Tetrahedron Vol. 45, No. 23, pp. 7311 to 7316, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00
Pergamon Press plc

PREPARATION OF ENANTIOMERICALLY PURE 3-ENDO-SULFONYLMETHYL SUBSTITUTED BICYCLO[2.2.1]HEPTANE-2-ENDO-CARBOXYLIC ACIDS

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(*Received in Germany* 10 *August* 1989)

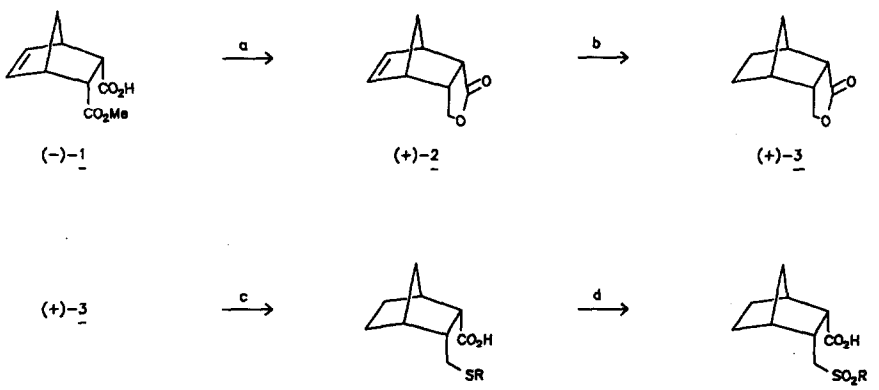
Abstract - Both enantiomers of title acids 5 were synthesized from mono-ester rac-1. An alternative approach via PLE catalyzed hydrolysis of a meso diester is described too.

Camphor derived C-3 substituted bicyclo[2.2.1]heptan-2-ols have proven to be very efficient chiral auxiliaries for asymmetric synthesis [1].

Searching for chiral conducting salts which would be able to act as nucleophiles towards electrochemically generated radical cations [2], there was interest in having access to carboxylic acids structurally analogous to the alcohols mentioned above. Since it was envisioned to synthesize these acids by ring-opening of γ-lactone 3 [3,4], chirality could be set up by resolution of a suitable diacid mono-ester precursor [5], by discrimination between enantiotopic groups of a meso starting compound, using an enzymatic [3], as well as a non-enzymatic [6] procedure, or via a Diels-Alder reaction of cyclopentadiene with a chiral dienophile [4,7]. The need to have both enantiomers of 3 available in large amounts was decisive in applying the resolution approach and in examining the potential use of a hydrolase [8].

Scheme 1 shows the synthesis of the desired acids (+)-5a and (+)-5b from mono-ester (-)-1, prepared by resolution of rac-1 with ephedrine [5].

Scheme 1



(-)-1 (+)-2 (+)-3

(+)-3

R = Ph : (+)-4a
R = i-Pr: (+)-4b

(+)-5a
(+)-5b

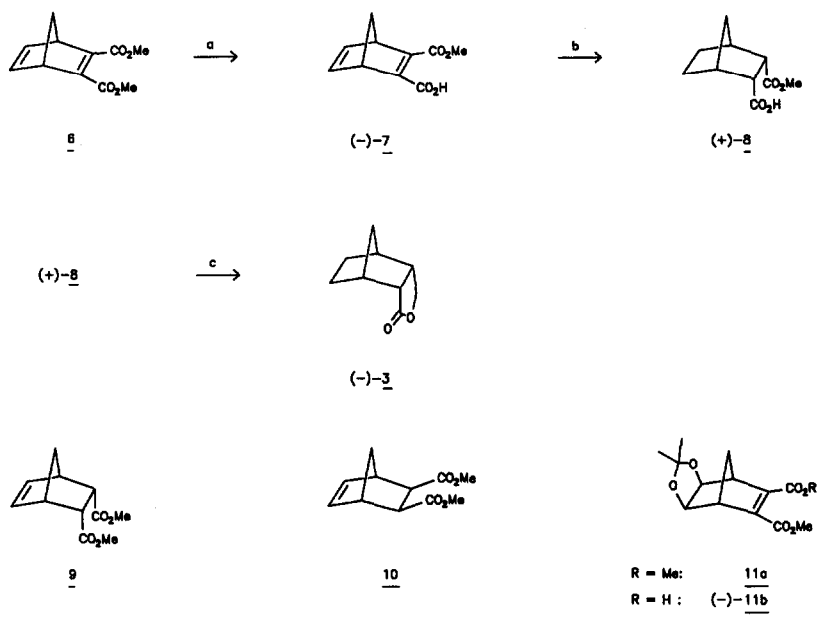
a: Na, NH_3, EtOH, -78 °C, acidic workup, 61 %. b: H_2, 10 % Pd on C, MeOH, rt, 100 %. c: RS-Na, DMF; for R = Ph: 100 °C, 81 %; for R = i-Pr: rt, 64 %. d: oxone, MeOH / H_2O, pH 6, rt; for R = Ph: 96 %; for R = i-Pr: 100 %.

