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Asymmetric [2+2+1] cyclopentannulation of olefins. Ring expansion of 2-*N*-methyl-*N*-tosyl-cyclobutanone

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Abstract—α-*N*-Methyl-*N*-tosyl cyclobutanones **2** which had been previously prepared in good yields and high enantiomeric excesses from olefins and chiral keteniminium salts have been converted into the corresponding oxiranes **3** by reaction with dimethylsulfonium methylid. The stereochemistry of this reaction was found to be dependent on several factors which have been analyzed. Treatment of these oxiranes with a stoichiometric amount of lithium iodide in refluxing tetrahydrofuran gave excellent yields of monocyclic or fused cyclopentenones **4** resulting from a β-elimination of *N*-methyl-*N*-tosylamide from a primarily formed cyclopentanone. The ring-expansion was totally selective but for oxiranes attached to a bicyclo[4.2.0]octanone system. In all cases, the enantiomeric purities of the starting cyclobutanones were preserved throughout the sequence which thus represents a useful [2+2+1] strategy for the cyclopentannulation of olefins.

1. Introduction

Cyclobutanones and cyclobutenones are very useful intermediates which have found applications in total syntheses of complex molecular structures.[1] As a consequence of their high angle strain, the electrophilicity of the carbonyl group is enhanced and carbon-carbon bonds are weakened offering possibilities for mild and chemoselective cleavage of the four-membered ring. The cheapest and most general method to prepare these four-membered ring ketones involves a [2+2] cycloaddition of in situ generated ketenes or keteniminium salts.[2] The cycloaddition of ketenes with olefins bearing a chiral substituent[3] or the use of keteniminium salts derived from amides bearing a chiral auxiliary[4] have opened a practical route towards enantiomerically pure cyclobutanones and further extended their utility in synthesis.

Early studies of our laboratory have shown that the asymmetric cycloadditions of keteniminium salt **1** to 1,2-disubstituted olefins followed by a regioselective Baeyer–Villiger oxidation of the resulting cyclobutanone was a unique method for the enantioselective vicinal acylation of an olefin (Scheme 1).[5] More recently, we have examined the transformation of these enantiomerically enriched cyclobutanones into cyclopentenones.[6] We report herein the full details of these studies.

Keywords: cyclopentannulation; rearrangement; cyclobutanone; cyclopentenone.

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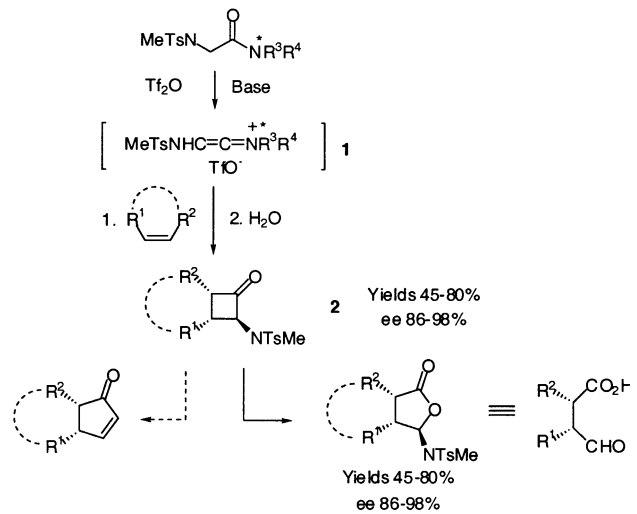
2. Results and discussion

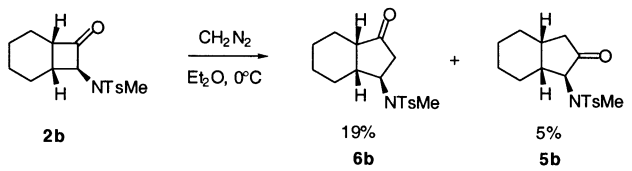
2.1. Preliminary results

The ring enlargement of cyclobutanones with diazomethane is well documented in spite of its limited preparative value.[1e] The regioselectivity of the reaction is subtly dependent on substitution at both α and β carbon atoms.[7] From our previous results on Baeyer–Villiger oxidation of **2**, we had anticipated that the reaction of **2b** with diazomethane would predominantly lead to regioisomer **6b**. This was indeed the case (Scheme 2). However bicyclo[4.2.0]octanone reacted sluggishly and yields were

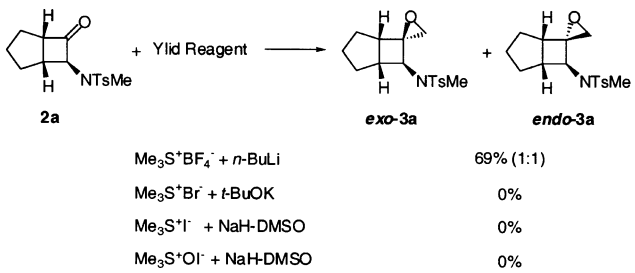


Scheme 1.

PII: S0040-4020(02)00694-4



Scheme 2.



Scheme 3.

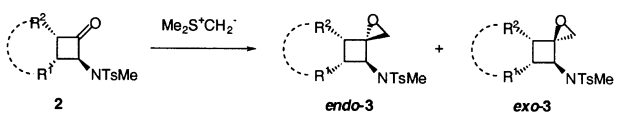
low. We therefore decided to study a sequence whereby we first generate an epoxide and then effect the rearrangement of this oxaspiropentane following the procedure developed by the groups of Leriverend and Trost.[8]

2.2. Synthesis of oxiranes

A preliminary study of the reaction of **2a** with sulfonium ylid reagents[9] showed that the reaction was only successful when the ylide was generated from trimethylsulfonium tetrafluoroborate and *n*-BuLi (Scheme 3). Other sources of dimethylsulfonium ylide or of the corresponding oxide gave complex reaction mixtures.

Thus a series of racemic and enantiomerically enriched α-*N*-methyl *N*-tosyl cyclobutanones **2a–j** (Table 1) previously prepared from the corresponding olefins have been converted into the corresponding oxiranes by treatment with dimethyl sulfonium ylid generated from trimethylsulfonium

