OPTICALLY PURE ALKOXYCHLOROSULFURANES. SYNTHESIS AND TRANSFORMATION TO CHIRAL SULFOXIDES, *N*-*p*-TOSYLSULFILIMINES, AND SULFONIUM YLIDES†

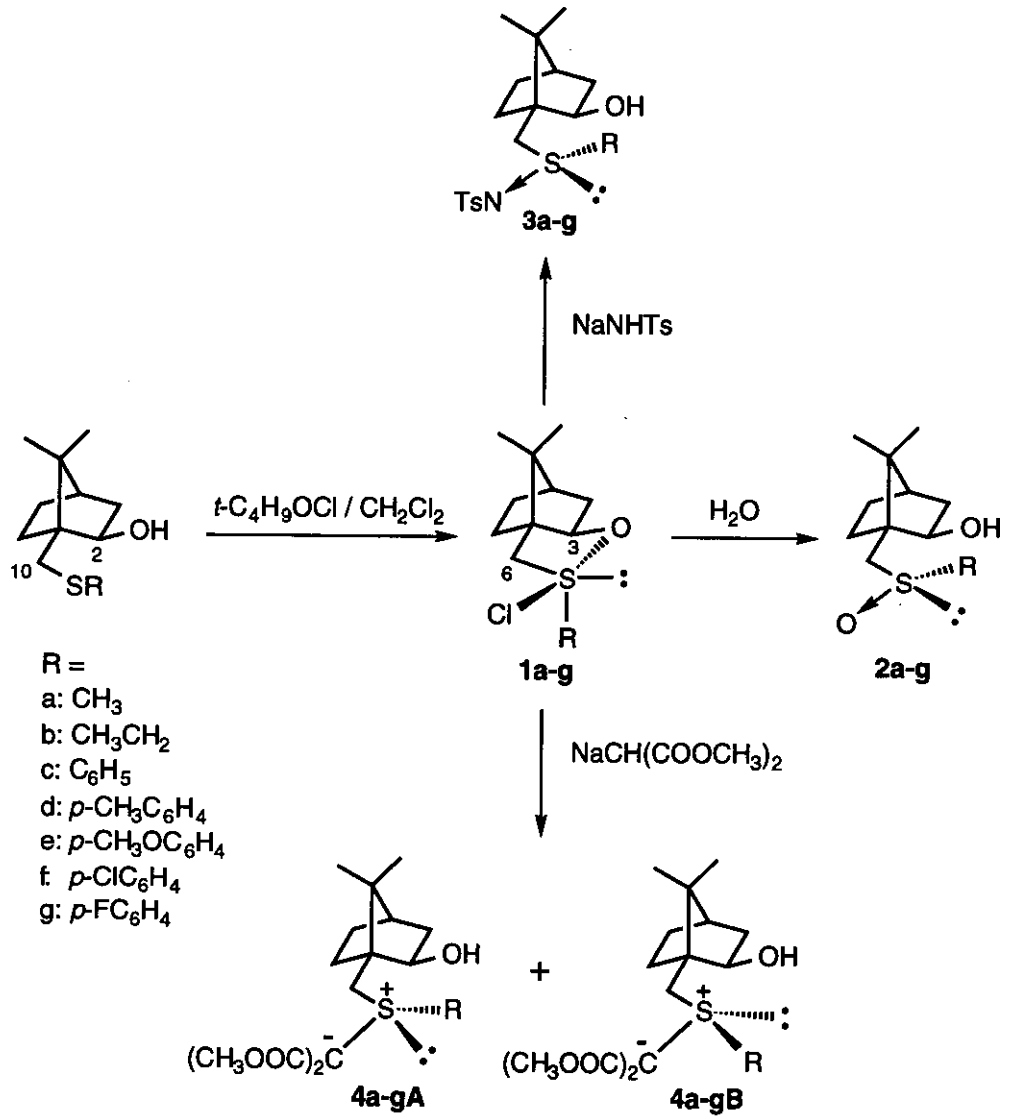
Jian Zhang, Tamiko Takahashi, and Toru Koizumi*

Faculty of Pharmaceutical Sciences, Toyama Medical & Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan

Abstract—Optically pure alkoxychlorosulfuranes (**1**) have been prepared by using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. The structure of sulfurane (**1a**) was confirmed by ^{1}H-nmr, ^{13}C-nmr, and mass spectra. Nucleophilic reaction of **1** with water and NaNHTs proceeded with retention of configuration to give optically pure sulfoxides (**2**) and *N*-*p*-tosylsulfilimines (**3**), respectively. Sulfonium ylides (**4**) were obtained as mixtures of diastereomers by the reaction of **1** with $NaCH(CO_2Me)_2$. The absolute configuration of sulfilimine (**3c**) was determined by X-ray analysis.

Hypervalent 10-S-4 organosulfur species (sulfuranes) are well-known as an intermediate in reactions of sulfoxides, sulfilimines, sulfonium salts, and sulfides.[1] Some of them have been isolated by using the "Martin type" or oximate five-membered ring as a ligand.[2] Synthesis of optically active sulfuranes is interesting not only as a synthetic goal but also from the mechanistic point of view. Martin[3a-c] and Kapovits[3d] have reported the synthesis of optically active sulfuranes. Hydrolysis of the sulfuranes proceeds with retention of configuration to give optically active sulfoxides. Recently, we have succeeded in the synthesis of optically pure selenuranes by using the 2-*exo*-hydroxy-10-bornyl group as a chiral

auxiliary.[4a] Nucleophilic reaction of the selenuranes with aqueous base, metal halides, and active methylene compounds gives selenoxides, haloselenuranes, and selenonium ylides, respectively, with retention of configuration.[4] In this paper, we wish to report the synthesis of optically pure alkoxychlorosulfuranes (**1**) which are available for transformation to chiral sulfoxides (**2**), *N-p*-tosylsulfilimines (**3**), and sulfonium ylides (**4**).



