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SYNTHESIS OF 3,4-DIHYDROSPIRO[2H-1-BENZOPYRAN-2,2'-BICYCLO[2.2.1]HEPTANE] RING SYSTEM.

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Abstract: Camphene oxide reacted with dilithiated o-methoxyphenylacetic acid to yield selectively the *exo* isomer of a spiro[γ-lactone-2,2'-bicyclo[2.2.1]heptane] which was stereoselectively converted into the *exo*-3,4-dihydrospiro[2H-1-benzopyran-2,2'-bicyclo[2.2.1]heptane] .

Synthesis of spiro ring systems, which comprise a benzopyran moiety joined to a terpene-derived ring, is of current interest since several natural products containing such spiro systems have been recently isolated from plants.[1] We wanted to construct the spiro system **1** consisting of a benzopyran synthon bound to a bicyclo[2.2.1]heptane moiety. Camphene oxide **4** seemed to be a logical electrophilic reagent to carry the camphane synthon.[2] In order for the synthesis to proceed efficiently it is necessary that: (i) the substituted norbornyl cation **2** should not undergo a Wagner-Meerwein rearrangement[3] and (ii) that the intramolecular attack on this cation by the OH group proceeds from the

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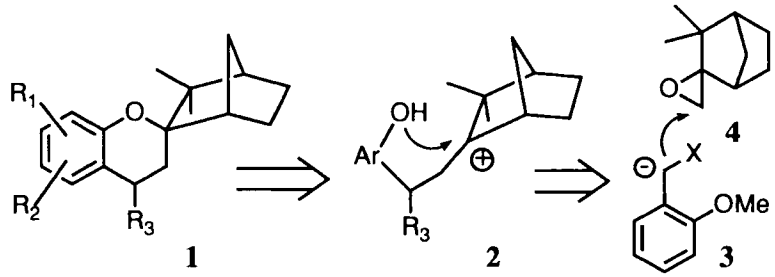
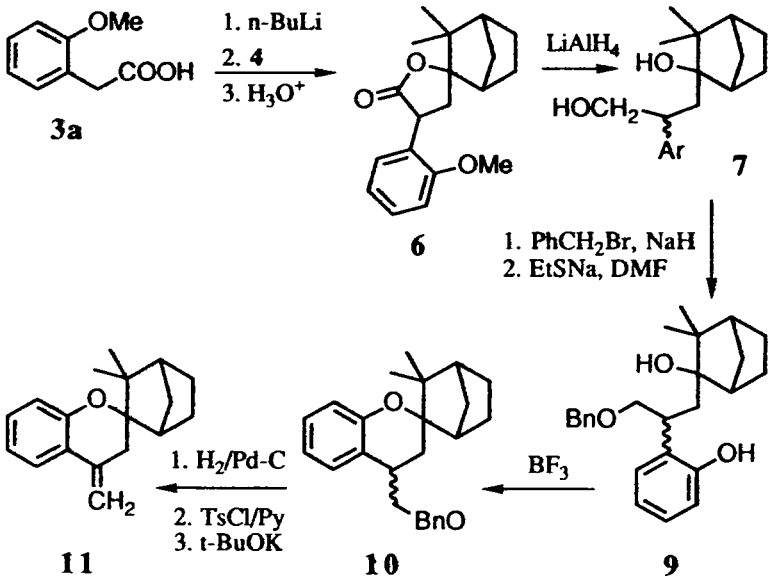
exo face. While we could predict the latter to be likely with reasonable confidence,[4] the possibility of a rearrangement was more worrisome.

