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Norpseudoephedrine-Derived 2-Methoxy-3-sulfonyl-1,3-oxazolidines: Chiral, Highly Diastereoselective Formyl Cation Equivalents

Kilian Conde-Frieboes, Dieter Hoppe*

Institut für Organische Chemie der Universität Kiel, Olshausenstr. 40, D-2300 Kiel, Germany

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Abstract: *(2S,4R,5R)-2-Methoxy-4-methyl-3-(4-methylbenzenesulfonyl)-5-phenyl-1,3-oxazolidine (2c) adds trimethylsilyl 1-cycloalkenyl ethers under Lewis acid catalysis with complete induced and high simple diastereoselectivity to yield homochiral oxazolidine-masked 2-formylalkanones.*

Key words: 2-methoxy-1,3-oxazolidine, enantioselective formylation, chiral 2-formylcycloalkanones.

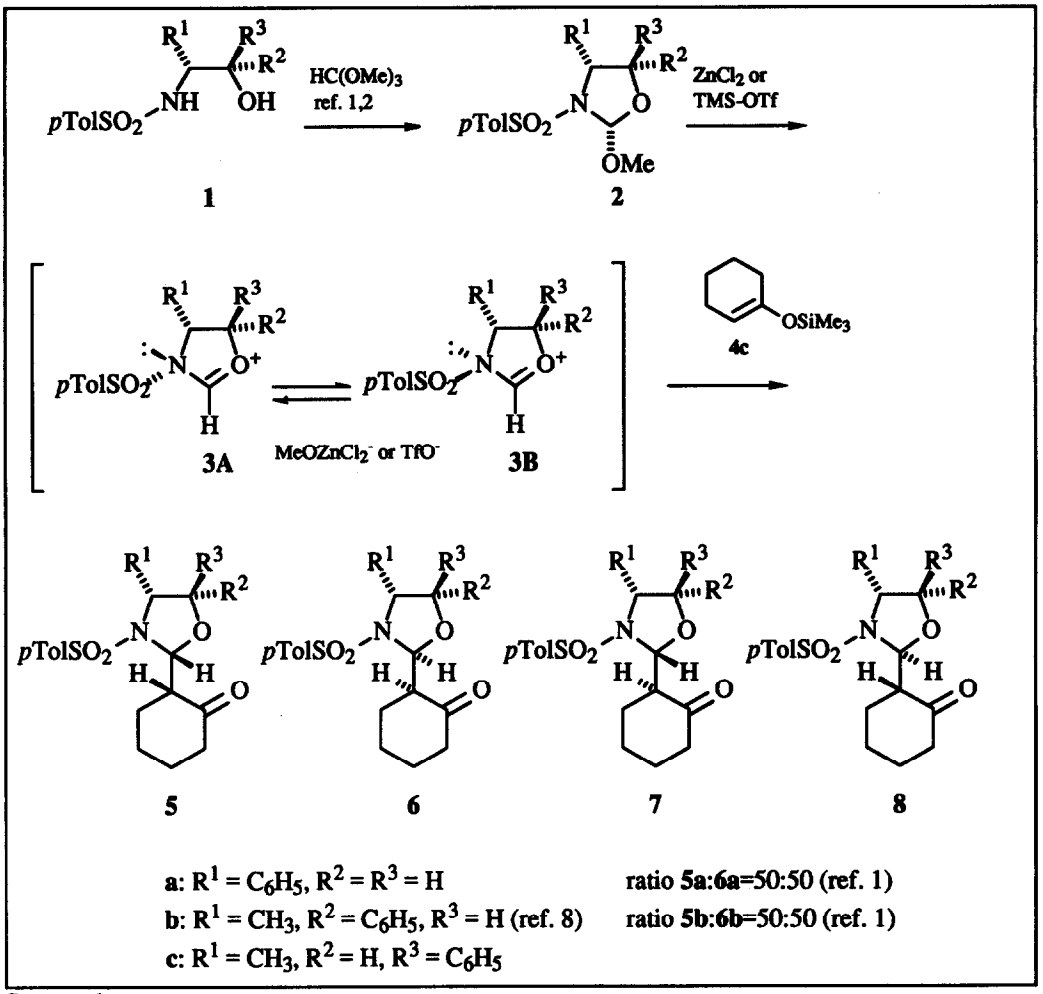
Recently, we[1] and others[2] introduced 2-methoxy-3-(*p*-toluenesulfonyl)-1,3-oxazolidines **2**,[3,4] derived from enantiomerically pure β-aminoalkanols like phenylglycinol (**1a**) or norephedrine (**1b**), as reagents for the asymmetric formylation[5] of silyl enol ethers and allylsilanes.

The Lewis-acid mediated condensation of **1a** or **1b** with 1-trimethylsilyloxy-cyclohexene affords out of the four possible diastereomers only **5a,b** and **6a,b** in an equal ratio.[1] From this result it must be concluded, that the simple diastereoselectivity is perfect, but the diastereofacial selectivity (which is expressed in the *cis* or *trans* relationship between C-2 and C-4) is poor.