Scheme 1

When the sulfides were treated with 1.05 equivalents of *tert*-butyl hypochlorite at 0 °C in CH_2Cl_2 for 5 min, the alkoxychlorosulfuranes (**1**) were obtained as white solids after evaporation of the excess reagent

and solvent under reduced pressure. Attempts to purify **1** by column chromatography or recrystallization were failed. Sulfuranes (**1**) were less stable than the corresponding selenuranes which could be purified by recrystallization.[4a] However, we confirmed the structure of sulfuranes (**1**) by ^{1}H-nmr, ^{13}C-nmr, and mass spectra. All of the following results for **1** were consistent with those for the chloroselenurane, (1*S*,R_{Se})-5-chloro-10,10-dimethyl-5-phenyl-5λ^{4}-selena-4-oxatricyclo[5.2.1.0^{3,7}]decane[4a] which had similar characteristics in the spectra. In the ^{1}H-nmr spectra, H_{6a} and H_{6b} of **1** appeared as doublets and had a large downfield shift (δ 4.04-4.57 and δ 4.48-4.70, respectively) relative to the corresponding hydrogen atoms (H_{10a} and H_{10b}) of sulfides (δ 2.88-2.96 and δ 3.15-3.23, respectively). Those of the chloroselenurane or (1*S*)-10-phenylselenenyl-2-*exo*-borneol (the selenide) showed peaks at δ 4.15 and δ 4.32, or at δ 3.00 and δ 3.18. In the ^{13}C-nmr spectra, C_3 of **1a** appeared at δ 101.6 whereas the corresponding carbon atom (C_2) of (1*S*)-10-methylthio-2-*exo*-borneol at δ 77.2. That of the chloroselenurane or the selenide showed a peak at δ 96.3 or δ 77.3. Molecular ion peaks appeared at *m/z* 234 (^{37}Cl) and 232 (^{35}Cl) for **1a** as well as at *m/z* 312 (^{37}Cl) and 310 (^{35}Cl) for **1d**, indicating the covalent character of S—Cl bond. Accordingly, the structure of **1** was proposed as shown in Scheme 1.

Table 1: Yield of the products (2-4)

compound	yield (%)	compound	yield (%)	compound	yield (%), (A:B)
2a	75	**3a**	76	**4a**	95 (1:2)
2b	74	**3b**	90	**4b**	91 (1:1)
2c	61	**3c**	81	**4c**	97 (1.5:1)
2d	80	**3d**	79	**4d**	96 (1.3:1)
2e	67	**3e**	97	**4e**	90 (1.4:1)
2f	56	**3f**	93	**4f**	98 (1.1:1)
2g	55	**3g**	84	**4g**	96 (1.3:1)

Then, transformation of **1** to the title compounds (**2-4**) was carried out *in situ* by nucleophilic reaction. Hydrolysis of **1** with 5% NaOH or saturated $NaHCO_3$ aqueous solution gave sulfoxides (**2**) in low yield (about 40%) along with complex mixture of unidentified compounds. Hydrolysis of **1** with water gave the sulfoxides (**2**) as single diastereomers in moderate to good yield (Table 1). These results also indicated the instability of **1** comparing to the selenuranes which were hydrolyzed to the selenoxide by treatment

with aqueous base.[4a] The absolute configuration of sulfoxides **(2a,b)** was determined as shown in Scheme 1 by comparison of their spectral data with those reported previously.[5] The structure of **2c-g** was assigned by analogy with **2a,b**.

When NaNHTs was used as a nucleophile, optically pure *N-p*-tosylsulfilimines **(3)** were obtained as single diastereomers in good to high yield (Table 1). The absolute configuration of the sulfur atom in **3c** was determined to be *R* by X-ray analysis (Figure 1). The distances of S(1)—N(1) [1.645(4) Å] and S(2)—N(1) [1.622(4) Å] bonds, as well as the S(1)—N(1)—S(2) angle [112.9(2)°] are consistent with those of dimethyl *N-p*-tosylsulfilimine.[6]

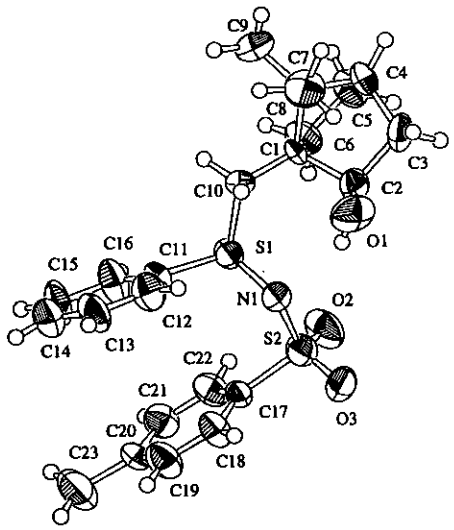
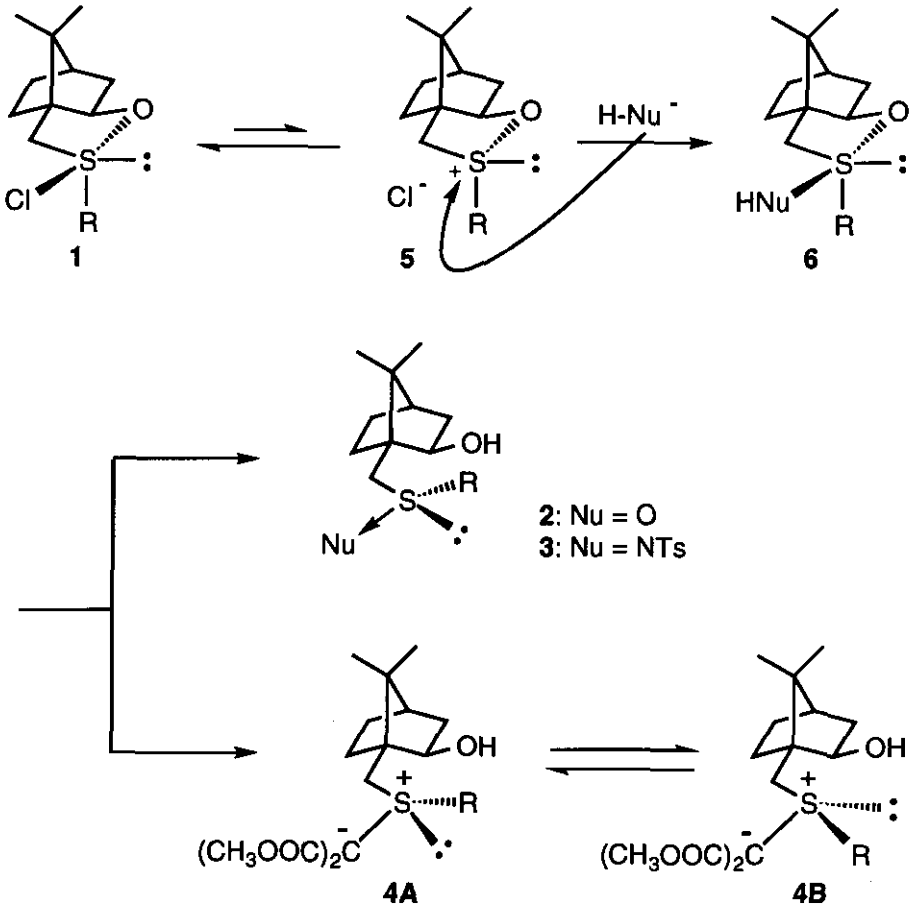


Figure 1. Perspective Structure of Compound **(3c)**.

