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TETRAHEDRON:  
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# An Improved Synthesis of 10-Isobornylsultone

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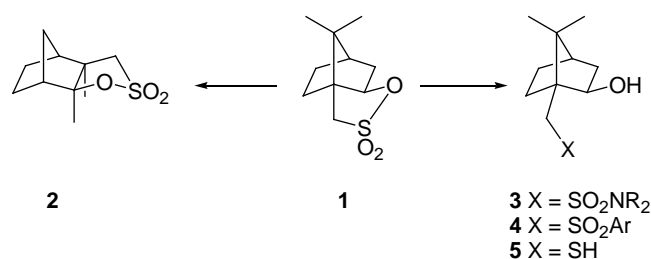
**Abstract**—A modified and improved synthesis of 10-isobornylsultone in three steps and in 81 % overall yield starting from (+)-camphor-10-sulfonic acid is described. The synthesis proceeds by methyl sulfonate ester formation, stereoselective reduction and base-catalyzed intramolecular cyclisation. © 2014 Elsevier Science. All rights reserved

## 1. Introduction

Derivatives of the bicyclic monoterpene (+)-camphor have been widely used both as chiral control elements in asymmetric synthesis and as chiral templates in enantiospecific natural product syntheses owing to its rigid bicyclic structure.<sup>1</sup> One such derivative is (–)-10-isobornylsultone **1** (Figure 1). The known<sup>2</sup> thermal rearrangement of sultone **1** to sultone **2** has been exploited in the enantiospecific total syntheses of β-santalol<sup>3</sup> and β-santalene,<sup>4</sup> which are the two main constituents of East Indian sandalwood oil. In addition, sultone **1** is a key precursor to several important chiral auxiliaries. Cleavage of the S–O bond of **1** with various nucleophiles gives rise to isborneol sulfonamides **3**,<sup>5</sup> isborneol arylsulfones **4**<sup>6</sup> and to 10-mercaptoisborneol **5**<sup>7</sup> which have all been frequently employed as chiral auxiliaries in asymmetric synthesis.<sup>8–11</sup>

Sultone **1** has been previously synthesized by the sulfonation of camphene using acetic anhydride/fuming sulfuric acid,<sup>2a</sup> or by the reduction of (+)-camphor-10-sulfonic acid with sodium borohydride followed by exposure of the intermediate sodium isobornylsulfonate salt to *p*-toluenesulfonyl chloride in pyridine.<sup>2c,3,5,6a</sup> In a more recent report, Kaye obtained sultone **1** as a minor by-product (4 % yield) during the reduction of phenyl (+)-camphor-10-sulfonate with sodium borohydride in H<sub>2</sub>O/EtOH at –8 °C, with the sultone **1** becoming the sole product (94 % yield) when the reduction was performed at 25 °C in absolute ethanol.<sup>12</sup> In this paper, we wish to report a modified and improved synthesis of sultone **1**<sup>13</sup> which we have serendipitously discovered.

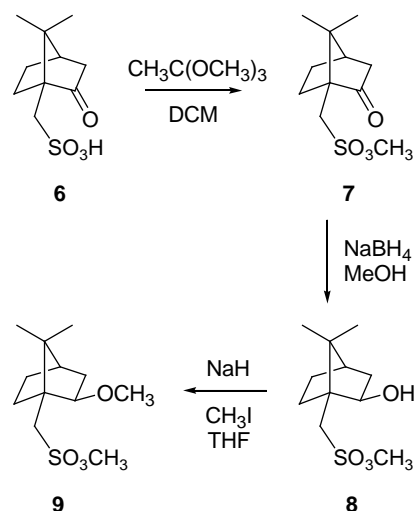
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**Figure 1.** The structures of isobornylsultone **1**, its thermal rearrangement isomer **2**, and its derived chiral auxiliaries **3**, **4** and **5**.