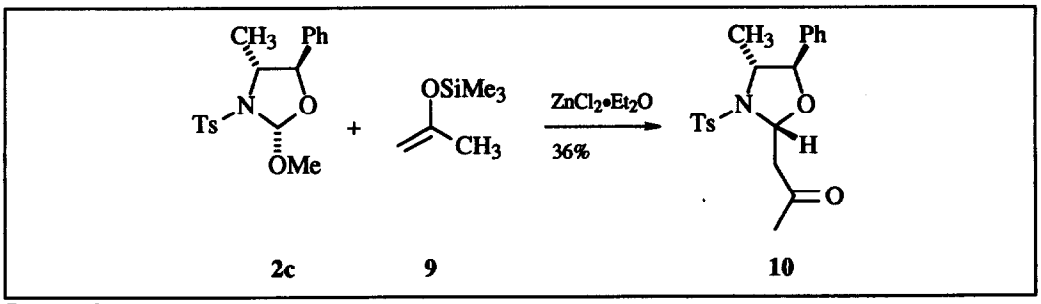
For an explanation, we assume that the intermediate cation exists as a mixture of rapidly equilibrating conformational isomers **3A** and **3B**, that differ in the configuration at the pyramidal nitrogen atom and where **3B** is favoured by the influence of the large substituent R^1. As a result, the steric differentiation of the nucleophile between the "front" and the "rear" face of the cation is low. On the base of our working hypothesis we concluded, that the introduction of a *small* substituent R^1 and a *large* substituent R^3 should suffice to shift the equilibrium of the cations in favour of **3B**. The shielding of the rear face is diminished and, thus, the formation of the *cis*-diastereomer **5c** in the nucleophilic addition step is supported.

The 2-methoxy-1,3-oxazolidine **2c** was obtained by the usual method[1] from the *p*-toluenesulfonamide **1c** of (1*R*,2*R*)-norpseudoephedrine as a single diastereomer with 100% yield. The assumption was impressively confirmed by the reaction of 2-trimethylsilyloxy-propene (**9**) with **2c**: The 2,4-*cis*-oxazolidine **10** was obtained with complete stereoselectivity, whereas **2b** furnishes the appropriate *trans*-isomer as the major product[1] (Scheme 2).

The condensation of **2c** with the cyclic prostereogenic silyl enol ether **4c** also gave rise to the formation of the diastereomer **5c** with 91% yield and >95% *ds*. Table 1 collects the results obtained with further cyclic silyl enol ethers.[6] It demonstrates, that in several cases both of the *cis*-diastereomers **5** and **7** are formed, although with different ratios. These arise from two competing diastereomorphous transition states **A** and **B** (Scheme 3).