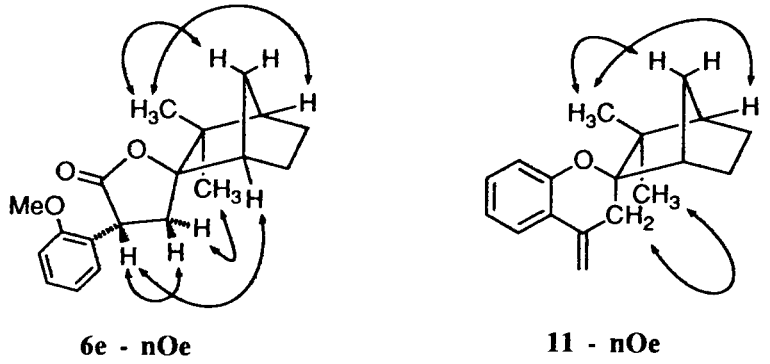


We have reacted camphene oxide, obtained by epoxidation of camphene with m-CPBA as a mixture of *exo* and *endo* diastereoisomers in a ratio of 4:1,[2] with dilithiated 2-methoxyphenylacetic acid.[5] The reaction proceeded slowly and required reflux in a mixture of THF and HMPA for 36 hours to attain a reasonable yield. After acidic work up a crystalline compound resulted which we identified as the *exo* lactone **6e** (45% yield). The stereochemistry of this compound was assigned on the basis of nuclear Overhauser effect studies (c.f **6e-nOe**, the nuclear Overhauser enhancements are indicated with arrows).

The lactone **6e** was reduced to the diol **7** with lithium aluminium hydride. During this reaction the benzylic stereogenic carbon atom underwent partial epimerization - two diastereoisomers were produced in a ratio of **3:1**. After protection of the primary OH the phenolic hydroxy group was deprotected using conditions developed by Salomon.[6] The resulting diol **9** cyclized smoothly, selectively (from the *exo* face), and without any evidence of a rearrangement of the camphane skeleton to produce required bicyclic system as a benzyl ether **10** which was formed as a mixture of two diastereoisomers. Deprotection of the primary alcohol followed by tosylation and elimination gave compound **11** (one isomer), structure of which was confirmed by nOe (c.f. **11-nOe**).

Thus a spirochromane system has been constructed starting from camphene oxide; this strategy is complementary to the most often used strategy based on condensation of acetophenones.[1e]





EXPERIMENTAL SECTION:

All air sensitive reactions were done under argon. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under nitrogen atmosphere prior to use. DMSO and DMF were dried with NaH

and CaH_2, respectively, distilled under vacuum and stored over 4A molecular sieves. n-BuLi (Aldrich) was titrated using 2,5-dimethoxybenzyl alcohol as indicator. Flash column chromatographic separations were carried out with Merck Kieselgel 60 (230-400 mesh ASTM). All thin layer chromatography was performed using precoated TLC plates with Silica Gel 60 F254. The spots were detected using UV light or phosphomolybdic acid/$Ce(SO_4)_2$ solution followed by charring on a hot plate.

Melting points are uncorrected. IR spectra were obtained using sodium chloride cells on a Perkin-Elmer 780 Infrared Spectrophotometer. Low resolution mass spectra were done with a retro-fit VG Analytical, MS-12. All ^1H and ^{13}C NMR spectra were recorded with Bruker AM-300 (at 300 MHz and 75 MHz respectively) using $CDCl_3$ as a solvent and TMS as internal standard, unless stated otherwise. The following abbreviations are used for ^1H NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; for ^{13}C NMR spectra: s', d', t', q' referring respectively to zero, one two, three, protons attached to the carbon atom.

exo-3'-(2-Methoxyphenyl)-3,3-dimethylspiro [bicyclo[2.2.1]heptane-2,5'-2(3H)-dihydrofuranone (6e)

To a solution of o-methoxyphenylacetic acid (2.46 g, 15 mmol) in THF (25 mL) was added TMEDA (5.1 mL, 34.1 mmol) and HMPA (15 mL). The reaction mixture was cooled to 0°C and n-BuLi (21.0 mL of a 1.6M solution in ethyl ether) was added and the mixture was stirred for two hours at room temperature. The mixture turned to a red homogeneous solution. A solution of camphene oxide **4** (2.5 g, 15 mmol; mixture of isomers exo:endo=4:1) in THF (10 mL) was added and the reaction mixture was heated under reflux for 36 hours then it was cooled to room temperature and quenched with aqueous NH_4Cl. The mixture was acidified with 6N HCl to a pH of 4-5 and stirred at room temperature for 2 hours and extracted with ethyl ether (three times). The combined organic layers were washed with saturated NaCl, dried with $MgSO_4$ and the solvent was removed. The crude product which contained some HMPA and starting material, was left overnight to crystallize. The resulting crystals were removed by vacuum filtration and washed with