## 2. Results and Discussion

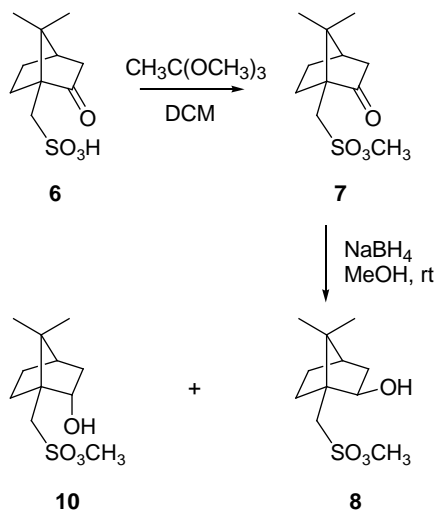
During the course of our ongoing studies on the utility of camphor-derived sulfones as novel chiral auxiliaries in asymmetric synthesis,<sup>14</sup> we required a short synthesis of the methyl sulfonate ether intermediate **9**. We proposed to synthesize **9** by the route outlined in Scheme 1.



**Scheme 1.**

Accordingly, methyl sulfonate ester **7** was conveniently obtained in 90 % yield by treating (+)-camphor-10-sulfonic acid **6** with trimethyl orthoacetate according to the procedure of Gopalan.<sup>15</sup> Reduction of **7** with excess sodium borohydride in methanol proceeded with high stereoselectivity to afford the novel *exo*-configured isoborneol sulfonate ester **8** along with ca. 10 % of its *endo*-configured borneol isomer **10** in 95 % combined yield as determined by <sup>1</sup>H NMR spectroscopy (Scheme 2). This mixture was used in the next step without further purification. The *exo*-alcohol **8** was characterized by a double doublet at ca.  $\delta$  4.1 ppm for the C2 *endo*-methine proton as well as a pair of doublets at ca.  $\delta$  3.0 and 3.6 ppm corresponding to the methylene protons adjacent to the sulfonate ester group.

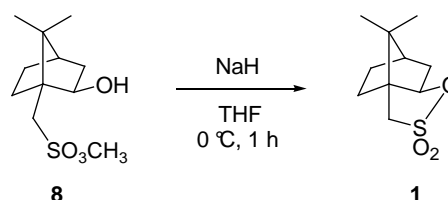
Treatment of **8** with sodium hydride in the presence of methyl iodide in dry THF at ambient temperature for 1 hour failed to afford the desired methyl ether **9** (Scheme 1). Instead, isobornyl sultone **1** was obtained as the sole product. When the reaction was repeated under identical conditions in the absence of methyl iodide, sultone **1** was obtained in 60 % yield. Performing the cyclisation reaction at 0 °C for 1 hour resulted in a greatly improved yield of **1** of 95 % (Scheme 3). The NMR spectroscopic details of **1** were identical to those published by Pinho e Melo.<sup>6b</sup> Interestingly, carrying out the reaction at ambient temperature for 24 hours afforded **1** in a much lower 15 % yield. Evaporation of the aqueous phase from this reaction furnished an off-white solid whose <sup>1</sup>H NMR spectrum in D<sub>2</sub>O suggested the presence of the corresponding sodium isobornylsulfonate salt,<sup>16</sup> which was most likely obtained by simple methanolysis or hydrolysis of the sulfonate ester group of **8**.



Scheme 2.

Inspired by Kaye's synthesis of **1** via reduction of the analogous phenyl sulfonate ester followed by cyclisation,<sup>12</sup> we next sought to synthesize the sultone **1** from the ester **7** in a one-pot procedure via reduction of **7** and subsequent base-catalyzed cyclisation *in situ*. However, these attempts met with limited success. Various reductions of **7** with excess (3–4 equivalents) sodium borohydride in methanol

or in isopropanol, and subsequent additions of potassium *tert*-butoxide (1 equivalent) led at best to mixtures of **8** and sultone **1** (**8**:**1** ratio ranging from 17:1 to 1:1.3) in overall yields no higher than 44 %. The reduced tendency of sulfonate ester **8** to cyclise to **1** under these conditions compared to Kaye's phenyl sulfonate ester (which cyclises smoothly to **1** in the absence of additional base)<sup>12</sup> can be attributed to the greater leaving group ability of the phenoxy-group in the latter compound.



Scheme 3.