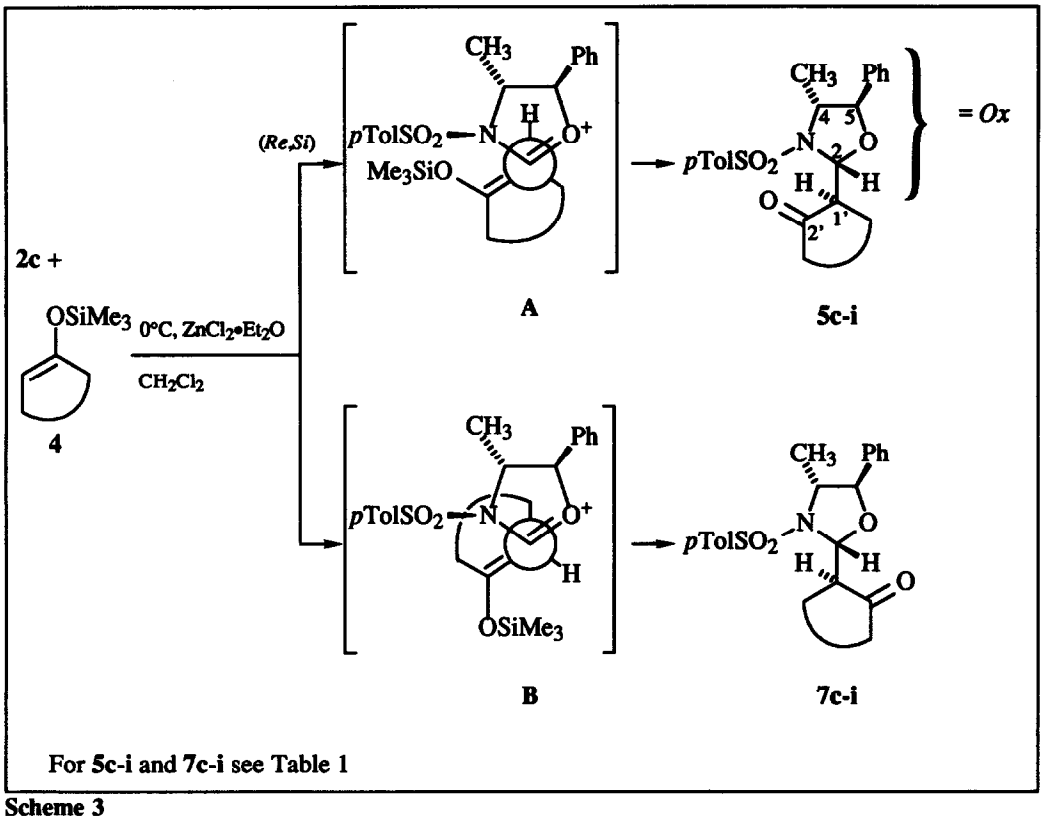


Scheme 1



Scheme 2

The stereochemical assignments of cyclohexanone **5c** and cyclopentanone **5d** base on NMR spectroscopical comparision with several analogues[1,3c] (Table 2). The assignment of the configuration for the 2-methylcyclohexanone derivative **5e** was concluded from its NMR spectra showing a stronger low-field shift

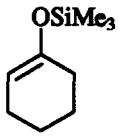
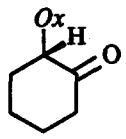
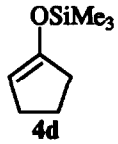
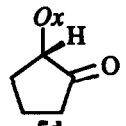
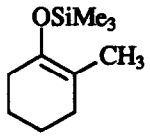
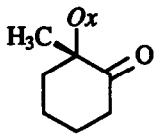
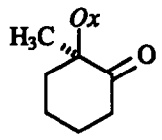
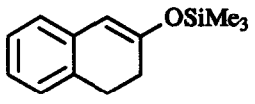
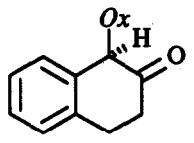
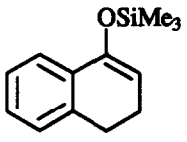
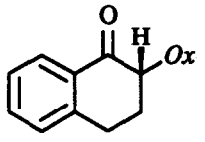
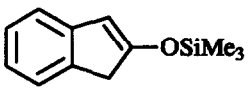
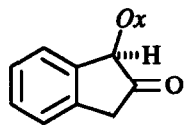
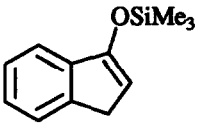
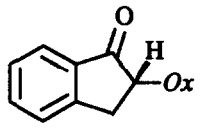


Scheme 3

for 2-H (6.11 ppm) and for C-2 (95.5 ppm) than recorded for the diastereomer **7e** (5.88 and 93.8). A similar trend is observed for the pair **5c** and **7c**.[7] The major diastereomer of the 2-tetralones was found to have the stereostructure **7f** on the base of a NOESY NMR experiment, revealing a synperiplanar relationship between the 2-H and 1'-H atom, which is unlikely to occur in the preferred conformation of diastereomer **5f**. From this results is to conclude that the unsubstituted cycloalkenyl trimethylsilyl ethers, like **4c** or **4d**, favour transition state **A** over **B** (Scheme 3). Here, besides minimized steric interaction in the antiperiplanar arrangement of the positively charged double bonds, a favourable dipol attraction between the negative oxygen atoms at the sulfonyl group and the positive carbon atom C-2' might play an important role. An additional methyl group in the enol ether **4e** increases the relative energy of transition state **A** by steric reasons.

The surprising preference of the silyl enol ethers **4f-i** to the formation of the diastereomers **7** through transition state **B** is surprising. Presumably, the origin is an attractive interaction of the benzene ring with the tosyl group. This can be better understood for the 1-indanone and 1-tetralone derivatives **4g** and **4i** than for the their isomers **4f** and **4h**, because a positive partial charge is developed in the aromatic ring of the first series. Compounds **5** and **7** constitute enantiomerically protected α-formyl-cycloalkanones, for which a high diastereofacial selectivity has been demonstrated for various nucleophilic and electrophilic substitution reactions, e.g. carbonyl additions,[3a] aldol reactions,[3b] Diels-Alder additions, and others. Thus, these compounds represent valuable intermediates for the synthesis of homochiral cycloalkane derivatives with few steps and high efficiency.

Table 1: Ketones 5 and 7 Prepared from the 2-Methoxy-1,3-oxazolidine 2c

Educt	Products[a]	Yield(%)	Ratio 5:7 [b]	$[\alpha]_D^{20}$, major product[c]
 **4c**	 **5c**	91[d]	>95:5	+2.0
 **4d**	 **5d**	75[d]	90:10	+51.5
 **4e**	 **5e**  **7e**	78[e]	50:50	**5e**: -19.0 **7e**: -52.5
 **4f**	 **7f**	77[d]	20:80	-139.2
 **4g**	 **7g**	52[d]	20:80	+53.0
 **4h**	 **7h**	46[d]	<5:95	-68.3
 **4i**	 **7i**	51[d]	<5:95	+63.0

a) For *Ox* see Scheme 2. b) Determined ^{1}H-NMR spectroscopically from the crude product.
c) c = 0.5-1.5, CH_2Cl_2. d) After crystallization from ether. e) After LC separation.

