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Diastereoselective Total Synthesis of (-)-Solavetivone *via* a Copper-Catalyzed Conjugate Addition of Me3Al to a Cyclohexa-2,5-dienone Intermediate

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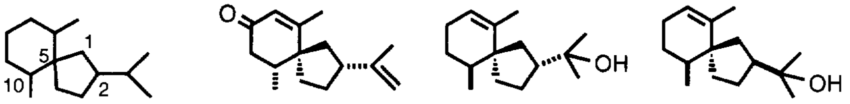
Abstract: We succeeded in a stereoselective total synthesis of (-)-solavetivone **1** by employing a new enantioselective copper-catalyzed conjugate addition of Me_3Al to a chiral cyclohexadienone **4**, which was prepared from a chiral cyclopropane derivative **9** by using a regioselective Hg(II)-mediated cyclopropyl ring-opening reaction, subsequent Pd(II)-mediated spiroannulation of the resulting alkylmercury chloride **8**, and a stereoselective Pd(0)-mediated hydrogenolysis of an allylic formate **15c** as the key reactions.

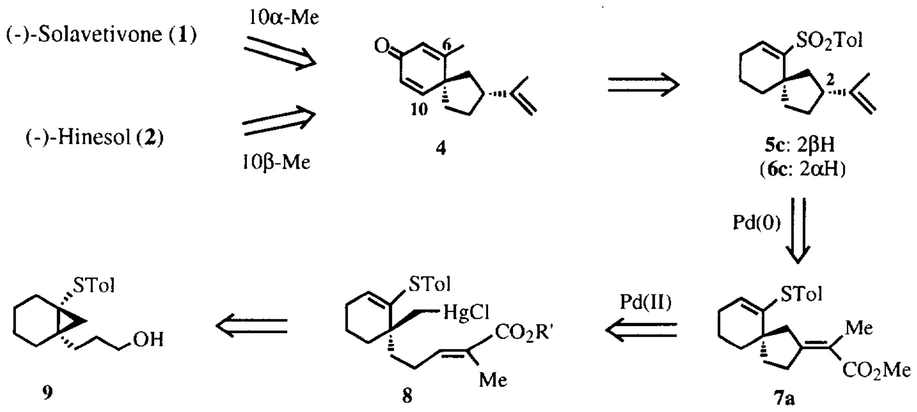
(-)-Solavetivone **1** is a representative phytoalexin,[1] which was isolated from potato tubers infected with the blight fungus *phytophthora infestans*[2a] or air-cured tobacco leaves.[2b] In general, phytoalexins can not be observed in normal plants and are only produced as defense substances by those plants after infection. **1** was structurally classified as *trans*-spirovetivane sesquiterpene characterized by trans configuration between a C1-C5 bond and a methyl group at C10 in the spiro[4.5]decane skeleton. Although the *trans*-spirovetivanes such as **1** possess inhibitory activity against several bacteria, *cis*-spirovetivanes, represented by hinesol **2** and agarospirol **3** known as fragrant principles, have no biological activity.[1c,d] From the viewpoint of evaluating the structure-activity relationship of the phytoalexins and identifying the defense mechanisms of plants, stereoselective construction of all the stereogenic centers in **1**-**3** (C2, C5, and C10) is considered very important. While, thus far, considerable attention has been directed towards the synthesis of these two types of sesquiterpenes, most of the work is limited to racemic preparation, and stereocontrols of the C2 and C10 chiral centers still remain to be resolved.[3,4] Recently, one group reported the asymmetric synthesis of (-)-solavetivone **1** starting from (+)-dihydrocarvone, which already contains the C2 chirality.[5]

In the course of our studies directed toward the asymmetric synthesis of all stereoisomers such as **1**-**3** by stereoselective chemical reactions, we have reported an asymmetric synthesis of a quaternary carbon center (C5) by using a Michael addition of an allylmagnesium chloride to a chiral vinylic sulfoxide, and a stereoselective introduction of the β-substituent at the C2 chiral center by a radical-mediated spiroannulation of an alkylmercury chloride.[6] Recently, we investigated alternative and efficient methods for controlling the remaining chiral centers; *i.e.*, C2 (α-isopropenyl) and C10 (α- and β-methyl), and found that the α-isopropenyl group at C2 and α-methyl group at C10 of **1** could be introduced stereoselectively by a Pd(0)-mediated Tsuji-Mandai reaction[7] (**7a**→**5c**) and a diastereoselective copper-catalyzed conjugate addition[8] of Me_3Al (**4**→**1** or **2**) in the presence of a chiral ligand, respectively (Scheme 1). In this paper, we wish to describe a second asymmetric total synthesis of (-)-solavetivone **1** starting from a chiral cyclopropyl sulfide (**9**)[6b] by using these novel diastereoselective reactions.[9]



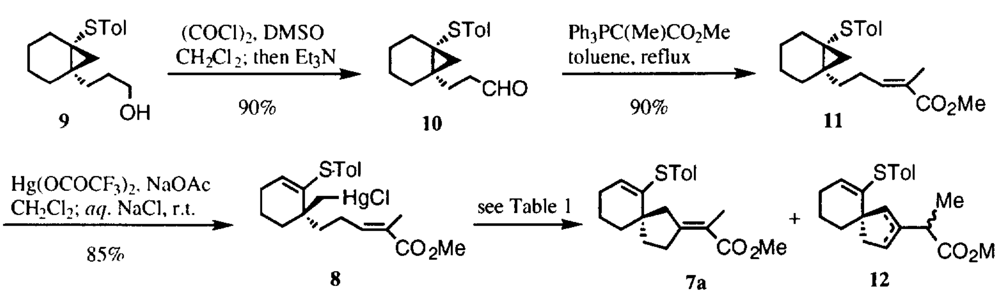
(-)-solavetivone **1** (-)-hinesol **2** (+)-agarospirol **3**

***Trans*- and *cis*-type spirovetivanes**



Scheme 1. Retrosynthetic analysis of *trans*-and *cis*-type spirovetivanes

Our initial efforts were focused on constructing the spiro[4.5]decane skeleton (Scheme 2). Swern oxidation of **9** afforded the aldehyde **10** (90%), Wittig reaction with (α-carbomethoxyethylidene)-triphenylphosphorane[10] of which provided α,β-unsaturated ester **11** effectively in 90% yield. Treatment of **11** with mercury(II) trifluoroacetate[6b] and sodium acetate in methylene chloride resulted in the anticipated chemo- and regio-selective ring-opening to give rise to **8** as a single isomer in 85% yield. We next investigated the palladium(II)-mediated spirocyclization of **8** (Table 1). When the spiroannulation reaction of **8** was performed with Li_2PdCl_4 in the presence of Et_3N,[6a,11a] several regioisomers **12** were produced along with the desired α,β-unsaturated ester **7a** irrespective of the amount of the base (entries 1 and 2). The addition of 1,3-dimethyl-2-imidazolidinone (DMI) in place of DMF had no effect on the C=C double bond isomerization (entry 3). In contrast, the spiroannulation reaction of **8** in the presence of $KHCO_3$ proceeded regioselectively and gave the spirocyclic product **7a** (49%) as a single isomer (entry 4). The regioselectivity of the double bond could be explained by the comparison of the nature of bases.[11b] That is, Et_3N, a weaker base than $KHCO_3$, could not convert the HPdCl, produced as the reaction proceeds, into the Pd(0) species effectively. Therefore, the remaining HPdCl catalyst would add to **7a** with no regioselectivity and subsequently undergo β-hydride elimination to give a mixture of **12** and **7a**. However, contrary to expectation of removing the HPdCl species more effectively, addition of more than 5 equiv. of $KHCO_3$ or 1 equiv. of a phase transfer catalyst ($^nBu_4NHSO_4$) was revealed to promote the isomerization of the double bond like Et_3N (entries 5-7).[11c] These facts suggest that the isomerization of **7a** to **12** occurs *via* two different processes, that is, a palladium hydride-mediated process and a base-catalyzed one. The relative stereochemistry of **7a** was determined by an X-ray crystallographic analysis (Fig. 1), which confirmed that **7a** possesses a (2*E*)-tetrasubstituted α,β-unsaturated ester and exists as a 1:1 mixture of two conformational isomers of a cyclohexene-ring in a solid state.



Scheme 2.

