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A short and convenient procedure for the stereoselective synthesis of 2-hydroxy-1-norbornanesulfonamides

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Abstract—A short and convenient procedure for the stereoselective synthesis of novel optically active 2-hydroxy-1-norbornanesulfonamides starting from commercially available natural camphor and fenchone is reported. The synthetic route involves a nucleophilic substitution at the sulfenyl sulfur atom of 2-methylene-1-norbornylthiotriflates followed by oxidation of the intermediate sulfenamides and highly diastereoselective reduction of the carbonyl group of the parent 2-oxo-1-norbornanesulfonamides.

1. Introduction

Chiral sulfonamides constitute an important class of chiral controllers, both as auxiliaries or catalysts, for a wide variety of asymmetric transformations.[1] Difunctional sulfonamides derived from chiral diamines and aminoalcohols are very versatile ligands, which have been employed with high enantioselectivity levels in a wide range of catalytic asymmetric reactions such as cyclopropanations by means of zinc bis(sulfonamide) complexes,[2] copper-catalyzed Michael additions of diethylzinc,[3] Diels–Alder cycloadditions catalyzed by aluminium bis(sulfonamide) complexes,[4] allylation of aldehydes by boron sulfonamides,[5] Mukaiyama aldol reaction catalyzed by lanthanide sulfonamide complexes[6] and titanium-promoted addition of dialkylzinc to aldehydes[7] (the last being one of the most studied) and ketones.[8] Some representative examples of chiral sulfonamides, which have been used as chiral controllers in stereoselective synthesis, are depicted in Figure 1.

C_2-Symmetrical bistriflamide **1**, for example, has found interesting applications in the enantioselective alkylation of a wide range of aldehydes.[7a,f,9] Other

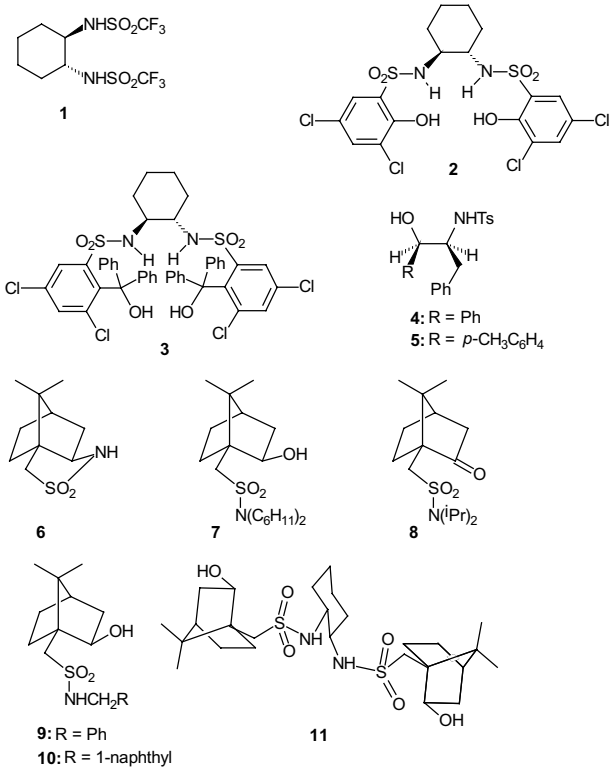

Figure 1.

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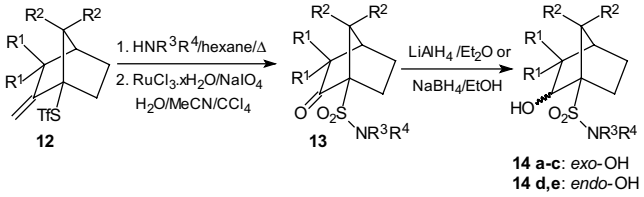
C_2-symmetrical hydroxysulfonamides such as **2**[10] and **3**,[11] as well as the acyclic β-hydroxysulfonamides **4**, **5**[7e] and related compounds[7g] have proven to be excellent ligands for the enantioselective alkylation of aldehydes.