methanol. The white crystals were determined to be lactone **6e** (990 mg, a single exo isomer). The recovered filtrate was concentrated and purified by column chromatography (10% ethyl acetate in hexane) to produce an off white solid which was a mixture of **6e** and its epimer (920 mg, in a ratio of 50:50). Lactone **6e** was recovered in a total yield of 45% (1.45 g). mp 112-114 °C ; ^{1}H NMR δ 0.88 (s, 3 H), 1.08 (s, 3 H), 1.24--1.37 (m, 3 H), 1.51--1.59 (m, 2 H), 1.87 (m, 1 H), 2.06--2.10 (m, 1 H), 2.25--2.34 (m, 2 H), 2.44--2.51 (m, 1 H), 2.25--2.34 (m, 2 H), 2.44--2.51 (m, 1 H), 3.82 (s, 3 H), 3.80--3.87 (m, 1 H), 6.88--6.94 (m, 2 H), 7.14--7.29 (m, 2 H); ^{13}C NMR δ 22.68 (t'), 23.95 (q'), 24.32 (t'), 25.16 (q'), 31.50 (t'), 34.93 (t'), 43.27 (s'), 44.16 (d'), 47.24 (d'), 48.46 (d'), 55.43 (q'), 94.66 (s'), 111.33 (d'), 120.87 (d'), 126.13 (s'), 128.98 (d'), 130.39 (d'), 157.03 (d'), 176.96 (s'); IR (nujol) 1760 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 301 (M+1, 100), 300 (67), 257 (55), 255 (34), 173 (29), 16 (129), 135 (32), 134 (61), 121 (36), 119 (41), 109 (27), 105 (17); Anal. Cald for $C_{19}H_{24}O_3$: C, 75.95; H, 8.07. Found: C, 75.97; H, 8.07.

2-[2'-(2-Methoxyphenyl)-3'-hydroxypropyl]-3,3-dimethyl bicyclo[2.2.1]heptan-2-ol (7)

A solution of **6e** (144 mg, 0.48 mmol) in THF (5 mL) was added to a suspension of lithium aluminum hydride (23 mg, 0.58 mmol) in THF (10 mL) at 0°C. The reaction mixture was stirred at room temperature for four hours and then quenched with ethyl acetate (1 mL) and stirred for an additional 30 minutes. The mixture was further diluted with ethyl acetate and extracted with aqueous NaCl solution (twice). The combined organic extracts were washed with water, dried with $MgSO_4$ and the solvent was removed. The crude product was a mixture of two isomers in a ratio of 74:26. The combined isomers were purified by column chromatography (25% ethyl acetate in hexane) to produce white solid of **7** (combined yield: 120 mg, 83%). **major isomer** ^{1}H NMR δ 0.87 (s, 3 H), 1.00 (s, 3 H), 1.00--1.24 (m, 5 H), 1.38--1.48 (m, 1 H), 1.68 (m, 1 H), 1.80--1.87 (m, 1 H), 1.95--2.03 (m, 2 H), 2.15 (m, 1 H), 3.42--3.46 (m, 1 H), 3.73 (d, J = 6.3 Hz, 2 H), 3.83 (s, 3 H), 6.83--6.93 (m, 2 H), 7.15--7.19 (m, 2 H); ^{13}C NMR δ 22.87 (t'), 23.15 (q'), 23.55 (t'), 25.23 (q'), 34.07 (t'), 37.31 (d'),