Chemoselective metal-ammonia reduction [5] of (-)-1 with $[\alpha]_D^{20}$ = -8.1° (CCl_4, c = 4.9), followed by acidic workup yielded unsaturated γ-lactone (+)-2 [3,5,7], which was hydrogenated to (+)-3 [3,5]. Nucleophilic ring-cleavage of (+)-3 proceeded smoothly and without concomitant epimerization α to the hydroxycarbonyl group when one equivalent of a sodium thiolate [9] in DMF was applied. In order to have a bulky and oxidatively stable 3-endo substituent, (+)-4a and (+)-4b were transformed to sulfones (+)-5a and (+)-5b, respectively, using oxone [10]. Again, no C-2 epimerization occurred when the oxidations were run in buffered medium. Conversion to the corresponding tetrabutylammonium salt was exemplified in case of acid (+)-5a. Stirring this acid with one equivalent of tetrabutylammonium hydroxide in methanol at room temperature and subsequent concentration furnished the pure salt of (+)-5a quantitatively. Starting from (+)-1 [5], (-)-5a and (-)-5b were prepared by the same route.

A peculiar observation was made when (+)-1 with $[\alpha]_D^{20}$ = +8.2° (CCl_4, c = 4.9) was treated successively with oxalyl chloride at room temperature, sodium borohydride in ethanol at -40 °C, and 6N HCl at room temperature. Here, lactone (+)-2 was obtained reproducibly with ee = 0 - 2 %. Whatever the reason for this unexpected result, the intermediate methyl (2S, 3R)-cis-endo-3-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate can be isolated in optically pure form [5].

The catalytic approach towards the enantioselective preparation of lactone 3 with the aid of a hydrolase is illustrated in Scheme 2.

Scheme 2



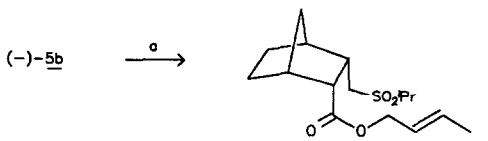
a: pig liver esterase, aqueous phosphate buffer pH 7 / acetone, rt, 77 %. **b**: H_2, PtO_2, EtOAc, rt, 87 %.
c: Na, NH_3, EtOH, -78 °C, acidic workup, 75 %.

Meso diester 6 [11] was subjected to PLE catalyzed hydrolysis. Maintaining pH 7 throughout the reaction course by dropwise addition of 2N NaOH, complete conversion to (-)-7 [12] was achieved within 5 h at room temperature. Hydrogenation of (-)-7 to (+)-8 [13] was always accompanied by some production of a trans-isomer of 8 [14], the best conditions found being those mentioned in Scheme 2 ((+)-8 : trans-isomer = 91 : 9). Metal-ammonia reduction of (+)-8 led to lactone (-)-3 with only 36 % enantiomeric excess, thus making the resolution method the route of choice.