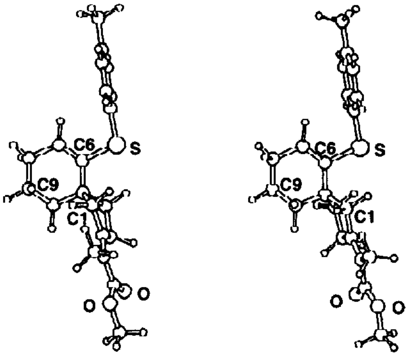


Fig. 1. A parallel View of **7a**

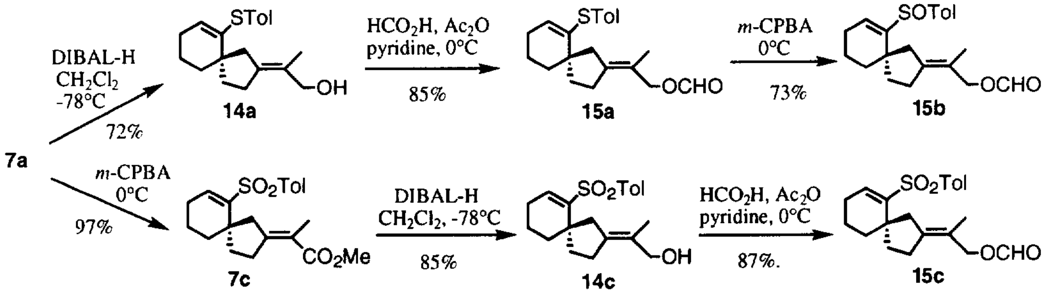
Table 1. The Pd(II)-mediated spiroannulation of **8** in the presence of a base

Entry	Solvent	Base (eq)	Time (hr)	**7a** : **12**[a]	Yield (%)
1	THF - DMF	Et_3N (1.2)	46	52 : 48	49[b]
2	THF - DMF	Et_3N (2.0)	48	50 : 50	51[b]
3	THF - DMI	Et_3N (2.0)	46	56 : 44	40[b]
4	THF - DMF	$KHCO_3$ (3.0)	57	93 : 7	49[c]
5	THF - DMF	$KHCO_3$ (5.0)	46	43 : 57	58[b]
6	THF - DMF	$KHCO_3$ (2.5)[d]	48	43 : 57	52[b]
7	CH_3CN	$KHCO_3$ (3.0)[d]	21	31 : 69	54[b]

[a] Determined by ^{1}H-NMR (200MHz) of crude products. [b] Isolated yields of a mixture of **7a** and **12**. [c] Isolated yield of **7a**. [d] 1.0 equiv. of $^n Bu_4NHSO_4$ was added to the reaction mixture.

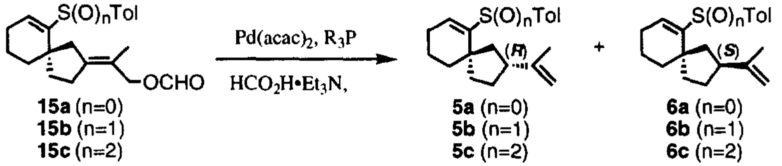
We next investigated a Pd(0)-mediated Tsuji-Mandai reaction[7] in expectation of an intramolecular hydride-transfer from the less-hindered side, resulting in predominant formation of (2*R*)-isomer **5a**. The requisite allylic formates (**15a-c**) were prepared from **7a** as shown in Scheme 3. Transformation of **7a** into the target **15a** was accomplished by the reduction with diisobutylaluminum hydride (DIBAL-H) (72%) and subsequent protection of the resulting alcohol **14a** (85%) as a formate with formic acid and acetic anhydride in pyridine. The sulfoxide **15b** was synthesized as a 1:1 diastereomeric mixture by the *m*-chloroperbenzoic acid (*m*-CPBA) oxidation of **15a**. Similarly, transformation of **7a** into the sulfone **15c** was performed by the three-step sequence *via* sulfones **7c** and **14c** [oxidation with *m*-CPBA (97%), reduction with DIBAL-H (85%), and protection (87%)].

We first investigated the palladium(0)-mediated hydrogenolysis of **15a** with a stoichiometric amount of palladium(0) acetylacetonate [$Pd(acac)_2$] in the presence of triphenyl- or tributyl-phosphine (Table 2). The reactions in benzene and THF gave better stereoselectivities than that in a more polar solvent such as DMF



Scheme 3

Table 2. The Pd(0)-mediated hydrogenolysis of allylic formate **15a-c**



Entry	n	Pd(acac)$_2$ (eq)	R$_3$P (eq)	HCO$_2$H$\cdot$ Et$_3$N (eq)	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)	5 : 6[b] (2*R* : 2*S*)
1	0	1.0	Ph$_3$P (1.0)	none	benzene	rt	48	60	67 : 33
2	0	1.0	Ph$_3$P (1.0)	none	THF	60	12	91	62 : 38
3	0	1.0	Ph$_3$P (1.0)	none	DMF	60	15	60	45 : 55
4	0	1.0	^{n}Bu$_3$P (1.0)	none	benzene	rt	16	76	79 : 21
5	1	1.0	^{n}Bu$_3$P (1.0)	none	benzene	rt	72	82	64 : 36
6	2	1.0	^{n}Bu$_3$P (1.0)	none	benzene	60	1	69	90 : 10
7	2	0.1	^{n}Bu$_3$P (0.4)	5.0	benzene	reflux	24	n.r.[c]	
8	2	0.1	^{n}Bu$_3$P (0.4)	none	THF	reflux	24	n.r.[c]	
9	2	0.1	^{n}Bu$_3$P (1.0)	5.0	THF	reflux	21	68	90 : 10

[a] Isolated yield. [b] Determined by ^{1}H-NMR (200MHz). [c] n.r. = no reaction

(entries 1-3). In addition, the phosphine ligands also affected the stereoselectivity, and use of ^{n}Bu$_3$P in place of Ph$_3$P gave improved results (entry 4). Although the hydrogenolysis of the sulfoxide (**15b**) decreased the stereoselectivity (**5b**/**6b**=64/36) even under the optimal conditions, the same treatment of the sulfone (**15c**) gave the best stereoselectivity (total yield 69%, **5c**/**6c**=90/10) (entries 5 and 6). Two diastereomers **5c** and **6c** could be separated by HPLC. Furthermore, the Pd(0)-mediated hydrogenolysis of **15c** proceeded smoothly with a 10 mol% of Pd(acac)$_2$ without loss of the stereoselectivity, but more than one equivalent of ^{n}Bu$_3$P and large excess amount of Et$_3$N$\cdot$HCO$_2$H as a hydrogen donor were required for the clean reaction (entries 7-9). According to Tsuji's report,[7] stereocontrol of the substrates without any chiral centers at the reaction site is generally difficult. Therefore, it is interesting to find that stereoselectivity of the C2 stereogenic center in the palladium-mediated hydrogenolysis of **15a-c** exhibited a pronounced dependency on the oxidation stage of the C6-sulfur atom. The impressive stereoselectivity of these processes is believed to arise as a consequence of both the steric hindrance of the phenylsulfonyl group and the varied coordinative ability of the sulfur atom. We presumed a mechanism of the Pd(0)-mediated hydrogenolysis as shown in Fig. 2. At first, Pd(0), which has been generated from Pd(acac)$_2$ and ^{n}Bu$_3$P, approaches from the upper-left side (opposite the sulfonyl group) to the olefin of **15c** due to a steric hindrance of the sulfonyl group, forming a π-allyl complex **A**. Then, the hydride transfer through decarboxylation of a σ-allyl complex which had been generated from **A**, gave **5c** stereoselectively. On the other hand, in the cases of **15a-b**, α-side approach of the Pd(0) catalyst *via* a π-allyl complex **B** is increased due to lesser steric hindrance of the sulfide and sulfoxide moieties, leading to the moderate selectivity. Although effect of the optically active sulfoxide moiety on the stereoselectivity could not be judged from the result using a 1/1 diastereomeric mixture of **15b**, the π-allyl complex **B** (n=0, 1) might be stabilized by the coordinative interaction, since the sulfide and sulfoxide would be prone to coordinate to the Pd(0) atom.[12]

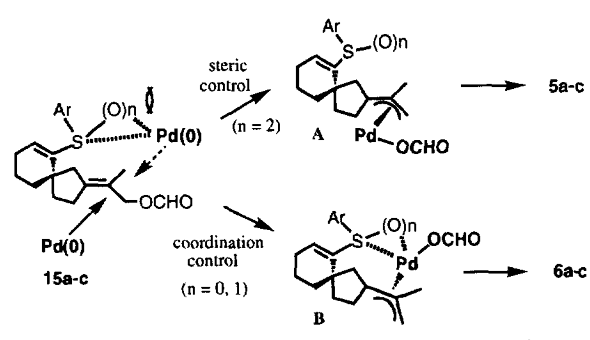
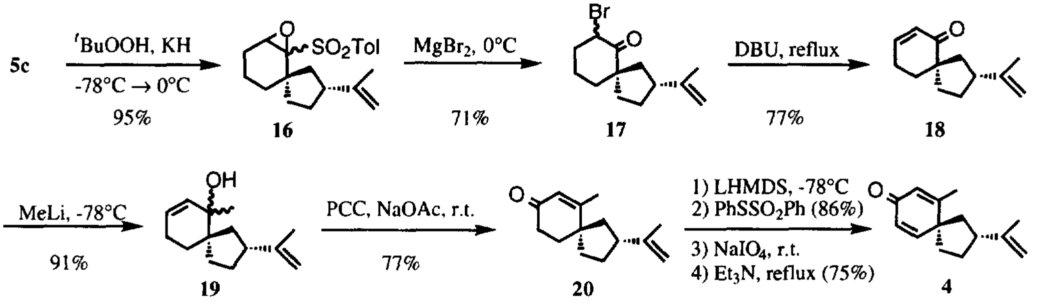


Fig. 2. Reaction process of the Pd(0)-mediated hydrogenation of **15a-c**



Scheme 4

At this stage, our efforts were focused on constructing the chiral dienone **4**. The requisite series of transformation, summarized in Scheme 4, began with the epoxidation of **5c** to epoxysulfone **16** with potassium *t*-butylperoxide and its conversion to α,β-unsaturated ketone **18** *via* bromo ketone **17**.[13] Submission of **18** to 1,2-addition of MeLi (91%) and subsequent oxidation of the resulting allylic alcohol **19** with pyridinium chlorochromate (PCC) (77%) gave the enone **20** with concomitant 1,3-migration of a ketone moiety. **20** was subjected to Trost's olefination reaction[14] to give the desired dienone **4** (86%). With arrival at the most important intermediate **4**, the stage was set for stereoselective introduction of a methyl group into C10. The structure of the dienone **4** was identified by comparing a racemic dienone **4**, which had been prepared as a C2-epimeric mixture by Torii.[4c] In addition, the stereochemical configuration of **4** was determined to be the desired 2*R*-configuration from observing a NOE (7.6%) between a proton at C2 and a proton at C10 (Fig. 3).