37.97 (t'), 45.07 (s'), 47.92 (d'), 49.30 (d'), 55.28 (q'), 67.32 (t'), 82.22 (s'), 110.61 (d'), 120.74 (d'), 127.15 (d'), 128.05 (d'), 133.10 (s'), 156.52 (s'); IR (nujol) 3050--3500 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 305 (M+1, 4), 288 (15), 275 (22), 274 (100), 270 (66), 151 (30), 148 (17), 147 (23), 121 (58), 111 (32), 105 (15). **minor isomer** ^1H NMR δ 0.94 (s, 3 H), 0.96 (s, 3 H), 0.94--1.02 (m, 1 H), 1.24--1.27 (m, 2 H), 1.52--1.56 (m, 1 H), 1.68--1.79 (m, 3 H), 1.92--1.94 (m, 1 H), 2.00--2.03 (m, 1 H), 2.18 (m, 1 H), 3.47--3.51 (m, 1 H), 3.66-3.72 (m, 2 H), 3.81 (s, 3 H), 6.84--6.94 (m, 2 H), 7.15--7.20 (m, 2 H); ^{13}C NMR δ 21.09 (t'), 22.04 (q'), 23.88 (t'), 26.47 (q'), 34.37 (t'), 37.31 (d'), 40.86 (t'), 43.38 (s'), 46.31 (d'), 49.64 (d'), 55.29 (q'), 67.42 (t'), 80.36 (s'), 110.63 (d'), 120.82 (d'), 127.45 (d'), 128.18 (d'), 133.17 (s'), 156.50 (s'); IR (nujol) 3050--3500 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 305 (M+1,1), 288 (18), 275 (23), 274 (100), 271 (17), 270 (78),151 (31),148 (20), 147 (22),139 (17), 121 (54),11 (31), 105 (15).

2-[2'-(2-Methoxyphenyl)-3'-phenylmethoxypropyl]-3,3-dimethylbicyclo[2.2.1]heptan-2-ol (8)

In a dry flask NaH (50% suspension in oil, 360 mg, 3.3 mmol) was washed several times with dry ethyl ether to remove the oil, and dry DMSO (40 mL) was added. A solution of diol **7** (900 mg, 2.96 mmol, two isomers in a ratio of 55:45) in DMSO (10 mL) and added to the NaH/DMSO solution via a syringe. Benzyl bromide (0.40 mL, 3.3 mmol) was added to the reaction mixture and the mixture was stirred at room temperature for one hour and then was slowly quenched with saturated aqueous NH_4Cl and extracted with ethyl ether (twice). The combined organic layers were washed with water, dried with $MgSO_4$ and the solvent was removed. The crude **8** was purified by chromatography (10% ethyl acetate in hexane) to produce colorless oil (1.12 g, 96%). **major isomer** ^1H NMR δ 0.89 (s, 3 H), 0.97--1.19 (m, 4 H), 1.04 (s, 3 H), 1.41--1.45 (m, 1 H), 1.68 (m, 1 H), 1.86--1.93 (m, 1 H), 2.03--2.11 (m, 3 H), 3.41 (s, 1 H), 3.60--3.68 (m, 3 H), 3.81 (s, 3 H), 4.54 (d, J = 12.3 Hz, 1 H), 4.60 (d, J = 12.3 Hz, 1 H) 6.84--6.94 (m, 2H), 7.17--7.34 (m, 7 H); ^{13}C NMR δ 22.92 (t'), 23.29 (q'), 23.80 (t'), 25.53 (q'), 34.15 (t'), 38.08 (t'), 44.77 (s'), 48.50 (d'), 49.36 (d'), 55.28 (q'), 72.79 (t'), 74.86 (t'), 81.07 (s'), 110.58