Chiral camphor-based sulfonamides play an important role in this field and their applications either as auxiliaries or ligands for enantioselective catalysis are well documented in the literature. Thus, high enantioselectivity levels have been achieved in different stereoselective synthetic processes controlled by auxiliaries such as **6** (the well-known Oppolzer's sultam),[12] **7** (one of the Oppolzer's alcohols)[13] and camphorsulfonamide **8**.[14] Concerning with the catalytic applications, ligand **9**, developed by Ramón and Yus[15] was found to catalyze the titanium-mediated enantioselective addition of diethylzinc to benzaldehyde with up to 72% ee. More importantly, in 1998 the same authors, using the ligands **9** and **10**, achieved the first enantioselective catalytic dialkylzinc addition to ketones with up to 89% ee.[8a] In further studies, Walsh[8b] and Yus[8c] have reported independently on this last reaction and found that the C_2-symmetrical bis(camphorsulfonamide) **11** is an excellent ligand promoting the alkylation of prochiral ketones with up to 99% ee. Very recently, Yus et al. have reported new applications of the ligand **11** in the enantioselective arylation of ketones[16] and catalytic enantioselective synthesis of frontalin[17] as well as on the synthesis of new C_2-symmetrical bis(hydroxycamphorsulfonamide) ligands and their application in the enantioselective addition of dialkylzinc to aldehydes and ketones with up to 90% ee.[18]

In order to obtain new data about the structural factors affecting the catalytic activity, the development of novel chiral camphor- or norbornane-based sulfonamides with different substitution patterns is of great interest. Following our studies on the synthesis and applications of chiral bridgehead norbornane derivatives,[19] we report herein a short and easy procedure for the stereoselective synthesis of new optically active 2-hydroxy-1-norbornanesulfonamides starting from commercially available natural camphor and fenchone. These ligands are very promising as chiral controllers and could find interesting applications in asymmetric syntheses.



Scheme 1.

2. Results and discussion

In previous studies we have shown[20] that the reaction of optically active thiocamphor and thiofenchone with Tf_2O leads to the corresponding 2-methylene-1-norbornylthiotriflates **12** through a Wagner–Meerwein rearrangement, allowing the introduction of a sulfur atom at the bridgehead position of the norbornane framework. The solvolysis of **12** in Et_2NH gives the bridgehead sulfenamides, which can be easily oxidized to the corresponding 2-oxo-1-norbornane sulfonamides.[19e] We have now extended this methodology to the synthesis of a new series of 2-hydroxy-1-norbornanesulfonamides **14** (Scheme 1). Our results are summarized in Table 1.

Thiotriflates **12** were prepared in two steps starting from natural camphor and fenchone.[20] The reaction of **12** with the primary or secondary amine followed by oxidation with $RuCl_3{\cdot}xH_2O/NaIO_4$[21] gave the corresponding 2-oxo-1-norbornanesulfonamide **13** in moderate to good yield. Oxidation of both sulfenyl sulfur and methylene group of the intermediate nonisolated sulfenamide takes place in a single step. The preparation of 7,7-dimethyl-substituted hydroxysulfonamides **14a–c** was carried out by reduction of the parent ketosulfonamides **13a–c** with $NaBH_4$/EtOH under similar conditions as reported by Ramón and Yus.[15] However, due to steric factors, a rate decrease and lower conversion was observed in the reduction of 3,3-dimethyl-substituted ketosulfonamides **13d** and **13e** under the same reaction conditions. Therefore, $LiAlH_4/Et_2O$ was straightforwardly used as a reducing agent for the preparation of **14d** and **14e**. It is noteworthy that in all

Table 1

Entry	Product	R^1	R^2	R^3	R^4	Yield (%)[a]
1	**13a**	H	Me	H	CH_2Ph	58
2	**13b**	H	Me	H	*i*-Pr	68
3	**13c**	H	Me	Et	Et	75[b]
4	**13d**	Me	H	H	CH_2Ph	66
5	**13e**	Me	H	H	*i*-Pr	55
6	**14a**	H	Me	H	CH_2Ph	86
7	**14b**	H	Me	H	*i*-Pr	80
8	**14c**	H	Me	Et	Et	79
9	**14d**	Me	H	H	CH_2Ph	83
10	**14e**	Me	H	H	*i*-Pr	76