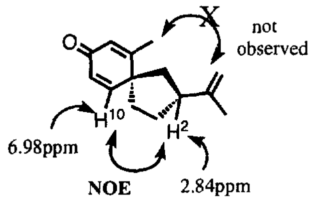
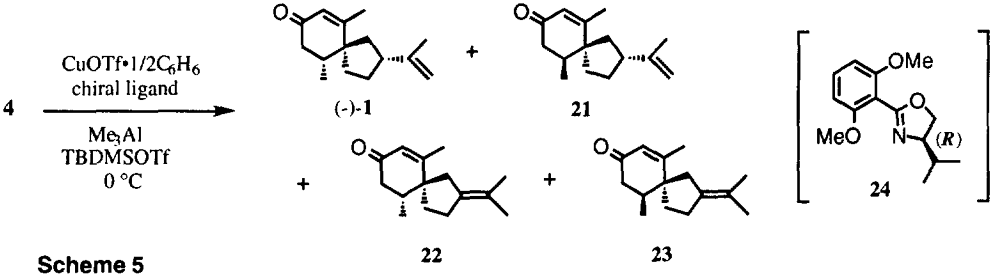


Fig. 3. The NOE experiment of **4**

Completion of the synthesis of (-)-solavetivone **1** is shown in Scheme 5. It was assumed from previous papers that the diastereoselective 1,4-addition of a methyl group to **4** bearing no stereodirecting groups is difficult.[3c,4c,15] The assumption could be also deduced from model studies of the dienone **4** (see Fig. 3). Therefore, we took advantage of the reagent-stereocontrolled reaction as the means for stereoselective introduction of a methyl group to C10. Since we recently developed an enantioselective copper-catalyzed conjugate addition of Me$_3$Al to a 2,5-cyclohexadienone in the presence of a chiral ligand **24**, application of this reaction to **4** was carried out under the optimized conditions [5mol% copper triflate•benzene complex (CuOTf·



Scheme 5

Table 3. Synthesis of **1** and **21** using the enantioselective conjugate addition

Entry	Ligand	Workup Conditions	Yield (%)^a	Products (**1** : **21** : **22** : **23**)
1	***ent*-24**	5% HCl	92	23 : 6 : 70 : trace
2	***ent*-24**	*aq*.NH$_4$Cl, then ^{n}Bu$_4$NF	93	81 : 19 : trace : trace
3	**24**	*aq*.NH$_4$Cl, then ^{n}Bu$_4$NF	93	37 : 63 : trace : trace

^{a} Isolated yield

1/2C_6H_6), 20mol% **24**, 2.0 equiv. Me_3Al, 1.2 equiv. *tert*-butyldimethylsilyl triflate (TBDMSOTf), THF, 0℃; then 5% HCl] (Table 3). Indeed, the conjugate addition proceeded smoothly and diastereoselectively, but gave rise to undesired isopropylidene products **22**/**23**[4c,16] along with small amounts of (-)-solavetivone **1** (entry 1). After many experiments, it was revealed that the strong acidic conditions in the presence of CuOTf promoted the isomerization of the isopropenyl group into the isopropylidene group.[17] Therefore, quenching the reaction mixture with a saturated aqueous NH_4Cl solution instead of 5% HCl and sequential removal of the TBDMS group with ^{n}Bu_4NF afforded the desired (-)-solavetivone **1** as a major product together with a *cis*-type spirovetivane, (-)-10-episolavetivone **21** (entry 2: total yield 93%, **1**/**21** = 81/19). These two compounds could be separated by HPLC, giving rise to enantiomerically pure (-)-solavetivone **1** in 72% yield. The synthetic sample was identical spectroscopically to an authentic sample reported previously.[2a,5] Interestingly, **1** showed the same positive Cotton effect at 300-350 nm (n-π*) in the CD spectrum as (5*S*)-3,4,4,5-tetramethyl-2-cyclohexenone previously synthesized in our laboratory (Fig. 4).[8] Since there are few methods to easily determine absolute stereochemistry of 2-cyclohexenones, the result suggests that absolute stereochemistries of 5-substituted-2-cyclohexenones like **1** could be easily deduced from their CD spectra.[18] On the other hand, by the same 1,4-addition reaction using the antipodal ligand ***ent*-24**, (-)-10-episolavetivone **21** was obtained as a major product (entry 3: **1**/**21**=37/63). Although the different stereoselectivities shown by the enantiomeric chiral ligands (**24** and **ent-24**) and mechanistic details are not clear, the asymmetric stereoselection at C10 of **4** in the diastereoselective conjugate addition is consistent with the previously reported asymmetric reaction.[8] In this way, we were able to synthesize both *trans*- and *cis*-types spirovetivanes by simply switching the chirality of the chiral ligand **24** or ***ent*-24** of the enantioselective copper-catalyzed conjugate addition, even though the latter diastereoselectivity was moderate.

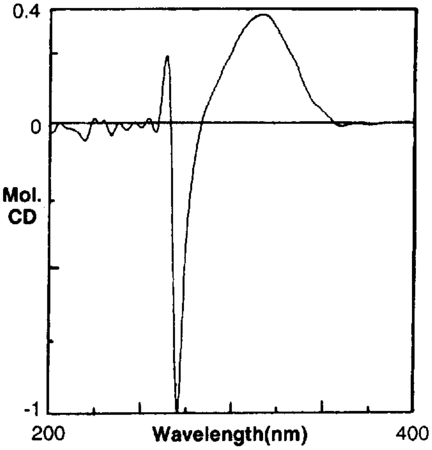


Fig. 4. CD spectrum of (-)-solavetivone 1 in 3.4mM-MeOH

In conclusion, we have established a stereoselective method for constructing all stereogenic centers involved in the spirovetivane sesquiterpenes **1**-**3** and, as an example, succeeded in the asymmetric synthesis of (-)-solavetivone with high stereoselectivity. We are sure that our synthetic approach would not only provide a useful tool for the syntheses of other natural products but also allow the stereo- and enantioselective syntheses of all types of spirovetivane sesquiterpenes, which would be very promising from the standpoint of evaluating the structure-activity relationship of the phytoalexins and identifying the defense mechanisms of plants.

Acknowledgment. We are grateful to Dr. T. Date, Mr. K. Okamura, and Mr. H. Hiramatsu (Analytical Research Laboratory, Tanabe Seiyaku Co., Ltd.) for an X-ray crystallographic structure solution of **7a** and a measurement of CD spectrum of **1**.

EXPERIMENTAL

General: Melting points are uncorrected. IR spectra were obtained using a HORIBA FT-210 and a Shimadzu IR-420 spectrometer. ^{1}H-NMR spectra were obtained using a JEOL JNM-GX-500 (500MHz), a HITACHI 250-RT (250MHz), a Varian VXR-200 (200MHz) and a Bruker AC-200 (200MHz) spectrometer. ^{13}C-NMR spectra were obtained using a JEOL JNM EX-270 (67.8MHz) and a Bruker AC-200 (50.3MHz) spectrometer. Optical rotations were measured with a JASCO DIP-360 polarimeter. Mass spectra (MS) were measured with a

Shimadzu GCMS-QP-1000 and a HITACHI M-2000A spectrometer. High resolution mass spectra (HI-MS) were measured with a JEOL JMS-D300 spectrometer. HPLC analysis were performed using a Shimadzu LC-6A. X-ray crystallographic analysis was performed using a RIGAKU AFC-5R diffractometer. Circular dichroism spectra (CD) were obtained using a JASCO J-720W spectropolarimeter. Column chromatography was carried out using Merck Kieselgel 60. All dry solvents were purchased from Kanto Chemical Co., Inc.

(+)-3-[(1*R*,6*S*)-6-(*p*-Tolylthio)bicyclo[4.1.0]heptyl]propanal (10). To a solution of oxalyl chloride (25.0 ml, 0.29 mol) in dry CH_2Cl_2 (100 ml) were successively added dry DMSO (43.0 ml, 0.61 mol) and a solution of **9**[6b] (49.5 g, 0.18 mol) in dry CH_2Cl_2 (100 ml) at -60 ℃ under a nitrogen atmosphere and the mixture was stirred for 15 min below -50 ℃. After Et_3N (165.0 ml, 1.18 mol) was added dropwise to the mixture at -50 ℃ and stirring was continued for 5 min, the resulting mixture was allowed to warm slowly up to room temperature and quenched with water. The mixture was extracted with CH_2Cl_2 and the organic layer was washed with a aqueous 10% HCl solution, water, a saturated aqueous $NaHCO_3$ solution, and brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=10/1) to give the aldehyde **10** (44.3 g, 90%) as a colorless viscous oil. $[\alpha]_D^{22}$ +75.7° (c = 1.00, $CHCl_3$). IR ($CHCl_3$): 2955, 2880, 1734 (CHO), 1509 (Ar), 1464 (Ar), 1100, 1026, 810 cm^{-1}. ^{1}H-NMR (200MHz, $CDCl_3$): δ 0.68 (d, 1H, *J* = 5.2 Hz, C7-H), 0.85 (dd, 1H, *J* = 5.2, 1.2 Hz, C7-H), 1.15-2.75 (m, 12H), 2.31 (s, 3H, Ar-Me), 7.09 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.17 (d, 2H, *J* = 8.2 Hz, Ar-H), 9.77 (t, 1H, *J* = 2.0 Hz, CHO). MS: 274 (M$^+$, 25), 230 (100), 217 (30), 123 (52). HI-MS: calcd for $C_{17}H_{22}OS$: 274.1390, found: 274.1385.