Table 1. Preparation of oxiranes **3**



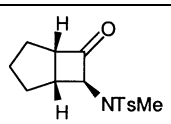
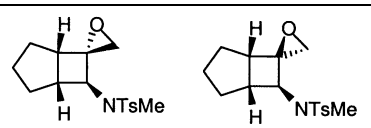
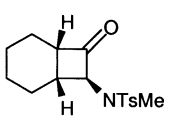
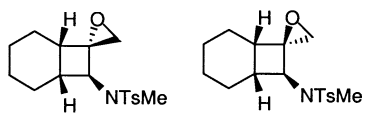
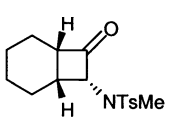
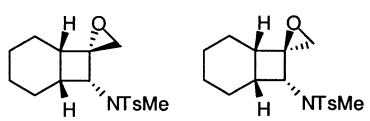
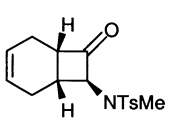
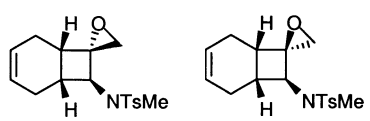
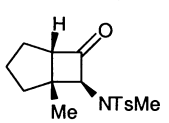
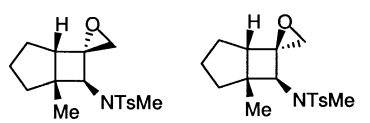
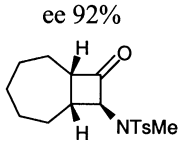
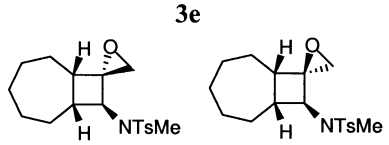
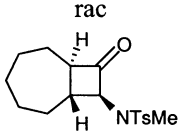
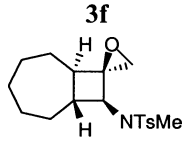
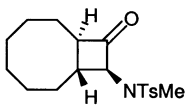
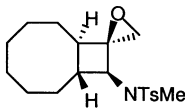
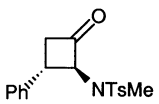
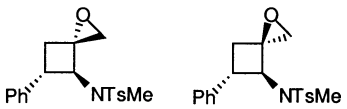
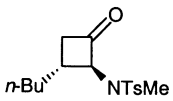
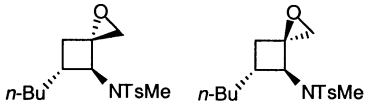
Entry	Cyclobutanone **2**	Oxirane **3**	*endo*:*exo*	Yield, % (ee%)
a	 ee 89%	 **3a**	1:1	69 (89)
b	 ee 92%	 **3b**	1.5:1	75 (92)
c	 rac	 **3c**	9:1	86
d	 ee 86%	 **3d**	6:1	72 (86)
e	 ee 92%	 **3e**	1:4	67 (92)
f	 rac	 **3f**	2.3:1	82
g	 ee 98%	 **3g**	–	71 (98)

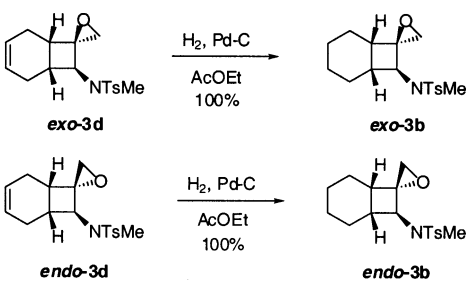
Table 1 (*continued*)

Entry	Cyclobutanone **2**	Oxirane **3**	*endo*:*exo*	Yield, % (ee%)
h	 ee 92%	 **3h**	–	59 (92)
i	 rac	 **3i**	1:9	81
j	 rac	 **3j**	1:9	61

tetrafluoroborate and *n*-BuLi (Table 1). *exo*- and *endo*-oxiranes could be easily separated by flash chromatography. Stereochemical assignments by ^{1}H NMR were not easy as the protons of the epoxide ring are too far away from the other ring to generate a significant nOe effect. The structure and stereochemistry of crystalline *exo*-**3a**, *exo*-**3b** and *exo*-**3e** were established by X-ray diffraction analysis.[10,11] In these compounds, the hydrogen geminal to the *N*TsMe group was deshielded with respect to that of the corresponding *endo*-isomers. The stereochemistry of compounds *exo*- and *endo*-**3d** was confirmed by hydrogenation to *exo*- and *endo*-**3b**, respectively (Scheme 4). By analogy, we tentatively assigned relative configurations for all oxiranes **3**.

Table 1 shows that oxiranes **3a**–**j** were formed in good to excellent yields. The facial selectivity can be rationalized by considering the approaches of the ylid reagent to the various cyclobutanones in their preferred conformation. The ^{1}H NMR spectra of cyclobutanones **2** showed fairly strong coupling between the proton at the ring junction and the neighbouring proton geminal to the *N*TsMe group and was in agreement with previous observations.[12] This indicated that the preferred conformations of the cyclobutanone ring are those shown in Fig. 1.

With *cis*-fused bicyclic ketones **2a**,**b**,**d**,**f** (A, Fig. 1), little selectivity was observed because both α and β faces are hindered. When the large *N*TsMe group sits on the α face as in **2c** (B), selectivity increased in favour of the *endo*-adduct *endo*-**3c**. The presence of a methyl group at the ring junction **2e** (C) further hides the β face and, as a result, the *exo*-adduct became the major isomer. With both the *trans*-fused bicyclic ketones **2g**–**h** (D) and the mono-substituted cyclobutanones **2i**–**j** (D), addition occurred preferentially from the α face.



Scheme 4.

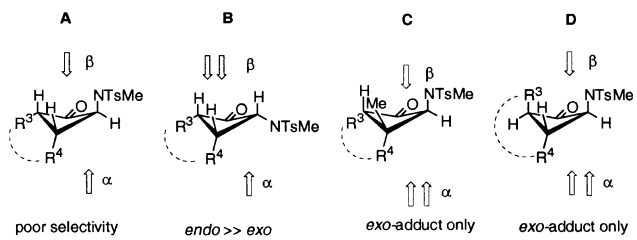
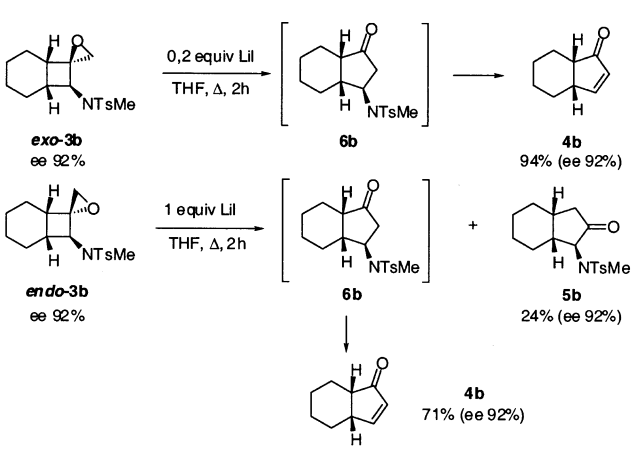


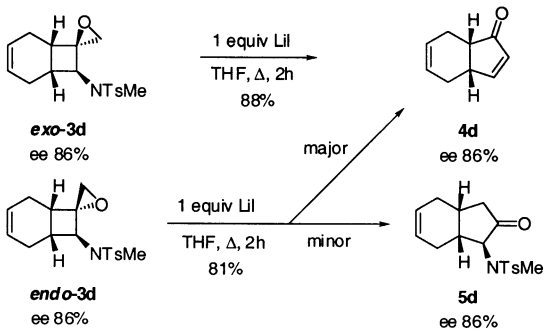
Figure 1.

2.3. Rearrangement of oxiranes

A model study of the rearrangement of oxiranes **3** was conducted on each of the two diastereomeric oxiranes *exo*-**3b** and *endo*-**3b** which had previously been prepared from the corresponding enantiomerically enriched bicyclo[4.2.0]-octan-7-one **2b** (ee 92%). The *exo*-isomer was selectively



Scheme 5.