It is interesting to compare the pig liver esterase catalyzed transformation of 6 with the corresponding reactions of meso diesters 9 and 10 with PLE. While cis-endo 9 suffers no hydrolysis at all [15] and cis-exo 10 is saponified virtually non-stereoselectively [15], a geometrically intermediate disposition of the ester groups as in 6 now allows for fast hydrolysis with significant discrimination between the enantiotopic ester functions. The stereochemical outcome of the PLE catalyzed reaction of 6 to (-)-7 illustrates the enzyme's sensitivity towards a structural modification of a substrate far from the reactive site, since 11a is known to yield (-)-11b [16] under similar conditions.

With the acids (+)-5 and (-)-5 at hand, some experiments were run to see as to whether the carboxyl group could be derivatized without epimerization at C-2.

Scheme 3



(-)-12

a: Ph_3P, EtO_2C-N=N-CO_2Et, (E)-2-butenol, THF, rt, 68 %.

According to Scheme 3, acid (-)-5b was esterified to trans-crotyl ester (-)-12. Using the Mitsunobu method [17], pure endo-ester (-)-12 was obtained, whereas application of the DCC/DMAP procedure [18] to (+)-5a and (E)-2-butenol gave 10 % exo-ester along with the desired product.

EXPERIMENTAL

General remarks - Flash chromatography was performed on silica gel 40 - 63 µm (Merck). HPLC separations were performed with a Knauer 64 pump, a Knauer differential refractometer and a 25 cm Knauer Polygosil 60 (5 µm) column, 3.2 cm i.d.. Capillary GC analyses were performed with a Shimadzu GC-9A, a Shimadzu CR3A integrator and a 25 m OV 225 CB column, 0.25 mm i.d., 0.25 µm film. Melting points were determined on a Kofler microscope-desk. Optical rotations were measured with a Perkin-Elmer 241 polarimeter.
IR spectra (Shimadzu IR-408): absorption frequencies reported in cm^{-1}, solvent $CHCl_3$. ^1H NMR spectra (Bruker WM 300, 300 MHz) and ^{13}C NMR spectra (Bruker WM 300, 75.47 MHz): chemical shifts in ppm relative to tetramethylsilane, coupling constants J in Hz, solvent $CHCl_3$, ^{13}C multiplicities were determined using INEPT pulse sequences. Mass spectra (Varian MAT CH-7A, Finnigan MAT 8230, Finnigan MAT 312; 70 eV): signals given in m/z with relative intensity (%) in brackets.
Pig liver esterase (EC 3.1.1.1) was obtained from Sigma.

(2S, 3R)-cis-endo-3-(Hydroxymethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid lactone ((+)-2): A solution of (-)-1 [5] (1.00 g, 5.10 mmol) in ethanol (3 ml) was added to liquid ammonia (30 ml, distilled from sodium) at -78 °C. Sodium (0.80 g, 34.8 mmol) was added in small pieces and the resulting mixture was stirred for 30 min at -78 °C. After addition of NH_4Cl, the ammonia and ethanol were evaporated and the residue was stirred with 6N HCl (10 ml) for 30 min at room temperature. The mixture was extracted with ether (3 x 20 ml) and the organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by HPLC (ethyl acetate / CH_2Cl_2 1 : 9) to yield (+)-2 (470 mg, 61 %) as a white solid:

m.p. 120 - 122 °C (lit.[3] m.p. 120 - 122 °C; lit[7] m.p. 65 - 67 °C). - $[\alpha]_D^{20}$ = +145° ($CHCl_3$, c = 5.2) [lit.[3] $[\alpha]_D^{25}$ = +143.2° ($CHCl_3$, c = 5.2); lit.[6] $[\alpha]_D^{25}$ = +136° ($CHCl_3$, c = 1.00); lit.[7] $[\alpha]_D^{26}$ = +147.52° ($CHCl_3$, c = 0.52)]. - IR: 1745 (C=O). - ^{1}H NMR: 1.47 (br. d, J = 8.6, 1 H), 1.65 (br. d, J = 8.6, 1 H), 3.05 - 3.16 (m, 2 H) including 3.10 (br. s), 3.25 (dd, J = 9.2, J = 4.6, 1 H), 3.34 (br. s, 1 H), 3.80 (dd, J = 9.7, J = 3.1, 1 H), 4.29 (dd, J = 9.7, J = 8.5, 1 H), 6.26 - 6.34 (m, 2 H). - MS: 150 (9, M^+), 91 (28), 85 (63), 67 (42), 66 (100), 65 (42).