Reaction of the alkoxychlorosulfuranes **(1)** with $NaCH(CO_2Me)_2$ gave sulfonium ylides **(4)** as mixtures of diastereomers at sulfur atom in quantitative yield (Table 1). We could not separate the diastereomers by column chromatography. The structure of diastereomers **(4A** and **4B)** was assigned as shown in Scheme 1 by comparison of their spectral data with those of (1*S*,S_{Se})- and (1*S*,R_{Se})-(2-*exo*-hydroxy-10-bornyl)(phenyl)selenonium 2-oxo-1-carbomethoxy-1-propyride.[4b] In the ^{1}H-nmr spectra, geminal methyl groups of **4A** and **4B** appeared at δ 0.87-0.94; δ 1.05-1.09 and at δ 0.83-0.86; δ 1.08-1.13, respectively. Those of the (S_{Se})- and (R_{Se})-selenonium ylides showed peaks at δ 0.94; δ 1.09 and at δ 0.85; δ 1.12, respectively. Lowering reaction temperature and/or changing the order of the reagent addition had no effect on the selectivity.

From the absolute configuration of the products (**2-4**), the nucleophilic reaction of **1** is likely to proceed through a similar pathway with that of the haloselenuranes[4] as shown in Scheme 2. Dissociation of S—Cl bond followed by stereoselective association of the resulting alkoxysulfonium ion (**5**) with nucleophiles would provide **6**. Concomitant cleavage of S—O bond of **6** would afford the products (**2**, **3** and **4A**). Pyramidal inversion at sulfur atom[7] in **4A** may readily proceed to give a thermodynamically controlled mixture of **4A** and **4B**.



Scheme 2

In conclusion, we developed a facile method for the highly diastereoselective synthesis of optically pure sulfoxides (**2**) and sulfilimines (**3**) using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand *via* alkoxychlorosulfuranes (**1**). Sulfonium ylides (**4**) were also prepared in this way in excellent yield as diastereomeric mixtures.

ACKNOWLEDGEMENT

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EXPERIMENTAL

Melting points were taken with a Yanaco micro melting point apparatus and are uncorrected. Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO DIP-1000 digital polarimeter; ir, Perkin-Elmer 1600 Series FTIR; mass (ms) and high resolution mass spectra (HRms), JEOL JMS-D 200 and JMS-AX 505H; ^{1}H-nmr, Varian Gemini-300 (300 MHz) for solutions in $CDCl_3$ with Me_4Si as an internal standard, *J* values in Hz; ^{13}C-nmr, Varian Gemini-300 (75 MHz) for solutions in $CDCl_3$. The chemical shifts from Me_4Si were calculated based on $CDCl_3$. All reactions were carried out in dried glassware under argon atmosphere. Dry CH_2Cl_2 was distilled over P_2O_5 and stored over 4Å molecular sieves. Column chromatogrphy and tlc were performed on Kiesel gel 60 (Merck, Art. 7734 and Art. 5715, respectively). (1*S*)-10-Methylthio-2-*exo*-borneol and (1*S*)-10-ethylthio-2-*exo*-borneol were prepared according to the literature.[5]

General Procedure for Preparation of 10-Arylthio-2-*exo*-borneol To a stirred suspension of NaH (60%, 566 mg, 14.2 mmol) in dry benzene (20 ml) was added dropwise thiophenol (1.3 ml, 13 mmol) at 0 °C. After completion of addition (5 min), DMF (20 ml) was added to the mixture at 0 °C and the solution was stirred until a clear solution was obtained (*ca.* 20 min). Then (1*S*)-(-)-10-bromo-2-*exo*-borneol (3.0 g, 13 mmol) in dry benzene (3 ml) was added dropwise to the mixture at 0 °C and the whole mixture was stirred at 50 °C for 4 h. The reaction was quenched with sat. NH_4Cl solution (5 ml) followed by H_2O (20 ml) and the mixture was extracted with AcOEt (60 ml × 4). The combined extracts were washed with water (20 ml × 3) followed by brine (20 ml) and dried over $MgSO_4$. After removal of the solvent, the residual oil was purified by column chromatography (hexane / AcOEt 20:1) to give pure (1*S*)-10-benzenethio-2-*exo*-borneol (2.80 g, 83%) as a colorless oil. (1*S*)-10-(*p*-Toluenethio)-2-*exo*-borneol,

(1*S*)-10-(4-methoxybenzenethio)-2-*exo*-borneol, (1*S*)-10-(4-chlorobenzenethio)-2-*exo*-borneol, and (1*S*)-10-(4-fluorobenzenethio)-2-*exo*-borneol were also prepared similarly.

(1*S*)-10-Benzenethio-2-*exo*-borneol: colorless oil. $[\alpha]_D^{24}$ -35.05° (*c* 2.44, $CHCl_3$). Ir ν_{max} (neat) cm^{-1}: 3463, 2952, 1480, 1438, 1071, 1026, 737, 690. ^{1}H-Nmr δ: 0.88 (3H, s), 1.09 (3H, s), 1.05-1.9 (7H, m), 2.19 (1H, br), 2.96 (1H, d, *J* = 11.0), 3.23 (1H, d, *J* = 11.0), 3.94 (1H, dd, *J* = 3.9, 7.7), 7.15-7.4 (5H, m). Ms *m/z*: 263 (M^++1), 262 (M^+), 245, 153, 135, 123. HRms: Calcd for $C_{16}H_{22}OS$: 262.1390. Found: 262.1353.

(1*S*)-10-(*p*-Toluenethio)-2-*exo*-borneol: From NaH (60%, 282 mg, 7.05 mmol), *p*-toluenethiol (798 mg, 6.44 mmol), and (1*S*)-(-)-10-bromo-2-*exo*-borneol (1.50 g, 6.44 mmol) was obtained (-)-10-(*p*-toluenethio)-2-*exo*-borneol (1.52 g, 86%) as a colorless oil. $[\alpha]_D^{27}$ -30.83° (*c* 1.00, $CHCl_3$). Ir ν_{max} (neat) cm^{-1}: 3463, 2953, 2880, 1590, 1490, 1228, 1071, 819. ^{1}H-Nmr δ: 0.86 (3H, s), 1.07 (3H, s), 1.0-1.8 (7H, m), 2.15-2.2 (1H, br), 2.32 (3H, s), 2.92 (1H, d, *J* = 11.5), 3.19 (1H, d, *J* = 11.5), 3.93 (1H, dd, *J* = 3.9, 7.7), 7.12 (2H, d, *J* = 8.2), 7.32 (2H, d, *J* = 8.2). Ms *m/z*: 277 (M^++1), 276 (M^+), 261, 260, 259, 243, 137, 135, 124, 107, 93, 91, 79, 69, 67, 55. HRms: Calcd for $C_{17}H_{24}OS$: 276.1547. Found: 276.1533.

