c** by the Lewis-acidic titanium enolate **4b**. Then, at higher temperatures (~−40°C) this signal disappears slowly whereas the signal of the formed product *cu*-**3c** at 6.28 ppm (2′-H) increases.[§] This signal of the 1,3-oxazolidine *cu*-**3c** is splitted below a temperature of 0°C (probably due to hindered bond rotations) and shifted downfield in comparison with the same signal (5.36 ppm) recorded in a solvent free of Lewis acids. We conclude that the abstraction of the ethoxy group at low temperature is the first step of the reaction; at higher temperatures the formed cation reacts with the enolate to give the product **3c**. This result reveals that the configuration of the C-2 in reagent **2c** will have no influence on the diastereomeric ratio of the formed 1,3-oxazolidine **3c**.

The variation of the chiral 2-ethoxy-3-sulfonyl-1,3-oxazolidine and its influence on the yield and diastereoselectivity of the studied reaction was of particular interest. Scheme 3 and Table 3 show the results of the preparation of eight new 2-ethoxy-1,3-oxazolidines **2d**–**k** from known chiral sulfonamides **5d**–**k**. Especially reagents such as **2g**–**k** bearing a bicyclic moiety have not been

[§] Some product was formed initially because of imperfect cooling during the placement of the NMR tube into the Bruker AM 360 instrument.

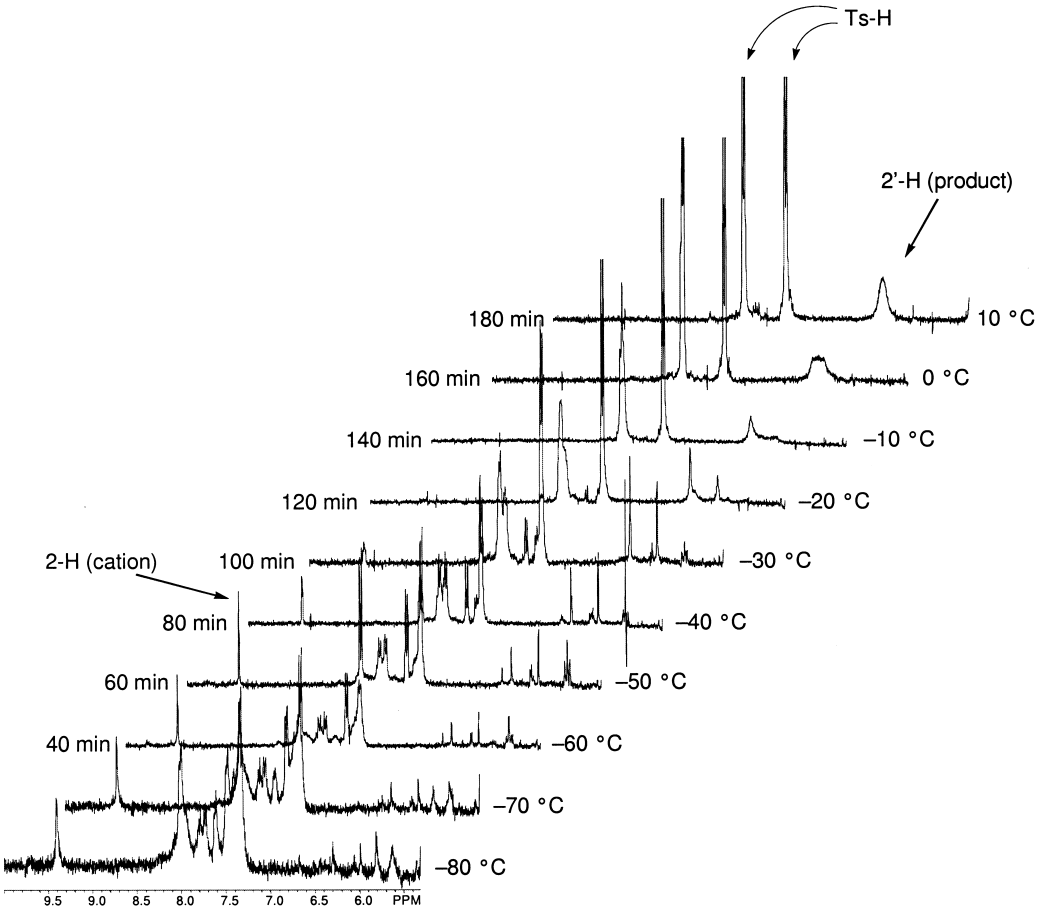
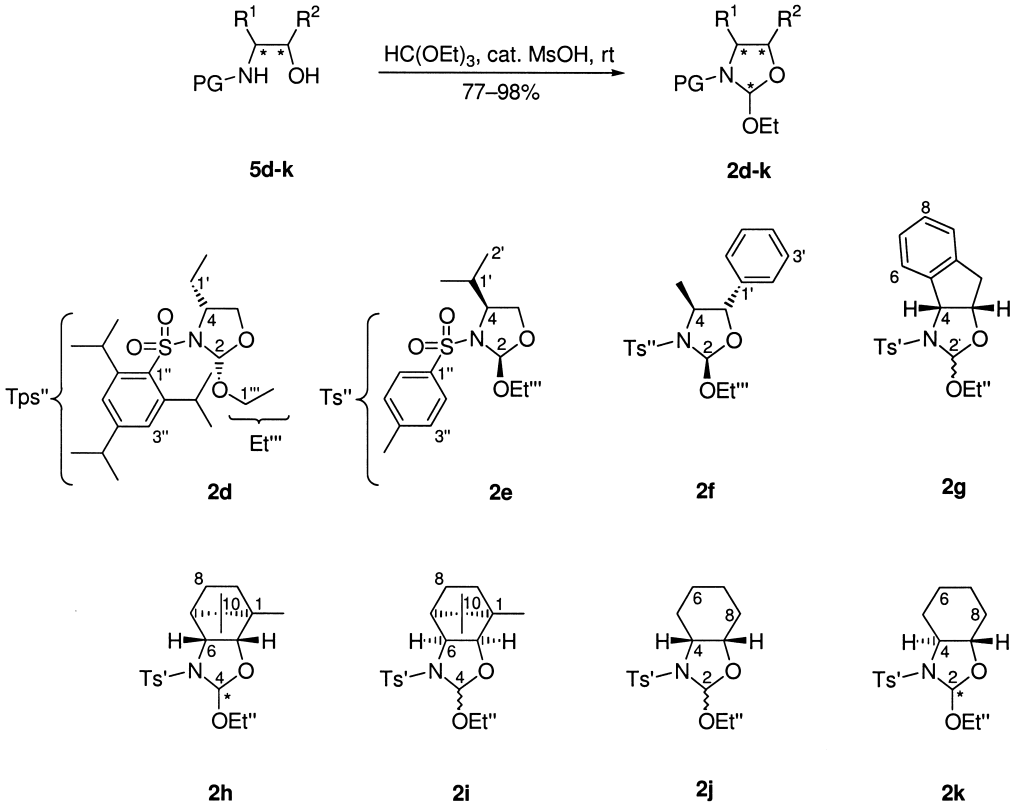


Figure 1. ^{1}H NMR-spectroscopic study of the reaction of the titanium enolate **4b** and the 2-ethoxy-1,3-oxazolidine **2c**.



Scheme 3.

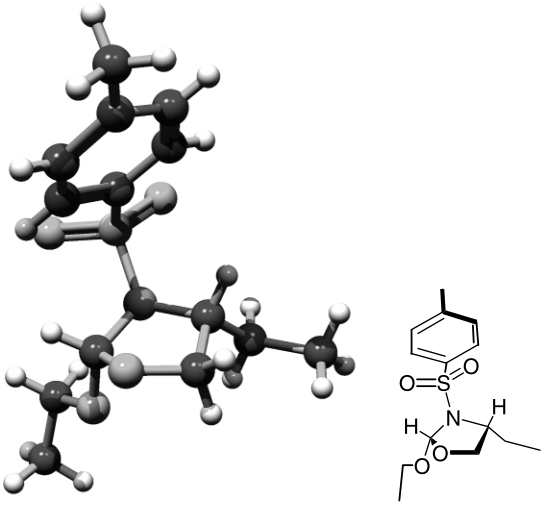
Table 3. Preparation of 2-ethoxy-3-sulfonyl-1,3-oxazolidines **2**

Entry	Educt	Product	Yield (%)[a]	dr[b]
1	**5d**[3j]	**2d**[c]	92	90:10
2	**5e**[3c]	**2e**	94	92:8
3	**5f**[1b]	**2f**	98	>97:3
4	**5g**[8]	**2g**	99	71:29[d]
5	**5h**[9]+**5i** (82:18)[e]	**2h**+**2i** (83:17)[f,g]	94	99:1
6	**5i**[9]+**5h** (92:8)[e]	**2i**+**2h** (96:4)	90	86:14
7	**5j**[10]	**2j**	77	54:46[d]
8	**5k**[11]	**2k**	90	73:27[h]

[a] All yields were determined after flash column chromatography.
[b] All diastereomeric ratios (*cis*/*trans*) were determined by ^{1}H NMR spectroscopy of the crude products.
[c] Contained 8% of triethyl orthoformate.
[d] The *cis*- and *trans*-isomer were separated by flash column chromatography.
[e] Sulfonamides **5h** and **5i** were synthesized as an inseparable mixture.
[f] Contained 12% of triethyl orthoformate.
[g] 2-Ethoxy-1,3-oxazolidines **2h** and **2i** were separated by crystallization.
[h] After flash column chromatography only the main diastereomer was isolated in 90% yield.

studied before. All compounds **2** were prepared in good to excellent yields and varying ratios of C-2 epimers. Interestingly, 2-ethoxy-1,3-oxazolidine **2k** seems to epimerize on silica gel and only traces of the minor diastereomer which was detected in the crude product were found after chromatography. In two cases (Table 3, entries 4 and 7) it was possible to separate the C-2 epimers by flash column chromatography. This allowed us to verify our hypothesis that the configuration in this position should have no effect on the diastereoselectivity in the reaction with trichlorotitanium enolates.

The structure of the main diastereomer of reagent **2c** was elucidated by X-ray analysis[12] (Fig. 2). As expected, the relative configuration of the substituents in the 2 and 4 position was proven to be *cis*. Table 4 shows selected NMR signals of the *cis*- and *trans*-isomers of the 2-ethoxy-1,3-oxazolines **2c**–**k**. With the exception of **2i** and **2j** the signals (2-H, C-2) of all major diastereomers are shifted more downfield than the signals of the corresponding minor isomers. This result may be an indication that in most cases the *cis*-isomers are favoured; only a strong steric shielding of one side of the 1,3-oxazolidine ring in compounds like **2i** or **2j** may lead to a preference for the *trans*-configuration.



cis-**2c**

Figure 2. Molecular structure of 2-ethoxy-3-sulfonyl-1,3-oxazolidine *cis*-**2c**.[12]

Table 4. Selected NMR data of the 2-ethoxy-1,3-oxazolidines **2**

Entry	Compound	Major diastereomer		Minor diastereomer	
		2-H	C-2	2-H	C-2
1	**2c**	**6.02**[a]	**108.0**	5.87	107.1
2	**2d**	6.02	107.7	5.78	106.7
3	**2e**	6.02	108.2	5.91	107.5
4	**2f**	6.22	107.6		
5	**2g**	6.18	108.8	5.81	107.4
6	**2h**	5.85[b]	108.2[c]	5.63[b]	–[d]
7	**2i**	6.08[b]	111.2[c]	6.13[b]	112.3[c]
8	**2j**	5.89	105.8	5.97	107.7
9	**2k**	5.85	107.1	5.02	–[d]

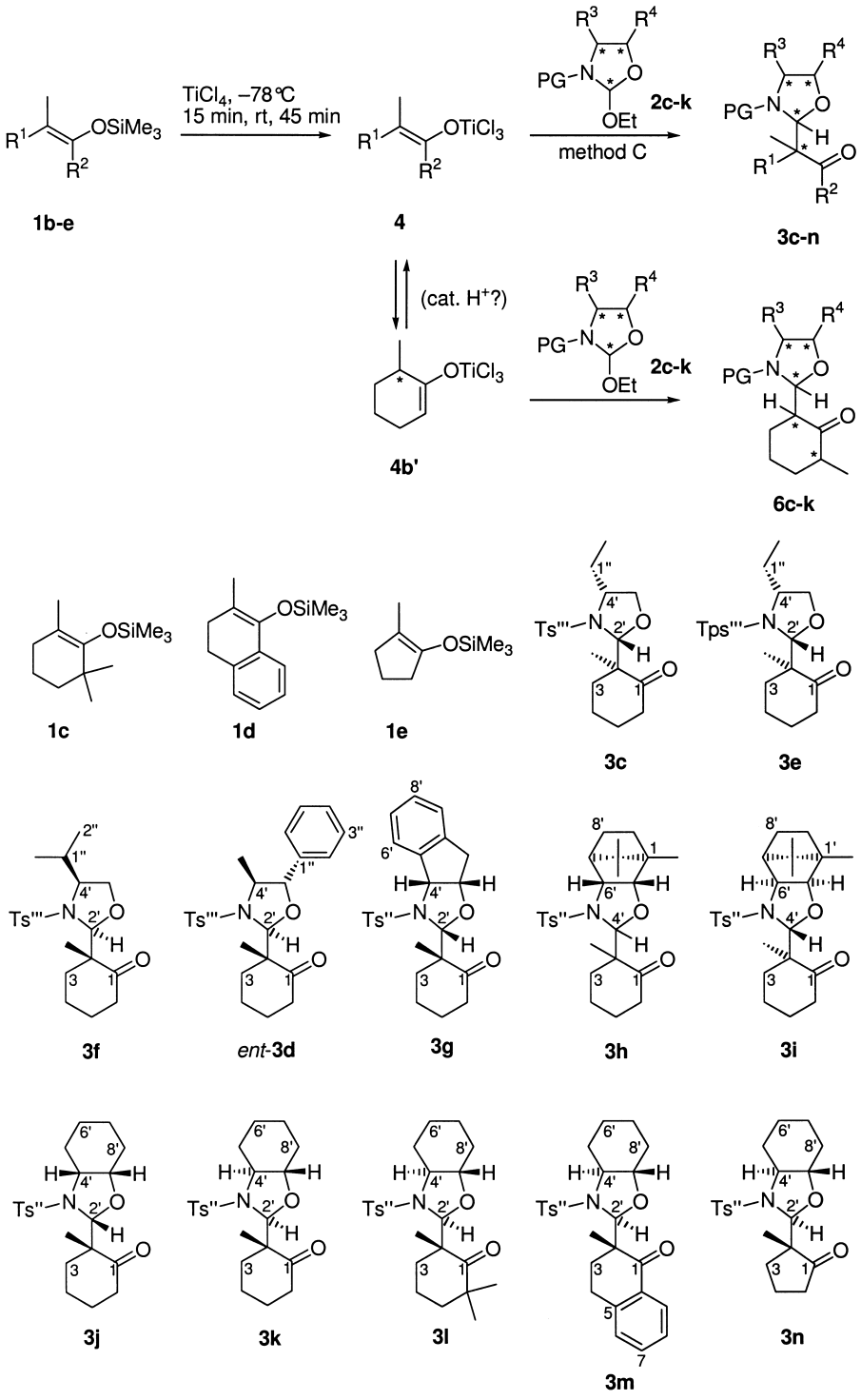
[a] Bold shifts indicate that the configuration was determined by X-ray analyses.
[b] 4-H is the corresponding proton.
[c] C-4 is the corresponding carbon atom.
[d] Not detected.

The results of the reactions of the titanium enolate **4b** and the 2-ethoxy-1,3-oxazolidines **2c**–**k** are presented in Scheme 4 and Table 5 (entries 1–11). In most cases the main product showed *cis-unlike*-configuration (Table 5, entries 1–4 and 11). In contrast to this, reagent **2i** (entry 8) furnished the *trans-unlike*-configured main product *tu*-**3i** in acceptable yield; the use of the diastereomeric **2h** (entry 7) gave no product. The application of 2-ethoxy-1,3-oxazolidines such as **2g** (entries 5 and 6) or **2j** (entries 9 and 10) gave mixtures of similar amounts of the *cis-unlike*- and *cis-like*-isomers. The *cis*- and *trans*-epimers of **2g** and also of **2j** were subjected separately to the reaction with the enolate **4b** (Table 5, entries 5 and 6, 9 and 10); as expected, the C-2 configuration showed no evident influence on the observed diastereomeric ratios. Good *cis-unlike*-selectivities were obtained with the 2-ethoxy-1,3-oxazolidines **2c**, **2f** and **2k** (entries 1, 4 and 11). The reagents **2c** and **2k** appeared to be most valuable because they provided the desired products **3c** and **3k** in good yields *and* selectivities.

Some experiments (Table 5, entries 3–5, 8, 9, 11) furnished up to 10% of the isomeric by-products **6**, which were identified easily by the ^{1}H NMR signal of the 2′-H (doublet instead of singlet). An isomerization of the titanium enolate **4b** might be responsible for this result (Scheme 4), since the used silyl enol ether **1b** was essentially isomerically pure[¶] (GC analysis: >97:3). Perhaps, traces of a proton source in some of the 2-ethoxy-1,3-oxazolidines are catalyzing this process.

The 2-ethoxy-1,3-oxazolidine **2k** was allowed to react with three other titanium enolates obtained from the known[4] silyl enol ethers **1c**–**e** (Table 5, entries 12–14). The *cis-unlike*-configured main products *cu*-**3** were produced in acceptable

[¶] Silyl enol ethers **1b** and **1e** were purified by spaltrohr distillation.



Scheme 4.

to excellent selectivities and moderate to good yields. In particular the cyclopentanone derivative *cu*-**3n** was formed with high selectivity.

The configurations of the synthesized 1,3-oxazolidines **3** were proven by X-ray analyses[12] (Figs. 3–5) in many cases; some more configurations could be determined by drawing conclusions from the NMR data, selected shifts are presented in Table 6. In accordance with the X-ray analyses the signals of the 2-H and C-2 of the *cu*-configured products *cu*-**3** are shifted more to high field than the signals of the other diastereomers.