Table 2: Comparison of Selected NMR Data of Ketones 5 and 7 (in $CDCl_3$, 300 MHz (^1H) and 75 MHz (^{13}C), δ)

	5c	7c	5d	7g	5g	7f	7i	7h
5-H	4.68	4.60	4.74	4.80	4.72	3.80	4.82	3.93
$J_{5,4}$	5.1 Hz	7.9 Hz	4.6 Hz	7.1 Hz	4.5 Hz	6.7 Hz	6.9 Hz	6.8 Hz
4-H	3.54	3.33	3.59	3.43	3.67	3.26	3.51	3.26
2-H	5.81	5.88	5.58	5.91	6.10	5.82	5.63	5.64
$J_{2,1'}$	2.6 Hz	9.1 Hz	2.6 Hz	7.8 Hz	2.3 Hz	3.4 Hz	5.7 Hz	3.5 Hz
1'-H	3.15	2.78	3.03	3.01[a]	3.39[a]	4.08	3.23[a]	4.17
5-Ph[b]	6.88	6.56	6.81	6.62	6.91	6.64	6.71	6.71
C-5	85.8	85.4	85.7	85.3	85.5	85.8	85.6	85.9
C-4	62.4	63.1	62.4	62.9	62.6	62.5	63.1	62.7
C-2	90.0	91.0	90.9	90.6	90.9	95.3	92.0	93.0
C-1'	55.5	54.3	54.8	51.2	52.9	59.0	51.7	59.1

[a] 2'-H. [b] *ortho*-protons of the phenyl group.

Experimental

CH_2Cl_2 and triethylamine were distilled from CaH_2 under Ar atmosphere. ^1H- and ^{13}C-NMR spectra were recorded on Bruker AM 300 and AM 200 spectrometer. IR spectra were recorded on Perkin-Elmer 283b spectrophotometer. Optical rotations were recorded on Perkin-Elmer 241 polarimeter.

The silyl enol ethers **4c-i** and **9** were prepared according to literature procedures.[5]

(1'R,2'R)-N-(2-Hydroxy-1-methyl-2-phenylethyl)-4-methylbenzenesulfonamide (**1c**): To a suspension of (1*R*,2*R*)-norpseudoephedrine hydrochloride (18.8 g, 0.10 mol) and triethylamine (30.0 ml, 0.22 mol) in CH_2Cl_2 (250 ml) at 0°C, 21.0 g (0.11 mol) *p*-toluenesulfonyl chloride in CH_2Cl_2 (150 ml) is slowly added and stirring continued for 14 h. After aqueous work-up (400 ml of water, followed by 400 ml of sat. aq. NaCl), **1c** was crystallized from ether/CH_2Cl_2 - yield 27.2 g (89%), mp 119°C, $[\alpha]_D^{20}$ = -35.3 (c = 1.2, CH_2Cl_2).

IR (KBr): 3495 (OH), 3305 (NH), 1310, 1150 cm^{-1} (SO_2).
200 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.64 (m, 2H, tosyl), 7.28-7.17 (m, 7H, tosyl and 2-Ph), 5.34 (d, 1H, NH, $J_{NH,1}$ = 7.7 Hz), 4.43 (dd, 1H, 2-H, $J_{2,1}$ = 6.6 Hz, $J_{2,OH}$ = 3.1 Hz), 3.39 (qdd, 1H, 1-H, $J_{1,methyl}$ = 6.6 Hz), 3.20 (d, 1H, OH), 2.38 (s, 3H, tosyl-CH_3), 0.90 (d, 3H, 1-CH_3).
50 MHz-^{13}C-NMR ($CDCl_3$): δ = 143.1 (tosyl-4), 140.3 (2-Ph), 137.3 (tosyl-1), 129.5 (2C, tosyl), 128.2 (2C, tosyl), 127.8 (2-Ph), 126.9 (2C, 2-Ph), 126.6 (2C, 2-Ph), 76.9 (C-2), 55.6 (C-1), 21.3 (tosyl-CH_3), 17.8 (1-CH_3).
$C_{16}H_{19}NO_3S$ (305.40) Calc.: C 62.93 H 6.27 Found: C 62.81 H 6.19.