(1*S*)-10-(4-Methoxybenzenethio)-2-*exo*-borneol: From NaH (60%, 311 mg, 7.78 mmol), 4-methoxybenzenethiol (990 mg, 7.07 mmol), and (1*S*)-(-)-10-bromo-2-*exo*-borneol (1.73 g, 7.42 mmol) was obtained (-)-10-(4-methoxybenzenethio)-2-*exo*-borneol (1.35 g, 62%) as a colorless oil. $[\alpha]_D^{27}$ -30.12° (*c* 1.00, $CHCl_3$). Ir ν_{max} (neat) cm^{-1}: 3474, 2952, 1592, 1494, 1285, 1244, 828. ^{1}H-Nmr δ: 0.84 (3H, s), 1.06 (3H, s), 1.0-1.8 (7H, m), 2.17 (1H, br), 2.88 (1H, d, *J* = 11.5), 3.15 (1H, d, *J* = 11.5), 3.80 (3H, s), 3.93 (1H, dd, *J* = 3.9, 8.2), 6.86 (2H, d, *J* = 8.8), 7.40 (2H, *J* = 8.8). Ms *m/z*: 293 (M^++1), 292 (M^+), 171, 167, 156, 140, 129, 121, 108, 93, 81, 55. HRms: Calcd for $C_{17}H_{24}O_2S$: 292.1496. Found: 292.1458.

(1*S*)-10-(4-Chlorobenzenethio)-2-*exo*-borneol: From NaH (60%, 402 mg, 10.1 mmol), 4-chlorobenzenethiol (1.32 g, 9.13 mmol), and (1*S*)-(-)-10-bromo-2-*exo*-borneol (2.13 g, 9.14 mmol) was obtained (-)-10-(4-chlorobenzenethio)-2-*exo*-borneol (2.16 g, 73%) as a yellow oil. $[\alpha]_D^{27}$ -34.78° (*c* 1.00, $CHCl_3$). Ir ν_{max} (neat) cm^{-1}: 3462, 2952, 1476, 1096, 1011, 811. ^{1}H-Nmr δ: 0.87 (3H, s), 1.09 (3H, s), 1.0-1.9 (7H, m), 2.15-2.2 (1H, br), 2.92 (1H, d, *J* = 11.0), 3.20 (1H, d, *J* = 11.0), 3.93 (1H, dd, *J* =

3.9, 7.7), 7.2-7.4 (4H, m). Ms *m/z*: 298 (M^+) (^{37}Cl), 296 (M^+) (^{35}Cl), 281, 279, 259,185, 157, 144, 135, 107, 93, 79, 67, 55. HRms: Calcd for $C_{16}H_{21}OClS$: 296.1001. Found: 295.0981.

(1*S*)-10-(4-Fluorobenzenethio)-2-*exo*-borneol: From NaH (60%, 282 mg, 7.05 mmol), 4-fluorobenzenethiol (823 mg, 6.43 mmol), and (1*S*)-(-)-10-bromo-2-*exo*-borneol (1.50 g, 6.44 mmol) was obtained (-)-10-(4-fluorobenzenethio)-2-*exo*-borneol (1.53 g, 85%) as a colorless oil. $[\alpha]_D^{27}$ -38.04° (*c* 1.00, $CHCl_3$). Ir ν_{max} (neat) cm^{-1}: 3474, 2952, 1492, 1072, 801. ^{1}H-Nmr δ: 0.86 (3H, s), 1.08 (3H, s), 1.0-1.9 (7H, m), 1.95-2.0 (1H, br), 2.92 (1H, d, *J* = 11.0), 3.18 (1H, d, *J* = 11.0), 3.94 (1H, dd, *J* = 3.9, 7.7), 6.95-7.05 (2H, m), 7.35-7.4 (2H, m). Ms *m/z*: 280 (M^+), 262, 185, 167, 135, 128, 109, 108, 95, 93, 91, 79, 67, 55. HRms: Calcd for $C_{16}H_{21}OFS$: 280.1296, Found: 280.1257.

General Procedure for Synthesis of Alkoxychlorosulfuranes (1a-g) To a solution of sulfides (1 mmol) in dry CH_2Cl_2 (5 ml) was added dropwise *t*-BuOCl (0.12 ml, 0.11 mmol) in dry CH_2Cl_2 (0.4 ml) at 0 °C under argon atomosphere. After completion of addition, the mixture was stirred at 0 °C for 5 min. Removal of the solvent and the excess reagent under reduced pressure gave alkoxychlorosulfuranes (**1a-g**) as white solids. Compounds (**1a-g**) were used for the next reaction without further purification because of their instability.

(1*S*, S_S)-5-Chloro-10,10-dimethyl-5-methyl-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1a): ^{1}H-Nmr δ: 0.95 (3H, s), 1.06 (3H, s), 1.1-2.4 (7H, m), 3.65 (3H, s), 4.13 (1H, d, *J* = 14.3), 4.52 (1H, d, *J* = 14.3), 4.88 (1H, dd, *J* = 2.5, 7.4). Ms *m/z*: 236 (M^+) (^{37}Cl), 234 (M^+) (^{35}Cl).

(1*S*, S_S)-5-Chloro-10,10-dimethyl-5-ethyl-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1b): ^{1}H-Nmr δ: 0.95 (3H, s), 1.08 (3H, s), 1.59 (3H, t, *J* = 7.7), 1.2-2.4 (7H, m), 3.51 (1H, qd, *J* = 6.8, 13.5), 4.04 (1H, d, *J* = 14.8), 4.47 (1H,qd, *J* = 6.6, 13.2), 4.48 (1H, d, *J* = 14.3), 4.76 (1H, dd, *J* = 2.7, 7.7).

(1*S*, R_S)-5-Chloro-10,10-dimethyl-5-phenyl-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1c): ^{1}H-Nmr δ: 0.99 (3H, s), 1.17 (3H, s), 0.8-2.35 (7H, m), 4.34 (1H, dd, *J* = 3.3, 7.7), 4.57 (1H, d, *J* = 15.4), 4.69 (1H, d, *J* = 14.8), 7.5-7.7 (3H, m), 7.9-8.05 (2H, m).

(1*S*, R_S)-5-Chloro-10,10-dimethyl-5-(*p*-tolyl)-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1d): ^{1}H-Nmr δ: 0.99 (3H, s), 1.16 (3H, s), 1.05-2.3 (7H, m), 2.44 (3H, s), 4.40 (1H, dd, *J* = 3.3, 7.7), 4.54 (1H, d, *J*

= 15.4), 4.67 (1H, d, J = 15.4), 7.39 (2H, d, J = 8.2), 7.84 (2H, d, J = 8.8). Ms *m/z*: 312 (M^+) (^{37}Cl), 310 (M^+) (^{35}Cl), 276, 274, 185, 171, 153, 135, 124, 107, 92, 91, 79, 67, 55.