Some relationships between the structures of the 2-ethoxy-1,3-oxazolidines **2** and the observed diastereoselectivities of their reaction with the titanium enolate **4b** can be recognized: To obtain a good selectivity in favour of the *cis-unlike*-product *cu*-**3**, 2-ethoxy-1,3-oxazolidines with a

Table 5. Results of the reactions of silyl enol ethers **1** and 2-ethoxy-3-sulfonyl-1,3-oxazolidines **2** (method C)

Entry	Educts[a]	Product	Yield (%)[b]	dr[c]	By-product[d]
1	**1b**[4a]+**2c** (99:1)	**3c**[3k]	79	81 (***cu***):19 (*cl*)	**6c**, 0%
2	**1b**+**2d** (90:10)[e]	**3e**	44	74 (*cu*):26 (*cl*)	**6e**, 0%
3	**1b**+**2e** (95:5)	**3f**	54	66 (***cu***):34 (*cl*)	**6f**, 8%, dr=50:50
4	**1b**+**2f** (>97:3)	*ent*-**3d**[1b]	50	92 (*cu*):8 (***cl***)	**6d**, 8%, dr=100:0
5	**1b**+**2g** (97:3)	**3g**	74	35 (***cl***):34 (*cu*):25 (***tl***):6 (*tu*)	**6g**, 10%, dr=60:40
6	**1b**+**2g** (6:94)	**3g**	–[f]	35 (***cl***):38 (*cu*):24 (***tl***):3 (*tu*)	**6g**, –[f]
7	**1b**+**2h** (100:0)[g]	**3h**	0	–	**6h**, 0%
8	**1b**+**2i** (86:14)[h]	**3i**	57	75 (***tu***):13:5:7	**6i**, 7%, dr=93:7
9	**1b**+**2j** (100:0)	**3j**	38	43 (***cl***):36 (***cu***):21 (*t*)	**6j**, 1%, dr=75:25
10	**1b**+**2j** (4:96)	**3j**	–[f]	45 (***cl***):36 (***cu***):19 (*t*)	**6j**, –[f]
11	**1b**+**2k** (100:0)	**3k**	74	89 (***cu***):11	**6k**, 2%, dr=100:0
12	**1c**[4b]+**2k** (100:0)	**3l**	47	78 (*cu*):13 (***cl***):9(*t*)	–
13	**1d**[4c]+**2k** (100:0)	**3m**	68	74 (***cu***):19:4:3	–
14	**1e**[4d]+**2k** (100:0)	**3n**	59	98 (***cu***):2	**6n**, 0%

[a] The diastereomeric ratios of the 2-ethoxy-1,3-oxazolidines **2** are given in parenthesis.
[b] All yields were determined after flash column chromatography.
[c] All diastereomeric ratios were determined by ^{1}H NMR spectroscopy of the crude products. Bold specifications of configurations were determined by X-ray analyses.
[d] All yields and diastereomeric ratios were determined after flash column chromatography.
[e] Contained 8% of triethyl orthoformate.
[f] Not determined.
[g] Contained 12% of triethyl orthoformate.
[h] Contained 4% of 2-ethoxy-1,3-oxazolidine **2h**.

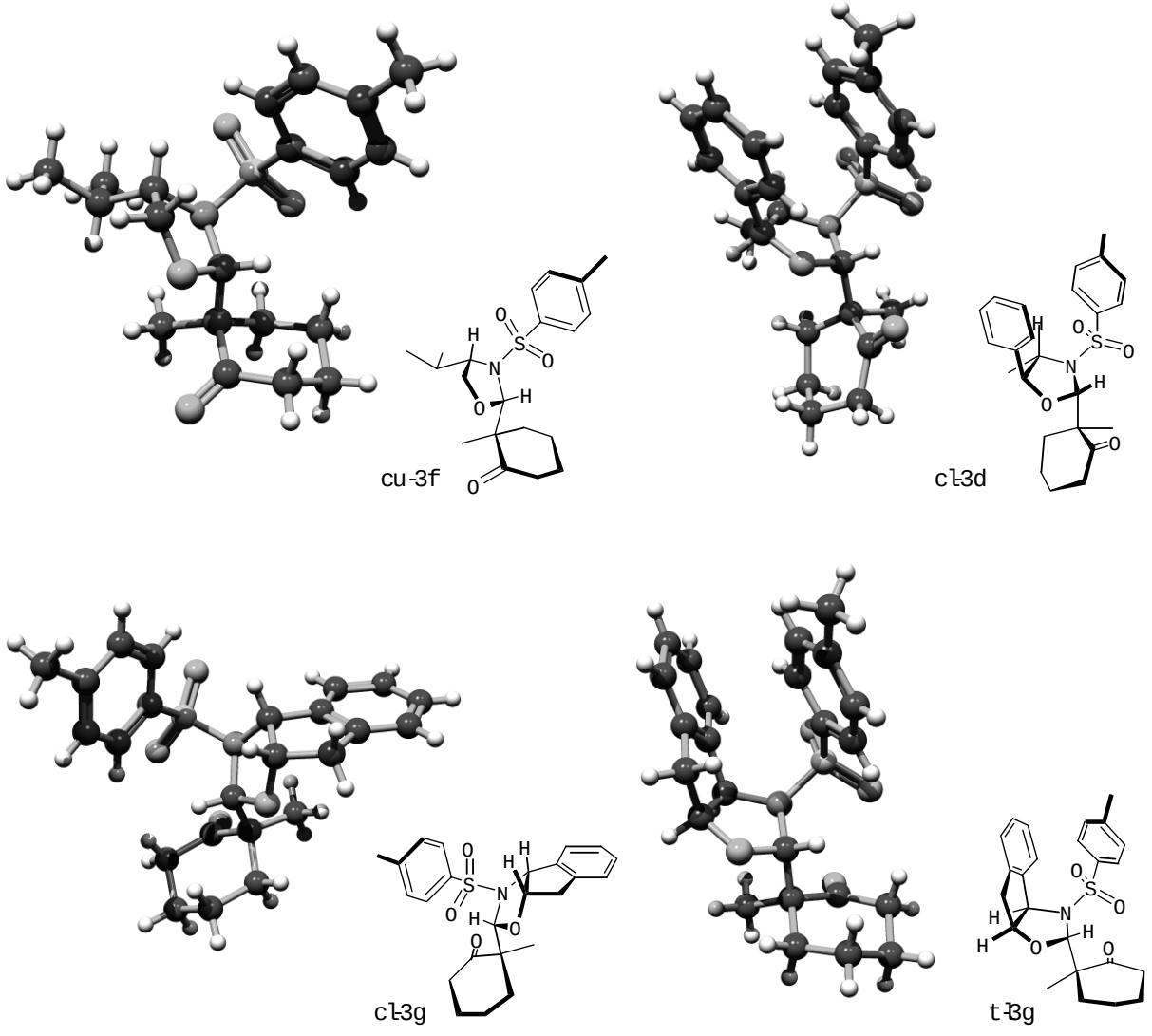


Figure 3. Molecular structures of 3-sulfonyl-1,3-oxazolidines *cu*-**3f**, *cl*-**3d**, *cl*-**3g** and *tl*-**3g**.[12]

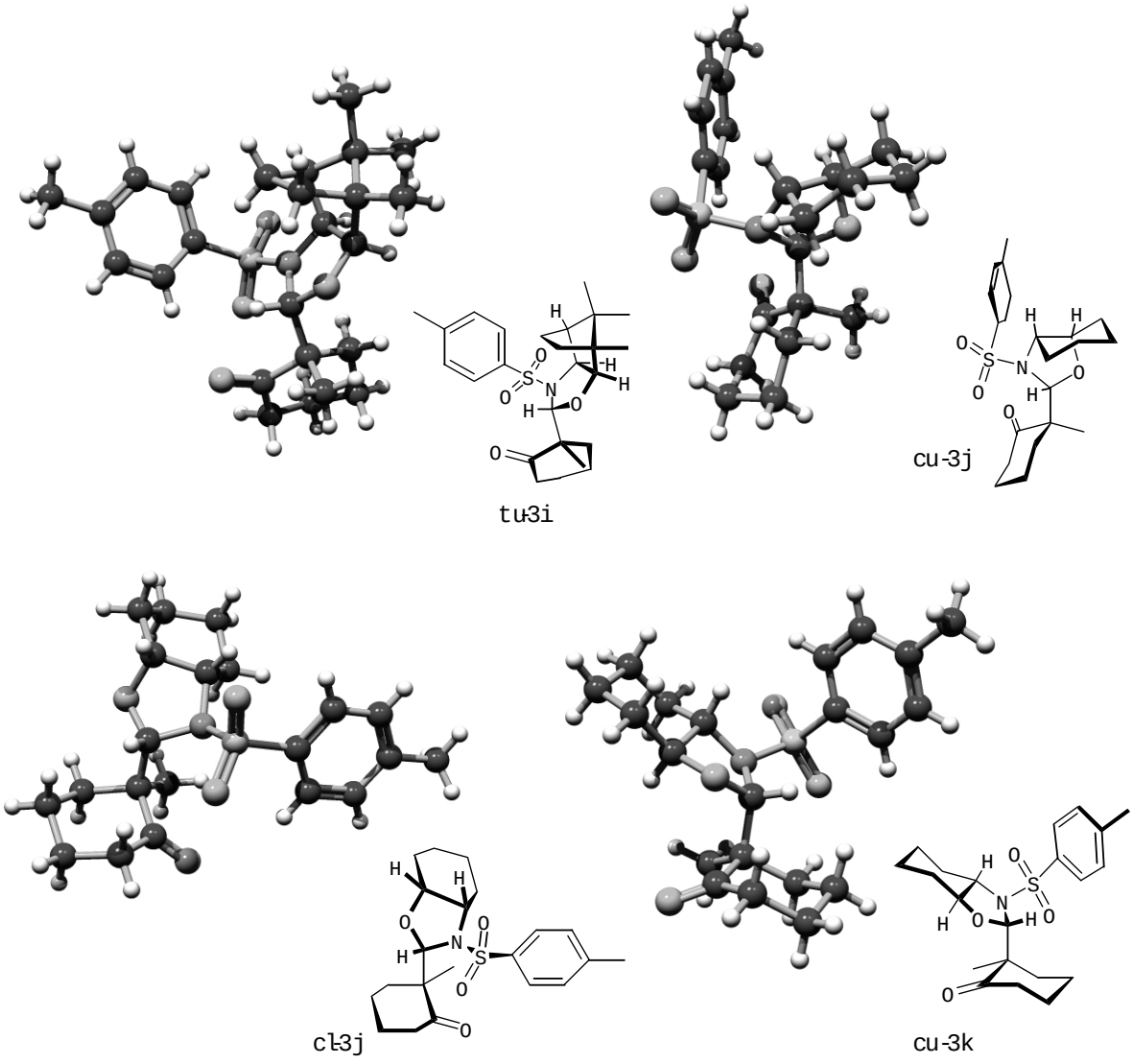


Figure 4. Molecular structures of 3-sulfonyl-1,3-oxazolidines *tu*-**3i**, *cu*-**3j**, *cl*-**3j** and *cu*-**3k**[12] (X-ray analysis for *cu*-**3j**, *cl*-**3j** and *cu*-**3k** were obtained from a racemic sample).

small group in the 4 position of the 1,3-oxazolidine ring (**2c**) or with two *trans*-configured groups in the 4 and 5 position (**2f**, **2k**) should be used. Two *cis*-orientated groups in the 4 and 5 position (**2g**, **2j**) lead to the formation of *cis-like*-product *cl*-**3** at the expense of *cis-unlike*-product *cu*-**3** and furthermore, *trans*-products *t*-**3** are detected or even become the main diastereomer (**2i**). A large group in 4 position (**2e**) or a large sulfonyl group (**2d**) support the formation of the *cis-like*-configured products *cl*-**3**, as well.

The observed *cis* selectivity in most reactions can be rationalized as an addition of the enolate *trans* to the bulky sulfonyl group, which is in a *trans* position relative to the adjacent C-4 substituent.[13] The formation of *trans*-products *t*-**3** instead of the generally preferred *cis*-products *c*-**3** may be consistent with the strong steric shielding of the *cis*-side in 2-ethoxy-1,3-oxazolidines like **2i** (and also **2g** and **2j**).

The *like* or *unlike* selectivity for the formation of the *cis*-isomers *c*-**3** is more difficult to understand. To explain the different results of the reactions of 2-alkoxy-1,3-oxazolidines **2** either with the silyl enol ether **1b** or the titanium enolate **4b** we suggest a cyclic transition state in the latter case. The titanium atom of the enolate may coordinate to the 1,3-oxazolidine oxygen atom or to the sulfonyl group (Fig. 6). Perhaps a coordination to the 1,3-oxazolidine oxygen atom (TS **A** and TS **B**) increases the electrophilicity of the cation and therefore promotes the reaction with the nucleophilic enolate, no matter which coordination may be thermodynamically favoured. We think that in this case TS **B** should be disfavoured because of steric interactions between the 1,3-oxazolidine ring and the cyclohexyl ring and this could be the reason for the *cis-unlike*-configuration of the main products in most cases.

A closer view at some of the possible geometries of the transition states TS **A** and TS **B** is given in Fig. 7. The transition states TS $\mathbf{A}^3$ and TS $\mathbf{B}^3$ appear to be disfavoured because of the titanium atom (and its ligands) placed at the top of a boat-like geometry; this creates a strong trans-annular strain. Two chair-like (TS $\mathbf{A}^1$ and TS $\mathbf{B}^2$) and two boat-like geometries (TS $\mathbf{A}^2$ and TS $\mathbf{B}^1$) can be regarded for explanations. Like in the corresponding aldol reactions[6b] of

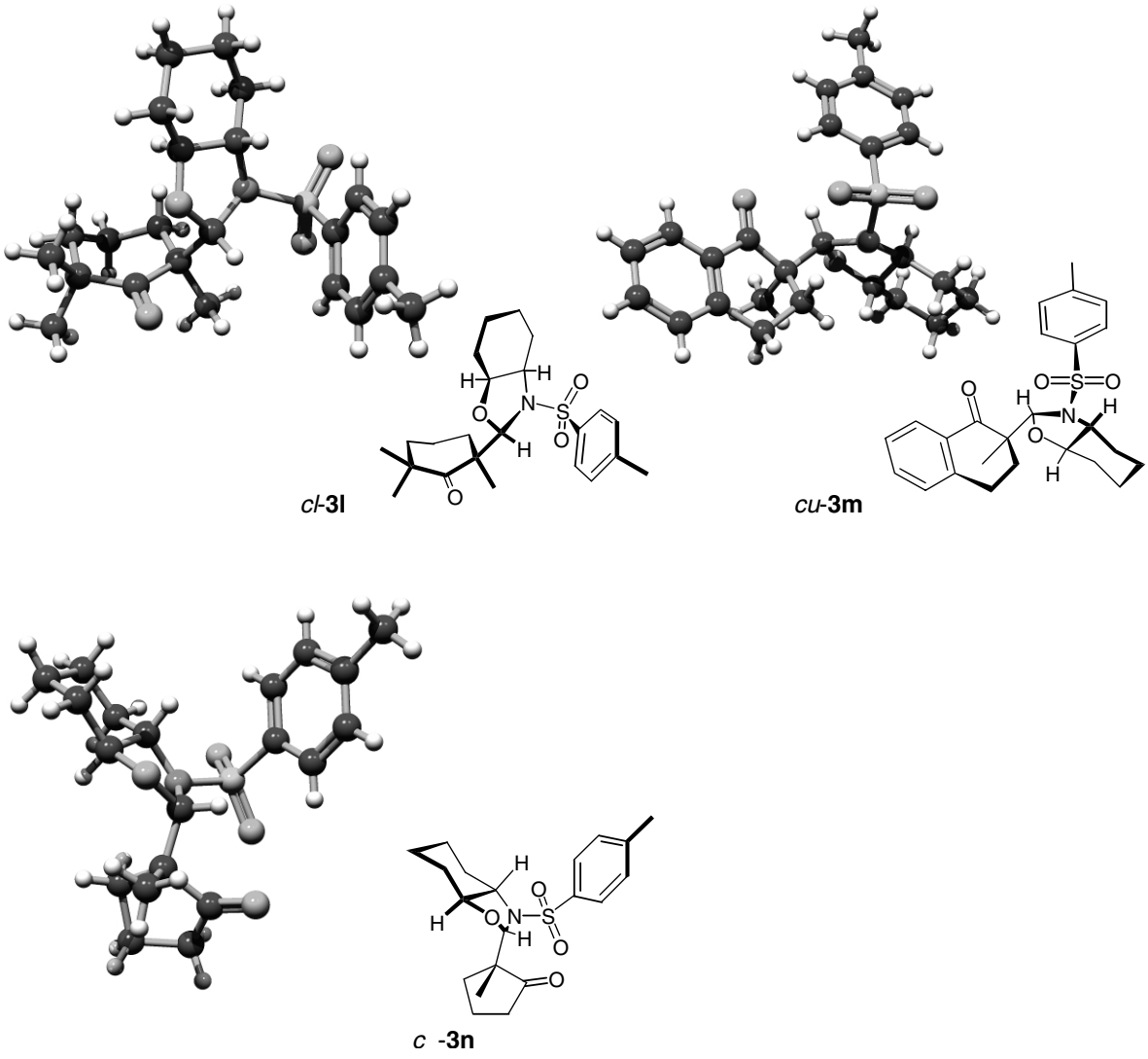


Figure 5. Molecular structures of 3-sulfonyl-1,3-oxazolidines *cl*-**3l**, *cu*-**3m** and *cu*-**3n**.[12]

Table 6. Selected NMR data of the 3-sulfonyl-1,3-oxazolidines **3**

Entry	Compound	*cu*		*cl*		*tu*		*tl*	
		2-H	C-2	2-H	C-2	2-H	C-2	2-H	C-2
1	**3c**	**5.36**[a]	**93.6**	5.69	94.3				
2	**3e**	5.97	91.4	6.01	92.5				
3	**3f**	**5.36**	**93.9**	5.66	94.6				
4	*ent*-**3d**	5.88	93.8	**6.11**	**95.5**				
5	**3g**	5.67	94.5	**5.89**	**95.4**	5.99	95.7	**6.36**	**99.0**
6	**3i**	5.71[b,c]	–[d]	6.03[b,c]	94.6[c,e]	**5.96**[b]	**97.7**[e]	6.36[b,c]	99.7[c,e]
7	**3j**	**5.34**	**93.0**	**5.65**	**92.9**	5.78[c]	90.8[c]		
8	**3k**	**5.42**	**92.3**	5.78	93.1				
9	**3l**	5.40	93.4	**5.44**	**96.4**	6.07[c]	95.6[c]		
10	**3m**	**5.56**	**93.2**	5.61[c]	93.7[c]	5.80[c]	–[d]	6.18[c]	–[d]
11	**3n**	**5.01**	**93.2**	5.13	–[d]				

[a] Bold shifts indicate that the corresponding configuration was determined by X-ray analyses.
[b] 4-H is the corresponding proton.
[c] The configuration of this product is uncertain.
[d] Not detected.
[e] C-4 is the corresponding carbon atom.