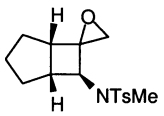
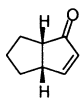
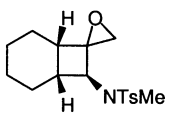
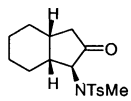
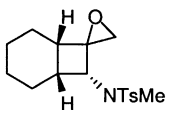
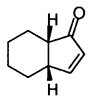
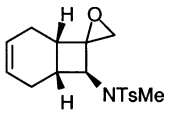
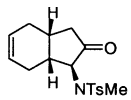
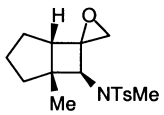
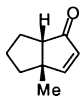
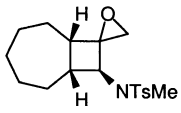
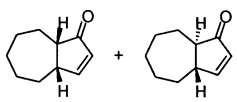
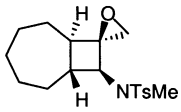
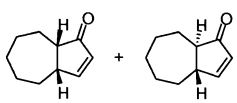
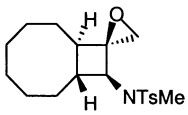
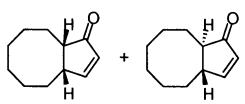
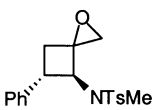
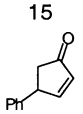
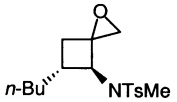


Scheme 6.

converted into (1*S*,6*S*) bicyclo[4.3.0]non-8-en-7-one **4b** (ee 92%) after 2 h in refluxing tetrahydrofuran containing a catalytic amount (0.2 equiv.) of lithium iodide. The formation of **4b** was believed to result from a β-elimination of *N*-methyl-*N*-tosyl amide from bicyclo[4.3.0]nonan-7-one **6b** which was the expected ring-expanded product. This was confirmed by the quantitative formation of **4b** when compound **6b** (previously isolated from the diazomethane ring expansion reaction, see Scheme 2) was refluxed in THF containing lithium iodide.

The *endo*-isomer reacted more slowly: a stoichiometric amount of lithium iodide was needed to bring the rearrangement to completion after 2 hours in refluxing

Table 2. Rearrangement of diastereomeric mixture of 3 in refluxing THF containing a stoichiometric amount of lithium iodide

Entry	Diastereomeric mixture of **3**	Enone **4**	Yield (%)	ee (%)	Other products
a			95	89	
b			81	92	 **5b** 14%
c			90	rac	
d			41	86	 **5d** 41%
e			95	92	
f		 85 : 15	95	rac	
g		 85 : 15	90	98	
h		 15 : 85	87	92	
i			94	rac	
j			96	rac	

THF. Also the ring expansion was less selective (3:1): the major product was still **4b** but there was a substantial amount of bicyclo[4.3.0]octan-8-one **5b** which is a structural isomer of **6b** (Scheme 5).[13]

The *exo*- and *endo* isomers of the corresponding unsaturated oxiranes *exo*- and *endo*-**3d** showed a similar behaviour (**4d**:**5d**=3:2) (Scheme 6). However all other *exo*- and *endo*-oxiranes gave exclusively the cyclopentenone derivatives in high yields when refluxed in THF containing a stoichiometric amount of lithium iodide. The results shown in Table 2 are those obtained from the mixture of *exo*- and *endo*-oxiranes obtained after flash chromatography of the crude product of the ylid addition to **2**. The rearrangement occurred with retention of configuration at the ring junction except when the five-membered ring was fused to a ring larger than six. A small amount of *trans*-isomer was observed when the cyclopentenone was fused to a seven-membered ring **4f**. Epimerization was completed with the corresponding eight-membered ring derivative **4h**.

Not surprisingly the enantiomeric purities of the original cyclobutanones were retained throughout the sequence.

3. Conclusions

In conclusion, the combined results of this and the previous publication[6] provide a unified approach towards the synthesis of enantiomerically pure four and five-membered rings. The previous paper dealt with the enantioselective synthesis of the four-membered ring. The present results showed that these could be readily converted into various types of enantiomerically enriched cyclopentenones. In this [2+2+1] strategy for the cyclopentannulation of olefins, the *N*TsMe group played a crucial role as a control element: as we had anticipated, it acts as an electron-releasing group controlling the regioselectivity of the ring expansion reaction. However, this electronic effect can be counter-balanced by what we believe to be conformational factors as shown in the ring-expansion of cyclobutanones fused to a six-membered ring. At this stage these factors are not well understood. Also, the *N*TsMe group provides the right oxidation state to allow the generation of the conjugate double bond at the end of sequence, thus increasing the synthetic utility of the products.

4. Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on Varian Gemini-200 or 300 spectrometers at 200 or 300 MHz at room temperature. ^{13}C NMR spectra were recorded in $CDCl_3$ at 50 or 75 MHz at room temperature. Chemical shifts are given in ppm relative to $(CH_3)_4Si$ (0 ppm, ^{1}H) or $CDCl_3$ (77.0 ppm, ^{13}C). Mass spectra were obtained on a Finnigan MAT-TSQ 700 spectrometer. IR spectra were recorded on a BIO-RAD TFS 135 FT-IR spectrometer. All absorption values are expressed in wavenumbers (cm-1). $[\alpha]_D$ values were obtained on a Perkin–Elmer 241 MC polarimeter. Melting points are uncorrected. Enantiomeric excesses were measured on hplc with a Millipore Waters 600 Controller, UV Millipore Waters 486 as detector and fitted with Diacel Chiralpack-AD, -AS, -OB, -OD analytical column. TLC were run on silica gel $60F_{254}$. Column chromatographies were performed with gel 40 (230–400 μm, Merck). All solvents were distilled before use. All reagents were of reagent grade.

4.1. General procedure for the preparation of epoxides

A solution of *n*-BuLi (2.5 M in hexanes, 1.2 equiv.) was added to a 0.05 M solution of trimethylsulfonium tetrafluoroborate (1 equiv.) in THF at −15°C. After 15 min, the mixture was cooled to −78°C and treated with a solution of cyclobutanone (1 equiv.) in THF. After 15 h at room temperature, the reaction mixture was diluted with ether and washed twice with water. The organic layer was dried over $MgSO_4$, filtered and concentrated. The product was purified by flash chromatography on silica gel (eluent AcOEt/cyclohexane 2:8).

4.2. Preparation of epoxides *exo*- and *endo*-3a

From **2a** (250 mg, 0.85 mmol), trimethylsulfonium tetrafluoroborate (168 mg, 1.02 mmol), *n*-BuLi (2.0 M in hexanes, 640 μL, 1.28 mmol). Yield: 85 mg (33%) of *exo*-**3a** and 95 mg (36%) of *endo*-**3a** (89% ee).

4.2.1. (1*R*,5*S*,6*R*,7*S*)-7-(Methyltosylamino)spiro[bicyclo[3.2.0]heptane-6,2′-oxirane] (*exo*-3a). Mp 88°C; $[\alpha]_D^{20}$=+38.8 (c=0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 4.29 (dd, J=4.2, 1.6 Hz, 1H), 3.06 (s, 3H), 2.87 (t, J=8.0 Hz, 1H), 2.71 (td, J=8.0, 4.4 Hz, 1H), 2.53 (d, J=5.2 Hz, 1H), 2.42 (s, 3H), 2.30 (d, J=5.2 Hz), 1.90–1.20 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.1, 136.4, 129.4, 127.1, 62.9, 62.4, 48.5, 45.1, 38.7, 31.5, 30.8, 29.4, 25.6, 21.5; IR (neat) ν 2943, 2851, 1338, 1157; M (IE): 238 (100%), 155 (56%), 91 (72%); elemental analysis calcd (%) for $C_{16}H_{21}O_3NS$: C 62.52, H 6.88, N 4.56, S 10.43; found: C 62.19, H 6.83, N 4.48, S 10.13; HPLC (AD column; eluent EtOH; flow: v=0.35 mL/min; λ=254 nm): 15.4 min (1*S*,5*R*,6*R*,7*R*) and 21.6 min (1*R*,5*S*,6*S*,7*S*).