However, the new synthesis of 10-isobornylsultone **1** reported herein has several advantages compared to previous syntheses reported in the literature. Firstly, the one-step esterification of (+)-camphor-10-sulfonic acid **6** to form **7** using trimethyl orthoacetate is superior to the literature synthesis of the analogous phenyl sulfonate ester,<sup>17</sup> which has to be carried out in two steps from **6** (ie: conversion of **6** into (+)-camphor-10-sulfonyl chloride using thionyl chloride, followed by treatment of the product with phenol in pyridine), and which employs toxic (phenol, pyridine) and corrosive (thionyl chloride) reagents.<sup>18</sup> Secondly, the optimized synthesis of **1** reported herein proceeds in higher overall yield (81 %) than previous syntheses of **1** from either (+)-camphor-10-sulfonyl chloride (76 %)<sup>12</sup> or from (+)-camphor-10-sulfonic acid **6** (44 % overall by Kaye's method,<sup>12</sup> 75 % overall when thionyl chloride is used to convert **6** to (+)-camphor-10-sulfonyl chloride<sup>19</sup>). Finally, our reduction of the sulfonate ester **7** to yield **8** requires a smaller excess of sodium borohydride (3 equivalents) than Kaye's reduction of the analogous phenyl sulfonate ester (which requires 10 equivalents of sodium borohydride).<sup>12</sup>

### 3. Conclusion

We report herein an unexpected and improved synthesis of (–)-10-isobornylsultone **1** from (+)-camphor-10-sulfonic acid **6**. This modified and convenient synthesis delivers **1** in three steps from **6** in a high overall yield of 81 % without the need for column chromatography or the use of toxic and corrosive reagents.

## 4. Experimental

### 4.1. General

NMR spectra were recorded using a Bruker AVANCE DPX 400 MHz spectrometer (400.1 MHz for <sup>1</sup>H and 100.6 MHz for <sup>13</sup>C). Chemical shifts are reported in parts per million. Coupling constants (*J*) are quoted in Hertz. Optical

rotations were measured using a Perkin-Elmer 141 polarimeter. IR spectra were recorded for Nujol mulls (N) or liquid films (L) on a Mattson Genesis II FTIR spectrometer. Mass spectra were obtained under electrospray conditions using a Micromass LCT instrument. Uncorrected melting points (Mp) were measured in unsealed capillary tubes using a Griffin melting point apparatus. Tetrahydrofuran (THF) was dried and distilled over sodium-benzophenone ketyl prior to use. All other solvents and reagents were purified by standard techniques. Organic extracts of reaction products were dried over anhydrous magnesium sulfate.

**(1S,4R)-Methyl (7,7-dimethyl-2-oxobicyclo[2.2.1]hept-1-yl)methanesulfonate 7.**

Following the procedure of Gopalan,<sup>15</sup> (+)-camphor-10-sulfonic acid **6** (3.0 g, 12.9 mmol) was suspended in DCM (50 mL) and trimethyl orthoacetate (8.21 mL, 64.5 mmol) was added. The resulting solution was stirred at ambient temperature for 90 minutes. The solution was then evaporated to yield an oil. Removal of excess trimethyl orthoacetate *in vacuo* (0.1 mm Hg) afforded the title compound **7** as a pale pink solid (2.88 g, 90 %). Mp 61–63 °C (DCM); Lit.<sup>20</sup> 61 °C;  $[\alpha]_D^{25} +42.7$  (c 1.61, CHCl<sub>3</sub>, 22 °C); Lit.<sup>20</sup> +43.6 (c 5 %, CHCl<sub>3</sub>, 23 °C); IR  $\nu_{\max}$  (N) 2923, 2723, 2669, 1741 (C=O), 1456, 1376, 1301, 1269, 1170 (S=O), 1054, 989 (S=O), 808, 747 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.88 (s, 3H, 7-CH<sub>3</sub>), 1.10 (s, 3H, 7-CH<sub>3</sub>), 1.41–1.48 (m, 1H), 1.63–1.70 (m, 1H), 1.95 (d, <sup>2</sup>J = 18.5, 1H, 3-CH<sub>2</sub> *endo*), 2.01–2.10 (m, 1H), 2.13 (t, <sup>3</sup>J = 4.5, 1H, 4-CH), 2.39 (dt, <sup>2</sup>J = 18.5, <sup>3</sup>J = 4.5, 1H, 3-CH<sub>2</sub> *exo*), 2.43–2.50 (m, 1H), 2.98 (d, <sup>2</sup>J = 15.0, 1H, CH<sub>2</sub>SO<sub>3</sub>CH<sub>3</sub>), 3.59 (d, <sup>2</sup>J = 15.0, 1H, CH<sub>2</sub>SO<sub>3</sub>CH<sub>3</sub>), 3.95 (s, 3H, SO<sub>3</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 19.2 (7-CH<sub>3</sub>), 19.2 (7-CH<sub>3</sub>), 24.3 (C-5), 26.4 (C-6), 42.0 (C-3), 42.2 (C-4), 45.5 (CH<sub>2</sub>SO<sub>3</sub>CH<sub>3</sub>), 47.5 (C-7), 55.7 (SO<sub>3</sub>CH<sub>3</sub>), 57.3 (C-1), 214.1 (C-2); HRMS (CI, MeOH) *m/z* calcd for C<sub>11</sub>H<sub>18</sub>O<sub>4</sub>S [M + Na]<sup>+</sup>: 269.0824; found: 269.0825.