[a] The yields are given in isolated product.
[b] See Ref. 19e.

cases studied, regardless of the reducing agent used as well as the *gem*-dimethyl position (C3 or C7) at the norbornane framework, the reduction of carbonyl group is virtually 100% diastereoselective. GC/MS and ^{1}H NMR analyses of the reaction crude reveal that only one of the two possible epimers of **14** is obtained. The absolute configuration at C2 was unambiguously established on the basis of ^{1}H–^{13}C HMQC and selective 1D NOESY NMR experiments (see experimental section). The stereochemical outcome of these reductions follows the same trends that we have previously observed in the reduction of several bridgehead-substituted 3,3- and 7,7-dimethyl-2-norbornanones,[22] being still more strongly dependent on the methyl substitution pattern in this case. Thus, the sulfonamides **13a**–**c**, bearing the *gem*-dimethyl group at C7, undergo *endo* hydride attack giving the corresponding *exo* epimers **14a**–**c** exclusively, whereas the 3,3-dimethylated **13d**,**e** give only the *endo* epimers **14d**,**e** by *exo* hydride attack. This enhanced diastereoselectivity is obviously an interesting feature, which allows an easy access to optically active 2-hydroxy-1-norbornanesulfonamides with different topological dispositions of hydroxy and sulfonamido groups as a function of the methyl substitution pattern.

3. Conclusions

In conclusion, we have developed a short and efficient procedure for the stereoselective synthesis of novel 2-hydroxy-1-norbornanesulfonamides starting from natural camphor and fenchone. An important feature of this method is the highly diastereoselective carbonyl group reduction in the parent 2-oxo-1-norbornanesulfonamides, which allows an easy and stereocontrolled access to a single epimer of the title compounds, absolute configuration at the stereogenic centre C2 being a function of the *gem*-dimethyl substitution pattern. These compounds offer interesting applications as bidentate ligands in several processes of catalytic asymmetric synthesis. The different spatial orientation of the hydroxy and sulfonamido groups provides opportunities to study the effect of the structure of the ligand on the stereochemical outcome and enantioselectivity. Further work in this field is currently in progress.

4. Experimental

4.1. General

NMR spectra were recorded on a Bruker-AC 200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) with TMS as the internal standard; *J* values are given in hertz. IR spectra were recorded on a Shimadzu FTIR spectrometer. Mass spectra were recorded on a GC–MS Shimadzu QP5000 (60 eV) mass spectrometer. For gas chromatography, a Shimadzu 17 AAF chromatograph equipped with a capillary SGL-1 column was used. Optical rotation data were recorded on a Perkin–Elmer 241 polarimeter; concentrations are given as g/100 mL of solvent.

4.2. Typical procedure for the synthesis of ketosulfonamides 13

A solution of thiotriflate **12** (2.0 mmol) and the corresponding amine (4.4 mmol) in hexane (25 mL) was refluxed for 5 h. After cooling to room temperature, the reaction mixture was diluted with hexane (20 mL), washed successively with 1 M tartaric acid solution (3×20 mL) and H_2O (20 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude was dissolved in CCl_4 (25 mL) and this solution then added to another solution of $NaIO_4$ (16.0 mmol) in H_2O (75 mL) and MeCN (25 mL) followed by addition of $RuCl_3{\cdot}xH_2O$ (0.05 mmol). After being vigorously stirred for 5 h at rt, the reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic layer was washed with H_2O (2×20 mL) and dried over $MgSO_4$. After filtration and solvent evaporation, the crude was purified by column chromatography (silica gel/CH_2Cl_2) to give pure **13**.