4.2.2. (1*R*,5*S*,6*S*,7*S*)-7-(Methyltosylamino)spiro[bicyclo[3.2.0]heptane-6,2′-oxirane] (*endo*-3a). $[\alpha]_D^{20}$=+29.2 (c=1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 4.31 (dd, J=4.7, 1.6 Hz, 1H), 2.88 (s, 3H), 2.88–2.80 (m, 1H), 2.65–2.55 (m, 1H), 2.59 (d, J=5.3 Hz, 1H), 2.43 (s, 3H), 2.29 (d, J=5.3 Hz, 1H), 1.90–1.20 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 136.9, 129.5, 127.2, 63.7, 61.0, 51.1, 41.6, 37.8, 31.9, 30.7, 26.6, 25.4, 21.5; IR (neat) ν 2950, 1340, 1159; M (IE): 308 (24%), 238 (100%), 155 (36%); HRMS calcd (%) for $C_{16}H_{21}O_3NS$: 307.1242; found: 307.1249; HPLC (AD column; eluent EtOH/hexane 10:90; flow: v=0.50 mL/min; λ=220 nm): 32.1 min (1*S*,5*R*,6*S*,7*R*) and 36.9 min (1*R*,5*S*,6*R*,7*S*).

4.3. Preparation of epoxides *exo*- and *endo*-3b

From **2b** (3.3 g, 10.8 mmol), trimethylsulfonium tetrafluoroborate (2 g, 12.3 mmol), *n*-BuLi (6.5 mL, 16.2 mmol). Yield: 0.95 g (47%) of *exo*-**3b** and 0.58 g (29%) of *endo*-**3b** (92% ee).

4.3.1. (1*R*,6*S*,7*R*,8*S*)-8-(Methyltosylamino)spiro[bicyclo[4.2.0]octane-7,2′-oxirane] (*exo*-3b). $[\alpha]_D^{20}=+10.6$ (c=0.85, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.61 (d, J=8.3 Hz, 2H), 7.22 (d, J=8.3 Hz, 2H), 4.61 (dd, J=8.3, 1.4 Hz, 1H), 2.91 (s, 3H), 2.58–2.70 (m, 1H), 2.55 (d, J=4.6 Hz, 1H), 2.36 (d, J=4.6 Hz, 1H), 2.42 (s, 3H), 2.25 (m, 1H), 1.70–0.70 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 136.7, 129.5, 126.9, 66.5, 57.5, 46.8, 35.6, 33.4, 31.4, 24.9, 24.1, 22.3, 21.5, 21.4; IR (neat) ν 2927, 2854, 1340, 1158; M (IE): 322 (2%), 238 (16%), 185 (24%), 155 (100%), 91 (72%); elemental analysis calcd (%) for $C_{17}H_{23}O_3NS$: C 63.52, H 7.21, N 4.35, S 9.97; found: C 63.43, H 7.34, N 4.13, S 10.04; HPLC (AD column; eluent EtOH; flow: v=0.35 mL/min; λ=254 nm): 14.1 min (1*S*,6*R*,7*S*,8*R*) and 22.0 min (1*R*,6*S*,7*R*,8*S*)

4.3.2. (1*R*,6*S*,7*S*,8*S*)-8-(Methyltosylamino)spiro[bicyclo[4.2.0]octane-7,2′-oxirane] (*endo*-3b). Mp 104°C; $[\alpha]_D^{20}=-0.95$ (c=0.85, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.70 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 4.83 (d, J=9.1 Hz, 1H), 2.79 (s, 3H), 2.72 (d, J=9.0 Hz, 1H), 2.49 (d, J=9.0 Hz, 1H), 2.42 (s, 3H), 2.38–2.26 (m, 2H), 1.90–0.90 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 136.4, 129.4, 127.2, 63.1, 57.9, 50.1, 32.9, 30.4, 29.6, 23.2, 22.4, 21.4, 21.3; IR (neat) ν 2929, 2852, 1340, 1161; M (IE): 321 (4%), 238 (72%), 166 (36%), 155 (32%), 91 (60%), 42 (100%); elemental analysis calcd (%) for $C_{17}H_{23}O_3NS$: C 63.52, H 7.21, N 4.35, S 9.97; found: C 63.46, H 7.25, N 4.29, S 10.35; HPLC (AD column; eluent EtOH/hexane 10:90; flow: v=1.00 mL/min; λ=254 nm): 12.7 min (1*R*,6*S*,7*R*,8*S*) and 14.4 min (1*S*,6*R*,7*S*,8*R*).

4.4. Preparation of epoxides *exo*- and *endo*-3c

From **2c** (500 mg, 1.6 mmol), trimethylsulfonium tetrafluoroborate (320 mg, 1.9 mmol), *n*-BuLi (975 μL, 2.4 mmol). Yield: 40 mg (8%) of *exo*-**3c** and 410 mg (78%) of *endo*-**3c**.

4.4.1. (1*R,6*S**,7*R**,8*R**)-8-(Methyltosylamino)spiro[bicyclo[4.2.0]octane-7,2′-oxirane] (*exo*-3c).** ^1H NMR (200 MHz, $CDCl_3$) δ 7.71 (d, J=8.4 Hz, 2H), 7.28 (d, J=8.4 Hz, 2H), 4.83 (d, J=8.5 Hz, 1H), 2.79 (s, 3H), 2.72 (d, J=5.1 Hz, 1H), 2.50 (d, J=5.1 Hz, 1H), 2.50–2.20 (m, 2H), 2.42 (s, 3H), 1.80–0.95 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 136.6, 129.5, 127.2, 63.2, 58.0, 50.1, 33.0, 30.4, 29.4, 23.2, 23.1, 22.4, 21.4, 21.3; IR (neat) ν 2933, 2851, 1341, 1160; M (IE): 322 (2%), 238 (100%), 166 (54%), 155 (40%), 91 (46%), 42 (48%).

4.4.2. (1*R,6*S**,7*S**,8*R**)-8-(Methyltosylamino)spiro[bicyclo[4.2.0]octane-7,2′-oxirane] (*endo*-3c).** Mp 148°C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.67 (d, J=8.2 Hz, 2H), 7.31 (d, J=8.2 Hz, 2H), 4.25 (d, J=9.1 Hz, 1H), 2.79 (s, 3H), 2.72–2.50 (m, 2H), 2.44 (s, 3H), 2.42 (d, J=9.1 Hz, 1H), 1.85–0.95 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 134.2, 129.5, 127.6, 68.5, 55.6, 44.5, 39.9, 33.3, 32.8, 23.8, 22.3, 22.1, 21.4, 19.3; IR (neat) ν 2927, 2842, 1340, 1158; M (IE): 322 (2%), 238 (100%), 166 (46%), 155 (36%), 91 (50%), 42 (44%); elemental analysis calcd (%) for $C_{17}H_{23}O_3NS$: C 63.52, H 7.21, N 4.35, S 9.97; found: C 63.49, H 7.37, N 4.23, S 10.26.