**(1S,2R,4R)-Methyl (2-hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl)methanesulfonate 8 and (1S,2S,4R)-Methyl (2-hydroxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl)methanesulfonate 10.**

Methyl sulfonate ester **7** (0.25 g, 1.01 mmol) was dissolved in methanol (10 mL) and solid sodium borohydride (0.115 g, 3.04 mmol) was added. The solution was stirred at ambient temperature for 1 hour. Acetic acid (2 mL) was added and sodium carbonate was added until the pH was neutral. The mixture was diluted with ethyl acetate (100 mL) and washed with water (50 mL) and saturated aqueous sodium hydrogen carbonate (2 × 50 mL), dried and evaporated to afford the title compound **8** as a colourless oil (0.24 g, 95 %) contaminated with ca. 10 % of the corresponding *endo* isomer **10**. IR  $\nu_{\max}$  (L) 3554 (O–H), 2957, 2883, 1456, 1352 (S=O), 1257, 1166 (S=O), 1076, 992, 879, 807, 746 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.86 (s, 3H, 7-CH<sub>3</sub>), 1.09 (s, 3H, 7-CH<sub>3</sub>), 1.13–1.17 (m, 1H), 1.45–1.51 (m, 1H), 1.69–1.88 (m, 5H), 2.83 (br s, 1H, O–H), 2.99 (d, <sup>2</sup>J = 14.0, 1H, CH<sub>2</sub>SO<sub>3</sub>CH<sub>3</sub>), 3.56 (d, <sup>2</sup>J = 14.0, 1H,

CH<sub>2</sub>SO<sub>3</sub>CH<sub>3</sub>), 3.94 (s, 3H, SO<sub>3</sub>CH<sub>3</sub>), 4.09 (dd, <sup>3</sup>J<sub>1</sub> = 7.5, <sup>3</sup>J<sub>2</sub> = 4.5, 1H, 2-CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 19.3 (7-CH<sub>3</sub>), 20.0 (7-CH<sub>3</sub>), 26.8 (C-5), 29.7 (C-6), 38.7 (C-3), 43.9 (C-4), 48.3 (C-7), 48.5 (CH<sub>2</sub>SO<sub>3</sub>CH<sub>3</sub>), 49.3 (C-1), 54.9 (SO<sub>3</sub>CH<sub>3</sub>), 75.7 (C-2); HRMS (CI, MeOH) *m/z* calcd for C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>S [M + H]<sup>+</sup>: 249.1161; found: 249.1153.