4.2.1. (1*R*)-*N*-Benzyl-7,7-dimethyl-2-oxobicyclo[2.2.1]-heptane-1-sulfonamide 13a. Yield 58%; $[\alpha]_D^{20}$ +1.5 (*c* 1.12, CH_2Cl_2); mp 115.4–116.9 °C. ^{1}H NMR δ: 7.37–7.27 (m, 5H), 5.30 (AB*X* system, $J_{AX} = 6.0$ Hz; $J_{BX} = 7.4$ Hz, 1H), 4.47 and 4.27 (*AB*X system, $J_{AB} = 14.4$ Hz, $J_{AX} = 6.0$ Hz; $J_{BX} = 7.4$ Hz, 2H), 2.27–2.51 (m, 2H), 2.28–2.10 (m, 2H), 2.02 (d, $J = 18.5$ Hz, 1H), 1.93–1.78 (m, 1H), 1.55–1.40 (m, 1H), 1.33 (s, 3H), 1.25 (s, 3H) ppm. ^{13}C NMR δ: 209.3, 137.6, 128.7, 127.7, 127.7, 79.9, 50.5, 47.0, 44.0, 43.7, 26.7, 26.6, 21.5, 20.6 ppm. FTIR (KBr) *v*: 3337, 1751, 1707, 1608, 1571, 1497, 1454, 1413, 1356, 1327, 1217, 1153 cm^{-1}. MS *m*/*z*: 243 (M^+−64, 2), 174 (4), 123 (7), 106 (100), 91 (19), 79 (9), 67 (13), 55 (8), 41 (14). Anal. Calcd for $C_{16}H_{21}NO_3S$: C, 62.51; H, 6.88; N, 4.56; S, 10.43. Found: C, 62.13; H, 6.79; N, 4.62; S, 10.32.

4.2.2. (1*R*)-*N*-Isopropyl-7,7-dimethyl-2-oxobicyclo[2.2.1]-heptane-1-sulfonamide 13b. Yield 68%; $[\alpha]_D^{20}$ +3.2 (*c* 1.34, CH_2Cl_2); mp 105.0–107.0 °C. ^{1}H NMR δ: 4.66 (br d, $J = 7.3$ Hz, 1H), 3.73 (dqq, $J = 7.3$, 6.6, 6.4 Hz, 1H), 2.63–2.44 (m, 2H), 2.21–2.00 (m, 2H), 1.94 (d, $J = 18.8$ Hz, 1H), 1.78 (ddd, $J = 13.4$, 9.3, 4.2 Hz, 1H), 1.47–1.33 (m, 1H), 1.24 (s, 3H), 1.19 (d, $J = 6.4$ Hz, 3H), 1.16 (s, 3H), 1.11 (d, $J = 6.6$ Hz, 3H) ppm. ^{13}C NMR δ: 209.3, 79.8, 50.1, 46.1, 44.0, 43.6, 26.8, 26.4, 25.6, 23.9, 21.5, 20.5 ppm. FTIR (KBr) *v*: 3290, 1738, 1319, 1294, 1140 cm^{-1}. MS *m*/*z*: 244 (M−15, 32), 137 (10), 123 (5), 109 (16), 95 (15), 79 (8), 67 (34), 58 (84), 44 (100), 41 (48). Anal. Calcd for $C_{12}H_{21}NO_3S$: C, 55.61; H, 8.10; N, 5.40; S, 12.37. Found: C, 55.79; H, 7.85; N, 5.12; S, 11.99.

4.2.3. (1*R*)-*N*-Benzyl-3,3-dimethyl-2-oxobicyclo[2.2.1]-heptane-1-sulfonamide 13d. Yield 66%; $[\alpha]_D^{20}$ +60.1 (*c* 0.30, CH_2Cl_2); mp 113.5–114.9 °C. ^{1}H NMR δ: 7.39–7.31 (m, 5H), 5.17 (AB*X* system, br t, $J = 6.2$ Hz, 1H), 4.43 and 4.31 (*AB*X system, $J_{AB} = 14.4$ Hz, $J_{AX} = J_{BX} = 6.2$ Hz, 2H), 2.47–2.30 (m, 3H), 2.12 (dd, $J = 10.5$, 1.7 Hz, 1H), 1.97–1.65 (m, 3H), 1.13 (s, 3H),