(+)-Methyl (1*R*,2*E*,6*S*)-5-[6-(*p*-Tolylthio)bicyclo[4.1.0]heptyl]-2-methylpent-2-enoate (11). To a solution of **10** (44.0 g, 0.16 mol) in dry toluene (440 ml) was added (α-carbomethoxyethylidene)-triphenylphosphorane[10] (61.7 g, 0.18 mol) and the mixture was refluxed for 30 min under a nitrogen atmosphere. After being cooled to room temperature, the mixture was filtered through a pad of celite and a solid residue was washed with toluene. The collected filtrates were concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=95/5) to give the α,β-unsaturated ester **11** (49.7 g, 90%) as a yellow viscous oil. $[\alpha]_D^{26}$ +114.7° (c = 1.00, $CHCl_3$). IR (KBr): 2929, 2908, 2850, 1713 (CO_2Me), 1651 (C=C), 1493 (Ar), 1448 (Ar), 1281, 802 cm^{-1}. ^{1}H-NMR (200MHz, $CDCl_3$): δ 0.71 (d, 1H, *J* = 5.2 Hz, C7-H), 0.86 (d, 1H, *J* = 5.2 Hz, C7-H), 1.21-2.44 (m, 12H), 1.83 (s, 3H, <u>Me</u>C=), 2.31 (s, 3H, Ar-Me), 3.71 (s, 3H, CO_2Me), 6.76 (t, 1H, *J* = 8.4 Hz, =CH), 7.08 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.17 (d, 2H, *J* = 8.2 Hz, Ar-H). MS: 344 (M$^+$, 2), 257 (2), 221 (100), 189 (36), 161 (67), 133 (58). HI-MS: calcd for $C_{21}H_{28}O_2S$: 344.1807, found: 344.1789.

(-)-(1*R*,2*E*)-[1-(4-Methoxycarbonyl-3-pentenyl)-2-*p*-tolylthio-2-cyclohexenyl]-methylmercury chloride (8). To a suspension of **11** (40.3 g, 0.12 mol) and NaOAc (11.5 g, 0.14 mol) in dry CH_2Cl_2 (403 ml) was added $Hg(II)(OCOCF_3)_2$ (75.0 g, 0.18 mol) and the resulting mixture was stirred for 21 h at room temperature under a nitrogen atmosphere. To the solution was added water and the mixture was extracted with CH_2Cl_2. The organic phase was washed with a saturated aqueous NaCl solution for 30 min, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=9/1) to give the alkylmercury chloride **8** (57.5 g, 85%) as a pale yellow viscous oil. $[\alpha]_D^{24}$ -10.4° (c = 1.03, $CHCl_3$). IR ($CHCl_3$): 2940, 1710 (CO_2Me), 1650 (C=C), 1490 (Ar), 1440 (Ar), 1245, 1130, 1040 cm^{-1}. ^{1}H-NMR (200MHz, $CDCl_3$): δ 1.50-2.30 (m, 12H), 1.85 (s, 3H, <u>Me</u>C=), 2.33 (s, 3H, Ar-Me), 3.74 (s, 3H, CO_2Me), 5.68 (t, 1H, *J* = 3.8 Hz, C3-H), 6.66 (t, 1H, *J* = 7.2 Hz, =CH), 7.15 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.33 (d, 2H, *J* = 8.2 Hz, Ar-H). MS: 580 (M$^+$, 2), 343 (31), 217 (100), 201 (17), 187 (17), 161 (18), 133 (10). HI-MS: calcd for $C_{21}H_{27}Cl^{35}Hg^{202}O_2S$: 580.1125, found: 580.1105. *Anal.* calcd for $C_{21}H_{27}ClHgO_2S$: C; 43.50, H; 4.71, found.: C; 43.37, H; 4.70.

(-)-Methyl (2*E*,5*S*)-2-[6-(*p*-tolylthio)spiro[4.5]dec-6-en-2-ylidene]propionate (7a). After a suspension of $PdCl_2$ (0.74 g, 4.2 mmol) and LiCl (0.36 g, 8.4 mmol) in dry THF (67 ml) and dry DMF (18 ml) was refluxed for 1 h under a nitrogen atmosphere (wine-red clear solution), a solution of **8** (2.21 g, 3.8 mmol) in dry THF (11 ml) was added to the whole was refluxed for 57 h. The cooled mixture was filtered through a pad of celite and a solid residue was washed with THF. The combined filtrates were concentrated *in* *vacuo* and a solution of the residue in AcOEt was washed with water. After the aqueous layer was extracted with AcOEt again, the combined organic extracts were washed with a saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=95/5) and crystallized from hexane to give the α,β-unsaturated ester **7a** (0.64 g, 49%) as colorless prisms. mp 69-70 °C. $[\alpha]_D^{29}$ -21.2°(c = 0.99, $CHCl_3$). IR (KBr): 2923, 1717 (CO_2Me), 1641 (C=C), 1494 (Ar), 1434 (Ar), 1285, 1209, 1100, 864, 814, 504 cm^{-1}. ^1H-NMR (500MHz, $CDCl_3$): δ 1.55-1.70 (m, 5H), 1.81 (s, 3H, C=C-Me), 2.12-2.19 (m, 3H), 2.27 (d, 1H, *J* = 18.0 Hz), 2.32 (s, 3H, Ar-Me), 2.68-2.76 (m, 1H), 2.84 (d, 1H, *J* = 18.0 Hz), 2.93 (dd, 1H, *J* = 19.7 Hz, 8.6), 3.70 (s, 3H, CO_2Me), 5.92 (t, 1H, *J* = 3.9 Hz), 7.08 (d, 2H, *J* = 7.7 Hz, Ar-H), 7.21 (d, 2H, *J* = 7.7 Hz, Ar-H). ^{13}C-NMR (67.8MHz, $CDCl_3$): δ 16.1 (C=C-Me), 19.2 (C9), 21.0 (Ar-Me), 27.4 (C10), 31.8 (C3), 34.6 (C8), 36.8 (C4), 45.5 (C5), 47.0 (C1), 51.0 ($CO_2\underline{Me}$), 119.2 (=$\underline{C}$- CO_2), 129.7 (Ar-Hx2), 130.1 (Ar-Hx2), 133.4 (C2), 135.9 (C7), 136.1 (Ar-Me), 138.6 (Ar-S), 159.3 (C6), 168.3 (C=O). MS: 343 (M^++1, 24), 342 (M^+, 100), 310 (24), 282 (13), 187 (13), 159 (13), 147 (10). HI-MS: calcd for $C_{21}H_{26}O_2S$: 342.1651, found: 342.1641. *Anal.* calcd for $C_{21}H_{26}O_2S$: C; 73.65, H; 7.65, S; 9.36. found.: C; 73.63, H; 7.63, S; 9.17.

X-Ray Crystallographic analysis of 7a. **7a** was recrystallized from 2-propanol and suitable crystal (0.5 x 0.3 x 0.2 mm^3) was subjected to an X-ray analysis. The crystal structure was solved by the direct method using the SHELXS-86[19] program. Full matrix least-squares refinement of positional and thermal parameters, using SHELXL-93[20], led to the final convergence with R=0.054 (Rw=0.130) for the (2*E*) relative stereochemistry: $C_{21}H_{26}O_2S$, M.W.=342.48, a=10.1928(11), b=13.6586(8), c=7.7719(8), α=93.465(7)°, β=109.798(9)°, γ=109.325(7)°, U=942.4(2)A^3, space group: P1, Z=2.

(+)-(2*E*,5*S*)-2-(1-Hydroxy-2-propylidene)-6-(*p*-tolylthio)spiro[4.5]dec-6-ene (14a). To a solution of **7a** (0.85 g, 2.5 mmol) in dry CH_2Cl_2 (17 ml) was added dropwise a 1.0 *M* solution of DIBAL-H in toluene (6.3 ml, 6.3 mmol) and the mixture was stirred at -78 °C for 1 h under a nitrogen atmosphere. After being quenched with a saturated aqueous NH_4Cl solution, the mixture was allowed to warm to room temperature and filtered through a pad of celite. A solid residue was washed with CH_2Cl_2 and the combined filtrates were washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=9/1) to give the alcohol **14a** (0.56 g, 72%) as a pale yellow viscous oil. $[\alpha]_D^{32}$ +11.0°(c = 0.90, $CHCl_3$). IR (KBr): 3375 (OH), 2939, 1490 (Ar), 1452 (Ar), 997, 804 cm^{-1}. ^1H-NMR (200MHz, $CDCl_3$): δ 1.44-2.44 (m, 13H), 1.68 (s, 3H, $\underline{Me}$C=), 2.32 (s, 3H, Ar-Me), 2.66 (d, 1H, *J* = 16.9 Hz), 4.01-4.14 (m, 2H, CH_2OH), 5.88 (t, 1H, *J* = 4.0 Hz, C7-H), 7.09 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.22 (d, 2H, *J* = 8.0 Hz, Ar-H). MS: 314 (M^+, 39), 298 (100), 268(22), 173 (27), 133 (37). HI-MS: calcd for $C_{20}H_{26}OS$: 314.1704, found: 314.1704.