4.5. Preparation of epoxides *exo*- and *endo*-3d

From **2d** (3.1 g, 10.2 mmol), trimethylsulfonium tetrafluoroborate (2 g, 12.3 mmol), *n*-BuLi (6.1 mL, 16.2 mmol). Yield: 338 mg (10%) of *exo*-**3d** and 2.02 g (62%) of *endo*-**3d** (86% ee).

4.5.1. (1*R*,6*S*,7*R*,8*S*)-8-(Methyltosylamino)spiro[bicyclo[4.2.0]oct-3-ene-7,2′-oxirane] (*exo*-3d). $[\alpha]_D^{20}=-5.5$ (c=0.11, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J=8.4 Hz, 2H), 7.28 (d, J=8.4 Hz, 2H), 5.95–5.85 (m, 2H), 4.38 (dd, J=6.1, 1.1 Hz, 1H), 3.06 (s, 3H), 2.90–2.65 (m, 2H), 2.53 (d, J=4.8 Hz, 1H), 2.42 (s, 3H), 2.22 (d, J=4.8 Hz, 1H), 2.10–1.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 136.9, 129.5, 127.9, 127.6, 127.0, 64.3, 61.1, 48.2, 37.1, 32.9, 31.6, 25.0, 23.4, 21.5; IR (neat) ν 3031, 2923, 2830, 1598, 1338, 1160; M (IE): 320 (1%), 212 (96%), 164 (28%), 91 (32%), 43 (100%); elemental analysis calcd (%) for $C_{17}H_{21}O_3NS$: C 63.93, H 6.63, N 4.39, S 10.04; found: C 63.80, H 6.58, N 4.38, S 10.24.

4.5.2. (1*R*,6*S*,7*S*,8*S*)-8-(Methyltosylamino)spiro[bicyclo[4.2.0]oct-3-ene-7,2′-oxirane] (*endo*-3d). Mp 123°C; $[\alpha]_D^{20}=+18.1$ (c=0.70, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 6.00–5.90 (m, 1H), 5.88–5.80 (m, 1H), 4.60 (d, J=6.5 Hz, 1H), 2.86 (s, 3H), 2.72–2.57 (m, 2H), 2.64 (d, J=5.1 Hz, 1H), 2.42 (s, 3H), 2.32 (d, J=5.1 Hz, 1H), 2.10–1.70 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 136.3, 129.4, 127.7, 127.1, 125.5, 62.3, 61.7, 50.8, 32.5, 30.8, 29.8, 23.9, 21.4, 20.4; IR (neat) ν 3030, 2963, 2836, 1598, 1339, 1159; M (IE):319 (4%), 238 (36%), 164 (100%), 155 (52%), 91 (80%); HRMS calcd (%) for $C_{17}H_{21}O_3NS$: 319.1242; found: 319.1240.

4.6. Preparation of epoxides *exo*- and *endo*-3e

From **2e** (250 mg, 0.85 mmol), trimethylsulfonium tetrafluoroborate (168 mg, 1.02 mmol), *n*-BuLi (610 μL, 1.5 mmol). Yield: 176 mg (54%) of *exo*-**3e** and 44 mg (13%) of *endo*-**3e** (92% ee).

4.6.1. (1*R*,5*S*,6*R*,7*S*)-1-Methyl-7-(methyltosylamino)-spiro[bicyclo[3.2.0]heptane-6,2′-oxirane] (*exo*-3e). $[\alpha]_D^{20}=+37.9$ (c=0.9, CH_2Cl_2); ^1H NMR (200 MHz, $CDCl_3$) δ 7.63 (d, J=7.8 Hz, 2H), 7.27 (d, J=7.8 Hz, 2H), 4.31 (d, J=1.5 Hz, 1H), 3.13 (s, 3H), 2.48 (d, J=5.0 Hz, 1H), 2.50–2.40 (m, 1H), 2.42 (s, 3H), 2.14 (d, J=5.0 Hz, 1H), 1.95–1.20 (m, 6H), 1.21 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.1, 137.0, 129.4, 126.8, 64.6, 61.8, 51.8, 48.3, 48.1, 40.4, 34.4, 29.5, 26.2, 21.4, 20.8; IR (neat) ν 2957, 2869, 1339, 1260, 1157; M (IE): 321 (4%), 239 (44%), 155 (28%), 91 (56%), 42 (100%); elemental analysis calcd (%) for $C_{17}H_{23}O_3NS$: C 63.52, H 7.21, N 4.36, S 9.97; found: C 63.38, H 6.99, N 4.07, S 9.97; HPLC (AD column; eluent EtOH; flow: v=0.35 mL/min; λ=254 nm): 13.2 min (1*S*,5*R*,6*R*,7*R*) and 15.8 min (1*R*,5*S*,6*S*,7*S*).

4.6.2. (1*R*,5*S*,6*S*,7*S*)-1-Methyl-7-(methyltosylamino)-spiro[bicyclo[3.2.0]heptane-6,2′-oxirane] (*endo*-3e). ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (d, J=8.1 Hz, 2H), 7.29 (d, J=8.1 Hz, 2H), 4.44 (d, J=1.6 Hz, 1H), 2.93 (s, 3H), 2.66 (d, J=5.1 Hz, 1H), 2.50–2.40 (m, 1H), 2.42 (s, 3H),

2.31 (d, J=5.1 Hz, 1H), 2.00–1.10 (m, 6H), 1.18 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 136.3, 129.5, 127.1, 66.0, 60.3, 52.1, 48.6, 48.0, 41.7, 33.6, 27.2, 26.4, 21.5, 20.4; IR (neat) ν 2957, 2869, 1339, 1260, 1157; M (IE): 321 (12%), 185 (60%), 155 (40%), 91 (100%); HRMS calcd (%) for $C_{17}H_{23}O_3NS$: 321.1402; found: 321.1399.

4.7. Preparation of epoxides *exo*- and *endo*-3f

From **2f** (400 mg, 1.2 mmol), trimethylsulfonium tetrafluoroborate (245 mg, 1.5 mmol), *n*-BuLi (2.3 M in hexanes, 830 μL, 1.9 mmol). Yield: 84 mg (20%) of *exo*-**3f** and 260 mg (62%) of *endo*-**3f**.

4.7.1. (1*R,7*S**,8*R**,9*S**)-9-(Methyltosylamino)spiro[bicyclo[5.2.0]nonane-8,2′-oxirane] (*exo*-3f).** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 4.45 (dd, J=6.8, 1.2 Hz, 1H), 3.03 (s, 3H), 2.80–2.50 (m, 2H), 2.55 (d, J=4.9 Hz, 1H), 2.42 (s, 3H), 2.29 (d, J=4.9 Hz, 1H), 1.90–1.00 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 137.0, 129.5, 127.0, 63.6, 60.5, 47.8, 44.0, 39.8, 31.9, 31.5, 31.4, 29.1, 28.7, 28.3, 21.5; IR (neat) ν 2990, 2918, 2847, 1376, 1160; M (IE): 335 (4%), 238 (100%), 180 (40%), 155 (28%), 91 (32%), 42 (26%); HRMS (CI) calcd (%) for $C_{18}H_{26}O_3NS$: 336.1633; found: 336.1627.