(2S,4R,5R)-2-Methoxy-4-methyl-3-(4-methylbenzenesulfonyl)-5-phenyl-1,3-oxazolidine (**2c**): A solution of sulfonamide **1c** (30.5 g, 0.10 mol) in trimethyl orthoformate (250 ml) and methanesulfonic acid (1 ml) were stirred at 15°C for 1 h. Solid K_2CO_3 (10 g) is added and the salt filtered off by suction. The solvent was evaporated in vacuum yielding 34.7 g (100%) of **2c** as a single diastereomer. The oily product was used without further purification; the analytical sample was obtained by LC on silica gel with ether/pentane (1:1).
$[\alpha]_D^{20}$ = -58.2 (c = 0.8, CH_2Cl_2).
IR (Film): 1350, 1160 cm^{-1} (SO_2).
300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.76 (m, 2H, tosyl), 7.40-7.20 (m, 5H, tosyl and 5-Ph), 6.84 (m, 2H, 5-Ph), 6.12 (s, 1H, 2-H), 4.84 (d, 1H, 5-H, $J_{5,4}$ = 8.0 Hz), 3.38 (s, 3H, CH_3-O), 3.47 (qd, 1H, 4-H, $J_{4,methyl}$ = 6.2 Hz), 2.49 (s, 3H, tosyl-CH_3), 1.39 (d, 3H, 4-CH_3).
75 MHz-^{13}C-NMR ($CDCl_3$): δ = 144.1 (tosyl-4), 136.8 (5-Ph), 135.5 (tosyl-1), 129.5 (2C, tosyl), 128.7 (5-Ph), 128.5 (2C, tosyl), 127.8 (2C, 5-Ph), 126.4 (2C, 5-Ph), 108.6 (C-2), 85.8 (C-5), 62.0 (C-4), 53.7 (CH_3-O), 21.5 (tosyl-CH_3), 18.7 (4-CH_3).
$C_{20}H_{21}NO_4S$ (347.44) Calc.: C 62.23 H 6.09 Found: C 62.33 H 6.17.

Lewis-Acid Mediated Condensation[1] of 2c with Silyl Enol Ethers; General Procedure:
To a solution of the 2-methoxy-1,3-oxazolidine **2c** (1.04 g, 3.0 mmol) and silyl enol ether **4** (3.3 mmol) in CH_2Cl_2, kept at 0°C, a 2.2M solution of $ZnCl_2$•Et_2O in CH_2Cl_2 (1.5 ml, 3.3 mmol) is added and stirring is continued at 0°C for 1 h. For work-up, sat. aq. NaCl (10 ml) is added and the aq. layer extracted with CH_2Cl_2 (2x20 ml). The CH_2Cl_2 solutions are dried with Na_2SO_4, the solvent is evaporated and the residue purified by crystallization from ether or chromatographed on silica gel with ether/pentane (1:2).

*(2R,4R,5R)-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(2-oxo-propyl)-5-phenyl-1,3-oxazolidine (**10**)*
With **9**, yield 36%, after LC.
$[\alpha]_D^{20}$ = -69.7 (c = 1.16, CH_2Cl_2).
IR (KBr): 1710 (C=O), 1345, 1160 (SO_2).
mp = 118°C (ether/pentane).
200 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.68 (m, 2H, tosyl), 7.31-7.10 (m, 5H, tosyl and 5-Ph), 6.81 (m, 2H, 5-Ph), 5.79 (ABX, 1H, 2-H, $J_{2,1'}$ = 4.3 Hz, $J_{2,1}$ = 7.5 Hz), 4.66 (d, 1H, 5-H, $J_{5,4}$ = 6.8 Hz), 3.38 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.3 Hz), 3.07 (ABX, 2H, 1'-H, J_{gem} = 16.3 Hz), 2.46 (s, 3H, CH_3-tosyl), 2.24 (s, 3H, CH_3-2').
50 MHz-^{13}C-NMR ($CDCl_3$): δ = 204.5 (C-2'), 144.3 (tosyl-4), 137.1 (5-Ph), 133.1 (tosyl-1), 129.9 (2C, tosyl), 128.5 (2C, tosyl), 128.3 (5-Ph), 128.0 (2C, 5-Ph), 126.00 (2C, 5-Ph), 88.5 (C-2), 85.3 (C-5), 62.6 (C-4), 50.4 (C-1'), 30.8 (C-3'), 21.5 (tosyl-CH_3), 19.9 (4-CH_3).
$C_{20}H_{23}NO_4S$ (373.47) Calc.: C 64.32 H 6.21 Found: C 64.28 H 6.25.

[2R,4R,5R,2(1R)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(2-oxo-cyclohexyl)-5-phenyl-1,3-oxazolidine (5c)
With **4c**, yield 91%, after crystallization.
$[\alpha]_D^{20}$ = +2.0 (c = 1.2, CH_2Cl_2).
IR (KBr): 1700 (C=O), 1340, 1165 cm^{-1} (SO_2).
mp = 163°C (ether).
300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.55 (m, 2H, tosyl), 7.19-7.08 (m, 5H, 5-Ph and tosyl), 6.89 (m, 2H, 5-Ph), 5.81 (d, 1H, 2-H, $J_{2,1'}$ = 2.6 Hz), 4.68 (d, 1H, 5-H, $J_{5,4}$ = 5.1 Hz), 3.54 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 3.15 (m, 1H, 1'-H), 2.39 (s, 3H, tosyl-CH_3), 2.57-2.31, 2.10-1.95 and 1.89-1.69 (m, 8H, cyclohexyl), 1.50 (d, 3H, 4-CH_3).
50 MHz-^{13}C-NMR ($CDCl_3$): δ = 209.8 (C-2'), 144.0 (tosyl-4), 138.2 (5-Ph), 132.5 (tosyl-1), 129.7 (2C, tosyl), 128.5 (2C, tosyl), 128.0 (2C, 5-Ph), 127.6 (5-Ph), 125.4 (2C, 5-Ph), 90.0 (C-2), 85.8 (C-5), 62.4 (C-4), 55.5 (C-1'), 42.0 (C-3'), 26.8 (C-6'), 25.7 (C-5'), 24.1 (C-4'), 21.5 (tosyl-CH_3), 20.5 (4-CH_3).
$C_{23}H_{27}NO_4S$ (413.53) Calc.: C 66.80 H 6.58 Found: C 66.97 H 6.39.