(+)-(2*E*,5*S*)-2-{6-(*p*-Tolylthio)spiro[4.5]dec-6-en-2-ylidene}propyl formate (15a). To a solution of **14a** (0.35 g, 1.1 mmol) in dry pyridine (3.5 ml) was added dropwise a mixture of HCO_2H (2.5 ml) and Ac_2O (1.1 ml) at 0 °C, and the mixture was stirred at 0 °C for 1 h and then at room temperature for another 1 h under a nitrogen atmosphere. Water and AcOEt were successively added to the mixture at 0 °C and stirring was continued for 2 h. The reaction mixture was extracted with AcOEt twice and the combined extracts were washed with a aqueous 5%-$KHSO_4$ solution and brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=95/5) to give the allylic formate **15a** (0.32 g, 85%) as a colorless viscous oil. $[\alpha]_D^{30}$ +4.4°(c = 1.00, $CHCl_3$). IR (KBr): 2935, 1724 (OCHO), 1490 (Ar), 1448 (Ar), 1165 (SO_2), 806 cm^{-1}. ^1H-NMR (200MHz, $CDCl_3$): δ 1.46-2.73 (m, 12H), 1.65 (s, 3H, $\underline{Me}$C=), 2.31 (s, 3H, Ar-Me), 4.62 (br s, 2H, $C\underline{H_2}OCHO$), 5.89 (t, 1H, *J* = 4.0 Hz, C7-H), 7.08 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.22 (d, 2H, *J* = 8.1 Hz, Ar-H), 8.10 (s, 1H, CHO). MS: 343 (M^++1, 25), 342 (M^+, 100), 298 (98), 268 (25), 173 (36). HI-MS: calcd for $C_{21}H_{26}O_2S$: 342.1651, found: 342.1649.

(+)-(2*E*,5*S*)-2-[6-(*p*-Tolylsulfinyl)spiro[4.5]dec-6-en-2-ylidene]propyl formate (15b). To a solution of **15a** (0.13 g, 0.38 mmol) in dry CH_2Cl_2 (5 ml) was added slowly *m*-CPBA (80% ; 0.10 g, 0.46 mmol) at 0 °C and the mixture was stirred for 30 min under a nitrogen atmosphere. After being quenched with a saturated aqueous $Na_2S_2O_3$ solution, the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, a saturated aqueous $NaHCO_3$ solution, and brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=3/1) to give the allylic formate **15b** (0.10 g, 73%) as a pale yellow viscous oil. $[\alpha]_D^{26}$ +13.8° (c = 0.99, CHCl$_3$). IR (KBr): 2935, 1722 (OCHO), 1452 (Ar), 1166 (SO$_2$), 1043, 811, 624 cm^{-1}. ^{1}H-NMR (200MHz, CDCl$_3$): δ 1.19-2.81 (m, 12H), 1.62 (s, 3H, $\underline{Me}$C=), 2.40 (s, 3H, Ar-Me), 4.57-4.62 (m, 2H, C$\underline{H}_2$OCHO), 6.72-6.79 (m, 1H, C7-H), 7.27 (d, 2H, *J* = 7.9 Hz, Ar-H), 7.48-7.55 (m, 2H, Ar-H), 8.090, 8.095 (s, total 1H, CHO). MS: 358 (M$^+$, 6), 342 (20), 312 (100), 295 (47), 189 (22), 173 (46), 131 (28), 105 (24). HI-MS: calcd for C$_{21}$H$_{26}$O$_3$S: 358.1602, found: 358.1597.

(-)-Methyl (2*E*,5*S*)-2-[(-6-(*p*-tolylsulfonyl)spiro[4.5]dec-6-en-2-ylidene]propionate (7c). To a solution of **7a** (15.5 g, 45.3 mmol) in dry CH$_2$Cl$_2$ (465 ml) was added slowly *m*-CPBA (80% ; 24.5 g, 113.3 mmol) at 0 °C and the mixture was stirred for 15 min under a nitrogen atmosphere. After being quenched with a saturated aqueous Na$_2$S$_2$O$_3$ solution, the mixture was extracted with CH$_2$Cl$_2$. The organic layer was washed with water, a saturated aqueous NaHCO$_3$ solution, and brine, dried over anhydrous MgSO$_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=8/2) to give the sulfone **7c** (16.4 g, 97%) as a yellow viscous oil. $[\alpha]_D^{26}$ -24.9°(c = 1.04, CHCl$_3$). IR (KBr): 2850, 1736 (CO$_2$Me), 1622, 1597 (C=C), 1454 (Ar), 1286, 1146 (SO$_2$) cm^{-1}. ^{1}H-NMR (200MHz, CDCl$_3$): δ 1.14-3.21 (m, 12H), 1.79 (s, 3H, $\underline{Me}$C=), 2.43 (s, 3H, Ar-Me), 3.69 (s, 3H, CO$_2$Me), 7.13 (t, 1H, *J* = 3.8 Hz, C7-H), 7.28-7.32 (m, 2H, Ar-H), 7.69-7.73 (m, 2H, Ar-H). MS: 374 (M$^+$, 11), 341 (46), 314 (100), 235 (25), 221 (21), 159 (43). HI-MS: calcd for C$_{21}$H$_{26}$O$_4$S: 374.1549, found: 374.1544.

(-)-(2*E*,5*S*)-2-(1-Hydroxy-2-propylidene)-6-(*p*-tolylsulfonyl)spiro[4.5]dec-6-ene (14c). To a solution of **7c** (0.90 g, 2.4 mmol) in dry CH$_2$Cl$_2$ (18 ml), was added dropwise a 1.0 *M* solution of DIBAL-H in toluene (6.0 ml, 6.0 mmol) and the mixture was stirred at -78 °C for 1 h under a nitrogen atmosphere. After being quenched with a saturated aqueous NH$_4$Cl solution, the mixture was allowed to warm to room temperature, and filtered through a pad of celite. A solid residue was washed with CH$_2$Cl$_2$ and the combined filtrates were washed with brine, dried over anhydrous MgSO$_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=6/4) to give the alcohol **14c** (0.71 g, 85%) as a colorless viscous oil. $[\alpha]_D^{25}$ -0.8°(c = 1.25, CHCl$_3$). IR (KBr): 3502 (OH), 2937, 1452 (Ar), 1286, 1143 (SO$_2$) 1088, 673 cm^{-1}. ^{1}H-NMR (200MHz, CDCl$_3$): δ 1.26-1.68 (m, 7H), 1.64 (s, 3H, $\underline{Me}$C=), 2.08 (d, 1H, *J* = 15.5), 2.27-2.41 (m, 4H), 2.43 (s, 3H, Ar-Me), 2.96 (br d, 1H, *J* = 16.5 Hz), 3.99-4.12 (m, 2H, C$\underline{H}_2$OH), 7.10 (t, 1H, *J* = 3.8 Hz, C7-H), 7.30 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.71 (d, 2H, *J* = 8.0 Hz, Ar-H). MS: 346 (M$^+$, 0.1), 328 (100), 249 (48), 221 (35), 172 (74), 157 (88). HI-MS: calcd for C$_{21}$H$_{26}$O$_3$S: 346.1600, found: 346.1598.

(-)-(2*E*,5*S*)-2-[6-(*p*-Tolylsulfonyl)spiro[4.5]dec-6-en-2-ylidene]propyl formate (15c). To a solution of **14c** (8.6 g, 24.8 mmol) in dry pyridine (86 ml) was added dropwise a mixture of HCO$_2$H (60 ml) and Ac$_2$O (26 ml) at 0 °C and the mixture was stirred at 0 °C for 3 h and then at room temperature for 2 h under a nitrogen atmosphere. After water and AcOEt were successively added to the mixture at 0 °C and the whole was stirred for 2 h, the mixture was extract with AcOEt twice. The combined extracts were washed with a aqueous 5%-KHSO$_4$ solution and brine, dried over anhydrous MgSO$_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=8/2) to give the allylic formate **15c** (8.1 g, 87%) as a colorless viscous oil. $[\alpha]_D^{30}$ -8.3°(c = 1.00, CHCl$_3$). IR (KBr): 2862, 1720 (OCHO), 1620, 1597, 1454 (Ar), 1286, 1144 (SO$_2$) cm^{-1}. ^{1}H-NMR (200MHz, CDCl$_3$): δ 1.29-1.70 (m, 6H), 1.61 (s, 3H, $\underline{Me}$C=), 2.11 (d, 1H, *J* = 17.0 Hz), 2.27-2.46 (m, 4H), 2.43 (s, 3H, Ar-Me), 3.00 (d, 1H, *J* = 17.0 Hz), 4.53-4.67 (m, 2H, C$\underline{H}_2$OH), 7.10 (t, 1H, *J* = 3.8 Hz, C7-H), 7.30 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.71 (d, 2H, *J* = 8.4 Hz, Ar-H), 8.09 (s, 1H, CHO). MS: 374 (M$^+$, 0.1), 329 (100), 250 (50), 222 (34), 173 (56), 158 (75). HI-MS: calcd for C$_{21}$H$_{26}$O$_4$S: 374.1550, found: 374.1548.