**(1S,5R,7R)-10,10-Dimethyl-4-oxa-3-thiatricyclo[5.2.1.0<sup>1,5</sup>]decane 3,3-dioxide 1.**

A solution of the sulfonate ester **8** (0.58 g, 2.33 mmol) in dry THF (10 mL) was added to a suspension of sodium hydride (0.14 g, 60 %, 3.50 mmol, 1.5 eq) in dry THF (5 mL) at 0 °C under an atmosphere of nitrogen. The solution was stirred at 0 °C for 1 hour. The solution was then diluted with H<sub>2</sub>O (50 mL) and extracted with DCM (3 × 50 mL). The combined organic extracts were dried and evaporated to yield a semi-solid material which crystallised *in vacuo* (0.1 mm Hg) to afford the title compound **1** as a white solid (0.48 g, 95 %). Mp 111–113 °C (ether); Lit.<sup>3</sup> 114–116 °C;  $[\alpha]_D^{25} -3.7$  (c 0.33, CCl<sub>4</sub>, 27 °C); Lit.<sup>2c</sup> -4.05 (c 10, CCl<sub>4</sub>, 25 °C); IR  $\nu_{\max}$  (N) 2920, 1459, 1412, 1375, 1345 (S=O), 1258, 1227, 1177 (S=O), 1149, 1111, 1079, 1026, 990, 940, 893, 864, 815, 737, 683 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.95 (s, 3H, 10-CH<sub>3</sub>), 1.12 (s, 3H, 10-CH<sub>3</sub>), 1.24–1.29 (m, 1H), 1.38–1.43 (m, 1H), 1.86–1.97 (m, 4H), 2.28 (dd, <sup>2</sup>J = 14.0, <sup>3</sup>J = 3.5, 1H), 3.19 (d, <sup>2</sup>J = 13.5, 1H, 2-CH<sub>2</sub>), 3.29 (d, <sup>2</sup>J = 13.5, 1H, 2-CH<sub>2</sub>), 4.38 (dd, <sup>3</sup>J<sub>1</sub> = 7.7, <sup>3</sup>J<sub>2</sub> = 3.5, 1H, 5-CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 19.3 (10-CH<sub>3</sub>), 19.4 (10-CH<sub>3</sub>), 26.2 (C-8), 28.6 (C-9), 35.3 (C-6), 43.9 (C-7), 46.9 (C-10), 48.6 (C-2), 55.0 (C-1), 87.5 (C-5); HRMS (CI, MeOH) *m/z* calcd for C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>S [M + H]<sup>+</sup>: 217.0899; found: 217.0898.

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### References

- (a) Oppolzer, W. *Tetrahedron* **1987**, *43*, 1969–2004. (b) Oppolzer, W. *Pure Appl. Chem.* **1990**, *62*, 1241–1250. (c) Polywka, M. E. C. *Chim. Oggi* **1992**, *10*, 33–35. (d) Kim, B. H.; Curran, D. P. *Tetrahedron* **1993**, *49*, 293–318. (e) Liu, W. In *Handbook of Chiral Chemicals*, 2nd ed.; Ager, D., Ed.; CRC LLC: Boca Raton, **2006**; pp 59–74. (f) Langlois, Y.; Kouklovsky, C. *Synlett* **2009**, 3065–3081.
- (a) Wolinsky, J.; Dimmel, D. R.; Gibson, T. W. *J. Org. Chem.* **1967**, *32*, 2087–2097. (b) Dimmel, D. R.; Fu, W. Y. *J. Org. Chem.* **1973**, *38*, 3778–3782. (c) Dimmel, D. R.; Fu, W. Y. *J. Org. Chem.* **1973**, *38*, 3782–3788.
- Solas, D.; Wolinsky, J. *J. Org. Chem.* **1983**, *48*, 1988–1991.
- Wolinsky, J.; Marhenke, R. L.; Lau, R. *Synth. Commun.* **1972**, *2*, 165–169.
- (a) Oppolzer, W.; Chapuis, C.; Kelly, M. J. *Helv. Chim. Acta* **1983**, *66*, 2358–2361. (b) Basavaiah, D.; Gowriswari, V. V.