[2R,4R,5R,2(1R)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(2-oxo-cyclopentyl)-5-phenyl-1,3-oxazolidine (5d)
With **4d**, yield 75%, after crystallization.
$[\alpha]_D^{20}$ = +51.5 (c = 1.1, CH_2Cl_2).
IR (KBr): 1735 (C=O), 1345, 1165 cm^{-1} (SO_2).
mp = 120°C (ether).
300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.55 (m, 2H, tosyl), 7.15-7.08 (m, 5H, tosyl, 5-Ph), 6.81 (m, 2H, 5-Ph), 5.58 (d, 1H, 2-H, $J_{2,1'}$ = 2.6 Hz), 4.74 (d, 1H, 5-H, $J_{5,4}$ = 4.6 Hz), 3.59 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 3.03 (m, 1H, 1'-H), 2.38 (s, 3H, tosyl), 2.40-1.98 and 1.91-1.80 (m, 6H, cyclopentyl), 1.53 (d, 3H, 4-CH_3).
50 MHz-^{13}C-NMR ($CDCl_3$): δ = 216.9 (C-2'), 144.0 (tosyl-4), 138.2 (5-Ph), 132.5 (tosyl-1), 129.7 (2C, tosyl), 128.5 (2C, 5-Ph), 127.8 (2C, tosyl), 127.6 (5-Ph), 125.3 (2C, 5-Ph), 90.9 (C-2), 85.7 (C-5), 62.4 (C-4), 54.8 (C-1'), 38.9 (C-3'), 23.5 (C-5'), 21.5 (tosyl-CH_3), 20.8 (4-CH_3), 20.5 (C-4').
$C_{22}H_{25}NO_4S$ (399.51) Calc.: C 66.14 H 6.31 Found: C 66.25 H 6.45.

[2R,4R,5R,2(1R)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(1-methyl-2-oxo-cyclohexyl)-5-phenyl-1,3-oxazolidine (5e)
With **4e**, yield 39%, after LC.
$[\alpha]_D^{20}$ = -19.0 (c = 1.1, CH_2Cl_2).
IR (KBr): 1700 (C=O), 1340, 1160 cm^{-1} (SO_2).
mp = 134°C (ether/pentane).
300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.75 (m, 2H, tosyl), 7.34 (m, 2H, tosyl), 7.22-7.09 (m, 3H, 5-Ph), 6.64 (m, 2H, 5-Ph), 6.11 (s, 1H, 2-H), 4.76 (d, 1H, 5-H, $J_{5,4}$ = 7.3 Hz), 3.55 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 2.68-2.48, 2.21-2.14 and 1.92-1.70 (m, 8H, cyclohexyl), 2.49 (s, 3H, tosyl-CH_3), 1.39 (d, 3H, 4-CH_3), 1.36 (s, 3H, 1'-CH_3).
75 MHz-^{13}C-NMR ($CDCl_3$): δ = 212.4 (C-2'), 144.2 (tosyl-4), 138.8 (5-Ph), 133.4 (tosyl-1), 129.8 (2C, tosyl), 128.6 (2C, tosyl), 128.3 (2C, 5-Ph), 128.1 (5-Ph), 125.7 (2C, 5-Ph), 95.5 (C-2), 87.4 (C-5), 64.2 (C-4), 55.3 (C-1'), 39.6 (C-3'), 34.5 (C-6'), 26.3 (C-5'), 21.5 (tosyl-CH_3), 20.7 (C-4'), 20.7 (1'-CH_3), 18.9 (4-CH_3).
$C_{24}H_{29}NO_4S$ (427.56) Calc.: C 67.42 H 6.84 Found: C 67.54 H 6.98.

[2R,4R,5R,2(1S)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(1-methyl-2-oxo-cyclohexyl)-5-phenyl-1,3-oxazolidine (7e)

With **4e**, yield 39%, after LC.

$[\alpha]_D^{20}$ = -52.5 (c = 1.2, CH_2Cl_2).

IR (KBr): 1700 (C=O), 1340, 1160 cm^{-1} (SO_2).

mp = 133°C (ether/pentane).

300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.70 (m, 2H, tosyl), 7.34 (m, 2H, tosyl), 7.20-7.08 (m, 3H, 5-Ph), 6.64 (m, 2H, 5-Ph), 5.88 (s, 1H, 2-H), 4.66 (d, 1H, 5-H, $J_{5,4}$ = 7.0 Hz), 3.54 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 2.63-2.39, 2.10-1.95 and 1.89-1.72 (m, 8H, cyclohexyl), 2.49 (s, 3H, tosyl-CH_3), 1.48 (d, 3H, 4-CH_3), 1.31 (s, 3H, 1'-CH_3).