(1*S*, R_S)-5-Chloro-10,10-dimethyl-5-(4-methoxylphenyl)-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1e): ^{1}H-Nmr δ: 1.00 (3H, s), 1.15 (3H, s), 1.2-2.35 (7H, m), 3.89 (3H, s), 4.5-4.6 (1H, m), 4.51 (1H, d, J = 14.8), 4.67 (1H, d, J = 14.8), 7.10 (2H, d, J = 9.3), 7.90 (2H, d, J = 9.3).

(1*S*, R_S)-5-Chloro-10,10-dimethyl-5-(4-chlorophenyl)-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1f): ^{1}H-Nmr δ: 0.99 (3H, s), 1.15 (3H, s), 1.0-2.4 (7H, m), 4.36 (1H, dd, J = 3.3, 7.7), 4.53 (1H, d, J = 15.4), 4.67 (1H, d, J = 15.4), 7.56 (2H, d, J = 8.8), 7.94 (2H, d, J = 8.8).

(1*S*, R_S)-5-Chloro-10,10-dimethyl-5-(4-fluorophenyl)-5λ^4-thia-4-oxatricyclo[5.2.1.0^{3,7}]decane (1g): ^{1}H-Nmr δ: 1.00 (3H, s), 1.16 (3H, s), 1.0-2.4 (7H, m), 4.41 (1H, dd, J = 3.3, 7.7), 4.54 (1H, d, J = 15.4), 4.70 (1H, d, J = 15.4), 7.29 (2H, dd, J = 7.7, 8.2), 8.02 (2H, dd, J = 4.7, 9.1).

General Procedure for Synthesis of Sulfoxides (2a-g) from Alkoxychlorosulfuranes (1a-g) To a solution of alkoxychlorosulfuranes **(1a-g)** (1 mmol) in dry CH_2Cl_2 (5 ml) was added H_2O (2 ml) at 0 °C, and the reaction mixture was stirred for 30 min and seperated. The aqueous layer was extracted with CH_2Cl_2 (25 ml × 3). The combined organic phase was washed with brine (8 ml) and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (hexane / AcOEt 4:1) to give sulfoxides **(2a-g)** as white solids. Yield from the corresponding sulfide is shown in Table 1. Mp and spectral data of (1*S*, S_S)-10-(methylsulfinyl)-2-*exo*-borneol **(2a)** and (1*S*, S_S)-10-(ethylsulfinyl)-2-*exo*-borneol **(2b)** were identical with those in the literature.[5]

(1*S*, R_S)-10-(Phenylsulfinyl)-2-*exo*-borneol (2c): mp 124-125 °C. $[\alpha]_D^{27}$ +133.0° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3375, 2956, 1446, 1032, 995. ^{1}H-Nmr δ: 0.80 (3H, s), 1.06 (3H, s), 1.2-2.0 (7H, m), 2.38 (1H, d, J = 13.2), 3.35 (1H, d, J = 13.7), 4.14 (1H, br d, J = 3.3), 4.20 (1H, ddd, J = 1.9, 3.8, 5.8), 7.5-7.65 (3H, m), 7.6-7.75 (2H, m). Ms *m/z*: 278 (M^+), 262, 260, 244, 229, 217, 201, 181, 153, 138, 135, 126, 110, 109, 93, 78, 57. *Anal.* Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.96. Found: C, 69.06; H, 7.92.

(1*S*, R_S)-10-(*p*-Tolylsulfinyl)-2-*exo*-borneol (2d): mp 142-144 °C. $[\alpha]_D^{27}$ +140.86° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3435, 2957, 1493, 1058, 1023, 813. ^{1}H-Nmr δ: 0.79 (3H, s), 1.05 (3H, s), 1.2-2.0 (8H, m), 2.35 (1H, d, *J* = 13.2), 2.44 (3H, s), 3.34 (1H, d, *J* = 13.2), 4.19 (1H, dd, *J* = 4.4, 7.7), 7.36 (2H, d, *J* = 8.2), 7.56 (2H, d, *J* = 8.2). Ms *m/z*: 293 (M^++1), 276, 274, 153, 140, 135, 109, 92, 91, 79, 67, 65, 55. *Anal.* Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.75; H, 8.24.

(1*S*, R_S)-10-(4-Methoxylphenylsulfinyl)-2-*exo*-borneol (2e): mp 118-120 °C. $[\alpha]_D^{27}$ +135.14° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3393, 2941, 1595, 1578, 1496, 1251, 1056, 1028, 999. ^{1}H-Nmr δ: 0.77 (3H, s), 1.05 (3H, s), 1.2-1.9 (7H, m), 2.32 (1H, d, *J* = 13.2), 3.33 (1H, d, *J* = 13.2), 3.85 (3H, s), 4.15-4.2 (1H, m), 4.18 (1H, br d, *J* = 1.6), 7.04 (2H, d, *J* = 8.8), 7.60 (2H, d, *J* = 8.8). Ms *m/z*: 309 (M^++1), 292, 290, 274, 259, 156, 140, 139, 135, 108, 93, 79, 67, 55. *Anal.* Calcd for $C_{17}H_{24}O_3S$: C, 66.20; H, 7.84. Found: C, 66.36; H, 7.82.

(1*S*, R_S)-10-(4-Chlorophenylsulfinyl)-2-*exo*-borneol (2f): mp 144-145 °C. $[\alpha]_D^{27}$ +137.30° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3401, 2930, 1474, 1078, 1033, 1020, 822. ^{1}H-Nmr δ: 0.80 (3H, s), 1.05 (3H, s), 1.2-1.9 (7H, m), 2.35 (1H, d, *J* = 13.7), 3.32 (1H, d, *J* = 13.7), 4.02 (1H, d, *J* = 3.3), 4.18 (1H, dd, *J* = 4.4, 8.2), 7.54 (2H, d, *J* = 8.8), 7.62 (2H, d, *J* = 8.2). Ms *m/z*: 315 (M^++1) (^{37}Cl), 313 (M^++1) (^{35}Cl), 295, 162, 160, 153, 135, 109, 107, 93, 79, 67, 55. *Anal.* Calcd for $C_{16}H_{21}O_2ClS$: C, 61.42; H, 6.76. Found: C, 61.16; H, 6.88.