(d'), 120.67 (d'), 127.18 (d'), 127.49 (d'), 127.56 (d'), 128.21 (d'), 128.26 (d'), 132.69 (s'), 137.91 (s'), 156.51 (s'); IR (neat) 3300--3650 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 395 (M+1, 17), 274 (100), 270 (47), 256 (26), 241 (18), 161 (16), 147 (23), 134 (29), 121 (42), 109 (77), 105 (22). **minor isomer** ^1H NMR δ 0.92-1.00 (m, 2 H), 0.98 (s, 6 H), 1.15--1.34 (m, 2 H), 1.52--1.58 (m, 1 H), 1.68--1.78 (m, 2 H), 1.96--2.08 (m, 3 H), 3.42 (s, 1 H), 3.55--3.58 (m, 2 H), 3.59--3.72 (m, 1 H), 3.82 (s, 3 H), 4.54--4.57 (m, 2 H), 6.85--6.93 (m, 2 H), 7.17--7.35 (m, 7 H); IR (neat) 3300--3650 cm^{-1}; MS (chemical ionization, isobutane) m/z (relative intensity) 395 (M+1, 16), 273 (100), 270 (84), 161 (16), 147 (27), 134 (22), 121 (47), 109 (80), 107 (22).

2-[2'-(2-Hydroxyphenyl)-3'-phenylmethoxypropyl]-3,3-dimethylbicylo[2.2.1]heptan-2-ol (9)

NaH (74 mg, 50% in oil, 0.53 mmol) was washed several times with dry ethyl ether to remove the oil and dry DMF (20 mL) was added. The mixture was cooled to 0°C and ethanethiol (0.14 mL, 1.9 mmol) was added slowly. The mixture was stirred for an additional 15 minutes at room temperature. A solution of compound **8** (151mg, 0.38 mmol) in DMF (5 mL) was added and the mixture was heated under refluxed for five hours, cooled to room temperature, quenched with aqueous NH_4Cl and extracted with ethyl ether (twice). The combined organic layers were washed with saturated aqueous NaCl, dried with $MgSO_4$ and the solvent was removed. The crude product was purified by column chromatography (10% ethyl acetate in hexane) to produce colorless oil of **9** (103 mg, 89%). **major isomer** ^1H NMR δ 0.87 (s, 3 H), 0.94 (s, 3 H), 0.91--1.15 (m, 3 H), 1.22--1.28 (m, 1 H), 1.38--1.45 (m, 1 H), 1.52--1.56 (m, 1 H), 1.78--1.82 (m, 1 H), 1.83--1.95 (m, 1 H), 3.82 (d, J = 9.0 Hz, 2 H), 4.50 (d, J = 15.0 Hz, 1 H), 4.67 (d, J = 9.0 Hz, 1 H) 6.26--6.91 (m, 2 H), 7.05--7.18 (m, 2 H), 7.28--7.42 (m, 5 H), 8.21 (s, 1 H); ^{13}C NMR δ 22.69 (t'), 23.02 (q'), 23.70 (t'), 25.15 (q'), 34.22 (t'), 34.54 (t'), 38.98 (d'), 45.22 (s'), 47.66 (d'), 49.09 (d'), 73.36 (t'), 75.79 (t'), 82.43 (s'), 117.33 (d'), 128.46 (d'), 129.77 (d'), 130.53 (s'), 137.04 (s'), 154.66 (s'). IR (nujol) 3250 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 381 (M+1, 3), 345 (9), 364 (31), 256 (50), 243 (20), 242 (100), 109 (21).

minor isomer ^{1}H NMR δ 0.91 (s, 3 H), 0.96 (s, 3 H), 1.12--1.27 (m, 2 H), 1.49--1.52 (m, 1 H), 1.59--1.73 (m, 3 H), 1.84--1.93 (m, 3 H), 2.13--2.20 (m, 1 H), 3.26--3.31 (m, 1 H), 3.75 (m, 2 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.59 (d, J = 12.0 Hz, 1 H) 6.81--6.88 (m, 2 H), 7.04--7.13 (m, 2 H), 7.24--7.36 (m, 5 H), 7.77 (s, 1 H); IR (nujol) 3320 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 381 (M+1, 20), 364 (19), 273 (21), 260 (41), 256 (93), 242 (100), 227 (18), 140 (17), 134 (19), 121 (20), 119 (27), 112 (25), 110 (69), 107 (46),

exo-3',3'-Dimethyl-4-phenylmethoxymethyl-3,4-dihydro-spiro[2H-1-benzopyran-2,2'-bicyclo[2.2.1]heptane] (10)