(2S, 3R)-cis-endo-3-(Hydroxymethyl)bicyclo[2.2.1]heptane-2-carboxylic acid lactone ((+)-3): (+)-2 (300 mg, 2.00 mmol) in methanol (10 ml) containing a catalytic amount of 10 % Pd on C was hydrogenated under H_2 (1 atm) at room temperature overnight. After filtration through celite to remove the catalyst, evaporation of the solvent in vacuo left (+)-3 (303 mg, 100 %) as a white solid. HPLC (ethyl acetate / CH_2Cl_2 1 : 9) provided an analytical sample:
m.p. 140 - 142 °C (lit[3]: m.p. 145 - 146 °C). - $[\alpha]_D^{20}$ = +152° ($CHCl_3$, c = 0.85) [lit.[3]: $[\alpha]_D^{25}$ = +123.7° ($CHCl_3$, c = 0.84); lit.[4] $[\alpha]_D^{26}$ = +153.28° ($CHCl_3$, c = 1.01)]. - IR: 1755 (C=O). - ^{1}H NMR: 1.40 - 1.65 (m, 6 H), 2.37 (br. s, 1 H), 2.67 (br. s , 1 H), 2.82 - 2.93 (m, 1 H), 2.98 (dd, J = 11.4, J = 5.6, 1 H), 4.21 - 4.34 (m, AB of ABX with δ_A = 4.30, δ_B = 4.25, J_{AB} = 10.0, J_{AX} = 8.4, J_{BX} = 2.7, 2 H). - MS: 152 (0.8, M^+), 85 (50), 80 (25), 67 (25), 66 (100).

(2S, 3R)-cis-endo-3-(Phenylthiomethyl)bicyclo[2.2.1]heptane-2-carboxylic acid ((+)-4a): Thiophenol (1.05 ml, 10.2 mmol) was added at 0 °C to a suspension of sodium hydride (240 mg of 99 % purity, 9.90 mmol) in DMF (5 ml). After stirring at room temperature for 10 min, the resulting solution was treated with a solution of (+)-3 (1.52 g, 9.99 mmol) in DMF (5 ml). The mixture was stirred at 100 °C for 4 h, cooled to room temperature, and then cold 2N HCl (50 ml) was added. After extraction with CH_2Cl_2 (4 x 30 ml), the organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography (ethyl acetate / hexane 1 : 2) to yield (+)-4a (2.13 g, 81 %) as a white solid:
m.p. 64 - 65 °C. - $[\alpha]_D^{20}$ = +55.8° (CCl_4, c = 1.8). - IR: 1710 (C=O). - ^{1}H NMR: 1.3 - 1.5 (m, 4 H), 1.56 - 1.68 (m, 1 H), 1.73 - 1.84 (m, 1 H), 2.24 - 2.37 (m, 1 H), 2.41 (br. s, 1 H), 2.56 (br. s, 1 H), 2.88 (br. dd, J = 4.1, J = 11.2, 1 H), 3.06 (dd, J = 9.4, J = 12.9, 1 H), 3.42 (dd, J = 7.1, J = 12.9, 1 H), 7.1 - 7.4 (m, 5 H). - MS (GC/MS of methyl ester prepared by treatment of (+)-4a with CH_2N_2): 276 (8, M^+), 245 (2), 168 (9), 167 (100), 135 (14), 107 (45), 79 (37). - MS (high resolution): 262.1030 (M^+) (calculated for $C_{15}H_{18}O_2S$: 262.1027). - Analysis: $C_{15}H_{18}O_2S$ (262.4) Calcd. C 68.66 H 6.92 Found C 68.52 H 6.92.