(1*S*, R_S)-10-(4-Fluorophenylsulfinyl)-2-*exo*-borneol (2g): mp 130-132 °C. $[\alpha]_D^{27}$ +134.84° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3387, 2954, 1588, 1491, 1216, 1058, 1006, 844. ^{1}H-Nmr δ: 0.81 (3H, s), 1.06 (3H, s), 1.2-1.9 (7H, m) 2.36 (1H, d, *J* = 13.2), 3.34 (1H, d, *J* = 13.2), 4.06 (1H, d, *J* = 3.3), 4.18 (1H, dd, *J* = 3.8, 7.7), 7.26 (2H, dd, *J* = 8.2, 8.8), 7.68 (2H, dd, *J* = 4.9, 8.8). Ms *m/z*: 297 (M^++1), 280, 278, 262, 153, 144, 135, 109, 96, 93, 79, 55. *Anal.* Calcd for $C_{16}H_{21}O_2FS$: C, 64.84; H, 7.14. Found: C, 64.83; H, 7.12.

General Procedure for Synthesis of *N*-*p*-Tosylsulfilimines (3a-g) from Alkoxychlorosulfuranes (1a-g) To a solution of alkoxychlorosulfuranes **(1a-g)** (1.00 mmol) in dry CH_2Cl_2 (5 ml) was added NaNHTs (290 mg, 1.50 mmol) (prepared from NH_2Ts and 1 equivalent of NaOMe in MeOH at 0 °C) at 0 °C under argon atmosphere. After being stirred for 1 h, the solvent was evaporated to give pale yellow

solids which were purified by column chromatography (hexane / AcOEt 4:1) or by recrystallization from CH_2Cl_2 / AcOEt to afford *N*-*p*-tosylsulfilimines (**3a-g**) as colorless crystals. Yield is shown in Table 1.

(1*S*, S_S)-Methyl 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3a): mp 169-170.5 °C. $[\alpha]_D^{27}$ +187.06° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3421, 2950, 1296, 1139, 1089, 1079, 972, 942. ^{1}H-Nmr δ: 0.80 (3H, s), 1.04 (3H, s), 0.9-1.8 (7H, m), 2.41 (3H, s), 2.48 (1H, d, *J* = 13.2), 2.68 (3H, s), 3.3-3.4 (1H, m), 3.59 (1H, d, *J* = 12.6), 3.73 (1H, br d, *J* = 2.7), 7.28 (2H, d, *J* = 8.2), 7.80 (2H, d, *J* = 8.2). Ms *m/z*: 370 (M^++1), 369 (M^+), 347, 326, 278, 222, 217, 198, 171, 155, 135, 108, 91, 65. *Anal.* Calcd for $C_{18}H_{27}NO_3S_2$: C, 58.50; H, 7.36; N, 3.79. Found: C, 58.27; H, 7.28; N, 3.90.

(1*S*, S_S)-Ethy 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3b): mp 197-198 °C. $[\alpha]_D^{27}$ +117.47° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3461, 2959, 1274, 1137, 1088, 970. ^{1}H-Nmr δ: 0.80 (3H, s), 1.03 (3H, s), 1.30 (3H, t, *J* = 7.7), 0.9-1.9 (7H, m), 2.40 (3H, s), 2.43 (1H, d, *J* = 13.2), 2.90 (2H, dq, 3.3, 7.7), 3.41 (1H, m), 3.52 (1H, d, *J* = 12.6), 3.64 (1H, br d, *J* = 3.9), 7.26 (2H, d, *J* = 8.2), 7.80 (2H, d, *J* = 8.2). Ms *m/z*: 384 (M^++1), 383 (M^+), 231, 172, 155, 139, 135, 107, 91, 76, 65, 55. *Anal.* Calcd for $C_{19}H_{29}NO_3S_2$: C, 59.50; H, 7.62; N, 3.65. Found: C, 59.52; H, 7.59; N, 3.85.

(1*S*, R_S)-Pheny 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3c): mp 213-214 °C. $[\alpha]_D^{27}$ +309.98° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3418, 2958, 1298, 1287, 1147, 1089, 1077, 943. ^{1}H-Nmr δ: 0.77 (3H, s), 0.99 (3H, s), 1.0-1.9 (7H, m), 2.35 (3H, s), 2.51 (1H, d, *J* = 13.2), 3.64 (1H, ddd, *J* = 3.8, 3.8, 7.7), 3.73 (1H, d, *J* = 13.2), 3.90 (1H, br d, *J* = 3.8), 7.17 (2H, d, *J* = 8.2), 7.5-7.6 (3H, m), 7.65-7.8 (4H, m). Ms *m/z*: 432 (M^++1), 431 (M^+), 306, 279, 260, 171, 155, 124, 110, 91, 65, 55. *Anal.* Calcd for $C_{23}H_{29}NO_3S_2$: C, 64.00; H, 6.77; N, 3.25. Found: C, 64.07; H, 6.73; N, 3.46.

Crystallographic Data for 3c: Orthorhombic, space group, $P2_12_12_1$ with *a* = 24.889(8) Å, *b* = 11.407(3) Å, *c* = 7.861(1) Å, *V* = 2231.8(9) Å^3, and *Z* = 4 (d_{calcd} = 1.284 g cm^{-3}), μ(MoKα) = 2.62 cm^{-1} absorption corrected by ω scans; 1951 unique reflection; 1244 with $I > 3.00\sigma(I)$ were used in refinement; *R* = 3.6%, R_w = 3.6%. The authors have deposited atomic coordinates for **3c** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(1*S*, R_S)-*p*-Tolyl 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3d): mp 143-144.5 °C. $[\alpha]_D^{27}$ +308.04° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3394, 2959, 1308, 1295, 1152, 1090, 1076, 945, 935.

^{1}H-Nmr δ: 0.76 (3H, s), 0.99 (3H, s), 1.0-1.9 (7H, m), 2.36 (3H, s), 2.41 (3H, s), 2.46 (1H, d, J = 12.6), 3.63 (1H, dd, J = 3.3, 7.7), 3.72 (1H, d, J = 12.6), 3.8-4.1 (1H, br), 7.17 (2H, d, J = 7.7), 7.31 (2H, d, J = 8.2), 7.58 (2H, d, J = 8.2), 7.72 (2H, d, J = 8.2). Ms *m/z*: 446 (M^++1), 445 (M^+), 293, 276, 274, 171, 165, 138, 124, 107, 91, 79, 65, 55. *Anal.* Calcd for $C_{24}H_{31}NO_3S_2$: C, 64.68; H, 7.01; N, 3.14. Found: C, 64.69; H, 6.93; N, 3.14.