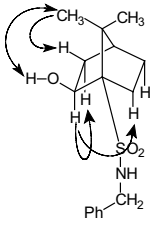
1.10 (s, 3H) ppm. ^{13}C NMR δ: 213.3, 137.4, 128.7, 127.8, 127.7, 76.8, 49.0, 47.0, 44.2, 37.9, 27.1, 24.6, 23.3, 21.5 ppm. FTIR (KBr) ν: 3356, 3290, 1738, 1410, 1321, 1144 cm^{-1}. MS m/z: 243 (M^+−64, 8), 123 (5), 106 (100), 91 (24), 77 (10), 69 (14), 41 (30). Anal. Calcd for $C_{16}H_{21}NO_3S$: C, 62.51; H, 6.88; N, 4.56; S, 10.43. Found: C, 62.34; H, 6.92; N, 4.53; S, 10.41.

4.2.4. (1*R*)-*N*-Isopropyl-3,3-dimethyl-2-oxobicyclo[2.2.1]-heptane-1-sulfonamide 13e. Yield 55%; $[\alpha]_D^{20}$ +54.8 (*c* 1.03, CH_2Cl_2); mp 112.6–114.2 °C. ^{1}H NMR δ: 4.55 (br d, $J = 7.6$ Hz, 1H), 3.78 (d septuplet, $J = 7.6$, 6.6 Hz, 1H), 2.46–2.29 (m, 3H), 2.10 (dd, $J = 10.6$, 1.8 Hz, 1H), 1.98–1.66 (m, 3H), 1.24 (d, $J = 6.6$ Hz, 3H), 1.18 (d, $J = 6.6$ Hz, 3H), 1.14 (s, 3H), 1.10 (s, 3H) ppm. ^{13}C NMR δ: 213.3, 76.9, 49.0, 46.2, 44.3, 37.8, 27.1, 25.2, 24.6, 24.3, 23.3, 21.5 ppm. FTIR (KBr) ν: 3274, 1745, 1465, 1437, 1305, 1134 cm^{-1}. MS m/z: 244 (M−15, 32), 137 (11), 123 (6), 109 (17), 95 (15), 67 (35), 58 (85), 44 (100), 41 (49). Anal. Calcd for $C_{12}H_{21}NO_3S$: C, 55.61; H, 8.10; N, 5.40; S, 12.37. Found: C, 55.73; H, 7.83; N, 5.39; S, 12.12.

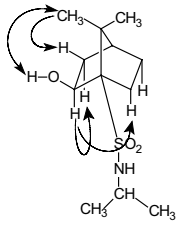
4.3. Typical procedure for the synthesis of hydroxysulfonamides 14a–c

To a suspension of $NaBH_4$ (6.0 mmol) in EtOH (30 mL) at 0 °C was added another solution of ketosulfonamide **13a**–**c** (0.75 mmol) in EtOH (10 mL). After being stirred for 15 h at room temperature, the reaction mixture was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic layer was washed with H_2O (2×20 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude was purified by column chromatography (silica gel, CH_2Cl_2) to give pure **14a**–**c**.

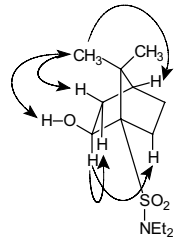
4.3.1. (1*R*,2*S*)-*N*-Benzyl-2-hydroxy-7,7-dimethylbicyclo-[2.2.1]-heptane-1-sulfonamide 14a. Yield 86%; $[\alpha]_D^{20}$ +5.1 (*c* 1.00, CH_2Cl_2); mp 126.4–127.9 °C. ^{1}H NMR δ: 7.37–7.26 (m, 5H), 5.06 (t, $J = 6.1$ Hz, 1H), 4.37 (d, $J = 6.1$ Hz, 2H), 4.09 (dd, $J = 7.7$, 3.5 Hz, 1H), 3.67 (br s, 1H), 2.47–2.28 (m, 1H), 2.04–1.73 (m, 4H), 1.50–1.31 (m, 1H), 1.22–1.05 (m, 1H), 1.38 (s, 3H), 1.18 (s, 3H) ppm. ^{13}C NMR δ: 137.7, 128.7, 127.9, 127.8, 77.0, 73.8, 49.5, 47.0, 46.2, 40.4, 29.8, 26.3, 21.7, 21.1 ppm. FTIR (KBr) ν: 3277, 3431, 3028, 1497, 1452, 1284, 1151, 1094 cm^{-1}. MS m/z: 186 (M^+−123, 2), 106 (100), 91 (50), 79 (17), 77 (17), 69 (15), 67 (17), 41 (42). Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53; S, 10.36. Found: C, 62.62; H, 7.46; N, 4.47; S, 9.94.