- L.; Sarma, P. K. S.; Dharma Rao, P. *Tetrahedron Lett.* **1990**, *31*, 1621–1624.
6. (a) Oppolzer, W.; Kelly, M. J.; Bernardinelli, G. *Tetrahedron Lett.* **1984**, *25*, 5889–5892. (b) Pinho e Melo, T. M. V. D.; Cardoso, A. L.; Rocha Gonsalves, A. M. d'A. *Tetrahedron* **2003**, *59*, 2345–2351.
7. Wolinsky, J.; Marhenke, R. L. *J. Org. Chem.* **1975**, *40*, 1766–1770.
8. For recent applications of isoborneol sulfonamides as chiral auxiliaries, see: (a) Fringuelli, F.; Matteucci, M.; Piermatti, O.; Pizzo, F.; Burla, M. C. *J. Org. Chem.* **2001**, *66*, 4661–4666. (b) Gerona-Navarro, G.; García-López, M. T.; González-Muñiz, R. *J. Org. Chem.* **2002**, *67*, 3953–3956. (c) Chairgulprasert, V.; Drew, M. G. B.; Jahans, A.; Harwood, L. M. *Arkivoc* **2002**, (ix) 37–45. (d) Keshava Murthy, K. S.; Rey, A. W.; Tjepkema, M. *Tetrahedron Lett.* **2003**, *44*, 5355–5358. (e) Gong, H.; Krische, M. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 7069–7071. (f) Lee, C. K. Y.; Herlt, A. J.; Simpson, G. W.; Willis, A. C.; Easton, C. J. *J. Org. Chem.* **2006**, *71*, 3221–3231.
9. For recent applications of isoborneol aryl sulfones as chiral auxiliaries, see: (a) Pinho e Melo, T. M. V. D.; Cardoso, A. L.; Rocha Gonsalves, A. M. d'A.; Storr, R. C.; Pessoa, J. C.; Paixão, J. A.; Beja, A. M.; Silva, M. R. *Tetrahedron Lett.* **2003**, *44*, 6409–6412. (b) Pinho e Melo, T. M. V. D.; Cardoso, A. L.; Rocha Gonsalves, A. M. d'A.; Pessoa, J. C.; Paixão, J. A.; Beja, A. M. *Eur. J. Org. Chem.* **2004**, 4830–4839.
10. For recent applications of 10-mercaptoisoborneol **5** as a chiral auxiliary, see: (a) Node, M.; Nishide, K.; Shigeta, Y.; Shiraki, H.; Obata, K. *J. Am. Chem. Soc.* **2000**, *122*, 1927–1936. (b) Nishide, K.; Ohsugi, S.; Shiraki, H.; Tamakita, H.; Node, M. *Org. Lett.* **2001**, *3*, 3121–3124. (c) Gonzalez-Temprano, I.; Sotomayor, N.; Lete, E. *Synlett* **2002**, 593–597. (d) Takahashi, T.; Yamakoshi, Y.; Okayama, K.; Yamada, J.; Ge, W.-Y.; Koizumi, T. *Heterocycles* **2002**, *56*, 209–220. (e) Aggarwal, V. K.; Lattanzi, A.; Fuentes, D. *Chem. Commun.* **2002**, 2534–2535. (f) Nishimura, K.; Tsubouchi, H.; Ono, M.; Hayama, T.; Nagaoka, Y.; Tomioka, K. *Tetrahedron Lett.* **2003**, *44*, 2323–2326. (g) Maezaki, N.; Yagi, S.; Ohsawa, S.; Ohishi, H.; Tanaka, T. *Tetrahedron* **2003**, *59*, 9895–9906. (h) Nishide, K.; Ozeki, M.; Kunishige, H.; Shigeta, Y.; Patra, P. K.; Hagimoto, Y.; Node, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 4515–4517. (i) Ozeki, M.; Nishide, K.; Teraoka, F.; Node, M. *Tetrahedron: Asymmetry* **2004**, *15*, 895–907. (j) Gonzalez-Temprano, I.; Osante, I.; Lete, E.; Sotomayor, N. *J. Org. Chem.* **2004**, *69*, 3875–3885. (k) Ozeki, M.; Hashimoto, D.; Nishide, K.; Kajimoto, T.; Node, M. *Tetrahedron: Asymmetry* **2005**, *16*, 1663–1671. (l) Gomez-Sanjuan, A.; Sotomayor, N.; Lete, E. *Eur. J. Org. Chem.* **2013**, 6722–6732.