(1*S*, R_S)-4-Methoxylphenyl 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3e): mp 138-139.5 °C. $[\alpha]_D^{27}$ +263.98° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3405, 2956, 1284, 1256, 1144, 1089, 945. ^{1}H-Nmr δ: 0.76 (3H, s), 1.00 (3H, s), 1.0-1.9 (7H, m), 2.35 (3H, s), 2.47 (1H, d, J = 13.2), 3.67 (1H, ddd, J = 3.9, 4.4, 8.2), 3.73 (1H, d, J = 13.2), 3.84 (3H, s), 3.94 (1H, d, J = 3.8), 6.97 (2H, d, J = 9.3), 7.15 (2H, d, J = 8.2), 7.61 (2H, d, J = 9.3), 7.69 (2H, d, J = 8.2). Ms *m/z*: 462 (M^++1), 461(M^+), 321, 309, 292, 290, 171, 154, 140, 108, 91, 65, 55. *Anal.* Calcd for $C_{24}H_{31}NO_4S_2$: C, 62.44; H, 6.77; N, 3.03. Found: C, 62.54; H, 6.75; N, 3.29.

(1*S*, R_S)-4-Chlorophenyl 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3f): mp 164-165 °C. $[\alpha]_D^{27}$ +246.28° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3360, 3262, 2953, 1306, 1160, 1097, 1076, 946. ^{1}H-Nmr δ: 0.77 (3H, s), 0.99 (3H, s), 1.0-1.85 (7H, m), 2.37 (3H, s), 2.48 (1H, d, J = 13.2), 3.62 (1H, dd, J = 3.9, 8.2), 3.71 (1H, d, J = 13.2), 3.80 (1H, d, J = 3.8), 7.19 (2H, d, J = 8.2), 7.49 (2H, d, J = 8.8), 7.64 (2H, d, J = 8.8), 7.72 (2H, d, J = 8.2). Ms *m/z*: 468 (M^++1) (^{37}Cl), 466 (M^++1) (^{35}Cl), 315, 313, 296, 294, 160, 158, 144, 135, 107, 93, 91, 81, 79, 67, 65, 55. *Anal.* Calcd for $C_{23}H_{28}NO_3ClS_2$: C, 59.27; H, 6.06; N, 3.01. Found: C, 59.06; H, 6.13; N, 2.71.

(1*S*, R_S)-4-Fluorophenyl 2-*exo*-Hydroxy-10-bornyl *N*-*p*-Tosylsulfilimine (3g): mp 161-162.5 °C. $[\alpha]_D^{27}$ +287.32° (*c* 1.00, $CHCl_3$). Ir ν_{max} (KBr) cm^{-1}: 3438, 2961, 1232, 1284, 1146, 1087, 947. ^{1}H-Nmr δ: 0.78 (3H, s), 0.99 (3H, s), 1.0-1.85 (7H, m), 2.36 (3H, s), 2.47 (1H, d, J = 13.2), 3.62 (1H, ddd, J = 3.8, 4.4, 8.2), 3.72 (1H, d, J = 12.6), 3.83 (1H, d, J = 3.8), 7.1-7.35 (4H, m), 7.6-7.8 (4H, m). Ms *m/z*: 450 (M^++1), 297, 278, 171, 155, 142, 128, 107, 91, 79, 67, 65, 55. *Anal.* Calcd for $C_{23}H_{28}NO_3FS_2$: C, 61.44; H, 6.28; N, 3.12. Found: C, 61.24; H, 6.28; N, 3.07.

General Procedure for Synthesis of Sulfonium Ylides (4a-g) from Alkoxychlorosulfuranes (1a-g)

To a solution of alkoxychlorosulfuranes **(1a-g)** (1.00 mmol) in dry CH_2Cl_2 (5 ml) was added

$NaCH(CO_2Me)_2$ (231 mg, 1.50 mmol) (prepared from dimethyl malonate and 1 equivalent of NaH in CH_2Cl_2 at 0 °C) at 0 °C under argon atmosphere. After being stirred for 1 h, the solvent was evaporated to give pale yellow solids which were purified by recrystallization from CH_2Cl_2 / AcOEt to afford sulfonium ylides (**4a-g**) as colorless crystals. Yield and the ratio of diastereomers are shown in Table 1.

Dimethyl [2-*exo*-Hydroxy-10-bornyl(methyl)sulfuranylidine]malonate (4a): (a mixture of **4aA** and **4aB**), mp 189.5-191 °C. Ir ν_{max} (KBr) cm^{-1}: 3449, 2953, 1628, 1332, 1078. ^{1}H-Nmr δ: **4aA**: 0.88 (3H, s), 1.05 (3H, s), 1.0-1.9 (8H, m), 2.92 (1H, d, J = 12.6), 2.89 (3H, s), 3.74 (6H, s), 3.85-3.95 (1H, m), 3.90 (1H, m), 4.01 (1H, d, J = 12.6). **4aB**: 0.83 (3H, s), 1.08 (3H, s), 1.0-1.9 (8H, m), 2.91 (3H, s), 3.00 (1H, d, J = 12.1), 3.73 (6H, s), 3.87 (1H, d, J = 12.1), 3.95-4.05 (1H, m). Ms *m/z*: 330 (M^+), 299, 199, 180, 178, 146, 108, 93, 79, 59. *Anal.* Calcd for $C_{16}H_{26}O_5S$: C, 58.16; H, 7.93. Found: C, 57.93; H, 7.87.

Dimethyl [Ethyl(2-*exo*-hydroxy-10-bornyl)sulfuranylidine]malonate (4b): (a mixture of **4bA** and **4bB**), mp 152-154 °C. Ir ν_{max} (KBr) cm^{-1}: 3480, 2953, 1633, 1329, 1082. ^{1}H-Nmr δ: **4bA**: 0.87 (3H, s), 1.05 (3H, s), 1.0-1.85 (8H, m), 1.26 (3H, t, J = 7.1), 2.83 (1H, d, J = 13.2), 2.85-3.05 (1H, m), 3.73 (6H, s), 3.65-3.85 (1H, m), 3.85-3.95 (1H, m), 3.97 (1H, d, J = 12.6). **4bB**: 0.83 (3H, s), 1.08 (3H, s), 1.0-1.85 (8H, m), 1.28 (3H, t, J = 7.1), 2.95 (1H, d, J = 12.1), 2.85-3.05 (1H, m), 3.73 (6H, s), 3.65-3.85 (1H, m), 3.80 (1H, d, J = 12.6), 3.95-4.05 (1H, m). Ms *m/z*: 344 (M^+), 313, 297, 213, 192, 161, 160, 128, 108, 93, 79, 59. *Anal.* Calcd for $C_{17}H_{28}O_5S$: C, 59.28; H, 8.19. Found: C, 59.45; H, 8.04.