4.7.2. (1*R,7*S**,8*S**,9*S**)-9-(Methyltosylamino)spiro[bicyclo[5.2.0]nonane-8,2′-oxirane] (*endo*-3f).** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 4.56 (d, J=6.3 Hz, 1H), 2.83 (s, 3H), 2.60 (d, J=5.0 Hz, 1H), 2.50–2.35 (m, 2H), 2.42 (s, 3H), 2.33 (d, J=5.0 Hz, 1H), 2.00–1.00 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 136.2, 129.4, 127.2, 63.5, 61.0, 50.0, 41.5, 36.9, 32.0, 30.7, 29.8, 28.1, 25.9, 21.4; IR (neat) ν 2918, 2847, 1337, 1151; M (IE): 335 (4%), 238 (100%), 180 (26%), 155 (20%), 150 (8%), 91 (30%), 42 (54%).

4.7.3. Preparation of epoxide (1*R*,7*R*,8*R*,9*S*)-9-(methyltosylamino)spiro[bicyclo[5.2.0]nonane-8,2′-oxirane] (*exo*-3g). From **2g** (348 mg, 1.1 mmol), trimethylsulfonium tetrafluoroborate (213 mg, 1.3 mmol), *n*-BuLi (2.1 M in hexanes, 785 μL, 1.6 mmol). Yield: 268 mg (74%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 (d, J=8.3 Hz, 2H), 7.29 (d, J=8.3 Hz, 2H), 4.34 (d, J=9.4 Hz, 1H), 2.93 (s, 3H), 2.51 (s, 2H), 2.42 (s, 3H), 2.45–2.30 (m, 1H), 2.30–2.15 (m, 1H), 1.70–1.10 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.1, 136.8, 129.5, 127.0, 66.9, 57.9, 45.9, 43.8, 40.6, 31.5, 31.3, 29.0, 28.0, 25.3, 23.5, 21.4; IR (neat) ν 2918, 2856, 1342, 1156; M (IE): 335 (4%), 238 (100%), 180 (26%), 155 (24%), 150 (10%), 91 (42%), 42 (52%); HRMS calcd (%) for $C_{18}H_{25}O_3NS$: 335.1555; found: 336.1555.

4.7.4. Preparation of epoxide (1*R*,8*R*,9*R*,10*S*)-10-(methyltosylamino)spiro[bicyclo[6.2.0]decane-9,2′-oxirane] (*exo*-3h). From **2h** (431 mg, 1.3 mmol), trimethylsulfonium tetrafluoroborate (253 mg, 1.5 mmol), *n*-BuLi (2.0 M in hexanes, 965 μL, 1.9 mmol). Yield: 264 mg (59%); mp 85°C; $[\alpha]_D^{20}=-30.7$ (c=0.8, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 4.31 (d, J=9.3 Hz, 1H), 2.96 (s, 3H), 2.45 (d, J=4.5 Hz, 1H), 2.42 (s, 3H), 2.36 (d, J=4.5 Hz, 1H), 2.30–2.15 (m, 1H), 1.90–1.65 (m, 4H), 1.60–1.45 (m, 1H), 1.40–1.10 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 137.0, 129.5, 127.0, 66.6, 59.2, 46.1, 44.6, 40.9, 34.4, 31.7, 28.2, 27.4, 27.0, 26.8, 26.0, 21.4; IR (neat) ν 2918, 2847, 1337, 1147; M (IE): 349 (12%), 306 (4%), 238 (100%), 194 (32%), 155 (24%), 91 (36%), 42 (72%); elemental analysis calcd (%) for $C_{19}H_{27}O_3NS$: C 65.30, H 7.74, N 4.01, S 9.17; found: C 65.14, H 7.85, N 3.90, S 9.80.

4.8. Preparation of epoxides *exo*- and *endo*-3i

From **2i** (146 mg, 0.4 mmol), trimethylsulfonium tetrafluoroborate (73 mg, 0.4 mmol), *n*-BuLi (2.0 M in hexanes, 266 μL, 0.5 mmol). Yield: 111 mg (73%) of *exo*-**3i** and 12 mg (8%) of *endo*-**3i**.

4.8.1. (1*R,2*S**,3*R**)-2-(Methyltosylamino)-3-phenylspiro[cyclobutane-1,2′-oxirane] (*exo*-3i).** ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40 (d, J=8.1 Hz, 2H), 7.30–7.00 (m, 5H), 7.00 (d, J=8.1 Hz, 2H), 4.96 (d, J=9.5 Hz, 1H), 3.89 (q, J=9.5 Hz, 1H), 3.10 (s, 3H), 2.70 (d, J=4.3 Hz, 1H), 2.55 (d, J=4.3 Hz, 1H), 2.48 (d, J=9.5 Hz, 1H), 2.46 (d, J=9.5 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.9, 141.3, 136.5, 129.4, 128.6, 126.9, 126.6, 126.5, 63.3, 62.2, 47.8, 41.5, 33.0, 31.6, 21.4; IR (neat) ν 2923, 2855, 1340, 1166; M (IE): 343 (2%), 287 (76%), 239 (36%), 188 (80%), 155 (32%), 106 (98%), 91 (100%), 42 (34%); HRMS calcd (%) for $C_{19}H_{21}O_3NS$: 343.1242; found: 343.1254.

4.8.2. (1*S,2*S**,3*R**)-2-(Methyltosylamino)-3-phenylspiro[cyclobutane-1,2′-oxirane] (*endo*-3i).** Mp 134°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44 (d, J=8.2 Hz, 2H), 7.30 (m, 5H), 7.05 (d, J=8.2 Hz, 2H), 5.00 (d, J=9.3 Hz, 1H), 3.40 (q, J=9.3 Hz, 1H), 2.91 (s, 3H), 2.81 (d, J=5.2 Hz, 1H), 2.60 (d, J=5.2 Hz, 1H), 2.52–2.40 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 141.0, 136.5, 129.3, 128.6, 127.0, 126.7, 126.7, 64.7, 59.5, 49.6, 36.3, 31.8, 30.9, 21.4; IR (neat) ν 2926, 2855, 1339, 1166; M (IE): 343 (2%), 287 (92%), 239 (24%), 188 (96%), 155 (32%), 91 (100%), 42 (48%).

4.9. Preparation of epoxides *exo*- and *endo*-3j

From **2j** (500 mg, 1.6 mmol), trimethylsulfonium tetrafluoroborate (300 mg, 1.9 mmol), *n*-BuLi (1.9 M in hexanes, 935 μL, 1.8 mmol). Yield: 320 mg (61%) of *exo*-**3j** and 25 mg (5%) of *endo*-**3j**.