50 MHz-^{13}C-NMR ($CDCl_3$): δ = 211.7 (C-2'), 144.3 (tosyl-4), 138.2 (5-Ph), 133.2 (tosyl-1), 129.9 (2C, tosyl), 128.4 (2C, tosyl), 128.2 (2C, 5-Ph), 128.2 (5-Ph), 125.9 (2C, 5-Ph), 93.8 (C-2), 86.3 (C-5), 64.2 (C-4), 54.6 (C-1'), 40.1 (C-3'), 36.3 (C-6'), 26.7 (C-5'), 21.5 (tosyl-CH_3), 21.2 (C-4'), 21.1 (1'-CH_3), 18.5 (4-CH_3).

$C_{24}H_{29}NO_4S$ (427.56) Calc.: C 67.42 H 6.84 Found: C 67.54 H 6.98.

[2R,4R,5R,2(1S)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(2-oxo-1,2,3,4-tetrahydronaphth-1-yl)-5-phenyl-1,3-oxazolidine (7f)

With **4f**, yield 77%, after crystallization.

$[\alpha]_D^{20}$ = -139.2 (c = 0.8, CH_2Cl_2).

IR (KBr): 1710 (C=O), 1350, 1165 cm^{-1} (SO_2).

mp = 147°C (ether/pentane).

300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.70 (m, 2H, tosyl), 7.57 (m, 1H, 9'-H), 7.49-7.07 (m, 8H, phenyl and tosyl), 6.64 (m, 2H, 5-Ph), 5.82 (d, 1H, 2-H, $J_{2,1'}$ = 3.4 Hz), 4.08 (d, 1H, 1'-H), 3.80 (d, 1H, 5-H, $J_{5,4}$ = 6.7 Hz), 3.30 (m, 1H, 4'α-H), 3.26 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 2.84 (m, 1H, 4'β-H), 2.75 (m, 1H, 3'α-H), 2.50 (m, 1H, 3'β-H), 2.43 (s, 3H, tosyl-CH_3), 0.93 (d, 3H, 4-CH_3).

50 MHz-^{13}C-NMR ($CDCl_3$): δ = 210.4 (C-2'), 144.3 (tosyl-4), 138.5 (C-10'), 137.4 (5-Ph), 132.7 (C-9'), 132.9 (tosyl-1), 132.3 (C-5'), 129.8 (2C, tosyl), 128.5 (2C, tosyl), 128.3 (C-8'), 128.1 (C-7'), 128.0 (2C, 5-Ph), 127.8 (5-Ph), 126.4 (C-6'), 125.8 (5-Ph), 95.3 (C-2), 85.8 (C-5), 62.5 (C-4), 59.0 (C-1'), 39.1 (C-3'), 27.2 (C-4'), 21.5 (tosyl-CH_3), 18.3 (4-CH_3).

$C_{27}H_{27}NO_4S$ (461.58) Calc.: C 70.26 H 5.90 Found: C 70.14 H 5.85.

[2R,4R,5R,2(2S)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(1-oxo-1,2,3,4-tetrahydronaphth-2-yl)-5-phenyl-1,3-oxazolidine (7g)

With **4g**, yield 52%, after crystallization.

$[\alpha]_D^{20}$ = +53.0 (c = 1.0, CH_2Cl_2).

IR (KBr): 1670 (C=O), 1340, 1165 cm^{-1} (SO_2).

mp = 163°C (ether/pentane).

300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.99 (dd, 1H, 9'-H, $J_{9',7'}$ = 1.5 Hz, $J_{9',8'}$ = 8.2 Hz), 7.73 (m, 2H, tosyl), 7.50 (m, 1H, 7'-H), 7.34-7.07 (m, 7H, phenyl and tosyl), 6.62 (m, 2H, 5-Ph), 5.91 (d, 1H, 2-H, $J_{2,2'}$ = 7.8 Hz), 4.80 (d, 1H, 5-H, $J_{5,4}$ = 7.1 Hz), 3.43 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 3.34 (m, 1H, 4'-H), 3.09 (m, 1H, 3'-H), 3.01 (m, 1H, 2'-H), 2.53-2.40 (m, 2H, 3'-H and 4'-H), 2.48 (s, 3H, tosyl-CH_3), 1.52 (d, 3H, 4-CH_3).

75 MHz-^{13}C-NMR ($CDCl_3$): δ = 196.2 (C-1'), 144.0 (tosyl-4), 143.5 (C-10'), 137.4 (5-Ph), 133.4 (C-5'), 133.3 (C-9'), 132.4 (tosyl-1), 129.7 (2C, tosyl), 128.7 (5-Ph), 128.1 (4C, 5-Ph and tosyl), 128.0 (C-5'), 127.4 (C-7'),

126.5 (C-6'), 125.8 (2C, 5-Ph), 90.6 (C-2), 85.3 (C-5), 62.9 (C-4), 51.2 (C-2'), 27.0 (C-3'), 24.9 (C-4'), 21.4 (tosyl-CH_3), 19.9 (4-CH_3).
$C_{27}H_{27}NO_4S$ (461.58) Calc.: C 70.26 H 5.90 Found: C 70.17 H 5.96.