To a solution of **9** (105 mg, 0.28 mmol) in dichloromethane (5 mL) was added boron trifluoride etherate (0.05 mL). After stirring for one minute the mixture was quenched with water and extracted with ethyl ether (twice). The combined organic layers were washed with aqueous NaCl, dried with $MgSO_4$ and the solvent was removed. The crude product was purified by chromatography (10% ethyl acetate in hexane) to produce colorless oil of **10** (97 mg, 93%). **Major isomer** ^{1}H NMR δ 0.98 (s, 3 H), 1.01 (s, 3 H), 1.05--1.44 (m, 5 H), 1.60--1.77 (m, 2 H), 2.04--2.27 (m, 3 H), 3.14--3.19 (m, 1 H), 3.53 (t, J = 9.0 Hz, 1 H), 3.78--3.83 (m, 1 H), 4.58 (m, 2 H), 6.77--6.83 (m, 2 H), 7.06--7.38 (m, 7 H); ^{13}C NMR δ 22.08 (t'), 23.08 (q'), 24.09 (t'), 28.68 (q'), 26.66 (t'), 33.01 (d'), 34.77 (t'), 46.30 (s'), 48.41 (d'), 49.71 (d'), 73.15 (t'), 74.32 (t'), 85.34 (s'), 117.27 (d'), 128.39 (d'), 138.21 (s'), 155.50 (s'); IR (neat) 1450 cm^{-1}, 1485 cm^{-1}; MS m/z (relative intensity) 262 (M$^+$, 3), 242 (19), 241 (100), 131 (9), 107 (12), 92 (49), 41 (14). **minor isomer** ^{1}H NMR δ 0.98 (s, 3 H), 1.05 (d, J = 9.0 Hz, 1 H), 1.13 (s, 3 H), 1.21--1.50 (m, 5 H), 1.59--1.63 (m, 1 H), 1.81 (s, 1 H), 2.08--2.11 (m, 3 H), 2.20--2.29 (m, 2 H), 2.98--3.11 (m, 1 H), 3.52, 3.54 (dd, J = 9.0, 9.0 Hz, 1 H), 3.86, 3.89 (dd, J = 6.0, 9.0 Hz, 1 H), 4.55 (d, J = 12.0 Hz, 1 H), 4.63 (d, J = 12.0 Hz, 1 H), 6.75--6.82 (m, 2 H), 7.05--7.10 (m, 1 H), 7.28--7.37 (m, 6 H); ^{13}C NMR δ 22.30 (q'), 22.75 (t'), 24.02 (q'), 25.03 (t'), 28.58 (t'), 33.28 (d'), 34.23 (t'), 44.10 (d'), 44.33 (s'), 49.32 (d'), 73.19 (t'), 74.32 (t'), 85.65 (s'), 117.57 (d'), 119.45 (d'), 123.43 (s'), 126.87 (d'), 127.36 (d'), 127.60 (d'), 127.66 (d'), 128.39 (d'), 138.80 (s'), 154.52 (s'); IR (neat) 1450 cm^{-1} 1485 cm^{-1}; MS m/z (relative

intensity) 362 (M^+, 5), 242 (21), 241 (100), 148 (13), 107 (14), 91 (60), 84 (12), 69 (12), 67 (11), 57 (11), 55 (11), 43 (12), 41 (21).

exo-3',3'-Dimethyl-3,4-dihydrospiro[2H-1-benzopyran-2,2'-bicyclo[2.2.1]heptane]-4-methanol (10a)