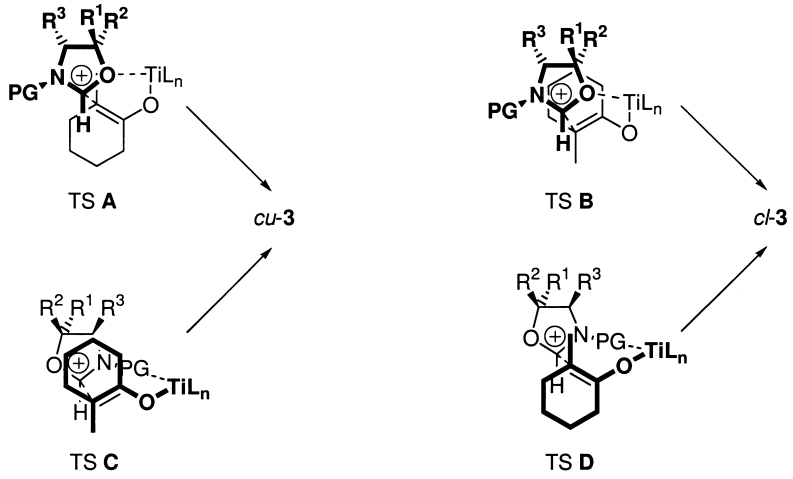


Figure 6. Proposed transition states **A**, **B**, **C** and **D**.

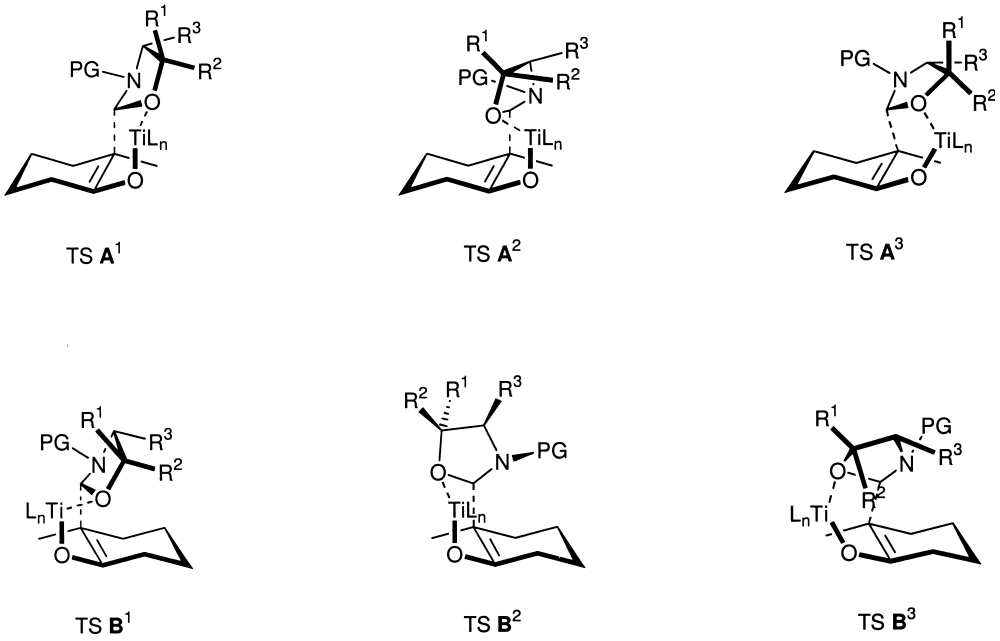


Figure 7. Proposed geometries of the transition states **A** and **B**.

trichlorotitanium enolates, only boat-like transition state geometries are able to explain the observed results. In the suggested model steric interactions between the titanium fragment and the groups R^2 and R^3 as well as repulsions between the sulfonyl group and the cyclohexyl ring disfavour the *cis-unlike*-configuration (TS $\mathbf{A}^2$); interactions between the R^1 group and the titanium atom and its ligands disfavour the formation of *cis-like*-configured products (TS $\mathbf{B}^1$). The chair-like geometries of TS $\mathbf{A}^1$ and TS $\mathbf{B}^2$ have the opposite 'configuration' at the 1,3-oxazolidine oxygen atom and would predict just the opposite influence of the groups R^1, R^2 and R^3.

3. Conclusions

In the present study, the reaction of chiral 2-ethoxy-3-sulfonyl-1,3-oxazolidines **2** and prochiral titanium enolates **4** has been investigated. It was found that the reaction of reagents like **2c** or **2k**, derived from the *N*-tosyl derivatives of 2-aminobutanol and *trans*-2-aminocyclohexanol with trichlorotitanium enolates in dichloromethane represents a useful method to install quaternary α-carbonyl stereocentres (after deprotection of the chirally masked formyl group). The *cis-unlike*-configured products *cu*-**3** are obtained in acceptable to good yields and selectivities. Some details of the possible mechanism of this reaction are described and the observed selectivities are interpreted. In summary, this new method is a valuable supplement to the known asymmetric formylation reactions and allows the stereoselective formation of synthetically interesting compounds.

4. Experimental

4.1. General

All reactions were performed under Ar in flame-dried glass-

ware. Flash column chromatography (FCC) was performed on Merck silical gel 60, 0.040–0.063 mm (PE=light petroleum ether, bp=36–46°C). R_F values were determined on Merck silica gel 60 F_{254} TLC plates. CH_2Cl_2 was distilled from CaH_2, toluene was distilled from sodium benzophenone ketyl. All commercially available reagents were used without purification.

NMR: Bruker ARX 300, AM 360 and AMX 400; chemical shifts are given with respect to $CHCl_3$ (δ_H=7.24) or $CDCl_3$ (δ_C=77.0). The ratios of isomers were determined from the ^{1}H NMR spectra, shifts of minor isomers are given in brackets. IR: Nicolet 5DXC. Optical rotations: Perkin–Elmer polarimeter 341. EI-MS: Finnigan MAT 8200. ESI-MS: Micromass Quattro LC-Z. Elemental analysis: Heraeus CHN–O-Rapid and Elementaranalysensysteme VarioEL III. Melting points: Gallenkamp MFB 595, uncorrected values.

4.2. Syntheses of 2-ethoxy-3-sulfonyl-1,3-oxazolidines 2

4.2.1. General procedure A (GP A). The sulfonamide **5** was dissolved in triethyl orthoformate, two drops of MsOH were added, and the mixture was stirred for 2–4 h (TLC monitoring) at room temperature. K_2CO_3 (0.5 g) was then added and the resulting suspension was stirred for 10 min. Filtration and removal of the triethyl orthoformate in vacuo gave the crude 2-ethoxy-1,3-oxazolidine **2**.

4.2.2. (4*R*)-2-Ethoxy-4-ethyl-3-[2,4,6-tri(1-methylethyl)-benzenesulfonyl]-1,3-oxazolidine (2d). According to GP A, sulfonamide **5d**[3j] (355 mg, 1.00 mmol) was treated with triethyl orthoformate (5.0 mL, 4.5 g, 30 mmol) to provide the crude product **2d** (*cis*/*trans*=90:10). FCC (125 cm^3 SiO_2, Et_2O/PE=1:2) afforded a mixture of *cis*-**2d** and *trans*-**2d** [390 mg, contained 8.3% triethyl orthoformate (^{1}H NMR)→378 mg, 0.918 mmol, 92%, dr=90:10] as a colourless oil. An analytical sample was obtained by removing the triethyl orthoformate in vacuo. *cis*-**2d**/*trans*-**2d**=90:10: R_F (SiO_2, Et_2O/PE=1:1)=0.57. $[\alpha]_D^{20}$=+4.7 (c=0.88, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 0.76 (t, J=7.5 Hz, 3H, 2′-H_3); 1.02 (t, J=7.2 Hz, 3H, 2‴-H_3); 1.22, 1.23, 1.23, 1.24, 1.25, 1.26 ('6s', 18H, 2″-CH(CH_3)$_2$, 4″-CH(CH_3)$_2$, 6″-CH(CH_3)$_2$); 1.40–1.55 (m, 1H, 1′-H_2); 1.55–1.70 (m, 1H, 1′-H_2); 2.89 (sept, J=6.9 Hz, 1H, 4″-CH(CH$_3$)$_2$); 3.28–3.41, 3.41–3.54 (2m, 2H, 1‴-H_2); 3.80–3.99 (m, 2H, 4-H, 5-H); 4.10–4.28 (m, 1H, 5-H); 4.27 (sept, J=6.9 Hz, 2H, 2″-CH(CH$_3$)$_2$, 6″-CH(CH$_3$)$_2$); 6.02 [5.78] (s, 1H, 2-H); 7.15 [7.12] (s, 2H, 3″-H, 5″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 10.0 [9.91] (q, C-2′); 14.5 [14.7] (q, C-2‴); 23.5 (q, 4″-CH(*C*H$_3$)$_2$); 24.7, 24.8 [24.6] (2q, 2″-CH(*C*H$_3$)$_2$, 6″-CH(*C*H$_3$)$_2$); 26.9 (t, C-1′); 29.2 [29.4] (d, 2″-*C*H(CH$_3$)$_2$, 6″-*C*H(CH$_3$)$_2$); 34.2 (d, 4″-*C*H(CH$_3$)$_2$); 58.6 [59.8] (t, C-1‴); 61.9 [61.6] (d, C-4); 70.5 [68.7] (t, C-5); 107.7 [106.7] (d, C-2); 123.9 [123.6] (d, C-3″, C-5″); 131.3 (s, C-4″); 151.7 [151.1] (s, C-2″, C-6″); 153.8 (s, C-1″). IR (KBr): 2960 (s); 2880 (s); 1605 (m); 1565 (w); 1470 (m); 1425 (m); 1375 (m); 1335 (s); 1175 (s); 1090 (s); 675 (m). EI-MS (70 eV): 411 (1, M^+); 366 (11); 267 (100); 251 (28); 218 (25); 202 (18); 187 (41); 175 (12); 159 (25); 145 (24); 131 (13); 119 (13); 114 (26); 105 (13); 100 (39); 91 (28); 71 (89). Anal. calcd for $C_{22}H_{37}NO_4S$ (411.61): C 64.20, H 9.06, N 3.40; found: C 64.10, H 9.39, N 3.66.

4.2.3. (4*S*)-2-Ethoxy-3-(4-methylbenzenesulfonyl)-4-(1-methylethyl)-1,3-oxazolidine (2e). According to GP A, sulfonamide **5e**[3c] (515 mg, 2.00 mmol) was treated with triethyl orthoformate (10 mL, 8.9 g, 60 mmol) to provide the crude product **2e** (*cis*/*trans*=92:8). FCC (125 cm^3 SiO_2, Et_2O/PE=1:4) afforded a mixture of *cis*-**2e** and *trans*-**2e** (572 mg, 1.83 mmol, 91%, dr=95:5) as a white solid and a mixture of *trans*-**2e** and *cis*-**2e** (22 mg, 70 mmol, 3.5%, dr=88:12) as a colourless oil. *cis*-**2e**/*trans*-**2e**=95:5: R_F (SiO_2, Et_2O/PE=1:1)=0.36. Mp (Et_2O/PE)=86.3–87.7°C. $[\alpha]_D^{20}$=+25.3 (c=0.90, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 0.87 (d, J=6.6 Hz, 3H, 2′-H_3); 0.96 (d, J=6.9 Hz, 3H, 1′-CH_3); 1.21 (t, J=7.2 Hz, 3H, 2‴-H_3); 1.95–2.11 (m, 1H, 1′-H); 2.41 (s, 3H, 4″-CH_3); 3.44 (dd, J=6.6, 7.2 Hz, 1H, 5-H_a); 3.55–3.75 (m, 3H, 1‴-H_2, 4-H); 3.86 (dd, J=6.6, 8.1 Hz, 1H, 5-H_b); 6.02 (s, 1H, 2-H); 7.29 ('d', J=8.7 Hz, 2H, 3″-H, 5″-H); 7.70 ('d', J=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.7 (q, C-2‴); 17.5, 19.7 (2q, C-2′, 1′-CH_3); 21.5 (q, 4″-CH_3); 31.2 (d, C-1′); 61.6 (t, C-1‴); 63.5 (d, C-4); 68.0 (t, C-5); 108.2 (d, C-2); 127.7 (d, C-2″, C-6″); 129.8 (d, C-3″, C-5″); 135.4 (s, C-4″); 144.0 (s, C-1″). IR (KBr): 2970 (m); 2915 (m); 1605 (w); 1470 (w); 1350 (s); 1175 (s); 1080 (s); 950 (m); 815 (m). EI-MS (70 eV): 270 (43); 268 (30, M^+−OEt); 196 (100); 155 (46); 139 (12); 91 (95). Anal. calcd for $C_{15}H_{23}NO_4S$ (313.42): C 57.48, H 7.40, N 4.47; found: C 57.60, H 7.50, N 4.36.

trans-**2e**/*cis*-**2e**=88:12: ^{1}H NMR (300 MHz, $CDCl_3$): 0.84 (d, J=7.2 Hz, 3H, 2′-H_3); 0.89 (d, J=5.4 Hz, 3H, 1′-CH_3); 1.15 (t, J=7.2 Hz, 3H, 2‴-H_3); 2.35–2.49 (m, 1H, 1′-H); 2.40 (s, 3H, 4″-CH_3); 3.45 (ddd, J=3.6, 3.6, 5.4 Hz, 1H, 4-H); 3.58 ('2q', J=7.2 Hz, 2H, 1‴-H_2); 3.85–3.90 (m, 2H, 5-H_2); 5.91 (s, 1H, 2-H); 7.25 ('d', J=8.4 Hz, 2H, 3″-H, 5″-H); 7.80 ('d', J=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.8 (q, C-2‴); 17.5, 19.2 (2q, C-2′, 1′-CH_3); 21.5 (q, 4″-CH_3); 29.9 (d, C-1′); 61.4 (t, C-1‴); 62.5 (d, C-4); 64.7 (t, C-5); 107.5 (d, C-2); 128.4 (d, C-2″, C-6″); 129.0 (d, C-3″, C-5″); 137.7 (s, C-4″); 143.2 (s, C-1″).

4.2.4. (2*R*,4*S*,5*S*)-2-Ethoxy-4-methyl-3-(4-methylbenzenesulfonyl)-5-phenyl-1,3-oxazolidine (*cis*-2f). According to GP A, sulfonamide **5f**[1b] (1.00 g, 3.27 mmol, dr>96:4) was treated with triethyl orthoformate (15 mL, 13 g, 90 mmol) to provide the crude product *cis*-**2f** (dr>97:3). FCC (565 cm^3 SiO_2, Et_2O/PE=1:1) afforded *cis*-**2f** (1.16 g, 3.21 mmol, 98%, dr>97:3) as a white solid. *cis*-**2f** (dr>97:3): R_F (SiO_2, Et_2O/PE=1:1)=0.50. Mp (Et_2O/PE)=113.0–115.6°C. $[\alpha]_D^{20}$=+46.4 (c=1.14, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 1.30 (t, J=7.2 Hz, 3H, 2‴-H_3); 1.40 (d, J=6.6 Hz, 3H, 4-CH_3); 2.48 (s, 3H, 4″-CH_3); 3.38–3.49 ('dd', J=6.6, 8.1 Hz, 1H, 4-H); 3.68–3.83 (m, 2H, 1‴-H_2); 4.86 (d, J=8.1 Hz, 1H, 5-H); 6.22 (s, 1H, 2-H); 6.82–6.90 ('d', J=8.1 Hz, 2H, 3′-H, 5′-H); 7.17–7.30 (m, 3H, 2′-H, 4′-H, 6′-H); 7.34 ('d', J=7.8 Hz, 2H, 3″-H, 5″-H); 7.77 ('d', J=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.8 (q, C-2‴); 18.7 (q, 4-CH_3); 21.5 (q, 4″-CH_3); 61.9 (d, C-4); 62.0 (t, C-1‴); 85.7 (d, C-5); 107.6 (d, C-2); 126.4, 127.8, 128.5, 128.6, 129.7 (5d, C-2′, C-3′, C-4′, C-5′, C-6′, C-2″, C-3″, C-5″, C-6″); 135.6 (s, C-1′); 136.9 (s, C-4″); 144.0 (s, C-1″). IR (KBr): 3080 (w); 2980 (m); 2930 (m); 1560 (m); 1460

(m); 1350 (s); 1180 (s); 1080 (s); 990 (s); 700 (s); 600 (s). EI-MS (70 eV): 361 (2, M^+); 316 (16); 288 (17); 164 (42); 155 (25); 139 (28); 135 (32); 132 (61); 117 (17); 105 (27); 100 (100); 91 (98); 79 (18); 77 (14). Anal. calcd for $C_{19}H_{23}NO_4S$ (361.46): C 63.14, H 6.41, N 3.87; found: C 63.16, H 6.67, N 3.81.