(-)-(5*S*)-2-Isopropenyl-6-(*p*-tolylthio)spiro[4.5]dec-6-ene (5a and 6a). To a solution of Pd(acac)$_2$ (12 mg, 0.039 mmol) and ^{n}Bu$_3$P (0.01 ml, 0.040 mmol) in dry benzene (5 ml) was added a solution of **15a** (13 mg, 0.038 mmol) in dry benzene (1 ml), and the mixture was stirred at room temperature for 16 h under a nitrogen atmosphere. The mixture was concentrated *in vacuo* and purified by column chromatography (hexane/AcOEt=8/1) to give the mixture of **5a** and **6a** (8 mg, 76%) as a yellow solid [**5a**/**6a** = 79/21 by ^{1}H-NMR (500MHz)]. mp 34-37 °C. $[\alpha]_D^{27}$ -5.9°(c = 1.00, CHCl$_3$). IR (KBr): 2927, 2856, 1734 (CO$_2$Me), 1645

(C=C), 1491 (Ar), 1454 (Ar) cm^{-1}. ^{1}H-NMR (500MHz, CDCl$_3$): δ 1.21-2.80 (m, 13H), 1.71 and 1.72* (s, total 3H, <u>Me</u>C=), 2.31 and 2.32* (s, total 3H, Ar-Me), 4.66 (s, 1H, =CH$_2$), 4.69 and 4.71* (s, total 1H, =CH$_2$), 5.62 and 5.70* (t, total 1H, J = 3.8 Hz, C7-H), 7.05-7.10 (m, 2H, Ar-H), 7.25-7.28 (m, 2H, Ar-H) [* indicates major product.]. MS: 299 (M$^+$+1, 24),298 (M$^+$, 100), 175 (35), 174 (37), 119 (32). HI-MS: calcd for $C_{20}H_{26}S$: 298.1753, found: 298.1753.

(+)-(5*S*)-2-Isopropenyl-6-(*p*-tolylsulfinyl)spiro[4.5]dec-6-ene (5b and 6b). To a solution of Pd(acac)$_2$ (34 mg, 0.11 mmol) and ^{n}Bu$_3$P (0.03 ml, 0.11 mmol) in dry benzene (5 ml) was added a solution of **15b** (39 mg, 0.11 mmol) in dry benzene (1 ml), and the mixture was stirred at room temperature for 72 h under a nitrogen atmosphere. The mixture was concentrated *in vacuo* and purified by column chromatography (hexane/AcOEt=3/1) to give the mixture of **5b** and **6b** (28 mg, 82%) as a yellow viscous oils [**5b**/**6b** = 64/36 by ^{1}H-NMR (200MHz)]. $[\alpha]_D^{27}$ +1.8° (c = 1.15, CHCl$_3$). IR (KBr): 2933, 2862, 1716, 1643 (C=C), 1595, 1493 (Ar), 1452 (Ar) cm^{-1}. ^{1}H-NMR (200MHz, CDCl$_3$): δ 1.18-2.42 (m, 13H), 1.58 and 1.70* (s, total 3H, <u>Me</u>C=), 2.40 (s, 3H, Ar-Me), 4.51 and 4.59* (br s, total 1H, =CH$_2$), 4.68 (s, 1H, =CH$_2$), 6.67 and 6.72* (t, total 1H, J = 3.9 Hz, C7-H), 7.24-7.29 (m, 2H, Ar-H) , 7.52-7.58 (m, 2H, Ar-H) [* indicates a major product]. MS: 314 (M$^+$, 11), 297 (100), 175 (34), 133 (15). HI-MS: calcd for $C_{20}H_{26}O_2S$: 314.1703, found: 314.1703.

(+)-(2*R*,5*S*)-2-Isopropenyl-6-(*p*-tolylsulfonyl)spiro[4.5]dec-6-ene (5c) and (+)-(2*S*,5*S*)-2-Isopropenyl-6-(*p*-tolylsulfonyl)spiro[4.5]dec-6-ene (6c). Method A (stoichiometrically): To a solution of Pd(acac)$_2$ (120 mg, 0.39 mmol) and ^{n}Bu$_3$P (0.10 ml, 0.39 mmol) in dry benzene (5 ml) was added a solution of **15c** (145 mg, 0.11 mmol) in dry benzene (1 ml), and the mixture was stirred at 60 °C for 1 h under a nitrogen atmosphere. After concentration *in vacuo*, the residue was purified by column chromatography (hexane/AcOEt=8/2) to give the mixture of **5c** and **6c** (89 mg, 69%) as a yellow viscous oils [**5c**/**6c** = 90/10 by ^{1}H-NMR (200MHz)]. Method B (catalytically): To a solution of Pd(acac)$_2$ (7.6 mg, 0.025 mmol) in dry THF (1 ml) was added ^{n}Bu$_3$P (60 μl, 0.25 mmol) and the mixture was stirred for 1 h at room temperature under a nitrogen atmosphere (yellow clear solution). A solution of **15c** (92 mg, 0.25 mmol) in dry THF (1 ml) and a 0.68 *M* solution of $Et_3N \cdot HCO_2H$ in THF (1.8 ml, 1.25 mmol) were successively added to the mixture, and the whole was refluxed for 21 h. After concentration *in vacuo*, a mixture of the residue and AcOEt was washed with a saturated aqueous NaHCO$_3$ solution and brine. The organic layer was.dried over anhydrous MgSO$_4$ and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=8/2) to give the mixture of **5c** and **6c** as a yellow viscous oil [**5c**/**6c** = 90/10 by ^{1}H-NMR (200MHz)]. Two compounds were separated by HPLC to give **5c** (56 mg, 68%) as a colorless viscous oil. [HPLC separation conditions : TOSOH SILICA-60, hexane/AcOEt = 100/1, flow rate 0.5 ml/min, column temp. 40 °C, t_R ; **5c** (2*S*) 15.1 min, **6c** (2*R*) 16.4 min]. **5c**: $[\alpha]_D^{25}$ +3.0° (c = 0.87, CHCl$_3$). IR (KBr): 2934, 1643 (C=C), 1597, 1497 (Ar), 1454 (Ar) cm^{-1}. ^{1}H-NMR (500MHz, CDCl$_3$): δ 1.32-1.44 (m, 2H), 1.51-1.62 (m, 2H), 1.62-1.68 (m, 2H), 1.71 (s, 3H, <u>Me</u>C=), 1.72-1.80 (m, 2H), 2.23-2.34 (m, 4H), 2.42 (s, 3H, Ar-Me), 2.54-2.62 (m, 1H), 4.66 (s, 2H, =CH$_2$), 7.03 (t, 1H, J = 3.7 Hz, C7-H), 7.31 (d, 2H, J = 7.9 Hz, Ar-H), 7.72 (d, 2H, J = 7.9 Hz, Ar-H). ^{13}C-NMR (50.3MHz, CDCl$_3$): δ 13.8 (C=C-Me), 18.0 (C9), 21.5 (Ar-Me), 26.2 (C8), 30.0 (C3), 35.9 (C4), 37.3 (C10), 42.2 (C1), 44.8 (C5), 45.3 (C2), 108.9 (=CH$_2$), 127.3 (Arx2), 129.6 (Arx2), 140.1 (Ar-Me), 141.8 (C7), 143.4 (quaternary carbon), 146.5 (quaternary carbon), 147.9 (quaternary carbon) [quaternary carbon=C6, Ar-SO$_2$, Me<u>C</u>=]. MS: 330 (M$^+$, 3), 329 (17), 250 (8), 176 (100), 131 (27). HI-MS: calcd for $C_{21}H_{26}O_2S$: 330.1654, found: 330.1660. **6c**: $[\alpha]_D^{25}$ +1.1° (c=0.81, CHCl$_3$). IR (KBr): 2934, 1643 (C=C), 1597, 1495 (Ar), 1454 (Ar), 1144, 1088 cm^{-1}. ^{1}H-NMR (200MHz, CDCl$_3$): δ 1.16-2.94 (m, 13H), 1.68 (s, 3H, <u>Me</u>C=), 2.43 (s, 3H, Ar-Me), 4.66 (br s, 2H, =CH$_2$), 6.94 (t, 3H, J = 3.9 Hz, C7-H), 7.30 (d, 2H, J = 8.0 Hz, Ar-H), 7.74 (d, 2H, J = 8.0 Hz, Ar-H). MS: 331 (M$^+$+1, 21), 330 (M$^+$, 100), 249 (20), 175 (62), 159 (22), 131 (47), 105 (20).