To a solution of **10** (80 mg, 0.22 mmol;) in absolute ethanol (5 mL) was added 30% Pd/C (60 mg) and acetic acid (2 drops). The reaction flask was fitted with a balloon filled with hydrogen. The reaction mixture was stirred at room temperature for two hours, filtered and the solvent was removed. The crude product was purified by chromatography (10% ethyl acetate in hexane) to give white solid of **10a** (45 mg, 75%). **Major isomer** ^{1}H NMR δ 0.93 (s, 3 H), 1.01 (s, 3 H), 1.04--1.20 (m, 1 H), 1.28--1.35 (m, 1 H), 1.41--1.47 (m, 2 H), 1.57--1.61 (m, 1 H), 1.75 (m, 1 H), 3.01 (m, 1 H), 3.81 (m, 1 H), 3.96 (m, 1 H), 6.77--6.83 (m, 2 H), 7.06--7.20 (m, 2 H); ^{13}C NMR δ 22.22 (t'), 23.07 (q'), 24.02 (t'), 25.68 (q'), 26.60 (t'), 34.76 (t'), 35.03 (d'), 46.00 (s'), 49.29 (d'), 50.03 (d'), 66.19 (t'), 85.50 (s'), 117.38 (d'), 119.48 (d'), 121.62 (s'), 127.44 (d'), 127.70 (d'), 155.40 (s'); IR (nujol) 3020--3500 cm^{-1}; MS m/z (relative intensity) 272 (M^+, 4), 242 (17), 241 (100), 171 (15), 147 (13), 107 (17), 95 (8), 71 (30), 69 (27), 57 (47), 41 (54). **minor isomer** ^{1}H NMR δ 0.98 (s, 3 H), 1.04 (d, J = 12.0 Hz, 1 H), 1.13 (s, 3 H), 1.25--1.42 (m, 3 H), 1.57--1.66 (m, 2 H), 1.81 (m, 1 H), 2.07--2.19 (m, 3 H), 2.88--2.95 (m, 1 H), 3.96--3.99 (m, 2 H), 6.77--6.85 (m, 2 H), 7.06--7.25 (m, 2 H); C NMR δ 22.25 (t'),22.72 (q'), 23.99 (t'), 24.99 (q'), 27.63 (t'), 34.16 (t'), 35.32 (d'), 44.00 (d') 44.31 (s'), 49.29 (d'), 65.57 (t'), 85.73 (s'), 117.94 (d'), 119.67 (d'), 122.30 (s'), 126.22 (d'), 127.60 (d'), 155.26 (s'); IR (nujol) 3020--3500 cm^{-1}; MS (chemical ionization, isobutane), m/z (relative intensity) 273 (M+1, 11), 256 (13), 243 (19), 242 (100), 171 (11), 131 (16), 107 (15).

exo-3',3'-Dimethyl-4-methylene-3,4-dihydrospiro[2H-1-benzopyran-2,2'-bicyclo[2.2.1]heptane] (11)

To a solution of alcohol **10a** (101 mg, 0.37 mmol) in dichloromethane (10 mL) was added t-BuOK (82 mg, 0.4 mmol) and tosyl chloride (105 mg, 0.55 mmol). After stirring for two hours, the solvent was removed and the crude mixture was redissolved in t-butanol (10 mL) and

heated at 100 °C for three hours. The reaction was quenched with aqueous NH_4Cl at room temperature and extracted with ethyl ether (twice). The combined organic extracts were washed with saturated aqueous NaCl, dried with $MgSO_4$ and the solvent was removed. The crude product was purified by chromatography (5% ethyl acetate in hexane) to give a single isomer of **11** (81 mg, 86%). ^1H NMR δ 1.01 (s, 3 H), 1.06--1.10 (m, 1 H), 1.12 (s, 3 H), 1.32--1.40 (m, 3 H), 1.60--1.63 (m, 1 H), 1.83 (m, 1 H), 2.12--2.17 (m, 2 H), 2.51--2.67 (m, 2 H), 4.89 (s, 1 H), 5.50 (s, 1 H), 6.82--6.87 (m, 2 H), 7.13--7.19 (m, 1 H), 7.53--7.56 (m, 1 H); ^{13}C NMR δ 22.01 (t'), 22.59 (q'), 24.12 (t'), 25.59 (q'), 33.93 (t'), 34.32 (t'), 44.43 (s'), 45.62 (d'), 50.06 (d'), 87.02 (s'), 107.22 (t'), 118.19 (d'), 120.09 (d'), 124.33 (d'), 129.67 (d'), 138.01 (s').

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