4.2.5. (3a*R*,8a*S*)-2-Ethoxy-3-(4-methylbenzenesulfonyl)-3,3a,8,8a-tetrahydro-2*H*-indeno[1,2-*d*][1,3]oxazole (2g). According to GP A, sulfonamide **5g**[8] (10.0 g, 33.0 mmol) was treated with triethyl orthoformate (0.10 L, 89 g, 0.60 mol) to provide the crude product **2g** (*a*/*b*[‖]=71:29). FCC (395 cm^3 SiO_2, Et_2O/PE=1:4→1:1) afforded a mixture of *a*-**2g** and *b*-**2g** (11.8 g, 32.8 mmol, 99%, dr=71:29) as a colourless oil. A sample of this product (1.00 g, 2.78 mmol, dr=71:29) was subjected twice to FCC (500 cm^3 SiO_2, Et_2O/PE=1:6→1:5). This provided a mixture of *a*-**2g** and *b*-**2g** (702 mg, 2.00 mmol, 72%, dr=97:3) and a mixture of *b*-**2g** and *a*-**2g** (270 mg, 0.751 mmol, 27%, dr=96:4), both as white solids. *a*-**2g**/*b*-**2g**=97:3: R_F (SiO_2, Et_2O/PE=1:1)=0.40. Mp (Et_2O/PE)=102.7–105.7°C. $[\alpha]_D^{20}$=−64.2 (*c*=0.99, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.80 (t, *J*=7.2 Hz, 3H, 2″-H_3); 2.45 (s, 3H, 4′-CH_3); 3.05–3.36 (m, 4H, 11-H_2, 1″-H_2); 4.61 (td, *J*=2.1, 6.3 Hz, 1H, 12-H); 5.29 (d, *J*=6.3 Hz, 1H, 4-H); 6.18 (s, 1H, 2-H); 7.12–7.19 (m, 1H, 9-H); 7.20–7.29 (m, 2H, 7-H, 8-H); 7.35 ('d', *J*=8.1 Hz, 2H, 3′-H, 5′-H); 7.47–7.51 (m, 1H, 6-H); 7.81 ('d', *J*=7.8 Hz, 2H, 2′-H, 6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (q, C-2″); 21.6 (q, 4′-CH_3); 39.0 (t, C-11); 59.9 (t, C-1″); 66.0 (d, C-12); 81.9 (d, C-4); 108.8 (d, C-2); 124.9, 125.7, 127.3, 127.6, 128.6, 129.9 (6d, C-6, C-7, C-8, C-9, C-2′, C-3′, C-5′, C-6′); 135.9 (s, C-4′); 139.6, 140.2 (2s, C-5, C-10); 144.2 (s, C-1′). IR (KBr): 3060 (w); 2950(m); 1610 (m); 1360(s); 1170 (s); 1060 (s); 760 (s); 670 (s). EI-MS (70 eV): 358 (0.1, M^+); 314 (24); 221 (28); 158 (36); 155 (21); 130 (100); 115 (31); 103 (37); 91 (92). Anal. calcd for $C_{19}H_{21}NO_4S$ (359.45): C 63.49, H 5.89, N 3.90; found: C 63.46, H 6.13, N 3.71.

b-**2g**/*a*-**2g**=94:6: R_F (SiO_2, Et_2O/PE=1:1)=0.45. Mp (Et_2O/PE)=104.7–107.3°C. $[\alpha]_D^{20}$=−226 (*c*=0.94, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.17 (t, *J*=7.2 Hz, 3H, 2″-H_3); 2.43 (s, 3H, 4′-CH_3); 3.01 (bs, 2H, 11-H_2); 3.50–3.66 (m, 2H, 1″-H_2); 4.80–4.93 (m, 1H, 12-H); 5.05 (d, *J*=5.7 Hz, 1H, 4-H); 5.81 (s, 1H, 2-H); 7.12–7.38 (m, 5H, 7-H, 8-H, 9-H, 3′-H, 5′-H); 7.90 ('d', *J*=8.4 Hz, 2H, 2′-H, 6′-H); 8.01–8.07 (m, 1H, 6-H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.7 (q, C-2″); 21.5 (q, 4′-CH_3); 36.0 (t, C-11); 62.7 (t, C-1″); 65.3 (d, C-12); 80.5 (d, C-4); 107.4 (d, C-2); 124.9, 127.4, 127.6, 128.6, 128.8, 129.0 (6d, C-6, C-7, C-8, C-9, C-2′, C-3′, C-5′, C-6′); 137.7 (s, C-4′); 139.6, 140.2 (2s, C-5, C-10); 143.4 (s, C-1′). IR (KBr): 2980 (w); 1360 (s); 1170 (s); 1070 (s); 680 (m); 570 (m). EI-MS (70 eV): 358 (0.3, M^+−H); 314 (71); 158 (81); 155 (43); 130 (75); 115 (51); 103 (33); 91 (100); 77 (16). Anal. calcd for $C_{19}H_{21}NO_4S$ (359.45): C 63.49, H 5.89, N 3.90; found: C 63.39, H 5.92, N 3.60.

‖ Diastereomeric compounds with unknown relative configuration are marked with small letters.

4.2.6. (1*R*,2*S*,6*R*,7*S*)-4-Ethoxy-1,10,10-trimethyl-5-(4-methylbenzenesulfonyl)-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]-decan (2h). According to GP A, sulfonamide **5h**[9] (1.00 g, 3.09 mmol, contained 18% **5i**) was treated with triethyl orthoformate (15 mL, 13 g, 90 mmol) to provide the crude product (*a*-**2h**/*a*-**2i**=83:17). FCC (280 cm^3 SiO_2, Et_2O/PE=1:4) afforded a mixture of *a*-**2h** and *a*-**2i** [1.15 g, contained 10% triethyl orthoformate (^1H NMR)→1.10 g, 2.90 mmol, 94%, dr=88:12] as a colourless oil. The mixture was dissolved in hexanes (2.0 mL) at 50°C and the resulting solution was cooled to −30°C. Filtration gave a mixture of *a*-**2h**, *a*-**2i** and *b*-**2h** (305 mg, 0.803 mmol, 26%, dr=60:38:2) as white crystals and removal of the solvent from the mother liquor furnished *a*-**2h** [800 mg, contained 12% triethyl orthoformate (^1H NMR)→760 mg, 2.00 mmol, 65%]. *a*-**2h**: R_F (SiO_2, Et_2O/PE=1:1)=0.56. Mp (Et_2O/PE)=88.6–92.8°C. $[\alpha]_D^{20}$=−104 (*c*=0.45, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.81, 0.94, 1.11 (3s, 9H, 1-CH_3, 10-$(CH_3)_2$); 0.80–0.90, 1.18–1.27, 1.39–1.50, 1.65–1.75 (4m, 4H, 8-H_2, 9-H_2); 1.11 (t, *J*=7.2 Hz, 3H, 2″-H_3); 2.31 (d, *J*=4.5 Hz, 1H, 7-H); 2.41 (s, 3H, 4′-CH_3); 3.24 (d, *J*=6.9 Hz, 1H, 6-H); 3.52 (q, *J*=7.2 Hz, 2H, 1″-H_2); 4.04 (d, 1H, *J*=7.2 Hz, 2-H); 5.85 (s, 1H, 4-H); 7.26 (d, *J*=8.1 Hz, 2H, 3′-H, 5′-H); 7.76 ('d', *J*=8.4 Hz, 2H, 2′-H, 6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 10.7 (q, 1-CH_3); 14.6 (q, C-2″); 19.4, 22.5 (2q, 10-$(CH_3)_2$); 21.5 (q, 4′-CH_3); 24.9 (t, C-9); 31.7 (t, C-8); 46.7, 47.7 (2s, C-1, C-10); 47.4 (d, C-7); 62.0 (t, C-1″); 63.5 (d, C-6); 90.0 (d, C-2); 108.2 (d, C-4); 128.8, 129.0 (2d, C-2′, C-3′, C-5′, C-6′); 135.8 (s, C-4′); 143.4 (s, C-1′). IR (KBr): 2960 (s); 2875 (s); 1600 (w); 1465 (m); 1355 (s); 1175 (s); 1100 (s); 1050 (s); 820 (m). EI-MS (70 eV): 379 (0.85, M^+); 350 (17); 334 (53); 224 (74); 210 (16); 194 (18); 155 (32); 150 (85); 133 (13); 123 (26); 109 (19); 103 (100); 91 (62).

a-**2h**/*a*-**2i**/*b*-**2h**=60:38:2: Mp (Et_2O/PE)=126.5–128.0°C. ^1H NMR (300 MHz, $CDCl_3$): 5.63 (s, 0.02H, 4-H); 5.85 (s, 0.60H, 4-H); 6.08 (s, 0.38H, 4-H). Anal. calcd for $C_{20}H_{29}NO_4S$ (379.52): C 63.30, H 7.70, N 3.69; found: C 63.60, H 7.77, N 3.47.

4.2.7. (1*R*,2*R*,6*S*,7*S*)-2-Ethoxy-1,10,10-trimethyl-5-(4-methylbenzenesulfonyl)-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]-decan (2i). According to GP A, sulfonamide **5i**[9] (666 mg, 2.06 mmol, contained 8% **5h**) was treated with triethyl orthoformate (10 mL, 8.9 g, 60 mmol) to provide the crude product (*a*-**2i**/*b*-**2i**/*a*-**2h**=83:13:4). FCC (140 cm^3 SiO_2, Et_2O/PE=1:5) afforded a mixture of *a*-**2i**, *b*-**2i** and *a*-**2h** (702 mg, 1.85 mmol, 90%, dr=83:13:4) as a white wax. *a*-**2i**/*b*-**2i**/*a*-**2h**=83:13:4: R_F (SiO_2, Et_2O/PE=1:1)=0.56. $[\alpha]_D^{20}$=+140 (*c*=1.32, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$)=0.84, 0.87, 0.92 (3s, 9H, 1-CH_3, 10-$(CH_3)_2$); 1.10 (t, *J*=7.2 Hz, 3H, 2″-H_3); 1.18–1.27, 1.51–1.62, 1.75–1.82, 1.82–1.92 (4m, 4H, 8-H_2, 9-H_2); 1.98 (t, *J*=4.8 Hz, 1H, 7-H); 2.40 (s, 3H, 4′-CH_3); 3.47–3.55 (m, 2H, 1″-H_2); 3.85 (ddd, *J*=1.6, 4.8, 9.2 Hz, 1H, 6-H); 4.41 (dd, *J*=1.6, 9.2 Hz, 1H, 2-H); 6.08 [6.13] (s, 1H, 4-H); 7.25 ('d', *J*=8.0 Hz, 2H, 3′-H, 5′-H); 7.74 ('d', *J*=8.4 Hz, 2H, 2′-H, 6′-H). ^{13}C NMR (100 MHz, $CDCl_3$)=14.0, 14.7 [15.0], 18.4 [18.5], 20.7 [20.8] (4q, 1-CH_3, 10-$(CH_3)_2$, C-2″); 19.9 (t, C-9); 21.5 (q, 4′-CH_3); 26.6 [27.1] (t, C-8); 48.9, 51.0 (2s, C-1, C-10); 49.2 [48.3] (d, C-7); 59.7 [61.7] (d, C-6); 61.9 [62.5] (t, C-1″); 88.7

[89.8] (d, C-2); 111.2 [112.3] (d, C-4); 128.6, 128.9 [127.6, 129.4] (2d, C-2′, C-3′, C-5′, C-6′); 136.3 (s, C-4′); 143.4 (s, C-1′). IR (KBr): 2965 (m); 2885 (m); 1730 (w); 1605 (w); 1360 (s); 1180 (s); 1105 (s); 1040 (s); 685 (s). EI-MS (70 eV): 379 (4, M^+); 350 (100); 334 (85); 224 (14); 196 (28); 155 (32); 150 (50); 135 (28); 123 (51); 109 (25); 91 (77). Anal. calcd for $C_{20}H_{29}NO_4S$ (379.52): C 63.30, H 7.70, N 3.69; found: C 62.93, H 7.66, N 3.72.

4.2.8. (3a*R*,7a*S*)-2-Ethoxy-3-(4-methylbenzenesulfonyl)-perhydro-1,3-benzoxazole (2j). According to GP A, sulfonamide **5j**[10] (328 mg, 1.22 mmol) was treated with triethyl orthoformate (10 mL, 8.9 g, 60 mmol) to provide the crude product **2j** (*a*/*b*=54:46). FCC (125 cm^3 SiO_2, Et_2O/PE=1:5→1:1) afforded *a*-**2j** (158 mg, 0.486 mmol, 40%) as a colourless oil and a mixture of *b*-**2j** and *a*-**2j** (148 mg, 0.455 mmol, 37%, dr=96:4) as a white wax. *a*-**2j**: R_F (SiO_2, Et_2O/PE=1:1)=0.70. $[\alpha]_D^{20}=-29.0$ (*c*=0.42, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.02–1.18, 1.30–1.71, 1.96–2.06, 2.17–2.28 (m, m, 'd', m, 8H, 5-H_2, 6-H_2, 7-H_2, 8-H_2); 1.13 (t, *J*=7.5 Hz, 3H, 2″-H_3); 2.39 (s, 3H, 4′-CH_3); 3.46–3.66, 4.15–4.20 (2m, 3H, 1H, 5-H, 9-H, 1″-H_2); 5.89 (s, 1H, 2-H); 7.23 (d, *J*=7.8 Hz, 2H, 3′-H, 5′-H); 7.80 ('d', *J*=8.4 Hz, 2H, 2′-H, 5′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.8 (q, C-2″); 19.5, 22.2 (2t, C-6, C-7); 21.5 (q, 4′-CH_3); 26.8, 29.8 (2t, C-5, C-8); 56.7 (d, C-4); 62.6 (t, C-1″); 73.7 (d, C-9); 105.8 (d, C-2); 127.7 (d, C-2′, C-6′); 129.1 (d, C-3′, C-5′); 138.6 (s, C-4′); 143.0 (s, C-1′). IR (KBr): 2940 (m); 2870 (w); 1605 (w); 1455 (w); 1355 (s); 1165 (s); 1070 (s); 950 (w); 815(w). EI-MS (70 eV): 325 (2.6, M^+); 280 (100); 210 (15); 200 (18); 170 (11); 155 (55); 96 (21); 91 (83). Anal. calcd for $C_{16}H_{23}NO_4S$ (325.43): C 59.05, H 7.12, N 4.30; found: C 59.08, H 7.16, N 4.26.

b-**2j**/*a*-**2j**=96:4: R_F (SiO_2, Et_2O/PE=1:1)=0.67. Mp (Et_2O/PE)>90°C. $[\alpha]_D^{20}=+10.3$ (*c*=0.74, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.02–1.17, 1.32–1.85, 1.95–2.04 (3m, 8H, 5-H_2, 6-H_2, 7-H_2, 8-H_2); 1.21 (t, *J*=6.9 Hz, 3H, 2″-H_3); 2.41 (s, 3H, 4′-CH_3); 3.55–3.81 (m, 4H, 5-H, 9-H, 1″-H_2); 5.97 [5.89] (s, 1H, 2-H); 7.28 (d, *J*=7.8 Hz, 2H, 3′-H, 5′-H); 7.75 ('d', *J*=8.4 Hz, 2H, 2′-H, 5′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.0 (q, C-2″); 19.7, 22.5 (2t, C-6, C-7); 21.5 (q, 4′-CH_3); 27.7, 28.7 (2t, C-5, C-8); 56.3 (d, C-4); 62.3 (t, C-1″); 75.9 (d, C-9); 107.7 (d, C-2); 127.4 (d, C-2′, C-6′); 129.7 (d, C-3′, C-5′); 137.3 (s, C-4′); 143.7 (s, C-1′). IR (KBr): 2950 (s); 2860 (m); 1730 (m); 1600 (m); 1350 (s); 1165 (s); 1080 (s); 980 (s); 680(s); 600(s). EI-MS (70 eV): 325 (1.8, M^+); 280 (95); 210 (18); 200 (17); 170 (13); 155 (59); 96 (27); 91 (100). Anal. calcd for $C_{16}H_{23}NO_4S$ (325.43): C 59.05, H 7.12, N 4.30; found: C 58.65, H 6.98, N 4.45.

4.2.9. (3a*S*,7a*S*)-2-Ethoxy-3-(4-methylbenzenesulfonyl)-perhydro-1,3-benzoxazole (2k). According to GP A, sulfonamide **5k**[11] (1.16 g, 4.31 mmol) was treated with triethyl orthoformate (15 mL, 13 g, 90 mmol) to provide the crude product **2k** (*a*/*b*=73:27). FCC (280 cm^3 SiO_2, Et_2O/PE=1:3→1:1) afforded *a*-**2k** (1.26 g, 3.87 mmol, 90%) as a colourless oil and only traces of *b*-**2k** (20 mg, ^1H NMR: 5.02 (s, 1H, 2-H), mixture with other compounds) as a colourless oil. *a*-**2k**: R_F (SiO_2, Et_2O/PE=1:1)=0.45. $[\alpha]_D^{20}=-2.8$ (*c*=0.50, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.13–1.45, 1.67–1.74, 1.99–2.09, 2.23–2.35 (4m, 4H, 2H, 1H, 1H, 5-H_2, 6-H_2, 7-H_2, 8-H_2); 1.22 (t, *J*=6.6 Hz, 3H, 2″-H_3); 2.40 (s, 3H, 4′-CH_3); 2.71, 3.60–3.82 (ddd, m, *J*=3.3, 9.9, 11.1 Hz, 1H, 3H, 4-H, 9-H, 1″-H_2); 5.85 (s, 1H, 2-H); 7.28 (d, *J*=8.7 Hz, 2H, 3′-H, 5′-H); 7.73 (d, *J*=8.4 Hz, 2H, 2′-H, 6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 15.0 (q, C-1″); 21.5 (4′-CH_3); 23.4, 23.8 (2t, C-6, C-7); 28.8, 29.0 (2t, C-5, C-8); 62.7 (t, C-2″); 64.4 (d, C-4); 80.3 (d, C-9); 107.1 (d, C-2); 127.5 (d, C-2′, C-6′); 129.6 (d, C-3′, C-5′); 136.1 (s, C-4′); 143.7 (s, C-1′). IR (KBr): 2965 (m); 2880 (m); 1605 (w); 1445 (w); 1360 (s); 1170 (s); 1140 (s); 1085 (s); 1045 (s); 830 (m); 660 (s); 590 (s). EI-MS (70 eV): 325 (3.3, M^+); 280 (35); 210 (27); 155 (44); 139 (10); 96 (60); 91 (100). Anal. calcd for $C_{16}H_{23}NO_4S$ (325.43): C 59.05, H 7.12, N 4.30; found: C 58.97, H 7.28, N 4.13.

4.3. Syntheses of 2-methyl-2-(3-sulfonyl-1,3-oxazolidin-2-yl)cycloalkanones 3

4.3.1. General procedure B (GP B). To a cold (−78°C) solution of the silyl enol ether **1** (1.00 mmol) in CH_2Cl_2 (10 mL), $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) was added dropwise. After stirring for 15 min at −78°C, the reaction mixture was allowed to warm to room temperature and stirred for a further 45 min. The deep-red solution was then cooled to −78°C once more, whereupon a solution of the 2-ethoxy-1,3-oxazolidine **2** (1.00 mmol) in CH_2Cl_2 (4.0 mL) was slowly added. The resulting mixture was allowed to warm to room temperature over a period of 15 h. The reaction was then stopped by the addition of satd. aqueous $NaHCO_3$ (20 mL) and the mixture was given to satd. aqueous NaCl (50 mL) and CH_2Cl_2 (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3×50 mL) and the combined organic layers were stirred with K_2CO_3 (2.0 g) for 15 min. The suspension was filtered (Celite) and the solvent was removed in vacuo to leave the crude 2-(1,3-oxazolidin-2-yl)-cycloalkanone **3**.