11. 10-Mercaptoisoborneol **5** has also been used to generate chiral ligands for asymmetric catalysis, see: (a) Nakano, H.; Okuyama, Y.; Hongo, H. *Tetrahedron Lett.* **2000**, *41*, 4615–4618. (b) Nakano, H.; Yanagida, H. *J. Org. Chem.* **2001**, *66*, 620–625. (c) Okuyama, Y.; Nakano, H.; Kabuto, C.; Nozawa, E.; Takahashi, K.; Hongo, H. *Heterocycles* **2002**, *58*, 457–469. (d) Nakano, H.; Suzuki, Y.; Kabuto, C.; Fujita, R.; Hongo, H. *J. Org. Chem.* **2002**, *67*, 5011–5014. (e) Okuyama, Y.; Nakano, H.; Takahashi, K.; Hongo, H.; Kabuto, C. *Chem. Commun.* **2003**, 524–525. (f) Nakano, H.; Takahashi, K.; Fujita, R. *Heterocycles* **2004**, *64*, 407–416. (g) Nakano, H.; Takahashi, K.; Suzuki, Y.; Fujita, R. *Tetrahedron: Asymmetry* **2005**, *16*, 609–614. (h) Okuyama, Y.; Nakano, H.; Saito, Y.; Takahashi, K.; Hongo, H. *Tetrahedron: Asymmetry* **2005**, *16*, 2551–2557.
12. Duggan, A. R.; Kaye, P. T.; Caira, M. R. *J. Chem. Res.* **2006**, 744–747.
13. For applications of the corresponding 10-isobornylsultine in asymmetric synthesis, see: (a) Kawęcki, R.; Urbańczyk-Lipkowska, Z. *Synthesis* **1996**, 603–605. (b) Kawęcki, R. *Tetrahedron: Asymmetry* **1999**, *10*, 4183–4190. (c) Kawęcki, R. *J. Org. Chem.* **1999**, *64*, 8724–8727.
14. (a) Lewis, F. W.; Egron, G.; Grayson, D. H. *Tetrahedron: Asymmetry* **2009**, *20*, 1531–1535. (b) Lewis, F. W.; McCabe, T. C.; Grayson, D. H. *Tetrahedron* **2011**, *67*, 7517–7528. (c) Lewis, F. W.; Grayson, D. H. *Tetrahedron: Asymmetry* **2012**, *23*, 643–649.
15. Trujillo, J. I.; Gopalan, A. S. *Tetrahedron Lett.* **1993**, *34*, 7355–7358.
16. This compound had <sup>1</sup>H NMR (D<sub>2</sub>O) 0.74 (s, 3H, 7-CH<sub>3</sub>), 0.90 (s, 3H, 7-CH<sub>3</sub>), 1.00–1.03 (m, 1H), 1.28–1.32 (m, 1H), 1.58–1.67 (m, 5H), 2.76 (d, <sup>2</sup>J = 14.6, 1H, CH<sub>2</sub>SO<sub>3</sub>Na), 3.21 (d, <sup>2</sup>J = 14.6, 1H, CH<sub>2</sub>SO<sub>3</sub>Na), 3.95–3.98 (m, 1H, 2-CH) ppm.
17. (a) Kaye, P. T.; Molema, W. E. *Chem. Commun.* **1998**, 2479–2480. (b) Procter, D. J.; Archer, N. J.; Needham, R. A.; Bell, D.; Marchington, A. P.; Rayner, C. M. *Tetrahedron* **1999**, *55*, 9611–9622.
18. Phenyl camphor-10-sulfonate was recently synthesized directly from (+)-camphor-10-sulfonic acid **6** in 68 % yield using diphenyliodonium salts, see: Jalalian, N.; Petersen, T. B.; Olofsson, B. *Chem. Eur. J.* **2012**, *18*, 14140–14149.
19. The highest reported yield for the conversion of **6** to (+)-camphor-10-sulfonyl chloride is 99 %, see: Jung, J.-C.; Kache, R.; Vines, K. K.; Zheng, Y.-S.; Bijoy, P.; Valluri, M.; Avery, M. A. *J. Org. Chem.* **2004**, *69*, 9269–9284.
20. Edminson, S. R.; Hilditch, T. P. *J. Chem. Soc.* **1910**, 223–231.

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