(2S, 3R)-cis-endo-3-(2-Propylthiomethyl)bicyclo[2.2.1]heptane-2-carboxylic acid ((+)-4b): Isopropyl thiol (310 µl, 3.34 mmol) was added at 0 °C to a suspension of sodium hydride (78.3 mg of 99 % purity, 3.23 mmol) in DMF (1.5 ml). After stirring at room temperature for 15 min, the suspension was treated at 0 °C with a solution of (+)-3 (492 mg, 3.23 mmol) in DMF (1.5 ml). The mixture was stirred at room temperature overnight and then worked up as described for (+)-4a. The crude product was purified by HPLC (ethyl acetate / hexane 1 : 3) to yield (+)-4b (474 mg, 64 %) as a waxy material:
$[\alpha]_D^{20}$ = +20.7° (CCl_4, c = 1.8). - IR: 1705 (C=O). - ^{1}H NMR: 1.25 and 1.26 (2 d, J= 6.7 each, 6 H), 1.35 -1.55 (m, 4 H), 1.55 - 1.69 (m, 1 H), 1.71 -1.85 (m, 1 H), 2.20 - 2.32 (m, 1 H), 2.37 (br. s, 1 H), 2.54 (br. s, 1 H), 2.69 (dd, J = 9.6, J = 12.1, 1 H), 2.83 - 2.99 (m, 3 H). - MS (GC/MS of methyl ester prepared by treatment of (+)-4b with CH_2N_2): 242 (32, M^+), 199 (37), 167 (100), 139 (46), 107 (47), 79 (42), 43 (69), 41 (96). - MS (high resolution): 228.1184 (M^+) (calculated for $C_{12}H_{20}O_2S$: 228.1184). - Analysis: $C_{12}H_{20}O_2S$ (228.4) Calcd. C 63.11 H 8.83 Found C 63.22 H 8.77.

(2S, 3R)-cis-endo-3-(Phenylsulfonylmethyl)bicyclo[2.2.1]heptane-2-carboxylic acid ((+)-5a): A solution of oxone (6.83 g, 22.2 mmol $KHSO_5$) in water (30 ml) was buffered to pH 6 with Na_2HPO_4 and then added to a solution of (+)-4a (1.94 g, 7.39 mmol) in methanol (30 ml), cooled to 0 °C. After the mixture was stirred at room temperature for 4 h, water (100 ml) was added, and methanol was removed in vacuo. The aqueous residue was extracted with CH_2Cl_2 (3 x 80 ml) and the organic layers were dried over $MgSO_4$. Removal of the solvent in vacuo left (+)-5a (2.08 g, 96 %) as a waxy material. The corresponding methyl ester (CH_2N_2) was homogeneous by capillary GC. Flash chromatography (ethyl acetate / hexane 4 : 1) provided an analytical sample of (+)-5a:
$[\alpha]_D^{20}$ = +43.8° (CCl_4, c = 1.9). - IR: 1715 (C=O), 1320 and 1160 (SO_2). - ^{1}H NMR: 1.3 - 1.7 (m, 6 H), 2.40 (br. s, 1 H), 2.57 - 2.74 (m, 2 H) including 2.61 (br. s), 3.02 (dd, J = 4.3, J = 11.0, 1 H), 3.20 (dd, J = 5.7, J = 14.0, 1 H), 4.03 (dd, J = 8.5, J = 14.0, 1 H), 7.5 - 7.75 (m, 3 H), 7.85 - 8.05 (m, 2 H). - ^{13}C NMR: 21.72 (CH_2), 24.13 (CH_2), 35.27 (CH), 39.77 (CH_2), 41.78 (CH), 41.91 (CH), 45.26 (CH), 54.55 (CH_2), 127.88 (CH), 129.28 (CH), 133.57 (CH), 139.85 (C), 179.18 (C). - MS (GC/MS of methyl

ester prepared by treatment of (+)-5a with CH_2N_2): 308 (0.2, M^+), 277 (5), 276 (4), 167 (100), 135 (21), 107 (69), 79 (45). - Analysis: $C_{15}H_{18}O_4S$ (294.4) Calcd. C 61.20 H 6.16 Found C 61.33 H 6.12.