4.3.2. 2-[(2*R*,4*R*)-4-Ethyl-3-(4-methylbenzenesulfonyl)-1,3-oxazolidin-2-yl]-2-methylcyclohexanone (3c).[3k] Method A: A 2.2 M solution of $ZnCl_2{\cdot}Et_2O$ in CH_2Cl_2 (7.3 mL, 16 mmol) was added to a solution of silyl enol ether **1b**[4a] (2.95 g, 16.0 mmol) and 2-ethoxy-1,3-oxazolidine *cis*-**2c**[3k] (4.79 g, 16.0 mmol) in CH_2Cl_2 (75 mL) at 0°C. After stirring at 0°C for 1 h, satd. aqueous NaCl (75 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried with $MgSO_4$ (5.0 g) and the solvent was removed in vacuo. Purification of the crude product **3c** (*cl*/*cu*=51:49) by FCC (825 cm^3 SiO_2, Et_2O/PE=1:5→1:2.5) provided *cu*-**3c**[3k] (2.33 g, 6.37 mmol, 40%) and *cl*-**3c**[3k] (2.49 g, 6.81 mmol, 43%) as white solids.

Method B: A 1.6 M solution of MeLi in Et_2O (0.63 mL, 1.0 mmol) was added to a solution of silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) in toluene (5.0 mL). The mixture was heated to 80°C for 1 h and then cooled to −78°C. A 1.0 M solution of $TiCl(OiPr)_3$ in toluene (1.0 mL, 1.0 mmol) was added and the resulting red suspension was stirred at room temperature for 30 min. After cooling to −78°C once more, a solution of 2-ethoxy-1,3-oxazolidine *cis*-**2c**[3k] (299 mg, dr=98:2) in toluene (1.0 mL) and then $BF_3{\cdot}Et_2O$ (0.25 mL, 0.28 g, 2.0 mmol) were added and the reaction

mixture was allowed to warm to 0°C over a period of 5 h. Satd. aqueous $NaHCO_3$ (20 mL) was added and the aqueous layer was extracted with toluene (3×15 mL). The combined organic layers were dried with $MgSO_4$ (1.0 g) and the solvent was removed in vacuo. The crude product **3c** (*cu*/*cl*=85:15) was subjected to FCC (125 cm^3 SiO_2, Et_2O/PE=1:4→1:2) and *cu*-**3c**[3k] (156 mg, 0.427 mmol, 43%) and *cl*-**3c**[3k] (31 mg, 0.085 mmol, 8.5%) were obtained, both as white solids.

Method C: According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *cis*-**2c**[3k] (299 mg, 1.00 mmol, dr=99:1) in toluene instead of CH_2Cl_2 as the solvent to provide the crude product **3c** (*cu*/*cl*=78:22). FCC (125 cm^3 SiO_2, Et_2O/PE=1:3) afforded *cu*-**3c**[3k] (135 mg, 0.369 mmol, 37%) and *cl*-**3c**[3k] (28 mg, 0.077 mmol, 7.7%), both as white solids.

NMR experiment: According to GP B, silyl enol ether **1b**[4a] (37 mg, 0.20 mmol) was treated with $TiCl_4$ (22 μL, 38 mg, 0.20 mmol) in CD_2Cl_2 (1.5 mL) as the solvent in a carefully sealed NMR tube. 2-Ethoxy-1,3-oxazolidine *cis*-**2c**[3k] (57 mg, 0.19 mmol, dr=99:1) was dissolved in CD_2Cl_2 (0.5 mL) and added to the reaction mixture. The NMR tube was placed into the NMR instrument at −80°C and ^1H NMR spectra were recorded periodically while the temperature was rising to 10°C within 180 min.

4.3.3. 2-{(2*R*,4*R*)-4-Ethyl-3-[2,4,6-tri(1-methylethyl)-benzenesulfonyl]-1,3-oxazolidin-2-yl}-2-methylcyclohexanone (3e). According to GP B, silyl enol ether **1b**[4a] (136 mg, 0.737 mmol) was treated with $TiCl_4$ (81 μL, 0.14 g, 0.74 mmol) and 2-ethoxy-1,3-oxazolidine *cis*-**2d** (306 mg, 743 mmol, dr=90:10) to provide the crude product **3e** (*cu*/*cl*=74:26). FCC (125 cm^3 SiO_2, Et_2O/PE=1:6) afforded *cu*-**3e** (115 mg, 0.241 mmol, 33%) and *cl*-**3e** (42 mg, 0.088 mmol, 12%), both as colourless oils. *cu*-**3e**: R_F (SiO_2, Et_2O/PE=1:1)=0.52. $[\alpha]_D^{20}$=+16.7 (*c*=0.26, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.50 (t, *J*=6.8 Hz, 3H, 2″-H_3); 0.79–0.88, 1.34–1.47, 1.60–1.72, 2.05–2.18, 2.35–2.45, 2.45–2.54, 2.54–2.64 (4m, 'd', 'dd', 'dt', 1H, 2H, 2H, 2H, 1H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 1″-H_2); 1.04 (s, 3H, 2-CH_3); 1.23, 1.24, 1.25, 1.26, 1.28 ('5s', 18H, 2‴-CH(CH_3)$_2$, 4‴-CH(CH_3)$_2$, 6‴-CH(CH_3)$_2$); 2.90 (sept, 1H, *J*=6.4 Hz, 4‴-C*H*(CH$_3$)$_2$); 3.52–3.56 (m, 1H, 4′-H); 3.75 (dd, *J*=2.4, 8.8 Hz, 1H, 5′-H_a); 3.86 (dd, *J*=6.0, 8.4 Hz, 1H, 5′-H_b); 4.28 (sept, *J*=7.2 Hz, 2H, 2‴-C*H*(CH$_3$)$_2$, 6‴-C*H*(CH$_3$)$_2$); 5.97 (s, 1H, 2′-H); 7.18 (s, 2H, 3‴-H, 5‴-H). ^{13}C NMR (75 MHz, $CDCl_3$): 10.9 (q, C-2″); 18.1 (q, 2-CH_3); 21.1 (t, C-4); 23.4, 23.5 (2q, 4‴-CH(*C*H$_3$)$_2$); 24.7, 25.0 (2q, 2‴-CH(*C*H$_3$)$_2$, 6‴-CH(*C*H$_3$)$_2$); 26.3, 28.2 (2t, C-1″, C-5); 29.6 (d, 2‴-*C*H(CH$_3$)$_2$, 6‴-*C*H(CH$_3$)$_2$); 34.2 (d, 4‴-*C*H(CH$_3$)$_2$); 37.6, 40.3 (2d, C-3, C-6); 53.9 (s, C-2); 61.9 (d, C-4′); 69.5 (d, C-5′); 91.4 (d, C-2′); 124.1 (d, C-3‴, C-5‴); 130.5 (s, C-4‴); 151.7 (s, C-2‴, C-6‴); 154.2 (s, C-1‴); 211.4 (s, C-1). IR (KBr): 2965 (s); 2870 (m); 1715 (s); 1600 (m); 1460 (m); 1325 (m); 1160 (s); 1120 (m); 960 (m). EI-MS (70 eV): 477 (0.2, M^+); 366 (95); 267 (100); 210 (26); 203 (41); 175 (45); 133 (22); 119 (32); 105 (33); 100 (74); 91 (48). Anal. calcd for $C_{27}H_{43}NO_4S$ (477.71): C 67.89, H 9.07, N 2.93; found: C 67.87, H 9.35, N 2.74.

cl-**3e**: R_F (SiO_2, Et_2O/PE=1:1)=0.60. $[\alpha]_D^{20}$=−5.0 (*c*=0.57, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.50 (t, *J*=7.2 Hz, 3H, 2″-H_3); 0.98–1.50, 1.32–1.48, 1.59–1.73, 1.80–1.96, 1.99–2.09, 2.27–2.35, 2.35–2.47, 2.90–3.01 (8m, 1H, 2H, 2H, 1H, 1H, 1H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 1″-H_2); 1.06 (s, 3H, 2-CH_3); 1.20, 1.21, 1.22, 1.24, 1.25, 1.27 ('6s', 18H, 2‴-CH(CH_3)$_2$, 4‴-CH(CH_3)$_2$, 6‴-CH(CH_3)$_2$); 2.88 (sept, *J*=6.4 Hz, 1H, 4‴-C*H*(CH$_3$)$_2$); 3.43–3.50 (m, 1H, 4′-H); 3.81 (dd, *J*=1.6, 8.4 Hz, 1H, 5′-H_a); 3.94 ('dd', *J*=5.6, 8.0 Hz, 1H, 5′-H_b); 4.10 (sept, *J*=6.8 Hz, 2H, 2‴-C*H*(CH$_3$)$_2$, 4‴-C*H*(CH$_3$)$_2$); 6.01 (s, 1H, 2′-H); 7.15 (s, 2H, 3‴-H, 5‴-H). ^{13}C NMR (75 MHz, $CDCl_3$): 10.9 (q, C-2″); 18.0 (q, 2-CH_3); 21.1 (t, C-4); 23.4, 23.5 (2q, 4‴-CH(*C*H$_3$)$_2$); 24.7, 25.0 (2q, 2‴-CH(*C*H$_3$)$_2$, 6‴-CH(*C*H$_3$)$_2$); 26.6, 28.3 (2t, C-1″, C-5); 29.4 (d, 2‴-*C*H(CH$_3$)$_2$, 6‴-*C*H(CH$_3$)$_2$); 34.2 (d, 4‴-*C*H(CH$_3$)$_2$); 38.7, 40.3 (2d, C-3, C-6); 54.2 (s, C-2); 61.5 (d, C-4′); 69.5 (d, C-5′); 92.5 (d, C-2′); 124.1 (d, C-3‴, C-5‴); 130.3 (s, C-4‴); 152.1 (s, C-2‴, C-6‴); 154.1 (s, C-1‴); 211.6 (s, C-1). IR (KBr): 2970 (s); 2880 (m); 1730 (s); 1610 (m); 1470 (m); 1310 (m); 1155 (s); 940 (m). EI-MS (70 eV)=366 (90, $M^+-C_7H_{11}O$); 267 (100); 210 (34); 203 (20); 175 (25); 119 (18); 105 (13); 100 (36); 91 (29). Anal. calcd for $C_{27}H_{43}NO_4S$ (477.71): C 67.89, H 9.07, N 2.93; found: C 68.02, H 9.29, N 2.61.

4.3.4. 2-Methyl-2-[(2*S*,4*S*)-3-(4-methylbenzenesulfonyl)-4-(1-methylethyl)-1,3-oxazolidin-2-yl]cyclohexanone (3f). According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *cis*-**2e** (313 mg, 1.00 mmol, dr=95:5) to provide the crude product **3f** (*cu*/*cl*=66:34). FCC (125 cm^3 SiO_2, Et_2O/PE=1:5→1:3) afforded a mixture of *cu*-**3f**, *a*-**6f** and *b*-**6f** (165 mg, 0.435 mmol, 43%, 82:9:9) and *cl*-**3f** (71 mg, 0.19 mmol, 19%), both as white solids. *cu*-**3f**/*a*-**6f**/*b*-**6f**=82:9:9: R_F (SiO_2, Et_2O/PE=1:1)=0.36. Mp (Et_2O/PE)=131.3–135.4°C. $[\alpha]_D^{20}$=−10.4 (*c*=0.46, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.85 (d, *J*=6.3 Hz, 3H, 2″-H_3); 1.03 (d, *J*=6.3 Hz, 3H, 1″-CH_3); 1.11 (s, 3H, 2-CH_3); 1.48–1.59, 1.59–1.86, 1.86–2.05, 2.35–2.62 (4m, 9H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 1″-H); 2.42 (s, 3H, 4‴-CH_3); 2.87 (dd, *J*=6.3, 8.4 Hz, 1H, 5′-H_a); 3.29 (dd, *J*=6.0, 9.3 Hz, 1H, 4′-H); 3.68 (d, *J*=8.7 Hz, 1H, 5′-H_b); 5.36 [5.40, 5.57] (s [d, d, *J*=9.0, 5.1 Hz], 1H, 2-H); 7.35 (d, *J*=7.8 Hz, 2H, 3‴-H, 5‴-H); 7.74 (d, *J*=8.1 Hz, 2H, 2‴-H, 6‴-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.7, 19.8, 19.9 (3q, 2-CH_3, C-2″, 1″-CH_3); 21.0 (t, C-4); 21.5 (q, 4‴-CH_3); 26.2 (t, C-5); 30.4 (d, C-1″); 34.9 (t, C-3); 39.6 (t, C-6); 52.8 (s, C-2); 66.8 (d, C-4′); 67.8 (t, C-5); 93.9 (d, C-2′); 128.4 (d, C-2‴, C-6‴); 129.9 (d, C-3‴, C-5‴); 134.3 (s, C-4‴); 144.3 (d, C-1‴); 212.1 (s, C-1). IR (KBr): 2950 (m); 2880 (w); 1715 (s); 1610 (w); 1460 (m); 1360 (s); 1175 (s); 1000 (m); 815 (m); 670 (s). EI-MS (70 eV)=268 (100, $M^+-C_7H_{11}O$); 224 (69); 155 (83); 138 (24); 112 (23); 99 (74); 91 (89). Anal. calcd for $C_{20}H_{29}NO_4S$ (379.52): C 63.30, H 7.70, N 3.69; found: C 63.27, H 7.60, N 3.62.

cl-**3f**: R_F (SiO_2, Et_2O/PE=1:1)=0.31. Mp (Et_2O/PE)=131.9–133.9°C. $[\alpha]_D^{20}$=−8.9 (*c*=0.63, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.82 (d, *J*=6.6 Hz, 3H, 2″-H_3); 0.89 (d, *J*=6.3 Hz, 3H, 1″-CH_3); 1.26 (s, 3H, 2-CH_3); 1.45–1.58, 1.58–1.89, 2.01–2.11, 2.45–2.64 (4m, 9H, 3-H_2, 4-H_2,

5-H_2, 6-H_2, 1″-H); 2.42 (s, 3H, 4‴-CH_3); 2.99 (dd, J=6.0, 8.4 Hz, 1H, 5′-H_a); 3.27 (ddd, J=0.9, 6.0, 11.1 Hz, 1H, 4-H); 3.68 (dd, J=1.2, 8.4 Hz, 1H, 5′-H_b); 5.66 (s, 1H, 2-H); 7.33 ('d', J=8.7 Hz, 2H, 3‴-H, 5‴-H); 7.74 ('d', J=8.1 Hz, 2H, 2‴-H, 6‴-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.5, 20.4, 20.5 (3q, 2-CH_3, C-2″, 1″-CH_3); 20.7 (t, C-4); 21.5 (q, 4‴-CH_3); 26.3 (t, C-5); 30.2 (d, C-1″); 33.6 (t, C-3); 39.5 (t, C-6); 53.2 (s, C-2); 67.1 (d, C-4′); 68.6 (t, C-5); 94.6 (d, C-2′); 128.7 (d, C-2‴, C-6‴); 129.9 (d, C-3‴, C-5‴); 134.7 (s, C-4‴); 144.4 (d, C-1‴); 212.9 (s, C-1). IR (KBr)=2950 (m); 2875 (w); 1710 (s); 1610 (w); 1470 (m); 1350 (s); 1160 (s); 1005 (s); 830 (m); 665 (s). EI-MS (70 eV)=268 (100, $M^+-C_7H_{11}O$); 224 (20); 171 (14); 155 (54); 91 (89). Anal. calcd for $C_{20}H_{29}NO_4S$ (379.52): C 63.30, H 7.70, N 3.69; found: C 63.29, H 7.92, N 3.62.

4.3.5. 2-Methyl-2-[(2*S*,4*S*,5*S*)-4-methyl-3-(4-methylbenzenesulfonyl)-5-phenyl-1,3-oxazolidin-2-yl]cyclohexanone (*ent*-3d).[1b] According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *cis*-**2f** (361 mg, 1.00 mmol, dr>97:3) to provide the crude product *ent*-**3d** (*cu*/*cl*=92:8). FCC (125 cm^3 SiO_2, Et_2O/PE=1:4⟶1:3) afforded a mixture of *ent-cu*-**3d**[1b] and **6d** [232 mg, 0.543 mmol, 54%, 85:15; ^{1}H NMR (**6d**): 6.90 (d, J=6.9 Hz, 2′-H)] and *ent-cl*-**3d**[1b] (18 mg, 0.042 mmol, 4.2%), both as white solids.