4.9.1. (1*R,2*S**,3*R**)-3-Butyl-2-(methyltosylamino)-spiro[cyclobutane-1,2′-oxirane] (*exo*-3j).** ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 (d, J=8.4 Hz, 2H), 7.29 (d, J=8.4 Hz, 2H), 4.40 (d, J=8.0 Hz, 1H), 3.03 (s, 3H), 2.80–2.40 (m, 1H), 2.54 (d, J=4.6 Hz, 1H), 2.42 (s, 3H), 2.32 (d, J=4.6 Hz, 1H), 2.15 (ddd, J=13.3, 9.8, 1.3 Hz, 1H), 1.92 (dd, J=13.3, 9.8 Hz, 1H), 1.45–1.00 (m, 6H), 0.92 (t, J=6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 137.2, 129.5, 127.0, 62.6, 60.8, 48.3, 36.8, 34.3, 31.7, 31.6, 29.3, 22.5, 21.4, 13.8; IR (neat) ν 2959, 2930, 1348, 1251, 1157; M (IE): 323 (6%), 267 (100%), 238 (42%), 168 (24%), 155 (48%), 91 (45%); elemental analysis calcd (%) for $C_{17}H_{25}O_3NS$: C 63.13, H 7.79, N 4.33, S 9.91; found: C 63.11, H 7.78, N 4.13, S 9.66.

4.9.2. (1*S,2*S**,3*R**)-3-Butyl-2-(methyltosylamino-spiro[cyclobutane-1,2′-oxirane] (*endo*-3j).** ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69 (d, J=8.1 Hz, 2H), 7.28 (d, J=8.1 Hz, 2H), 4.49 (d, J=7.2 Hz, 1H), 2.81 (s, 3H), 2.65 (d, J=4.9 Hz, 1H), 2.42 (s, 3H), 2.33 (d, J=4.9 Hz, 1H), 2.25–2.10 (m, 2H), 1.90–1.70 (m, 1H), 1.50–1.30 (m, 4H), 1.40 (q, J=6.7 Hz, 2H), 0.84 (t, J=6.7 Hz, 3H),; ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 136.6, 129.4, 127.2, 63.2, 59.5, 49.8, 34.5, 32.1, 30.8, 30.4, 29.3, 22.5, 21.4, 13.8.

4.10. Reaction of 2b with diazomethane

A 1 M solution of diazomethane in ether (10 mL) was added to a solution of **2b** (350 mg, 1.2 mmol) in a 1:1 mixture of ether and ethyle actetate at −10°C. After one day, drops of acetic acid were added and the mixture was concentrated in vacuo and purified by flash chromatography on silica gel (eluent AcOEt/cyclohexane 2:8). Yield 75 mg (19%) of **6** and 20 mg (5%) of **5** and 245 mg (70%) of starting material **2b**.

4.10.1. (1*R,6*S**,9*S**)-9-(Methyltosylamino)-bicyclo-[4.3.0]nonan-7-one (6b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=7.9 Hz, 2H), 7.29 (d, J=7.9 Hz, 2H), 4.59 (q, J=9.0 Hz, 1H), 2.71 (s, 3H), 2.41 (s, 3H), 2.32 (m, 1H), 2.22 (m, 1H), 2.14 (dd, J=19.0, 8.0 Hz, 1H), 1.95 (ddd, J=19.0, 9.0, 1.0 Hz, 1H), 1.68–1.58 (m, 3H), 1.50–1.37 (m, 3H), 1.33–1.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.3, 143.5, 136.1, 129.8, 127.0, 53.8, 47.8, 38.0, 37.4, 28.0, 23.8, 23.2, 22.9, 21.4, 20.7; IR (neat) ν 2928, 2856, 1742, 1339, 1159; M (IC+): 322 (2%), 186 (100%); HRMS calcd (%) for $C_{17}H_{23}O_3NS$: 321.1397; found: 321.1392.

4.10.2. (1*S,6*R**,7*S**)-7-(Methyltosylamino)bicyclo-[4.3.0]nonan-8-one (5b).** Mp 104°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=8.0 Hz, 2H), 7.31 (d, J=8.0 Hz, 2H), 4.66 (d, J=12.4 Hz, 1H), 2.59 (s, 3H), 2.43 (s, 3H), 2.29 (m, 1H), 2.25 (m, 2H), 2.02 (m, 1H), 1.92 (m, 1H), 1.76 (m, 1H), 1.72 (m, 1H), 1.59 (m, 2H), 1.57 (m, 1H), 1.28 (m, 1H), 1.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 143.2, 136.8, 129.4, 127.6, 63.7, 43.9, 36.7, 31.4, 30.0, 29.2, 25.0, 21.4, 19.6; IR (neat) ν 2927, 2854, 1749, 1338, 1156; M (IE): 321 (28%), 165 (100%), 136 (100%), 91 (56%); elemental analysis calcd (%) for $C_{17}H_{23}O_3NS$: C 63.52, H 7.21, N 4.36, S 9.97; found: C 63.27, H 7.16, N 4.22, S 10.14.

4.11. General procedure for the rearrangement of epoxides

Lithium iodide (1 equiv.) was added to a 0.05 M solution of epoxide (1 equiv.) in THF at room tempreature. The mixture was heated for two hours at 65°C. The mixture was cooled to room tempretaure and concentrated in vacuo. The product was purified by flash chromatography on silica gel (eluent AcOEt/cyclohexane 2:8). When the separation of oxiranes was not required, the crude reaction mixture was purified by flash chromatography to afford a mixture of epoxides. The rearrangement was done on these mixtures.

4.12. Rearrangement of 3a

From *exo*-**3a** and *endo*-**3a** (400 mg, 1.2 mmol), lithium iodide (170 mg, 1.2 mmol). Yield: 130 mg (86%) of **4a** (90% ee). (1*S*,5*S*)-Bicyclo[3.3.0]oct-3-en-2-one (**4a**): RN 1388665-76-6; $[\alpha]_D^{20}$=+291.5 (c=1.1, CH_2Cl_2); HPLC (OB column; eluent iPrOH/hexane 2:98; flow: v=1.00 mL/min; λ=232 nm): 10.6 min (1*R*,5*R*) and 12.2 min (1*S*,5*S*).

4.13. Rearrangement of 2b

From *exo*-**2b** (200 mg, 0.62 mmol), lithium iodide (83 mg, 0.62 mmol). Yield: 80 mg (95%) of **4b** (92% ee). From *endo*-**2b** (200 mg, 0.62 mmol), lithium iodide (8 mg, 0.62 mmol). Yield: 60 mg (71%) of **4b** and 48 mg (24%) of **5b** (92% ee).

(1*S*,6*S*)-Bicyclo[4.3.0]non-8-en-7-one (**4b**): RN 81255-91-6; $[\alpha]_D^{20}$=+35.3 (c=0.1, CH_2Cl_2); HPLC (OB column; eluent *i*PrOH/hexane 2:98; flow: v=1.00 mL/min; λ=232 nm): 8.0 min (1*S*,6*S*) and 17.0 min (1*R*,6*R*).

4.13.1. (1*S*,6*R*,7*S*)-7-(Methyltosylamino)bicyclo[4.3.0]-nonan-8-one (5b). $[\alpha]_D^{20}$=+93.4 (c=1.1, $CHCl_3$); HPLC (AD column; eluent EtOH; flow: v=0.35 mL/min; λ=254 nm): 17.9 min (1*R*,6*S*,7*R*) and 30.9 min (1*S*,6*R*,7*S*).

4.14. Rearrangement of 3c

From *exo*-**3c**-rac (100 mg, 0.3 mmol), lithium iodide (27 mg, 0.3 mmol) heated overnight. Yield: 36 mg (90%) of **4a**.