(2S, 3R)-cis-endo-3-(2-Propylsulfonylmethyl)bicyclo[2.2.1]heptane-2-carboxylic acid ((+)-5b): (+)-4b (278 mg, 1.22 mmol) was oxidized as described for (+)-4a to yield (+)-5b (316 mg, 100 %) as a white solid. The corresponding methyl ester (CH_2N_2) was homogeneous by capillary GC. HPLC (ethyl acetate / hexane 4 : 1) provided an analytical sample of (+)-5b: m.p. 99 - 100 °C. - $[\alpha]_D^{20}$ = +37.3° ($CHCl_3$, c = 1.0). - IR: 1705 (C=O), 1305 and 1120 (SO_2). - ^{1}H NMR: 1.39 (d, J = 6.8, 3H), 1.42 - 1.55 (m, 5H), 2.45 (br. s, 1H), 2.84 (br. s, 1H), 2.84 - 2.77 (m, 1H), 2.96 - 3.13 (m, 3H), 3.36 (dd, J = 3.4, J = 13.3, 1 H). - ^{13}C NMR: 15.17 (CH_3), 15.29 (CH_3), 21.71 (CH_2), 24.09 (CH_2), 33.86 (CH), 39.71 (CH_2), 41.60 (CH), 41.85 (CH), 45.27 (CH), 46.63 (CH_2), 53.86 (CH), 179.15 (C). - MS: 243 (0.9, M - OH), 217 (0.8), 153 (100), 107 (54), 79 (47), 67 (41), 43 (68), 41 (61). - Analysis: $C_{12}H_{20}O_4S$ (260.4) Calcd. C 55.35 H 7.74 Found C 55.51 H 7.78.

Tetrabutylammonium salt of (+)-5a: A solution of tetrabutylammonium hydroxide in methanol (0.81M, 500 µl, 0.405 mmol) was added to a solution of (+)-5a (119 mg, 0.404 mmol) in methanol (1.5 ml), cooled to 0 °C. After warming to room temperature, the mixture was concentrated in vacuo to leave the tetrabutylammonium salt of (+)-5a (216 mg, 100 %) as an oil:
$[\alpha]_D^{20}$ = +0.9° ($CHCl_3$, c = 1.0). - IR: 1565 (C=O). - ^{1}H NMR: 0.97 (t, J = 7.3, 12 H), 1.22 - 1.49 (m, 12 H), 1.52 - 1.73 (m, 10 H), 2.34 - 2.50 (m, 3 H) including 2.37 and 2.46 (2 br. s), 2.78 (dd, J = 3.7, J = 11.4, 1 H), 3.24 - 3.37 (m, 8 H), 3.63 (dd, J = 10.8, J = 14.8, 1 H), 4.19 (dd, J = 3.4, J = 14.8, 1 H), 7.45 - 7.65 (m, 3 H), 7.85 - 7.95 (m, 2 H). - ^{13}C NMR: 13.23 (CH_3, NBu_4^+), 19.26 (CH_2, NBu_4^+), 22.20 (CH_2), 23.51 (CH_2, NBu_4^+), 23.91 (CH_2), 34.45 (CH), 39.41 (CH_2), 40.28 (CH), 40.86 (CH), 50.42 (CH), 55.71 (CH_2), 58.28 (CH_2, NBu_4^+), 127.34 (CH), 128.54 (CH), 132.66 (CH), 148.54 (C), 176.27 (C).

(1S)-3-(Methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid ((-)-7): To a solution of 6 [11] (1.04 g, 5.00 mmol) in acetone (20 ml) and aqueous phosphate buffer pH 7 (0.075M, 180 ml) was added pig liver esterase (10 mg, 1600 units). The mixture was stirred at room temperature for 5 h, while the pH was kept between 6.9 and 7.0 by dropwise addition of 2N NaOH. After acidification with 2N HCl (30 ml), the mixture was extracted with ethyl acetate (5 x 50 ml). The organic layers were filtered to remove the enzyme and dried over $MgSO_4$. Evaporation of the solvent in vacuo left (-)-7 (750 mg, 77 %) as a white solid. HPLC (acetone / hexane 3 : 1) provided an analytical sample:
m.p. 100 - 102 °C (lit [12] for rac-7 m.p. 108 - 109 °C). - $[\alpha]_D^{20}$ = -9.3° ($CHCl_3$, c = 1.07). - IR: 1720 (C=O). - ^{1}H NMR: 2.12 - 2.21 (m, 1 H), 2.22 - 2.31 (m, 1 H), 3.95 (s, 3H), 4.12 (br. s, 1 H), 4.28 (br. s, 1 H), 6.87 - 6.98 (m, 2H). - MS (high resolution): 194.0570 (M^+) (calculated for $C_{10}H_{10}O_4$: 194.0579). - Analysis: $C_{10}H_{10}O_4$ (194.2) Calcd. C 61.85 H 5.19 Found C 61.69 H 5.30.