4.3.6. 2-Methyl-2-{(3a*R*,8a*S*)-3-(4-methylbenzenesulfonyl)-3,3a,8,8a-tetrahydro-2*H*-indeno[1,2-*d*][1,3]oxazol-2-yl}cyclohexanone (3g). (A) According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2g** (359 mg, 1.00 mmol, dr=97:3) to provide the crude product **3g** (*cl*/*cu*/*tl*/*tu*=35:34:25:6). FCC (280 cm^3 SiO_2, Et_2O/PE=1:4⟶1:2) afforded *tu*-**3g** (67 mg, 0.16 mmol, 16%) as a white solid, a mixture of *tu*-**3g**, *cu*-**3g** and *a*-**6g** (40 mg, 0.094 mmol, 9.4%, 22:30:48) as a colourless resin, a mixture of *cu*-**3g**, *a*-**6g** and *b*-**6g** (101 mg, 0.237 mmol, 24%, 81:5:14) as a colourless resin, a mixture of *cu*-**3g**, *cl*-**3g**, *a*-**6g** and *b*-**6g** (29 mg, 0.068 mmol, 6.8%, 29:61:2:8) as a colourless resin, *cl*-**3g** (102 mg, 0.240 mmol, 24%) as a white solid and *tl*-**3g** (19 mg, 0.044 mmol, 4.4%) as a white solid. B) According to GP B, silyl enol ether **1b**[4a] (92 mg, 0.50 mmol) was treated with $TiCl_4$ (55 μL, 95 mg, 0.5 mmol) and 2-ethoxy-1,3-oxazolidine *b*-**2g** (180 mg, 0.50 mmol, dr=94:6) to provide the crude product **3g** (*cl*/*cu*/*tl*/*tu*=35:38:24:3). *tu*-**3g**: R_F (SiO_2, Et_2O/PE=1:1)=0.60. Mp (Et_2O/PE)=81.3–83.2°C. $[\alpha]_D^{20}$=+51.0 (c=0.62, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 1.23 (s, 3H, 2-CH_3); 1.58–1.88, 1.88–2.09, 2.33–2.63 (3m, 9H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 11′-H_2); 2.28 (s, 3H, 4″-CH_3); 2.91 (dd, J=7.2, 16.8 Hz, 1H, 11′-H_2); 5.05 (ddd, J=5.1, 6.3, 7.2 Hz, 1H, 12′-H); 5.23 (d, J=6.0 Hz, 1H, 4′-H); 5.99 (s, 1H, 2′-H); 6.80–6.86 (m, 1H, 9′-H); 6.82 ('d', J=8.1 Hz, 2H, 3″-H, 5″-H); 7.11 (d, J=8.1 Hz, 2H, 2″-H, 6″-H); 7.14–7.22 (m, 2H, 7′-H, 8′-H); 7.55–7.60 (m, 1H, 6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.9 (t, C-4); 21.1, 21.3 (2q, 2-CH_3, 4″-CH_3); 25.6 (t, C-5); 33.5 (t, C-3); 37.6, 39.2 (2t, C-6, C-11′); 54.7 (s, C-2); 68.0 (d, C-12′); 83.7 (d, C-4′); 95.7 (d, C-2′); 124.6, 126.7, 126.8, 128.9, 129.5, 130.0 (6d, C-6′, C-7′, C-8′, C-9′, C-2″, C-3″, C-5″, C-6″); 135.4 (s, C-4″); 137.9 (s, C-5′, C-10′); 142.6 (s, C-1″); 212.1 (s, C-1). IR (KBr)=2935 (m); 2860 (w); 1715 (s); 1455 (m); 1340 (m); 1165 (s); 1085 (m); 760 (w); 675 (m); 600 (m); 545 (m). EI-MS (70 eV)=424 (0.5, M^+-H); 314 (86); 270 (10); 155 (49); 115 (84); 91(100). Anal. calcd for $C_{24}H_{27}NO_4S$ (425.55): C 67.74, H 6.39, N 3.29; found: C 67.37, H 6.50, N 2.99.

cu-**3g**/*a*-**6g**/*b*-**6g**=81:5:14: R_F (SiO_2, Et_2O/PE=1:1)=0.52. $[\alpha]_D^{20}$=−48.8 (c=0.53, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 0.47 (s, 3H, 2-CH_3); 0.79–0.90, 1.20–1.31, 1.50–1.68, 1.68–1.93, 2.18–2.41 (5m, 8H, 3-H_2, 4-H_2, 5-H_2, 6-H_2); 2.46 (s, 3H, 4″-CH_3); 2.87 (dd, J=4.8, 17.4 Hz, 1H, 11′-H_2); 3.00 (d, J=17.4 Hz, 1H, 11′-H_2); 4.08 ('t', J=5.1 Hz, 1H, 12′-H); 5.25 [5.12, 5.33] (d, 1H, J=5.4 Hz [J=5.7, 6.0 Hz], 4′-H); 5.67 [5.51, 5.73] (s [d,d, J=3.6, 8.4 Hz], 1H, 2′-H); 7.09–7.19 (m, 1H, 9′-H); 7.19–7.30 (m, 2H, 7′-H, 8′-H); 7.39 (d, J=7.8 Hz, 2H, 3″-H, 5″-H); 7.43–7.50 (m, 1H, 6′-H); 7.86 (d, J=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 18.4 (q, 2-CH_3); 20.9 (t, C-4); 21.6 (q, 4″-CH_3); 26.7 (t, C-5); 34.7, 36.9, 39.3 (3t, C-3, C-6, C-11′); 53.2 (s, C-2); 68.9 (d, C-12′); 80.3 (d, C-4′); 94.5 (d, C-2′); 125.2, 126.3, 127.4, 128.3, 128.7, 130.1 (6d, C-6′, C-7′, C-8′, C-9′, C-2″, C-3″, C-5″, C-6″); 134.6 (s, C-4″); 139.6, 140.0 (s, C-5′, C-10′); 144.5 (s, C-1″); 212.7 (s, C-1). IR (KBr): 2935 (m); 2875 (w); 1715 (s); 1470 (m); 1360 (m); 1170 (s); 1100 (w); 760 (w); 660 (m); 605 (m). EI-MS (70 eV)=424 (0.1, M^+-H); 314 (80); 270 (21); 155 (40); 115 (76); 91(100). Anal. calcd for $C_{24}H_{27}NO_4S$ (425.55): C 67.74, H 6.39, N 3.29; found: C 67.77, H 6.61, N 3.17.

cl-**3g**: R_F (SiO_2, Et_2O/PE=1:1)=0.44. Mp (Et_2O/PE)=123.3–124.4°C. $[\alpha]_D^{20}$=−59.4 (c=0.56, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 0.90 (s, 3H, 2-CH_3); 0.78–0.90, 1.10–1.30, 1.30–1.50, 1.50–1.75, 2.30–2.52 (5m, 8H, 3-H_2, 4-H_2, 5-H_2, 6-H_2); 2.46 (s, 3H, 4″-CH_3); 2.86 (dd, J=4.5, 17.4 Hz, 1H, 11′-H_2); 3.02 (d, J=17.4 Hz, 1H, 11′-H_2); 4.16 ('t', J=4.8 Hz, 1H, 12′-H); 5.27 (d, J=5.1 Hz, 1H, 4′-H); 5.89 (s, 1H, 2′-H); 7.05–7.28 (m, 4H, 6′-H, 7′-H, 8′-H, 9′-H); 7.38 (d, J=8.1 Hz, 2H, 3″-H, 5″-H); 7.86 (d, J=8.1 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.2 (q, 2-CH_3); 20.6 (t, C-4); 21.6 (q, 4″-CH_3); 26.2 (t, C-5); 32.6 (t, C-3); 37.0, 39.4 (2t, C-6, C-11′); 53.4 (s, C-2); 68.9 (d, C-12′); 80.7 (d, C-4′); 95.4 (d, C-2′); 125.1, 126.1, 127.3, 128.5, 128.7, 130.0 (6d, C-6′, C-7′, C-8′, C-9′, C-2″, C-3″, C-5″, C-6″); 135.0 (s, C-4″); 139.5, 140.1 (s, C-5′, C-10′); 144.6 (s, C-1″); 213.3 (s, C-1). IR (KBr): 2925 (m); 2855 (w); 1710 (s); 1600 (w); 1465 (m); 1355 (m); 1170 (s); 1125 (m); 1090 (m); 755 (w); 670 (m); 590 (m); 545 (m). EI-MS (70 eV)=314 (90, $M^+-C_7H_{11}O$); 270 (10); 155 (46); 115 (70); 91(100). Anal. calcd for $C_{24}H_{27}NO_4S$ (425.55): C 67.74, H 6.39, N 3.29; found: C 67.69, H 6.56, N 3.04.

tl-**3g**: R_F (SiO_2, Et_2O/PE=1:1)=0.24. Mp (Et_2O/PE)= 164.9–166.0°C. $[\alpha]_D^{20}$=+93.6 (c=0.48, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 1.36 (s, 3H, 2-CH_3); 0.79–0.91, 1.13–1.32, 1.50–1.55, 1.72–1.97, 1.97–2.12, 2.45–2.58 (6m, 9H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 11′-H_2); 2.28 (s, 3H, 4″-CH_3); 2.88 (dd, J=6.6, 16.5 Hz, 1H, 11′-H_2); 5.08–5.19 (m, 2H, 4′-H, 12′-H); 6.36 (s, 1H, 2′-H); 6.66 (d, J=6.6 Hz, 1H, 9′-H); 6.90 ('d', J=8.7 Hz, 2H, 3″-H, 5″-H); 6.98 ('d', J=8.7 Hz, 2H, 2″-H, 6″-H); 7.15–7.28

(m, 2H, 7′-H, 8′-H); 7.63 (dd, J=1.2, 6.9 Hz, 1H, 6′-H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.5 (t, C-4); 20.7 (q, 2-CH_3); 21.4 (q, 4″-CH_3); 26.2 (t, C-5); 33.6 (t, C-3); 39.2, 39.3 (2t, C-6, C-11′); 56.4 (s, C-2); 68.1 (d, C-12′); 85.5 (d, C-4′); 99.0 (d, C-2′); 124.3, 126.7, 126.9, 128.8, 129.8, 130.9 (6d, C-6′, C-7′, C-8′, C-9′, C-2″, C-3″, C-5″, C-6″); 133.7 (s, C-4″); 137.6, 142.6 (s, C-5′, C-10′); 143.5 (s, C-1″); 212.8 (s, C-1). IR (KBr): 2930 (m); 2860 (w); 1710 (s); 1610 (w); 1470 (w); 1380 (m); 1170 (s); 1070 (m); 760 (w); 675 (m); 610 (m). EI-MS (70 eV): 424 (0.3, M^+-H); 314 (87); 286 (7); 155 (52); 115 (88); 91(100). Anal. calcd for $C_{24}H_{27}NO_4S$ (425.55): C 67.74, H 6.39, N 3.29; found: C 67.81, H 6.66, N 3.03.

4.3.7. 2-Methyl-2-{(1*R*,2*R*,6*S*,7*S*)-1,10,10-trimethyl-5-(4-methylbenzenesulfonyl)-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]-dec-4-yl}cyclohexanone (3i). According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2i** (379 mg, 1.00 mmol, dr=83:13:4) to provide the crude product **3i** (*tu*/*a*/*b*/*c*=75:13:5:7). FCC (125 cm^3 SiO_2, Et_2O/PE/CH_2Cl_2=1:8:0.4→1:3:0.2) afforded a mixture of *tu*-**3i** and *b*-**3i** (231 mg, 0.518 mmol, 52%, dr=96:4), a mixture of *a*-**3i** and *c*-**3i** (25 mg, 0.056 mmol, 5.6%, dr=75:25) and a mixture of *a*-**6i** and *b*-**6i** (33 mg, 0.074 mmol, 7.4%, dr=93:7), all as colourless resins. *tu*-**3i**/*b*-**3i**=96:4: R_F (SiO_2, Et_2O/PE=1:1)=0.59. Mp (Et_2O/PE)>145°C. $[\alpha]_D^{20}$=+127 (c=0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): 0.58–0.68, 1.02–1.09, 1.48–1.55, 1.56–1.73, 1.77–1.92, 1.92–2.05, 2.26–2.40, 2.46-–2.55 (8m, 1H, 2H, 1H, 2H, 2H, 1H, 2H, 1H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 8′-H_2, 9′-H_2); 0.81, 0.90, 1.17 (3s, 6H, 3H, 3H, 2-CH_3, 1′-CH_3, 10′-$(CH_3)_2$); 1.96 (t, J=3.6 Hz, 1H, 7′-H); 2.39 (s, 3H, 4″-CH_3); 4.29 (d, J=8.8 Hz, 1H, 2′-H); 4.52 (ddd, J=1.6, 3.2, 7.6 Hz, 1H, 6′-H); 5.96 [5.71] (s, 1H, 4′-H); 7.27 (d, J=8.0 Hz, 2H, 3″-H, 5″-H); 7.75 (d, J=8.0 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0 (q, 1′-CH_3); 19.0, 20.4, 23.2 (3q, 2-CH_3, 10′-$(CH_3)_2$); 20.0, 20.6 (2t, C-4, C-9′); 21.5 (q, 4″-CH_3); 24.1 (t, C-5); 26.7 (t, C-8′); 30.6 (t, C-3); 38.5 (t, C-6); 48.5 (d, C-7′); 50.0, 50.7 (2s, C-1′, C-10′); 54.2 (s, C-2); 65.2 (d, C-6′); 87.8 (d, C-2′); 97.7 (d, C-4′); 127.3 (d, C-2″, C-6″); 129.4 (d, C-3″, C-5″); 138.3 (s, C-4″); 143.1 (s, C-1″); 212.2 (s, C-1). IR (KBr): 2955 (m); 2875 (w); 1703 (m); 1460 (w); 1355 (s); 1170 (s); 1120 (m); 685 (s); 620 (m); 550 (m). EI-MS (70 eV): 444 (0.5, M^+-H); 334 (100); 306 (16); 290(8); 155(15); 135 (38); 93 (32); 91 (26). Anal. calcd for $C_{25}H_{35}NO_4S$ (445.63): C 67.38, H 7.92, N 3.14; found: C 67.21, H 7.87, N 2.84.

a-**3i**/*c*-**3i**=75:25: R_F (SiO_2, Et_2O/PE=1:1)=0.55. Mp (Et_2O/PE)>75°C. $[\alpha]_D^{20}$=+113 (c=0.31, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): 0.73, 0.87, 0.88, 0.91 [0.83, 0.85, 0.88] (4s, 12H, 2-CH_3, 1′-CH_3, 10′-$(CH_3)_2$); 0.99, 1.15–1.40, 1.51–1.62, 1.62–1.75, 1.75–1.90, 2.00–2.06, 2.25–2.32, 2.43–2.50, 2.97 [3.05–3.11] (d, J=6.4 Hz, 7m, dt [m], J=6.4, 13.6 Hz, 1H, 1H, 2H, 2H, 2H, 1H, 1H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 8′-H_2, 9′-H_2); 2.08 [1.98] (t, J=4.4 Hz, [J=4.0 Hz,] 1H, 7′-H); 2.40 [2.42] (s, 3H, 4″-CH_3); 3.90 [4.26] (ddd, J=2.0, 4.4, 8.8 Hz, [J=1.6, 4.0, 7.6 Hz,] 1H, 6′-H); 4.40 [4.34] (d, J=8.0 Hz, [J=7.6 Hz,] 1H, 2′-H); 6.36 [6.03] (s, 1H, 4′-H); 7.28 (d, J=8.0 Hz, 2H, 3″-H, 5″-H); 7.65 (d, J=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.2, 17.3, 18.9, 20.2, 20.7, 21.4, 21.5 [14.1, 14.3, 18.8, 20.2, 20.5, 21.5] (1′-CH_3, 2-CH_3, 10′-$(CH_3)_2$, C-4, C-9′, 4″-CH_3); 26.6, 29.4, 40.1, 40.7 [24.3, 26.4, 26.5, 35.8] (C-5, C-8′, C-3, C-6); 49.7, 50.3, 50.8 [45.6, 49.7, 50.5] (C-1′, C-7′, C-10′); 58.0 [54.7] (C-2); 62.9 [63.3] (C-6′); 91.0 [90.2] (C-2′); 99.7 [94.6] (C-4′); 127.6 [126.9] (C-2″, C-6″); 129.3 [129.6] (C-3″, C-5″); 137.4 [138.2] (C-4″); 143.3 [143.4] (C-1″); 212.3 (C-1). IR (KBr): 2960 (s); 2875 (m); 1715 (s); 1460 (m); 1355 (s); 1170 (s); 1110 (s); 820 (m); 675 (s); 610 (m); 540 (m). EI-MS (70 eV): 444 (0.25, M^+-H); 334 (100); 306 (17); 290 (16); 155 (17); 135 (43); 93 (39); 91 (30). Anal. calcd for $C_{25}H_{35}NO_4S$ (445.63): C 67.38, H 7.92, N 3.14; found: C 67.30, H 7.85, N 2.72.

a-**6i**/*b*-**6i**=93:7: R_F (SiO_2, Et_2O/PE=1:1)=0.56. $[\alpha]_D^{20}$=+143 (c=0.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): 0.82, 0.85, 0.90 (3s, 9H, 1′-CH_3, 10′-$(CH_3)_2$); 0.80–0.90, 1.10–1.63, 1.71–1.79, 1.80–1.88, 2.45–2.52 (5m, 1H, 7H, 1H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 6-H, 8′-H_2, 9′-H_2); 1.09 (d, J=7.2 Hz, 3H, 6-CH_3); 2.01 (t, J=4.8 Hz, 1H, 7′-H); 2.41 (s, 3H, 4″-CH_3); 3.07 (ddd, J=2.0, 5.6, 10.0 Hz, 1H, 2-H); 4.30 (ddd, J=1.6, 4.4, 8.8 Hz, 1H, 6′-H); 4.38 (dd, J=0.8, 8.8 Hz, 1H, 2′-H); 5.91 [6.03] (d, J=2.0 Hz, 1H, 4′-H); 7.29 (d, J=8.0 Hz, 2H, 3″-H, 5″-H); 7.70 (d, J=8.8 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (100 MHz, $CDCl_3$): 14.1 (q, 1′-CH_3); 16.3, 18.8, 20.6 (3q, 6-CH_3, 10′-$(CH_3)_2$); 19.8, 20.2 (2t, C-4, C-9′); 21.5 (q, 4″-CH_3); 24.1, 26.6, 31.8 (3t, C-3, C-5, C-8′); 44.0, 49.8, 51.9 (3d, C-2, C-6, C-7′); 49.7, 50.6 (2s, C-1′, C-10′); 63.5 (d, C-6′); 90.0 (d, C-2′); 95.9 (d, C-4′); 127.0 (d, C-2″, C-6″); 129.6 (d, C-3″, C-5″); 138.1 (s, C-4″); 143.5 (s, C-1″); 213.2 (s, C-1). IR (KBr): 2955 (s); 2870 (m); 1715 (s); 1470 (w); 1350 (s); 1170 (s); 1105 (s); 690 (s); 605 (m). EI-MS (70 eV): 334 (86, $M^+-C_7H_{11}O$); 306 (18); 290 (100); 194 (14); 155 (20); 135 (55); 93 (47); 91 (30). Anal. calcd for $C_{25}H_{35}NO_4S$ (445.63): C 67.38, H 7.92, N 3.14; found C 67.11, H 7.42, N 2.83.