(2*R*,5*S*)-2-Isopropenyl-6-(*p*-tolylsulfonyl)-6,7-epoxyspiro[4.5]decane (16). To a suspension of KH (30% in oil; 7.3 g, 54.5 mmol) in dry THF (72 ml) a 2.0 M solution of ^{t}BuOOH in hexane (8.2 ml, 16.4 mmol) was added dropwise at -78 °C under a nitrogen atmosphere. After 20 min, a solution of **5c** (3.6 g, 10.9 mmol) in dry THF (36 ml) was added to the mixture and the whole was stirred for 1 h. The mixture was allowed to warm slowly up to -15 ℃, and stirring was continued for 15 min at this temperature, and then 0 ℃ for 1h. After being quenched with a saturated aqueous $Na_2S_2O_3$ solution, the mixture was extracted with Et_2O. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. to give the epoxy **16** (3.6 g, 95%) as a colorless viscous oil. IR (KBr): 2924, 1645 (C=C), 1597, 1495 (Ar), 1456, 1315, 1301, 1146 (SO_2), 1088, 885 (C=C), 816 (epoxy) cm^{-1}. ^{1}H-NMR (500MHz, $CDCl_3$): δ 1.2-3.07 (m, 13H), 1.70 and 1.77 (s, total 3H, $\underline{\text{Me}}$C=), 2.436 and 2.443 (s, total 3H, Ar-Me), 3.28 and 3.33 (t, total 1H, J = 2.4 Hz, C7-H), 4.67-4.78 (m, 2H, =CH_2), 7.32 (d, 2H, J = 7.9 Hz, Ar-H), 7.80 (d, 2H, J = 7.9 Hz, Ar-H). MS: 346 (M^+, 0.4), 249 (9), 175 (53), 81 (100). HI-MS: calcd for $C_{20}H_{26}O_3S$: 346.1603, found: 346.1611.

(2*R*,5*S*)-7-Bromo-2-isopropenylspiro[4.5]decan-6-one (17). To a suspension of Mg (40.0 mg, 1.7 mmol) in dry Et_2O (5 ml) was added dropwise 1,2-$BrCH_2CH_2Br$ (0.13 ml, 1.5 mmol) at 0 ℃, and the mixture was stirred at 0 ℃ for 30 min and then for another 30 min at room temperature. To this were successively added 1,1,2-trimethylethene (10.7 ml, 2.3 mmol) and a solution of **16** (78.7 mg, 0.23 mmol) in dry Et_2O (3 ml) at 0 ℃, and the whole was stirred for 1 h. After being quenched with a saturated aqueous NH_4Cl solution, the mixture was extracted with Et_2O. The extract was washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=95/5) to give the bromo ketone **17** (43.3 mg, 71%) as a colorless viscous oil. IR (KBr): 2935, 2866, 1722 (C=O), 1645 (C=C), 1444 (Ar), 887 (C=C), 563 (C-Br) cm^{-1}. ^{1}H-NMR (500MHz, $CDCl_3$): δ 1.25-2.17 (m, 10H), 1.70 and 1.73 (s, total 3H, $\underline{\text{Me}}$C=), 2.41 and 2.69 (t and ddd, total 1H, J = 12.8 Hz, and J = 2.6, 8.6, 12.8 Hz), 2.51-2.58 (m, 2H), 4.70 (br s, 2H, =CH_2), 4.75 and 4.80 (dd, total 1H, J = 6.0, 12.0 Hz and J = 6.0, 11.1 Hz, CHBr). MS: 272 (M^+ for Br^{81}, 1), 270 (M^+ for Br^{79}, 1), 191 (100), 173 (27), 111 (47), 107 (53). HI-MS: calcd for $C_{13}H_{19}Br^{79}$: 270.0620, found: 270.0620 and calcd for $C_{13}H_{19}Br^{81}$: 272.0600, found: 272.0600.

(-)-(2*R*,5*R*)-2-Isopropenyspiro[4.5]dec-7-en-6-one (18). A mixture of **17** (75.0 mg, 0.28 mmol), DBU (0.06 ml, 0.39 mmol), and dry toluene (4 ml) was refluxed for 3.5 h under a nitrogen atmosphere. Water was added to the cooled mixture and the resulting mixture was extracted with AcOEt. The extract was washed with brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=8/2) to give the enone **18** (41.0 mg, 77%) as a colorless viscous oil. $[\alpha]_D^{22}$ -7.3°(c = 0.68, $CHCl_3$). IR (KBr): 2935, 1672 (C=O), 1645 (C=C), 1444 (Ar), 1387, 1219, 887 (C=C) cm^{-1}. ^{1}H-NMR (500MHz, $CDCl_3$): δ 1.48 (ddd, 1H, J = 6.8, 10.3, 12.8 Hz), 1.56-2.00 (m, 7H), 1.74 (s, 3H, MeC=), 2.11 (ddd, 1H, J = 2.6, 7.7, 12.0 Hz), 2.36-2.39 (m, 2H), 4.70 (s, 1H, =CH_2), 4.75 (s, 1H, =CH_2), 5.96 (dt, 1H, J = 10.3, 2.3 Hz, C7-H), 6.86 (dt, 1H, J = 10.3, 4.2 Hz, C8-H). ^{13}C-NMR (67.8MHz, $CDCl_3$): δ 20.8 (C=C$\underline{\text{Me}}$), 23.8 (C10), 30.9 (C3), 34.8 (C4), 34.8 (C9), 38.2 (C1), 46.6 (C2), 51.9 (C5), 109.0 (=CH_2), 128.8 (C7), 127.7 (C9), 147.5 ($\underline{\text{C}}$Me=CH_2), 18.7 (C8), 203.5 (C6). MS: 190 (M^+, 49), 147 (44), 122 (42), 109 (100). HI-MS: calcd for $C_{13}H_{18}O$: 190.1355, found: 190.1340.

(2*R*,5*R*)-2-Isopropeny-6-methylspiro[4.5]dec-7-en-6-ol (19). To a solution of **18** (0.55 g, 2.9 mmol) in dry Et_2O (22 ml) was added dropwise a 1.0 *M* solution of MeLi in Et_2O (5.8 ml, 5.8 mmol) at -78 ℃ under a nitrogen atmosphere and the mixture was stirred for 30 min. After being quenched with a saturated aqueous NH_4Cl solution, the mixture was allowed to warm up to room temperature and extracted with Et_2O. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=97/3) to give the 1,2-adduct **19** (0.54 g, 91%) as a colorless viscous oil. IR (KBr): 3456 (OH), 2935, 1705, 1645 (C=C), 1452 (Ar), 1434, 1373, 1122, 1082, 885 (C=C) cm^{-1}. ^{1}H-NMR (250MHz, $CDCl_3$): δ 1.14-2.12 (m, 11H), 1.24 (s, 3H, C6-Me), 1.75 (s, 3H, $\underline{\text{Me}}$C=), 2.45-2.51 (m, 1H), 4.69 (s, 1H, =CH_2), 4.74 (s, 1H, =CH_2), 5.57-5.69 (m, 2H, C7 and C8-H). MS: 206 (M^+, 5), 191 (9), 188 (7), 173 (6), 123 (89), 84 (100). HI-MS: calcd for $C_{14}H_{22}O$: 206.1670, found: 206.1670.

(-)-(2*R*,5*R*)-2-Isopropeny-6-methylspiro[4.5]dec-6-en-8-one (20). To a suspension of PCC (0.79 g, 3.7 mmol) and NaOAc (0.20 g, 2.4 mmol) in dry CH_2Cl_2 (15 ml) was added a solution of **19** (0.50 g, 2.9 mmol) in dry CH_2Cl_2 (15 ml) and the mixture was stirred at room temperature for 2 h. After the mixture was filtered through a pad of celite and a solid residue was washed with CH_2Cl_2, the combined filtrates were washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=9/1) to give the methyl enone **20** (0.36 g, 77%) as a colorless viscous oil. $[\alpha]_D^{25}$ -86.2°(c = 0.59, $CHCl_3$). IR (KBr): 2947, 1674 (C=O), 1614 (C=C), 1446 (Ar), 1377, 887 (C=C) cm^{-1}. ^1H-NMR (250MHz, $CDCl_3$): δ 1.56-2.06 (m, 8H), 1.77 (s, 3H, <u>Me</u>C=), 1.95 (s, 3H, C6-Me), 2.41-2.45 (m, 2H), 2.60-2.69 (m, 1H), 4.75 (s, 2H, $=CH_2$), 5.80 (s, 1H, C7-H). MS: 204 (M^+, 62), 189 (42), 176 (51), 162 (51), 148 (92), 123 (100). HI-MS: calcd for $C_{14}H_{20}O$: 204.1514, found: 204.1504.