Dimethyl [2-*exo*-Hydroxy-10-bornyl(phenyl)sulfuranylidine]malonate (4c): (a mixture of **4cA** and **4cB**), mp 199-200 °C. Ir ν_{max} (KBr) cm^{-1}: 3396, 2951, 1698, 1608, 1322, 1072. ^{1}H-Nmr δ: **4cA**: 0.94 (3H, s), 1.09 (3H, s), 1.05-1.9 (8H, m), 3.23 (1H, d, J = 12.6), 3.73 (6H, s), 3.89 (1H, dd, J = 3.3, 8.8), 4.61 (1H, d, J = 13.2), 7.5-7.6 (3H, m), 7.7-7.8 (2H, m). **4cB**: 0.86 (3H, s), 1.13 (3H, s), 1.05-1.9 (8H, m), 3.45 (1H, d, J = 12.6), 3.72 (6H, s), 4.13 (1H, dd, J = 4.1, 7.4), 4.43 (1H, d, J = 12.6), 7.4-7.5 (3H, m), 7.6-7.7 (2H, m). Ms *m/z*: 392 (M^+), 361, 261, 240, 208, 149, 121, 105, 93, 77, 67, 59. *Anal.* Calcd for $C_{21}H_{28}O_5S$: C, 64.26; H, 7.19. Found: C, 64.07; H, 7.15.

Dimethyl [2-*exo*-Hydroxy-10-bornyl(*p*-tolyl)sulfuranylidine]malonate (4d): (a mixture of **4dA** and **4dB**), mp 172-173 °C. Ir ν_{max} (KBr) cm^{-1}: 3422, 2951, 1615, 1318, 1084. ^{1}H-Nmr δ: **4dA**: 0.94 (3H, s),

1.09 (3H, s), 1.60 (3H, s), 1.0-1.9 (8H, m), 3.24 (1H, d, J = 13.2), 3.73 (6H, s), 3.85-3.95 (1H, m), 4.60 (1H, d, J = 12.6), 7.45-7.55 (2H, m), 7.7-7.8 (2H, m). **4dB**: 0.86 (3H, s), 1.13 (3H, s), 1.61 (3H, s), 1.0-1.9 (8H, m), 3.45 (1H, d, J = 12.6), 3.72 (6H, s), 4.1-4.2 (1H, m), 4.43 (1H, d, J = 12.6), 7.4-7.5 (2H, m), 7.65-7.75 (2H, m). Ms *m/z*: 406 (M^+), 375, 334, 276, 254, 222, 195, 163, 135, 124, 108, 93, 67, 55. *Anal.* Calcd for $C_{22}H_{30}O_5S$: C, 65.00; H, 7.44. Found: C, 64.90; H, 7.42.

Dimethyl [2-*exo*-Hydroxy-10-bornyl(4-methoxylphenyl)sulfuranylidine]malonate (4e): (a mixture of **4eA** and **4eB**), mp 128-129.5 °C. Ir ν_{max} (KBr) cm^{-1}: 3396, 2950, 1645, 1326, 1083. ^{1}H-Nmr δ: **4eA**: 0.90 (3H, s), 1.07 (3H, s), 1.0-1.9 (8H, m), 3.17 (1H, d, J = 12.6), 3.71 (6H, s), 3.84 (3H, s), 3.87 (1H, ddd, J = 2.7, 3.3, 6.0), 4.57 (1H, d, J = 12.6), 6.97 (2H, d, J = 8.8), 7.75 (2H, d, J = 8.8). **4eB**: 0.85 (3H, s), 1.10 (3H, s), 1.0-1.9 (8H, m), 3.37 (1H, d, J = 12.1), 3.72 (6H, s), 3.82 (3H, s), 4.08 (1H, ddd, J = 1.6, 2.5, 4.1), 4.43 (1H, d, J = 12.6), 6.95 (2H, d, J = 8.8), 7.66 (2H, d, J = 9.3). Ms *m/z*: 422 (M^+), 391, 291, 270, 238, 209, 151, 140, 135, 129, 108, 93, 79, 67, 55. *Anal.* Calcd for $C_{22}H_{30}O_6S$: C, 62.54; H, 7.16. Found: C, 62.37; H, 7.08.

Dimethyl [(4-Chlorophenyl)(2-*exo*-hydroxy-10-bornyl)sulfuranylidine]malonate (4f): (a mixture of **4fA** and **4fB**), mp 201-202.5 °C. Ir ν_{max} (KBr) cm^{-1}: 3440, 2951, 1612, 1391, 1298, 1077. ^{1}H-Nmr δ: **4fA**: 0.93 (3H, s), 1.09 (3H, s), 1.05-1.95 (8H, m), 3.21 (1H, d, J = 13.2), 3.73 (6H, s), 3.85-3.95 (1H, m), 4.59 (1H, d, J = 12.6), 7.47 (2H, d, J = 8.2), 7.70 (2H, d, J = 8.8). **4fB**: 0.85 (3H, s), 1.12 (3H, s), 1.05-1.95 (8H, m), 3.41 (1H, d, J = 12.6), 3.72 (6H, s), 4.1-4.2 (1H, m), 4.42 (1H, d, J = 12.6), 7.44 (2H, d, J = 8.2), 7.63 (2H, d, J = 8.8). Ms *m/z*: 428 (M^+) (^{37}Cl), 426 (M^+) (^{35}Cl), 397, 396, 395, 297, 296, 295, 274, 276, 244, 242, 215, 185, 183, 157, 155, 108, 93, 67, 59. *Anal.* Calcd for $C_{21}H_{27}O_5ClS$: C, 59.08; H, 6.37. Found: C, 59.07; H, 6.33.

Dimethyl [(4-Fluorophenyl)(2-*exo*-hydroxy-10-bornyl)sulfuranylidine]malonate (4g): (a mixture of **4gA** and **4gB**), mp 193-195 °C. Ir ν_{max} (KBr) cm^{-1}: 3447, 2951, 1617, 1436, 1086. ^{1}H-Nmr δ: **4gA**: 0.93 (3H, s), 1.08 (3H, s), 1.0-1.9 (8H, m), 3.18 (1H, d, J = 12.6), 3.73 (6H, s), 3.85-3.95 (1H, m), 4.62 (1H, d, J = 13.2), 7.17 (2H, dd, J = 1.6, 8.8), 7.81 (2H, dd, J = 4.7, 9.1). **4gB**: 0.86 (3H, s), 1.12 (3H, s), 1.0-1.9 (8H, m), 3.39 (1H, d, J = 12.6), 3.72 (6H, s), 4.1-4.2 (1H, m), 4.46 (1H, d, J = 12.6), 7.14 (2H, dd, J = 1.6, 8.8), 7.71 (2H, dd, J = 4.9, 8.8). Ms *m/z*: 410 (M^+), 379, 280, 258, 226,

199, 167, 139, 128, 108, 93, 67, 59. *Anal.* Calcd for $C_{21}H_{27}O_5FS$: C, 61.44; H, 6.63. Found: C, 61.43; H, 6.52.

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