[2R,4R,5R,2(1S)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(2-oxo-indan-1-yl)-5-phenyl-1,3-oxazolidine (7h)
With **4h**, yield 46%, after crystallization.
$[\alpha]_D^{20}$ = -68.3 (c = 1.0, CH_2Cl_2).
IR (KBr): 1740 (C=O), 1350, 1160 cm^{-1} (SO_2).
mp = 127°C (ether).
200 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.85 (m, 1H, 8'-H), 7.71 (m, 2H, tosyl), 7.42-7.05 (m, 8H, 5-Ph, tosyl, 5'-H, 6'-H and 7'-H), 6.71 (m, 2H, 5-Ph), 5.64 (d, 1H, 2-H, $J_{2,1'}$ = 3.5 Hz), 4.17 (dt, 1H, 1'-H, $J_{1',3'}$ = 1.1 Hz), 3.93 (d, 1H, 5-H, $J_{5,4}$ = 6.8 Hz), 3.63 (dt, 1H, 3'-H, J_{gem} = 22.7 Hz), 3.46 (dt, 1H, 3'-H), 3.26 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.3 Hz), 2.44 (s, 3H, tosyl-CH_3), 1.30 (d, 3H, 4-CH_3).
50 MHz-^{13}C-NMR ($CDCl_3$): δ = 213.6 (C-2'), 144.4 (tosyl-4), 138.8 (5-Ph), 137.3 (C-4'), 137.0 (C-9'), 132.2 (tosyl-1), 129.9 (2C, tosyl), 128.5 (2C, 5-Ph), 128.4 (C-6'), 128.2 (C-7'), 128.1 (2C, tosyl), 127.9 (5-Ph), 127.0 (C-5'), 125.9 (2C, 5-Ph), 124.7 (C-8'), 93.0 (C-2), 85.9 (C-5), 62.7 (C-4), 59.1 (C-1'), 43.9 (C-3'), 21.5 (tosyl-CH_3), 18.1 (4-CH_3).
$C_{26}H_{25}NO_4S$ (447.55) Calc.: C 69.46 H 6.05 Found: C 69.47 H 5.98.

[2R,4R,5R,2(2S)]-4-Methyl-3-(4-methylbenzenesulfonyl)-2-(1-oxo-indan-2-yl)-5-phenyl-1,3-oxazolidine (7i)
With **4i**, yield 51%, after crystallization.
$[\alpha]_D^{20}$ = +63.0 (c = 1.2, CH_2Cl_2).
IR (KBr): 1705 (C=O), 1345, 1160 cm^{-1} (SO_2).
mp = 148°C (ether).
300 MHz-^{1}H-NMR ($CDCl_3$): δ = 7.76 (m, 1H, 8'-H), 7.67 (m, 2H, tosyl), 7.60 (m, 1H, 6'-H), 7.52 (m, 1H, 5'-H), 7.37 (m, 1H, 7'-H), 7.26 (m, 2H, tosyl), 7.19 (m, 1H, 5-Ph), 7.11 (m, 2H, 5-Ph), 6.71 (m, 2H, 5-Ph), 5.63 (d, 1H, 2-H, $J_{2,2'}$ = 5.7 Hz), 4.82 (d, 1H, 5-H, $J_{5,4}$ = 6.9 Hz), 3.61 (dd, 1H, 3'-H, J_{gem} = 17.2 Hz, $J_{3',2'}$ = 3.7 Hz), 3.51 (dq, 1H, 4-H, $J_{4,methyl}$ = 6.4 Hz), 3.37 (dd, 1H, 3'-H, $J_{3',2'}$ = 8.2 Hz), 3.23 (ddd, 1H, 2'-H), 2.44 (s, 3H, tosyl-CH_3), 1.54 (d, 3H, 4-CH_3).
75 MHz-^{13}C-NMR ($CDCl_3$): δ = 203.2 (C-1'), 153.1 (C-9'), 144.1 (tosyl-4), 137.5 (5-Ph), 136.7 (C-4'), 134.8 (C-8'), 133.4 (tosyl-1), 129.7 (2C, tosyl), 128.3 (2C, 5-Ph), 128.2 (2C, tosyl), 128.1 (5-Ph), 127.4 (C-6'), 126.6 (C-5'), 125.9 (2C), 123.9 (C-7'), 92.0 (C-2), 85.6 (C-5), 63.1 (C-4), 51.7 (C-2'), 29.3 (C-3'), 21.5 (tosyl-CH_3), 19.7 (4-CH_3).
$C_{26}H_{25}NO_4S$ (447.55) Calc.: C 69.79 H 5.63 Found: C 69.91 H 5.55.

References and Footnotes

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3. For further application of 3-sulfonyl-1,3-oxazolidines see:
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7. A sample of **7c** was obtained by base-catalyzed epimerization of **5c** by means of cesium carbonate.

8. Actually, the enantiomers of series **b** were prepared.[1,2]