(+)-(2*R*,5*S*)-2-Isopropeny-6-methylspiro[4.5]deca-6,9-dien-8-one (4). To a solution of **20** (200 mg, 1.0 mmol) in dry THF (10 ml) was added dropwise a 1.0 *M* solution of lithium bis(trimethylsilyl)amide (LHMDS) in hexane (2.0 ml, 2.0 mmol), and the mixture was stirred at -78 °C for 30 min under a nitrogen atmosphere. Then to the solution was added a solution of $PhSSO_2Ph$ (491 mg, 2.0 mmol) in dry THF (3 ml) at 0 °C and the whole was stirred for 1 h. After being quenched with a saturated aqueous NH_4Cl solution, the resulting mixture was allowed to warm to room temperature and extracted with Et_2O. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=9/1) to give the sulfide (264 mg, 86%) as a colorless viscous oil. IR (KBr): 3062, 2868, 1672 (C=O), 1473 (Ar), 1441, 1327, 1146 cm^{-1}. ^1H-NMR (200MHz, $CDCl_3$): δ 1.00-2.80 (m, 9H), 1.74 (s, 3H, <u>Me</u>C=), 1.95 (br s, 3H, C6-Me), 3.93-4.05 (m, 1H, C9-H), 4.73 (br s, 2H, $=CH_2$), 5.87-5.88 (m, 1H, C7-H), 7.24-7.48 (m, 5H, Ar-H). MS: 312 (M^+, 65), 176 (100), 109 (49). To a solution of the above sulfide (85 mg, 0.27 mmol) in MeOH (8.5 ml) was added a solution of $NaIO_4$ (173 mg, 0.81 mmol) in water (2 ml) at room temperature and the mixture was stirred for 24 h. After concentration *in vacuo*, water was added to the residue and the resulting mixture was extracted with Et_2O. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo* to give the sulfoxide (115 mg) as a colorless viscous oil. ^1H-NMR (200MHz, $CDCl_3$): δ 1.26-2.90 (m, 9H), 3.41-3.51 (m, 1H, C9-H), 4.64-4.78 (m, 2H, $=CH_2$), 5.92-5.94 and 6.11-6.15 (m, total 1H, C7-H), 7.26-7.72 (m, 5H, Ar-H). MS: 329 (M^++1, 100), 203 (53), 147 (61), 121 (29). A mixture of the crude sulfoxide, Et_3N (0.04 ml, 0.3 mmol), and CCl_4 (8.5 ml) was refluxed for 1.5 h. After concentration *in vacuo*, an ethereal solution of the residue was washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=9/1) to give the dienone **4** (41 mg, 75%) as a colorless viscous oil. $[\alpha]_D^{23}$ +2.2°(c = 0.33, $CHCl_3$). IR (KBr): 2924, 1732, 1664 (C=O), 1625 (C=C), 1603, 1454, 881 (C=C) cm^{-1}. ^1H-NMR (500MHz, $CDCl_3$): δ 1.78 (s, 3H, <u>Me</u>C=), 1.75-1.85 (m, 3H), 1.92 (m, 1H), 1.96-2.04 (m, 1H), 2.02 (s, 3H, C6-Me), 2.12 (m, 1H), 2.84 (m, 1H, C2-H), 4.78 (s, 2H, $=CH_2$), 6.11-6.14 (m, 2H, C7 and C9-H), 6.98 (d, 1H, *J* = 9.4 Hz, C10-H). ^{13}C-NMR (50.3MHz, $CDCl_3$): δ 19.7 (<u>Me</u>C=), 21.3 (C10-Me), 32.2 (C3), 35.9 (C4), 41.9 (C1), 46.9 (C2), 50.1 (C5), 109.7 ($=CH_2$), 124.7 (C7), 127.7 (C9), 146.4 (<u>C</u>Me=CH_2), 155.9 (C10), 163.0 (C6), 186.4 (C=O). MS: 202 (M^+, 28), 187 (29), 174 (29), 159 (60), 146 (70), 121 (100). HI-MS: calcd for $C_{14}H_{18}O$: 202.1358, found: 202.1358.

(-)-Solavetivone (1). A solution of CuOTf•1/2C_6H_6 complex (2.1 mg, 10.0 μ mol) and ligand **24**[8] (10.0 mg, 0.04 mmol) in dry THF (8 ml) was stirred at room temperature for 30 min (pale greenish yellow clear solution). After a solution of **4** (40.0 mg, 0.15 mmol) in THF (2 ml) was added to the mixture, a 1.0 *M* solution of Me_3Al in hexane (0.40 ml, 0.40 mmol) and TBDMSOTf (0.05 ml, 0.24 mmol) were successively added to the reaction mixture at 0 °C and the whole was stirred at the same temperature for 1 h. Then the mixture was quenched with a saturated NH_4Cl solution (10 ml) at 0 °C and extracted with AcOEt. The organic layer was washed with a saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. To a solution of the residue in THF (10 ml) was added a 1.0 *M* solution of Bu_4NF in THF (0.2 ml, 0.20 mmol) and then the mixture was stirred for 30 min at room temperature. Water was added to the mixture and then the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane/AcOEt=9/1) to give the mixture of **1** and **21** (40.2 mg, 93%) as a colorless oil (**1**/**21** = 81/19 by HPLC). The diastereomers (30.0 mg) were purified by HPLC to give **1** (21.7 mg, 72%) and **21** (2.9 mg, 9%) as a colorless oil. [HPLC separation conditions: TOSOH SILICA-60, hexane/AcOEt = 100/4, flow rate 1.0 ml/min, column temp. 40 °C, t_R; **1** 26.5 min, **21** 31.6 min]. **1**; (>99% by HPLC); colorless oil. $[\alpha]_D^{24}$ -121.6°

(c = 0.63, EtOH). [for synthetic 1[5]; $[\alpha]_D^{25}$ -135.0° (c = 0.23, EtOH). for authentic 1[2a], $[\alpha]_D$ -119.0° (concentration and temperature were not given, EtOH)]. IR (KBr): 3080, 2960, 2877, 1670 (C=O), 1614 (C=C), 1454 (Ar), 1344, 1238, 889 cm^{-1}. CD (3.4 mM, MeOH): $\Delta\ \varepsilon$ = +0.38 (316 nm), -1.00 (270 nm), +0.24 (263 nm). ^1H-NMR (500MHz, $CDCl_3$): δ 0.99 (d, 3H, J = 6.8 Hz, C10-Me), 1.55-1.72 (m, 3H), 1.76 (s, 3H, <u>Me</u>C=), 1.91-1.95 (m, 2H), 1.95 (s, 3H, C6-Me), 2.07-2.16 (m, 2H), 2.21 (dd, 1H, J = 17.1, 4.3, C9-H), 2.52-2.59 (m, 1H, C2-H), 2.66 (dd, 1H, J = 17.1, 5.0 Hz, C9-H), 4.74 (br d, 2H, J = 4.3 Hz, $=CH_2$), 5.75 (s, 1H, C7-H). MS: 219 (M^++1, 22), 218 (M^+, 100), 203 (40), 190 (80), 176 (82), 161 (65), 147 (67), 137 (70), 120 (57), 108 (90). HI-MS: calcd for $C_{15}H_{22}O$: 218.1671, found: 218.1654. **21**; (88% by HPLC); colorless oil. $[\alpha]_D^{22}$ -107.6°(c = 0.15, EtOH). IR (KBr): 2956, 2887, 1672 (C=O), 1614 (C=C), 1454 (Ar), 1378, 1288, 1184, 887 cm^{-1}. ^1H-NMR (500MHz, $CDCl_3$): δ 1.04 (d, 3H, J = 6.5 Hz, C10-Me), 1.40-1.65 (m, 3H), 1.76 (s, 3H, <u>Me</u>C=), 1.81-1.91 (m, 1H), 1.96-2.03 (m, 2H), 1.97 (s, 3H, C6-Me), 2.09-2.13 (m, 1H), 2.23 (dd, 1H, J=16.5, 10.5 Hz, C9-H), 2.42 (dd, 1H, J = 16.5, 4.0 Hz, C9-H), 2.53-2.58 (m, 1H, C2-H), 4.74 (s, 2H, $=CH_2$), 5.76 (s, 1H, C7-H). MS: 219 (M^++1, 15), 218 (M^+, 77), 203 (49), 190 (69), 175 (100), 161 (64), 147 (86), 137 (56), 120 (81), 108 (81).

(-)-10-*Epi*solavetivone (21). A mixture of **21** and **1** was prepared in 93% yield from $CuOTf\bullet 1/2C_6H_6$ complex (0.6 mg, 2.5 μ mol), ***ent*-24**[8] (2.5 mg, 0.01 mmol), **4** (10.0 mg, 0.05 mmol), a 1.0 M solution of Me_3Al in hexane (0.10 ml, 0.10 mmol), and TBDMSOTf (0.01 ml, 0.06 mmol) according to the standard procedure described for (-)-solavetivone [**21**/**1** = 63/37 by HPLC].

10-Epi-β-vetivone (22). 10-Epi-β-vetivone **22** was prepared in 92% yield as a mixture of (-)-solavetivone **1**, 10-episolavetivone **21**, and β-vetivone **23** [**22**/**23**/**1**/**24** = 70/1/23/6 by HPLC, HPLC separation conditions: TOSOH SILICA-60, hexane/AcOEt = 100/4, flow rate 1.0 ml/min, column temp. 40 ℃, t_R; **22** 22.6 min, **23** 25.1 min]. from $CuOTf\bullet 1/2C_6H_6$ complex (0.6 mg, 2.5 μ mol), **24**[8] (2.5 mg, 0.01 mmol), **4** (10.0 mg, 0.05 mmol), a 1.0 M solution of Me_3Al in hexane (0.10 ml, 0.10 mmol), and TBDMSOTf (0.01 ml, 0.06 mmol) according to the standard procedure described for (-)-solavetivone except for the quenching with a aqueous 5% HCl solution (10 ml) in place of a saturated NH_4Cl solution. **22**; (70% by HPLC); colorless oil. ^1H-NMR (200MHz, $CDCl_3$): δ 0.98 (d, 3H, J = 6.9 Hz, C10-Me), 1.63-1.67 (m, 3Hx2, $=Me_2$), 1.91 (d, 3H, J = 1.3 Hz, C6-Me), 1.76-2.71 (m, 9H), 5.80 (s, 1H, C7-H). MS: 219 (M^++1, 15), 218 (M^+, 100), 203 (15), 175 (50), 133 (70).

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