4.3.2. (1*R*,2*S*)-2-Hydroxy-*N*-isopropyl-7,7-dimethylbicyclo[2.2.1]heptane-1-sulfonamide 14b. Yield 80%; $[\alpha]_D^{20}$ +10.3 (*c* 1.73, CH_2Cl_2); mp 111.6–113.9 °C. ^{1}H NMR δ: 4.25 (br d, $J = 8.3$ Hz, 1H), 4.09 (ddd, $J = 7.7$, 3.9, 3.6 Hz, 1H), 3.76 (d septuplet, $J = 8.3$, 6.6 Hz, 1H), 3.63 (d, $J = 3.9$ Hz, 1H), 2.45–2.28 (m, 1H), 2.08–1.76 (m, 4H), 1.50–1.34 (m, 1H), 1.39 (s, 3H), 1.25 (d, $J = 6.6$ Hz, 6H), 1.22–0.98 (m, 1H), 1.17 (s, 3H) ppm. ^{13}C NMR δ: 77.1, 73.4, 49.4, 46.4, 46.3, 40.5, 29.9, 26.3, 25.0, 24.9, 21.8, 21.2 ppm. FTIR (KBr) ν: 3516, 3333, 1300, 1132 cm^{-1}. MS m/z: 232 (M−29, 2), 123 (11), 110 (35), 95 (40), 79 (26), 69 (43), 67 (48), 55 (33), 46 (100), 41 (81). Anal. Calcd for $C_{12}H_{23}NO_3S$: C, 55.18; H, 8.81; N, 5.36; S, 12.27. Found: C, 54.91; H, 8.49; N, 5.45; S, 12.18.



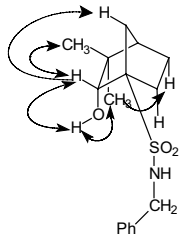
4.3.3. (1*R*,2*S*)-*N*,*N*-Diethyl-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptane-1-sulfonamide 14c. Yield 79%; $[\alpha]_D^{20}$ +5.6 (*c* 0.96, CH_2Cl_2); mp 121.0–122.0 °C. ^{1}H NMR δ: 4.27 (d, $J = 2.7$ Hz, 1H), 4.00 (ddd, $J = 7.6$, 3.1, 2.7 Hz, 1H), 3.38 (m, 4H), 2.38–2.21 (m, 1H), 2.10–1.70 (m, 4H), 1.40 (s, 3H), 1.38–1.09 (m, 2H), 1.21 (t, $J = 7.1$ Hz, 6H), 1.17 (s, 3H) ppm. ^{13}C NMR δ: 76.2, 74.0, 50.3, 45.9, 41.4, 40.8, 29.7, 26.9, 22.2, 21.0, 14.6 ppm. FTIR (KBr) ν: 3489, 1458, 1313, 1140 cm^{-1}. MS m/z: 232 (M^+−43, 2), 123 (10), 110 (33), 95 (41), 81 (12), 79 (25), 77 (15), 69 (43), 67 (48), 46 (100), 41 (82). Anal. Calcd for $C_{13}H_{25}NO_3S$: C, 56.69; H, 9.15; N, 5.08; S, 11.64. Found: C, 56.39; H, 9.03; N, 5.11; S, 11.67.