4.3.8. 2-Methyl-2-[(3a*R*,7a*S*)-3-(4-methylbenzenesulfonyl)perhydro-1,3-benzoxazol-2-yl]cyclohexanone (3j). (A) According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2j** (325 mg, 1.00 mmol) to provide the crude product **3j** (*cl*/*cu*/*a*=43:36:21). FCC (125 cm^3 SiO_2, Et_2O/PE=1:6→1:4) afforded *cl*-**3j** (59 mg, 0.15 mmol, 15%), a mixture of *cu*-**3j**, *a*-**3j** and *a*-**6j** (52 mg, 0.13 mmol, 13%, 91:4:5) and a mixture of *a*-**3j**, *cu*-**3j**, *a*-**6j** and *b*-**6j** (43 mg, 0.11 mmol, 11%, 89:5:3:3), all as colourless resins. (B) According to GP B, silyl enol ether **1b** (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *b*-**2j** (325 mg, 1.00 mmol, dr=96:4) to provide the crude product **3j** (*cl*/*cu*/*a*=45:36:19). *cl*-**3j**: R_F (SiO_2, Et_2O/PE=1:1)=0.38. Mp (Et_2O/PE)=162.3–163.7°C. $[\alpha]_D^{20}$=+17.7 (c=0.51, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): 0.79–0.88, 0.95–2.08, 2.25–2.35, 2.43–2.54, 2.71–2.83 (m, 16H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.21 (s, 3H, 2-CH_3); 2.40 (s, 3H, 4″-CH_3); 3.42–3.48, 3.55–3.65 (2m, 2H, 4′-H, 9′-H); 5.65 (s, 1H, 2′-H); 7.29 ('d', J=8.7 Hz, 2H, 3″-H, 5″-H); 7.72 (d, J=8.1 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.9, 21.0, 23.3, 27.2, 27.3, 28.0, 36.4, 39.9 (8t, C-3, C-4, C-5, C-6, C-5′, C-6′, C-7′, C-8′); 20.0 (q, 2-CH_3); 21.5 (q,

4″-CH_3); 53.3 (s, C-2); 58.6 (d, C-4′); 74.8 (d, C-9′); 92.9 (d, C-2′); 128.1 (d, C-2″, C-6″); 129.7 (d, C-3″, C-5″); 135.9 (s, C-4″); 144.0 (s, C-1″); 212.5 (s, C-1). IR (KBr): 2940 (s); 2870 (m); 1705 (s); 1460 (m); 1355 (m); 1175 (s); 1091 (m); 1005 (m); 670 (s); 595 (s). EI-MS (70 eV): 390 (0.1, M^+-H); 280 (93); 252 (66); 236 (87); 200 (90); 155 (94); 139 (29); 111 (17); 91 (100). Anal. calcd for $C_{21}H_{29}NO_4S$ (391.53): C 64.42, H 7.47, N 3.58; found: C 64.25, H 7.47, N 3.45.

cu-**3j**/*a*-**3j**/*a*-**6j**=91:4:5: R_F (SiO_2, Et_2O/PE=1:1)=0.43. Mp (Et_2O/PE)=159.3–161.0°C. $[\alpha]_D^{20}=+24.4$ (*c*=0.39, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.79–0.88, 0.98–2.02, 2.29–2.40, 2.47–2.63 (m, 16H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.17 (s, 3H, 2-CH_3); 2.41 (s, 3H, 4″-CH_3); 3.15–3.22, 3.56 (m, ddd, *J*=4.8, 6.9, 11.7 Hz, 2H, 4′-H, 9′-H); 5.34 [5.78, 5.50] (s, [s, d, *J*=2.7 Hz,] 1H, 2′-H); 7.32 (d, *J*=7.8 Hz, 2H, 3″-H, 5″-H); 7.75 (‘d’, *J*=8.1 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.9, 20.8, 23.3, 24.9, 27.2, 29.6, 32.8, 39.1 (8t, C-3, C-4, C-5, C-6, C-5′, C-6′, C-7′, C-8′); 21.5 (q, 4″-CH_3); 22.1 (q, 2-CH_3); 51.6 (s, C-2); 58.9 (d, C-4′); 74.6 (d, C-9′); 93.0 (d, C-2′); 127.9 (d, C-2″, C-6″); 129.9 (d, C-3″, C-5″); 135.2 (s, C-4″); 143.8 (s, C-1″); 212.1 (s, C-1). IR (KBr): 2950 (s); 2870 (m); 1715 (s); 1460 (m); 1350 (s); 1170 (s); 670 (s); 600 (s). EI-MS (70 eV): 390 (0.25, M^+-H); 280 (99); 236 (100); 200 (37); 155 (51); 139 (14); 111 (15); 91 (95). Anal. calcd for $C_{21}H_{29}NO_4S$ (391.53): C 64.42, H 7.47, N 3.58; found: C 64.47, H 7.92, N 3.28.

a-**3j**/*cu*-**3j**/*a*-**6j**/*b*-**6j**=89:5:3:3: R_F (SiO_2, Et_2O/PE=1:1)=0.49. Mp (Et_2O/PE)=161.1–163.0°C. $[\alpha]_D^{20}=+1.2$ (*c*=0.38, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.75–1.02, 1.10–1.38, 1.39–2.04, 2.21–2.36, 2.42–2.60 (m, 16H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.22 (s, 3H, 2-CH_3); 2.39 (s, 3H, 4″-CH_3); 3.90–4.05, 4.05–4.09 (2m, 2H, 4′-H, 9′-H); 5.78 [5.34, 5.13, 5.50] (s, [s, 2d, *J*=2.7, 3.0 Hz] 1H, 2′-H); 7.27 (d, *J*=8.7 Hz, 2H, 3″-H, 5″-H); 7.84 (‘d’, *J*=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.2, 20.8, 22.5, 23.6, 26.0, 27.4, 31.1, 38.4 (8t, C-3, C-4, C-5, C-6, C-5′, C-6′, C-7′, C-8′); 21.5 (q, 4″-CH_3); 24.2 (q, 2-CH_3); 53.5 (s, C-2); 59.8 (d, C-4′); 74.4 (d, C-9′); 90.8 (d, C-2′); 127.8 (d, C-2″, C-6″); 129.5 (d, C-3″, C-5″); 139.0 (s, C-4″); 143.2 (s, C-1″); 212.8 (s, C-1). IR (KBr): 2935 (s); 2875 (m); 1700 (s); 1455 (s); 1345 (s); 1165 (s); 1165 (s); 1090 (s). EI-MS (70 eV)=391 (0.25, M^+); 280 (100); 236 (42); 200 (23); 155 (33); 114 (14); 91 (60). Anal. calcd for $C_{21}H_{29}NO_4S$ (391.53): C 64.42, H 7.47, N 3.58; found: C 64.23, H 7.24, N 3.51.

4.3.9. 2-Methyl-2-[(3a*S*,7a*S*)-3-(4-methylbenzenesulfonyl)perhydro-1,3-benzoxazol-2-yl]cyclohexanone (3k). According to GP B, silyl enol ether **1b**[4a] (184 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2k** (325 mg, 1.00 mmol) to provide the crude product **3k** (*cu*/*a*=89:11). FCC (125 cm^3 SiO_2, Et_2O/PE=1:5) afforded *cu*-**3k** (256 mg, 0.654 mmol, 65%) and a mixture of *a*-**3k** and **6k** (39 mg, 0.10 mmol, 10%, 83:17), both as white foams. *cu*-**3k**: R_F (SiO_2, Et_2O/PE=1:1)=0.40. Mp (Et_2O/PE)=131.5–132.6°C. $[\alpha]_D^{20}=+21.3$ (*c*=0.54, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.06–1.27, 1.35–1.54, 1.64–1.85, 1.85–2.05, 2.29–2.59 (5m, 3H, 2H, 4H, 3H, 4H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.18 (s, 3H, 2-CH_3); 2.43 (s, 3H, 4″-CH_3); 2.60–2.71, 3.35–3.48 (2m, 2H, 4′-H, 9′-H); 5.42 (s, 1H, 2′-H); 7.34 (d, *J*=8.1 Hz, 2H, 3″-H, 5″-H); 7.70 (d, *J*=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.1, 23.3, 24.0, 25.4 (4t, C-4, C-5, C-6′, C-7′); 21.6 (q, 4″-CH_3); 22.9 (q, 2-CH_3); 29.7 (2t, C-5′, C-8′); 35.2 (t, C-3); 39.8 (t, C-6); 54.4 (s, C-2); 65.7 (d, C-4′); 81.6 (d, C-9′); 92.3 (d, C-2′); 128.4 (d, C-2″, C-6″); 129.8 (d, C-3″, C-5″); 132.3 (s, C-4″); 144.2 (s, C-1″); 211.7 (s, C-1). IR (KBr): 2945 (s); 2880 (m); 1715 (s); 1605 (w); 1465 (m); 1350 (s); 1170 (s); 990 (m); 830 (m); 690 (s). EI-MS (70 eV): 391 (0.25, M^+); 280 (89); 252 (37); 236 (10); 184 (31); 155 (51); 113 (12); 99 (30); 91 (100). Anal. calcd for $C_{21}H_{29}NO_4S$ (391.53): C 64.42, H 7.47, N 3.58; found: C 64.53, H 7.72, N 3.37.

a-**3k/6k**=83:17: R_F (SiO_2, Et_2O/PE=1:1)=0.33. Mp (Et_2O/PE)>55°C. $[\alpha]_D^{20}=-10.4$ (*c*=0.97, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.09–1.35, 1.45–1.95, 1.95–2.11, 2.29–2.54, 2.68–2.79 (5m, 16H, 3-H_2, 4-H_2, 5-H_2, 6-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.19 (s, 3H, 2-CH_3); 2.41 (s, 3H, 4″-CH_3); 2.79–2.92, 3.51–3.67 (2m, 2H, 4′-H, 9′-H); 5.78 [5.39] (s, [d, *J*=3.3 Hz,] 1H, 2′-H); 7.31 (‘d’, *J*=8.4 Hz, 2H, 3″-H, 5″-H); 7.69 (d, *J*=8.1 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 20.1 (q, 2-CH_3); 21.2, 23.3, 24.0 (3t, C-4, C-6′, C-7′); 21.5 (q, 4″-CH_3); 27.9, 28.9, 30.0 (3t, C-5, C-5′, C-8′); 38.1 (t, C-3); 40.3 (t, C-6); 56.3 (s, C-2); 65.9 (d, C-4′); 82.4 (d, C-9′); 93.1 (d, C-2′); 128.3 (d, C-2″, C-6″); 129.6 (d, C-3″, C-5″); 134.8 (s, C-4″); 144.2 (s, C-1″); 212.6 (s, C-1). IR (KBr): 2960 (s); 2880 (s); 1715 (s); 1595 (m); 1465 (m); 1370 (s); 1170 (s); 1130 (m); 985 (m); 675 (s); 600 (m). EI-MS (70 eV): 280 (54, $M^+-C_7H_{11}O$); 252 (20); 205 (9); 184 (10); 155 (27); 91 (44); 85 (88); 83 (100). Anal. calcd for $C_{21}H_{29}NO_4S$ (391.53): C 64.42, H 7.47, N 3.58; found: C 64.56, H 7.60, N 3.45.

4.3.10. 2,6,6-Trimethyl-2-[(3a*S*,7a*S*)-3-(4-methylbenzenesulfonyl)perhydro-1,3-benzoxazol-2-yl]cyclohexanone (3l). According to GP B, silyl enol ether **1c**[4b] (212 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2k** (325 mg, 1.00 mmol) to provide the crude product **3l** (*cu*/*cl*/*a*=78:13:9). FCC (125 cm^3 SiO_2, Et_2O/PE=1:6→1:3) afforded *cu*-**3l** (154 mg, 0.367 mmol, 37%), *cl*-**3l** (27 mg, 0.064 mmol, 6.4%) and a mixture of *a*-**3l** and *cl*-**3l** (18 mg, 0.043 mmol, 4.3%, dr=91:9), all as colourless resins. *cu*-**3l**: R_F (SiO_2, Et_2O/PE=1:1)=0.59. $[\alpha]_D^{20}=-8.8$ (*c*=0.97, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.10–1.30, 1.42–1.55, 1.55–1.65, 1.69–1.90, 2.31–2.40, 2.51–2.61 (6m, 4H, 1H, 1H, 6H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.17, 1.17, 1.19 (3s, 9H, 2-CH_3, (6-CH_3)$_2$); 2.41 (s, 3H, 4″-CH_3); 2.66–2.79, 3.27–3.37 (2m, 2H, 4′-H, 9′-H); 5.40 (s, 1H, 2′-H); 7.33 (d, *J*=8.1 Hz, 2H, 3″-H, 5″-H); 7.67 (d, *J*=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 17.6 (t, C-4); 21.5 (q, 4″-CH_3); 23.2, 23.9 (2t, C-6′, C-7′); 25.2 (q, 2-CH_3); 27.3, 29.5 (2q, (6-CH_3)$_2$); 29.6, 29.8 (2t, C-5′, C-8′); 33.1 (t, C-3); 37.8 (t, C-5); 44.2 (s, C-6); 53.7 (s, C-2); 65.4 (d, C-4′); 81.1 (d, C-9′); 93.4 (d, C-2′); 128.5 (d, C-2″, C-6″); 129.7 (d, C-3″, C-5″); 131.8 (s, C-4″); 144.0 (s, C-1″); 217.6 (s, C-1). IR (KBr)=2935 (s); 2875 (s); 1700 (s); 1600 (m); 1475 (s); 1360 (s); 1165 (s); 1165 (s); 1010 (m); 670 (s). EI-MS

(70 eV)=419 (0.05, M^+); 280 (100); 252 (40); 184 (27); 155 (38); 91 (75). Anal. calcd for $C_{23}H_{33}NO_4S$ (419.53): C 65.84, H 7.93, N 3.34; found: C 65.82, H 8.25, N 3.25.

cl-**3l**: R_F (SiO_2, Et_2O/PE=1:1)=0.53. Mp (Et_2O/PE)= 124.2–125.6°C. $[\alpha]_D^{20}$=+9.1 (*c*=0.27, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.10, 1.14, 1.33 (3s, 9H, 2-CH_3, (6-CH_3)$_2$); 1.10–1.30, 1.38–1.57, 1.62–1.86, 1.89–1.98, 2.10–2.22, 2.45–2.58, 3.69–3.78 (7m, 4H, 1H, 6H, 1H, 1H, 2H, 1H, 3-H_2, 4-H_2, 5-H_2, 4′-H, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2, 9′-H); 2.41 (s, 3H, 4″-CH_3); 5.44 (s, 1H, 2′-H); 7.32 (d, *J*=7.8 Hz, 2H, 3″-H, 5″-H); 7.71 (‘d’, *J*=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$, no DEPT): 17.5 (C-4); 21.5 (4″-CH_3); 23.4 (2-CH_3); 24.2, 24.6 (C-6′, C-7′); 27.5, 28.0, 28.7, 30.1, 30.2 (C-5′, C-8′, (6-CH_3)$_2$); 32.0 (C-3); 38.1 (C-5); 44.3 (C-6); 54.7 (C-2); 67.1 (C-4′); 81.3 (C-9′); 96.4 (C-2′); 128.8 (C-2″, C-6″); 129.7 (C-3″, C-5″); 132.2 (C-4″); 144.3 (C-1″); 218.8 (C-1). IR (KBr): 2940 (s); 2875 (m); 1710 (s); 1605 (w); 1455 (m); 1350 (s); 1170 (s); 1120 (s); 980 (m); 825 (w); 745 (w). EI-MS (70 eV): 280 (100, $M^+-C_9H_{15}O$); 252 (42); 184 (21); 155 (39); 91 (64). Anal. calcd for $C_{23}H_{33}NO_4S$ (419.53): C 65.84, H 7.93, N 3.34; found: C 65.92, H 7.86, N 3.27.

a-**3l**/*cl*-**3l**=91:9: R_F (SiO_2, Et_2O/PE=1:1)=0.48. $[\alpha]_D^{20}$= +20.0 (*c*=0.21, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.08, 1.15, 1.36 (3s, 9H, 2-CH_3, (6-CH_3)$_2$); 1.10–1.32, 1.50–1.75, 1.75–1.88, 1.88–2.03, 2.15–2.24, 2.74–2.80 (6m, 4H, 7H, 1H, 2H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 4′-H, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2, 9′-H); 2.40 [2.41] (s, 3H, 4″-CH_3); 6.07 [5.44] (s, 1H, 2′-H); 7.27 (dd, *J*=0.6, 9.0 Hz, 2H, 3″-H, 5″-H); 7.79 (‘d’, *J*=8.4 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$, no DEPT): 17.1 (C-4); 21.5 (4″-CH_3); 23.0, 23.5 (C-6′, C-7′); 25.3 (2-CH_3); 26.9, 27.4, 28.3, 29.9, 30.7 (C-3, C-5′, C-8′, (6-CH_3)$_2$); 38.4 (C-5); 44.4 (C-6); 53.8 (C-2); 65.6 (C-4′); 79.8 (C-9′); 95.6 (C-2′); 128.1 (C-2″, C-6″); 129.7 (C-3″, C-5″); 138.7 (C-4″); 143.7 (C-1″); 218.9 (C-1). IR (KBr): 2930 (s); 2880 (s); 1710 (s); 1605 (m); 1470 (s); 1360 (s); 1170 (s); 1125 (s); 985 (m); 820 (m). EI-MS (70 eV): 280 (100, $M^+-C_9H_{15}O$); 252 (47); 186 (32); 155 (46); 111 (32); 96 (82); 91 (89). HR-ESI-MS calcd for $C_{23}H_{33}NO_4S+H^+$: 420.2209; found: 420.2256; calcd for $C_{23}H_{33}NO_4S+Na^+$: 442.2028; found: 442.2069.