(2R, 3S)-cis-endo-3-(Methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid ((+)-8): (-)-7 (97.1 mg, 0.500 mmol) in ethyl acetate (5 ml) containing a catalytic amount of PtO_2 was hydrogenated under H_2 (1 atm) at room temperature overnight. After filtration to remove the catalyst, evaporation of the solvent in vacuo left an oily product (94.0 mg, 95 %) consisting of 91 % (+)-8 (see lit. [13] for rac-8) and 9 % trans-isomer(s) [14]:
$[\alpha]_D^{20}$ = +3.6° ($CHCl_3$, c = 1.06) for the mixture. - ^{1}H NMR: 1.35 - 1.55 (m, 4 H), 1.7 - 1.85 (m, 2 H), 2.55 and 2.58 (2 br. s, 2 H), 2.96 (dd, J = 3.6, J = 11.8, 1 H), 3.03 (dd, J = 3.6, J = 11.8, 1 H), 3.63 (s, 3 H). - MS: 180 (19, M - H_2O), 167 (36), 148 (37), 132 (64), 114 (70), 67 (84), 66 (100).

(-)-3 from (+)-8: The above mixture containing 91 % (+)-8 was subjected to sodium-ammonia reduction as described for (-)-1. HPLC (ethyl acetate / CH_2Cl_2 1 : 9) yielded (-)-3 (75 % on cis-endo starting compound) as a white solid:
$[\alpha]_D^{20}$ = -55.1° ($CHCl_3$, c = 1.09). - Spectral data as for (+)-3.

(E)-2-Butenyl (2R,3S)-cis-endo-3-(2-propylsulfonylmethyl)bicyclo[2.2.1]heptane-2-carboxylate ((-)12): To a solution of (-)-5b (260 mg, 1.00 mmol), triphenylphosphine (262 mg, 1.00 mmol), and (E)-2-butenol (108 mg, 1.50 mmol) in THF (4 ml) was added a solution of diethyl azodicarboxylate (174 mg, 1.00 mmol) in THF (1 ml). After stirring the mixture at room temperature for 17 h, the solvent was removed in vacuo. Flash chromatography (ethyl acetate / hexane 1 : 3) of the residue yielded (-)-12 (213 mg, 68 %) as a colourless oil:

$[\alpha]_D^{20}$ = -41.8° ($CHCl_3$, c = 1.1). - IR: 1720 (C=O), 1295 and 1120 (SO_2), 960 (C=C). - ^1H NMR: 1.34 - 1.58 (m, 12 H) including 1.38 and 1.39 (2 d, J = 6.9 each), 1.72 (dd, J = 6.4, J = 1.1, 3 H), 2.44 (br. s, 1 H), 2.55 (br. s, 1 H), 2.69 (m_c, 1 H), 2.95 - 3.13 (m, 3 H) consisting of 2.99 (ddd, J = 11.1, J = 4.3, J = 1.4) and 3.06 (sept, J = 6.9) and 3.06 (dd, J = 13.4, J = 6.5), 3.82 (dd, J = 13.4, J = 7.8, 1 H), 4.46 (br. d, J = 6.4, 2 H), 5.57 (dtq, J_d = 15.3, J_t = 6.4, J_q = 1.5, 1 H), 5.78 (dqt, J_d = 15.3, J_q = 6.4, J_t = 1.1, 1 H). - MS (GC/MS): 243 (64, M - OCH_2-CH=CH-CH_3), 153 (100), 107 (94), 79 (43), 55 (77), 43 (48), 41 (30). - Analysis: $C_{16}H_{26}O_4S$ (314.4) Calcd. C 61.13 H 8.34 Found C 61.13 H 8.42.

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