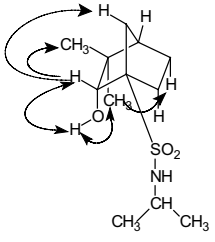
4.4. Typical procedure for the synthesis of hydroxysulfonamides 14d,e

To a suspension of $LiAlH_4$ (2.5 mmol) in Et_2O (30 mL) at 0 °C under argon atmosphere was added another solution of ketosulfonamide **13** (0.50 mmol) in Et_2O (10 mL). After being stirred for 15 h at room temperature, the reaction mixture was carefully quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic layer was washed with H_2O (2×20 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude was purified by column chromatography (silica gel, CH_2Cl_2) to give pure **14d**,**e**.

4.4.1. (1*R*,2*R*)-*N*-Benzyl-2-hydroxy-3,3-dimethylbicyclo-[2.2.1]heptane-1-sulfonamide 14d. Yield 83%; $[\alpha]_D^{20}$ −7.5 (*c* 0.93, CH_2Cl_2); mp 107.6–108.7 °C. ^1H NMR δ: 7.38–7.28 (m, 5H), 4.70 (AB*X* system, $J_{AX} = J_{BX} = 6.1$ Hz, 1H), 4.34 and 4.30 (*AB*X system, $J_{AB} = 14.2$ Hz; $J_{AX} = J_{BX} = 6.1$ Hz; 2H), 4.04 (m, 1H), 2.47 (d, $J =$ 2.9 Hz, 1H), 2.23–2.09 (m, 1H), 2.00–1.77 (m, 4H), 1.69–1.48 (m, 2H), 1.04 (s, 3H), 0.92 (s, 3H) ppm. ^{13}C NMR δ: 137.4, 128.8, 127.9, 127.8, 78.6, 74.2, 47.7, 46.9, 40.1, 36.9, 30.3, 26.6, 20.3, 19.8 ppm. FTIR (KBr) *v*: 3523, 3319, 1306, 1170, 1140, 1082 cm^{-1}. MS *m*/*z*: 172 (M^+−137, 2), 156 (4), 123 (5), 106 (100), 91 (46), 79 (15), 69 (30), 43 (31), 41 (36). Anal. Calcd for $C_{16}H_{23}NO_3S$: C, 62.11; H, 7.49; N, 4.53; S, 10.36. Found: C, 62.18; H, 7.27; N, 4.57; S, 10.15.



4.4.2. (1*R*,2*R*)-2-Hydroxy-*N*-isopropyl-3,3-dimethylbicyclo[2.2.1]heptane-1-sulfonamide 14e. Yield 76%; $[\alpha]_D^{20}$ −1.7 (*c* 1.07, CH_2Cl_2); mp 78.7–79.9 °C. ^1H NMR δ: 4.04 (br d, $J = 8.8$ Hz, 1H), 4.02 (d, $J = 2.2$ Hz, 1H), 3.65 (d septuplet, $J = 8.8$, 6.4 Hz, 1H), 2.48 (d, $J = 2.2$ Hz, 1H), 2.20–2.07 (m, 1H), 2.02–1.76 (m, 4H), 1.71–1.56 (m, 2H), 1.26 (d, $J = 6.4$ Hz, 6H), 1.09 (s, 3H), 0.95 (s, 3H) ppm. ^{13}C NMR δ: 78.5, 74.1, 47.0, 46.8, 40.1, 36.9, 30.4, 25.7, 24.9, 24.7, 20.1, 19.8 ppm. FTIR (KBr) *v*: 3549, 3284, 1467, 1387, 1367, 1296, 1117, 1085 cm^{-1}. MS *m*/*z*: 246 (M^+−15, 16), 138 (16), 123 (16), 109 (12), 95 (44), 81 (16), 70 (71), 60 (79), 44 (100), 41 (85). Anal. Calcd for $C_{12}H_{23}NO_3S$: C, 55.18; H, 8.81; N, 5.36; S, 12.27. Found: C, 55.16; H, 8.50; N, 5.42; S, 12.28.



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