4.3.11. 2-Methyl-2-[(3a*S*,7a*S*)-3-(4-methylbenzenesulfonyl)perhydro-1,3-benzoxazol-2-yl]-1,2,3,4-tetrahydronaphthalinone (3m). According to GP B, silyl enol ether **1d**[4c] (232 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2k** (325 mg, 1.00 mmol) to provide the crude product **3m** (*cu*/*a*/*b*/*c*=74:19:4:3). FCC (125 cm^3 SiO_2, Et_2O/PE= 1:5→1:4) afforded a mixture of *cu*-**3m** and *b*-**3m** (229 mg, 0.521 mmol, 52%, dr=93:7) and a mixture of *a*-**3m** and *c*-**3m** (72 mg, 0.16 mmol, 16%, dr=90:10), both as white solids. *cu*-**3m**/*b*-**3m**=93:7: R_F (SiO_2, E/PE=1:1)=0.55. Mp (E/PE)=175.6–176.5°C. $[\alpha]_D^{20}$=−52.8 (*c*=0.83, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.10–1.37, 1.42–1.58, 1.71–1.86, 1.93–2.02, 2.35–2.45, 2.49–2.58 (5m, ‘d’, 3H, 1H, 3H, 1H, 1H, 1H, 3-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.27 (s, 3H, 2-CH_3); 2.43 (s, 3H, 4″-CH_3); 2.83–2.96, 2.96–3.07, 3.42–3.53 (3m, 1H, 2H, 1H, 4-H_2, 4′-H, 9′-H); 5.56 [5.80] (s, 1H, 2′-H); 7.19 (d, *J*=7.8 Hz, 1H, 6-H); 7.28 (‘dt’, *J*=1.2, 7.8 Hz, 1H, 8-H); 7.35 (dd, *J*=0.6, 8.7 Hz, 2H, 3″-H, 5″-H); 7.42 (‘dt’, *J*=1.5, 7.5 Hz, 1H, 7-H); 7.74 (‘d’, *J*=8.4 Hz, 2H, 2″-H, 6″-H); 8.07 (dd, *J*=1.2, 7.8 Hz, 1H, 9-H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.1 (q, 2-CH_3); 21.6 (q, 4″-CH_3); 23.4, 24.0 (2t, C-6′, C-7′); 25.3 (t, C-4); 29.7, 29.8, 30.9 (3t, C-3, C-5′, C-8′); 50.8 (s, C-2); 65.5 (d, C-4′); 81.7 (d, C-9′); 93.2 (d, C-2′); 126.7, 128.2, 128.3 (3d, C-6, C-8, C-9); 128.6 (d, C-2″, C-6″); 129.7 (d, C-3″, C-5″); 131.8 (s, C-10); 132.5 (s, C-4″); 132.9 (d, C-7); 142.3 (s, C-5); 144.1 (s, C-1″); 199.0 (s, C-1). IR (KBr)=2930 (m); 2860 (w); 1690 (s); 1600 (m); 1465 (m); 1360 (s); 1170 (s); 1000 (m); 750 (m); 685 (s); 595 (s). EI-MS (70 eV)=439 (0.25, M^+); 280 (100); 252 (42); 184 (30); 155 (49); 91 (94). Anal. calcd for $C_{25}H_{29}NO_4S$ (439.58): C 68.31, H 6.65, N 3.18; found: C 68.13, H 6.38, N 2.83.

a-**3m**/*c*-**3m**=90:10: R_F (SiO_2, Et_2O/PE=1:1)=0.48. Mp (Et_2O/PE)>75°C. $[\alpha]_D^{20}$=−5.6 (*c*=0.45, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.09–1.44, 1.56–1.80, 1.90–2.02, 2.06, 2.28–2.45 (m, m, m, ddd, m, 4H, 2H, 1H, 1H, 2H, 3-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 1.38 (s, 3H, 2-CH_3); 2.40 (s, 3H, 4″-CH_3); 2.59, 2.90–3.14, 3.64 (ddd, *J*=5.4, 7.5, 12.9 Hz, m, ddd, *J*=3.3, 10.2, 11.4 Hz, 1H, 2H, 1H, 4-H_2, 4′-H, 9′-H); 5.61 [6.18] (s, 1H, 2′-H); 7.20 (d, *J*=7.8 Hz, 1H, 6-H); 7.26 (d, *J*=7.8 Hz, 2H, 3″-H, 5″-H); 7.30 (‘dt’, *J*=6.9 Hz, 1H, 8-H); 7.45 (‘dt’, *J*=1.2, 7.2 Hz, 1H, 7-H); 7.54 (d, *J*=8.1 Hz, 2H, 2″-H, 6″-H); 8.03 (dd, *J*=1.2, 7.8 Hz, 1H, 9-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.2 (q, 2-CH_3); 21.5 (q, 4″-CH_3); 23.4, 24.1 (2t, C-6′, C-7′); 25.1 (t, C-4); 29.7, 30.1, 31.6 (3t, C-3, C-5′, C-8′); 52.1 (s, C-2); 66.5 (d, C-4′); 82.1 (d, C-9′); 93.7 (d, C-2′); 126.7, 128.4, 128.8 (3d, C-6, C-8, C-9); 128.7 (d, C-2″, C-6″); 129.7 (d, C-3″, C-5″); 132.7, 133.2 (2s, C-10, C-4″); 132.8 (d, C-7); 142.5 (s, C-5); 144.2 (s, C-1″); 200.0 (s, C-1). IR (KBr): 2955 (m); 2870 (w); 1695 (s); 1610 (m); 1350 (s); 1175 (s); 1130 (m); 1100 (m); 980 (m); 755 (m); 675 (m); 595 (m). EI-MS (70 eV)=438 (0.25, M^+-H); 284 (64); 280 (95); 252 (79); 184 (62); 155 (84); 131 (37); 91 (100). Anal. calcd for $C_{25}H_{29}NO_4S$ (439.58): C 68.31, H 6.65, N 3.18; found: C 68.10, H 6.52, N 2.85.

4.3.12. (2*R*)-2-Methyl-2-[(2*S*,3a*S*,7a*S*)-3-(4-methylbenzenesulfonyl)perhydro-1,3-benzoxazol-2-yl]cyclopentanone (3n). According to GP B, silyl enol ether **1e**[4d] (170 mg, 1.00 mmol) was treated with $TiCl_4$ (0.11 mL, 0.19 g, 1.0 mmol) and 2-ethoxy-1,3-oxazolidine *a*-**2k** (325 mg, 1.00 mmol) to provide the crude product **3n** (*cu*/*a*=98:2). FCC (125 cm^3 SiO_2, Et_2O/PE=1:5) afforded a mixture of *cu*-**3n** and *a*-**3n** (223 mg, 0.591 mmol, 59%, dr=98:2) as a white foam. *cu*-**3n**/*a*-**3n**=98:2: R_F (SiO_2, Et_2O/PE= 1:1)=0.33. Mp (Et_2O/PE)=169.1–171.8°C. $[\alpha]_D^{20}$=+57.9 (*c*=0.76, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 0.98 (s, 3H, 2-CH_3); 1.15–1.32, 1.42–1.57, 1.59–1.68, 1.72–1.87, 1.93–2.01, 2.02–2.14, 2.23–2.35, 2.39–2.51, 2.51–2.62 (9m, 4H, 1H, 1H, 3H, 1H, 1H, 1H, 1H, 1H, 3-H_2, 4-H_2, 5-H_2, 5′-H_2, 6′-H_2, 7′-H_2, 8′-H_2); 2.41 (s, 3H, 4″-CH_3); 2.75, 3.27 (ddd, *J*=7.2, 11.4, 11.4 Hz, ddd, *J*=3.6, 9.6, 10.5 Hz, 2H, 4′-H, 9′-H); 5.01 [5.13] (s, 1H, 2′-H); 7.33 (dd, *J*=0.3, 8.7 Hz, 2H, 3″-H, 5″-H); 7.66 (‘d’, *J*=8.1 Hz, 2H, 2″-H, 6″-H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.5 (t, C-4); 20.7 (q, 2-CH_3); 21.5 (q, 4″-CH_3); 23.3, 24.0 (2t, C-6′, C-7′); 29.4, 30.0, 32.7 (3t, C-3, C-5′, C-8′); 37.2 (t, C-5);

53.9 (s, C-2); 65.7 (d, C-4′); 80.6 (d, C-9′); 93.2 (d, C-2′); 128.4 (d, C-2″, C-6″); 129.7 (d, C-3″, C-5″); 131.7 (s, C-4″); 144.1 (s, C-1″); 220.0 (s, C-1). IR (KBr): 2975 (m); 2945 (m); 2875 (m); 1740 (s); 1360 (s); 1165 (s); 985(w); 830 (w); 685 (s). EI-MS (70 eV): 280 (100, $M^+-C_6H_9O$); 252 (32); 184 (13); 155 (37); 91 (58). Anal. calcd for $C_{20}H_{27}NO_4S$ (377.51): C 63.63, H 7.21, N 3.71; found: C 63.62, H 7.16, N 3.41.

4.4. X-Ray structure analyses

4.4.1. Crystal data for *cis*-2c. Formula $C_{14}H_{21}NO_4S$, M=299.38, colourless crystal 0.35×0.15×0.05 mm^3, a=6.288(1), b=7.560(1), c=33.057(5) Å, V=1571.4(4) Å^3, ρ_{calc}=1.265 g cm^{-3}, μ=12.65 cm^{-1}, empirical absorption correction via ψ scan data ($0.550 \le T \le 0.909$), Z=4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 1904 reflections collected ($-h,+k,+l$), [(sin θ)/λ]=0.62 Å^{-1}, 1904 independent and 1319 observed reflections [$I \ge 2\sigma(I)$], 184 refined parameters, R=0.054, wR^2=0.135, max. residual electron density 0.26 (−0.35) e Å^{-3}, Flack parameter 0.04(5), hydrogens calculated and refined as riding atoms.

4.4.2. Crystal data for *cu*-3f. Formula $C_{20}H_{29}NO_4S$, M=379.50, colourless crystal 0.50×0.40×0.10 mm^3, a=9.799(2), b=12.090(2), c=16.772(4) Å, V=1987.0(7) Å^3, ρ_{calc}=1.269 g cm^{-3}, μ=16.46 cm^{-1}, empirical absorption correction via ψ scan data ($0.493 \le T \le 0.853$), Z=4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 4385 reflections collected ($\pm h,+k,+l$), [(sin θ)/λ]=0.62 Å^{-1}, 4059 independent (R_{int}=0.061) and 3863 observed reflections [$I \ge 2\sigma(I)$], 240 refined parameters, R=0.071, wR^2=0.219, max. residual electron density 0.63 (−0.67) e Å^{-3}, Flack parameter 0.04(3), hydrogens calculated and refined as riding atoms.

4.4.3. Crystal data for *cl*-3d. Formula $C_{24}H_{29}NO_4S$, M=427.54, colourless crystal 0.60×0.50×0.20 mm^3, a=7.606(1), b=11.749(1), c=12.606(1) Å, β=101.63(1)°, V=1103.4(2) Å^3, ρ_{calc}=1.287 g cm^{-3}, μ=15.47 cm^{-1}, empirical absorption correction via ψ scan data ($0.457 \le T \le 0.747$), Z=2, monoclinic, space group $P2_1$ (No. 4), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 2540 reflections collected ($-h,-k,\pm l$), [(sin θ)/λ]=0.62 Å^{-1}, 2361 independent (R_{int}=0.047) and 2351 observed reflections [$I \ge 2\sigma(I)$], 275 refined parameters, R=0.032, wR^2=0.091, max. residual electron density 0.29 (−0.18) e Å^{-3}, Flack parameter 0.00(2), hydrogens calculated and refined as riding atoms.

4.4.4. Crystal data for *cl*-3g. Formula $C_{24}H_{27}NO_4S$, M=425.53, colourless crystal 0.30×0.20×0.10 mm^3, a=10.219(1), b=10.276(1), c=12.180(1) Å, α=86.46(1), β=66.27(1), γ=70.75(1)°, V=1101.7(2) Å^3, ρ_{calc}=1.283 g cm^{-3}, μ=15.49 cm^{-1}, empirical absorption correction via ψ scan data ($0.654 \le T \le 0.861$), Z=2, triclinic, space group $P1$ (No. 1), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 4751 reflections collected ($\pm h,+k,\pm l$), [(sin θ)/λ]=0.62 Å^{-1}, 4751 independent and 4534 observed reflections [$I \ge 2\sigma(I)$], 545 refined parameters, R=0.034, wR^2=0.088, max. residual electron density 0.19 (−0.42) e Å^{-3}, Flack parameter −0.004(11), hydrogens calculated and refined as riding atoms.

4.4.5. Crystal data for *tl*-3g. Formula $C_{24}H_{27}NO_4S$, M=425.53, colourless crystal 0.20×0.20×0.10 mm^3, a=8.385(2), b=10.850(2), c=23.712(5) Å, β=92.11(2)°, V=2155.8(8) Å^3, ρ_{calc}=1.311 g cm^{-3}, μ=15.84 cm^{-1}, empirical absorption correction via ω scan data ($0.742 \le T \le 0.858$), Z=4, monoclinic, space group $P2_1$ (No. 4), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 9372 reflections collected ($+h,\pm k,\pm l$), [(sin θ)/λ]=0.62 Å^{-1}, 8756 independent (R_{int}=0.037) and 6871 observed reflections [$I \ge 2\sigma(I)$], 545 refined parameters, R=0.054, wR^2=0.137, max. residual electron density 1.11 (−0.49) e Å^{-3} close to S, Flack parameter 0.01(2), two almost identical molecules in the asymmetric unit, hydrogens calculated and refined as riding atoms.

4.4.6. Crystal data for *tu*-3i. Formula $C_{25}H_{35}NO_4S$, M=445.60, colourless crystal 0.50×0.20×0.05 mm^3, a=10.748(0), b=10.989(1), c=11.308(1) Å, β=117.34(1)°, V=1186.4(2) Å^3, ρ_{calc}=1.247 g cm^{-3}, μ=14.55 cm^{-1}, empirical absorption correction via ψ scan data ($0.530 \le T \le 0.931$), Z=2, monoclinic, space group $P2_1$ (No. 4), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 2679 reflections collected ($\pm h,-k,-l$), [(sin θ)/λ]=0.62 Å^{-1}, 2553 independent (R_{int}=0.047) and 1813 observed reflections [$I \ge 2\sigma(I)$], 285 refined parameters, R=0.052, wR^2=0.122, max. residual electron density 0.34 (−0.51) e Å^{-3}, Flack parameter 0.03(3), hydrogens calculated and refined as riding atoms.

4.4.7. Crystal data for *cu*-3j. Formula $C_{21}H_{29}NO_4S$, M=391.51, colourless crystal 0.25×0.10×0.10 mm^3, a=14.047(4), b=9.959(2), c=15.269(3) Å, β=108.27(2)°, V=2028.4(8) Å^3, ρ_{calc}=1.282 g cm^{-3}, μ=16.30 cm^{-1}, empirical absorption correction via ψ scan data ($0.686 \le T \le 0.854$), Z=4, monoclinic, space group $P2_1/c$ (No. 14), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 4292 reflections collected ($\pm h,+k,+l$), [(sin θ)/λ]=0.62 Å^{-1}, 4128 independent (R_{int}=0.029) and 3549 observed reflections [$I \ge 2\sigma(I)$], 247 refined parameters, R=0.037, wR^2=0.097, max. residual electron density 0.29 (−0.33) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.4.8. Crystal data for *cl*-3j. Formula $C_{21}H_{29}NO_4S$, M=391.51, colourless crystal 0.70×0.50×0.30 mm^3, a=13.793(2), b=10.545(2), c=14.527(3) Å, β=105.45(2)°, V=2036.6(6) Å^3, ρ_{calc}=1.277 g cm^{-3}, μ=16.24 cm^{-1}, empirical absorption correction via ψ scan data ($0.396 \le T \le 0.642$), Z=4, monoclinic, space group $P2_1/c$ (No. 14), λ=1.54178 Å, T=223 K, $\omega/2\theta$ scans, 8394 reflections collected ($\pm h,\pm k,+l$), [(sin θ)/λ]=0.62 Å^{-1}, 4157 independent (R_{int}=0.049) and 3562 observed reflections [$I \ge 2\sigma(I)$], 247 refined parameters, R=0.044, wR^2=0.116, max. residual electron density 0.37 (−0.31) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.4.9. Crystal data for *cu*-3k. Formula $C_{21}H_{29}NO_4S$, M=391.51, colourless crystal 0.25×0.20×0.15 mm^3, a=10.178(1), b=10.610(1), c=19.318(2) Å, β=101.75(1)°, V=2042.4(3) Å^3, ρ_{calc}=1.273 g cm^{-3}, μ=16.19 cm^{-1}, empirical absorption correction via ψ scan data

($0.688 \le T \le 0.793$), $Z=4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 4304 reflections collected ($\pm h,+k,-l$), [(sin θ)/λ]=0.62 Å^{-1}, 4174 independent ($R_{int}=0.021$) and 3128 observed reflections [$I \ge 2\sigma(I)$], 246 refined parameters, $R=0.041$, $wR^2=0.106$, max. residual electron density 0.21 (−0.45) e Å^{-3}, hydrogens calculated and refined as riding atoms.

4.4.10. Crystal data for *cl*-3l. Formula $C_{23}H_{33}NO_4S$, $M=419.56$, colourless crystal 0.25×0.20×0.10 mm^3, $a=10.087(3)$, $b=11.272(4)$, $c=19.863(3)$ Å, $V=2258.4(8)$ Å^3, $\rho_{calc}=1.234$ g cm^{-3}, $\mu=14.96$ cm^{-1}, empirical absorption correction via ψ scan data ($0.706 \le T \le 0.865$), $Z=4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 2607 reflections collected ($+h,+k,+l$), [(sin θ)/λ]=0.62 Å^{-1}, 2607 independent and 1791 observed reflections [$I \ge 2\sigma(I)$], 267 refined parameters, $R=0.047$, $wR^2=0.111$, max. residual electron density 0.20 (−0.26) e Å^{-3}, Flack parameter 0.07(4), hydrogens calculated and refined as riding atoms.

4.4.11. Crystal data for *cu*-3m. Formula $C_{25}H_{29}NO_4S$, $M=439.55$, colourless crystal 0.45×0.20×0.10 mm^3, $a=8.010(1)$, $b=8.542(3)$, $c=32.041(3)$ Å, $V=2192.3(8)$ Å^3, $\rho_{calc}=1.332$ g cm^{-3}, $\mu=15.74$ cm^{-1}, empirical absorption correction via ψ scan data ($0.538 \le T \le 0.859$), $Z=4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 2575 reflections collected ($-h,-k,-l$), [(sin θ)/λ]=0.62 Å^{-1}, 2575 independent and 2277 observed reflections [$I \ge 2\sigma(I)$], 283 refined parameters, $R=0.053$, $wR^2=0.134$, max. residual electron density 0.35 (−0.44) e Å^{-3}, Flack parameter −0.05(4), hydrogens calculated and refined as riding atoms.

4.4.12. Crystal data for *cu*-3n. Formula $C_{20}H_{27}NO_4S$, $M=377.49$, colourless crystal 0.35×0.15×0.10 mm^3, $a=9.834(2)$, $b=12.360(2)$, $c=16.166(3)$ Å, $V=1964.9(6)$ Å^3, $\rho_{calc}=1.276$ g cm^{-3}, $\mu=16.64$ cm^{-1}, empirical absorption correction via ψ scan data ($0.594 \le T \le 0.851$), $Z=4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda=1.54178$ Å, $T=223$ K, $\omega/2\theta$ scans, 2290 reflections collected ($-h,+k,+l$), [(sin θ)/λ]=0.62 Å^{-1}, 2290 independent and 2150 observed reflections [$I \ge 2\sigma(I)$], 237 refined parameters, $R=0.033$, $wR^2=0.092$, max. residual electron density 0.24 (−0.26) e Å^{-3}, Flack parameter 0.04(2), hydrogens calculated and refined as riding atoms.

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1997), graphics MOPICT 3.2 (Brüggemann, M., Universität Münster, 2001). Crystallographic data (excluding structure factors) for structures *cis*-**2c**, *cu*-**3f**, *cl*-**3d**, *cl*-**3g**, *tl*-**3g**, *tu*-**3i**, *cu*-**3j**, *cl*-**3j**, *cu*-**3k**, *cl*-**3l**, *cu*-**3m** and *cu*-**3n** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-166227, CCDC-166228, CCDC-166229, CCDC-166230, CCDC-166231, CCDC-166232, CCDC-166233, CCDC-166234, CCDC-166235, CCDC-166236, CCDC-166237 and CCDC-166238. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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