4.15. Rearrangement of 3d

From *exo*-**3d** (100 mg, 0.31 mmol), lithium iodide (42 mg, 0.31 mmol). Yield: 37 mg (88%) of **4d** (86% ee). From *endo*-**3d** (1 g, 3.13 mmol), lithium iodide (419 mg, 3.13 mmol). Yield: 205 mg (32%) of **4d** and 320 mg (49%) of **5d** (86% ee).

4.15.1. (1*S*,6*S*)-Bicyclo[4.3.0]non-3,8-dien-7-one (4d). RN 94344-47-5; $[\alpha]_D^{20}$=+99.5 (c=0.6, CH_2Cl_2); HPLC (OB column; eluent *i*PrOH/hexane 2:98; flow: v=1.00 mL/min; λ=220 nm): 11.9 min (1*S*,6*S*) and 19.5 min (1*R*,6*R*).

4.15.2. (1*S*,6*R*,7*S*)-7-(Methyltosylamino)bicyclo[4.3.0]-non-3-en-8-one (5d). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75 (d, J=8.4 Hz, 2H), 7.30 (d, J=8.4 Hz, 2H), 5.80–5.70 (m, 2H), 4.33 (d, J=11.9 Hz, 1H), 2.65 (s, 3H), 2.43 (s, 3H), 2.50–2.15 (m, 6H), 1.80–1.55 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 212.7, 143.0, 136.7, 129.2, 127.2, 124.3, 123.9, 65.6, 44.6, 35.0, 30.1, 27.2, 26.8, 23.4, 21.2; IR (neat) ν 2922, 2840, 1749, 1338, 1153; M (IE): 319 (2%), 185 (28%), 155 (16%), 91 (26%), 43 (100%); HRMS calcd (%) for $C_{17}H_{21}O_3NS$: 319.1242; found: 319.1247; $[\alpha]_D^{20}$=+101.7 (c=0.7, CH_2Cl_2); HPLC (AD column; eluent EtOH; flow: v=0.35 mL/min; λ=254 nm): 16.4 min (1*R*,6*S*,7*R*) and 21.0 min (1*S*,6*R*,7*S*).

4.16. Rearrangement of 3e

From *exo*-**3e** and *endo*-**3e** (400 mg, 1.2 mmol), lithium iodide (170 mg, 1.2 mmol). Yield: 160 mg (95%) of **4e** (92% ee).

4.16.1. (1*S*,5*S*)-5-Methyl-bicyclo[3.3.0]oct-3-en-2-one (4e). RN 39163-28-5; $[\alpha]_D^{20}=+14.8$ ($c=0.5$, CH_2Cl_2); HPLC (AS column; eluent *i*PrOH/hexane 3:97; flow: $v=0.35$ mL/min; $\lambda=220$ nm): 15.9 min (1*S*,5*S*) and 19.7 min (1*R*,5*R*).

4.17. Rearrangement of 3f

From *exo*-**3f**-rac and *endo*-**3f**-rac (200 mg, 0.62 mmol), lithium iodide (83 mg, 0.62 mmol). Yield: 80 mg (95%) of a mixture of *cis*-**4f** and *trans*-**4f** in a ratio 85:15.

4.18. Rearrangement of *exo*-3g

From *exo*-**3g** (260 mg, 0.78 mmol), lithium iodide (104 mg, 0.78 mmol). Yield: 105 mg (90%) of a mixture of *cis*-**4f** and *trans*-**4f** in a ratio 85:15 (92% ee). HPLC (AS column; eluent *i*PrOH/hexane 3:97; flow: $v=1.00$ mL/min; $\lambda=220$ nm): 15.7 min (1*R*,7*S*), 17.3 min (1*R*,7*R*), 19.3 min (1*S*,7*S*) and 21.4 min (1*S*,7*R*).

4.18.1. (1*R*,7*S*)-Bicyclo[6.3.0]dec-9-en-8-one (*cis*-4f). RN 81255-92-7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, $J=5.6$, 2.0 Hz, 1H), 6.16 (dd, $J=5.6$, 2.0 Hz, 1H), 3.13 (m, 1H), 2.50 (dt, $J=10.5$, 6.5 Hz, 1H), 2.02 (m, 1H), 1.92 (m, 1H), 2.10–1.20 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.7, 168.7, 132.3, 50.4, 47.4, 31.0, 30.6, 28.1, 27.5; M (GC-IE): 150 (100%), 107 (60%), 95 (48%).

4.18.2. (1*R*,7*R*)-Bicyclo[6.3.0]dec-9-en-8-one (*trans*-4f). RN 81255-93-8; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46 (d, $J=5.8$ Hz, 1H), 6.28 (d, $J=5.8$ Hz, 1H), 2.62 (d, $J=9.4$ Hz, 1H), 2.15–1.85 (m, 2H), 1.80–1.20 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 209.1 163.3, 134.8, 53.4, 47.4, 32.8, 31.1, 27.1, 27.0, 22.8; M (GC-IE): 150 (100%), 107 (60%), 95 (48%).

4.19. Rearrangement of *exo*-3h

From *exo*-**3h** (167 mg, 0.48 mmol), lithium iodide (64 mg, 0.48 mmol). Yield: 68 mg (87%) of a mixture of *cis*-**4h** and *trans*-**4h** in a ratio 15:85 (98% ee). HPLC (AS column; eluent *i*PrOH/hexane 3:97; flow: $v=1.00$ mL/min; $\lambda=220$ nm): 12.5 min (1*R*,8*S*), 15.5 min (1*R*,8*R*), 21.4 min (1*S*,8*S*), and 26.0 min (1*S*,8*R*).

4.19.1. (1*R*,8*S*)-Bicyclo[6.3.0]dec-9-en-8-one (*cis*-4h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, $J=5.6$, 2.8 Hz, 1H), 6.11 (dd, $J=5.6$, 2.3 Hz, 1H), 2.94 (m, 1H), 2.15 (m, 1H), 2.10–1.20 (m, 8H); M (GC-IE): 164 (100%), 135 (68%).

4.19.2. (1*R*,8*R*)-Bicyclo[6.3.0]dec-9-en-8-one (*trans*-4h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, $J=5.6$, 2.2 Hz, 1H), 6.20 (ddd, $J=5.6$, 2.2, 0.9 Hz, 1H), 2.72 (d, $J=12.5$ Hz, 1H), 2.15–1.85 (m, 3H), 1.85–1.65 (m, 4H), 1.60–1.30 (m, 4H), 1.20–1.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.3167.9, 131.6, 129.2, 51.5, 47.4, 34.1, 29.6, 27.3, 26.8, 25.3, 25.1; M (GC-IE): 164 (100%), 135 (36%), 120 (44%), 107 (48%), 94 (36%).

4.20. Rearrangement of 3i

From *exo*-**3i**-rac and *endo*-**3i**-rac (150 mg, 0.44 mmol), lithium iodide (60 mg, 0.44 mmol). Yield: 65 mg (94%) of **4i**. 4-Phenylcyclopent-2-en-1-one (**4i**): RN 81255-96-1.

4.21. Rearrangement of 3j

From *exo*-**3j**-rac and *endo*-**3j**-rac (166 mg, 0.5 mmol), lithium iodide (70 mg, 0.5 mmol). Yield: 68 mg (96%) of **4j**. 4-Butylcyclopent-2-en-1-one (**4j**): RN 54814-22-1.

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13. Compound **5b** was assigned a wrong structure in our preliminary account of this work.[6]